High Purity Hydrogen Production with In-Situ Carbon Dioxide and Sulfur Capture in a Single Stage Reactor

FINAL REPORT

Reporting Period Start Date: July 1, 2007

Reporting Period End Date: July 31, 2011

Authors

Nihar Phalak

Shwetha Ramkumar

Daniel Connell

Zhenchao Sun

Fu-Chen Yu

Niranjani Deshpande

Dr. Robert M. Statnick

Professor Liang-Shih Fan

Report Issue Date: October 31, 2011

DOE Contract No.: DE-FC26-07NT43059

Name and Address of Submitting Organization:

William G. Lowrie Department of Chemical and Biomolecular Engineering
The Ohio State University
140 W 19th Avenue
Columbus OH 43210

Contact Information of Principal Investigator:

Professor Liang-Shih Fan

Phone: 614-688-3262

Fax: 614-292-3769

Email: fan.1@osu.edu

Disclaimer

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

SUMMARY

Enhancement in the production of high purity hydrogen (H_2) from fuel gas, obtained from coal gasification, is limited by thermodynamics of the water gas shift (WGS) reaction. However, this constraint can be overcome by conducting the WGS in the presence of a CO_2 -acceptor. The continuous removal of CO_2 from the reaction mixture helps to drive the equilibrium-limited WGS reaction forward. Since calcium oxide (CaO) exhibits high CO_2 capture capacity as compared to other sorbents, it is an ideal candidate for such a technique.

The Calcium Looping Process (CLP) developed at The Ohio State University (OSU) utilizes the above concept to enable high purity H_2 production from synthesis gas (syngas) derived from coal gasification. The CLP integrates the WGS reaction with in-situ CO_2 , sulfur and halide removal at high temperatures while eliminating the need for a WGS catalyst, thus reducing the overall footprint of the hydrogen production process. The CLP comprises three reactors – the carbonator, where the thermodynamic constraint of the WGS reaction is overcome by the constant removal of CO_2 product and high purity H_2 is produced with contaminant removal; the calciner, where the calcium sorbent is regenerated and a sequestration-ready CO_2 stream is produced; and the hydrator, where the calcined sorbent is reactivated to improve its recyclability.

As a part of this project, the CLP was extensively investigated by performing experiments at lab-, bench- and subpilot-scale setups. A comprehensive techno-economic analysis was also conducted to determine the feasibility of the CLP at commercial scale. This report provides a detailed account of all the results obtained during the project period.

TABLE OF CONTENTS

List of Figures	iv
List of Tables	x
Executive Summary	1
Introduction	3
Literature Review	7
Conventional coal-to-H ₂ process	7
Novel technologies for efficient conversion of coal to H ₂	8
Calcium sorbent based processes	10
How is CLP different from past and current calcium-based processes?	12
Prior findings support the CLP concept	13
Thermodynamic Analyses	19
Introduction	19
CLP Configuration and Thermodynamics	19
System Thermodynamics Analysis	32
Enhanced Non-Catalytic H ₂ Production from Syngas	46
Materials and Methods	46
Results and Discussion	51
HCl and COS removal using CaO	80
Design and Operation of Sub-Pilot Scale CLP Carbonator	89
Description of the Sub-Pilot Scale CLP Carbonator	89
Experimental Methods	94
Results and Discussion	96
Challenges during the Operation of the Sub-Pilot Scale Reactor	108
Reaction Kinetics-based Model to Predict CLP Carbonator Performance	109
Techno-Economic Analysis	115
Conclusions and Recommendations	120
References	123
Attachment 1 – Techno-Economic Analysis of the Calcium Looping Process (Detailed Report by CONSOL Energy Inc.)	
Appendix	

List of Figures

Figure 1. Implementation of Carbon Capture and Sequestration (CCS) in fossil fuel combustion and gasification.....	3
Figure 2. Schematic of the CLP.....	21
Figure 3. Thermodynamic data illustrating the equilibrium constants of the WGS reaction and the combined WGS and carbonation reaction.....	23
Figure 4. Thermodynamic data for the hydration and carbonation of CaO sorbent.....	25
Figure 5. Thermodynamic data for the sulfidation (H_2S) of CaO with varying steam partial pressures ($P_{\text{total}} = 30 \text{ atm}$).....	26
Figure 6. Thermodynamic data for predicting the equilibrium COS concentration for the CaO sulfidation with varying CO_2 concentration.....	27
Figure 7. Thermodynamic data for predicting the equilibrium HCl concentration for CaO reaction with HCl with varying steam concentration ($P_{\text{total}} = 30 \text{ atm}$).....	28
Figure 8. Thermodynamic data for the carbonation of CaO.....	29
Figure 9. Thermodynamic data for hydration of CaO.....	31
Figure 10. Comparison of the P_{CO_2} in the carbonator with the equilibrium P_{CO_2} for the carbonation of CaO for S:C of 1.....	35
Figure 11. Comparison of the P_{CO_2} in the carbonator with the equilibrium P_{CO_2} for the carbonation of CaO for S:C of 3.....	36
Figure 12. Comparison of the $P_{\text{H}_2\text{O}}$ in the carbonator with the equilibrium $P_{\text{H}_2\text{O}}$ for the hydration of CaO for a S:C of 1.....	37
Figure 13. Comparison of the $P_{\text{H}_2\text{O}}$ in the carbonator with the equilibrium $P_{\text{H}_2\text{O}}$ for the hydration of CaO for a S:C of 3.....	38

Figure 14. Effect of temperature on equilibrium CO conversion in the WGS reactor at S:C of 1.....	39
Figure 15. Effect of temperature on equilibrium CO conversion in the WGS reactor at S:C of 3.....	40
Figure 16. Effect of temperature on equilibrium CO conversion in the presence of CaO in the carbonator of the CLP at a S:C of 1.....	41
Figure 17. Effect of temperature on equilibrium CO conversion in the presence of CaO in the carbonator of the CLP at a S:C of 3.....	42
Figure 18. Effect of temperature on equilibrium H ₂ purity in the presence of CaO at a S:C of 1.....	43
Figure 19. Effect of temperature on equilibrium H ₂ purity in the presence of CaO at a S:C of 3.....	44
Figure 20. Effect of temperature and S:C on the % carbon captured in the CLP using syngas from different gasifiers as the feed.....	45
Figure 21. Bench-scale fixed bed reactor setup.....	48
Figure 22. Effect of reaction temperature and S:C on the conversion of CO by WGS reaction at 1 atm.....	53
Figure 23. Effect of reaction temperature and S:C on the conversion of CO by WGS reaction at 21 atm.....	54
Figure 24. Typical breakthrough curves for the production of H ₂ in the presence of CaO without catalyst – outlet gas composition (mole%) – at 600 °C, 21 atm and S:C=3.....	55

Figure 25. Typical breakthrough curves for the production of H ₂ in the presence of CaO without catalyst – CO conversion – at 600 °C, 21 atm and S:C=3.....	56
Figure 26. Effect of pressure on CO conversion obtained in the presence of CaO without catalyst at 650 °C and S:C=3.....	57
Figure 27. Effect of S:C on CO conversion obtained in the presence of CaO without catalyst at 1 atm and 650 °C.....	58
Figure 28. Effect of S:C on CO conversion obtained in the presence of CaO without catalyst at 11 atm and 650 °C.....	59
Figure 29. Effect of S:C on CO conversion obtained in the presence of CaO without catalyst at 21 atm and 650 °C.....	60
Figure 30. Effect of temperature on CO conversion obtained in the presence of CaO without catalyst at a S:C of 1 at 1 atm.....	61
Figure 31. Effect of temperature on CO conversion obtained in the presence of CaO without catalyst at a S:C of 3 at 1 atm.....	62
Figure 32. Effect of CO concentration in the feed on CO conversion in the presence of CaO without catalyst at 11 atm, 600 °C and S:C=3.....	63
Figure 33. Effect of CO concentration in the feed on the purity of H ₂ in the presence of CaO without catalyst at 11 atm, 600 °C and S:C=3.....	64
Figure 34. SEM image of the (a) initial CaCO ₃ sorbent (b) CaO obtained from the calcination of CaCO ₃	66
Figure 35. SEM image of the sorbent at the end of the WGS and carbonation reaction in the absence of a catalyst at (a) 1 atm (b) 21 atm at 600 °C and S:C=3.....	66

Figure 36. Comparison in the product H ₂ purity in the presence of CaO and the presence of CaO and catalyst mixture at 1 atm, 650 °C and S:C=1	68
Figure 37. Comparison in the product H ₂ purity in the presence of CaO and the presence of CaO and catalyst mixture at 21 atm and 650 °C.....	69
Figure 38. Product H ₂ purity obtained over multiple reaction and regeneration cycles in the presence of CaO without catalyst at 4.5 atm at 600 °C and S:C=3.....	70
Figure 39. Product H ₂ purity obtained over multiple reaction and regeneration cycles in the presence of CaO without catalyst at 21 atm at 600 °C and S:C=3.....	71
Figure 40. Effect of S:C on the extent of H ₂ S removal during combined WGS, carbonation and sulfidation reaction in the presence of CaO only at 1 atm and 600 °C.....	73
Figure 41. Effect of S:C on the purity of H ₂ produced during combined WGS, carbonation and sulfidation reaction in the presence of CaO only at 1 atm and 600 °C.....	74
Figure 42. Effect of temperature on the extent of H ₂ S removal during combined WGS, carbonation and sulfidation reaction in the presence of CaO at 1 atm and S:C=1.....	75
Figure 43. Effect of temperature on the purity of H ₂ produced during combined WGS, carbonation and sulfidation reaction in the presence of CaO at 1 atm and S:C=1.....	76
Figure 44. Effect of pressure on the extent of H ₂ S during combined WGS, carbonation and sulfidation reaction in the presence of CaO at 600 °C and S:C=1	77

Figure 45. Effect of pressure on the purity of H_2 produced during combined WGS, carbonation and sulfidation reaction in the presence of CaO at 600 °C and S:C=1.....	78
Figure 46. SEM image of the (a) initial $CaCO_3$ sorbent; (b) CaO sorbent obtained from the calcination of $CaCO_3$; (c) sorbent at the end of the WGS, carbonation and sulfidation reaction at 1 atm (600 °C, S:C=1); (d) sorbent at the end of the WGS, carbonation and sulfidation reaction at 21 atm (600 °C, S:C=1).....	80
Figure 47. Wt% capture of COS for $Ca(OH)_2$	82
Figure 48. Wt% capture of COS for limestone.....	82
Figure 49. Wt% capture of COS for PCC.....	83
Figure 50. Comparison of wt% capture of COS on all three sorbents at the end of 20 minutes.....	83
Figure 51. Effect of chloridation temperature on the chloridation reaction rates of limestone-CaO and PCC-CaO sorbents (HCl concentration: 1500 ppm; particle size: below 180 μm).....	85
Figure 52. Effect of HCl concentration on the chloridation reaction rate of PCC-CaO (particle size: below 180 μm).....	86
Figure 53. Effect of PCC particle size on the chloridation reaction rate of PCC-CaO (HCl concentration: 1500 ppm).....	87
Figure 54. Schematic of the sub-pilot scale CLP carbonator at OSU.....	90
Figure 55. Snapshot of the sub-pilot scale CLP carbonator at OSU.....	91
Figure 56. Assembly of the gas mixing panel. (Reproduced by permission from Swagelok Company).....	92

Figure 57. Effect of Ca:C on CO conversion.....	97
Figure 58. Effect of Ca:C on %CO ₂ removal. Original figure adapted from Wang et.al., 2010. Green squares represent the data points obtained from testing in the CLP carbonator.....	98
Figure 59. Effect of S:C on H ₂ purity in the product gas (Ca:C = 1.5).....	102
Figure 60. Replicate runs – Ca:C = 1.5, S:C = 3.....	103
Figure 61(a). Sorbent fed to the reactor – Ca(OH) ₂ . (b). Solids recovered from the reactor wall after the completion of the experiment.....	105
Figure 62. Product gas composition for test conducted with syngas-like mixture (S:C = 3, Ca:C = 1.5).....	107
Figure 63. Comparison of experimental and model results (Ca:C = 1.5, T = 600 °C, P = 1 atm).....	112
Figure 64. Effect of residence time on H ₂ purity achieved in the CLP carbonator as predicted by the model (S:C = 3, Ca:C = 1.5, T = 600 °C, P = 1 atm).....	113

List of Tables

Table 1. Typical flue gas compositions obtained from different gasifiers.....	33
Table 2. Fuel gas composition entering the WGS reactor after steam addition (S:C = 1).....	33
Table 3. Fuel gas composition entering the WGS reactor after steam addition (S:C = 3).....	34
Table 4. Composition of the feed gas used in the experiment with syngas-like mixture.....	106

EXECUTIVE SUMMARY

Efforts to develop non-renewable sources of energy notwithstanding, fossil fuels like coal and natural gas are being perceived to be major energy providers in the near future. However, since the use of fossil fuels in general, and coal in particular, results in large amount of CO₂ emissions, recent research efforts have focused on the development of novel clean coal technologies in the lieu of rising awareness about climate change due to greenhouse gas emissions. In U.S., coal combustion provides approximately 50% of the electricity. Coal gasification, which is a relatively new technology, can provide flexibility in coal usage by offering a variety of products besides electric power such as hydrogen, liquid fuels, and chemical products. The Calcium Looping Process (CLP) investigated as a part of this work is a pre-combustion CO₂ capture technology that integrates the water gas shift (WGS) reaction with in-situ carbon dioxide (CO₂), sulfur and halide removal from synthesis gas (syngas) at high temperatures (~600 °C) in a single reactor. Thus, the integrated process combines several unit operations, such as the WGS reactor, the CO₂ capture system, sulfur removal step, halide removal, and H₂ production in one process module thereby reducing the overall foot print of the process.

In the CLP, the thermodynamic limitation of the WGS reaction is overcome by the in-situ removal of CO₂ by the calcium oxide (CaO) sorbent leading to the production of high purity H₂ in the absence of a catalyst. The purity of H₂ achieved depends on the pressure of operation of this integrated reactor, referred to as the ‘carbonator’. In addition to CO₂ removal, the calcium sorbent has also demonstrated superior performance for the removal of sulfur – hydrogen sulfide (H₂S) and carbonyl sulfide (COS) – and hydrogen chloride (HCl) impurities.

To begin with, detailed thermodynamic analyses of the different reactions involved in the CLP were performed. Based on the information obtained from these analyses, suitable temperatures were identified for the experimental investigation of the reactions. Thermogravimetric analyzer (TGA) was used for preliminary screening of CaO from different precursors and study of reaction kinetics. Based on the results obtained from these tests, detailed parametric investigation was conducted using a bench-scale fixed bed reactor. Different parameters like temperature, pressure, steam to carbon ratio (S:C) were studied in the fixed bed. This work was accomplished in the first two years of the project. Based on the data obtained from the above tests, a sub-pilot scale fluidized bed reactor was designed and constructed. This system was designed for once-through operation. The investigation of parameters like S:C, calcium to carbon mol ratio (Ca:C) in this reactor provided further information on the scalability of the CLP. The data obtained from this testing also provides guidance on the further improvements and experiments that may be necessary. This work was accomplished in the final two years of the project. Process simulations using ASPEN Plus and detailed techno-economic analyses were performed in collaboration with CONSOL Energy Inc. throughout the length of the project. The experimental results obtained by OSU were used to guide this analysis.

The thermodynamic analysis indicated that 600-700 °C is a suitable operating range for the CLP carbonator. The carbonation of CaO exhibits occurs favorably in this range

enabling high purity H_2 as the product gas. The reaction of CaO with other contaminants like H_2S , COS and HCl was also possible at such temperatures. The results from the thermodynamic analysis were confirmed by the experimental findings obtained from the fixed bed reactor testing. It was also determined from these tests that the purity of H_2 was dependent on the operating pressure of the carbonator – at 1 atm, ~70% H_2 was obtained and at >3 atm, >95% H_2 was obtained at stoichiometric S:C. From the sub-pilot scale carbonator testing, it was found that ~50% H_2 could be produced at 1 atm using S:C of 3 and Ca:C of 1.5. Finally, the techno-economic analysis conducted by CONSOL Energy Inc. revealed that CLP has a potential to reduce the cost of producing H_2 and electricity by 9-12% as compared to conventional processes, in a carbon-constrained scenario.

This technical report provides all experimental results and analyses as well as results from the techno-economic analyses.

1. INTRODUCTION

The world energy demand is projected to increase by 40% from 2007 to 2030 (EIA, 2009). Although the energy generation from renewable resources is expected to grow, fossil fuels are still projected to contribute a major portion of the energy needs in the near future. A growing need for the reduction in anthropogenic carbon dioxide (CO₂) emission has led to a global push towards the development of efficient, economical, and reliable carbon capture and sequestration technologies (CCS) for application to fossil fuel based power plants. The implementation of CO₂ capture in fossil fuel based systems could be through post-combustion capture, oxy-combustion and pre-combustion capture.

Figure 1. Implementation of Carbon Capture and Sequestration (CCS) in fossil fuel combustion and gasification.

Post-combustion capture involves the combustion of fossil fuel like coal, natural gas, etc. to produce hot flue gas which is used to generate steam. The CO_2 from the flue gas is then captured. The capture of CO_2 from the flue gas results in a large increase in parasitic energy and cost of electricity (COE) due to the large volumes of flue gas and the low concentration of CO_2 (10-15% in case of coal combustion and 3-4% for natural gas). In oxy-combustion, the fuel is burnt in oxygen (O_2) and the flue gas is recycled, to produce a concentrated stream containing CO_2 and steam which is then dried, compressed and transported for sequestration. Oxy-combustion requires an Air Separation Unit (ASU) which is energy intensive and expensive. Pre-combustion capture involves gasification of coal or reforming of natural gas (methane) to produce synthesis gas (syngas). The syngas is then cleaned and sent to shift reactors to convert the carbon monoxide (CO) to hydrogen (H_2) and CO_2 in the presence of steam. Downstream of the shift reactors, the CO_2 is removed using solvents like amines, rectisol, selexol, etc. and the H_2 is further purified in a pressure swing adsorber (PSA) for high H_2 purity applications.

The application of CCS to gasification systems has been found to be more efficient and economical when compared to CCS for post-combustion systems. It has been estimated that with the implementation of CCS using solvent based systems, the increase in COE for an integrated gasification combined cycle (IGCC) will be 25 to 40% while that for pulverized coal (PC) boilers will be 60 to 85% (MIT, 2007). In a carbon constrained scenario, it has been estimated that the cost of a super critical PC boiler will be \$2140/kWe while that of an IGCC will be \$1890/kWe. In addition to being more

economical and efficient, gasification is also very versatile and capable of producing H_2 and liquid fuels in addition to electricity.

Several options are being investigated for the implementation of CCS on pre-combustion systems including using solvent, sorbents, membranes and chemical looping processes. The Calcium Looping Process (CLP) which is a calcium sorbent based chemical looping process, has the potential to reduce the cost and increase the efficiency of CCS implementation (Abanades et.al., 2007; Ramkumar et.al., 2009). Under the current work, the CLP concept and application to various feed streams (syngas, natural gas, etc.) has been studied using thermodynamic analysis and lab-, bench-, and subpilot-scale experiments. A detailed techno-economic analysis has also been performed.

Section 2 provides an overview of the state-of-the-art coal-to- H_2 process and different techniques that have been employed to improve this process with respect to product yield and process efficiency and economics. A summary of different calcium processes that have been developed is also provided and the special features of the CLP have been highlighted. Section 3 describes the thermodynamics of the different reactions occurring in the CLP as well as analyses of the overall system.

Section 4 describes the non-catalytic production of H_2 using the CLP. The process conditions for which the WGS catalyst can be eliminated without any decrease in H_2 purity have been identified.

Section 5 describes the scale-up of the CLP for H₂ production from bench to subpilot scale. The subpilot scale unit was designed based on the information discussed in the previous sections. The operational results from of the subpilot scale reactor are also discussed here.

Section 6 discusses the techno-economic analysis for the production of H₂ and electricity from coal and natural gas. The application of the CLP to three cases – coal-to-H₂, IGCC and steam methane reforming (SMR) – was investigated in detail. The techno-economic analysis predicts that the CLP has a potential to reduce the cost of H₂ and electricity production as compared to conventional processes.

Section 7 contains the summary of all results and conclusions. Recommendations for improvement and future work have also been included.

2. LITERATURE REVIEW

Conventional coal-to-H₂ process

H₂ can be produced conventionally from coal by the gasification process, natural gas by SMR process and higher hydrocarbons by the partial oxidation process. In a typical coal gasification system, the coal is fed along with steam and/or a water quench. The quench system also provides the excess steam required for the WGS reaction (Holt, 2005; MIT, 2007). While higher temperatures enhance the kinetics of the WGS reaction, the equilibrium limitation of it adversely affects H₂ production and the H₂ yield falls with rising temperature. Hence, a high steam to carbon ratio (S:C) is required to enhance the CO conversion and the consequent H₂ yield. The S:C required at 550 °C can be as high as 50 in a single stage operation or 7.5 for a more expensive dual-stage operation to obtain >99% pure H₂ (Haussinger et.al., 2000). Numerous research studies have focused on the development of low temperature catalysts to improve H₂ production (Haussinger et.al., 2000). Commercially, the dual-stage sweet WGS reaction is carried out in series, with a high temperature shift (HTS) (300-450 °C) stage containing iron oxide catalyst and a low temperature shift (LTS) (180-270 °C) stage containing copper catalyst (Loyd et.al., 1996). The commercial iron oxide catalyst has a lower tolerance to sulfur and chloride impurities (Haussinger et.al., 2000). Hence syngas clean up is required upstream of the shift reactors which is achieved in conventional scrubbing towers using physical or chemical sorbents. This low temperature syngas clean up process is energy intensive due to the gas cooling and reheating requirements. In a sour gas shift system, where the sulfur content on syngas is greater than 1000 ppm, a sulfided catalyst is used in a series of reactors at a temperature of 250-500 °C and the desulfurization unit is located

downstream of the WGS reactors (Lloyd et.al., 1996; Hiller et.al., 2007). After the shift reaction, the syngas is subjected to scrubbing using solvents to remove the CO₂ and is sent to the PSA to produce pure H₂. The PSA tailgas is used as a fuel for power generation.

Novel technologies for efficient conversion of coal to H₂

Several methods to enhance the purity of H₂ with the simultaneous separation of CO₂ have been cited in literature. A slight advancement in the commercial method of H₂ production has been to remove the CO₂ from the reaction mixture between the two stages of the shift reaction. However, solvents operate at ambient temperatures and this method involves severe energy penalties due to cooling and reheating of the reaction gas mixture.

An effective technique to shift the WGS reaction to higher conversion for the enhanced H₂ generation has been to remove H₂ from the reaction mixture. This concept has led to the development of H₂ separation membranes. The syngas from the gasifier is shifted at a high temperature over a sulfur tolerant catalyst (STC) followed by a WGS H₂ membrane reactor which aids in producing more H₂ and separating it from the gas mixture (Kreutz et.al., 2002). However, ceramic membranes have a very low H₂ permeability and the intermediate temperature composites are difficult to fabricate and are very susceptible to poisoning, in spite of having a high H₂ flux. The cermet membranes are superior to the other two classes of membranes but they are susceptible to poisoning and are expensive (Roark et.al., 2002). It has been reported that, for optimum performance of Pd membrane reactors, two stages are required with a S:C of 3 (Ma & Lund, 2003). However, these

reactors suffer from inhibition effects of CO₂, which reduces the yield of H₂ from 90% to 50%. In addition, membranes cannot completely remove H₂ from the mixture and suffer from a considerable pressure drop across them. Any remaining H₂ in the main stream would dilute the CO₂ and would lead to poor process economics.

High temperature CO₂ membranes have been developed which operate in the same temperature range as that of the WGS reaction. Although polymeric membranes for the removal of CO₂ from H₂ have been found to have several advantages like simplicity of operation, high energy efficiency and lower cost, most polymers have a poor H₂/CO selectivity. Hence they are not very effective in shifting the equilibrium of the WGS reaction and producing high purity H₂ (Chung et.al., 2006).

An alternative concept to drive the WGS reaction forward has been to remove the CO₂ from the reaction mixture using solid sorbents which either physisorb or react with the CO₂ in the WGS reactor. The separation of CO₂ from the reaction mixture at high temperatures removes the equilibrium constraint of the WGS reaction and enhances H₂ production. Sorbents that operate at higher temperatures are beneficial to the process as the WGS reaction has superior kinetics due to the high temperature and enhanced thermodynamic extent due to the removal of CO₂ from the product gas. Faster rates of reaction and larger CO₂ capture capacities allow use of smaller reactors and require a smaller amount of solids circulation through the system. CaO has a high CO₂ capture capacity and removes CO₂ to ppm levels at a high temperature of 600 °C making it one of the most suitable sorbents for this application (Gupta and Fan, 2002).

Calcium sorbent based processes

The concept of utilizing CaO for CO₂ capture has existed for well over a century. It was first introduced by DuMotay and Marechal in 1869 for enhancing the gasification of coal (Squires, 1967) and followed by CONSOL's CO₂ Acceptor Process (Curran et.al., 1967) a century later when this concept was tested in a 40 ton/day plant. A variation of this process, the HyPr-RING process, (Lin et.al., 2005) was developed in Japan for the production of H₂ at high pressures. Several other processes have also been developed to enhance H₂ production using calcium sorbents such as the ZECA (Ziock et.al., 2001), ALSTOM (Andrus, 2006) and GE Process (Rizeq et.al., 2001).

The CO₂ Acceptor Process was developed by the Consolidation Coal Company and later Conoco Coal Development Company. It was designed to produce synthesis pipeline gas from pulverized lignite or sub-bituminous coal. The Ca-based sorbent was circulated between two fluidized bed reactors – a gasifier and a regenerator – and aided in the conversion of coal to H₂. The process was proved to be technically feasible after being successfully tested in a pilot plant facility located at Rapid City, South Dakota. However, the activity of CO₂ acceptor decreased with increasing number of cycles which was attributed to CaO crystalline growth. Attempts were made improve the recyclability of the acceptor using different approaches like reactivation, structure modifications, etc. and the results were found to be encouraging.

In the HyPr-RING (Hydrogen Production by Reaction-Integrated Novel Gasification) process, coal is gasified with high pressure steam in the presence of CaO/Ca(OH)₂

sorbent. In order that the CaO hydrates to form Ca(OH)_2 , excess steam is used. The heat required for the endothermic gasification reaction is supplied by the hydration and carbonation of CaO, both of which are exothermic. The purity of hydrogen obtained from this process is only about 90% and the process also has a disadvantage of being operated at elevated pressures (~ 70 bar). Besides this, the sorbent does not display a robust CO_2 capture ability, which is mainly due to the interaction between the CaO/ Ca(OH)_2 and the minerals contained in coal.

The ZECA (Zero Emission Coal Alliance) process is another process which is based on a similar concept. This process is based on hydrogasification of coal, i.e. coal is gasified using hydrogen instead of oxygen. The pressure for this gasification is approximately 70 bar, and the main product is methane (via the methanation reaction $\text{C} + 2\text{H}_2 \rightarrow \text{CH}_4$). An integrated reactor is used as a next stage, in which the reforming of methane and the WGS reaction occur simultaneously in the presence of CO_2 acceptor (CaO). One of the advantages of the ZECA process is that an air separation unit (ASU), which is very energy-intensive, is not necessary. However, the use of hydrogen for gasification itself means that a part of the product hydrogen will be used up in the process and this translates into more consumption of coal, when compared to traditional coal gasification.

In the Lime-Enhanced Gasification (LEGS) process to produce a hydrogen-rich product, the gasifier itself contains the CaO sorbent and is coupled with one more reactor (regenerator), in which the sorbent is continuously calcined (or regenerated). One of the disadvantages of this process is that along with the spent calcium sorbent, even the coal

ash enters the calciner and a higher amount of purge would be necessary to be maintained, as compared to other processes where the fuel in the gasifier does not come in contact with the sorbent.

The limestone based chemical looping process developed by ALSTOM makes use of calcium sulfide as the oxygen carrier. Coal is first gasified in the presence of CaSO_4 , which acts as an oxygen carrier. This step produces CO and H_2 , simultaneously reducing CaSO_4 to CaS. Using the WGSR, the CO is converted to CO_2 and H_2 and the CO_2 is then captured using CaO, to form CaCO_3 . The CaO is regenerated and CaS is oxidized to form CaSO_4 so that the loop continues.

How is CLP different from past and current calcium-based processes?

The CLP comprises of three reactors – carbonator, calciner and hydrator. The CO_2 capture and other contaminant removal along with high purity H_2 production occurs in the carbonator. The calcium sorbent is regenerated in the calciner and reactivated by hydration in the hydrator. Details regarding the reactions occurring in each of these 3 steps and operating conditions etc. have been provided in subsequent sections.

In the CLP, the calcium sorbent (CaO) does not come in contact with coal directly, unlike the HyPr-RING and the CO_2 Acceptor Process. The coal is first gasified in a traditional gasifier to produce syngas which is then directed to the carbonator. Such a scheme prevents exposure of the sorbent to different coal constituents (minerals, etc.) thus protecting its CO_2 capture capacity from declining rapidly. However, as has been

reported by several researchers, the capture capacity of CaO decreases over traditional CaO-CaCO₃ cycles due to the phenomenon of high temperature sintering. To overcome this, a third step – CaO hydration – has been integrated in the CLP. Independent investigations performed by OSU (details provided in the Appendix) and several other researchers have confirmed the effectiveness of hydration in maintaining the capture capacity of CaO over multiple cycles. Thus, the inclusion of hydration makes the sorbent go through CaO-CaCO₃-Ca(OH)₂ in every cycle. The higher CO₂ capture capacity of the sorbent over many cycles helps to reduce the purge and make up rates as compared to other traditional calcium processes. Since CaO derived from Ca(OH)₂ is more reactive than that obtained from CaCO₃, good CO₂ capture can be achieved at comparatively lower calcium to carbon (Ca:C) loadings. These factors will result in significant cost savings when the process is scaled up further. Further, since hydration of CaO is a highly exothermic reaction, it also provides high quality heat which can be used to produce electricity in addition to H₂.

Prior findings support the CLP concept

The idea of the CLP is based on prior work conducted at OSU and also reported by several other researchers. In the CLP carbonator, the CaO reacts mainly with CO₂ and also with other acid gas contaminants like H₂S, HCl, COS, etc. The kinetics of each of these reactions has been thoroughly studied and is summarized below. Thermodynamic calculations and CLP-specific analyses were performed as a part of this work and have been provided in next section.

Kinetic of carbonation of CaO

The carbonation of CaO, given by the following reaction, has been investigated by for application in high temperature CO₂ removal from flue and fuel gases –

It has been established that the gas-solid CO₂-CaO reaction proceeds through two regimes. The reaction occurs rapidly in the first regime and this regime is referred to as ‘kinetically controlled’, followed by a ‘diffusion limited’ regime in which the rate of reaction decreases due to the diffusion limitation imposed on the CO₂ by the CaCO₃ product layer formed on the surface. The shrinking core model has been used to model this behavior –

$$t/\tau = 1 - (1 - X)^{1/3}$$

$$t/\tau = 1 - 3(1 - X)^{2/3} + 2(1 - X)$$

where t is the time, X is the conversion of CaO and τ is the time required to reach complete conversion.

The first equation is for the kinetically controlled regime, while the second represents the diffusion limited regime. Bhatia and Perlmutter (1983) have also used the random pore model to describe the carbonation reaction.

A much simpler model, proposed by Lee (2004), is as follows –

$$r_{\text{CO}_2} = \frac{1}{M_{\text{CaO}}} \left(\frac{dX}{dt} \right)$$

where,

$$\frac{dX}{dt} = k \left(1 - \frac{X}{X_u} \right)^2$$

X_u = ultimate conversion

This model is found to fit experimental data available in the literature and is more useful for process design, modeling and reactor performance prediction. This model has also been used in the later section where the H_2 purity from CLP carbonator is predicted using a reaction kinetics-based model.

While the different models proposed in literature fit the existing laboratory-scale data fairly well, OSU has investigated the kinetics of the carbonation reaction in terms of the actual residence time of required for the reaction and the Ca:C. These results have been detailed elsewhere (Wang et.al., 2010). It was found that at Ca:C>1.4, 100% CO_2 capture could be achieved when the reactor residence time was of the order of few seconds.

Kinetics of reaction of CaO with HCl

The kinetics of HCl capture using calcium based sorbents has been widely investigated due to applications in IGCC gas cleanup (Dou et.al., 2001).

HCl is also present in coal-fired power plant flue gas and is a hazardous species for both process hardware and environmental health. For such applications, the operating temperature is similar to the one encountered in the CLP carbonator where the calcium sorbent is expected to capture HCl from the coal-derived syngas (500 – 700 °C). Hence the data reported from prior studies by different researchers can be used for predicting the kinetics of HCl capture that will occur in the CLP carbonator.

Weineu and Jensen (1992) investigated the reaction between HCl and CaO in the temperature range of 60-1000 °C. They report that the capacity for HCl binding to the sorbent is the largest in the range of 500–600 °C. OSU has also confirmed these findings by performing independent investigations (Sun et.al., 2011). 600 °C was found to be a favorable temperature for operating the CLP carbonator and hence good HCl capture is expected to occur in the CLP carbonator. The rate of HCl capture by CaO was also found to peak in the temperature range 550-600 °C. Given that the CaO loading in the CLP carbonator will be large enough to achieve 90-100 % CO₂ capture, and since the HCl concentration in the syngas will be in ppm levels, fast and complete HCl capture can be expected to occur in the carbonator.

The kinetics of this reaction is found to be first-order as a function of HCl concentration and zero order for the sorbent (Dou et.al., 2001; Mura and Lallai, 1992). The overall process is believed to occur as follows:

1. Diffusion of HCl in the gas film outside the particle
2. Diffusion of HCl in the pores inside the particle
3. Diffusion through solid product layer
4. Chemical reaction

Li and Shaw (2000) applied the Arrhenius equation to correlate the rate constants from their experimental data. They determined the activation energy to be 31.1 kJ/mol with a corresponding pre-exponential factor of 0.241 1/(g min). The rate constant as a function of temperature is given by the following expression –

$$k = 0.241 \exp (-31100/RT)$$

where T is the temperature in K and R = 8.314 J/mol.K.

Kinetics of reaction of CaO with COS and H₂S

Similar to HCl, the removal of sulfur compounds is important in developing coal gasification processes. In addition to being detrimental to the environment and corroding agents, sulfur compounds are also known to be catalyst poisons. This has been the driving force for the studies that have been extensively conducted since 1970s for the removal of H₂S using metal oxides as sorbents. Among them, CaO in particular has received a lot of attention. CaO reacts with H₂S and COS according to the following reactions –

Westmoreland et.al. (1977) report the kinetics of high temperature reaction of H₂S with CaO. They report that the reaction is first order with to H₂S and obeys the Arrhenius equation

$$k_s = k_0 \exp (-E/RT)$$

where $k_0 = 0.038 \text{ cm}^4/\text{min.mg.mol}$ and $E = 5160 \text{ cal/mol}$.

Yang and Chen (1979) have performed similar studies for reaction of COS and CaO. They have employed a grain model to satisfactorily correlate the overall rates in the temperature range of 600 – 900 °C, where chemical reaction was the rate-limiting step. The rate of COS uptake by CaO followed the form:

$$dX/dt = 78 \exp(-2160/T) P_{\text{COS}} (1-X)$$

where P_{COS} is the partial pressure of COS

Bench-scale fixed bed tests conducted at OSU for the co-capture of H_2S and CO_2 during WGS reaction in the CLP carbonator indicated that at 600 °C and 21 atm, the H_2S concentration in the product gas can be reduced to as low as 1ppm. It was found that higher pressures favored the H_2S uptake by CaO. Yang and Chen (1979) report that the rate of sorption of COS by CaO is slightly higher than that of H_2S . Hence, it can be expected that even faster uptake of COS will happen at the above mentioned conditions. Even though independent tests for co-capture using COS were not performed, based on the existing data in the literature, it can be concluded with reasonable degree of confidence that the CLP carbonator can achieve complete sulfur (H_2S and COS) removal.

3. THERMODYNAMIC ANALYSES

Introduction

Most H_2 production processes reported in literature require a separate sulfur cleanup unit to prevent poisoning of the sorbent used for CO_2 capture. Sulfur is present in syngas in the form of H_2S and carbonyl sulfide (COS). According to equilibrium calculations, at temperatures below $1027\text{ }^\circ\text{C}$ which exist in the gasifier, all sulfur radicals combine to form predominantly H_2S which is close to 95% of the total sulfur content and COS forms the other 5% (Jazbec et.al., 2004). There have been studies conducted on the simultaneous calcination and sulfidation of calcium based sorbents at temperatures higher than $600\text{ }^\circ\text{C}$ (De Diego et.al., 2004). There have also been studies on the sulfidation of $CaCO_3$ in the presence of CO_2 but the CO_2 was used only to maintain a high enough partial pressure to prevent the calcination of $CaCO_3$ (Fenouil et.al., 1994; De Deigo et.al., 1999). However, there is no mention of studies conducted on simultaneous CO_2 and sulfur capture integrated with H_2 production in the literature. In the CLP described in the sections below, simultaneous CO_2 and H_2S capture is achieved during the production of H_2 .

CLP Configuration and Thermodynamics

Several options are being investigated for the implementation of CCS on coal gasification systems including using solvents, sorbents, membrane and chemical looping processes. The CLP which is a calcium sorbent based chemical looping process, has the potential to reduce the cost and increase the efficiency of H_2 and/or electricity production from coal derived syngas by implementing the principles of process intensification (Ramkumar

et.al., 2010). The CLP integrates the WGS reaction with in-situ CO₂, sulfur, and halide removal at high temperatures in a single stage reactor. It utilizes a high temperature regenerable CaO sorbent which in addition to capturing the CO₂, enhances the yield of H₂ and simultaneously captures sulfur and halide impurities.

The advantages of the CLP include:

1. The simplification of the coal to H₂ process by integration of the reaction and separation steps. This results in a decrease in the number of process units and combines the two staged WGS reactors (HTS and LTS), the CO₂, sulfur and halide capture units into a single stage reactor.
2. The enhancement in H₂ yield at high temperatures due to elimination of the equilibrium limitation of the WGS reaction.
3. The potential to reduce excess steam requirement for the WGS reaction due to the enhanced thermodynamics of H₂ production by the combined WGS and carbonation reactions.
4. The potential to eliminate the requirement of WGS reaction catalyst due to H₂ production at high temperatures.
5. Although energy needs to be supplied for the endothermic calcination reaction, the carbonation reaction is exothermic at high temperatures of 500-750 °C resulting in the production of high quality heat. By using a good strategy of heat integration it is possible to achieve high process efficiencies.
6. The calcination reaction results in the production of a pure sequestration ready CO₂ stream.

Figure 2. Schematic of the CLP.

A schematic of the CLP is shown in Figure 2. The CLP comprises the carbonation reactor, the calciner and the hydrator. In the carbonation reactor high-purity H_2 is produced while contaminant removal is achieved, in the calciner the calcium sorbent is regenerated and a sequestration-ready CO_2 stream is produced and in the hydrator the sorbent is reactivated. Thermodynamic analyses are conducted for the reactions occurring in each reactor using HSC Chemistry v 5.0 (Outokumpu Research Oy, Finland) software. All the reactions shown in Figure 2 are found to be thermodynamically spontaneous but reversible and the extent of each of these reactions depends on the partial pressure of the

respective gas species and the reaction temperature. The following sections give a description of the three reactors using thermodynamic analyses.

Carbonation Reactor (Carbonator)

The carbonation reactor comprises either a fluidized bed or an entrained flow reactor that operates at pressures ranging from 1 to 30 atm and temperatures of 500-750 °C. The exothermic heat released from the carbonation reactor can be used to generate steam or electricity. In the carbonator, the thermodynamic constraint of the WGS reaction is overcome by the incessant removal of the CO₂ product from the reaction mixture, which enhances H₂ production and obviates the need for excess steam addition. This is achieved by the concurrent WGS reaction and carbonation reaction of CaO to form CaCO₃ thereby removing the CO₂ product from the reaction mixture. In addition, the CaO sorbent is also capable of reducing the concentration of sulfur and halides in the outlet stream to ppm levels. The in-situ removal of CO₂ removes the equilibrium limitation of the WGS reaction thereby obviating the need for excess steam addition. Thermodynamic analysis, presented subsequently, predicts that the removal of H₂S using CaO is inhibited by the presence of steam. Since almost all the steam is consumed in the enhanced WGS reaction, the removal of H₂S is favored in the system. The reactions occurring in the carbonator are:

Halide capture (HCl): $\text{CaO} + \text{HCl} \leftrightarrow \text{CaCl}_2 + \text{H}_2\text{O}$ ($\Delta H = -218 \text{ kJ/mol}$) [5]

The equilibrium constants for the WGS reaction and the combined WGS and carbonation reaction for various temperatures are shown in Figure 3.

Figure 3. Thermodynamic data illustrating the equilibrium constants of the WGS reaction and the combined WGS and carbonation reaction.

The equilibrium calculations have been performed using HSC Chemistry v 5.0. The equilibrium constant for the WGS reaction can be defined as shown below:

$$K_{\text{eq1}} = \frac{P_{\text{H}_2} P_{\text{CO}_2}}{P_{\text{H}_2\text{O}} P_{\text{CO}}}$$

where P_{CO_2} , P_{H_2} , P_{CO} , $P_{\text{H}_2\text{O}}$ are the partial pressures of CO_2 , H_2 , CO and H_2O at equilibrium. The combined WGS and carbonation reaction is as follows:

The equilibrium constant for the combined reaction is defined as follows:

$$K_{\text{eq2}} = \frac{P_{\text{H}_2}}{P_{\text{H}_2\text{O}} P_{\text{CO}}}$$

where $K_{\text{eq2}} = K_{\text{eq1}} \times K_{\text{carb}}$ and K_{carb} is the equilibrium constant of the carbonation reaction.

The equilibrium constant of the WGS reaction decreases with an increase in the temperature resulting in low H_2 yields at higher temperatures. Hence, in the conventional WGS system, a LTS is used after the HTS to convert the CO slip and to increase the yield of H_2 in the presence of a LTS catalyst. The equilibrium constant of the combined reaction is significantly higher than the equilibrium constant of the WGS reaction alone, in the desired temperature of operation ranging from 500 to 750 °C. Hence, the CLP is capable of producing a much higher H_2 yield, and hence purity, due to almost complete CO conversion, when compared to the conventional H_2 production process.

Equilibrium curves for the partial pressures of H_2O , CO_2 and H_2S as a function of temperature, for the hydration, carbonation and sulfidation reactions with CaO were also obtained using HSC Chemistry v 5.0. The relationship between reaction temperature and equilibrium partial pressure of CO_2 and H_2O for the carbonation and hydration reaction with CaO sorbent is shown in Figure 4.

Figure 4. Thermodynamic data for the hydration and carbonation of CaO sorbent.

Hydration: $\text{CaO} + \text{H}_2\text{O} \leftrightarrow \text{Ca(OH)}_2$ [7]

Carbonation and hydration of CaO are reversible reactions which occur depending on the conditions of temperature and partial pressures of CO_2 and H_2O respectively. Carbonation of CaO occurs at conditions above the equilibrium P_{CO_2} curve while calcination of CaCO_3 occurs at conditions below the curve. Similarly hydration of CaO occurs above the $P_{\text{H}_2\text{O}}$ curve while dehydration occurs at conditions below the curve.

For the reversible sulfidation of CaO, the extent of H_2S removal will depend on the temperature and $P_{\text{H}_2\text{O}}$ in the carbonation reactor. Figure 5 depicts the equilibrium H_2S

concentrations in the product H_2 stream, in ppm, for varying moisture concentrations (P_{H_2O}) at 30 atm total system pressure. It can be seen that the equilibrium H_2S concentration in the product H_2 increases with the increase in P_{H_2O} . At a temperature of 600 °C, the H_2S concentration is 0.1 ppm for a P_{H_2O} of 0.02 atm and 1 ppm for a P_{H_2O} of 0.2 atm. By operating the carbonator at near-stoichiometric steam requirement, it is possible to obtain low concentrations of steam in the reactor system leading to low H_2S concentrations of less than 1 ppm in the product. It can also be seen that the reactor will favor H_2S removal using CaO at around 500-650 °C, which is suitable for the carbonation reaction as well.

Figure 5. Thermodynamic data for the sulfidation (H_2S) of CaO with varying steam partial pressures ($P_{total} = 30$ atm).

Similarly, the removal of COS is dependent on temperature and partial pressure of CO_2 in the carbonator. Figure 6 illustrates the equilibrium COS concentrations in the product H_2 stream for varying CO_2 concentrations at 30 atm total system pressure. The equilibrium COS concentration in the product H_2 stream increases with the increase in temperature and partial pressure of CO_2 . Since CO_2 in the carbonator can be reduced to very low concentrations in the product stream by CaO, COS capture by CaO will be favored. The equilibrium partial pressure of CO_2 for carbonation with CaO at 600 °C is less than 0.01 atm as shown in Figure 4. Hence the equilibrium COS concentration in the product H_2 can be predicted from Figure 6 to be lower than 0.001 atm.

Figure 6. Thermodynamic data for predicting the equilibrium COS concentration for the CaO sulfidation with varying CO_2 concentration.

CaO is also capable of capturing HCl in the carbonator. Similar to the removal of H₂S by CaO, the extent of HCl capture is also dependent on the temperature and the partial pressure of steam in the carbonator. The equilibrium HCl concentration in the product H₂ stream from the carbonator for varying temperatures and steam partial pressures is shown in Figure 7. Hence the reduction of S:C in the carbonator will improve the extent of HCl removal.

Figure 7. Thermodynamic data for predicting the equilibrium HCl concentration for CaO reaction with HCl with varying steam concentration ($P_{\text{total}} = 30 \text{ atm}$).

Calciner

The spent sorbent at the exit of the carbonator is a mixture consisting of CaCO₃, CaO, CaS and calcium chloride (CaCl₂). The CaCO₃ in the spent sorbent mixture is regenerated

back to CaO in the calciner. The calciner is operated at atmospheric pressure in a rotary or a fluidized bed system. The heat can be supplied directly or indirectly using a mixture of fuel and oxidant. From the thermodynamic curve for CaO and CO₂ shown in Figure 8, calcination is found to occur at temperatures above 890 °C in the presence of 1 atm CO₂. Dilution of CO₂ in an indirectly fired calciner with steam, or oxy-combustion of a fuel (syngas, natural gas, coal, etc) in a direct fired calciner will permit the calcination to be conducted at temperatures lower than 890 °C. The reaction occurring in the calciner is:

Figure 8. Thermodynamic data for the carbonation of CaO.

The regenerability of CaO sorbents over multiple cycles has been the major drawback of high temperature calcium based CO₂ capture processes. CaO sorbents are prone to

sintering during the high-temperature calcination step. There is a decrease in sorbent reactivity even when steam is present in the calcination atmosphere. Over multiple cycles, the percentage of sintered CaO progressively increases and reduces the CO₂ capture capacity (Curran et.al., 1967; Iyer et.al., 2004; Bhatia and Perlmutter, 1983). Due to sintering, higher solid circulation or make up rates need to be used to maintain a high level of CO₂ removal (Romeo et.al., 2009). Pretreatment methods have been developed to reduce the decay in reactivity, which involve hydration of the sorbent (Koji et.al., 2003; Sun et.al., 2008), preheating and grinding of the sorbent (Manovic and Anthony, 2008) and synthesis of novel sorbents by physical or chemical modification of the precursor (Gupta and Fan, 2002; Salvador, 2003). In CLP, the addition of a sorbent reactivation step by hydration, as part of the carbonation-calcination cycle is used to reverse the effect of sintering during each cycle and thus maintain the sorbent reactivity (Fan et.al., 2008).

Hydrator

The calcination process causes sintering of the sorbent which results in a reduction in its reactivity and hence, the overall CO₂ capture capacity. The hydration process reverses this effect by increasing the pore volume and surface area available for reaction with the gas mixture. Figure 9 shows the partial pressure of steam required for hydration of the sorbent at various temperatures. Hydration occurs at atmospheric pressure at temperatures below 500 °C. At temperatures of 600 °C and above hydration occurs at steam partial pressures of above 4 atm. Operation of the hydrator at high temperatures reduces the extent of cooling and reheating of the solids required between the calciner and the carbonator. This aids in reducing the parasitic energy consumption of the process.

Hydration at higher temperatures also produces high quality heat which can be used to produce steam or electricity.

Figure 9. Thermodynamic data for hydration of CaO.

Depending on the reactivity of the calcined sorbent, a fraction of the calcined sorbent or the entire stream of sorbent could be hydrated. The reactivity of the calcined sorbent will depend on a variety of factors including the type of calciner (direct or indirect), mode of calcination (rotary kiln, fluidized bed or entrained bed), the temperature of calcination and the atmosphere within the calciner. The Ca(OH)_2 from the hydrator is conveyed to the carbonator where it dehydrates to produce high reactivity CaO and steam. The steam obtained from the dehydration reaction is consumed in the WGS reaction. The advantage of this reactivation process is that no excess steam is required for hydration. Part or all of

the steam required for the WGS reaction is supplied to the hydrator depending on the fraction of the calcined sorbent that is sent to the hydrator for reactivation.

System Thermodynamics Analysis

Thermodynamic analysis was conducted for the reactions occurring in the carbonator with syngas feed compositions from different gasifiers. The equilibrium constants for the reactions occurring in the carbonator were obtained using HSC Chemistry v 5.0 software as shown earlier. Table 1 shows the syngas compositions from different gasifiers. It is noted that air is used as the oxidant in the moving bed dry gasifier, while oxygen is used in all the other gasifiers. Using the composition of the syngas, the feasibility of the simultaneous WGS, carbonation and sulfidation reaction in the temperature range of 500-750 °C was determined. The temperature range of 500-750 °C was chosen as the preferred operating range primarily because the kinetics of CO₂ capture by CaO is high and the equilibrium partial pressure of CO₂ is low as shown earlier. Steam is added to syngas before it is fed to the carbonator to adjust the S:C for the WGS reaction. Tables 2 and 3 list the compositions of the syngas-steam mixture for S:C of 1 and 3, respectively. Depending on the thermodynamic extent of the WGS reaction occurring in the carbonator, the P_{CO2} in the carbonator can be determined.

Table 1. Typical flue 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 (atm)	20.1	31.6	9.9	41.8	24.8
CO (mol %)	17.4	46	48.2	41	60.3
H ₂ (mol %)	23.3	26.4	30.6	29.8	30
CO ₂ (mol %)	14.8	2.9	8.2	10.2	1.6
H ₂ O (mol %)	-	16.3	9.1	17.1	2
N ₂ (mol %)	38.5	2.8	0.7	0.8	4.7
CH ₄ + HC _s (mol %)	5.8	4.2	2.8	0.3	-
H ₂ S + COS (mol %)	0.2	1.1	0.4	1.1	1.3

Table 2. Fuel gas composition entering the WGS reactor after steam addition (S:C = 1) (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
total pressure (atm)	20.1	31.6	9.9	41.8	24.8
CO (atm)	2.97	11.24	3.42	13.81	9.46
H ₂ (atm)	3.98	6.45	2.17	10.04	4.71
CO ₂ (atm)	2.53	0.71	0.58	3.44	0.25
H ₂ O (atm)	2.97	11.24	3.42	13.81	9.46
N ₂ (atm)	6.58	0.68	0.05	0.27	0.74
CH ₄ + HC _s (atm)	0.99	1.03	0.2	0.1	0
H ₂ S + COS (atm)	0.03	0.27	0.03	0.37	0.2

Table 3. Fuel gas composition entering the WGS reactor after steam addition (S:C = 3)
(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
total pressure (atm)	20.1	31.6	9.9	41.8	24.8
CO (atm)	2.29	6.57	2.02	8.32	5.37
H ₂ (atm)	3.07	3.77	1.28	6.05	2.67
CO ₂ (atm)	1.95	0.41	0.34	2.07	0.14
H ₂ O (atm)	6.88	19.72	6.06	24.96	16.11
N ₂ (atm)	5.08	0.4	0.03	0.16	0.42
CH ₄ + HCs (atm)	0.76	0.6	0.12	0.06	0
H ₂ S + COS (atm)	0.03	0.16	0.02	0.22	0.12

Figure 10 illustrates the P_{CO_2} in the carbonator, after WGS reaction has occurred in the syngas-steam mixture with a S:C = 1 from various gasifiers. It also shows the equilibrium P_{CO_2} required for the carbonation reaction with CaO. It can be seen that the P_{CO_2} in the carbonator for various gasifiers is higher than the equilibrium P_{CO_2} for the carbonation of CaO and hence it can be inferred that in the temperature range of 500-750 °C, CO₂ removal is achieved by CaO to greater than 90%. Figure 11 illustrates the same for S:C=3.

Figure 10. Comparison of the P_{CO_2} in the carbonator with the equilibrium P_{CO_2} for the carbonation of CaO for S:C of 1.

Figure 11. Comparison of the P_{CO_2} in the carbonator with the equilibrium P_{CO_2} for the carbonation of CaO for S:C of 3.

In order to determine whether CaO will undergo hydration, the P_{H_2O} in the carbonator was determined after the combined WGS and carbonation reaction has occurred to equilibrium for S:C of 1 and 3. Figure 12 shows the P_{H_2O} in the carbonator for S:C of 1. Since P_{H_2O} in the carbonator is lower than equilibrium P_{H_2O} for hydration of CaO, hydration will not occur for any syngas composition in the temperature range under

consideration. Figure 13 shows P_{H_2O} in the carbonator for S:C of 3 and it can be seen that hydration will occur at lower temperatures. Hydration of CaO will occur at temperatures below 600 °C for fluidized bed and moving bed (dry), below 670 °C for entrained flow (dry), below 680 °C for moving bed (slagging) and below 700 °C for entrained flow (slurry) gasifier syngas.

Figure 12. Comparison of the P_{H_2O} in the carbonator with the equilibrium P_{H_2O} for the hydration of CaO for a S:C of 1.

Figure 13. Comparison of the P_{H_2O} in the carbonator with the equilibrium P_{H_2O} for the hydration of CaO for a S:C of 3.

Figure 14 and 15 depict the equilibrium CO conversion obtained in a conventional WGS reactor. The CO conversion for all syngas compositions and S:C ratios decreases with the increase in temperature due to the equilibrium limitation of the exothermic WGS reaction. The CO conversion increases with the increase in S:C from 1 to 3 for all

compositions of syngas. Figures 16 and 17 illustrate the CO conversion obtained in the carbonation reactor of the CLP for different syngas feed compositions. It can be seen that the CO conversion is enhanced in the presence of CaO in the CLP in comparison to the conventional WGS reactor. It can be seen that greater than 95% CO conversion can be obtained for syngas from all the gasifiers by operating in the temperature range of 550 to 650 °C. Although greater CO conversions can be obtained at temperatures lower than 550 °C, the kinetics of the WGS reaction and CO₂ removal by CaO will decrease, resulting in the need for the use of larger reactors.

Figure 14. Effect of temperature on equilibrium CO conversion in the WGS reactor at S:C of 1.

Figure 15. Effect of temperature on equilibrium CO conversion in the WGS reactor at S:C of 3.

Figure 16. Effect of temperature on equilibrium CO conversion in the presence of CaO in the carbonator of the CLP at a S:C of 1.

Figure 17. Effect of temperature on equilibrium CO conversion in the presence of CaO in the carbonator of the CLP at a S:C of 3.

Figures 18 and 19 illustrate the purity of H_2 produced by the carbonator in the CLP at S:C of 1 and 3. High H_2 purities can be obtained at both S:C of 3 and 1 in all gasifiers where O_2 is used as the oxidant. In the moving bed, dry gasifier, lower H_2 purities are obtained due to dilution by N_2 since air is used as the oxidant in the gasifier.

Figure 18. Effect of temperature on equilibrium H₂ purity in the presence of CaO at a S:C of 1.

Figure 19. Effect of temperature on equilibrium H₂ purity in the presence of CaO at a S:C of 3.

Figure 20 depicts the total equilibrium carbon capture obtained in the CLP at S:C of 1 and 3. The % carbon captured is defined as the total moles of carbon in the form of CO, CO₂ and CH₄ that is removed from the process gas. The % carbon captured for all syngas compositions and S:C ratios decreases with the increase in temperature. This decrease is due to the decrease in not only CO conversion but also CO₂ capture by CaO at high temperatures. It can be seen that greater than 95% carbon capture can be obtained from all the gasifiers by operating in the temperature range of 550 to 650 °C. Although greater CO conversions can be obtained at temperatures lower than 550 °C, the kinetics of the WGS reaction and CO₂ removal by CaO will decrease, resulting in the need of larger

reactors. The % carbon captured increases with the increase in S:C from 1 to 3 for all compositions of syngas.

Figure 20. Effect of temperature and S:C on the % carbon captured in the CLP using syngas from different gasifiers as the feed.

4. ENHANCED NON-CATALYTIC H₂ PRODUCTION FROM SYNGAS

In prior work conducted by OSU (Ramkumar et.al., 2008), H₂ production with contaminant removal in the presence of CaO sorbent and a WGS catalyst was investigated. The presence of the sorbent and catalyst in the carbonator results in the production of high purity H₂ with low levels of CO, CO₂ and sulfur but introduces issues and costs associated with the separation of the sorbent and catalyst prior to calcination or pretreatment of the catalyst to the active form after its deactivation in the presence of CO₂ in the calciner at high temperatures, replacement of the spent catalyst, deactivation of the catalyst in the presence of sulfur impurities (H₂S) and the use of expensive STC. In an attempt to further simplify the process, the non-catalytic CLP was investigated in this work. The feasibility of enhancing the purity of H₂ and the optimum process conditions for H₂ production in the absence of a WGS catalyst were determined.

Material and Methods

Chemicals, sorbents and gases

The HTS catalyst was procured from Sud-Chemie Inc., Louisville, KY. The HTS catalyst consists of iron (III) oxide supported on chromium oxide. CaO was obtained by calcining PCC. PCC was synthesized from calcium hydroxide (Ca(OH)₂) obtained from Fisher Scientific (Pittsburgh, PA). The high surface area PCC (BET analysis; surface area 49.2 m²/g; pore volume 0.17 cm³/g) was synthesized using a dispersant modified wet precipitation technique. The anionic dispersant used in this process was N40 V, supplied by Ciba Specialty Chemicals (Basel, Switzerland). PCC was synthesized by bubbling CO₂ through a slurry of hydrated lime. The neutralization of the positive surface charges

on the CaCO_3 nuclei by negatively charged N_4O^- molecules forms CaCO_3 particles characterized by a higher surface area/pore volume and a predominantly mesoporous structure. Details of this synthesis procedure have been reported elsewhere (Fan and Gupta, 2006). The feed gas for all the H_2 production tests was a mixture of 10% CO and 90% nitrogen (N_2).

Fixed bed reactor setup

Figure 21 shows the integrated experimental setup used for the bench scale studies of the CLP. The bench scale reactor is coupled with a set of continuous gas analyzers which detect concentrations of CO, CO_2 , H_2S , CH_4 , and H_2 in the product stream. The reactor setup is capable of handling high pressures and temperatures of up to 21 atm and 900 °C, respectively, which are representative of the conditions in a commercial syngas to H_2 system.

Figure 21. Bench-scale fixed bed reactor setup.

The mixture of gases from the cylinders is regulated and sent into the fixed bed reactor by means of mass flow controllers that can handle pressures of about 21 atm. From the mass flow controllers the reactant gases flow to the steam-generating unit. The steam-generating unit is maintained at a temperature of 200 °C and contains a packing of quartz chips which provide a large surface area of contact and mixing between the reactant gases and steam. The steam-generating unit not only facilitates the complete evaporation of the water being pumped into the steam generating unit, but it also serves to preheat the reactant gases entering the reactor. The reactor, which is heated by a tube furnace, is provided with a pressure gauge and a thermocouple to monitor the pressure and

temperature within. The reactor consists of two concentric sections: the inner section is filled with the catalyst or sorbent-catalyst mixture and the outer section provides a preheating zone for the gases before they come in contact with the bed of solids. The sorbent and catalyst loading section of the reactor is detachable, which enables easy removal and loading of the sorbent. The reactant gases leaving the reactor enter a back-pressure regulator, which builds pressure by regulating the flow rate of the gases and is capable of building pressures of up to 68.9 atm. The back-pressure regulator is very sensitive, and the pressure within the reactor can be changed quickly without any fluctuations. In addition, the back-pressure regulator is also capable of maintaining a constant pressure for a long period of time. The valve seat material of the regulator is made of PEEK, which is corrosion resistant to acidic H_2S vapors, which makes it suitable for conducting sulfur removal experiments. As shown in Figure 10, the inlet of the back-pressure regulator is connected to the reactor rod and the outlet is connected to a heat exchanger. Since the entire section of the equipment setup upstream of the back-pressure regulator will be exposed to high pressures, flexible stainless steel lines are used to withstand the pressure and the reactor is constructed from Inconel, which is resistant to corrosion due to the high pressure, high temperature steam and H_2S gas. The product gas mixture exiting the back-pressure regulator is then cooled in a heat exchanger using a chilled ethylene glycol-water mixture to condense the unconverted steam. The product gas at the exit of the heat exchanger is dried in a desiccant bed and is sent to a set of continuous analyzers capable of determining the concentrations of CO , CO_2 , H_2S , CH_4 , and H_2 in the gas stream.

WGS reaction in the presence and absence of HTS catalyst

The extent of the WGS reaction was determined at different temperatures in an empty stainless steel reactor. The reactant gases were made to flow through the empty heated reactor and were analyzed by means of continuous analyzers. The extent of the WGS reaction was also determined in the presence of the HTS catalyst obtained from Sud-Chemie. A 0.25 g portion of the catalyst was loaded into the reactor, and the pressure, temperature, and gas flow rates were adjusted for each run. The dry gas compositions at the outlet of the reactor were monitored continuously using the CO, CO₂, H₂S, CH₄, and H₂ gas analyzers. The total flow rate of the gases through the reactor was maintained a constant at 725 sccm for all the experiments, and the concentration of CO in the reaction mixture was maintained at 10.3%.

Simultaneous WGS and CO₂ removal

The combined WGS and carbonation reaction was conducted either using a catalyst-sorbent mixture or non-catalytically, using only the sorbent without the WGS catalyst. The combined experiments were conducted using a sorbent (CaO) to catalyst ratio of 10:1 by weight or only CaO sorbent. The effect of various temperatures (600, 650, and 700 °C), S:C ratios (3:1, 2:1, 1:1), and pressures (1–21 atm) was investigated. The CaCO₃ sorbent was calcined by heating the sorbent–catalyst mixture or only the sorbent to 700 °C in a stream of N₂ until the CO₂ analyzer confirmed the absence of CO₂ in the outlet stream. Multicyclic experiments were conducted in the fixed bed reactor with only CaO sorbent by alternating the carbonation and calcination steps, and switching between the above-mentioned temperatures and feed gas streams. The total flow rate of the gases

through the reactor was maintained a constant at 725 sccm for all the experiments, and the concentration of carbon monoxide (CO) in the reaction mixture was maintained at 10.3%.

Combined H_2 production with H_2S removal

To study the effect of sulfur on the CLP, 5000 ppm of H_2S was mixed with the CO, N_2 and steam being sent to the reactor. The H_2 production tests were conducted in the presence of CaO only, as described above.

Results and Discussion

Baseline WGS reaction testing

Baseline experiments in an empty stainless steel reactor and in the presence of a HTS catalyst were conducted to study the kinetics of the WGS reaction in a bench scale reactor system. A comparison of the extent of WGS reaction in the presence and absence of a catalyst gives a perspective of the feasibility of eliminating the WGS catalyst in the carbonation reactor of the CLP. Figure 22 shows the CO conversion obtained when a 10% CO and 90% N_2 feed stream is reacted with steam at different temperatures in an empty stainless steel reactor and in a stainless steel reactor with HTS catalyst at atmospheric pressure. The CO conversion in the presence of HTS catalyst was higher than in the empty reactor at temperatures lower than 800 °C. In both the presence and absence of the catalyst, the CO conversion increases with the increase in temperature due to higher kinetics of the WGS reaction. Beyond a particular optimum temperature, the CO conversion decreases with increase in temperature due to the thermodynamic

limitation of the WGS reaction. It can be seen that, as expected the CO conversion increases with increasing S:C ratio. The effects of reaction temperatures and S:C ratios on CO conversion at 21 atm, shown in Figure 23, follow the same trend as that at 1 atm. These baseline experiments show that CO conversion occurs even in the absence of a catalyst due to rapid kinetics in the temperature range of 500–750 °C which is the temperature range at which CO₂ removal occurs with CaO sorbent. Hence, this CO conversion achieved in the empty reactor can be further improved by the addition of CaO sorbent to the reaction system and removing the thermodynamic constraint of the WGS reaction.

Figure 22. Effect of reaction temperature and S:C on the conversion of CO by WGS reaction at 1 atm.

Figure 23. Effect of reaction temperature and S:C on the conversion of CO by WGS reaction at 21 atm.

WGS reaction in the presence of CaO only

The results obtained above lead to the conclusion that the WGS reaction takes place to a considerable extent even in the absence of a catalyst at relatively higher temperatures than the conventional WGS reaction. Hence, it is possible to increase the yield of H_2 from the WGS reactor by shifting the equilibrium of the reaction in the forward direction by removing the CO_2 product formed. The CO_2 formed by the WGS reaction is removed using CaO sorbent. Figure 24 shows the N_2 and steam free gas concentration at the outlet of the reactor due to the combined WGS and carbonation reaction at 600 °C and 21 atm.

High purity H_2 is produced with very low levels of CO and CO_2 during the prebreakthrough region of the curve when the CaO sorbent is active. As the CaO sorbent gets consumed, the purity of H_2 reduces and the concentration of CO and CO_2 increase in the breakthrough region of the curves. In the post-breakthrough region of the curve, CaO sorbent is completely consumed and the composition of the outlet gas is similar to the composition at the outlet of the non-catalytic WGS reaction. Figure 25 illustrates the CO conversion obtained with time for the gas compositions obtained in Figure 24. Almost complete conversion of CO is obtained in the prebreakthrough region of the curve where the combined WGS and carbonation reaction takes place.

Figure 24. Typical breakthrough curves for the production of H_2 in the presence of CaO without catalyst – outlet gas composition (mole%) – at 600 °C, 21 atm and S:C=3.

Figure 25. Typical breakthrough curves for the production of H_2 in the presence of CaO without catalyst – CO conversion – at 600 °C, 21 atm and S:C=3.

Effect of pressure and S:C

Pressure has been found to have an important role in increasing the purity of H_2 by the combined WGS and carbonation reaction in the presence of CaO sorbent. Figure 26 shows the effect of the change in pressure on CO conversion at a temperature of 650 °C and S:C ratio of 3:1. The CO conversion is found to increase with increasing pressure. At 1 atm, a clear prebreakthrough region is not obtained and a 90–95% CO conversion is obtained in the initial part of the breakthrough curve. As the pressure is increased to 4.5 atm, a prebreakthrough CO conversion of greater than 98% is observed and at a pressure of 21 atm, almost 100% CO conversion is observed in the pre-breakthrough region.

Figure 26. Effect of pressure on CO conversion obtained in the presence of CaO without catalyst at 650 °C and S:C=3.

Since pressure has been found to be an important variable, the combined effect of pressure and S:C ratio was investigated to determine conditions where the S:C ratio can be decreased without causing a large decrease in CO conversion or H₂ purity. Combined WGS and carbonation experiments were conducted in the absence of a catalyst for various S:C ratios and pressures ranging from 1 to 21 atm. When the S:C ratio is decreased from 3:1 to 1:1 at ambient pressure, the CO conversion decreases in the breakthrough curve as shown in Figure 27. At higher pressures of 11 and 21 atm, there is almost no decrease in the initial pre-breakthrough CO conversion with the decrease in

S:C ratio. As illustrated in Figure 28, the CO conversion remains at 98% to near 100% for both S:C ratios of 3:1 and 1:1. At 21 atm, a near 100% CO conversion is obtained in the pre-breakthrough curve for all S:C ratios of 3:1, 2:1, and 1:1 as shown in Figure 29. Hence, by operating the carbonation reactor at high pressures, it is possible to reduce the excess steam addition without causing a decrease in the CO conversion and corresponding H₂ purity.

Figure 27. Effect of S:C on CO conversion obtained in the presence of CaO without catalyst at 1 atm and 650 °C.

Figure 28. Effect of S:C on CO conversion obtained in the presence of CaO without catalyst at 11 atm and 650 °C.

Figure 29. Effect of S:C on CO conversion obtained in the presence of CaO without catalyst at 21 atm and 650 °C.

Effect of temperature

The effect of temperature was investigated at various S:C ratios for the combined WGS and carbonation reaction. Figures 30 and 31 illustrates the change in CO conversion obtained when the temperature is varied from 600 to 700 °C at two S:C ratios of 3:1 and 1:1 at atmospheric pressure. At both S:C ratios, it can be seen that the highest CO conversion in the prebreakthrough region is obtained at 600 °C and the CO conversion decreases with the increase in temperature due to the highly exothermic nature of the combined WGS and carbonation reaction. A reverse trend is obtained in the post-

breakthrough region where the WGS reaction occurs in the absence of both sorbent and catalyst, and its rate increases with the increase in temperature.

Figure 30. Effect of temperature on CO conversion obtained in the presence of CaO without catalyst at a S:C of 1 at 1 atm.

Figure 31. Effect of temperature on CO conversion obtained in the presence of CaO without catalyst at a S:C of 3 at 1 atm.

Effect of CO concentration in the feed gas

The effect of CO concentration in the reactant gas was investigated at a pressure of 150 psig on the CO conversion and purity of H₂ produced for the same amount of sorbent loaded. As shown in Figures 32 and 33, near 100% CO conversion and high purity H₂ was produced for both 10% and 15% CO in the feed stream. With an increase in the CO concentration, the pre-breakthrough region of the curve becomes shorter. This is due to the higher flow rate of CO₂ produced from the CO in the feed by the WGS reaction, which results in the faster conversion of the CaO bed to CaCO₃.

Figure 32. Effect of CO concentration in the feed on CO conversion in the presence of CaO without catalyst at 11 atm, 600 °C and S:C=3.

Figure 33. Effect of CO concentration in the feed on the purity of H₂ in the presence of CaO without catalyst at 11 atm, 600 °C and S:C=3.

Sorbent characterization and morphology analysis

Scanning electron microscopy (SEM) analysis was conducted on the sorbent samples to visualize the changes in the physical structure of the sorbent. PCC sorbent was examined using SEM as shown in Figure 34a. It can be seen that the surface of PCC is rough, and the structure is porous and not dense like the structure of the limestone sample observed by Abanades and Alvarez (Abanades & Alvarez, 2003). It can be clearly observed that the structure of PCC has been modified to improve the porosity by introducing mesopores in the structure using surface modifying agents. The PCC was then calcined to form PCC–CaO which was also examined under the SEM. Figure 34b is the image of a

freshly calcined sample of PCC, and it shows smaller sized clusters than the PCC precursor. The calcined sorbent is then used in the WGS reactor at atmospheric pressure to remove the CO_2 produced and to shift the equilibrium of the WGS reaction in the forward direction, thereby increasing the yield and purity of H_2 . Figure 35a shows the surface characteristics and pore structure of the PCC sorbent which has undergone carbonation during the WGS reaction at atmospheric pressure. During H_2 production, 70% conversion of CaO to CaCO_3 was obtained. It can be seen that the structure and surface of the first carbonated sample is different from the fresh PCC sample shown in Figure 34a. Elongated structures can be observed on the surface of the first carbonated sample. Figure 35b shows the surface structure for calcium sorbent which has undergone carbonation during H_2 production at 21 atm. At 21 atm, it is found that 85% conversion of CaO to CaCO_3 is obtained. It can be seen that the surface structure formed during carbonation at 21 atm is similar to that formed during carbonation at 1 atm but is denser due to the compaction at higher pressure.

Figure 34. SEM image of the (a) initial CaCO_3 sorbent (b) CaO obtained from the calcination of CaCO_3 .

Figure 35. SEM image of the sorbent at the end of the WGS and carbonation reaction in the absence of a catalyst at (a) 1 atm (b) 21 atm at 600 °C and S:C=3.

H₂ production in the presence of CaO only and a mixture of CaO and catalyst

The effect of the presence of WGS catalyst in the carbonation reactor was investigated at atmospheric pressure and a high pressure of 21 atm. Figure 36 depicts the H₂ purity obtained in the presence and absence of the catalyst at atmospheric pressure. It can be seen that the H₂ purity obtained in the presence of the catalyst is 90% while it is 70% in the absence of the catalyst. In addition, a clear pre-breakthrough region is observed in the presence of the catalyst for H₂ purity while there is almost no pre-breakthrough region in the absence of the catalyst. In contrast, at a high pressure of 21 atm, there is no difference in the purity of H₂ produced in the absence and presence of the catalyst. Almost 100% pure H₂ is produced in both cases. The same effect is observed at both S:C ratios of 3:1 and 2:1 as shown in Figure 37. Hence, although the catalyst can be eliminated without causing a decrease in H₂ purity at high pressures, the same is not true at atmospheric pressure. However, in commercial facilities, most of the H₂ production applications are typically deployed at high pressures.

Figure 36. Comparison in the product H₂ purity in the presence of CaO and the presence of CaO and catalyst mixture at 1 atm, 650 °C and S:C=1.

Figure 37. Comparison in the product H_2 purity in the presence of CaO and the presence of CaO and catalyst mixture at 21 atm and 650 °C.

Multicyclic investigation of H_2 production in the presence of CaO only

Multicyclic reaction and regeneration of the calcium sorbent was conducted to determine the effect of the number of cycles on the purity of H_2 produced in the fixed bed reactor. During the reaction step, H_2 was produced from a 10% CO/90% N_2 feed stream in the presence of CaO sorbent. The gas compositions for CO, CO_2 , H_2 , and hydrocarbons were recorded using continuous analyzers connected to a computer program. At the end of the reaction step, the sorbent was calcined at 750 °C in N_2 for the same amount of time in every cycle. Figure 38 illustrates the purity of H_2 obtained when the reaction step is conducted at a pressure of 4.5 atm for 10 cycles. The purity of H_2 in the product stream is

found to decrease with sorbent cycling from near 100% to 97% at the end of 10 cycles. In addition, it can be observed that for each additional cycle, the pre-breakthrough region is shorter than the previous one. This trend might be due to the reduction in useful porosity available for the carbonation of CaO due to sintering of the sorbent.

Figure 38. Product H₂ purity obtained over multiple reaction and regeneration cycles in the presence of CaO without catalyst at 4.5 atm at 600 °C and S:C=3.

Figure 39 illustrates the N₂ and steam free H₂ purity obtained from a 10% CO/90% N₂ feed stream in the presence of CaO sorbent at an operating pressure of 21 atm. The purity of H₂ in the pre-breakthrough region remains almost constant for 10 cycles. However, the time for which the pre-breakthrough region lasts, decreases with the increase in the cycle

number, but to a lower extent than at 4.5 atm. The shortening of the pre-breakthrough region with each progressive cycle again can be attributed to sorbent sintering.

Figure 39. Product H₂ purity obtained over multiple reaction and regeneration cycles in the presence of CaO without catalyst at 21 atm at 600 °C and S:C=3.

Enhanced H₂ production with CO₂ and sulfur capture

In the CLP, the CaO sorbent assumes the role of a multipollutant capture sorbent, in addition to enhancing the WGS reaction. Hence, the influence of various process variables such as temperature, S:C, and pressure was determined on the purity of H₂ produced and the extent of H₂S removed during the combined WGS, carbonation, and sulfidation reaction of CaO.

Effect of S:C ratio

Figures 40 and 41 illustrate the effect of varying S:C ratio on the extent of H_2S removal and the purity of H_2 produced in the combined WGS, carbonation, and sulfidation reaction. The extent of H_2S removal by the CaO sorbent was found to increase with decreasing S:C in the carbonation reactor. As shown in Figure 40, the concentration of H_2S in the product H_2 stream decreased from 100 to <1 ppm as the S:C decreased from 3:1 to 0.75:1. This decrease in H_2S concentration was due to a reduction in the inhibiting effect of steam on the reaction between H_2S and CaO . The same inference was drawn from the thermodynamic analysis shown earlier. The effect of the change in S:C on the purity of H_2 is illustrated in Figure 41. Similar to observations made earlier, at atmospheric pressure, the purity of H_2 was found to decrease with decreasing S:C in the breakthrough region of the curves.

Figure 40. Effect of S:C on the extent of H₂S removal during combined WGS, carbonation and sulfidation reaction in the presence of CaO only at 1 atm and 600 °C.

Figure 41. Effect of S:C on the purity of H₂ produced during combined WGS, carbonation and sulfidation reaction in the presence of CaO only at 1 atm and 600 °C.

Effect of temperature

Figures 42 and 43 illustrate the effect of temperature on the extent of H₂S removal through breakthrough curves and the purity of H₂ produced, respectively. A low concentration of H₂S in the order of ~10 ppm was detected in the outlet H₂ stream at temperatures ranging from 560 to 600 °C at atmospheric pressure. With an increase in the temperature above 600 °C, the H₂S concentration in the outlet was found to increase to 50 ppm at 650 °C and 90 ppm at 700 °C. The effect of temperature on the purity of H₂ is illustrated in Figure 43. The H₂ purity was found to be the highest (70%) within the temperature range of 600–650 °C. The purity of H₂ was found to decrease to 60% with a

decrease in temperature to 560 °C. A similar effect was observed with an increase in temperature to 700 °C. Hence, from Figures 42 and 43, it can be inferred that the optimum temperature of operation for simultaneous H₂ production and H₂S removal is ~ 600 °C.

Figure 42. Effect of temperature on the extent of H₂S removal during combined WGS, carbonation and sulfidation reaction in the presence of CaO at 1 atm and S:C=1.

Figure 43. Effect of temperature on the purity of H_2 produced during combined WGS, carbonation and sulfidation reaction in the presence of CaO at 1 atm and S:C=1.

Effect of pressure

Pressure has been found to be a very important variable for the non-catalytic production of high-purity H_2 at low S:C. The effect of an increase in pressure on the extent of H_2S removal and the purity of H_2 produced is illustrated in Figures 44 and 45. The concentration of H_2S in the product H_2 stream was found to decrease from 10 to <1 ppm when the pressure was increased from 1 to 21 atm. Hence, the combined effect of operating at a low S:C and high pressure resulted in the production of a H_2 stream with <1 ppm of sulfur impurities. Figure 45 illustrates the effect of an increase in pressure on the purity of H_2 produced during the combined WGS, carbonation, and sulfidation

reaction. At a temperature of 600 °C and a stoichiometric S:C, the purity of H₂ was found to increase from 70% to >99% with an increase in pressure from 1 to 21 atm. Hence, the CLP is capable of producing high-purity H₂ (>99%) with <1 ppm of sulfur impurities in it at stoichiometric S:C.

Figure 44. Effect of pressure on the extent of H₂S during combined WGS, carbonation and sulfidation reaction in the presence of CaO at 600 °C and S:C=1.

Figure 45. Effect of pressure on the purity of H₂ produced during combined WGS, carbonation and sulfidation reaction in the presence of CaO at 600 °C and S:C=1.

Sorbent characterization and morphology analysis

Scanning electron microscopy (SEM) analysis was conducted on the sorbent samples to visualize the changes in the physical structure of the sorbent. PCC sorbent was examined by SEM as shown in Figure 46a. It can be seen that the surface of PCC was rough and the structure was porous. The PCC was then calcined to form PCC-CaO, which was also examined by SEM. Figure 46b is the image of a freshly calcined sample of PCC and it shows smaller-sized clusters than were found in the PCC precursor. The calcined sorbent was then used in the carbonation reactor at atmospheric pressure to remove the CO₂ and

H₂S and shift the equilibrium of the WGS reaction in the forward direction, thereby increasing the yield and purity of H₂. Figure 46c shows the surface characteristics and pore structure of PCC sorbent that had undergone carbonation and sulfidation during the WGS reaction at atmospheric pressure. It can be seen that the structure and surface of the first carbonated sample was different from that of the fresh PCC sample shown in Figure 46a. Elongated structures can be observed on the surface of the first carbonated sample. Figure 46d shows the surface structure of calcium sorbent that had undergone carbonation and sulfidation during H₂ production at 21 atm. It can be seen that the surface structure formed during carbonation at 21 atm was similar to that formed during carbonation at 1 atm but denser because of compaction at the higher pressure.

Figure 46. SEM image of the (a) initial CaCO_3 sorbent; (b) CaO sorbent obtained from the calcination of CaCO_3 ; (c) sorbent at the end of the WGS, carbonation and sulfidation reaction at 1 atm (600 °C, S:C=1); (d) sorbent at the end of the WGS, carbonation and sulfidation reaction at 21 atm (600 °C, S:C=1).

HCl and COS removal using CaO

In the CLP carbonator, CaO reacts simultaneously with CO_2 , H_2S , HCl and COS . Comprehensive investigations of co-capture of CO_2 and H_2S with simultaneous H_2 production have been performed in the fixed bed reactor as described in this section. For the reactions of CaO with COS and HCl , the experiments have been performed in the TGA.

Study of the removal of COS by CaO

The capture of COS using different calcium-based sorbents was tested in the TGA. PCC, Ca(OH)_2 and limestone were used in these tests. The calcination of the samples was carried out in N_2 at 700 °C. A constant COS concentration of 20 ppm was maintained for all tests, with N_2 as the carrier gas. The total flow rate of the gas was 120 ml/min in each case and the reaction time was 20 minutes. COS capture using CaO was studied at temperatures of 400, 500, 600 and 700 °C.

The reactions occurring in the TGA during the calcination step and reaction step are shown below:

The reactivity of the sorbent for COS capture is represented by its weight % capture which is the grams of COS captured per gram of the CaO –

Weight % Capture (C_t):

$$C_t = (W_t - W_0) / W_0 * 100$$

W_t : weight of sample at time t;

W_0 : weight of calcined sample;

In general, for all the sorbents in the temperature range of 400 to 700 °C, the wt% capture was found to be fairly linear with time. For limestone and Ca(OH)_2 , the wt% capture of COS was found to decrease with the increase in temperature, in the range of 400 to 700 °C as shown in Figures 47 and 48 respectively. The wt% capture of COS with PCC was also found to increase with temperature although the capture at 400 and 500 °C was

found to be almost equal as shown in Figure 49. Among the three sorbents, PCC was found to have the highest wt% capture at all temperatures, at the end of the reaction time of 20 minutes as shown in Figure 50.

Figure 47. Wt% capture of COS for Ca(OH)₂.

Figure 48. Wt% capture of COS for limestone.

Figure 49. Wt% capture of COS for PCC.

Figure 50. Comparison of wt% capture of COS on all three sorbents at the end of 20 minutes.

Study of HCl capture by CaO

The capture of HCl using CaO obtained from different precursors was also investigated and the results are presented here. The chloridation reaction is as follows:

The chloridation reaction rate is defined as follows:

$$R = \frac{dC_t}{dt} (\%/ \text{min})$$

On the basis of the definitions of these two parameters, a larger R refers to a faster reaction rate. The weight capture rates reported in this study are initial reaction rates at the early stage of chloridation (0–120 min), when the weight increase is approximately linear.

Effect of chloridation temperature

The performances of limestone-CaO and PCC-CaO were also tested toward HCl capture using the TGA. External mass transfer resistance was minimized by placing the tested samples in a thin layer in the TGA quartz sample holder. Limestone-CaO and PCC-CaO were obtained by calcining limestone and PCC at 700 °C under N₂, respectively. Introduction of HCl immediately followed the completion of calcination. Effect of temperature on chloridation reaction rate was investigated at four representative temperatures: 500, 550, 600, and 650 °C, which is shown in Figure 51. As can be seen from Figure 51, the fastest HCl capture rate for both sorbents occurs at 550 °C. Similar results were reported in some previous studies. A reasonable explanation to the decrease of HCl capture rate above this optimal temperature is that, as chloridation temperature

elevates further above 550 °C, the increase of HCl absorption by CaO is offset by the faster increase of HCl desorption from the CaCl_2 . At each given chloridation temperature, PCC-CaO has higher capture capacity than limestone-CaO. The reason of the enhanced performance of this specially tailored PCC-CaO sorbent can be explained by its more favorable morphology.

Figure 51. Effect of chloridation temperature on the chloridation reaction rates of limestone-CaO and PCC-CaO sorbents (HCl concentration: 1500 ppm; particle size: below 180 μm).

Effects of HCl concentration and sorbent particle size

The effects of HCl concentration and sorbent particle size on the chloridation reaction rate were tested on the PCC-CaO sorbent. As to the effect of HCl concentration, three HCl concentrations (25 ppm, 500 ppm, and 1500 ppm) were obtained by mixing a 3000 ppm HCl stream and a pure N₂ stream at three different ratios. The effect of HCl concentration is given in Figure 52. Figure 52 indicates that at higher the HCl concentrations the chloridation reaction of PCC-CaO.

Figure 52. Effect of HCl concentration on the chloridation reaction rate of PCC-CaO (particle size: below 180 μm).

In addition, PCC solid was ground and screened into three size ranges: below 180 μm , 180–250 μm , and above 250 μm . At each given temperature shown in Figure 53, the chloridation reaction rate of PCC-CaO sorbent decreases as the particle size increases. This property can be explained by the fact that a smaller particle has a relatively larger surface area and pore volume, which leads to faster chloridation reaction rate.

Figure 53. Effect of PCC particle size on the chloridation reaction rate of PCC-CaO (HCl concentration: 1500 ppm).

Since the Ca:C in the CLP carbonator would be maintained such that 90% or greater CO_2 removal can be achieved, it is expected that complete removal of other impurities like

HCl, H₂S and COS would occur in the carbonator. This is because the concentration of these contaminants – HCl, H₂S and COS – in the syngas is in the ppm range as compared to higher concentrations of CO₂. The experiments to show simultaneous CO₂ and H₂S capture have been performed in the fixed bed reactor and based on the TGA results shown here, the same can be extended to HCl and COS.

5. DESIGN AND OPERATION OF SUB-PILOT SCALE CLP CARBONATOR

As discussed in the previous sections, the CLP has been thoroughly investigated at lab- and bench-scale for H₂ production from syngas. Based on the results obtained, a sub-pilot scale carbonator was constructed to demonstrate the process. The design of the sub-pilot scale unit is based on the thermodynamic, kinetic and sorbent reactivity studies detailed in the previous sections. In this section, the design of this unit is described followed by a discussion of the experimental results. A reaction kinetics based model has been setup to predict the performance (H₂ purity) of the sub-pilot scale reactor at conditions which could not be actually investigated due to safety and hardware limitations. Finally, the results obtained from different sources – lab and bench-scale, sub-pilot scale and the model – have been compared.

Description of the sub-pilot scale CLP carbonator

The CLP comprises three reactors – carbonator, calciner and hydrator. The detailed design of the sub-pilot scale carbonator is provided as follows. The existing setup does not include the calciner and the hydrator.

The sub-pilot scale CLP carbonator is a fluidized bed reactor designed for once-through testing. Figure 54 provides the detailed design of this reactor. The riser section of the reactor is 11.5' in height and 4" I.D. It is mainly composed of 4 identical flanged sections. A 3-dimensional view of one such section has also been provided in Figure 54. Each section has ports for measuring temperature and pressure, and for drawing product gas for analyses. The entire assembly has been constructed using SS 304. To achieve the

desired operating temperature, high-temperature ceramic heaters (OMEGA Engineering, Inc.) are used along the length of the riser. Appropriate ceramic wool insulation has been provided to minimize heat losses. Multiple Type K thermocouples monitor the temperature of the riser. These thermocouples also provide feedback to the ceramic heaters so that the desired operating temperature is achieved and maintained throughout the experiment. The feedback process control loop has been programmed in LabVIEW (National Instruments, Inc.). Figure 55 provides a snapshot of the reactor.

Figure 54. Schematic of the sub-pilot scale CLP carbonator at OSU.

The calcium sorbent is continuously delivered to the reactor using a Schenck-Accurate mid-range volumetric hopper and screw feeder. The rpm of the motor-driven screw decides the solids feed rate and it is kept constant throughout the experiment. The solid

feeding section also consists of two pneumatically-operated gate valves, which open and close alternately and thus, imitate a double dump valve. This action prevents the gas entering the reactor from escaping through the solids feeding section. The opening and closing sequence of the valves has also been programmed in LabVIEW and the time intervals in the sequence can be specified by the operator. The screw feeder feeds the sorbent in the stand pipe containing these valves. An inclined section then carries the solids into the reactor.

Figure 55. Snapshot of the sub-pilot scale CLP carbonator at OSU.

A gas mixing panel (shown in Figure 56), designed and constructed by Swagelok Company, is used to deliver the reactant gases to the reactor. The gas mixing panel

consists of independent mass flow controllers (MFCs) (Brooks Instruments) for CO, H₂, CO₂ and N₂. The MFCs are controlled using a dedicated digital read-out box. The mixing panel has been provided with a manual ball valve and pneumatically-operated diaphragm valve for each gas. Gas cylinders are used to supply the gases to the gas mixing panel. For the flammable gases – H₂ and CO – the gas cylinders are stored in gas cabinets (Air Liquide) provided with independent ventilation. Automatic switchover valves (Scott Specialty Gases) have been installed for each gas to enable cylinder changeover during an experiment. For the safety of the operators, flash arrestors, check valves and maximum flow limit shut-off valves have been installed in the gas lines.

Figure 56. Assembly of the gas mixing panel. (Reproduced by permission from Swagelok Company).

The gaseous mixture delivered by the gas mixing panel is preheated to a suitable temperature before injecting into the reactor. The gas preheater is a stainless steel helical coil (~25' length, ~0.6" I.D.) surrounded by a high temperature ceramic heater. Two such preheaters are used in series. The preheated gas is then mixed with steam, produced using a combination of high precision Optos 3HM water pump (Eldex Laboratories) and HGA-S steam generator (Micropyretics Heaters International). The steam generator is capable of producing steam up to a maximum temperature of 500 °C. The steam-gas mixture then enters the reactor through a sintered hastelloy plate. The sintered plate is porous enough to allow minimum pressure drop across it; however, it has suitable strength to support the weight of the solids in the reactor.

A slipstream of the gas exiting the reactor is drawn through one of the gas sampling ports provided on the riser. The gas sampling port contains a 2-micron Swagelok in-line filter to prevent the solids from entering the gas analysis equipment – micro-GC (Varian). An independent diaphragm micro-pump (KNF Neuberger) has been installed to pull the sample gas from the port. The pump allows sample gas in excess of 1 l/min to be delivered to the micro-GC. Prior to entering the micro-GC, the product gas is passed through a desiccant bed (anhydrous calcium sulfate) to remove the moisture. The gas-solid mixture from the reactor is diluted with air before it enters the Donaldson Torit downflow baghouse. The air dilution cools the exit gas to a suitable temperature for the baghouse and also maintains the gas composition outside the explosion limits. The solid-free gas from the exit of the baghouse is vented out of the facility. The reacted solids are recovered from the baghouse for analysis.

Experimental Methods

Chemicals

Pure gases – CO, CO₂ and H₂ – supplied by Praxair were used to simulate a syngas mixture for all the tests. Nitrogen (N₂) was used as the carrier gas. Since large volumetric flowrates of N₂ were required, liquid N₂ dewars were used as the source of gaseous N₂. High purity helium and argon were used as carrier gases in the micro-GC. The calibration of the micro-GC was conducted using certified standard gases – 9.5% CO, 3% CO₂ and 5% H₂. Compressed air, available at the facility, was used to dilute the vent gas.

The sorbent used in all the tests was commercial-grade, high-calcium Ca(OH)₂, obtained from Graymont Inc. The manufacturer-specified composition of the sorbent and other sorbent characteristics have been provided elsewhere (Wang et.al., 2010). In prior research conducted at OSU, extensive studies have been performed on naturally-occurring and synthetically modified CaO precursors (Gupta and Fan, 2002; Iyer et.al., 2004). Precipitated Calcium Carbonate (PCC) was identified to be a superior sorbent as compared to naturally available precursors like limestone and dolomite. The performance of PCC was found to be better because of a predominantly mesoporous structure in the 5-20 nm range with larger surface area and pore volume. Based on these results, it was proposed that PCC would be used as the CaO-precursor in the experiments to be performed as a part of this project. However, subsequent investigation performed at laboratory- and pilot-scale reactors (Wang et.al., 2010) revealed that PCC may not be the best sorbent for the following reasons –

1. When subjected to high temperature calcination ($>900\text{ C}$), it was found that the decay in reactivity of PCC-CaO was similar to naturally occurring precursors. Though earlier studies had pointed out that PCC-CaO would exhibit robust performance over multiple cycles, these studies were conducted at milder calcination conditions (700 C in $100\%\text{ N}_2$).
2. Compared to the cost of natural calcium sorbents ($\$20\text{-}30/\text{ton}$), PCC was very expensive ($>\$100/\text{ton}$).

Further work conducted at OSU investigated the use of a reactivation step – CaO hydration – to restore the reactivity of CaO and enable good CO_2 capture over multiple cycles. It was found that if an intermediate hydration step was incorporated into the traditional carbonation-calcination process, high CO_2 capture capacity of the sorbent could be maintained over multiple cycles. The effectiveness of hydration was believed to be independent of CaO precursor and hence in the experiments performed in the sub-pilot scale reactor, commercially available hydrated lime (procured from Graymont Inc.) was used as the CaO precursor. However, as detailed earlier, all investigations performed in the fixed bed reactor utilized PCC-CaO.

Operating Procedures

The reactor was heated to the operating temperature and maintained at that temperature. The feed gas to the reactor was also preheated to the same temperature. During preheating, only N_2 was flowed through the reactor. Once the desired temperatures were attained, the reactive component (CO or CO , CO_2 and H_2 mixture) was introduced in the feed gas and the sorbent was injected using the screw feeder. The product gas was

analyzed using the micro-GC. Prior to each experimental run, the micro-GC was calibrated using certified standard gases. Based on the results obtained from the bench-scale tests, all the experiments in the current work were conducted at 600 °C. The pressure in all the experiments was 1 atm.

At the completion of every experimental run, solids from the baghouse were collected and analyzed using a thermogravimetric analyzer (TGA). The data obtained from the micro-GC was also analyzed. The data obtained from gas analyses was in good agreement with the data obtained from the solids analyses.

Results and Discussion

Effect of calcium to carbon mol ratio (Ca:C)

The Ca:C, which quantifies the calcium loading in the carbonator, was investigated and Figure 57 shows the results. Two Ca:C – 1.5 and 2.3 – were used. The Ca:C is calculated based on the carbon entering the feed gas. For Ca:C investigation, the experiments were performed using CO, and hence the ratio of moles of Ca(OH)_2 to moles of CO is the Ca:C. Since both the molar flowrates were kept constant throughout the experiment, the Ca:C at the inlet to the reactor is constant. Similarly, in experiments in which the feed gas contained both CO and CO_2 (section 3.4), the Ca:C was calculated as the ratio of moles of Ca(OH)_2 to combined moles of CO and CO_2 .

Figure 57. Effect of Ca:C on CO conversion.

The selection of Ca:C was based on the results obtained in prior work conducted at OSU (Wang et.al., 2010). In this work, the effect of Ca:C was investigated on the extent of CO₂ removal from a coal combustion flue gas and it was found that the CO₂ removal achieved is a strong function of Ca:C. For e.g. using Ca(OH)₂, it was found that 50% CO₂ removal is possible at Ca:C ~0.7 and for 90% and 100% CO₂ removal, the Ca:C required is ~1.3 and ~1.6, respectively. To validate these prior results in the CLP carbonator, the effect of Ca:C was investigated on CO₂ capture alone and the results are shown in Figure

58. The new data points are represented by the green squares and it can be seen that they fit fairly well with the previous data (Wang et.al., 2010).

Figure 58. Effect of Ca:C on %CO₂ removal. Original figure adapted from Wang et.al., 2010. Green squares represent the data points obtained from testing in the CLP carbonator.

In the present work, to begin with, a Ca:C of 1.3 was chosen, which meant that if all the CO sent to the carbonator got converted via the WGS reaction, then 90% of the CO₂ produced would be captured. However, from the fixed bed tests conducted earlier, it was shown that a CO conversion of 70% could be achieved at 600 °C and 1 atm. Moreover, this conversion was recorded during the initial period of the fixed bed experiment, when the Ca:C is practically infinite, making it the maximum conversion possible. (For a fixed bed experiment, where breakthrough curves are obtained for gas conversion, a parameter

like Ca:C cannot be calculated. Nonetheless, since all the sorbent is fresh when the experiment begins, the Ca:C can be said to be infinite.) Hence it was expected that CO conversion would never exceed 70%. Assuming 70% CO conversion is achieved, the effective operating Ca:C in the reactor would exceed 1.6, which is sufficient to achieve 100% CO₂ capture.

Although the design Ca:C was set at 1.3, the calculation of the actual Ca:C ‘delivered’ to the reactor was performed post-experiment. This is because of the variability introduced during the operation of the solids feeder. As stated earlier, the screw feeder is a volumetric-based feeder and prior to each experiment, the feeder was calibrated for mass-based solids feedrate. However, during the course of the experiment, this feedrate (being a function of the bulk density of the solids) can fluctuate due to the way the solids ‘pack’ themselves in the storage hopper, etc. Hence, at the end of each experiment, the mass of the sorbent left in the hopper was found out and subtracted from the initial amount of sorbent fed to the hopper. The difference is equal to the mass of the sorbent delivered to the reactor over the duration of the experiment. Knowing the duration of the experiment, the actual (average) sorbent feedrate can be calculated which leads to a slightly different value of Ca:C. When Ca:C was set at 1.3 and 2, post-experiment calculations indicated that the actual inlet Ca:C during the experiment was 1.5 and 2.3, respectively.

From Figure 57, it can be seen that a change in Ca:C did not significantly alter CO conversion. In both cases, approximately 45-50% CO conversion was achieved. However, results from the tests conducted previously at OSU indicate that the CO₂

removal achieved is a strong function of Ca:C (Wang et.al., 2010). Since CO₂ capture drives the equilibrium-limited WGS reaction in the CLP carbonator, it is reasonable to expect a similar trend here – higher the Ca:C, higher the CO conversion. Since such a trend was not observed, it is hypothesized that for the given scale of operation, the difference between the two Ca:C that were selected for investigation, is not large enough to significantly affect CO conversion. 100% CO₂ capture was, however, observed in all the experiments that were conducted. Figure 57 also shows that the CO conversion is low initially and then increases as the experiment progresses, ultimately reaching a steady value. The initial low conversion is mainly due to the large response-time of the micro-GC toward CO. The start-up of the experiment, where the system is essentially in an unsteady-state, also contributes to this profile. A similar profile was observed in all the experiments. For the case where Ca:C of 2.3 was used, sudden drop in conversion can be observed at 20 and 40 minutes. This was due to the clogging of the gas sampling line by the sorbent. The sample gas flow to the micro-GC was momentarily suspended for cleaning of the line which affected the concentration of CO.

Another phenomenon which is believed to have hampered the CO conversion in the experiments was the contact of ‘cold’ solids with hot gas. As stated earlier, the current design of this system allows for once-through testing only. Thus, the solids which were fed to the reactor were at room temperature while the preheated gas was fed at operating temperature (600 °C). At the point of contact of the gas and the solid sorbent, a temperature drop is inevitable. Lower temperatures will lead to poor kinetics, especially for the carbonation reaction. Since the carbonation reaction is expected to drive the WGS

reaction, this ultimately affects the final conversion of CO. If this phenomenon is significantly more important, then the Ca:C will cease to have a bearing on the final CO conversion.

If a significantly higher Ca:C (5 to 10 or higher) would have been used, a higher CO conversion may have been possible. However, these experiments were not performed for two reasons. First, from the point of view of the overall process, a higher Ca:C will increase the solids circulation among the different units of the CLP, leading to less attractive process economics and other solids handling and waste disposal issues. As a result, there exists a trade-off between superior performance in the carbonator and the overall feasibility of the CLP. Second, as outlined above, the current experimental setup posed some unavoidable limitations and hence future work is expected to overcome them so that more accurate conclusions can be drawn.

Effect of steam to carbon mol ratio (S:C)

As described earlier, ‘excess steam’ could be added to the reactor using a water pump-steam generator combination. Hence, to investigate the effect of S:C, experimental results of two runs – with and without excess steam – were compared. The calculation of the S:C was based on the total steam available for the reaction including the steam resulting from the dehydration of Ca(OH)_2 . E.g. when the Ca:C was maintained at 1.5 and 1.5 moles of excess steam was supplied per mole of C fed to the reactor, the overall S:C was 3. In absence of the excess steam, the overall S:C was the same as Ca:C (=1.5).

The effect of S:C on H_2 purity is shown in Figure 59. When no excess steam was supplied and dehydration of $Ca(OH)_2$ was the only source of steam for the WGS reaction, a H_2 purity of 37% was obtained. The H_2 purity increased to 49% when excess steam was supplied to the carbonator. This result is expected as per Le Chatelier's principle – increase in the concentration of one of more reactants drives the reaction in the forward direction. Replicate runs were conducted which confirmed the reproducibility of these results (Figure 60).

Figure 59. Effect of S:C on H_2 purity in the product gas (Ca:C = 1.5).

Figure 60. Replicate runs – Ca:C = 1.5, S:C = 3.

Figure 57, which shows the effect of Ca:C on CO conversion also inherently represents the effect of S:C on CO conversion and hence, H₂ purity. In Figure 57, the S:C is equal to the Ca:C in each case. But unlike Figure 59, no significant difference in CO conversion is observed. Comparing results from Figures 57 and 59, it can be hypothesized that the enhancement provided by externally supplied steam is superior to the one provided by increasing the supply of steam via increment in the moles of Ca(OH)₂. The externally supplied excess steam is readily available for the WGS reaction while in the other scenario, Ca(OH)₂ has to decompose to provide the steam in-situ. When the steam is

readily available, it is likely to be well distributed through out the reactor and cause a more pronounced effect on the forward reaction.

Carbon formation via Boudouard reaction

In addition to enhancing the product H₂ purity, the presence of excess steam also aided in suppressing the Boudouard reaction. In the Boudouard reaction, CO cracks to form CO₂ and carbon (C), as follows –

This reaction is thermodynamically feasible in the operating conditions used in the CLP carbonator in this work. The occurrence of the above reaction is undesirable for the CLP because it results in loss of the reactant CO. In the absence of Boudouard reaction, a one-to-one ratio exists between the moles of CO reacted and the moles of H₂ produced.

It is difficult to accurately quantify the extent of the Boudouard reaction because the product CO₂ gets captured by the calcium sorbent and the C is left behind in the reactor, mainly as a deposition on the reactor walls. The difference in total CO conversion and CO converted to H₂, as obtained from the micro-GC data, provided an indication of the extent of the Boudouard reaction. In the case where excess steam was supplied to the reactor, the difference between the two conversions was found to be negligible. However, approximately 15% of the CO that was converted did not result in the production of H₂ when no excess steam was supplied. Figure 61 presents the comparison between the sorbent that was fed in the reactor and the sorbent that was recovered from the walls of

the reactor after the experiment was completed. The difference is clearly visible – the sorbent in Figure 61(b) is discolored due to the C formed during the experiment. It is believed that the presence of more steam favors the occurrence of the WGS reaction over the Boudouard reaction.

Figure 61(a). Sorbent fed to the reactor – $\text{Ca}(\text{OH})_2$.

Figure 61(b). Solids recovered from the reactor wall after the completion of the experiment.

Testing with Syngas-like Mixture

For the parametric investigations discussed in the preceding sections, the experiments were conducted with only CO as the reactive component in the feed gas. Experiments using the major syngas constituents – CO, CO₂ and H₂ – in the feed gas were also

performed. The result from one such experiment is shown in Figure 62. The composition of the feed gas used in this experiment is provided in Table 4. This composition is based on a typical syngas composition derived from a GE entrained flow gasifier (DOE, 2010). The S:CO was maintained at 3, due to which the overall S:C reduced to ~2.2. The overall S:C is lower in this case because the C contributed by CO₂ is also considered in the calculation.

Table 4. Composition of the feed gas used in the experiment with syngas-like mixture.

Gas	Vol%	N ₂ -free vol%
CO	6.5	42.8
H ₂	6.17	40.7
CO ₂	2.5	16.5
N ₂	balance	-

Figure 62. Product gas composition for test conducted with syngas-like mixture (S:C = 3, Ca:C = 1.5).

As can be seen from Figure 62, the final product contained only H₂ and CO. All the CO₂ – the one supplied in the feed and the one generated in-situ – was captured. On a N₂-free and steam-free basis, the product was found to contain ~70% H₂ and balance CO. Based on the data obtained from the micro-GC, it was found that the CO conversion was 50%, which is similar to the conversion observed in the tests conducted using CO only. Theoretically, all other conditions remaining the same, presence of H₂ and CO₂ in the feed should lower the CO conversion by Le Chatelier's principle. However, since such an effect was not observed, it can be concluded that the presence of a CO₂ acceptor helps to overcome this limitation.

Challenges during the operation of the sub-pilot scale reactor

Following difficulties were encountered during operation:

Limitation of the gas preheater

The gas preheater currently in use has been designed in-house at OSU. It was found that the maximum achievable temperature of the preheated gas was highly dependent on the gas flow rate itself. As a result, conducting tests using lower gas flowrates/velocities (higher gas residence times) became difficult since suitable temperatures could not be attained by the preheated gas. It was also found that the preheater required ~5-6 hours to preheat the gas from room temperature to 600 °C.

Temperature drop

It was found that there was a substantial temperature drop due to the contact of the cold solids with the preheated gas. Since the system has been designed only for once-through testing, the solids coming into the reactor are at ambient temperature and the specific heat of solids combined with the endothermic dehydration of Ca(OH)_2 causes the temperatures to drop significantly in the zone where the solids get injected. The lower temperatures are likely to lead to inferior kinetics of the carbonation of the calcium sorbent, affecting the overall WGS reaction conversion.

Operating regime of the reactor

Though majority of Ca(OH)_2 , which is a fine powder, was expected to fully entrain at the operating conditions, it was found that there was agglomeration of the fines which led to a solids build up in the reactor over time.

Reaction Kinetics-based Model to Predict CLP Carbonator Performance

The CLP carbonator test facility, as described earlier, posed some unavoidable limitations due to which certain operating conditions could not be investigated. Primary among them was the effect of providing additional residence time for the gas-solid reaction. In the results presented above, a constant gas residence time (henceforth referred to as 'X') was employed at which 50% H₂ purity could be achieved when the carbonator was operated at 600 C with Ca:C = 1.5 and S:C = 3. The residence time X was of the order of seconds. It is believed that if greater residence times were provided for the gas-solid reaction, for same conditions, higher H₂ purities could be achieved. Since the height of the carbonator is fixed, actual experiments could not be performed to test this hypothesis. Hence, a reaction kinetics-based model was developed to predict the CLP carbonator performance and give an indication of the enhancement in H₂ purity that could be possible for larger residence times.

Model setup

As mentioned earlier, the model was based purely on the reaction kinetics. Existing models for the WGS and carbonation reactions were obtained from literature (Corella et.al., 2005; Lee, 2004). The mass balance equations were setup in the form ordinary differential equations (ODEs) and solved simultaneously using MATLAB (ode23t solver). The reaction conditions used in the model were identical to the actual experimental conditions. The model was designed such that it was sensitive to the following parameters:

- Temperature (T)

- S:C
- Ca:C
- Voidage – gas volume fraction (ϵ)
- Initial CO concentration
- Residence time (t)

Model Assumptions

The model made the following simplifying assumptions –

- Gas and solids both in plug flow
- Complete radial mixing and negligible axial mixing
- Gas velocity = solids velocity (entrained flow mode)
- Negligible heat and mass transfer limitations
- Constant volume fraction of solids along the height of the riser (ϵ constant)
- Constant temperature
- Dehydration of Ca(OH)_2 was assumed to be instantaneous
- Only two reactions considered – WGS and carbonation of CaO
- Enhancement factor ‘q’ to account for underestimation of CO_2 capture rate by the selected carbonation kinetic model

Kinetic equations

WGS reaction (Corella et.al., 2005)

$$r_{\text{WGS}} = k_1 \left([\text{CO}][\text{H}_2\text{O}] - \frac{[\text{CO}_2][\text{H}_2]}{K_w} \right)$$

where,

$$k_1 = 10^6 \exp\left(\frac{-6370}{T}\right)$$

$$K_w = 520 \exp\left(\frac{-7230}{T}\right)$$

Carbonation of CaO (Lee, 2004)

$$r_{\text{CO}_2} = \frac{1}{M_{\text{CaO}}} \left(\frac{dX}{dt} \right)$$

where,

$$\frac{dX}{dt} = k \left(1 - \frac{X}{X_u} \right)^2$$

X_u = ultimate conversion

Mass balances

The following equations represent the ODEs that were solved simultaneously in MATLAB –

$$\frac{d[\text{CO}]}{dt} = -r_{\text{WGS}}$$

$$\frac{d[\text{H}_2\text{O}]}{dt} = -r_{\text{WGS}}$$

$$\frac{d[\text{H}_2]}{dt} = r_{\text{WGS}}$$

$$\frac{d[\text{CO}_2]}{dt} = r_{\text{WGS}} - c \frac{1}{M_{\text{CaO}}} \frac{dX}{dt}$$

$$\frac{dX}{dt} = k \left(1 - \frac{X}{X_u} \right)^2$$

$$c = [\text{CO}] \times (\text{Ca:C}) \times (\text{S:C}) \times q$$

q = enhancement factor (dimensionless)

Results and discussion

Figures 63 and 64 show the results of the kinetic model.

Figure 63. Comparison of experimental and model results (Ca:C = 1.5, T = 600 °C, P = 1 atm).

Figure 64. Effect of residence time on H₂ purity achieved in the CLP carbonator as predicted by the model (S:C = 3, Ca:C = 1.5, T = 600 °C, P = 1 atm).

From Figure 63, it can be seen that model predicts the experimental results fairly well. The differences could be due to the underestimation of the CO₂ removal by the calcium sorbent, which is accounted for by the enhancement factor. The value of ϵ was set at 0.9, which represents a dilute solid phase. From Figure 64, it can be concluded that higher residence times could help achieve greater H₂ purities. For a residence time of 3X, ~70% purity H₂ could be produced.

As discussed in the section 4, a maximum H₂ purity of ~70% was observed at 600 °C and 1 atm, when the experiments were performed in the fixed bed reactor. Hence, future investigations need to focus on higher residence times in the carbonator to match the fixed bed reactor results.

6. TECHNO-ECONOMIC ANALYSIS

As part of this project, CONSOL Energy Inc. (CONSOL) completed a comprehensive techno-economic evaluation to forecast the performance and cost of the CLP at commercial scale. The details of this evaluation are provided in Attachment 1 and summarized here.

The techno-economic evaluation considered application of the CLP to three different advanced energy systems: (1) an oxygen-blown coal gasification plant for high-purity hydrogen production (“coal-to-hydrogen case”), (2) a steam methane reforming plant for high-purity hydrogen production (“SMR case”), and (3) an oxygen-blown, coal-based integrated gasification-combined cycle plant for electricity production (“IGCC case”). For each case, the technical performance and cost of a plant using the CLP (“CLP plant”) were compared with the technical performance and cost of a plant using conventional WGS and acid gas removal technologies (“base plant”). All base and CLP plants were designed for $\geq 90\%$ CO₂ capture. Cost and performance results for the base coal-to-hydrogen and SMR plants were taken from Cases 2-1 and 1-1, respectively, in the U.S. Department of Energy report titled *Assessment of Hydrogen Production with CO₂ Capture Volume 1: Baseline State-of-the-Art Plants*.¹ Cost and performance results for the IGCC plant with CO₂ capture were taken from Case 2 in the U.S. DOE report titled *Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity*.² Cost and performance results for the CLP plants were developed by CONSOL using Aspen Plus[®] and spreadsheet-based models. Each CLP plant was sized to use the same gasifiers or reformer used in the corresponding base

plant. A common design basis was used for all of the base and CLP plants, including specifications for the coal (Illinois No. 6 containing 2.51% sulfur, 11,666 Btu/lb higher heating value (HHV) as received), natural gas (22,792 Btu/lb HHV), hydrogen product ($\geq 99.9\%$ purity, ≥ 315 psia delivery pressure), and CO₂ product (dehydrated and compressed to 2,215 psia). The process economics for all plants also were evaluated using a consistent methodology and common assumptions. All costs were estimated as “overnight” costs expressed in 2007 dollars. Capital costs were estimated as total overnight costs, which include bare erected costs, engineering and home office costs, process and project contingencies, and owner’s costs. Fixed operating and maintenance (O&M) costs were approximated using common cost estimating practices, and variable O&M costs were computed using consistent unit price assumptions and assuming capacity factors of 90% for the coal-to-hydrogen and SMR plants and 80% for the IGCC plants. The prices for coal and natural gas were assumed to be \$1.64/mmBtu and \$6.55/mmBtu, respectively. The economic performance of the base and CLP plants was compared on the basis of the first-year cost of hydrogen (COH) and first-year cost of electricity (COE). The first-year capital charge factors used to compute these costs were derived based on each plant’s product mix and expected capital expenditure period. For the CLP coal-to-hydrogen and SMR plants, which co-produce significant amounts of hydrogen and electricity, any economic advantage was distributed equally between the hydrogen and electric power products, such that the changes in COH and COE relative to the base plant were equivalent on a percentage basis.

The techno-economic evaluation led to the following principal conclusions:

- The CLP has the potential to reduce the cost of producing H₂ and electricity in a carbon constrained world, when compared with conventional approaches based on coal gasification and natural gas reforming. In each of the coal-to-hydrogen, SMR, and IGCC cases evaluated in this report, use of the CLP results in a 9-12% reduction in the cost of hydrogen or cost of electricity when compared with the use of conventional CO₂ capture and WGS technologies. Application of the CLP to a coal gasification or SMR plant essentially amounts to integrating the base plant and a pulverized coal power plant (i.e., the coal-fired calciner in the CLP) around a common CO₂ capture technology. The synergies arising from this integration, coupled with the availability of high-quality heat from the calcium sorbent-based CO₂ capture process, result in the observed economic advantage for the CLP plant.
- Application of the CLP to a hydrogen production plant necessarily results in substantial co-production of electricity. The economic advantage afforded by the CLP is only realized if the large amount of high-quality heat produced in the process is recovered to raise steam for electricity generation. This heat arises from the combustion of additional coal in the CLP calciner (which results in significantly greater heat input and fuel costs in the CLP plant than in the base plant) and from the exothermicity of the CO₂ absorption, water-gas shift, and hydration reactions, which are carried out at high temperature (i.e., $\geq 500^{\circ}\text{C}$) in the CLP. Process simulations show that a 26,000 kg H₂/h coal-to-hydrogen plant using the CLP will co-produce about 320 MW_e of net electric power, and a 26,000 kg H₂/h SMR plant using the CLP will co-produce about 190 MW_e of net electric power. By contrast, an identically-sized coal-to-hydrogen plant using conventional CO₂ capture technology generates

only about 7 MW_e of net electric power, and an identically-sized SMR plant using conventional CO₂ capture technology consumes more than 30 MW_e of electric power.

- Although the CLP can reduce the cost of producing hydrogen from coal, the lowest-cost route to H₂ production with CO₂ capture is achieved by applying the CLP (with a coal-fired calciner) to a steam methane reforming plant. The CLP is capable of achieving a greater-than 10% reduction in the cost of producing high-purity hydrogen from coal with $\geq 90\%$ CO₂ capture, when compared with conventional CO₂ capture and WGS technologies. However, for assumed coal and natural gas prices of \$1.64/mmBtu and \$6.55/mmBtu, respectively, the first-year COH for a CLP-based coal-to-hydrogen plant (\$2.77/kg H₂) is still significantly greater than the first-year COH for an SMR plant equipped with conventional CO₂ capture technology (\$2.20/kg H₂). Application of the CLP to an SMR plant results in a first-year COH of <\$2.00/kg H₂. The economic advantage afforded by the CLP SMR plant over the conventional SMR plant with CO₂ capture grows from 9% to 12% if the assumed natural gas price is reduced to \$4.00/mmBtu, which is more consistent with actual prices as of the writing of this report.
- Additional research is required to resolve technical uncertainties related to the commercial application of the CLP technology. In particular, work should be conducted to evaluate sulfur chemistry in the oxyfuel calciner, develop and demonstrate the high-temperature hydrator with internal heat recovery, evaluate the carbonator performance at a larger scale and wider range of operating conditions, evaluate cyclone performance with very high solids loadings and small particle sizes, and demonstrate solids handling in the integrated process at a relevant scale. This

work would enable further refinements in the performance and economic estimates presented in this report.

- Improvements in air separation technology could help to improve the technical and cost performance of the CLP. The flash calciner in the CLP uses oxy-fired, pulverized coal burners and, therefore, consumes a substantial amount of high-purity O₂. In each of the three cases studied in this report, the calciner ASU accounts for 15-27% of the capital cost for CLP process equipment and a large portion of the energy penalty associated with the CLP. Hence, the successful commercialization of advanced air separation technologies such as ion transport membranes, which show potential for reducing both the capital cost and parasitic power requirement for air separation, would widen the advantage afforded by the CLP over conventional pre-combustion CO₂ capture technologies.
- Several additional process configurations, including an air-blown IGCC plant equipped with the CLP and a CLP-based SMR plant that integrates the reformer and carbonator into a single reactor vessel, should be evaluated to better understand the potential benefits afforded by the CLP, but this is beyond the scope of this project.

7. CONCLUSIONS AND RECOMMENDATIONS

Summary

This work shows the ability of the CLP to enhance H_2 yield and purity produced from syngas, on the basis of experiments conducted on lab-, bench-, and subpilot-scale reactors. The CLP provides a single non-catalytic step to

- capture CO_2 ,
- remove other impurities like H_2S , COS , HCl etc., and
- simultaneously produce high purity H_2 at stoichiometric S:C.

The purity of H_2 achieved in the CLP carbonator depends on the operating pressure (70% H_2 at 1atm, >95% H_2 at 3 atm). Independent investigation (discussed in section A of the Appendix) of intermediate steam hydration has shown that the CO_2 capture capacity of CaO can be maintained over many cycles. This distinguishes CLP from other processes which utilize the traditional CaO - $CaCO_3$ loop.

The CLP carbonator was scaled to a sub-pilot unit and operated on a once through basis. Although the maximum H_2 purity (at atmospheric pressure) achieved in the sub-pilot scale carbonator (~50%) was lower than that achieved at bench-scale (~70%), it is believed that this difference can be minimized if certain existing hardware limitations are overcome.

Techno-economic analyses for integration of the CLP in a coal-to- H_2 plant, IGCC plant and SMR plant show that CLP has the potential to reduce the cost of H_2 and electricity production as compared to conventional processes.

Recommendations for future work

Based on the results obtained from this work, further research can be performed to develop the CLP as well as to validate certain assumptions used in the analysis of the process. Following are some of the important tests that need to be conducted –

1. As predicted by the kinetic model, higher H₂ purity may be achievable for larger gas residence times. Hence, larger residence times need to be investigated in the sub-pilot scale carbonator to determine the maximum H₂ purity that can be obtained.
2. Experiments with a simulated gas mixture that is closer to syngas need to be performed. Most experiments in the current work were performed using 9% CO, which is substantially lower than the CO encountered in syngas obtained from actual gasifiers.
3. Longer duration runs need to be conducted in the sub-pilot scale carbonator to investigate system stability over a larger period of time.
4. Laboratory tests to investigate the effect of CaSO₄ (produced in the calciner) on H₂ production need to be performed as also the evaluation of the sulfur chemistry in an oxyfuel calciner.
5. The tests conducted in the bench-scale fixed bed reactor indicate that 100% co-capture of all unwanted species – CO₂, H₂S, HCl, COS – will occur in the CLP carbonator. However, a test in which all these components are co-fed to the carbonator has not been performed. Such a test can also be performed to validate previous results.

Besides the above stated experimental work, the Aspen models can be constantly updated based on new data obtained at OSU as well as upcoming improvements in other technologies.

References

- Abanades, J. C.; Alvarez, D. Conversion Limits in the Reaction of CO₂ with Lime. *Energy and Fuels*. 2003, 17, 308-315.
- Abanades et.al. Cost Structure of a Postcombustion CO₂ Capture System Using CaO. *Environ. Sci. Technol.* **2007**, 41, 5523-5527.
- Andrus, H. E.; Burns, G.; Chiu, J. H.; Liljedahl, G. N.; Stromberg, P. T.; Thibeault, P. R. Hybrid Combustion-Gasification Chemical Looping Coal Power Technology Development. ALSTOM Technical Report for Project DE-FC26-03Nt41866. 2006
- Bhatia, S. K.; Perlmutter, D. D. Effect of the product later on kinetics of the CO₂-lime reaction. *AIChE J.* **1983**, 29, 79-86.
- Chung, T.-S.; Shao, L.; Tin, P. S. Surface Modification of Polyimide Membranes by Diamines for H₂ and CO₂ Separation. *Macromolecular Rapid Communication*, 2006, 27, 998-1003.
- Curran, G. P.; Fink, C. E.; Gorin, E. CO₂ Acceptor Gasification Process – Studies of Acceptor Properties. *Advances in Chemistry Series*. 1967, 69, 141-165.
- Corella, J.; Sanz, A. *Fuel Proc. Technol.* **2005**, 86, 1021-1053.
- De Diego, L. F.; Garcia-Labiano, F.; Adanez, J.; Palacios, J. M. Factors Affecting the H₂S Reaction with Noncalcined Limestones and Half-Calcined Dolomites. *Energy Fuels*. 1999, 3, 146.
- De Diego, L. F.; Abad, A.; Garcia-Labiano, F.; Adanez, J.; Gayan, P.; Simultaneous calcination and sulfidation of calcium based sorbents. *Ind. Eng. Chem. Res.* 2004, 42, 3261-3269.
- Dou, B.; Gao, J; Sha, X. A study on the reaction kinetics of HCl removal using high temperature coal gas. *Fuel Processing Technology* **2001**, 72, 23-33.
- EIA, 2009. International Energy Outlook 2009. Washington, D.C.: U.S. Department of Energy, Report DOE/EIA-0484 (2009).
- Fan, L.-S.; Ramkumar, S.; Wang, W.; Statnick, R. Separation of Carbon Dioxide from Gas Mixtures by Calcium Based Reaction Separation Process. The Ohio State University, USA. Provisional Patent Application No. 61/116,172, 2008.
- Fenouil, L. A.; Towler, G. P.; Lynn, S. Removal of H₂S from Coal Gas Using Limestone: Kinetic considerations. *Ind. Eng. Chem. Res.* 1994, 33, 265.

- Gupta, H.; Fan, L.-S. Carbonation-Calcination Cycle Using High Reactivity Calcium Oxide for Carbon Dioxide Separation from Flue Gas. *Ind. Eng. Chem. Res.* 2002, 41, 4035-4042.
- Haussinger, P.; Lohmuller, R.; Watson, A. M. (2000). "Hydrogen" Ullmann's Encyclopedia of Industrial Chemistry. Wiley-VCH Verlag GmbH and Co. KGaA.
- Hiller et.al. Gas Production. In: M. Bohnet et.al., Editors, Ullmann's Encyclopedia of Industrial Chemistry, Online Edition, Wiley-VCH Verlag, Weinheim (2007).
- Holt, N.A.H. Gasification & IGCC – design, issues & opportunities, Proceeding of GCEP Advanced Coal Workshop Provo. 2005.
- Hughes, R. W.; Lu, D.; Anthony, E. J.; Wu, Y. Improved Long-Term Conversion of Limestone-Derived Sorbents for In Situ Capture of CO₂ in a Fluidized Bed Combustor *Ind. Eng. Chem. Res.* **2004**, 43, 5529-5539.
- Iyer, M. V.; Gupta, H.; Sakadjian, B. B.; Fan, L.-S. Multicyclic Study on the Simultaneous Carbonation and Sulfation of High-Reactivity CaO. *Ind. Eng. Res. Chem.* 2004, 43, 3939-3947.
- Jazbec, M.; Sendt, K.; Haynes, B. S. Kinetic and thermodynamic analysis of the fate of sulphur compounds in gasification products. *Fuel*. 2004, 83, 2133-2138.
- Koji, K.; Shinji, F.; Atsuko, S. S.; Yoshizo, S.; Hiroyuki, H.; Lin, S.-Y.; Michiaki, H.; Takayuki, T. Repetitive Carbonation-Calcination Reactions of Ca-based Sorbents for Efficient CO₂ Sorption at Elevated Temperatures and Pressures. *Ind. Eng. Chem. Res.* 2003, 42, 975-981.
- Kreutz, T. G.; Williams, R. H.; Socolow, R. H.; Chiesa, P.; Lozza, G. Production of Hydrogen and Electricity from Coal with CO₂ Capture. Sixth Greenhouse Gas Control Technologies Conference, Kyoto, Japan, 2002.
- Lee, D. K. *Chem. Eng. J.* **2004**, 100, 71-77.
- Li, M.; Shaw, H. Reaction Kinetics of Hydrogen Chloride with Calcium Oxide by Fourier Transform Infrared Spectroscopy. *Ind. Eng. Chem. Res.* **2000**, 39, 1898-1902.
- Li, Y.; Zhao, C.; Qu, C.; Duan, L.; Li, Q.; Liang, C. CO₂ Capture Using CaO Modified with Ethanol/Water Solution during Cyclic Calcination/Carbonation *Chem. Eng. Technol.* **2008**, 31, 237-244.
- Lin, S. Y.; Harada, M.; Suzuki, Y.; Hatano, H. Process Analysis for Hydrogen Production by Reaction Integrated Novel Gasification (HyPr-RING). *Energy Conversion and Management*. 2005, 46(6), 869-880.

- Loyd, L.; Ridler, D. E.; Twigg, M. V. The water gas shift reaction. In: M.V. Twigg, Editor, *Catalyst Handbook* (Second Edition), Manson Publishing Ltd, London (1996).
- Lu, H.; Reddy, E. P.; Smirniotis, P. G. Calcium Oxide Based Sorbents for Capture of Carbon Dioxide at High Temperatures. *Ind. Eng. Chem. Res.* **2006**, 45, 3944-3949.
- Ma, D.; Lund, C. R. F. Assessing High-Temperature Water Gas Shift Membrane Reactors. *Ind. Eng. Chem. Res.* 2003, 42, 711-717.
- MIT, “The Future of Coal: Options for a Carbon-Constrained World”, 2007.
- Manovic, V.; Anthony, E. J. Thermal activation of CaO-based sorbent and self-reactivation during CO₂ capture looping cycles. *Environ. Sci. Technol.* **2008**, 42, 4170-4174.
- Ramkumar, S.; Iyer, M.; Wong, D.; Gupta, H.; Sakadjian, B.; Fan, L.-S. Enhanced Hydrogen Production Integrated with CO₂ separation in a Single-Stage Reactor – Final Technical Report, 2008. DOE Contract No. DE-FC26-03NT41853.
- Ramkumar et.al. Calcium Looping Process for Clean Fossil Fuel Conversion. Proceedings of the 1st Meeting of the High Temperature Solid Looping Cycles Network, Oviedo, Spain, September 15-17, 2009.
- Ramkumar, S.; Iyer, M. V.; Fan, L.-S. Calcium Looping Process (CLP) for enhanced, catalytic hydrogen production with integrated carbon dioxide and sulfur capture. *Ind. Eng. Res. Chem.* 2011, 50, 1716-1729.
- Rizeq, R. G.; Lyon, R. K. Zamansky, V. M.; Das, K. Fuel-flexible AGC technology for production of H₂, power, and sequestration-ready CO₂. Proceedings of the International Technical Conference on Coal Utilization & Fuel Systems. 2001.
- Roark, S. E.; Mackay, R.; Sammells, A. F. Hydrogen Separation Membranes for Vision 21 Energy Plants. Proceedings of the International Technical Conference on Coal Utilization & Fuel Systems. 2002, 27 (Vol. 1), 101-112.
- Romeo, L. M.; Lara, Y.; Lisbona, P.; Escosa, J. M. Optimizing make-up flow in a CO₂ capture system using CaO. *Chem. Eng. J.* 2009, 147, 252-258.
- Ross, H. U. Physical Chemistry Part I: Thermodynamics in Direct Reduced Iron-technology and economics of production and use; Stephenson, R. L.; Smailer, R. M., Eds.; The Iron & Steel Society of AIME: Warrendale, PA, 1980.

- Salvador, C.; Lu, D.; Anthony, E. J.; Abanades, J. C. Enhancement of CaO for CO₂ capture in an FBC environment. *Chem. Eng. J.* 2003, 96, 187-195.
- Squires, A. M. Cyclic Use of Calcined Dolomite to Desulfurize Fuels Undergoing Gasification. *Advances in Chemistry Series.* 1967, 69, 205-209.
- Stultz, S. C.; Kitto, J. B. Babcock & Wilcox Company. *Steam, Its Generation and Use.* 40th edition, 1992.
- Sun, P.; Lim, J.; Grace, J. R. Cyclic CO₂ Capture by Limestone-Derived Sorbent During Prolonged Calcination/Carbonation Cycling. *AIChE J.* 2008, 54, 1668-1677.
- Sun, Z.; Yu, F.; Li, F.; Li, S.; Fan, L.-S. Experimental Study of HCl Capture Using CaO Sorbents: Activation, Deactivation, Reactivation, and Ionic Transfer Mechanism. *Ind. Eng. Chem. Res.* **2011**, 44, 6034-6043.
- U. S Department of Energy – National Energy Technology Laboratory *Assessment of Hydrogen Production with CO₂ Capture Volume 1: Baseline State-of-the Art Plants* DOE/NETL-2010/1434.
- Wang, W.; Ramkumar, S.; Wong, D.; Fan, L.-S. Simulations and Process Analysis of the Carbonation-Calcination Reaction Process with Intermediate Hydration. *Fuel* **2011**, doi:10.1016/j.fuel.2011.06.059
- Weineu, C.; Jensen, P. *Ind. Eng. Chem. Res.* **1992**, 31, 164.
- Westmoreland, P.; Gibson, J. Harrison, D. Comparative Kinetics of High Temperature Reaction Between H₂S and Selected Metal Oxides. *Environ. Sci. Technol.* **1977**, 11, 488-491.
- Yang, R.; Chen, J. Kinetics of Desulfurization of Hot Fuel Gas with Calcium Oxide. Reaction between Carbonyl Sulfide and Calcium Oxide. *Environ. Sci. Technol.* **1979**, 13, 549-553.
- Zeman, F. Effect of steam hydration on performance of lime sorbent for CO₂ capture *International Journal of Greenhouse Gas Control* **2008**, 2, 203-209.
- Ziock, H.-J; Lackner, K.-S.; Harrison, D. P. Zero Emission Coal Power, a New Concept. 2001.

Attachment 1

Techno-Economic Analysis of the Calcium Looping Process
(Detailed Report by CONSOL Energy Inc.)

TECHNO-ECONOMIC ANALYSIS OF THE CALCIUM LOOPING PROCESS

**Final Report of Work Performed
July 5, 2007 – July 31, 2011**

***Principal Author*
Daniel P. Connell**

October 2011

**U.S. Department of Energy Cooperative Agreement
DE-FC26-07NT43059
Tasks 8.1-8.5**

**CONSOL Energy Inc.
Research & Development
4000 Brownsville Road
South Park, PA 15129**

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

ABSTRACT

Calcium oxide (CaO) sorbents are well suited for capturing carbon dioxide (CO₂) in a variety of applications involving both fuel gas and flue gas streams. The exothermic absorption of CO₂ by CaO, when carried out at high temperature (e.g., 550-700°C), produces high-quality heat that can be used to raise steam for electricity generation. Sorbent regeneration also occurs at high temperature (>850°C), in a coal or gas-fired calciner, yielding additional recoverable heat. The availability of high-quality heat reduces the energy penalty associated with CO₂ capture and differentiates CaO sorbents from conventional chemical or physical solvent technologies, which operate at comparatively low temperatures and produce little useful heat. Calcium oxide also absorbs sulfur and halide impurities at the process operating conditions, enabling it to be used for multi-pollutant control.

One promising application of calcium oxide sorbents is the Calcium Looping Process (CLP) for high-purity hydrogen production from synthesis gas. The process integrates CO₂, sulfur, and halide removal with the water-gas shift (WGS) reaction in a single-stage reactor. The continual removal of CO₂ from the synthesis gas by the calcium sorbent drives the water-gas shift reaction forward via Le Chatelier's principle, obviating the need for WGS catalyst. Lab-scale experiments have shown that the CLP can produce >99% pure hydrogen with less than 1 ppm sulfur impurity in the presence of a low steam-to-carbon ratio and with no WGS catalyst. Experiments also have demonstrated that steam hydration of the calcium oxide sorbent upstream of the hydrogen production reactor (after the calciner) enables its activity to be maintained over multiple carbonation-calcination cycles, improving the performance of the process.

The Ohio State University recently completed a four-year research project aimed at lab-scale development of the Calcium Looping Process to facilitate CO₂ capture during the production of hydrogen from coal. The project was funded by the U.S. Department of Energy, through its National Energy Technology Laboratory, under Cooperative Agreement No. DE-FC26-07NT43059. As part of the project, CONSOL Energy Inc. (CONSOL) completed a comprehensive techno-economic evaluation to forecast the performance and cost of the CLP at commercial scale.

This report summarizes the results of CONSOL's techno-economic evaluation. The evaluation considered application of the Calcium Looping Process to several different advanced energy systems, including a coal-to-hydrogen plant, an integrated gasification-combined cycle plant, and a steam methane reforming plant, all with ≥90% CO₂ capture. Differences in the design strategy for these applications are discussed, and process simulation results and economics for the CLP plants are compared with those for similar plants that use commercially available water-gas shift and acid gas removal technologies. Results indicate that the CLP has the potential to reduce the cost of producing hydrogen and electricity with CO₂ capture by 9-12% when compared with the conventional technologies, and they indicate a logical path for further research and development of the process.

TABLE OF CONTENTS

1.	EXECUTIVE SUMMARY	1
2.	INTRODUCTION	3
3.	METHODOLOGY	6
3.1	Process Modeling	7
3.2	Economic Analysis	12
3.2.1	Capital Costs	12
3.2.2	Fixed Operating and Maintenance Costs	13
3.2.3	Variable Operating and Maintenance Costs	14
3.2.4	Project Financing and Process Economics	15
4.	RESULTS	17
4.1	Coal-to-Hydrogen Case	18
4.1.1	Process Design	18
4.1.2	Process Simulation Results	23
4.1.3	Process Economics	25
4.2	Steam Methane Reforming Case	30
4.2.1	Process Design	30
4.2.2	Process Simulation Results	37
4.2.3	Process Economics	38
4.3	Integrated Gasification-Combined Cycle Case	44
4.3.1	Process Design	44
4.3.2	Process Simulation Results	46
4.3.3	Process Economics	51
5.	DISCUSSION	56
5.1	Technical Performance of the Calcium Looping Process	56
5.2	Economic Performance of the Calcium Looping Process	60
5.3	Other Potential Applications and Process Configurations	64
6.	CONCLUSIONS	67
	REFERENCES	70
	ACRONYMS AND ABBREVIATIONS	72
	CHEMICAL SYMBOLS	75

LIST OF FIGURES

Figure 1. General process concept for the Calcium Looping Process (U.S. Patent Application No. 61/116, 172; Patent Application WO2008039783).....	5
Figure 2. Block flow diagram for the base coal-to-hydrogen plant.....	18
Figure 3. Block flow diagram for the CLP coal-to-hydrogen plant.....	19
Figure 4. Process flow diagram for the Calcium Looping Process in the coal-to-hydrogen case.....	20
Figure 5. Block flow diagram for the base SMR plant.....	31
Figure 6. Block flow diagram for the CLP SMR plant.....	32
Figure 7. Process flow diagram for the Calcium Looping Process in the SMR case.....	33
Figure 8. Block flow diagram for the base IGCC plant.....	45
Figure 9. Block flow diagram for the CLP IGCC plant.....	46
Figure 10. Process flow diagram for the Calcium Looping Process in the IGCC case.....	47
Figure 11. Block flow diagram for a conceptual air-blown IGCC plant using the CLP.....	66
Figure 12. Conceptual process flow diagram for the Calcium Looping Process as applied for post-combustion CO ₂ capture in an air-blown IGCC plant.	67

LIST OF TABLES

Table 1. Design criteria for the base and CLP coal-to-hydrogen plants.....	7
Table 2. Design criteria for the base and CLP SMR plants.....	8
Table 3. Design criteria for the base and CLP IGCC plants.....	9
Table 4. Specification for design coal (Illinois No. 6).....	10
Table 5. Specification for design natural gas.....	10
Table 6. Composition of design limestone.....	11
Table 7. Methodology and assumptions for estimating owner's costs.	13
Table 8. Methodology and assumptions for estimating fixed operating and maintenance costs.	14
Table 9. Unit price assumptions for variable O&M cost calculations.	14
Table 10. Global economic assumptions used to calculate COH and COE.	16
Table 11. Finance structure for high-risk hydrogen projects.	16
Table 12. Finance structure for high-risk electric power projects (investor owned utility).	16
Table 13. Capital charge factors used to calculate the COH or COE for each of the plants evaluated in this report.	17
Table 14. Stream table for the Calcium Looping Process in the coal-to-hydrogen case.	21
Table 15. Summary of process performance results (at full load) for the coal-to-hydrogen case.....	24
Table 16. Total Plant Cost estimates for the coal-to-hydrogen case.	26
Table 17. Owner's cost and TOC estimates for the coal-to-hydrogen case.....	28
Table 18. Estimated annual fixed O&M costs for the coal-to-hydrogen case.	29
Table 19. Estimated annual variable O&M costs for the coal-to-hydrogen case.	29
Table 20. First-year cost of hydrogen estimates for the coal-to-hydrogen case.	30
Table 21. Stream table for the Calcium Looping Process in the SMR case.	34
Table 22. Summary of process performance results (at full load) for the SMR case.....	38
Table 23. Total Plant Cost estimates for the SMR case.....	39
Table 24. Owner's cost and TOC estimates for the SMR case.....	41
Table 25. Estimated annual fixed O&M costs for the SMR case.....	42
Table 26. Estimated annual variable O&M costs for the SMR case.	43

Table 27. First-year cost of hydrogen estimates for the SMR case.	44
Table 28. Stream table for the Calcium Looping Process in the IGCC case.	48
Table 29. Summary of process performance results for the IGCC case.....	50
Table 30. Total Plant Cost estimates for the IGCC case.....	52
Table 31. Owner's cost and TOC estimates for the IGCC case.....	54
Table 32. Estimated annual fixed O&M costs for the IGCC case.....	55
Table 33. Estimated annual variable O&M costs for the IGCC case.	55
Table 34. First-year cost of electricity estimates for the IGCC case.	56
Table 35. Summary of technical performance results for the base and CLP plants in each of the coal-to-hydrogen, IGCC, and SMR cases. For each case, the CLP and base plants were designed using the same gasifier/reformer, gasifier/reformer fuel feed rate and composition, and CO ₂ and H ₂ product specifications, as detailed in the text.	57
Table 36. Comparison of the efficiency of the CLP IGCC plant with the efficiencies of the base IGCC plant, a base subcritical PC plant, and a hypothetical base plant including IGCC and PC components in the same ratio as the CLP plant. All plants include ≥90% CO ₂ capture and compression. CO ₂ capture is accomplished using a Selexol system in the base IGCC cases and an MEA scrubbing system in the base PC cases.....	57
Table 37. Summary of economic analysis results for the coal-to-hydrogen and SMR cases.	60
Table 38. Summary of economic analysis results for the IGCC case.	61
Table 39. Effect of project finance structure on economic analysis results for the coal-to-hydrogen case.....	62
Table 40. Effect of project finance structure on economic analysis results for the SMR case.....	62
Table 41. Sensitivity analysis results for the coal-to-hydrogen, SMR, and IGCC cases.....	63

1. Executive Summary

The Ohio State University (OSU) is developing the Calcium Looping Process (CLP) to reduce the cost of capturing CO₂ during the production of hydrogen and electricity from coal and other fuels. The CLP integrates CO₂, sulfur, and halide removal with the water-gas shift (WGS) reaction in a single-stage reactor. In the process, a regenerable calcium oxide sorbent is used to chemically absorb CO₂, sulfur, and halide impurities from the syngas during the production of hydrogen. The removal of CO₂ drives the water-gas shift reaction forward via Le Chatelier's principle, obviating the need for WGS catalyst and enabling the production of high-purity hydrogen. The process operates at high temperature (e.g., 550-700°C), allowing the exothermic heat of the CO₂ absorption and water-gas shift reactions to be recovered for use in generating steam. This reduces the energy penalty associated with CO₂ capture. The spent sorbent is heated in a coal-fueled, oxy-fired calciner to regenerate CaO for reuse in the process and to release a concentrated CO₂ stream, which can be dried and sequestered. The regenerated sorbent is reactivated in a high-temperature hydrator, to improve the recyclability of the sorbent, before being reintroduced into the hydrogen production reactor (the "carbonator"). A small amount of sorbent is also purged from the system and replaced with naturally occurring limestone during each carbonation-calcination-hydration cycle to prevent the buildup of inert solids (e.g., sulfur compounds and ash) in the calcium loop. Heat recovered from the carbonator, hydrator, and calciner off-gas is used to raise steam for electricity generation.

OSU recently completed a four-year research project aimed at lab-scale development of the Calcium Looping Process to facilitate CO₂ capture during the production of hydrogen from coal. The project was funded by the U.S. Department of Energy (DOE), through its National Energy Technology Laboratory (NETL), under Cooperative Agreement No. DE-FC26-07NT43059. As part of the project, CONSOL Energy Inc. (CONSOL) completed a comprehensive techno-economic evaluation to forecast the performance and cost of the CLP at commercial scale. The details of that evaluation are summarized in this report.

The techno-economic evaluation considered application of the Calcium Looping Process to three different advanced energy systems: (1) an oxygen-blown coal gasification plant for high-purity hydrogen production ("coal-to-hydrogen case"), (2) a steam methane reforming plant for high-purity hydrogen production ("SMR case"), and (3) an oxygen-blown, coal-based integrated gasification-combined cycle plant for electricity production ("IGCC case"). For each case, the technical performance and cost of a plant using the CLP ("CLP plant") were compared with the technical performance and cost of a plant using conventional WGS and acid gas removal technologies ("base plant"). All base and CLP plants were designed for ≥90% CO₂ capture. Cost and performance results for the base coal-to-hydrogen and SMR plants were taken from Cases 2-1 and 1-1, respectively, in the U.S. Department of Energy report titled *Assessment of Hydrogen Production with CO₂ Capture Volume 1: Baseline State-of-the-Art Plants*.¹ Cost and performance results for the IGCC plant with CO₂ capture were taken from Case 2 in the U.S. DOE report titled *Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity*.² Cost and performance results for the CLP plants were developed by CONSOL using Aspen Plus® and spreadsheet-based models. Each CLP plant was sized to use the same gasifiers or reformer used in the corresponding base plant. A common design basis was used for all of the base and CLP plants, including specifications for the coal (Illinois No. 6 containing 2.51% sulfur, 11,666 Btu/lb higher heating value (HHV) as received), natural gas (22,792 Btu/lb HHV), hydrogen product (≥99.9% purity, ≥315 psia delivery pressure), and CO₂ product (dehydrated and compressed to 2,215 psia). The process economics for all plants also were evaluated using a consistent methodology and common assumptions. All costs were estimated as "overnight" costs expressed in 2007 dollars. Capital costs were estimated as total overnight costs, which include bare erected costs, engineering and home office costs, process and project contingencies, and owner's costs. Fixed operating and maintenance (O&M) costs were approximated using common cost estimating practices, and variable O&M costs were computed using consistent unit price assumptions and assuming capacity factors of 90% for the coal-to-hydrogen and SMR plants and 80% for the IGCC plants. The prices for coal and natural gas were assumed to be \$1.64/mmBtu and \$6.55/mmBtu, respectively. The economic performance of the base and CLP plants was compared on the basis of the first-year cost of hydrogen (COH) and first-year cost of electricity (COE). The first-year capital charge factors used to compute these costs were derived based on each plant's product mix and expected capital expenditure period. For the CLP coal-to-hydrogen and SMR plants, which co-produce significant amounts of hydrogen and electricity, any economic advantage was distributed equally between the

hydrogen and electric power products, such that the changes in COH and COE relative to the base plant were equivalent on a percentage basis.

The techno-economic evaluation led to the following principal conclusions:

- The Calcium Looping Process has the potential to reduce the cost of producing H₂ and electricity in a carbon constrained world, when compared with conventional approaches based on coal gasification or natural gas reforming. In each of the coal-to-hydrogen, SMR, and IGCC cases evaluated in this report, use of the CLP results in a 9-12% reduction in the cost of hydrogen or cost of electricity when compared with the use of conventional CO₂ capture and WGS technologies. Application of the CLP to a coal gasification or SMR plant essentially amounts to integrating the base plant and a pulverized coal power plant (i.e., the coal-fired calciner in the CLP) around a common CO₂ capture technology. The synergies arising from this integration, coupled with the availability of high-quality heat from the calcium sorbent-based CO₂ capture process, result in the observed economic advantage for the CLP plant.
- Application of the Calcium Looping Process to a hydrogen production plant necessarily results in substantial co-production of electricity. The economic advantage afforded by the CLP is only realized if the large amount of high-quality heat produced in the process is recovered to raise steam for electricity generation. This heat arises from the combustion of additional coal in the CLP calciner (which results in significantly greater heat input and fuel costs in the CLP plant than in the base plant) and from the exothermicity of the CO₂ absorption, water-gas shift, and hydration reactions, which are carried out at high temperature (i.e., ≥500°C) in the CLP. Process simulations show that a 26,000 kg H₂/h coal-to-hydrogen plant using the CLP will co-produce about 320 MW_e of net electric power, and a 26,000 kg H₂/h SMR plant using the CLP will co-produce about 190 MW_e of net electric power. By contrast, an identically-sized coal-to-hydrogen plant using conventional CO₂ capture technology generates only about 7 MW_e of net electric power, and an identically-sized SMR plant using conventional CO₂ capture technology consumes more than 30 MW_e of electric power.
- Although the Calcium Looping Process can reduce the cost of producing hydrogen from coal, the lowest-cost route to H₂ production with CO₂ capture is achieved by applying the CLP (with a coal-fired calciner) to a steam methane reforming plant. The CLP is capable of achieving a greater-than 10% reduction in the cost of producing high-purity hydrogen from coal with ≥90% CO₂ capture, when compared with conventional CO₂ capture and water-gas shift technologies. However, for assumed coal and natural gas prices of \$1.64/mmBtu and \$6.55/mmBtu, respectively, the first-year COH for a CLP-based coal-to-hydrogen plant (\$2.77/kg H₂) is still significantly greater than the first-year COH for an SMR plant equipped with conventional CO₂ capture technology (\$2.20/kg H₂). Application of the CLP to an SMR plant results in a first-year COH of <\$2.00/kg H₂. The economic advantage afforded by the CLP SMR plant over the conventional SMR plant with CO₂ capture grows from 9% to 12% if the assumed natural gas price is reduced to \$4.00/mmBtu, which is more consistent with actual prices as of the writing of this report.
- Additional research is required to resolve technical uncertainties related to the commercial application of the CLP technology. In particular, work should be conducted to evaluate sulfur chemistry in the oxyfuel calciner, develop and demonstrate the high-temperature hydrator with internal heat recovery, evaluate the carbonator performance at a larger scale and wider range of operating conditions, evaluate cyclone performance with very high solids loadings and small particle sizes, and demonstrate solids handling in the integrated process at a relevant scale. This work would enable further refinements in the performance and economic estimates presented in this report.
- Improvements in air separation technology could help to improve the technical and cost performance of the Calcium Looping Process. The flash calciner in the CLP uses oxy-fired, pulverized coal burners and, therefore, consumes a substantial amount of high-purity O₂. In each of the three cases studied in this report, the calciner ASU accounts for 15-27% of the capital cost for CLP process equipment and a large portion of the energy penalty associated with the CLP. Hence, the successful commercialization of advanced air separation technologies such as ion transport membranes, which show potential for reducing both the capital cost and parasitic power requirement for air separation, would widen the advantage afforded by the CLP over conventional pre-combustion CO₂ capture technologies.
- Several additional process configurations, including an air-blown IGCC plant equipped with the CLP and a CLP-based SMR plant that integrates the reformer and carbonator into a single reactor vessel, should be evaluated to better understand the potential benefits afforded by the Calcium Looping Process, but this is beyond the scope of this project.

2. Introduction

Numerous technologies are being developed to capture and sequester carbon dioxide from coal-based energy systems, so that this valuable fossil fuel resource can continue to be utilized if constraints are imposed on greenhouse gas emissions. Current technologies for capturing CO₂ from coal-derived flue and fuel gases are generally characterized by high capital costs and high parasitic power consumption. For example, application of an amine scrubbing system for post-combustion CO₂ capture from a new supercritical pulverized coal (PC) power plant may reduce the plant's net electric output by ~30% and increase its capital cost by ~80%.² Application of a physical absorption process for pre-combustion CO₂ capture from a new integrated gasification-combined cycle (IGCC) power plant may reduce the plant's net electric output by 15-25% and increase its capital cost by 35-50%.² Hence, there is a need to develop advanced technologies that can reduce the cost and energy penalty associated with capturing CO₂.

The Ohio State University (OSU) is developing several novel carbon dioxide capture technologies based on regenerable calcium sorbents. The overall goal of this work is to reduce the cost of capturing CO₂ during the production of electricity, hydrogen, and chemicals from coal and other fuels. The technologies, which include the Calcium Looping Process (CLP) for syngas applications and the Carbonation-Calciation Reaction (CCR) process for flue gas applications, use calcium oxide particles to chemically absorb CO₂ according to the following carbonation reaction:

As with most CO₂ capture processes, the CO₂ absorption reaction is exothermic, producing 178 kJ of heat per mole of CO₂ captured. The reaction can be reversed by supplying an equal amount of heat (under a different set of process conditions), thereby liberating the captured CO₂ so that it can be sequestered and regenerating the CaO sorbent for reuse in the process. However, unlike most physical and chemical absorption processes, in which CO₂ capture occurs at low temperature (i.e., <100°C) and much of the exothermic heat of absorption is wasted because of its low quality, CO₂ capture in the CLP and CCR processes occurs at high temperature (i.e., 550-700°C). As a result, the exothermic heat of the absorption reaction can be recovered to raise steam for electricity generation or process use. This offsets much of the energy required for sorbent regeneration (some energy is still lost because of process inefficiencies), reducing the energy penalty of the calcium sorbent technologies relative to conventional CO₂ capture technologies.

Regeneration of the calcium sorbent is accomplished via calcination at high temperature (i.e., >850°C). The calcination process can sinter the sorbent, significantly reducing its activity. For example, laboratory experiments showed that the activity of the CaO sorbent was reduced by approximately two-thirds after a single carbonation-calcination cycle when the calcination was carried out at 1,000°C.³ A deactivation rate of this magnitude would require very large sorbent purge and makeup rates to maintain CO₂ capture performance, compromising the economic viability of the process. However, experiments conducted by OSU also have demonstrated that hydrating the calcined sorbent (using either liquid water or steam) essentially restores its original activity, enabling it to perform effectively over many cycles. Hence, a hydration step, given by Equation 2, is included between the calcination and carbonation steps.

OSU has tested the CO₂ capture performance of Ca(OH)₂ sorbent at the sub-pilot (120 kW_t) scale using coal-derived flue gas.⁴ These tests showed that the hydrated sorbent can achieve greater than 90% CO₂ capture at a calcium-to-carbon molar ratio of 1.3. The calcium hydroxide formed by Equation 2 decomposes back to CaO and H₂O under the operating conditions for carbonation. This decomposition, which is an endothermic reaction, consumes much of the exothermic heat generated by the carbonation reaction. The efficiency of the overall process can be approximately maintained, however, if the exothermic heat of the hydrate formation reaction is recovered in the hydrator to offset this effect.

OSU recently completed a four-year research project aimed at lab-scale development of the Calcium Looping Process to facilitate carbon dioxide capture during the production of hydrogen from coal. The project was funded by the U.S. Department of Energy (DOE), through its National Energy Technology Laboratory (NETL), under Cooperative Agreement No. DE-FC26-07NT43059.

In the conventional process for producing hydrogen from coal, coal is first gasified to make syngas consisting primarily of CO, H₂, CO₂, and H₂O. The water-gas shift (WGS) reaction is then employed to generate additional hydrogen via the reaction of CO and H₂O, as shown in Equation 3.

Since the equilibrium conversion of the water-gas shift reaction moves to the left at high temperature, catalysts are used to enable the reaction to be carried out at lower temperatures (i.e., <500°C) where the equilibrium is more favorable. Finally, additional separation processes are performed to remove acid gases, including CO₂, H₂S, COS, and HCl, from the shifted syngas, producing a hydrogen product stream. These separation processes also occur at low temperatures (i.e., <50°C). The hydrogen product then can be sent to a pressure swing adsorber (PSA) to purify it for commercial sale, or it can be sent to a combined cycle power block to generate electricity (as in an integrated gasification-combined cycle power plant).

This process is attractive because the CO₂ that is removed from the shifted syngas can be geologically sequestered, enabling the production of electricity or high-purity hydrogen from coal with very low greenhouse gas emissions. In the future, this high-purity hydrogen potentially could be used in hydrogen fuel cells, which are being considered as a strategy for reducing greenhouse gas emissions from the transportation sector and small stationary sources. However, as discussed above, advanced CO₂ capture technologies with reduced costs and energy requirements are needed to make the coal-to-hydrogen process commercially viable.

The overall objective of Project DE-FC26-07NT43059 was to simplify and improve the hydrogen production process by using OSU's calcium looping scheme to integrate the water-gas shift reaction and acid gas removal into a single, high-temperature reactor (the carbonator), while eliminating the need for water-gas shift catalyst. The process concept is illustrated in Figure 1. When the water-gas shift reaction is carried out in the presence of CaO sorbent, the CaO reacts with CO₂ to form solid CaCO₃ according to Equation 1 above. The continuous removal of CO₂ from the syngas drives the water-gas shift reaction forward via Le Chatelier's principle, enabling high equilibrium conversions, even at high temperatures. This obviates the need for WGS catalyst and reduces the amount of steam required for the WGS reaction. Much or all of the required steam is provided by the dissociation of Ca(OH)₂, eliminating the need to raise process steam for this purpose. In addition to capturing CO₂, the CaO sorbent reacts with other acid

gases (i.e., H_2S , COS , and HCl) to form solid products. Most importantly, as discussed above, the carbonator operates at high temperature, enabling recovery of the exothermic heat of the acid gas absorption and water-gas shift reactions to raise steam. Laboratory experiments conducted as part of the current project showed that the CLP can produce >99% purity hydrogen with less than 1 ppm sulfur impurity when operated at 600°C and 22 bar.³ As discussed above, the solid products from the carbonator are calcined to produce a sequestrable CO_2 stream and regenerate the CaO sorbent for reuse in the process. The CaO is then reactivated in a high-temperature hydrator before being reintroduced into the carbonator. Solids purge and makeup streams are used to prevent the accumulation of inert solids (e.g., sulfided sorbent, ash, etc.) in the system. The sorbent feedstock to the process is limestone, a naturally occurring material that is widely available, relatively inexpensive, and environmentally benign.

Figure 1. General process concept for the Calcium Looping Process (U.S. Patent Application No. 61/116, 172; Patent Application WO2008039783).

OSU issued a subcontract to CONSOL Energy Inc. (CONSOL) to evaluate the projected technical and economic performance of the Calcium Looping Process at commercial scale. Techno-economic evaluations were performed periodically throughout the project period, in iterative fashion, in order to incorporate the latest results from OSU's research and provide feedback to help guide this research toward the development of commercially viable technology. Several applications of the Calcium Looping Process were considered, including its application to a coal gasification plant for high-purity hydrogen production and its application to a coal-based integrated gasification-combined cycle plant for electricity production. In addition, because most commercial hydrogen plants currently use natural gas rather than coal as a feedstock, the evaluation also considered application of the CLP to a steam methane reforming

(SMR) plant, in order to provide a basis for gauging the performance of the coal-to-hydrogen plant.

This report summarizes the final techno-economic analysis results for the coal-to-hydrogen, IGCC, and SMR cases. For each case, the technical performance and cost of a plant using the Calcium Looping Process are compared with the technical performance and cost of a plant using conventional water-gas shift and acid gas removal technologies. All cases, including both the CLP plants and the conventional plants, include $\geq 90\%$ CO₂ capture. Performance results for the CLP plants were estimated using the best process designs and experimental data available at the end of the project period. Because the Calcium Looping Process is still at a relatively early stage of development, many of the assumptions used in this evaluation are based on laboratory-scale experimental results, thermodynamic predictions, and good engineering judgment. Hence, the results presented here will likely change as the process is scaled up and additional data are developed. Nevertheless, these results provide an initial assessment of the potential for the Calcium Looping Process to reduce the cost and improve the performance of producing hydrogen and electricity from coal.

3. Methodology

As discussed in the Introduction, detailed techno-economic evaluations were performed for three cases representing three different potential applications of the Calcium Looping Process:

1. An oxygen-blown coal gasification plant for high-purity hydrogen production (“coal-to-hydrogen case”)
2. A steam methane reforming plant for high-purity hydrogen production (“SMR case”), and
3. An oxygen-blown, coal-based integrated gasification-combined cycle plant for electricity production (“IGCC case”).

For each case, the cost and technical performance of a plant using the Calcium Looping Process (“CLP plant”) were compared with the cost and technical performance of a plant using conventional water-gas shift, CO₂ capture, and gas cleanup technologies (“base plant”). The base plants were adopted from baseline systems analysis studies published by the U.S. Department of Energy. The base plants in the coal-to-hydrogen and SMR cases are represented by Cases 2-1 and 1-1, respectively, in the U.S. Department of Energy report titled *Assessment of Hydrogen Production with CO₂ Capture Volume 1: Baseline State-of-the-Art Plants*¹ (referred to hereafter as the “DOE hydrogen baseline report”). The base plant in the IGCC case is represented by Case 2 in the U.S. DOE report titled *Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity*² (referred to hereafter as the “DOE bituminous baseline report”). Unless noted otherwise, the technical and economic performance results for the base plants in this report were taken directly from these U.S. DOE systems analysis studies.

Technical and economic performance results for the CLP plants were developed by CONSOL according to the same design basis and assumptions that were used for the corresponding base plants. Care was taken to ensure that the CLP plant and base plant results are directly comparable for each case. Details of our methodology are described in the following subsections.

3.1 Process Modeling

Process modeling results for the base plants were taken directly from the U.S. DOE systems analysis studies referenced above. Results for the coal-to-hydrogen and SMR base plants were taken from Cases 2-1 and 1-1, respectively, in the DOE hydrogen baseline report,¹ and results for the IGCC base plant were taken from Case 2 in the DOE bituminous baseline report.²

The technical performance of the CLP plants was modeled by CONSOL. Each CLP plant was modeled using the same design basis as the corresponding base plant. The design criteria used for the coal-to-hydrogen, SMR, and IGCC cases are shown in Tables 1-3, respectively.

Table 1. Design criteria for the base and CLP coal-to-hydrogen plants.

Parameter	Design Basis
Plant Site	Midwestern U.S., greenfield site, 300 acres
Ambient Temperature / Pressure	15°C (59°F) / 1.0 bar (15 psia)
Gasifier Type	GE Energy slurry-fed, oxygen-blown with radiant syngas cooler
Coal Feed Rate to Gasifier	220,904 kg/h (487,011 lb/h), as received
Coal Type	Illinois No. 6
Gasifier Performance	Per DOE process model, Hydrogen Baseline report Case 2-1
Gasifier Outlet Temperature / Pressure	1,316°C / 56.2 bar (2,400°F / 815 psia)
Radiant Syngas Cooler Outlet Temperature / Pressure	677°C / 55.5 bar (1,250°F / 805 psia)
Hydrogen Recovery in PSA	80%
Hydrogen Product Purity	≥99.9%
Hydrogen Product Delivery Pressure	≥21.7 bar (≥315 psia) at plant gate
Steam Cycle Main Steam Temperature / Pressure	538°C / 125.1 bar (1,000°F / 1,815 psia)
Steam Cycle Reheat Steam Temperature	538°C (1,000°F)
CO ₂ Capture Efficiency	≥90%
CO ₂ Dehydration	Triethylene glycol system
CO ₂ Product Pressure	152.7 bar (2,215 psia)
Water Supply	Municipal (50%) / Groundwater (50%)
Cooling Water System Wet Bulb / Cold Water / Hot Water Temperatures	11°C (51.5°F) / 16°C (60°F) / 27°C (80°F)
Solid Waste Disposal	Off site
Plant Capacity Factor	90%

As indicated in these tables, each CLP plant was designed to use the same gasifier or reformer as the corresponding base plant. The coal feed rate to the gasifier was fixed at 220,904 kg/h (487,011 lb/h) for the CLP and base plants in the coal-to-hydrogen and IGCC cases. The natural gas feed rate to the reformer (not including the supplemental gas that is required for external heating of the reformer tubes) was fixed at 84,947 kg/h (187,276 lb/h) for the CLP and base plants in the SMR case. These fuel feed rates do not include the additional coal or natural gas that is required to provide heat for sorbent calcination in the CLP plants. Hence, the total

fuel input is greater in the CLP plants than in the base plants. We chose to fix the gasifier or reformer fuel input, rather than the total fuel input, in order to provide for similar hydrogen production rates among the CLP and base plants in the coal-to-hydrogen and SMR cases, and to provide for consistent sizing of key equipment items (e.g., gasifiers, reformers, combustion turbines, etc.) among the CLP and base plants in all of the cases.

Table 2. Design criteria for the base and CLP SMR plants.

Parameter	Design Basis
Plant Site	Midwestern U.S., greenfield site, 300 acres
Ambient Temperature / Pressure	15°C (59°F) / 1.0 bar (15 psia)
Reformer Type	Vertical tube, single-stage, Ni-based catalyst, externally heated
Natural Gas Feed to Reformer (Tube Side) ^a	84,947 kg/h (187,276 lb/h)
Natural Gas Feed Pressure	31.0 bar (450 psia)
Natural Gas Desulfurization	Zinc oxide guard bed
Reformer External Heat Source (Shell Side)	PSA tail gas and supplemental natural gas fired in air
Reformer Performance	Per DOE process model, Hydrogen Baseline report Case 1-1
Reformer Syngas Outlet Temperature / Pressure	866°C / 30.3 bar (1,590°F / 440 psia)
Reformer Flue Gas Outlet Temperature / Pressure	643°C / 1.1 bar (1,190°F / 16 psia)
Hydrogen Recovery in PSA	80%
Hydrogen Product Purity	≥99.9%
Hydrogen Product Delivery Pressure	≥21.7 bar (≥315 psia) at plant gate
CO ₂ Dehydration	Triethylene glycol system
CO ₂ Capture Efficiency	≥90%
CO ₂ Product Pressure	152.7 bar (2,215 psia)
Water Supply	Municipal (50%) / Groundwater (50%)
Cooling Water System Wet Bulb / Cold Water / Hot Water Temperatures	11°C (51.5°F) / 16°C (60°F) / 27°C (80°F)
Solid Waste Disposal	Off site
Plant Capacity Factor	90%

^aDoes not include supplemental gas that is combusted on the shell side of the reformer to provide heat for the endothermic reforming reactions.

All of the cases evaluated in this report were designed using a common set of specifications for coal, natural gas, hydrogen product, and CO₂ product. The design coal is an Illinois No. 6 bituminous coal with the characteristics shown in Table 4. The design natural gas specification, which is presented in Table 5, is based on the average composition of natural gas in 26 U.S. cities.⁵ The hydrogen product produced in the coal-to-hydrogen and SMR cases must be delivered at ≥99.9% purity and at least 21.7 bar (315 psia). All of the plants in this report were designed for at least 90% CO₂ capture efficiency and include CO₂ dehydration (via triethylene glycol) and compression to 152.7 bar (2,215 psia).

Table 3. Design criteria for the base and CLP IGCC plants.

Parameter	Design Basis
Plant Site	Midwestern U.S., greenfield site, 300 acres
Ambient Temperature / Pressure	15°C (59°F) / 1.0 bar (15 psia)
Gasifier Type	GE Energy slurry-fed, oxygen-blown with radiant syngas cooler
Coal Feed Rate to Gasifier	220,904 kg/h (487,011 lb/h), as received
Coal Type	Illinois No. 6
Gasifier Performance	Per DOE process model, Bituminous Baseline report Case 2
Gasifier Outlet Temperature / Pressure	1,316°C / 56.2 bar (2,400°F / 815 psia)
Radiant Syngas Cooler Outlet Temperature / Pressure	677°C / 55.5 bar (1,250°F / 805 psia)
Combustion Turbine	2x Advanced F Class (232 MW _e output each)
Steam Cycle Main Steam Temperature / Pressure	534°C / 125.1 bar (994°F / 1,815 psia)
Steam Cycle Reheat Steam Temperature	534°C (994°F)
CO ₂ Capture Efficiency	≥90%
CO ₂ Dehydration	Triethylene glycol system
CO ₂ Product Pressure	152.7 bar (2,215 psia)
Water Supply	Municipal (50%) / Groundwater (50%)
Cooling Water System Wet Bulb / Cold Water / Hot Water Temperatures	11°C (51.5°F) / 16°C (60°F) / 27°C (80°F)
Solid Waste Disposal	Off site
Plant Capacity Factor	80%

For plants that raise steam to generate electricity, the steam cycle was modeled on the basis of a commercially available advanced steam turbine with main and reheat steam temperatures of 534-538°C (994-1000°F) and a main steam pressure of 125.1 bar (1,815 psia). The IGCC plants also generate electricity using gas combustion turbines. Both the base IGCC plant and the CLP IGCC plant were designed to use two advanced F Class gas combustion turbines, with each turbine rated at 232 MW_e output.

All plants were assumed to be constructed on a 300-acre, greenfield site in the Midwestern United States, with design ambient conditions of 15°C (59°F) and 1.01325 bar (14.696 psia). It was assumed that 50% of the raw water makeup for each plant could be obtained from groundwater, with the other 50% provided by a publicly owned treatment works. The cooling water system for each plant was designed based on an ambient wet bulb temperature of 10.8°C (51.5°F), an approach of 4.7°C (8.5°F), and a cooling water range of 11.1°C (20°F). These assumptions result in cold water and hot water temperatures of 15.6°C (60°F) and 26.7°C (80°F), respectively. The solid waste generated by each plant was assumed to be transported offsite for disposal in a landfill.

A 90% capacity factor was assumed for the coal-to-hydrogen and SMR plants. This capacity factor is consistent with the availability typically achieved by commercial steam methane reforming plants.¹ (For this study, it was assumed that each plant would be dispatched at maximum capacity any time it is available). An 80% capacity was assumed for the IGCC plants, based on the rationale set forth in Section 2.5 of the DOE bituminous baseline report.² The

equipment design and sparing philosophy for each plant was developed to achieve the specified capacity factor. For example, the IGCC plants in this report include two, 50% capacity gasifier trains to achieve an 80% capacity factor, whereas the coal-to-hydrogen plants include three, 50% capacity gasifier trains (i.e., two operating trains plus one hot standby train) to achieve a 90% capacity factor.

Table 4. Specification for design coal (Illinois No. 6).

	As Received	Dry
Proximate Analysis, % w/w		
Moisture	11.12	0.00
Ash	9.70	10.91
Volatile Matter	34.99	39.37
Fixed Carbon	44.19	49.72
Total	100.00	100.00
Higher Heating Value, kJ/kg	27,133	30,506
Higher Heating Value, Btu/lb	11,666	13,126
Ultimate Analysis, % w/w		
Moisture	11.12	0.00
Carbon	63.75	71.72
Hydrogen	4.50	5.06
Nitrogen	1.25	1.41
Chlorine	0.29	0.33
Sulfur	2.51	2.82
Ash	9.70	10.91
Oxygen (by difference)	6.88	7.75
Total	100.00	100.00

Table 5. Specification for design natural gas.

Methane (CH ₄), % v/v	93.15
Ethane (C ₂ H ₆), % v/v	3.17
Propane (C ₃ H ₈), % v/v	0.69
n-Butane (C ₄ H ₁₀), % v/v	0.40
Carbon Dioxide (CO ₂), % v/v	1.29
Nitrogen (N ₂), % v/v	1.29
Higher Heating Value, kJ/kg	53,014
Higher Heating Value, Btu/lb	22,792

Material and energy balances and thermodynamic calculations for the CLP plants were performed using Aspen Plus[®] Version 7.1 software (Aspen Technology, Inc., Burlington, MA). The STEAM-TA property method (ASME 1967 steam table correlations) was used to model the steam cycle, and the RKS-BM property method (Redlich-Kwong-Soave equation of state with Boston-Mathias modifications) was used to model all other process units. Pure component properties were obtained from the PURE13, INORGANIC, and SOLIDS databanks in Aspen

Plus[®], and the HCOALGEN and DCOALIGT property models were used to calculate the enthalpy and density, respectively, of coal and ash.

Where applicable, the assumptions used to model the CLP plants were chosen to match those used in the base plants. As indicated in Tables 1-3, the gasifier and reformer performance results from the base plants were incorporated directly into the CLP plant process models. The steam cycle and combustion turbine models for the CLP plants were also tuned to mimic the models used for the base plants. Auxiliary power requirements, water requirements, and cooling loads for certain equipment items in the CLP plants were scaled directly from corresponding equipment items in the base plants.

Process operating conditions for equipment items specific to the Calcium Looping Process were selected based on OSU's experimental results and engineering considerations. The carbonators in the CLP plants were modeled using operating temperatures of 550-700°C (1022-1292°F) and a calcium-to-carbon molar ratio of 1.3:1, consistent with the optimal conditions identified by OSU in its experimental program. The entrained bed calciners in the CLP plants were designed for an exit gas temperature of $\geq 875^{\circ}\text{C}$ ($\geq 1607^{\circ}\text{F}$), based on thermodynamic considerations and input from a commercial vendor of this technology. The hydrators in the CLP plants were assumed to operate at $\sim 500^{\circ}\text{C}$ (932°F) and 2.5 bar (36.3 psia) total pressure, based on OSU's experimental results, thermodynamic considerations, and heat integration considerations.

For purposes of this techno-economic evaluation, it was assumed that all reactions proceed to thermodynamic equilibrium (i.e., the reactions are not kinetically limited at the design residence times). Chemical reactors were simulated in Aspen Plus[®] using RGibbs blocks, which simultaneously model chemical and phase equilibria by minimizing the Gibbs free energy of the reactor products, subject to atom balance constraints. Turboexpanders were modeled using an isentropic efficiency of 0.8. Cyclones were modeled assuming a particle collection efficiency of 95-99% (for multiple cyclones in series), based on the results of cold flow modeling conducted by OSU. Fabric filters and metallic filters were modeled assuming a particle collection efficiency of $\sim 100\%$. The performance of the atmospheric-pressure air separation units that supply oxygen to the entrained bed calciners in the CLP plants was based on Cases 5 and 5b in the U.S. Department of Energy report titled *Pulverized Coal Oxycombustion Power Plants Volume 1: Bituminous Coal to Electricity*.⁶ The performance of the pressure swing adsorber in each of the CLP plants was based on specifications provided by a PSA technology vendor for the CLP process conditions.

All of the CLP plants consume a substantial amount of limestone, which is used as sorbent makeup in the Calcium Looping Process. The composition of limestone varies geographically, and these variations can impact the performance of the Calcium Looping Process. (Specifically, the calcium-to-carbon molar ratio that is required to achieve a given level of CO₂ removal can vary as a function of limestone source and composition). For purposes of this evaluation, all of the CLP plants were modeled using the limestone composition shown in Table 6, which is based on a commercial specification for a quarry with access to the Midwestern U.S. market.

Table 6. Composition of design limestone.

Component	Weight Percent
Calcium Carbonate (CaCO ₃)	97.6
Magnesium Carbonate (MgCO ₃)	1.3
Other (SiO ₂ , Al ₂ O ₃ , Fe ₂ O ₃)	1.1

3.2 Economic Analysis

The commercial viability of the Calcium Looping Process ultimately depends upon its economic competitiveness with other technologies. Hence, economic analyses were completed to compare the cost of the CLP plants with the cost of the base plants for each of the coal-to-hydrogen, SMR, and IGCC cases.

The process economics for all plants were computed using a common set of assumptions, which are described in detail in the following subsections. All capital costs and operating and maintenance (O&M) costs presented in this report are “overnight” costs expressed in 2007 dollars. As discussed above, all plants are assumed to be built in a Midwest U.S. location. The process economics presented in this report include the costs associated with capturing at least 90% of the carbon dioxide produced by each plant and compressing the captured CO₂ to 2,215 psia, but they do not include any costs associated with CO₂ transport, storage, or monitoring.

3.2.1 Capital Costs

The capital cost metric used in this report is the total overnight cost (TOC), which includes the following components:

- Bare erected cost
- Costs for engineering, construction management, home office, and fees
- Process contingency
- Project contingency
- Owner's costs

The bare erected cost (BEC) consists of the direct costs for process equipment and construction materials, as well as the direct and indirect labor costs associated with the construction and installation of equipment and on-site facilities (e.g., buildings, roadways, etc). Bare erected costs for the base coal-to-hydrogen and SMR plants were taken from the DOE hydrogen baseline report,¹ and bare erected costs for the base IGCC plant were taken from the DOE bituminous baseline report.² Bare erected costs for the CLP coal-to-hydrogen, SMR, and IGCC plants were factored from these DOE baseline reports, other U.S. DOE reports, vendor quotes, literature sources, and engineering cost estimating equations. Costs were escalated or deescalated to 2007 dollars, as necessary, using the Chemical Engineering Plant Cost Index.⁷

Costs for engineering, construction management, home office, and fees were estimated as 8.6 to 12.2% of the bare erected cost of each equipment item, according to the conventions established in the DOE baseline reports.^{1,2}

Project contingencies are included in the capital cost estimate to compensate for uncertainties resulting from the limited level of project definition in this study. These contingencies are intended to cover the costs for additional equipment items, materials, and construction labor that would likely result from a more detailed plant design. Process contingencies are applied to certain equipment items to account for cost uncertainties that result from technology risks associated with the early developmental stage of those items. For the base plants in each of the coal-to-hydrogen, SMR, and IGCC cases, project and process contingencies for all

equipment items were taken from the DOE baseline reports.^{1,2} These same contingencies were also applied to any corresponding equipment items in the CLP plants. A project contingency of 20% was applied to all equipment items that are unique to the CLP plants. In addition, process contingencies were applied to unconventional or unproven CLP equipment items. These include contingencies of 25% on the carbonator, 15% on the entrained bed calciner, 30% on the hydrator, and 10% on the lockhoppers for all cases.

The Total Plant Cost (TPC) is defined as the sum of the BEC, costs for engineering, construction management, home office, and fees, and costs for process and project contingencies. The Total Overnight Cost is computed as the sum of the TPC and owner's costs. Owner's costs include preproduction costs (start-up costs), inventory capital, initial costs for catalyst and chemicals, land costs, financing costs, and other owner's costs (e.g., costs for front-end engineering and design, off-site infrastructure improvements, legal fees, permitting, owner's engineering, owner's contingency, etc.) These costs were estimated according to the same methodology used in the DOE baseline reports, which is summarized in Table 7.

Table 7. Methodology and assumptions for estimating owner's costs.

Cost Element	Basis of Estimate
Preproduction Costs	<ul style="list-style-type: none"> • 6 months of operating, maintenance, and administrative & support labor • 1 month of maintenance materials at 100% capacity factor • 1 month of non-fuel consumables at 100% capacity factor • 1 month of waste disposal at 100% capacity factor • 25% of one month's fuel cost at 100% capacity factor • 2% of TPC
Inventory Capital	<ul style="list-style-type: none"> • 0.5% of TPC for spare parts • 60-day supply of coal at 100% capacity factor • 60-day supply of non-fuel consumables at 100% capacity factor
Initial Costs for Catalyst and Chemicals	<ul style="list-style-type: none"> • Estimated for each plant based on initial catalyst/chemical fill requirements and the unit costs for these consumables
Land	<ul style="list-style-type: none"> • \$3,000/acre
Financing Cost	<ul style="list-style-type: none"> • 2.7% of TPC
Other Owner's Costs	<ul style="list-style-type: none"> • 15% of TPC

The capital costs presented in this report are consistent with an Association for the Advancement of Cost Engineering International (AACE) Class 4 estimate, which represents a feasibility study with 1 to 15% project definition. The expected accuracy range for such an estimate is -15% to +30%.

3.2.2 Fixed Operating and Maintenance Costs

Fixed operating and maintenance costs include costs for operating labor, maintenance labor and materials, administrative and support labor, property taxes, and insurance. These costs do not depend strongly on the plant's capacity factor. The fixed O&M costs for all of the plants evaluated in this report were approximated using common cost estimating practices, which are described in Table 8.

Table 8. Methodology and assumptions for estimating fixed operating and maintenance costs.

Cost Element	Basis of Estimate
Operating Labor	<ul style="list-style-type: none"> Operating labor base rate = \$34.65/h Operating labor burden = 30% of base rate 16 full-time operators
Maintenance Labor	<ul style="list-style-type: none"> 1.0% of TPC
Administrative and Support Labor	<ul style="list-style-type: none"> 25% of operating and maintenance labor
Maintenance Materials	<ul style="list-style-type: none"> 2.4% of TPC x Capacity Factor
Property Taxes and Insurance	<ul style="list-style-type: none"> 2.0% of TPC

3.2.3 Variable Operating and Maintenance Costs

Variable operating and maintenance costs include costs for fuel, consumables, waste disposal, and emissions credits, all of which are expected to vary as a function of the plant's capacity factor. The variable O&M costs for each plant were estimated based on process simulation results and the unit prices shown in Table 9.

Table 9. Unit price assumptions for variable O&M cost calculations.

Cost Element	Standard Unit	Unit Cost
Coal (delivered)	ton	\$38.19
Natural gas	mmBtu	\$6.55
Limestone (delivered)	ton	\$17.25
Water	1,000 gal	\$1.08
Water treatment chemicals	lb	\$0.17
Selexol solution	gal	\$13.40
MDEA solution	gal	\$8.70
MEA solution	lb	\$1.12
Shift catalyst	ft ³	\$498.83
Reforming catalyst	ft ³	\$440.00
Claus catalyst	ft ³	\$131.27
Carbon sorbent (mercury removal)	lb	\$1.05
CO ₂ emissions	ton	\$27.22
Solid waste disposal	ton	\$16.23
Elemental sulfur byproduct	ton	\$0.00

As indicated in the table, to account for differences in CO₂ removal performance among the various plants evaluated in this report, the net CO₂ emissions from each plant were taxed at a rate of \$30/tonne (\$27.22/ton). The delivered cost for limestone (\$17.25/ton) is based on information from a commercial supplier, assuming barge delivery and a transport distance of 150 miles. The elemental sulfur byproduct produced by the base coal-to-hydrogen and base IGCC plants was assumed to be sold for the cost of transportation, resulting in zero net cost to the plant. All other price assumptions were taken from the DOE hydrogen baseline and bituminous baseline reports.^{1,2}

Electricity is a variable operating cost (or credit) when calculating the cost of hydrogen for the coal-to-hydrogen and SMR plants. The base coal-to-hydrogen, CLP coal-to-hydrogen, and CLP SMR plants are net producers of electricity, and the base SMR plant is a net consumer of electricity. For the base coal-to-hydrogen and base SMR plants, an electricity price of \$105/MWh was used to calculate the value of electricity sold to or purchased from the grid. This assumed base price for electricity is consistent with the first-year cost of electricity for a coal-fired power plant equipped with commercially-available technology to achieve 90% CO₂ capture.² For the CLP coal-to-hydrogen and CLP SMR plants, the price of electricity was adjusted as described in Section 3.2.4 to account for any economic advantage associated with using the Calcium Looping Process instead of conventional technology.

3.2.4 Project Financing and Process Economics

The economic performance of the base and CLP plants is compared on the basis of the first-year cost of hydrogen (COH) and first-year cost of electricity (COE), expressed in dollars per kilogram of hydrogen produced and dollars per megawatt-hour of electricity produced, respectively. The first-year COH and first-year COE, which are expressed in base-year (2007) dollars, are computed according to Equations 4 and 5, respectively:

$$COH = \frac{(CCF)(TOC) + OC_{FIX} + (CF)(OC_{VAR})}{(CF)(KG)} \quad (4)$$

$$COE = \frac{(CCF)(TOC) + OC_{FIX} + (CF)(OC_{VAR})}{(CF)(MWH)} \quad (5)$$

Here, CCF is the capital charge factor; TOC is the total overnight capital cost; OC_{FIX} is the sum of all fixed O&M costs over a 1-year period; OC_{VAR} is the sum of all variable O&M costs over a 1-year period at 100 percent capacity factor; CF is the plant capacity factor; KG is the total kilograms of hydrogen that would be generated by the plant over a 1-year period at 100 percent capacity factor, and MWH is the total net megawatt-hours of electric power that would be generated by the plant over a 1-year period at 100 percent capacity factor.

The values of TOC, OC_{FIX}, and OC_{VAR} were calculated according to the methodology described in Sections 3.2.1, 3.2.2, and 3.2.3, respectively. As discussed in Section 3.1, the capacity factor is assumed to equal 90% for the coal-to-hydrogen and SMR cases and 80% for the IGCC case. The values of KG and MWH were obtained from the process simulation results for each plant.

The capital charge factors for the plants evaluated in this report were derived from the U.S. DOE Power Systems Financial Model⁸ using the economic assumptions shown in Table 10 and the finance structures shown in Tables 11-12. These assumptions are consistent with those used in the DOE hydrogen baseline and bituminous baseline reports. Because all of the plants in this report include carbon dioxide capture, which is not currently a widely-deployed technology, they all were evaluated using high-risk finance structures. As shown in Tables 11-12, different finance structures are assumed for hydrogen plants and for electric power plants. The lower cost of debt and lower required rate of return on equity for electric power plants, as compared to hydrogen plants, reflect the lower technology and commodity risk for electricity production (as opposed to hydrogen production) and the greater certainty provided by rate-based electricity tariffs (assuming the electric power plants are developed by investor owned utilities).⁹ As a result of these differences in finance structure, different CCFs were used for the

hydrogen and electric power plants evaluated in this report. The CCF is also affected by the duration of the capital expenditure (construction) period. In this report, a five-year capital expenditure period is assumed for the coal-to-hydrogen and IGCC plants, and a three-year capital expenditure period is assumed for the SMR plants.

Table 10. Global economic assumptions used to calculate COH and COE.

TAXES	
Income tax rate	38%
Capital depreciation	20 years, 150% declining balance
Investment tax credit	0%
Tax holiday	0 years
PROJECT DURATION	
Capital expenditure period	Coal-to-hydrogen and IGCC plants: 5 years SMR plants: 3 years
Operational period	30 years
FINANCING TERMS	
Repayment term of debt	15 years
Grace period on debt repayment	0 years
Debt reserve fund	None
TREATMENT OF CAPITAL COSTS	
Capital cost escalation during construction (nominal annual rate)	3.6%
Distribution of TOC over the capital expenditure period (before escalation)	5-year period: 10%, 30%, 25%, 20%, 15% 3-year period: 10%, 60%, 30%
Working capital	None
Percent of TOC that is depreciated	100%
INFLATION OF OPERATING REVENUES AND COSTS	
Inflation of COH, COE, O&M costs, and fuel costs (nominal annual rate)	3.0%

Table 11. Finance structure for high-risk hydrogen projects.

Type of Security	% of Total	Current (Nominal) Dollar Cost	Weighted Current Cost of Capital	After Tax Weighted Cost of Capital
Debt	50	9.5%	4.75%	
Equity	50	20%	10.0%	
Total			14.75%	12.945%

Table 12. Finance structure for high-risk electric power projects (investor owned utility).

Type of Security	% of Total	Current (Nominal) Dollar Cost	Weighted Current Cost of Capital	After Tax Weighted Cost of Capital
Debt	45	5.5%	2.475%	
Equity	55	12%	6.6%	
Total			9.075%	8.13%

Table 13 shows the CCFs used to compute the COH and COE for each of the six plants evaluated in this study. For the base and CLP IGCC plants, first-year capital charges were calculated using a CCF of 0.1240 (high-risk electric power project, 5-year capital expenditure period). A CCF of 0.2470 (high-risk hydrogen project, 5-year capital expenditure period) was used for the base coal-to-hydrogen plant, and a CCF of 0.2044 (high-risk hydrogen project, 3-year capital expenditure period) was used for the base SMR plant. As indicated in Table 13 and discussed later in this report, the CLP coal-to-hydrogen plant and CLP SMR plant produce significant quantities of both hydrogen and electricity. For these plants, weighted average CCFs were computed from the appropriate high-risk hydrogen and high-risk electric power CCFs based on the relative contributions of hydrogen and electricity to the plant's total energy output. (The energy content of the H₂ product was multiplied by a factor of 0.6 to convert it to an electric power-equivalent basis). The resulting CCFs were 0.2048 for the CLP coal-to-hydrogen plant and 0.1853 for the CLP SMR plant. Finally, for these two co-production plants, any economic advantage was distributed equally between the hydrogen and electric power products, such that the changes in COE and COH relative to the base plant values were equivalent on a percentage basis.

Table 13. Capital charge factors used to calculate the COH or COE for each of the plants evaluated in this report.

Case	% Hydrogen ^a	% Electricity	Financial Model	CCF
Base Coal-to-Hydrogen	99	1	High-risk hydrogen 5-yr capital expenditure	0.2470
CLP Coal-to-Hydrogen	66	34	Weighted average ^b	0.2048
Base SMR	100	0	High-risk hydrogen 3-yr capital expenditure	0.2044
CLP SMR	76	24	Weighted average ^b	0.1853
Base IGCC	0	100	High-risk electric power 5-yr capital expenditure	0.1240
CLP IGCC	0	100	High-risk electric power 5-yr capital expenditure	0.1240

^aThe energy content of the hydrogen product produced by each plant was multiplied by a factor of 0.6 to convert it to an electric power-equivalent basis. ^bFor cases with significant co-production of hydrogen and electricity, a weighted average CCF was computed from the appropriate high-risk hydrogen and high-risk electric power CCFs based on the relative contributions of hydrogen and electricity to the plant's total energy output.

4. Results

The process design, process simulation results, and process economics for the base and CLP plants in each of the coal-to-hydrogen, SMR, and IGCC cases are presented in the following subsections. For each plant, the process design was developed and the process simulation carried out according to the design basis and methodology described in Section 3.1, and the process economics were evaluated according to the methodology described in Section 3.2. The implications of the results presented in this section are discussed in Section 5 of this report.

4.1 Coal-to-Hydrogen Case

4.1.1 Process Design

Figure 2 presents a block flow diagram for the base coal-to-hydrogen plant. In this plant, high-purity hydrogen is produced from 220,904 kg/h (244 ton/h) of coal using an oxygen-blown GE Energy radiant-only gasifier followed by a water quench, a syngas scrubber, water-gas shift reactors, syngas coolers, a mercury removal system, a two-stage Selexol unit for H₂S and CO₂ removal, and a pressure swing adsorber. (The radiant-only gasifier includes a radiant syngas cooler ahead of the water quench). The H₂S captured in the Selexol unit is sent to a Claus plant to produce elemental sulfur. The CO₂ captured in the Selexol unit is dried and compressed for sequestration. A cryogenic air separation unit (ASU) is used to supply 95% (by volume) purity oxygen to the gasifier and Claus plant. The tailgas from the PSA is combusted with air in an auxiliary boiler to generate steam. This steam, along with steam raised in the radiant syngas cooler, is sent to a turbine-generator to produce electricity. The plant includes three, 50% capacity gasifier trains (two active trains plus one spare train on hot standby) to achieve 90% availability. Additional information regarding the base coal-to-hydrogen plant design, including a detailed process description, process flow diagram, and heat and material balance results, can be found in Sections 3 and 5 of the DOE hydrogen baseline report.¹

Figure 2. Block flow diagram for the base coal-to-hydrogen plant.

As discussed in Section 3 above, the CLP coal-to-hydrogen plant was designed to use the same gasifier as the base plant. Figure 3 presents a block flow diagram for the CLP coal-to-

hydrogen plant. Per the discussion in the Section 2 of this report, the Calcium Looping Process is designed to accomplish several key process steps, including the water-gas shift reaction and acid gas removal. As a result, a number of components from the base plant, including the water quench, syngas scrubber, shift reactors, syngas coolers, 2-stage Selexol unit, Claus plant, and auxiliary boiler, are not required in the CLP plant.

Figure 4 presents a process flow diagram (PFD) for the Calcium Looping Process as applied to the coal-to-hydrogen plant. The system boundaries for this PFD correspond to the red box in Figure 3. Table 14 provides temperature, pressure, enthalpy, mass flow rate, and chemical composition data for the streams that are labeled in Figure 4. These data were derived from material and energy balances performed in Aspen Plus®.

Figure 3. Block flow diagram for the CLP coal-to-hydrogen plant.

As shown in Figures 3 and 4, syngas is fed to the Calcium Looping Process just after it exits the gasifier's radiant cooler, where its temperature and pressure are about 677°C (1,251°F) and 56 bar (805 psia), respectively. This syngas, which contains about 36% CO, 14% H₂O, 34% H₂, 14% CO₂, and 0.73% H₂S (by volume), passes through a high-efficiency cyclone to remove particulate matter and a ruggedized turboexpander to reduce its pressure to 23 bar (334 psia). It then enters the carbonator, which is a fluidized bed reactor operating at 650°C and 23 bar. Hydrated lime is fed to the carbonator at a calcium-to-carbon molar ratio of ~1.3. The dissociation of this hydrated lime provides all of the steam required for the water-gas shift reaction. The resulting CaO chemically reacts with the CO₂, H₂S, COS, and HCl in the syngas to form CaCO₃, CaS, and CaCl₂. As discussed in the Introduction, the removal of CO₂ drives the water-gas shift reaction forward, obviating the need for WGS catalyst. The net exothermic heat of reaction in the carbonator is recovered to produce steam.

Figure 4. Process flow diagram for the Calcium Looping Process in the coal-to-hydrogen case.

Table 14. Stream table for the Calcium Looping Process in the coal-to-hydrogen case.

	1	2	3	4	5	6	7	8	9	10
Temperature (°C)	677	536	650	149	43	650	15	15	38	15
Pressure (bar)	56	23	22	22	22	1	1	1	1	1
Enthalpy (kJ/kg)	-5,243	-5,494	-8,435	-7,859	-335	-8,975	-12,110	-2,116	-1,062	-97
Mass Flow (kg/hr)	465,270	465,270	231,988	125,355	48,167	1,742,540	47,674	116,703	22,411	1,355,250
Vapor-Liquid Components (kg/h)										
Ar	7,944	7,944	7,944	7,943	7,943	0	0	0	7,943	17,261
CH ₄	408	408	408	408	408	0	0	0	408	0
C ₂ H ₆	0	0	0	0	0	0	0	0	0	0
C ₃ H ₈	0	0	0	0	0	0	0	0	0	0
C ₄ H ₁₀	0	0	0	0	0	0	0	0	0	0
CO	231,602	231,602	395	395	395	0	0	0	395	0
CO ₂	140,428	140,428	812	811	811	0	0	0	811	620
COS	278	278	0	0	0	0	0	0	0	0
H ₂	15,876	15,876	32,195	32,195	32,195	0	0	0	6,439	0
H ₂ O	57,026	57,026	184,773	78,149	975	0	0	0	975	8,377
H ₂ S	5,753	5,753	139	139	138	0	0	0	138	0
N ₂	4,534	4,534	4,822	4,822	4,822	0	0	0	4,822	1,017,300
NH ₃	748	748	398	393	380	0	0	0	380	0
O ₂	0	0	0	0	0	0	0	0	0	311,697
SO ₂	0	0	0	0	0	0	0	0	0	0
Other	674	674	101	100	100	0	0	0	100	0
Solid Components (kg/h)										
CaCO ₃	0	0	0	0	0	1,144,230	46,530	0	0	0
CaO	0	0	0	0	0	189,249	0	0	0	0
Ca(OH) ₂	0	0	0	0	0	0	0	0	0	0
CaS	0	0	0	0	0	15,634	0	0	0	0
CaSO ₄	0	0	0	0	0	0	0	0	0	0
Coal	0	0	0	0	0	0	0	116,703	0	0
Ash / Other	0	0	0	0	0	393,428	1,144	0	0	0

Table 14. (continued)

	11	12	13	14	15	16	17	18	19	20
Temperature (°C)	17	13	950	132	132	132	21	875	204	493
Pressure (bar)	1	2	1	1	1	1	1	1	3	2
Enthalpy (kJ/kg)	-123	-11	-8,043	-9,247	-9,088	-9,088	-8,621	-7,467	-13,090	-9,690
Mass Flow (kg/hr)	1,032,830	322,422	1,876,110	68,675	863,644	943,788	829,860	1,239,280	357,267	1,509,250
Vapor-Liquid Components (kg/h)										
Ar	3,665	13,597	41,250	0	19,710	21,539	21,539	0	0	0
CH ₄	0	0	0	0	0	0	0	0	0	0
C ₂ H ₆	0	0	0	0	0	0	0	0	0	0
C ₃ H ₈	0	0	0	0	0	0	0	0	0	0
C ₄ H ₁₀	0	0	0	0	0	0	0	0	0	0
CO	0	0	1	0	0	0	0	0	0	0
CO ₂	620	0	1,522,430	0	723,361	790,487	790,471	0	0	0
COS	0	0	0	0	0	0	0	0	0	0
H ₂	0	0	0	0	0	0	0	0	0	0
H ₂ O	8,377	0	229,617	0	109,829	120,021	6,109	0	357,267	0
H ₂ S	0	0	0	0	0	0	0	0	0	0
N ₂	1,012,720	4,578	21,392	0	10,222	11,171	11,171	0	0	0
NH ₃	0	0	0	0	0	0	0	0	0	0
O ₂	7,450	304,247	882	0	417	456	456	0	0	0
SO ₂	0	0	12	0	0	0	0	0	0	0
Other	0	0	1,130	0	104	114	114	0	0	0
Solid Components (kg/h)										
CaCO ₃	0	0	0	18,788	0	0	0	0	0	99
CaO	0	0	11,235	0	0	0	0	840,278	0	0
Ca(OH) ₂	0	0	0	0	0	0	0	0	0	1,110,150
CaS	0	0	0	0	0	0	0	0	0	0
CaSO ₄	0	0	36,016	36,042	0	0	0	6,450	0	6,450
Coal	0	0	0	0	0	0	0	0	0	0
Ash / Other	0	0	12,141	13,846	0	0	0	392,555	0	392,555

The product stream exiting the carbonator travels to a high-efficiency cyclone for gas/solids separation. The gaseous hydrogen stream leaving this cyclone, which contains a substantial amount of water vapor and some impurities, then passes through a firetube boiler and a condensing heat exchanger, which cool the hydrogen while recovering heat for the plant's steam cycle. The hydrogen finally passes through a condenser for further cooling and moisture removal before entering the pressure swing adsorber. Although the CLP produces purer hydrogen upstream of the PSA than the conventional process, a PSA is still required to attain 99.9% purity. Hydrogen product exits the PSA at 49°C (120°F) and 22 bar (315 psia); the PSA tailgas is sent for use as fuel in the calciner.

The solid products from the carbonator, which include CaCO_3 , CaS , CaCl_2 , CaO , and ash, are depressurized using lockhoppers and sent to the calciner for regeneration. Fresh limestone is added just ahead of the calciner to compensate for solids that are purged from the calcium loop later in the process. In the calciner, the solids are heated to $>875^\circ\text{C}$ ($>1,607^\circ\text{F}$) at atmospheric pressure, causing the CaCO_3 to dissociate into CaO and CO_2 . The calciner is an entrained bed design (i.e., a flash calciner) and is fired using coal and PSA tailgas, which are combusted in oxygen and recycled CO_2 (i.e., oxyfuel combustion) to produce combustion products consisting largely of CO_2 and H_2O . (The coal that is fed to the calciner is in addition to the 220,904 kg/h that is fed to the gasifier). Oxygen (95% purity by volume) for the calciner is produced in a cryogenic ASU. (This ASU is separate from the elevated-pressure ASU that is used for the gasifier and Claus plant). The CaS in the carbonator solid products can react with O_2 , CO_2 , or H_2O in the calciner to form either CaSO_4 or SO_2 . SO_2 is the desired product, as it enables sulfur to be purged from the solids loop as a gaseous compound and recaptured downstream for disposal, as described below.

Most of the solids exiting the calciner are recovered in a high-efficiency cyclone and sent to the hydrator, where the CaO reacts with steam to produce Ca(OH)_2 . As discussed in Section 3.1, the hydrator is designed to operate at high temperature ($\sim 500^\circ\text{C}$) and slightly elevated pressure (~ 2.5 bar) in order to enable the exothermic heat of the hydration reaction to be recovered for use in the plant's steam cycle. The Ca(OH)_2 and other solids from the hydrator are returned to the carbonator, reinitiating the calcium loop.

Meanwhile, the gaseous CO_2 stream exiting the cyclone at the calciner outlet is sent to a heat recovery steam generator (HRSG) to raise steam. The solids that are not removed in the calciner outlet cyclone (about 3% of the total solids flow), which contain a substantial amount of CaO , absorb SO_2 from the CO_2 stream as it is cooled in the HRSG, forming CaSO_4 . These solids are then separated from the CO_2 stream using a fabric filter and purged from the system to prevent a buildup of sulfur compounds and inerts in the calcium loop. The CO_2 exiting the fabric filter, now free of SO_2 and particulate matter, is cooled in a condenser to remove water vapor. (First, a portion of this CO_2 is recycled to the calciner for use as a diluent in the oxyfuel combustion process). The CO_2 is then sent for further drying and compression to 153 bar (2,215 psia).

4.1.2 Process Simulation Results

Table 15 summarizes the modeled performance of the CLP coal-to-hydrogen plant and compares this with the performance of the base coal-to-hydrogen plant (taken from Case 2-1 of the DOE hydrogen baseline report).

Table 15. Summary of process performance results (at full load) for the coal-to-hydrogen case.

	Base Plant	CLP Plant
Coal Feed Rate, kg/h (lb/h)		
Gasifier	220,904 (487,011)	220,904 (487,011)
Calciner	0 (0)	116,703 (257,286)
Total	220,904 (487,011)	337,607 (744,297)
Total HHV Heat Input, kW _t (mmBtu/h)	1,665,075 (5,681)	2,544,727 (8,683)
Hydrogen Production, kg/h (lb/h)	25,689 (56,634)	25,756 (56,782)
Gross Electric Power Output, kW _e		
Steam Turbine	155,600	567,090
Turboexpander	0	32,350
Total	155,600	599,440
Auxiliary Load, kW _e		
Coal Handling, Prep, and Feed	2,930	4,380
Gasifier ASU and O ₂ Compressors	79,010	77,800
Slag Handling	1,160	1,160
Quench Water Pump	540	0
Scrubber Pumps	230	0
Selexol System	19,230	0
Claus Plant	2,090	0
Calciner Air Separation Unit	0	75,690
Limestone Handling, Prep, and Feed	0	1,830
Spent Sorbent Handling	0	2,030
Hydrator Auxiliaries	0	7,590
Lockhopper Feed Systems	0	6,810
CLP System Fans	0	3,860
CO ₂ Compressor	31,160	67,810
Feedwater Pumps	2,850	10,390
Condensate Pump	150	480
Steam Turbine Auxiliaries	100	360
Ground Water Pumps	380	850
Circulating Water Pump	3,110	8,510
Cooling Tower Fans	1,600	4,380
Miscellaneous Balance of Plant	3,000	3,000
Transformer Losses	900	3,470
Total	148,440	280,400
Net Electric Power Output, kW _e	7,160	319,040
CO ₂ Capture Efficiency, % ^a	90	~100
Net CO ₂ Emissions, kg/h (lb/h)	49,331 (108,755)	~0
Oxygen Demand, kg/h (lb/h) ^b		
Gasifier	177,828 (392,044)	177,828 (392,044)
Claus Plant	3,198 (7,050)	0
Calciner	0	322,422 (710,818)
Total	181,026 (399,094)	500,250 (1,102,862)
Raw Water Demand, m ³ /min (gpm)	16.1 (4,253)	36.1 (9,530)
Cooling Tower Load, GJ/h (mmBtu/h)	1,573 (1,491)	3,760 (3,564)
Elemental Sulfur Byproduct, kg/h (lb/h)	5,525 (12,181)	0 (0)
Solid Waste, kg/h (lb/h)	24,237 (53,433)	92,912 (204,836)

^aCO₂ capture efficiency = (carbon in product for sequestration) ÷ (carbon in fuel + carbon in limestone makeup – carbon in slag – carbon in spent sorbent purge); ^bFlow rates shown are for 95% (v/v) purity O₂

As shown in the table, the base plant and CLP plant produce approximately equal amounts of hydrogen (25,689 kg/h and 25,756 kg/h, respectively) from a common gasifier coal feed rate of 220,904 kg/h (487,011 lb/h). The CLP plant consumes an additional 116,703 kg/h (257,286 lb/h) of coal to fuel the entrained bed calciner. In addition to providing heat for sorbent regeneration, this additional coal contributes to significantly greater net electric power production in the CLP plant than in the base plant. (The difference in net electric power generation between the plants is also attributable, in part, to the recovery of the exothermic heat from the carbonation and hydration reactions in the CLP plant. The exothermic heat of the CO₂ absorption reaction in the base plant is not of sufficient quality for use in electricity generation). As shown in Table 15, the net electric power output from the CLP plant is about 312 MW_e greater than the net electric power output from the base plant. Although the CLP plant produces significantly more CO₂ than the base plant (owing to the additional CO₂ produced from coal combustion in the calciner and from calcination of the makeup limestone sorbent), it achieves a CO₂ capture efficiency of nearly 100%, compared to the base plant capture efficiency of ~90%. As a result, the CLP plant has a CO₂ emission rate of essentially zero, whereas the base plant has a CO₂ emission rate of 49,331 kg/h (108,755 lb/h). (Most of the CO₂ emissions in the base plant arise from the combustion of PSA tailgas in the air-fired auxiliary boiler).

The CLP coal-to-hydrogen plant consumes significantly more water and produces significantly more solid waste than the base coal-to-hydrogen plant. The difference in water consumption is largely related to the difference in electric power generation between the CLP plant and the base plant. The cooling tower water makeup requirement in the CLP plant is 5,536 gpm greater than in the base plant, due mostly to the much larger steam cycle condenser cooling load in the CLP plant. The difference in solid waste production between these plants results from the use of a solid sorbent (with 3% purge rate) in the CLP plant and from the greater overall coal feed rate (and, therefore, greater ash production) in the CLP plant than in the base plant.

Process performance results for the coal-to-hydrogen case are discussed further and compared with results for the SMR and IGCC cases in Section 5 of this report.

4.1.3 Process Economics

Tables 16-17 summarize the capital cost estimates for the base coal-to-hydrogen plant and CLP coal-to-hydrogen plant. Table 16 shows the estimated Bare Erected Cost and Total Plant Cost for each plant, as well as a breakdown of these costs by major equipment item. Table 17 shows the estimated owner's costs and Total Overnight Cost for each plant. The TOC for the CLP coal-to-hydrogen plant (\$2.588 billion) is about 39% greater than the TOC for the base coal-to-hydrogen plant (\$1.866 billion). This result might be expected, given the greater overall coal consumption and significantly greater co-production of electricity in the CLP plant relative to the base plant. As discussed in Section 4.1.1 and shown in Table 16, many base plant equipment items, including the syngas scrubber, shift reactors, syngas coolers, 2-stage Selexol unit, elemental sulfur plant, and auxiliary boiler, are not required in the CLP plant. The elimination of these equipment items results in a Total Plant Cost savings of about \$319 million. However, the Calcium Looping Process equipment (i.e., Account 15 in Table 16) adds about \$728 million of TPC, of which 45% is for the oxy-fired, entrained bed calciner and the corresponding ASU. Moreover, because of its greater coal consumption and electric power generation, the capital costs for the coal handling equipment, coal preparation and feed equipment, feedwater and miscellaneous balance of plant (BOP) systems, CO₂ compression and drying equipment, steam

Table 16. Total Plant Cost estimates for the coal-to-hydrogen case.

Acct No.	Item/Description	Base Plant					CLP Plant				
		Bare Erected Cost (\$ 000)	Engineering, Construction Management, Home Office, & Fee (%)	Process Contingency (%)	Project Contingency (%)	Total Plant Cost (\$ 000)	Bare Erected Cost (\$ 000)	Engineering, Construction Management, Home Office, & Fee (%)	Process Contingency (%)	Project Contingency (%)	Total Plant Cost (\$ 000)
1	Coal Handling	\$28,008	10.00%	0.00%	20.00%	\$36,971	\$41,027	10.00%	0.00%	20.00%	\$54,156
2	Coal Prep and Feed	\$43,489	10.00%	3.63%	20.00%	\$59,299	\$50,449	10.00%	3.63%	20.00%	\$68,789
3	Feedwater and Misc. BOP Systems	\$18,574	10.00%	0.00%	23.69%	\$25,271	\$44,178	10.00%	0.00%	23.69%	\$60,108
4	Gasifier Island										
4.1	GEE Syngas Cooler Gasifier System	\$341,298	10.00%	13.88%	15.60%	\$488,749	\$341,298	10.00%	13.88%	15.60%	\$488,749
4.2	Syngas Cooler (w/Gasifier-4.1)	\$0	10.00%	0.00%	0.00%	\$0	\$0	10.00%	0.00%	0.00%	\$0
4.3	ASU / Oxidant Compression	\$193,147	10.00%	0.00%	10.00%	\$233,708	\$190,956	10.00%	0.00%	10.00%	\$231,057
4.4	Scrubber & Low Temperature Cooling	\$16,102	10.00%	0.00%	20.00%	\$21,254	\$0	10.00%	0.00%	20.00%	\$0
4.4-4.9	Other Gasification Equipment	\$16,352	10.00%	0.00%	25.00%	\$22,484	\$16,352	10.00%	0.00%	25.00%	\$22,484
5A	Gas Cleanup and Piping										
5A.1	Double Stage Selexol	\$137,069	10.00%	20.00%	20.00%	\$213,828	\$0	10.00%	20.00%	20.00%	\$0
5A.2	Elemental Sulfur Plant	\$25,719	10.00%	0.00%	20.00%	\$33,949	\$0	10.00%	0.00%	20.00%	\$0
5A.3	Mercury Removal	\$2,436	10.00%	5.01%	19.99%	\$3,362	\$2,436	10.00%	5.01%	19.99%	\$3,362
5A.4	Shift Reactors	\$13,487	10.00%	0.00%	20.00%	\$17,803	\$0	10.00%	0.00%	20.00%	\$0
5A.7	Fuel Gas Piping	\$1,080	10.00%	0.00%	20.03%	\$1,426	\$0	10.00%	0.00%	20.03%	\$0
5A.9	HGCU Foundations	\$1,058	10.00%	0.00%	20.02%	\$1,397	\$0	10.00%	0.00%	20.02%	\$0
5B	CO ₂ Compression and Drying	\$29,448	10.00%	0.00%	20.00%	\$38,872	\$43,132	10.00%	0.00%	20.00%	\$56,935
6.1	Pressure Swing Adsorber	\$40,412	10.00%	0.00%	20.00%	\$53,344	\$42,493	10.00%	0.00%	20.00%	\$56,091
7.1	Off-Gas Fired Boiler and Stack	\$20,309	10.00%	0.00%	30.00%	\$29,042	\$0	10.00%	0.00%	30.00%	\$0
8	Steam Turbine Generator										
8.1	Steam TG & Accessories	\$21,606	10.00%	0.00%	20.00%	\$28,520	\$53,423	10.00%	0.00%	20.00%	\$70,518
8.2	Turbine Plant Auxiliaries and Steam Piping	\$11,976	10.00%	0.00%	20.00%	\$15,809	\$26,020	10.00%	0.00%	20.00%	\$34,347
9	Cooling Water System	\$15,715	10.00%	0.00%	20.00%	\$20,744	\$26,511	10.00%	0.00%	20.00%	\$34,994
10	Slag Handling System	\$56,865	10.00%	0.00%	15.00%	\$71,935	\$56,865	10.00%	0.00%	15.00%	\$71,935
11	Accessory Electric Plant	\$20,017	10.00%	0.00%	20.00%	\$26,423	\$37,782	10.00%	0.00%	20.00%	\$49,873
12	Instrumentation and Control	\$21,083	10.00%	5.00%	20.00%	\$29,094	\$21,083	10.00%	5.00%	20.00%	\$29,094
13	Improvements to Site	\$15,813	10.00%	0.00%	30.00%	\$22,612	\$19,766	10.00%	0.00%	30.00%	\$28,265
14	Buildings and Structures	\$16,867	10.00%	0.00%	20.00%	\$22,265	\$16,867	10.00%	0.00%	20.00%	\$22,265
15	CLP Equipment										
15.1	Carbonator	\$0	10.00%	25.00%	20.00%	\$0	\$20,390	10.00%	25.00%	20.00%	\$33,032
15.2	Flash Calciner	\$0	10.00%	15.00%	20.00%	\$0	\$87,015	10.00%	15.00%	20.00%	\$130,523

Table 16. (continued)

Acct No.	Item/Description	Base Plant					CLP Plant				
		Bare Erected Cost (\$ 000)	Engineering, Construction Management, Home Office, & Fee (%)	Process Contingency (%)	Project Contingency (%)	Total Plant Cost (\$ 000)	Bare Erected Cost (\$ 000)	Engineering, Construction Management, Home Office, & Fee (%)	Process Contingency (%)	Project Contingency (%)	Total Plant Cost (\$ 000)
15.3	Hydrator	\$0	10.00%	30.00%	20.00%	\$0	\$56,154	10.00%	30.00%	20.00%	\$94,339
15.4	Hydrator Auxiliaries	\$0	10.00%	0.00%	20.00%	\$0	\$17,862	10.00%	0.00%	20.00%	\$23,579
15.5	Calcliner ASU	\$0	10.00%	0.00%	20.00%	\$0	\$151,528	10.00%	0.00%	20.00%	\$200,017
15.6	Carbonator Product Lockhoppers	\$0	10.00%	10.00%	20.00%	\$0	\$20,837	10.00%	10.00%	20.00%	\$30,005
15.7	Hydrated Lime Lockhoppers	\$0	10.00%	10.00%	20.00%	\$0	\$26,886	10.00%	10.00%	20.00%	\$38,716
15.8	Cyclones	\$0	10.00%	0.00%	20.00%	\$0	\$5,686	10.00%	0.00%	20.00%	\$7,505
15.9	Firetube Boiler	\$0	10.00%	0.00%	20.00%	\$0	\$4,626	10.00%	0.00%	20.00%	\$6,106
15.10	Condensing Heat Exchanger	\$0	10.00%	0.00%	20.00%	\$0	\$5,310	10.00%	0.00%	20.00%	\$7,009
15.11	Hydrogen Stream Condenser	\$0	10.00%	0.00%	20.00%	\$0	\$4,429	10.00%	0.00%	20.00%	\$5,846
15.12	Calcliner Off-Gas HRSG	\$0	10.00%	0.00%	20.00%	\$0	\$39,235	10.00%	0.00%	20.00%	\$51,790
15.13	CO ₂ Stream Condenser	\$0	10.00%	0.00%	20.00%	\$0	\$5,895	10.00%	0.00%	20.00%	\$7,781
15.14	Solids Purge Fabric Filter	\$0	10.00%	0.00%	20.00%	\$0	\$13,865	10.00%	0.00%	20.00%	\$18,302
15.15	Calcliner Off-Gas ID Fan	\$0	10.00%	0.00%	20.00%	\$0	\$4,162	10.00%	0.00%	20.00%	\$5,494
15.16	CO ₂ Recycle Fan	\$0	10.00%	0.00%	20.00%	\$0	\$459	10.00%	0.00%	20.00%	\$606
15.17	Syngas Expander	\$0	10.00%	20.00%	20.00%	\$0	\$7,644	10.00%	20.00%	20.00%	\$11,925
15.18	Limestone Storage and Make-up System	\$0	10.00%	0.00%	20.00%	\$0	\$19,850	10.00%	0.00%	20.00%	\$26,202
15.19	Solid Byproduct Handling System	\$0	10.00%	0.00%	20.00%	\$0	\$21,941	10.00%	0.00%	20.00%	\$28,962
	TOTAL	\$1,107,930				\$1,518,161	\$1,544,412				\$2,110,761

Table 17. Owner's cost and TOC estimates for the coal-to-hydrogen case.

	Base Plant		CLP Plant	
	Quantity	Cost	Quantity	Cost
Total Plant Cost (TPC)				
From Table 16		\$1,518,161,000		\$2,110,761,000
Preproduction Costs				
6 Months All Labor		\$13,434,448		\$17,138,198
1 Month Maintenance Materials @ 100% CF		\$3,036,322		\$4,221,522
1 Month Non-fuel Consumables @ 100% CF		\$475,997		\$1,470,737
1 Month Waste Disposal @ 100% CF		\$316,534		\$1,213,432
25% of 1 Month's Fuel Cost @ 100% CF		\$1,697,154		\$2,593,754
2% of TPC		\$30,363,220		\$42,215,220
Inventory Capital				
60-day Supply of Consumables @ 100% CF		\$938,953		\$2,901,180
60-day Supply of Coal @ 100% CF		\$13,391,244		\$20,465,786
0.5% of TPC (spare parts)		\$7,590,805		\$10,553,805
Land				
300 acres @ \$3,000/acre		\$900,000		\$900,000
Financing Costs				
2.7% of TPC		\$40,990,347		\$56,990,547
Other Owner's Costs				
15% of TPC		\$227,724,150		\$316,614,150
Initial Cost for Catalyst and Chemicals				
Carbon (Mercury Removal) (lb)	76,126	\$79,932	76,126	\$79,932
Shift Catalyst (ft ³)	6,290	\$3,137,641	0	\$0
Selexol Solution (gal)	298,541	\$4,000,449	0	\$0
Limestone (ton)	0	\$0	2,181	\$37,622
Total Overnight Cost (TOC)		\$1,866,238,197		\$2,588,156,886

turbine-generator and auxiliary equipment, cooling water system, and accessory electric plant in the CLP plant are significantly greater than the costs for these equipment items in the base plant, helping to explain the difference in TOC between these plants.

Tables 18 and 19 show the estimated fixed O&M costs and variable O&M costs, respectively, for the base and CLP coal-to-hydrogen plants. The CLP plant has greater estimated fixed O&M costs than the base plant, as its larger TPC results in greater expected maintenance costs, property taxes, and insurance costs. It also has greater variable O&M costs than the base plant, arising from its greater coal consumption, water consumption, and solid waste disposal and from its significant consumption of limestone. (The variable O&M costs associated with the WGS catalyst, Selexol solution, and Claus catalyst in the base plant, which total \$1,221,793/y, are much less than the \$7,146,951/y required for limestone in the CLP plant). The difference in CO₂ emissions between the CLP and base plants is accounted for via the \$11,669,764/y tax applied to the base plant.

Table 18. Estimated annual fixed O&M costs for the coal-to-hydrogen case.

	Base Plant	CLP Plant
Operating Labor	\$6,313,507	\$6,313,507
Maintenance Labor	\$15,181,610	\$21,107,610
Maintenance Material	\$32,792,278	\$45,592,438
Administrative and Support Labor	\$5,373,779	\$6,855,279
Property Taxes and Insurance	\$30,363,220	\$42,215,220
Total Fixed O&M Cost	\$90,024,394	\$122,084,054

Table 19. Estimated annual variable O&M costs for the coal-to-hydrogen case.

Cost Element	Unit Cost	Unit	Base Plant				CLP Plant		
			Consumption	Unit Rate	Annual Variable O&M Cost		Consumption	Unit Rate	Annual Variable O&M Cost
Coal	\$38.19	ton	5,844	ton/day	\$73,317,061		8,932	ton/day	\$112,050,177
CO ₂ Emission Tax	\$27.22	ton	1,305	ton/day	\$11,669,764		0	ton/day	\$0
Water	\$1.08	1000 gal	6,124	1000 gal/day	\$2,172,786		13,723	1000 gal/day	\$4,868,717
Water Treatment Chemicals	\$0.17	lb	30,626	lb/day	\$1,710,310		68,626	lb/day	\$3,832,414
Carbon (Mercury Removal)	\$1.05	lb	104	lb/day	\$35,878		104	lb/day	\$35,878
Shift Catalyst	\$498.83	ft ³	4	ft ³ /day	\$705,659		0	ft ³ /day	\$0
Selexol Solution	\$13.40	gal	95	gal/day	\$418,126		0	gal/day	\$0
Claus Catalyst	\$131.27	ft ³	2	ft ³ /day	\$98,008		0	ft ³ /day	\$0
Solid Waste Disposal	\$16.23	ton	641	ton/day	\$3,418,572		2,458	ton/day	\$13,105,069
Elemental Sulfur Byproduct	\$0.00	ton	146	ton/day	\$0		0	ton/day	\$0
Limestone	\$17.25	ton	0	ton/day	\$0		1,261	ton/day	\$7,146,951
Total Annual Fuel Cost					\$73,317,061				\$112,050,177
Total Annual CO₂ Emission Tax Cost					\$11,669,764				\$0
Total Annual Other Variable O&M Cost					\$8,559,339				\$28,989,030

Table 20 shows the estimated first-year cost of hydrogen for the base coal-to-hydrogen plant and the CLP coal-to-hydrogen plant. As discussed in Section 3.2.4, different first-year capital charge factors were used when computing the first-year COH for these plants, based on differences in the relative proportions of hydrogen and electricity produced by each plant. If it is assumed that the electricity produced by the base coal-to-hydrogen plant is sold at the base price of \$105/MWh, then the first-year COH for this plant is \$3.15/kg H₂. Use of the Calcium Looping Process results in a 12% reduction in the costs of hydrogen and electricity relative to the base plant. The first-year COH for the CLP coal-to-hydrogen plant is \$2.77/kg H₂ at an electricity price of \$92.07/MWh. Hence, although the CLP plant has higher capital costs, fixed O&M costs, and variable O&M costs than the base plant on an absolute basis, this cost differential is outweighed by the significant co-production of electricity in the Calcium Looping Process, resulting in an economic advantage for the CLP plant. (As discussed in Section 3.2.4, the economic advantage afforded by the CLP plant was distributed equally between the hydrogen and electric power products, such that the changes in cost of electricity and cost of hydrogen relative to the base plant values are equivalent on a percentage basis).

Table 20. First-year cost of hydrogen estimates for the coal-to-hydrogen case.

	Base Plant			CLP Plant	
First-Year Capital Charge Factor	0.2470			0.2048	
Hydrogen Production (kg/y)	202,532,076			203,060,304	
Electric Power Production (MWh/y)	56,449			2,515,311	
Cost of Electricity (\$/MWh)	\$105.00			\$92.07	
First-Year Cost of Hydrogen	Cost (\$/y)	COH (\$/kg H ₂)		Cost (\$/y)	COH (\$/kg H ₂)
Capital	\$460,960,835	\$2.28		\$529,926,331	\$2.61
Fixed O&M	\$90,024,394	\$0.44		\$122,084,054	\$0.60
Fuel	\$73,317,061	\$0.36		\$112,050,177	\$0.55
CO ₂ Emissions	\$11,669,764	\$0.06		\$0	\$0.00
Other Variable O&M	\$8,559,339	\$0.04		\$28,989,030	\$0.14
Electric Power ^a	-\$5,927,191	-\$0.03		-\$231,584,717	-\$1.14
Total	\$638,604,203	\$3.15		\$561,464,875	\$2.77

^aComputed using an electricity price equal to the plant-specific cost of electricity shown in the table.

4.2 Steam Methane Reforming Case

4.2.1 Process Design

Figure 5 presents a block flow diagram for the base steam methane reforming plant. In this plant, high-purity hydrogen is produced from 84,947 kg/h (94 ton/h) of natural gas. The gas passes through a sulfur guard and is sent to the reformer, where it reacts with steam to form syngas. The reforming reaction takes place over a nickel-based catalyst contained inside a system of high-alloy steel tubes. Energy for this endothermic reaction is supplied by combusting PSA tailgas and supplemental natural gas on the outside of the catalyst tubes. The syngas stream leaving the reformer is processed using a syngas cooler, water-gas shift reactors, a methyldiethanolamine (MDEA) unit for CO₂ capture, and a pressure swing adsorber

to produce high-purity hydrogen. The flue gas (produced from combustion of the PSA tailgas and supplemental natural gas) is cooled in a HRSG to raise process steam and sent to a monoethanolamine (MEA) unit for CO₂ capture. The CO₂ recovered in the MDEA and MEA units is dried and compressed to 153 bar (2,215 psia) for sequestration. Additional information regarding the base SMR plant design, including a detailed process description, process flow diagram, and heat and material balance results, can be found in Sections 3 and 4 of the DOE hydrogen baseline report.¹

Figure 5. Block flow diagram for the base SMR plant.

As discussed in Section 3 of this report, the CLP steam methane reforming plant was designed to use the same reformer as the base plant. Figure 6 presents a block flow diagram for this CLP plant. Because the water-gas shift reaction and CO₂ capture are carried out in the Calcium Looping Process, the shift reactors, MDEA unit, and MEA unit from the base plant are not required in the CLP plant.

Figure 7 presents a process flow diagram for the Calcium Looping Process as applied to the SMR plant. The system boundaries for this PFD correspond to the red box labeled “Calcium Looping Process” in Figure 6. Table 21 provides temperature, pressure, enthalpy, mass flow rate, and chemical composition data for the streams that are labeled in Figure 7. These data were derived from material and energy balances performed in Aspen Plus®.

The process design for the Calcium Looping Process in the SMR plant is similar to that for the CLP in the coal-to-hydrogen plant (see Section 4.1.1), with several noteworthy exceptions. In the SMR case, two separate carbonators are used: one for the syngas stream and one for the

flue gas stream from the reformer. Less heat is generated in these carbonators than in the coal-to-hydrogen case, owing to the lower carbon content of natural gas-derived syngas and flue gas relative to coal-derived syngas. As a result, the carbonators in the SMR case do not include internal heat recovery, and they are designed as entrained rather than fluidized beds. The syngas and flue gas streams are cooled to appropriate inlet temperatures ahead of the carbonators to allow for the temperature rise resulting from the exothermic heat of the carbonation and WGS reactions. As with the coal-to-hydrogen case, both carbonators in the SMR case operate at calcium-to-carbon molar ratios of ~1.3.

Figure 6. Block flow diagram for the CLP SMR plant.

The solid products from the carbonators are captured using high-efficiency cyclones, combined, and sent to a common entrained bed calciner. (The solids from the syngas carbonator are first depressurized using lockhoppers). Although the reformer uses natural gas, the process is most economical if the calciner is fired with coal (a small amount of supplemental natural gas is also used in the simulation presented here). The calcination and hydration process designs for the SMR case are essentially the same as those used in the coal-to-hydrogen case. However, a lower solids purge rate is used in the SMR case (2%) than in the coal-to-hydrogen case (3%), because the syngas and stack gas from the reformer do not contain any sulfur compounds. (Some sulfur and fly ash are still introduced into the solids loop through the coal-fired calciner, so the purge stream cannot be eliminated completely).

As with the coal-to-hydrogen case, the gaseous hydrogen stream leaving the syngas carbonator in the SMR case is cooled and purified using a firetube boiler, a condensing heat exchanger, a condenser, and a PSA. The gaseous effluent from the flue gas carbonator is cooled in a HRSG, treated in a fabric filter to remove residual particulate matter, and exhausted through a stack.

Figure 7. Process flow diagram for the Calcium Looping Process in the SMR case.

Table 21. Stream table for the Calcium Looping Process in the SMR case.

	1	2	3	4	5	6	7	8	9
Temperature (°C)	866	625	695	173	38	643	550	587	132
Pressure (bar)	30	30	30	28	27	1	1	1	1
Enthalpy (kJ/kg)	-7,659	-8,348	-8,285	-9,608	-1,608	-2,184	-2,304	-2,326	-2,787
Mass Flow (kg/hr)	424,813	424,813	1,057,310	194,903	54,233	791,689	791,689	772,671	755,922
Vapor-Liquid Components (kg/h)									
Ar	0	0	0	0	0	9,712	9,712	9,712	9,712
CH ₄	9,111	9,111	9,111	9,109	9,109	0	0	0	0
C ₂ H ₆	4,675	4,675	4,675	4,673	4,673	0	0	0	0
C ₃ H ₈	1,539	1,539	1,539	1,539	1,539	0	0	0	0
C ₄ H ₁₀	1,106	1,106	1,106	1,106	1,106	0	0	0	0
CO	62,118	62,118	853	853	853	0	0	0	0
CO ₂	80,845	80,845	2,247	2,244	2,242	84,435	84,435	3,541	3,541
COS	0	0	0	0	0	0	0	0	0
H ₂	27,700	27,700	31,976	31,974	31,974	0	0	0	0
H ₂ O	235,942	235,942	292,672	141,282	630	116,724	116,724	161,852	161,852
H ₂ S	0	0	319	317	314	0	0	0	0
N ₂	1,778	1,778	1,636	1,636	1,636	562,072	562,072	562,071	562,071
NH ₃	0	0	172	169	157	0	0	0	0
O ₂	0	0	0	0	0	18,746	18,746	18,745	18,745
SO ₂	0	0	0	0	0	0	0	0	0
Other	0	0	0	0	0	0	0	2	2
Solid Components (kg/h)									
CaCO ₃	0	0	398,853	0	0	0	0	9,227	0
CaO	0	0	74,650	0	0	0	0	1,870	0
Ca(OH) ₂	0	0	0	0	0	0	0	0	0
CaS	0	0	237	0	0	0	0	0	0
CaSO ₄	0	0	0	0	0	0	0	41	0
Coal	0	0	0	0	0	0	0	0	0
Ash / Other	0	0	237,268	0	0	0	0	5,612	0

Table 21. (continued)

	10	11	12	13	14	15	16	17	18
Temperature (°C)	695	15	646	15	15	15	17	13	899
Pressure (bar)	1	1	1	1	31	1	1	2	1
Enthalpy (kJ/kg)	-7,731	-12,110	-7,838	-2,116	-4,571	-102	-128	-11	-8,081
Mass Flow (kg/hr)	711,008	16,400	1,062,400	70,625	4,907	720,178	548,448	171,730	1,038,480
Vapor-Liquid Components (kg/h)									
Ar	0	0	0	0	0	9,372	1,990	7,383	15,138
CH ₄	0	0	0	0	4,223	0	0	0	0
C ₂ H ₆	0	0	0	0	269	0	0	0	0
C ₃ H ₈	0	0	0	0	86	0	0	0	0
C ₄ H ₁₀	0	0	0	0	66	0	0	0	0
CO	0	0	0	0	0	0	0	0	0
CO ₂	0	0	0	0	160	330	330	0	900,278
COS	0	0	0	0	0	0	0	0	0
H ₂	0	0	0	0	0	0	0	0	0
H ₂ O	0	0	0	0	0	4,676	4,676	0	95,213
H ₂ S	0	0	0	0	0	0	0	0	0
N ₂	0	0	0	0	102	539,917	537,488	2,430	7,001
NH ₃	0	0	0	0	0	0	0	0	0
O ₂	0	0	0	0	0	165,882	3,965	161,918	798
SO ₂	0	0	0	0	0	0	0	0	1
Other	0	0	0	0	0	0	0	0	272
Solid Components (kg/h)									
CaCO ₃	398,853	16,006	599,393	0	0	0	0	0	0
CaO	74,650	0	112,045	0	0	0	0	0	6,393
Ca(OH) ₂	0	0	0	0	0	0	0	0	0
CaS	237	0	237	0	0	0	0	0	0
CaSO ₄	0	0	815	0	0	0	0	0	6,250
Coal	0	0	0	70,625	0	0	0	0	0
Ash / Other	237,268	394	349,908	0	0	0	0	0	7,133

Table 21. (continued)

	19	20	21	22	23	24	25	26
Temperature (°C)	132	132	132	49	875	130	493	493
Pressure (bar)	1	1	1	1	1	3	2	2
Enthalpy (kJ/kg)	-8,477	-9,054	-9,054	-8,891	-6,086	-13,304	-8,242	-8,242
Mass Flow (kg/hr)	24,929	519,253	494,297	467,098	790,435	164,411	632,501	299,223
Vapor-Liquid Components (kg/h)								
Ar	0	7,755	7,383	7,383	0	0	0	0
CH ₄	0	0	0	0	0	0	0	0
C ₂ H ₆	0	0	0	0	0	0	0	0
C ₃ H ₈	0	0	0	0	0	0	0	0
C ₄ H ₁₀	0	0	0	0	0	0	0	0
CO	0	0	0	0	0	0	0	0
CO ₂	0	458,643	436,600	436,595	0	0	0	0
COS	0	0	0	0	0	0	0	0
H ₂	0	0	0	0	0	0	0	0
H ₂ O	0	48,802	46,456	19,262	0	164,411	0	0
H ₂ S	0	0	0	0	0	0	0	0
N ₂	0	3,587	3,415	3,415	0	0	0	0
NH ₃	0	0	0	0	0	0	0	0
O ₂	0	406	386	386	0	0	0	0
SO ₂	0	0	0	0	0	0	0	0
Other	0	60	57	57	0	0	0	0
Solid Components (kg/h)								
CaCO ₃	11,200	0	0	0	0	0	1,190	563
CaO	0	0	0	0	438,384	0	0	0
Ca(OH) ₂	0	0	0	0	0	0	392,321	185,599
CaS	0	0	0	0	0	0	0	0
CaSO ₄	6,252	0	0	0	2,537	0	1,722	815
Coal	0	0	0	0	0	0	0	0
Ash / Other	7,477	0	0	0	349,514	0	237,268	112,246

Unlike the conventional SMR plant, the CLP SMR plant includes ample opportunities to recover high-quality heat. As shown in Figure 7, heat is recovered from the syngas cooler, firetube boiler, condensing heat exchanger, two flue gas HRSGs, CO₂ stream HRSG, and hydrator to raise steam. Some of this steam is used to satisfy process requirements, but most is sent to a steam turbine-generator to produce electricity. (The conventional SMR plant does not include a steam turbine-generator).

4.2.2 Process Simulation Results

Table 22 summarizes the modeled performance of the CLP steam methane reforming plant and compares this with the performance of the base SMR plant (taken from Case 1-1 of the DOE hydrogen baseline report).

The base plant and CLP plant produce approximately equal amounts of hydrogen (25,689 kg/h and 25,579 kg/h, respectively) from a common reformer natural gas feed rate of 84,947 kg/h (187,276 lb/h). Both plants also consume 10,319 kg/h (22,750 lb/h) of supplemental natural gas for external heating of the reformer catalyst tubes. In addition, the CLP plant consumes 70,625 kg/h (155,701 lb/h) of coal and 4,907 kg/h (10,818 lb/h) of natural gas to fuel the entrained bed calciner, such that its total fuel consumption is greater than that of the base plant. As with the coal-to-hydrogen case, the additional fuel consumed by the CLP plant in the SMR case provides heat for sorbent regeneration and also contributes to significant co-production of electric power. Whereas the base SMR plant must purchase 34.2 MW_e of externally generated electric power in order to operate, the CLP SMR plant generates 188.9 MW_e of excess electric power that can be sold to the grid. (The difference in net electric power generation between the plants is also attributable, in part, to the recovery of the exothermic heat from the carbonation and hydration reactions in the CLP plant. The exothermic heat of the CO₂ absorption reactions in the base plant is not of sufficient quality for use in electricity generation). Although the CLP plant produces significantly more CO₂ than the base plant (owing to the additional CO₂ produced from coal and natural gas combustion in the calciner and from calcination of the makeup limestone sorbent), it achieves a CO₂ capture efficiency of >99%, compared to the base plant capture efficiency of ~90%. (The MDEA and MEA systems in the base plant are only designed for 90% CO₂ capture efficiency). As a result, the CLP plant CO₂ emission rate is 21,754 kg/h (47,959 lb/h) less than the base plant CO₂ emission rate.

The CLP steam methane reforming plant consumes significantly more water and produces significantly more solid waste than the base SMR plant. The difference in water consumption between the base and CLP plants arises largely from the added steam cycle condenser cooling load in the CLP plant, which results in a larger cooling tower water makeup requirement in that plant. The base SMR plant does not consume any solids (apart from the fixed sulfur guard bed and fixed catalyst beds, which are only changed periodically) and therefore produces essentially zero solid waste. Solid waste in the CLP plant results from the use of a solid sorbent (with 2% purge rate) and from the combustion of coal in the calciner, which leads to the production of ash, CaSO₄, and CaCl₂ as solid wastes.

Process performance results for the SMR case are discussed further and compared with results for the coal-to-hydrogen and IGCC cases in Section 5 of this report.

Table 22. Summary of process performance results (at full load) for the SMR case.

	Base Plant	CLP Plant
Natural Gas Feed Rate, kg/h (lb/h)		
Reformer	84,947 (187,276)	84,947 (187,276)
Reformer External Heating	10,319 (22,750)	10,319 (22,750)
Calciner	0 (0)	4,907 (10,818)
Total	95,266 (210,026)	100,173 (220,844)
Coal Feed Rate (Calciner), kg/h (lb/h)	0 (0)	70,625 (155,701)
Total HHV Heat Input, kW _t (mmBtu/h)	1,402,906 (4,787)	2,007,503 (6,850)
Hydrogen Production, kg/h (lb/h)	25,689 (56,634)	25,579 (56,392)
Gross Electric Power Output, kW _e		
Steam Turbine	0	309,250
Total	0	309,250
Auxiliary Load, kW _e		
Coal Handling, Prep, and Feed	0	1,220
Primary Air Fans	2,350	2,350
MDEA and MEA Systems	3,200	0
Calciner Air Separation Unit	0	40,310
Limestone Handling, Prep, and Feed	0	630
Spent Sorbent Handling	0	740
Hydrator Auxiliaries	0	8,180
Lockhopper Feed Systems	0	2,810
CLP System Fans	0	2,070
CO ₂ Compressor	23,020	46,490
Feedwater Pumps	450	5,660
Condensate Pump	0	240
Steam Turbine Auxiliaries	0	200
Ground Water Pumps	300	460
Circulating Water Pump	2,560	4,080
Cooling Tower Fans	1,320	2,100
Miscellaneous Balance of Plant	1,000	1,000
Transformer Losses	0	1,790
Total	34,200	120,330
Net Electric Power Output, kW _e	-34,200	188,920
CO ₂ Capture Efficiency, % ^a	90	>99
Net CO ₂ Emissions, kg/h (lb/h)	24,954 (55,014)	3,200 (7,055)
Oxygen Demand (Calciner), kg/h (lb/h) ^b	0 (0)	171,730 (378,599)
Raw Water Demand, m ³ /min (gpm)	12.4 (3,265)	19.0 (5,012)
Cooling Tower Load, GJ/h (mmBtu/h)	1,304 (1,236)	2,078 (1,970)
Solid Waste, kg/h (lb/h)	0 (0)	24,929 (54,959)

^aCO₂ capture efficiency = (carbon in product for sequestration) ÷ (carbon in fuel + carbon in limestone makeup – carbon in slag – carbon in spent sorbent purge); ^bFlow rates shown are for 95% (v/v) purity O₂

4.2.3 Process Economics

Tables 23-24 summarize the capital cost estimates for the base SMR plant and CLP SMR plant. Table 23 shows the estimated Bare Erected Cost and Total Plant Cost for each plant, as well as a breakdown of these costs by major equipment item. Table 24 shows the estimated owner's costs and Total Overnight Cost for each plant.

Table 23. Total Plant Cost estimates for the SMR case.

Acct No.	Item/Description	Base Plant					CLP Plant				
		Bare Erected Cost (\$ 000)	Engineering, Construction Management, Home Office, & Fee (%)	Process Contingency (%)	Project Contingency (%)	Total Plant Cost (\$ 000)	Bare Erected Cost (\$ 000)	Engineering, Construction Management, Home Office, & Fee (%)	Process Contingency (%)	Project Contingency (%)	Total Plant Cost (\$ 000)
SMR-1	Methanation Reactor	\$57,841	10.00%	0.00%	20.00%	\$76,350	\$57,841	10.00%	0.00%	20.00%	\$76,350
ZnO-1	Sulfur Polisher	\$243	10.00%	0.00%	20.00%	\$321	\$243	10.00%	0.00%	20.00%	\$321
COMP-1	Primary Air Compressor	\$861	10.00%	0.00%	20.00%	\$1,137	\$861	10.00%	0.00%	20.00%	\$1,137
WGS-1	Water-Gas Shift Reactor	\$12,918	10.00%	0.00%	20.00%	\$17,052	\$0	10.00%	0.00%	20.00%	\$0
AGR-1	MDEA CO ₂ Removal Process	\$95,985	10.00%	20.00%	20.00%	\$149,737	\$0	10.00%	20.00%	20.00%	\$0
COMP-2	CO ₂ Compressor/Drier	\$16,494	10.00%	0.00%	20.00%	\$21,772	\$21,544	10.00%	0.00%	20.00%	\$28,438
AGR-2	MEA CO ₂ Removal Process	\$68,176	10.00%	20.00%	20.00%	\$106,354	\$0	10.00%	20.00%	20.00%	\$0
PSA-1	Pressure Swing Adsorber	\$38,047	10.00%	0.00%	20.00%	\$50,222	\$38,212	10.00%	0.00%	20.00%	\$50,440
SMR B-1	SMR Additional Boiler Surface	\$7,306	10.00%	0.00%	20.00%	\$9,644	\$0	10.00%	0.00%	20.00%	\$0
BOP-1	Balance of Plant	\$44,681	10.00%	0.00%	22.00%	\$59,962	with CLP	with CLP	with CLP	with CLP	with CLP
CLP	CLP Equipment										
CLP-1	Syngas Carbonator	\$0	10.00%	25.00%	20.00%	\$0	\$15,622	10.00%	25.00%	20.00%	\$25,308
CLP-2	Flue Gas Carbonator	\$0	10.00%	25.00%	20.00%	\$0	\$8,032	10.00%	25.00%	20.00%	\$13,012
CLP-3	Flash Calciner	\$0	10.00%	15.00%	20.00%	\$0	\$44,836	10.00%	15.00%	20.00%	\$67,254
CLP-4	Hydrator	\$0	10.00%	30.00%	20.00%	\$0	\$35,913	10.00%	30.00%	20.00%	\$60,334
CLP-5	Hydrator Auxiliaries	\$0	10.00%	30.00%	20.00%	\$0	\$18,260	10.00%	0.00%	20.00%	\$24,103
CLP-6	Calciner ASU	\$0	10.00%	0.00%	20.00%	\$0	\$78,892	10.00%	0.00%	20.00%	\$104,137
CLP-7	Syngas Carbonator Product Lockhoppers	\$0	10.00%	10.00%	20.00%	\$0	\$11,749	10.00%	10.00%	20.00%	\$16,919
CLP-8	Hydrated Lime Lockhoppers	\$0	10.00%	10.00%	20.00%	\$0	\$15,370	10.00%	10.00%	20.00%	\$22,133
CLP-9	Cyclones	\$0	10.00%	0.00%	20.00%	\$0	\$3,356	10.00%	0.00%	20.00%	\$4,430
CLP-10	Syngas Cooler	\$0	10.00%	0.00%	20.00%	\$0	\$5,631	10.00%	0.00%	20.00%	\$7,433
CLP-11	Hydrogen Stream Firetube Boiler	\$0	10.00%	0.00%	20.00%	\$0	\$8,999	10.00%	0.00%	20.00%	\$11,879
CLP-12	Hydrogen Stream Condensing Heat Exchanger	\$0	10.00%	0.00%	20.00%	\$0	\$5,827	10.00%	0.00%	20.00%	\$7,692
CLP-13	Hydrogen Stream Condenser	\$0	10.00%	0.00%	20.00%	\$0	\$6,383	10.00%	0.00%	20.00%	\$8,426
CLP-14	Flue Gas HRSG	\$0	10.00%	0.00%	20.00%	\$0	\$3,523	10.00%	0.00%	20.00%	\$4,650
CLP-15	Flue Gas Carbonator Off-gas HRSG	\$0	10.00%	0.00%	20.00%	\$0	\$12,171	10.00%	0.00%	20.00%	\$16,066
CLP-16	Flue Gas Carbonator Off-Gas Fabric Filter	\$0	10.00%	0.00%	20.00%	\$0	\$5,552	10.00%	0.00%	20.00%	\$7,329
CLP-17	Calciner Off-Gas HRSG	\$0	10.00%	0.00%	20.00%	\$0	\$22,698	10.00%	0.00%	20.00%	\$29,961
CLP-18	CO ₂ Stream Condenser	\$0	10.00%	0.00%	20.00%	\$0	\$2,471	10.00%	0.00%	20.00%	\$3,262
CLP-19	Solids Purge Fabric Filter	\$0	10.00%	0.00%	20.00%	\$0	\$5,349	10.00%	0.00%	20.00%	\$7,061

Table 23. (continued)

Acct No.	Item/Description	Base Plant					CLP Plant				
		Bare Erected Cost (\$ 000)	Engineering, Construction Management, Home Office, & Fee (%)	Process Contingency (%)	Project Contingency (%)	Total Plant Cost (\$ 000)	Bare Erected Cost (\$ 000)	Engineering, Construction Management, Home Office, & Fee (%)	Process Contingency (%)	Project Contingency (%)	Total Plant Cost (\$ 000)
CLP-20	Calcliner Off-Gas ID Fan	\$0	10.00%	0.00%	20.00%	\$0	\$2,205	10.00%	0.00%	20.00%	\$2,911
CLP-21	CO ₂ Recycle Fan	\$0	10.00%	0.00%	20.00%	\$0	\$261	10.00%	0.00%	20.00%	\$345
CLP-22	Coal Handling	\$0	10.00%	0.00%	20.00%	\$0	\$10,651	10.00%	0.00%	20.00%	\$14,059
CLP-23	Coal Prep and Feed	\$0	10.00%	0.00%	20.00%	\$0	\$6,693	10.00%	0.00%	20.00%	\$8,835
CLP-24	Feedwater and Misc. BOP	\$0	10.00%	0.00%	20.00%	\$0	\$29,428	10.00%	0.00%	20.00%	\$38,845
CLP-25	Steam TG & Auxiliaries	\$0	10.00%	0.00%	20.00%	\$0	\$34,945	10.00%	0.00%	20.00%	\$46,127
CLP-26	Turbine Plant Auxiliaries and Steam Piping	\$0	10.00%	0.00%	20.00%	\$0	\$18,084	10.00%	0.00%	20.00%	\$23,871
CLP-27	Cooling Water System	\$0	10.00%	0.00%	20.00%	\$0	\$18,573	10.00%	0.00%	20.00%	\$24,516
CLP-28	Accessory Electric Plant	\$0	10.00%	0.00%	20.00%	\$0	\$22,166	10.00%	0.00%	20.00%	\$29,259
CLP-29	I&C, Site Improvements, and Buildings	\$0	10.00%	0.00%	20.00%	\$0	\$30,333	10.00%	0.00%	20.00%	\$40,039
CLP-30	Limestone Storage and Make-up	\$0	10.00%	0.00%	20.00%	\$0	\$9,920	10.00%	0.00%	20.00%	\$13,094
CLP-31	Solid Byproduct Handling System	\$0	10.00%	0.00%	20.00%	\$0	\$12,493	10.00%	0.00%	20.00%	\$16,491
	TOTAL	\$342,552				\$492,551	\$625,087				\$856,467

Table 24. Owner's cost and TOC estimates for the SMR case.

	Base Plant		CLP Plant	
	Quantity	Cost	Quantity	Cost
Total Plant Cost (TPC) From Table 23		\$492,551,000		\$856,467,000
Preproduction Costs				
6 Months All Labor		\$7,024,386		\$9,298,861
1 Month Maintenance Materials @ 100% CF		\$985,102		\$1,712,934
1 Month Non-fuel Consumables @ 100% CF		\$3,065,973		\$694,176
1 Month Waste Disposal @ 100% CF		\$494		\$325,568
25% of 1 Month's Fuel Cost @ 100% CF		\$5,711,132		\$6,547,893
2% of TPC		\$9,851,020		\$17,129,340
Inventory Capital				
60-day Supply of Consumables @ 100% CF		\$876,906		\$1,369,333
60-day Supply of Coal @ 100% CF		\$0		\$4,281,279
0.5% of TPC (spare parts)		\$2,462,755		\$4,282,335
Land				
300 acres @ \$3,000/acre		\$900,000		\$900,000
Financing Costs				
2.7% of TPC		\$13,298,877		\$23,124,609
Other Owner's Costs				
15% of TPC		\$73,882,650		\$128,470,050
Initial Cost for Catalyst and Chemicals				
Shift Catalyst (ft ³)	1,574	\$785,158	0	\$0
MDEA Solution (gal)	28,187	\$245,227	0	\$0
MEA Solution (lb)	255,152	\$285,770	0	\$0
Limestone (ton)	0	\$0	266	\$4,592
Total Overnight Cost (TOC)		\$611,926,450		\$1,054,607,970

The TOC for the CLP steam methane reforming plant (\$1.055 billion) is about 72% greater than the TOC for the base steam methane reforming plant (\$612 million). As discussed in Section 4.2.1 and shown in Table 23, several base plant equipment items, including the water-gas shift reactors, MDEA system, and MEA system, are not required in the CLP plant. The elimination of these equipment items results in Total Plant Cost savings of about \$273 million. However, these savings are more-than offset by the capital for equipment and balance of plant facilities required for oxyfuel coal combustion and co-production of electricity in the Calcium Looping Process. As shown in Table 23, the capital cost for the CLP steam methane reforming plant includes costs for coal handling, preparation, and feed equipment and for a steam turbine and auxiliary equipment. These items, which are not required in the base plant, have a combined Total Plant Cost of \$93 million. As with the CLP coal-to-hydrogen plant, the coal-fired oxyfuel flash calciner and associated air separation unit account for a substantial portion (\$171 million) of the TPC associated with the CLP steam methane reforming plant. Moreover, because the CLP plant includes a steam cycle for electricity generation, it requires much more extensive

balance of plant facilities (e.g., feedwater system, cooling water system, accessory electric plant, instrumentation and controls, buildings and structures, and miscellaneous BOP) than the base plant requires. As a result, the TPC for balance of plant systems in the CLP plant is more-than double the TPC for BOP systems in the base plant. The capital costs for other major CLP equipment items (e.g., carbonators, hydrator, lockhoppers, heat exchangers, gas/solids separation equipment, solids handling equipment, etc.) also contribute to the TOC differential between the CLP and base plants.

Tables 25 and 26 show the estimated annual fixed O&M costs and variable O&M costs, respectively, for the base and CLP steam methane reforming plants. The CLP plant has greater estimated fixed O&M costs than the base plant, as its larger TPC results in greater expected maintenance costs, property taxes, and insurance costs. It also has greater variable O&M costs than the base plant, arising from its greater fuel consumption, water consumption, and solid waste disposal and from its significant consumption of limestone. (The variable O&M costs associated with WGS catalyst, MDEA solution, and MEA solution in the base plant, which total \$1,065,361/y, are less than the \$2,458,590/y required for limestone in the CLP plant). The difference in CO₂ emissions between the CLP and base plants is accounted for via the CO₂ emission taxes applied to both plants.

Table 27 shows the estimated first-year cost of hydrogen for the base steam methane reforming plant and the CLP steam methane reforming plant. As discussed in Section 3.2.4, different first-year capital charge factors were used when computing the first-year COH for these plants, based on differences in the relative proportions of hydrogen and electricity produced by each plant. If it is assumed that the electricity produced by the base SMR plant is sold at the base price of \$105/MWh, then the first-year COH for this plant is \$2.20/kg H₂. Use of the Calcium Looping Process results in a 9% reduction in the costs of hydrogen and electricity relative to the base plant. The first-year COH for the CLP steam methane reforming plant is \$1.99/kg H₂ at an electricity price of \$95.24/MWh. Hence, as with the coal-to-hydrogen case, the significant co-production of electricity in the CLP steam methane reforming plant more-than compensates for its greater capital, fixed O&M, and variable O&M costs (relative to the base SMR plant), resulting in an economic advantage over the base plant. (As discussed in Section 3.2.4, the economic advantage afforded by the CLP plant was distributed equally between the hydrogen and electric power products, such that the changes in cost of electricity and cost of hydrogen relative to the base plant values are equivalent on a percentage basis).

Table 25. Estimated annual fixed O&M costs for the SMR case.

	Base Plant	CLP Plant
Operating Labor	\$6,313,507	\$6,313,507
Maintenance Labor	\$4,925,510	\$8,564,670
Maintenance Material	\$10,639,102	\$18,499,687
Administrative and Support Labor	\$2,809,754	\$3,719,544
Property Taxes and Insurance	\$9,851,020	\$17,129,340
Total Fixed O&M Cost	\$34,538,893	\$54,226,749

Table 26. Estimated annual variable O&M costs for the SMR case.

Cost Element	Unit Cost	Unit	Base Plant				CLP Plant		
			Consumption	Unit Rate	Annual Variable O&M Cost		Consumption	Unit Rate	Annual Variable O&M Cost
Natural Gas	\$298.00	ton	2,520	ton/day	\$246,720,903		2,650	ton/day	\$259,428,980
Coal	\$38.19	ton	0	ton/day	\$0		1,868	ton/day	\$23,440,004
CO ₂ Emission Tax	\$27.22	ton	669	ton/day	\$5,983,991		73	ton/day	\$655,225
Water	\$1.08	1000 gal	4,702	1000 gal/day	\$1,668,034		7,217	1000 gal/day	\$2,560,547
Water Treatment Chemicals	\$0.17	lb	13,731	lb/day	\$766,806		21,078	lb/day	\$1,177,100
Reforming Catalyst	\$440.00	ft ³	9	ft ³ /day	\$1,300,860		9	ft ³ /day	\$1,300,860
Shift Catalyst	\$498.83	ft ³	5	ft ³ /day	\$819,328		0	ft ³ /day	\$0
MDEA Solution	\$8.70	gal	40	gal/day	\$114,318		0	gal/day	\$0
MEA Solution	\$1.12	lb	358	lb/day	\$131,715		0	lb/day	\$0
Solid Waste Disposal	\$16.23	ton	1	ton/day	\$5,332		659	ton/day	\$3,516,139
Limestone	\$17.25	ton	0	ton/day	\$0		434	ton/day	\$2,458,590
Total Annual Fuel Cost					\$246,720,903				\$282,868,984
Total Annual CO₂ Emission Tax Cost					\$5,983,991				\$655,225
Total Annual Other Variable O&M Cost					\$4,806,393				\$11,013,235

Table 27. First-year cost of hydrogen estimates for the SMR case.

	Base Plant			CLP Plant	
First-Year Capital Charge Factor	0.2044			0.1853	
Hydrogen Production (kg/y)	202,532,076			201,664,836	
Electric Power Production (MWh/y)	-269,633			1,489,295	
Cost of Electricity (\$/MWh)	\$105.00			\$95.24	
First-Year Cost of Hydrogen	Cost (\$/y)	COH (\$/kg H ₂)		Cost (\$/y)	COH (\$/kg H ₂)
Capital	\$125,077,766	\$0.62		\$195,385,491	\$0.97
Fixed O&M	\$34,538,893	\$0.17		\$54,226,749	\$0.27
Fuel	\$246,720,903	\$1.22		\$282,868,984	\$1.40
CO ₂ Emissions	\$5,983,991	\$0.03		\$655,225	\$0.00
Other Variable O&M	\$4,806,393	\$0.02		\$11,013,235	\$0.05
Electric Power ^a	\$28,311,444	\$0.14		-\$141,841,991	-\$0.70
Total	\$445,439,389	\$2.20		\$402,307,694	\$1.99

^aComputed using an electricity price equal to the plant-specific cost of electricity shown in the table.

4.3 Integrated Gasification-Combined Cycle Case

4.3.1 Process Design

Figure 8 presents a block flow diagram for the base IGCC plant. This plant, like the base coal-to-hydrogen plant, uses an oxygen-blown GE Energy radiant-only gasifier to produce syngas from 220,904 kg/h of coal. However, in the IGCC plant, the syngas is used to produce electricity rather than high-purity hydrogen, and two, 50% capacity gasifier trains are used to achieve 80% availability. As with the base coal-to-hydrogen plant, the syngas produced in the conventional IGCC plant is cooled, shifted, and cleaned using a water quench, a syngas scrubber, water-gas shift reactors, syngas coolers, a mercury removal system, and a two-stage Selexol unit for H₂S and CO₂ removal. The H₂S captured in the Selexol unit is sent to a Claus plant to produce elemental sulfur, and the CO₂ captured in the Selexol unit is dried and compressed to 153 bar (2,215 psia) for sequestration. A cryogenic ASU is used to supply 95% (by volume) purity oxygen to the gasifier and Claus plant. In the base IGCC plant, however, the clean syngas leaving the Selexol unit is reheated using high-pressure boiler feedwater, expanded to 31.7 bar (460 psia) using a turboexpander, diluted with nitrogen (obtained from the gasifier ASU) to achieve a lower heating value (LHV) of 4.4-4.7 MJ/Nm³ (119-125 Btu/scf), and sent to a combined cycle power island to generate electricity. The power island includes two advanced F Class combustion turbines, each rated at 232 MW_e. The hot flue gas from these turbines is cooled to 132°C (270°F) in a HRSG to raise steam. This steam, along with steam raised in the radiant syngas cooler, is sent to a steam turbine-generator to produce additional electricity. Additional information regarding the base IGCC plant design, including a detailed process description, process flow diagram, and heat and material balance results, can be found in Sections 3.1 and 3.2 of the DOE bituminous baseline report.²

Figure 8. Block flow diagram for the base IGCC plant.

Figure 9 presents a block flow diagram for the CLP integrated gasification-combined cycle plant. As discussed above, the CLP plant is designed for the same gasifiers and F Class combustion turbines that are used in the base plant. As with the coal-to-hydrogen case, use of the Calcium Looping Process eliminates the need for the water quench, syngas scrubber, shift reactors, syngas coolers, 2-stage Selexol unit, and Claus plant in the IGCC case.

Figure 10 provides a process flow diagram for the Calcium Looping Process as applied to the IGCC plant. The system boundaries for this PFD correspond to the red box in Figure 9. Table 28 provides temperature, pressure, enthalpy, mass flow rate, and chemical composition data for the streams that are labeled in Figure 10. These data were derived from material and energy balances performed in Aspen Plus®.

As shown in Figure 10, the CLP process design for the IGCC case is very similar to that for the coal-to-hydrogen case (see Section 4.1.1), with three noteworthy exceptions. First, the carbonator operates at a greater pressure in the IGCC case than in the coal-to-hydrogen case, because the combustion turbine inlet pressure (31.7 bar) is greater than the pressure specification for high-purity hydrogen product (22 bar). As a result, a higher carbonator operating temperature (700°C) is also used in the IGCC case to provide for $\text{Ca}(\text{OH})_2$ dissociation at this higher pressure. Second, because the desired product in the IGCC case is electricity rather than hydrogen, the clean, shifted syngas leaving the carbonator is treated differently than in the coal-to-hydrogen case to meet the inlet specifications for the combustion turbine. In particular, H_2O is not condensed from the syngas stream in the IGCC case; the H_2O serves as a diluent and reduces the amount of nitrogen that must be compressed to dilute the syngas to the required LHV. In addition to cooling and dehydrating the syngas, the condensers in the coal-to-hydrogen case serve to remove residual particulate matter from the syngas. Hence, in the absence of these condensers, a metallic filter is required in the IGCC case to

capture particulate matter ahead of the combustion turbine. Finally, because there is no PSA tailgas in the IGCC case, the calciner is fired exclusively using coal. Hence, more coal is required than in the coal-to-hydrogen case.

Figure 9. Block flow diagram for the CLP IGCC plant.

4.3.2 Process Simulation Results

Table 29 summarizes the modeled performance of the CLP integrated gasification-combined cycle plant and compares this with the performance of the base IGCC plant (taken from Case 2 of the DOE bituminous baseline report).

As discussed above, both plants are designed for a gasifier coal feed rate of 220,904 kg/h (487,011 lb/h), and both generate ~460 MW_e of electric power from their gas combustion turbines. However, the CLP plant also consumes 152,850 kg/h (336,976 lb/h) of coal to fuel its entrained bed calciner. As with the coal-to-hydrogen and SMR cases, this additional fuel provides the heat for sorbent regeneration as well as significant excess heat that can be used to raise steam for electricity generation. This heat, combined with heat recovered from the exothermic reactions in the carbonator and hydrator, contributes to significantly greater electric power generation from the steam cycle in the CLP plant than in the base plant. The gross steam turbine electric power output is 775 MW_e in the CLP plant and 264 MW_e in the base plant. After accounting for differences in turboexpander electricity generation and auxiliary load, the CLP plant produces 390 MW_e more net electric power than the base plant, in spite of using the same gasifiers and gas combustion turbines. (The auxiliary load in the CLP plant is 127 MW_e greater than the auxiliary load in the base plant. Much of this difference arises from the parasitic power associated with the calciner ASU and significantly larger CO₂ compression

Figure 10. Process flow diagram for the Calcium Looping Process in the IGCC case.

Table 28. Stream table for the Calcium Looping Process in the IGCC case.

	1	2	3	4	5	6	7	8	9
Temperature (°C)	677	592	700	196	15	662	15	15	17
Pressure (bar)	56	33	32	32	1	1	1	1	1
Enthalpy (kJ/kg)	-5,243	-5,396	-8,196	-10,066	-12,110	-8,470	-2,116	-97	-123
Mass Flow (kg/hr)	465,270	465,270	320,010	228,307	46,595	1,880,670	152,850	1,441,410	1,098,490
Vapor-Liquid Components (kg/h)									
Ar	7,944	7,944	7,944	7,944	0	0	0	18,359	3,898
CH ₄	408	408	408	408	0	0	0	0	0
C ₂ H ₆	0	0	1	1	0	0	0	0	0
C ₃ H ₈	0	0	0	0	0	0	0	0	0
C ₄ H ₁₀	0	0	0	0	0	0	0	0	0
CO	231,602	231,602	1,139	1,139	0	0	0	0	0
CO ₂	140,428	140,428	1,796	1,796	0	0	0	660	660
COS	278	278	0	0	0	0	0	0	0
H ₂	15,876	15,876	32,106	32,106	0	0	0	0	0
H ₂ O	57,026	57,026	179,320	179,320	0	0	0	8,909	8,909
H ₂ S	5,753	5,753	203	203	0	0	0	0	0
N ₂	4,534	4,534	4,821	4,821	0	0	0	1,081,970	1,077,110
NH ₃	748	748	400	400	0	0	0	0	0
O ₂	0	0	0	0	0	0	0	331,513	7,923
SO ₂	0	0	0	0	0	0	0	0	0
Other	674	674	169	169	0	0	0	0	0
Solid Components (kg/h)									
CaCO ₃	0	0	56,965	0	45,477	1,184,780	0	0	0
CaO	0	0	8,643	0	0	172,861	0	0	0
Ca(OH) ₂	0	0	0	0	0	0	0	0	0
CaS	0	0	791	0	0	15,813	0	0	0
CaSO ₄	0	0	0	0	0	0	0	0	0
Coal	0	0	0	0	0	0	152,850	0	0
Ash / Other	0	0	25,305	0	1,118	507,211	0	0	0

Table 28. (continued)

	10	11	12	13	14	15	16	17	18
Temperature (°C)	13	951	132	132	132	21	875	204	493
Pressure (bar)	2	1	1	1	1	1	1	3	2
Enthalpy (kJ/kg)	-11	-7,979	-8,760	-9,001	-9,001	-8,765	-6,781	-13,090	-8,980
Mass Flow (kg/hr)	342,920	2,116,800	71,903	1,073,710	971,192	899,337	1,333,340	365,000	1,597,110
Vapor-Liquid Components (kg/h)									
Ar	14,461	30,449	0	15,988	14,461	14,461	0	0	0
CH ₄	0	0	0	0	0	0	0	0	0
C ₂ H ₆	0	0	0	0	0	0	0	0	0
C ₃ H ₈	0	0	0	0	0	0	0	0	0
C ₄ H ₁₀	0	0	0	0	0	0	0	0	0
CO	0	2	0	0	0	0	0	0	0
CO ₂	0	1,841,440	0	963,123	871,165	871,155	0	0	0
COS	0	0	0	0	0	0	0	0	0
H ₂	0	0	0	0	0	0	0	0	0
H ₂ O	0	164,950	0	86,726	78,445	6,601	0	365,000	0
H ₂ S	0	0	0	0	0	0	0	0	0
N ₂	4,869	14,274	0	7,495	6,780	6,780	0	0	0
NH ₃	0	0	0	0	0	0	0	0	0
O ₂	323,590	526	0	270	244	244	0	0	0
SO ₂	0	17	0	0	0	0	0	0	0
Other	0	1,070	0	107	96	96	0	0	0
Solid Components (kg/h)									
CaCO ₃	0	0	15,556	0	0	0	0	0	82
CaO	0	9,396	0	0	0	0	820,977	0	0
Ca(OH) ₂	0	0	0	0	0	0	0	0	1,084,660
CaS	0	0	0	0	0	0	0	0	0
CaSO ₄	0	39,049	39,086	0	0	0	7,044	0	7,044
Coal	0	0	0	0	0	0	0	0	0
Ash / Other	0	15,629	17,261	0	0	0	505,323	0	505,323

Table 29. Summary of process performance results for the IGCC case.

	Base Plant	CLP Plant
Coal Feed Rate, kg/h (lb/h)		
Gasifier	220,904 (487,011)	220,904 (487,011)
Calciner	0 (0)	152,850 (336,976)
Total	220,904 (487,011)	373,754 (823,987)
Total HHV Heat Input, kW _t (mmBtu/h)	1,665,075 (5,681)	2,817,184 (9,613)
Gross Electric Power Output, kW _e		
Gas Turbine	464,000	455,850
Steam Turbine	263,500	774,810
Turboexpander	6,500	19,790
Total	734,000	1,250,450
Auxiliary Load, kW _e		
Coal Handling, Prep, and Feed	2,930	4,830
Gasifier ASU and O ₂ Compressors	78,970	77,810
Nitrogen Compressors	35,640	19,350
Slag Handling	1,160	1,160
Quench Water Pump	540	0
Scrubber Pumps	230	0
Selexol System	19,230	0
Claus Plant	2,030	0
Calciner ASU	0	80,500
Limestone Handling, Prep, and Feed	0	1,790
Spent Sorbent Handling	0	2,130
Hydrator Auxiliaries	0	7,760
Lockhopper Feed Systems	0	7,190
CLP System Fans	0	4,150
CO ₂ Compressor	31,160	73,490
Feedwater Pumps	4,180	12,290
Condensate Pump	280	610
Steam Turbine Auxiliaries	100	100
Gas Turbine Auxiliaries	1,000	1,000
Ground Water Pumps	530	1,070
Circulating Water Pump	4,620	9,610
Cooling Tower Fans	2,390	4,970
Miscellaneous Balance of Plant	3,000	3,000
Transformer Losses	2,760	4,700
Total	190,750	317,510
Net Electric Power Output, kW _e	543,250	932,940
CO ₂ Capture Efficiency, %	90	>99
Net CO ₂ Emissions, kg/h (lb/h)	49,131 (108,316)	4,709 (10,381)
Oxygen Demand, kg/h (lb/h)		
Gasifier	177,828 (392,044)	177,828 (392,044)
Claus Plant	3,080 (6,791)	0 (0)
Calciner	0 (0)	342,920 (756,008)
Total	180,908 (398,835)	520,748 (1,148,052)
Raw Water Demand, m ³ /min (gpm)	22.0 (5,815)	44.3 (11,716)
Cooling Tower Load, GJ/h (mmBtu/h)	2,350 (2,227)	4,461 (4,228)
Elemental Sulfur Byproduct, kg/h (lb/h)	5,524 (12,178)	0 (0)
Solid Waste, kg/h (lb/h)	24,237 (53,433)	96,140 (211,952)

^aCO₂ capture efficiency = (carbon in product for sequestration) ÷ (carbon in fuel + carbon in limestone makeup – carbon in slag – carbon in spent sorbent purge); ^bFlow rates shown are for 95% (v/v) purity O₂

requirement in the CLP plant.) The overall net efficiency of the CLP plant (33.1%, HHV basis) is slightly greater than that of the base plant (32.7%, HHV basis).

Although the CLP plant produces significantly more CO₂ than the base plant (owing to the additional CO₂ produced from coal combustion in the calciner and from calcination of the makeup limestone sorbent), it achieves a CO₂ capture efficiency of >99%, compared to the base plant capture efficiency of ~90%. (The Selexol system in the base plant is only designed for 90% CO₂ capture efficiency). As a result, the CLP plant CO₂ emission rate is 44,422 kg/h (97,935 lb/h) less than the base plant CO₂ emission rate.

As with the coal-to-hydrogen and SMR cases, the CLP integrated gasification-combined cycle plant consumes significantly more water and produces significantly more solid waste than the base IGCC plant. The difference in water consumption between these plants arises largely from greater cooling load in the CLP plant, which results in 5,129 gpm of additional cooling tower water makeup relative to the base plant. (The CLP plant has a greater cooling load than the base plant because of its larger steam cycle condenser duty, its larger CO₂ compressor intercooling requirement, and the added cooling load associated with the calciner ASU). The difference in solid waste production between the CLP and base plants results from the use of a solid sorbent (with 3% purge rate) in the CLP plant and from the greater overall coal feed rate (and, therefore, greater ash production) in the CLP plant than in the base plant.

Process performance results for the IGCC case are discussed further and compared with results for the coal-to-hydrogen and SMR cases in Section 5 of this report.

4.3.3 Process Economics

Tables 30-31 summarize the capital cost estimates for the base IGCC plant and CLP IGCC plant. Table 30 shows the estimated Bare Erected Cost and Total Plant Cost for each plant, as well as a breakdown of these costs by major equipment item. Table 31 shows the estimated owner's costs and Total Overnight Cost for each plant. The TOCs for the base and CLP plants in the IGCC case (\$1.811 billion and \$2.700 billion, respectively) are similar to those for the base and CLP plants in the coal-to-hydrogen case (\$1.866 and \$2.588 billion, respectively). This result is expected, as the process designs for these cases are very similar. As with the coal-to-hydrogen case, the CLP plant in the IGCC plant has a substantially higher capital cost than the corresponding base plant (for fixed gasifier and gas combustion turbine sizes). This difference, again, is largely attributable to the costs associated with oxy-fired coal combustion in the entrained bed calciner and the production of significant additional electricity in the Calcium Looping Process (i.e., the costs for the calciner and calciner ASU, as well as the costs for expanding the coal handling, preparation, and feed equipment, feedwater and miscellaneous BOP systems, CO₂ compression and drying equipment, steam turbine-generator and auxiliary equipment, cooling water system, and accessory electric plant in the CLP plant). When capital costs are normalized by net electric power output, however, the TOC for the CLP plant (\$2,894/kW_{net}) is less than the TOC for the base plant (\$3,335/kW_{net}).

Table 30. Total Plant Cost estimates for the IGCC case.

Acct No.	Item/Description	Base Plant					CLP Plant				
		Bare Erected Cost (\$ 000)	Engineering, Construction Management, Home Office, & Fee (%)	Process Contingency (%)	Project Contingency (%)	Total Plant Cost (\$ 000)	Bare Erected Cost (\$ 000)	Engineering, Construction Management, Home Office, & Fee (%)	Process Contingency (%)	Project Contingency (%)	Total Plant Cost (\$ 000)
1	Coal Handling	\$28,008	9.08%	0.00%	20.00%	\$36,660	\$44,960	9.08%	0.00%	20.00%	\$58,849
2	Coal Prep and Feed	\$43,489	9.09%	3.63%	20.00%	\$58,826	\$52,277	9.09%	3.63%	20.00%	\$70,713
3	Feedwater and Misc. BOP Systems	\$28,309	9.44%	0.00%	23.13%	\$38,146	\$58,312	9.44%	0.00%	23.13%	\$78,575
4	Gasifier Island										
4.1	GEE Syngas Cooler Gasifier System	\$176,251	9.16%	13.88%	15.33%	\$250,109	\$176,251	9.16%	13.88%	15.33%	\$250,109
4.2	Syngas Cooler (w/Gasifier-4.1)	\$0	0.00%	0.00%	0.00%	\$0	\$0	0.00%	0.00%	0.00%	\$0
4.3	ASU / Oxidant Compression	\$193,046	9.69%	0.00%	10.00%	\$232,934	\$190,936	9.69%	0.00%	10.00%	\$230,388
4.4-4.9	Other Gasification Equipment	\$32,449	9.49%	0.00%	21.83%	\$43,282	\$32,449	9.49%	0.00%	21.83%	\$43,282
5A	Gas Cleanup and Piping										
5A.1	Double Stage Selexol	\$137,025	9.67%	20.00%	20.00%	\$213,218	\$0	9.67%	20.00%	20.00%	\$0
5A.2	Elemental Sulfur Plant	\$25,713	9.71%	0.00%	20.00%	\$33,853	\$0	9.71%	0.00%	20.00%	\$0
5A.3	Mercury Removal	\$2,423	9.66%	4.99%	20.01%	\$3,334	\$2,423	9.66%	4.99%	20.01%	\$3,334
5A.4	Shift Reactors	\$13,456	9.59%	0.00%	20.00%	\$17,695	\$0	9.59%	0.00%	20.00%	\$0
5A.6	Blowback Gas Systems	\$1,605	12.21%	0.00%	19.99%	\$2,161	\$0	12.21%	0.00%	19.99%	\$0
5A.7	Fuel Gas Piping	\$1,078	9.28%	0.00%	20.03%	\$1,414	\$1,078	9.28%	0.00%	20.03%	\$1,414
5A.9	HGCU Foundations	\$1,056	9.19%	0.00%	30.01%	\$1,499	\$1,056	9.19%	0.00%	30.01%	\$1,499
5B	CO ₂ Compression and Drying	\$29,446	9.63%	0.00%	20.00%	\$38,738	\$44,470	9.63%	0.00%	20.00%	\$58,503
6	Combustion Turbine/Accessories										
6.1	Combustion Turbine Generator	\$98,609	9.48%	10.00%	10.00%	\$129,600	\$97,394	9.48%	10.00%	10.00%	\$128,003
6.2	Syngas Expander	\$6,316	9.50%	0.00%	15.01%	\$7,954	\$7,560	9.50%	0.00%	15.01%	\$9,521
6.9	Combustion Turbine Foundations	\$1,868	9.37%	0.00%	30.00%	\$2,656	\$1,868	9.37%	0.00%	30.00%	\$2,656
7	HRSG, Ducting, and Stack	\$47,336	9.46%	0.00%	11.18%	\$57,610	\$47,519	9.46%	0.00%	11.18%	\$57,833
8	Steam Turbine Generator										
8.1	Steam TG & Accessories	\$32,931	9.60%	0.00%	10.00%	\$39,700	\$70,064	9.60%	0.00%	10.00%	\$84,466
8.2	Turbine Plant Auxiliaries and Steam Piping	\$18,253	9.11%	0.00%	19.83%	\$23,865	\$34,864	9.11%	0.00%	19.83%	\$45,583
9	Cooling Water System	\$28,483	9.29%	0.00%	20.39%	\$37,477	\$44,197	9.29%	0.00%	20.39%	\$58,153
10	Ash/Spent Sorbent Handling System	\$37,910	9.63%	0.00%	10.77%	\$46,038	\$37,910	9.63%	0.00%	10.77%	\$46,038
11	Accessory Electric Plant	\$69,237	8.60%	0.00%	18.97%	\$89,451	\$99,434	8.60%	0.00%	18.97%	\$128,464
12	Instrumentation and Control	\$20,849	9.06%	5.00%	16.66%	\$27,742	\$20,849	9.06%	5.00%	16.66%	\$27,742
13	Improvements to Site	\$14,140	9.87%	0.00%	30.00%	\$20,197	\$17,675	9.87%	0.00%	30.00%	\$25,246

Table 30. (continued)

Acct No.	Item/Description	Base Plant					CLP Plant				
		Bare Erected Cost (\$ 000)	Engineering, Construction Management, Home Office, & Fee (%)	Process Contingency (%)	Project Contingency (%)	Total Plant Cost (\$ 000)	Bare Erected Cost (\$ 000)	Engineering, Construction Management, Home Office, & Fee (%)	Process Contingency (%)	Project Contingency (%)	Total Plant Cost (\$ 000)
14	Buildings and Structures	\$14,716	9.11%	0.00%	16.37%	\$18,684	\$14,716	9.11%	0.00%	16.37%	\$18,684
15	CLP Equipment										
15.1	Carbonator	\$0	9.41%	25.00%	20.00%	\$0	\$15,029	9.41%	25.00%	20.00%	\$24,241
15.2	Flash Calciner	\$0	9.41%	15.00%	20.00%	\$0	\$108,916	9.41%	15.00%	20.00%	\$162,605
15.3	Hydrator	\$0	9.41%	30.00%	20.00%	\$0	\$60,187	9.41%	30.00%	20.00%	\$100,689
15.4	Hydrator Auxiliaries	\$0	9.41%	0.00%	20.00%	\$0	\$15,930	9.41%	0.00%	20.00%	\$20,915
15.5	Calciner ASU	\$0	9.41%	0.00%	20.00%	\$0	\$157,625	9.41%	0.00%	20.00%	\$206,952
15.6	Carbonator Product Lockhoppers	\$0	9.41%	10.00%	20.00%	\$0	\$24,109	9.41%	10.00%	20.00%	\$34,547
15.7	Hydrated Lime Lockhoppers	\$0	9.41%	10.00%	20.00%	\$0	\$27,887	9.41%	10.00%	20.00%	\$39,960
15.8	Cyclones	\$0	9.41%	0.00%	20.00%	\$0	\$3,839	9.41%	0.00%	20.00%	\$5,039
15.9	Firetube Boiler	\$0	9.41%	0.00%	20.00%	\$0	\$8,508	9.41%	0.00%	20.00%	\$11,170
15.10	Metallic Filter	\$0	9.41%	0.00%	20.00%	\$0	\$25,740	9.41%	0.00%	20.00%	\$33,795
15.11	Calciner Off-Gas HRSG	\$0	9.41%	0.00%	20.00%	\$0	\$42,132	9.41%	0.00%	20.00%	\$55,317
15.12	CO ₂ Stream Condenser	\$0	9.41%	0.00%	20.00%	\$0	\$4,741	9.41%	0.00%	20.00%	\$6,225
15.13	Solids Purge Fabric Filter	\$0	9.41%	0.00%	20.00%	\$0	\$6,664	9.41%	0.00%	20.00%	\$8,749
15.14	Calciner Off-Gas ID Fan	\$0	9.41%	0.00%	20.00%	\$0	\$4,431	9.41%	0.00%	20.00%	\$5,818
15.15	CO ₂ Recycle Fan	\$0	9.41%	0.00%	20.00%	\$0	\$537	9.41%	0.00%	20.00%	\$705
15.16	Limestone Storage and Make-Up	\$0	9.41%	0.00%	20.00%	\$0	\$19,557	9.41%	0.00%	20.00%	\$25,677
15.17	Solid Byproduct Handling System	\$0	9.41%	0.00%	20.00%	\$0	\$22,514	9.41%	0.00%	20.00%	\$29,559
	TOTAL	\$1,104,002				\$1,472,843	\$1,646,608				\$2,201,018

Table 31. Owner's cost and TOC estimates for the IGCC case.

	Base Plant		CLP Plant	
	Quantity	Cost	Quantity	Cost
Total Plant Cost (TPC)				
From Table 30		\$1,472,843,000		\$2,201,018,000
Preproduction Costs				
6 Months All Labor		\$13,487,622		\$18,205,037
1 Month Maintenance Materials @ 100% CF		\$2,997,896		\$4,480,059
1 Month Non-fuel Consumables @ 100% CF		\$381,679		\$1,187,234
1 Month Waste Disposal @ 100% CF		\$316,534		\$1,255,599
25% of 1 Month's Fuel Cost @ 100% CF		\$1,697,154		\$2,871,464
2% of TPC		\$29,456,860		\$44,020,360
Inventory Capital				
60-day Supply of Consumables @ 100% CF		\$752,901		\$2,341,941
60-day Supply of Coal @ 100% CF		\$13,391,244		\$22,657,033
0.5% of TPC (spare parts)		\$7,364,215		\$11,005,090
Land				
300 acres @ \$3,000/acre		\$900,000		\$900,000
Financing Costs				
2.7% of TPC		\$39,766,761		\$59,427,486
Other Owner's Costs				
15% of TPC		\$220,926,450		\$330,152,700
Initial Cost for Catalyst and Chemicals				
Carbon (Mercury Removal) (lb)	79,786	\$83,775	79,786	\$83,775
Shift Catalyst (ft ³)	6,246	\$3,115,692	0	\$0
Selexol Solution (gal)	298,502	\$3,999,927	0	\$0
Limestone (ton)	0	\$0	2,256	\$38,924
Total Overnight Cost (TOC)		\$1,811,481,711		\$2,699,644,703

Tables 32 and 33 show the estimated fixed O&M costs and variable O&M costs, respectively, for the base and CLP integrated gasification-combined cycle plants. The CLP plant has greater estimated fixed O&M costs than the base plant, as its larger TPC results in greater expected maintenance costs, property taxes, and insurance costs. It also has greater variable O&M costs than the base plant, arising from its greater coal consumption, water consumption, and solid waste disposal and from its significant consumption of limestone. (The variable O&M costs associated with the WGS catalyst, Selexol solution, and Claus catalyst in the base plant, which total \$1,072,131/y, are much less than the \$6,209,049/y required for limestone in the CLP plant). The difference in CO₂ emissions between the CLP and base plants is accounted for via the CO₂ emission taxes applied to both plants.

Table 32. Estimated annual fixed O&M costs for the IGCC case.

	Base Plant	CLP Plant
Operating Labor	\$6,313,507	\$6,313,507
Maintenance Labor	\$15,266,687	\$22,814,552
Maintenance Material	\$28,779,806	\$43,008,570
Administrative and Support Labor	\$5,395,049	\$7,282,015
Property Taxes and Insurance	\$29,456,860	\$44,020,360
Total Fixed O&M Cost	\$85,211,909	\$123,439,004

Table 33. Estimated annual variable O&M costs for the IGCC case.

Cost Element	Unit Cost	Unit	Base Plant				CLP Plant		
			Consumption	Unit Rate	Annual Variable O&M Cost		Consumption	Unit Rate	Annual Variable O&M Cost
Coal	\$38.19	ton	5,844	ton/day	\$65,170,721		9,888	ton/day	\$110,264,228
CO ₂ Emission Tax	\$27.22	ton	1,350	ton/day	\$10,726,766		163	ton/day	\$1,293,637
Water	\$1.08	1000 gal	4,187	1000 gal/day	\$1,320,349		8,436	1000 gal/day	\$2,660,226
Water Treatment Chemicals	\$0.17	lb	24,944	lb/day	\$1,238,220		50,257	lb/day	\$2,494,753
Carbon (Mercury Removal)	\$1.05	lb	109	lb/day	\$33,419		109	lb/day	\$33,419
Shift Catalyst	\$498.83	ft ³	4	ft ³ /day	\$623,418		0	ft ³ /day	\$0
Selexol Solution	\$13.40	gal	95	gal/day	\$371,668		0	gal/day	\$0
Claus Catalyst	\$131.27	ft ³	2	ft ³ /day	\$77,045		0	ft ³ /day	\$0
Solid Waste Disposal	\$16.23	ton	641	ton/day	\$3,038,730		2,543	ton/day	\$12,053,750
Elemental Sulfur Byproduct	\$0.00	ton	146	ton/day	\$0		0	ton/day	\$0
Limestone	\$17.25	ton	0	ton/day	\$0		1,233	ton/day	\$6,209,049
Total Annual Fuel Cost					\$65,170,721				\$110,264,228
Total Annual CO₂ Emission Tax Cost					\$10,726,766				\$1,293,637
Total Annual Other Variable O&M Cost					\$6,702,850				\$23,451,197

Table 34 shows the estimated first-year cost of electricity for the base IGCC plant and the CLP IGCC plant. As discussed in Section 3.2.4, a first-year capital charge factor of 0.1240 was used when computing the first-year COE for both IGCC plants. Use of the Calcium Looping Process results in a 12% reduction in the cost of electricity relative to the base plant. The first-year COE for the CLP IGCC plant is \$90.73/MWh, whereas the first-year COE for the base plant is \$103.08/MWh.

Table 34. First-year cost of electricity estimates for the IGCC case.

	Base Plant			CLP Plant	
First-Year Capital Charge Factor	0.1240			0.1240	
Electric Power Production (MWh/y)	3,807,096			6,538,079	
First-Year Cost of Electricity	Cost (\$/y)	COE (\$/MWh)		Cost (\$/y)	COE (\$/MWh)
Capital	\$224,623,732	\$59.00		\$334,755,943	\$51.20
Fixed O&M	\$85,211,909	\$22.38		\$123,439,004	\$18.88
Fuel	\$65,170,721	\$17.12		\$110,264,228	\$16.86
CO ₂ Emissions	\$10,726,766	\$2.82		\$1,293,637	\$0.20
Other Variable O&M	\$6,702,850	\$1.76		\$23,451,197	\$3.59
Total	\$392,435,978	\$103.08		\$593,204,009	\$90.73

5. Discussion

5.1 Technical Performance of the Calcium Looping Process

Detailed process simulation results for the coal-to-hydrogen, SMR, and IGCC cases are presented in Tables 15, 22, and 29, respectively, in Section 4 of this report. Table 35 summarizes several key performance results from all three cases.

As shown in the table, in each of the cases studied in this report, the CLP plant consumes significantly more fuel and oxygen than the base plant. The additional fuel and oxygen are required to satisfy the energy demand for sorbent regeneration in the oxyfuel calciner, but they also contribute to significant co-production of electricity in the CLP plants. As discussed above, unlike conventional chemical and physical solvent processes, the Calcium Looping Process enables much of the energy associated with CO₂ capture to be recovered as high-quality heat that can be used to raise steam for electricity generation. This energy includes both the exothermic heat of the CO₂ absorption reaction and the extra energy that must be supplied to achieve the temperatures required for sorbent regeneration. The data presented in Table 35 indicate that, for an IGCC plant with fixed gasifier and combustion turbine sizes, use of the CLP results in about 72% greater net electric output than the use of conventional WGS and acid gas removal technologies. The CLP plant also is more efficient than the conventional IGCC plant with CO₂ capture. The CLP plant has a net efficiency (HHV basis) of 33.1%, compared with 32.7% for the base IGCC plant. Although this difference might appear to be small, it is important to remember that 41% of the heat input in the CLP plant is fed to the calciner rather than the gasifier. The calciner is a pulverized coal combustor, and the efficiency of producing electricity via pulverized coal combustion with CO₂ capture is expected to be significantly less than the efficiency of producing electricity via coal-based IGCC with CO₂ capture. Whereas the

base IGCC plant, which includes 90% CO₂ capture, has a net efficiency of 32.7%, the projected efficiency for a comparable subcritical PC power plant equipped with an MEA scrubbing system for 90% CO₂ capture is only 26.2%.² (The efficiency of a PC oxycombustion power plant with CO₂ capture is expected to be similar to or slightly better than the efficiency of a PC power plant with MEA scrubbing).⁶ Hence, the efficiency of the CLP IGCC plant, which essentially integrates a subcritical PC power plant with a coal-based IGCC power plant, might be more appropriately compared with the efficiency of a hypothetical “blended” base plant including IGCC and PC components in the same proportion as the CLP plant. This comparison is shown in Table 36. The efficiency of the CLP plant is 3.1 percentage points (or 10% on a relative basis) greater than the efficiency of the “blended” base plant, indicating the potential performance improvement afforded by the Calcium Looping Process over conventional CO₂ capture technologies.

Table 35. Summary of technical performance results for the base and CLP plants in each of the coal-to-hydrogen, IGCC, and SMR cases. For each case, the CLP and base plants were designed using the same gasifier/reformer, gasifier/reformer fuel feed rate and composition, and CO₂ and H₂ product specifications, as detailed in the text.

	Coal-to-Hydrogen Case		SMR Case		IGCC Case	
	Base Plant	CLP Plant	Base Plant	CLP Plant	Base Plant	CLP Plant
Coal Feed (ton/h)	244	372	0	78	244	412
Natural Gas Feed (ton/h)	0	0	105	110	0	0
O ₂ Consumption ^a (ton/h)	199	550	0	189	199	574
Solid Waste (ton/h)	27	102	<1	27	27	106
CO ₂ Sequestered (ton/h)	503	871	250	481	503	960
Net CO ₂ Emissions (ton/h)	54	0	28	4	54	5
H ₂ Production (ton/h)	28	28	28	28	0	0
Net Electric Power (MW _e)	7	319	-34	189	543	933

Note: Mass flow rates are expressed in short tons per hour; multiply by 907.18 to convert to kg/h. ^a95% (v/v) purity.

Table 36. Comparison of the efficiency of the CLP IGCC plant with the efficiencies of the base IGCC plant, a base subcritical PC plant, and a hypothetical base plant including IGCC and PC components in the same ratio as the CLP plant. All plants include ≥90% CO₂ capture and compression. CO₂ capture is accomplished using a Selexol system in the base IGCC cases and an MEA scrubbing system in the base PC cases.

	Base IGCC Plant with ≥90% CO ₂ Capture	Base PC Plant with ≥90% CO ₂ Capture	Base “Blended” IGCC + PC Plant with ≥90% CO ₂ Capture	CLP Plant with ≥90% CO ₂ Capture
IGCC Heat Input, % of total	100	0	59	59
PC Heat Input, % of total	0	100	41	41
Net HHV Efficiency, %	32.7	26.2	30.0	33.1
Net HHV Heat Rate, Btu/kWh	10,458	13,046	11,381	10,304

Because of the significant availability of high-quality, recoverable heat, the Calcium Looping Process necessarily results in co-production of electricity when it is applied to a hydrogen production plant. As shown in Table 35, for the coal-to-hydrogen and SMR cases, the base plant and the CLP plant produce roughly equal amounts of hydrogen. However, whereas the base coal-to-hydrogen and SMR plants generate little or no net electric power, the CLP coal-to-hydrogen and SMR plants generate 319 MW_e and 189 MW_e, respectively. In effect, then, application of the Calcium Looping Process amounts to integrating the hydrogen plant with a commercial-scale pulverized coal power plant with CO₂ capture. The efficiency of hydrogen production facilities is typically reported as either the cold gas efficiency (CGE = Hydrogen Product HHV ÷ Fuel HHV) or the effective thermal efficiency (ETE = [Hydrogen Product HHV + Net Electric Power] ÷ Fuel HHV). The CLP coal-to-hydrogen and SMR plants have cold gas efficiencies of 39.9% and 50.2%, respectively, which are significantly lower than the corresponding base plant CGEs of 60.8% and 72.2%. Similarly, the effective thermal efficiencies of 52.4% for the CLP coal-to-hydrogen plant and 59.6% for the CLP SMR plant are significantly less than the ETEs of 61.2% and 69.7% for the corresponding base plants. However, these measures are unduly biased by the significant co-production of electricity in the CLP plants, as electricity production is inherently less efficient than hydrogen production. Viewed from a different perspective, if the performance of the hydrogen production portion of each CLP plant is assumed to be equivalent to the performance of the corresponding base plant, then the electric power production portion has an implied net efficiency (HHV basis) of 35.7% for the coal-to-hydrogen case and 36.5% for the SMR case. These efficiencies are substantially greater than the efficiencies reported above for conventional PC and IGCC plants with CO₂ capture, again illustrating the reduction in energy penalty that results from heat recovery in the Calcium Looping Process. (In reality, the efficiency improvement resulting from the CLP is distributed among the hydrogen and electricity products, rather than being applied wholly to the electricity product as is done in the illustrative calculation above).

Based on the data presented in Tables 15, 22, and 29, the auxiliary load in the CLP coal-to-hydrogen, SMR, and IGCC plants is dominated by the energy required for cryogenic air separation and CO₂ compression. Excluding the parasitic load associated with the steam required for the hydrator (which is not itemized as an auxiliary load in these tables because it is already accounted for in the estimated steam turbine gross electric power output), air separation and CO₂ compression account for 70-80% of the total auxiliary power requirement in each of these three plants. It is unlikely that the hydrator steam requirement can be reduced significantly; hence, the greatest opportunities for reducing the parasitic power associated with the Calcium Looping Process lie with the air separation and CO₂ compression units. The U.S. Department of Energy and others are funding the development of several advanced air separation and CO₂ compression technologies, such as ion transport membranes and supersonic shockwave compression technology. These technologies, if successfully commercialized, could potentially be applied to improve the performance of the CLP.

All three CLP plants examined in this report produce more carbon dioxide than the corresponding base plants, owing to the CO₂ that is formed from combustion of additional fuel in the calciner and the CO₂ that is liberated from the calcination of the limestone makeup stream. However, the CLP plants also achieve greater CO₂ capture efficiencies than the conventional plants. Based on the data presented in Table 35, the conventional coal-to-hydrogen, IGCC, and SMR plants all achieve about 90% overall CO₂ capture efficiency, while the corresponding CLP plants all achieve greater than 99% overall CO₂ capture efficiency. Aspen Plus® simulations indicate that, at the carbonator operating conditions, the calcium sorbent will capture 95-99% of the carbon in the gasifier syngas (coal-to-hydrogen and IGCC cases), reformer syngas (SMR case), and reformer flue gas (SMR case). Additional experimental testing is needed to confirm

this result. Moreover, for all three cases, essentially all of the carbon in the calciner fuel and the limestone makeup is captured as part of the oxycombustion process in the calciner. In combination, these factors result in much lower projected net CO₂ emissions from the CLP plants than from the corresponding base plants.

Unlike the base plants, which use liquid solvents to capture CO₂ and other acid gases, the CLP is based on the use of a solid sorbent. As discussed earlier, a portion of the sorbent must be purged from the system during each carbonation-calcination-hydration cycle, in order to prevent a buildup of inert solids in the system. Therefore, the CLP plants generate more solid waste than the conventional plants. The success of the CLP will depend in part upon the ability to effectively handle the large quantity of solids used in the process. For the three CLP cases studied here, the solid sorbent makeup rates range from 18-53 ton/h (16,400-47,674 kg/h), the solids purge rates range from 27-79 ton/h (24,929-71,904 kg/h), and the solids circulation rates (measured at the calciner inlet) range from 1,171 to 2,073 ton/h (1,062,399-1,880,671 kg/h). These solids flow rates would be considerably larger without the hydration step, which preserves sorbent activity over many cycles, enabling the use of relatively low solids purge and makeup rates and the use of a relatively low calcium-to-carbon molar ratio in the carbonator. Certain commercial processes, such as fluid catalytic cracking and circulating fluidized bed dry scrubbing, demonstrate the feasibility of handling large quantities of circulating solids. Nevertheless, use of a solid sorbent is expected to introduce certain design challenges (e.g., regarding solids transport, solids fluidization, and gas/solids separation) and operating and maintenance challenges (e.g., resulting from erosion, plugging, scaling, etc.) that would not be encountered with a solvent-based system. Further demonstration of the integrated process at relevant scale will be needed to better understand and resolve these challenges.

Raw water demand in the CLP plants is 54-124% greater than the demand in the corresponding base plants for each of the three cases studied in this report. As discussed in Section 4, the greater water demand in the CLP plants largely arises from the significantly greater production of electricity in these plants, which in turn leads to greater steam cycle condenser cooling loads and greater cooling tower water makeup requirements. Given the differences in net output between the base and CLP plants, it is more appropriate to compare water usage after normalizing it by net plant output. Using the IGCC case as an example, raw water demand per kW_e of net electric output is only 17% greater in the CLP plant than in the base plant (as opposed to 124% greater when the comparison is done on an absolute basis). The difference that remains after normalizing by plant output results from differences in process water consumption, opportunities for internal recycle, and the relative proportion of electricity that is generated from the steam turbine (this proportion is greater in the CLP plant than in the base plant; more water is consumed when generating electricity from the steam turbine than when generating electricity from the gas combustion turbine).

Principal technical uncertainties regarding the performance of the Calcium Looping Process include the performance of the high-temperature hydrator with internal heat recovery, which has not been demonstrated at relevant scale, and the use of oxycombustion in the coal-fired flash calciner, which represents a new mode of operation for this technology. Further development and demonstration of these equipment items are required to resolve these uncertainties. Moreover, sulfur chemistry in the calciner can have an appreciable effect on the performance of the Calcium Looping Process, especially in the coal-to-hydrogen and IGCC cases. In these cases, sulfur enters the calciner in the form of CaS from the carbonator, as well as SO₂ (or SO₃) from the oxy-fired coal burner. The CaS that enters the calciner can remain unreacted, or it can react with O₂, CO₂, H₂O, or calcium compounds to form SO₂ or CaSO₄.¹⁰⁻¹³ Possible reaction pathways include:

The SO₂ produced from coal combustion in the calciner also can react with sorbent to form CaSO₄. Formation of SO₂ in the calciner is desirable, as it enables sulfur to be purged from the solids loop as a gaseous compound and captured downstream for disposal. Any unreacted CaS is undesirable, because it may pose a waste disposal problem. The formation of CaSO₄ also is undesirable, as any CaSO₄ formed in the calciner is recycled back to the carbonator, where it can react with either CO or H₂ according to the following reactions:

Reactions (13) and (14) both reduce the amount of hydrogen produced by the Calcium Looping Process (as discussed above, H₂ is formed from CO in the carbonator via the water-gas shift reaction), diminishing its economic attractiveness. The CLP process simulation results presented in this report are based on a calciner design that produces an operating environment that favors SO₂ formation over CaSO₄ formation. Additional experimental work must be conducted to confirm the effectiveness of this design, which was invented under Cooperative Agreement No. DE-FC26-07NT43059. The project team is still deciding whether to pursue a patent for this invention.

5.2 Economic Performance of the Calcium Looping Process

Table 37 summarizes the economic analysis results for the coal-to-hydrogen and SMR cases, and Table 38 summarizes the results for the IGCC case. More detailed results can be found in Section 4.1.3 for the coal-to-hydrogen case, Section 4.2.3 for the SMR case, and Section 4.3.3 for the IGCC case. As shown in the tables, for all three cases, use of the CLP results in a 9-12% lower COH and/or COE than use of conventional CO₂ capture and WGS technologies.

Table 37. Summary of economic analysis results for the coal-to-hydrogen and SMR cases.

	Coal-to-Hydrogen Case		SMR Case	
	Base Plant	CLP Plant	Base Plant	CLP Plant
Capital (\$/kg H ₂)	\$2.28	\$2.61	\$0.62	\$0.97
Fixed O&M (\$/kg H ₂)	\$0.44	\$0.60	\$0.17	\$0.27
Fuel (\$/kg H ₂)	\$0.36	\$0.55	\$1.22	\$1.40
Electric Power (\$/kg H ₂) ^a	-\$0.03	-\$1.14	\$0.14	-\$0.70
CO ₂ Emissions (\$/kg H ₂)	\$0.06	\$0.00	\$0.03	\$0.00
Other Variable O&M (\$/kg H ₂)	\$0.04	\$0.14	\$0.02	\$0.05
TOTAL COH (\$/kg H ₂)	\$3.15	\$2.77	\$2.20	\$1.99
TOTAL COE (\$/MWh)	\$105.00	\$92.07	\$105.00	\$95.24

^aComputed using an electricity price equal to the total COE value shown in the table.

Table 38. Summary of economic analysis results for the IGCC case.

	Base Plant	CLP Plant
Capital (\$/MWh)	\$59.00	\$51.20
Fixed O&M (\$/MWh)	\$22.38	\$18.88
Coal (\$/MWh)	\$17.12	\$16.86
CO ₂ Emissions (\$/MWh)	\$2.82	\$0.20
Other Variable O&M (\$/MWh)	\$1.76	\$3.59
TOTAL (\$/MWh)	\$103.08	\$90.73

Techno-economic modeling suggests that, when it is applied to an oxygen-blown IGCC plant for electricity production with CO₂ capture, the CLP can achieve a first-year COE of ~\$91/MWh. This is less than the estimated first-year COE of >\$100/MWh for an IGCC or PC plant using conventional solvent-based CO₂ capture technology.² As discussed above, the CLP IGCC plant essentially integrates an IGCC plant and a PC plant (i.e., the coal-fired calciner) around a common CO₂ capture technology. The synergies arising from this integration, coupled with the availability of high-quality heat from the calcium sorbent-based CO₂ capture process, result in the observed economic advantage for the CLP plant.

The data in Table 38 indicate that the lower capital cost of the CLP IGCC plant accounts for about 60% of its economic advantage over the base IGCC plant. When expressed on a \$/kW_{net} basis, the Total Overnight Cost for the CLP plant (\$2,894/kW_{net}) plant is 13% less than the TOC for the base plant (\$3,335/kW_{net}). The TOC for the CLP plant is also substantially less than the TOC for a 550 MWe (net), subcritical PC power plant with an MEA scrubbing system for 90% CO₂ capture (\$3,610/kW_{net}). A small amount of the difference between the CLP and base plants might be attributed to economies of scale, given the significant difference in net electric output between these plants. However, many of the high-cost equipment items in the CLP plant, including the gasifier, gasifier ASU, gas turbine, calciner, calciner ASU, and hydrator, are divided into two trains in the design evaluated in this report. Hence, it should be possible to cut the size of the CLP plant in half (i.e., to 466 MW_e net, which is slightly smaller than the base plant output) while maintaining a similar capital cost on a net plant output basis.

The CLP also is capable of achieving a greater-than 10% reduction in the cost of producing high-purity hydrogen from coal with >90% CO₂ capture, per the data in Table 37. However, the resulting cost of hydrogen for the CLP coal-to-hydrogen plant (\$2.77/kg) is still significantly greater than the COH for a steam methane reforming plant equipped with commercially-available WGS and CO₂ capture technologies (\$2.20/kg), even at an assumed natural gas price of \$6.55/mmBtu. As shown in Table 37, the lowest cost of hydrogen with CO₂ capture is achieved by applying the CLP (with a coal-fired calciner) to a steam methane reforming plant. This configuration, which effectively integrates a natural gas-based hydrogen plant with a pulverized coal electric power plant, results in a COH of <\$2.00/kg.

One of the greatest uncertainties in the economic analysis results for the coal-to-hydrogen and SMR cases comes from the finance structures used to compute the first-year capital costs in these cases. As discussed in Section 3.2.4, first-year capital charges for the base coal-to-hydrogen and SMR plants, which produce essentially 100% hydrogen with little or no co-production of electricity, were computed assuming a high-risk hydrogen project finance structure. (A five-year capital expenditure period was assumed for the coal-to-hydrogen plant, resulting in a first-year capital charge factor of 0.2470, and a three-year capital expenditure

period was assumed for the SMR plant, resulting in a first-year capital charge factor of 0.2044). For the CLP coal-to-hydrogen and SMR plants, which produce significant amounts of both hydrogen and electricity, weighted average CCFs were computed from the finance structures for high-risk hydrogen projects and high-risk electric power projects based on the relative contributions of hydrogen and electricity to each plant's total energy output. The resulting CCFs of 0.2048 for the CLP coal-to-hydrogen plant and 0.1853 for the CLP SMR plant were used to compute the first-year capital charges for these plants. However, the finance structures used for actual commercial projects could differ from the ones assumed in this study, particularly for the plants that co-produce hydrogen and electricity, and as shown in Tables 39-40, the economic analysis results are particularly sensitive to the choice of finance structure. For example, if a high-risk hydrogen project finance structure is assumed for both the base plant and the CLP plant, then the cost advantage afforded by the CLP plant shrinks from 9% to 6% in the SMR case and disappears in the coal-to-hydrogen case. On the other hand, if a high-risk electric power project finance structure is assumed for both the base plant and the CLP plant, then the advantage afforded by the CLP plant grows from 9% to 13% in the SMR case and from 12% to 13% in the coal-to-hydrogen case. Hence, although the results for both cases are sensitive to the choice of finance structure, the Calcium Looping Process appears to have less downside potential and more upside potential in the SMR case than in the coal-to-hydrogen case.

Table 39. Effect of project finance structure on economic analysis results for the coal-to-hydrogen case.

Base Plant Finance Structure (CCF)	CLP Plant Finance Structure (CCF)	Base Plant COH (COE)	CLP Plant COH (COE)	% Change
High-risk hydrogen (0.2470)	Weighted average ^a (0.2048)	\$3.15/kg (\$105.00/MWh)	\$2.77/kg (\$92.07/MWh)	-12
High-risk hydrogen (0.2470)	High-risk hydrogen (0.2470)	\$3.15/kg (\$105.00/MWh)	\$3.15/kg (\$104.77/MWh)	0
High-risk electric power (0.1240)	High-risk electric power (0.1240)	\$2.02/kg (\$105.00/MWh)	\$1.75/kg (\$90.95/MWh)	-13

^aFor cases with significant co-production of hydrogen and electricity, a weighted average CCF was computed from the appropriate high-risk hydrogen and high-risk electric power CCFs based on the relative contributions of hydrogen and electricity to the plant's total energy output.

Table 40. Effect of project finance structure on economic analysis results for the SMR case.

Base Plant Finance Structure (CCF)	CLP Plant Finance Structure (CCF)	Base Plant COH (COE)	CLP Plant COH (COE)	% Change
High-risk hydrogen (0.2044)	Weighted average ^a (0.1853)	\$2.20/kg (\$105.00/MWh)	\$1.99/kg (\$95.24/MWh)	-9
High-risk hydrogen (0.2044)	High-risk hydrogen (0.2044)	\$2.20/kg (\$105.00/MWh)	\$2.07/kg (\$98.77/MWh)	-6
High-risk electric power (0.1240)	High-risk electric power (0.1240)	\$1.96/kg (\$105.00/MWh)	\$1.70/kg (\$91.39/MWh)	-13

^aFor cases with significant co-production of hydrogen and electricity, a weighted average CCF was computed from the appropriate high-risk hydrogen and high-risk electric power CCFs based on the relative contributions of hydrogen and electricity to the plant's total energy output.

Sensitivity analyses also were conducted to explore the effect of changes in other key variables, such as the price of fuel, the value of the CO₂ emission tax, and the capital cost of CLP process equipment, on the economic competitiveness of the Calcium Looping Process. Results are summarized in Table 41.

Table 41. Sensitivity analysis results for the coal-to-hydrogen, SMR, and IGCC cases.

Deviation from Base Case Assumptions	% Change in COH or COE (Relative to Base Plant) Resulting from Calcium Looping Process		
	Coal-to-Hydrogen Case	SMR Case	IGCC Case
Base case assumptions	-12	-9	-12
25% increase in coal cost (to \$47.74/ton)	-11	-8	-12
25% decrease in coal cost (to \$28.64/ton)	-14	-10	-12
Natural gas price = \$4.00/mmBtu	-12	-12	-12
CO ₂ emission tax = \$50/tonne	-13	-10	-13
CO ₂ emission tax = \$10/tonne	-12	-9	-11
10% increase in TPC of CLP equipment	-10	-6	-10
10% decrease in TPC of CLP equipment	-15	-13	-14
Site plant next to quarry with solid waste backfilling	-13	-10	-13

The CLP plants in the coal-to-hydrogen, SMR, and IGCC cases consume more coal than the corresponding base plants. As a result, the economic attractiveness of the CLP plants tends to decrease with increasing coal price. However, as shown in Table 41, the effect of coal price on process economics is relatively small. A $\pm 25\%$ change in coal price yields at most a two percentage point change in the cost advantage associated with the Calcium Looping Process in each of the three cases studied in this report.

Among these three cases, only the SMR plants consume natural gas. As shown in Table 41, if the assumed natural gas price is reduced from \$6.55/mmBtu to \$4.00/mmBtu, which is more consistent with current and projected future natural gas prices as of the writing of this report, then the cost advantage afforded by the Calcium Looping Process in the SMR case widens from 9% to 12%. Moreover, as the spread between natural gas and coal prices narrows, the possibility of switching from coal to natural gas firing in the calciner should be considered for all three CLP plants. Such an analysis is beyond the scope of this report, however.

As discussed in Section 3.2.3, the economic evaluations presented here assume that CO₂ emissions are taxed at a rate of \$30/tonne. However, the future cost of emitting CO₂ is highly uncertain, depending on factors such as regulatory requirements and control technology costs. For this sensitivity analysis, the CO₂ emission tax was varied between \$10/tonne, which might represent the cost during the early stages of a phased regulatory program for greenhouse gases, and \$50/tonne, which is more consistent with the CO₂ avoidance cost of current CO₂ control technologies for coal-fired power plants and similar large point sources. As shown in Table 41, these variations have only a minor ($\pm$ one percentage point) impact on the cost differential between the CLP and base plants in each of the coal-to-hydrogen, SMR, and IGCC cases.

The economic analysis results are somewhat more sensitive to changes in the estimated capital cost of the Calcium Looping Process equipment. These changes could result from the inaccuracy associated with the AACE Class 4 estimates used in this report (as discussed in Section 3.2.1, these estimates have an expected accuracy range of -15% to +30%) or from advances in technology that reduce the capital cost of one or more equipment items. The results presented in Table 41 show that a $\pm 10\%$ change in the estimated Total Plant Cost of the Calcium Looping Process equipment (i.e., those equipment items listed in Account 15 in Table 16 for the coal-to-hydrogen case, Account CLP in Table 23 for the SMR case, and Account 15 in Table 30 for the IGCC case) yields a two-to-four percentage point change in the cost differential between the CLP and base plants. Advanced air separation technologies provide one potential avenue for reducing the capital cost of the Calcium Looping Process. Based on the capital cost estimates provided in Sections 4.1.3, 4.2.3, and 4.3.3, the cryogenic ASU accounts for 15-27% of the Total Plant Cost for CLP equipment in the three cases evaluated in this report. Emerging technologies such as ion transport membranes show the potential to reduce air separation capital costs by as much as 35%.¹⁴ Such a reduction would bring about a 5-10% decrease in CLP capital cost. Any accompanying reduction in the parasitic power required for air separation would further improve the cost competitiveness of the CLP.

Finally, a small improvement in the economic performance of the CLP plants could be realized by siting these plants next to a limestone quarry. This would eliminate much of the transportation cost associated with the limestone makeup that is consumed by the Calcium Looping Process. It could also substantially reduce waste disposal costs if the solid waste produced by the CLP can be disposed in mined-out areas of the quarry. The large limestone demand created by the CLP might enable such a siting arrangement.

The sensitivity analysis results presented in Table 41 collectively help to establish error bars around the economic performance of the Calcium Looping Process. In general, substantial changes in the assumed fuel price, CO₂ emission tax, CLP capital cost, and sorbent and waste disposal costs lead to only modest changes in the projected economic performance of the CLP. The reduction in COH or COE associated with using the Calcium Looping Process instead of conventional technology is between 6 and 15% for all of the scenarios and cases considered in Table 41. This lends confidence to our economic analysis results.

5.3 Other Potential Applications and Process Configurations

In addition to the three cases studied in this report, several other applications and process configurations for the Calcium Looping Process warrant consideration.

The results presented above indicate that, unless natural gas and coal prices change dramatically, the lowest-cost route to hydrogen production with CO₂ capture is achieved by applying the Calcium Looping Process to a steam methane reforming plant (rather than by applying it to a coal-to-hydrogen plant). Experimental work conducted by The Ohio State University (outside the scope of this project) suggests that it might be possible to integrate the reformer with the carbonator in a CLP-based SMR plant, combining the reforming, CO₂ capture, and WGS steps into a single reactor vessel.¹⁵ This configuration, which would further simplify the CLP SMR plant and could allow further reductions in the cost of producing high-purity hydrogen with CO₂ capture, deserves further study.

Moreover, as discussed in the Introduction and illustrated in the SMR case evaluated in this report, calcium sorbents can be used to capture CO₂ from flue gas streams as well as syngas streams. OSU is developing the calcium sorbent-based CCR process (outside the scope of this project) for post-combustion CO₂ capture applications in pulverized coal and natural gas combined cycle power plants. Preliminary experimental and modeling results indicate that the process shows potential for reducing the cost of CO₂ capture in these applications.

Calcium looping also should be considered as a CO₂ capture option for air-blown IGCC plants. The technical performance and economics of conventional air-blown IGCC plants have not been published in sufficient detail to permit a comprehensive techno-economic evaluation of this application of the CLP. However, a conceptual process flow scheme for a CLP-based air-blown IGCC plant was developed as part of the current project.

The base plant for our air-blown IGCC design was adapted from a Southern Company paper titled "Power Systems Development Facility Update on Six TRIG Studies".¹⁶ This base plant uses an air-blown KBR Transport Gasifier firing Powder River Basin coal (8,760 Btu/lb HHV, 27% moisture, 0.26% sulfur as received). In the absence of CO₂ capture, the syngas from the gasifier is cooled in a syngas cooler, filtered in a metallic filter to remove particulate matter, and then sent directly to a combined cycle power island (including a gas combustion turbine and a heat recovery steam generator) to generate electricity. Contaminants from the coal (i.e., SO₂, HCl, and HF) are removed after the power island, by treating the HRSG exit gas with a wet scrubber. (Some sulfur is also removed by injecting limestone into the gasifier).

Figure 11 presents a block flow diagram showing the application of the Calcium Looping Process to the air-blown IGCC plant. The CLP could be applied to capture CO₂ either upstream or downstream of the gas combustion turbine (i.e., in either a pre- or post-combustion capture configuration). We selected the post-combustion capture configuration (i.e., in which the CLP is installed downstream of the gas turbine) for our conceptual design, based on the following considerations:

1. The carbonator chemistry is simplified in the post-combustion capture configuration. Specifically, this configuration eliminates the need to carry out the water-gas shift reaction, which has slower kinetics than the CO₂ absorption reaction. The temperature rise across the carbonator is also reduced in the post-combustion capture configuration. As a result, the carbonator can be designed as a relatively simple entrained flow reactor (rather than as a fluidized bed reactor with internal heat recovery), with smaller residence time requirements than would be required in a pre-combustion capture configuration.
2. The post-combustion capture configuration eliminates the possibility that CaSO₄ formed in the calciner could react with H₂ or CO in the carbonator, as discussed in Section 5.1. This simplifies the design and operating requirements for the calciner.
3. In the post-combustion capture configuration, the carbonator operating pressure is ~1 bar, rather than ~27 bar as in the pre-combustion configuration. This eliminates the need for lockhoppers to transport solids between the carbonator and the calciner and hydrator, which also operate at or near atmospheric pressure, reducing capital costs, maintenance requirements, and parasitic power consumption.
4. The flue gas leaving the gas combustion turbine is already at the proper inlet temperature (~600°C) for the carbonator.

Figure 11. Block flow diagram for a conceptual air-blown IGCC plant using the CLP.

Figure 12 presents a conceptual process flow diagram for the Calcium Looping Process in the air-blown IGCC plant. The system boundaries for this PFD correspond to the red areas of Figure 11; as indicated in that figure, the HRSG downstream of the combustion turbine is integrated into the CLP design. As shown in Figure 12, the flue gas leaving the combustion turbine, which is at 608°C (1126°F) and 1 bar (15 psia) and contains ~8.5% CO₂, travels directly to the entrained flow carbonator. Hydrated lime is injected into the carbonator at a calcium-to-carbon molar ratio of 1.3:1. The hydrated lime reacts with the CO₂ in the flue gas to form CaCO₃. It also reacts with any SO₂ and HCl in the flue gas to form CaSO₄ and CaCl₂, respectively. The gas and solid products leaving the carbonator are separated in a high-efficiency cyclone. The clean flue gas then passes through a HRSG to raise steam and a fabric filter for residual particulate removal before it is exhausted through the stack. As with the other CLP process designs described in this report, the CaCO₃ formed in the carbonator is regenerated (to form CaO and CO₂) in an entrained bed calciner that is fired via oxycombustion of coal, and the resulting CaO is reactivated in a high-temperature steam hydrator and then recycled to the carbonator. Heat is recovered from the CO₂ stream leaving the calciner and from the hydrator to raise steam for electricity generation. The CO₂ stream is dehydrated and compressed to 153 bar (2,215 psia) for sequestration.

The process flow scheme shown in Figure 12 for the Calcium Looping Process in an air-blown IGCC plant is somewhat simpler than the flow schemes shown in Figures 4, 7, and 10 for coal-to-hydrogen, SMR, and oxygen-blown IGCC applications. Moreover, the CLP is expected to afford similar cost and performance advantages when applied in an air-blown IGCC configuration as it does in these other applications. Hence, further evaluation of this configuration should be performed.

Figure 12. Conceptual process flow diagram for the Calcium Looping Process as applied for post-combustion CO₂ capture in an air-blown IGCC plant.

6. Conclusions

In summary, our techno-economic evaluation of the Calcium Looping Process leads to the following primary conclusions:

- **The Calcium Looping Process has the potential to reduce the cost of producing hydrogen and electricity in a carbon constrained world, when compared with conventional approaches based on coal gasification and natural gas reforming.** In each of the coal-to-hydrogen, steam methane reforming, and IGCC cases evaluated in this report, use of the Calcium Looping Process results in a 9-12% reduction in the cost of hydrogen or cost of electricity when compared with the use of conventional CO₂ capture and water-gas shift technologies. Application of the CLP to a coal gasification or steam methane reforming plant essentially amounts to integrating the base plant and a pulverized coal power plant (i.e., the coal-fired calciner in the CLP) around a common CO₂ capture technology. The synergies arising from this integration, coupled with the availability of high-quality heat from the calcium sorbent-based CO₂ capture process, result in the observed economic advantage for the CLP plant.
- **Application of the Calcium Looping Process to a hydrogen production plant necessarily results in substantial co-production of electricity.** The economic advantage afforded by the CLP is only realized if the large amount of high-quality heat produced in the process is recovered to raise steam for electricity generation. This heat arises from the combustion of additional coal in the CLP calciner (which results in

significantly greater heat input and fuel costs in the CLP plant than in the base plant) and from the exothermicity of the CO₂ absorption, water-gas shift, and hydration reactions, which are carried out at high temperature (i.e., $\geq 500^{\circ}\text{C}$) in the CLP. Process simulations show that a 26,000 kg H₂/h coal-to-hydrogen plant using the CLP will co-produce about 320 MW_e of net electric power, and a 26,000 kg H₂/h SMR plant using the CLP will co-produce about 190 MW_e of net electric power. By contrast, an identically-sized coal-to-hydrogen plant using conventional technology generates only about 7 MW_e of net electric power, and an identically-sized SMR plant using conventional technology consumes more than 30 MW_e of electric power.

- Although the Calcium Looping Process can reduce the cost of producing hydrogen from coal, the lowest-cost route to hydrogen production with CO₂ capture is achieved by applying the CLP (with a coal-fired calciner) to a steam methane reforming plant.** The CLP is capable of achieving a greater-than 10% reduction in the cost of producing high-purity hydrogen from coal with >90% CO₂ capture, when compared with conventional CO₂ capture and water-gas shift technologies. However, for assumed coal and natural gas prices of \$1.64/mmBtu and \$6.55/mmBtu, respectively, the first-year cost of hydrogen for a CLP-based coal-to-hydrogen plant (\$2.77/kg H₂) is still significantly greater than the first-year COH for a steam methane reforming plant equipped with conventional technology (\$2.20/kg H₂). Application of the CLP to a steam methane reforming plant results in a first-year COH of <\$2.00/kg H₂. The economic advantage afforded by the CLP steam methane reforming plant over the conventional SMR plant grows from 9% to 12% if the assumed natural gas price is reduced to \$4.00/mmBtu, which is more consistent with actual prices as of the writing of this report.
- Additional research is required to resolve technical uncertainties related to the commercial application of the CLP technology.** In particular, work should be conducted to evaluate sulfur chemistry in the oxy-fired calciner, develop and demonstrate the high-temperature hydrator with internal heat recovery, evaluate the carbonator performance at a larger scale and wider range of operating conditions, evaluate cyclone performance with very high solids loadings and small particle sizes, and demonstrate solids handling in the integrated process at a relevant scale. This work would enable further refinements in the cost and performance estimates presented in this report.
- Improvements in air separation technology could help to improve the technical and cost performance of the Calcium Looping Process.** The flash calciner in the CLP uses oxy-fired, pulverized coal burners and, therefore, consumes a substantial amount of high-purity oxygen. In each of the three cases studied in this report, the calciner ASU accounts for 15-27% of the capital cost for CLP process equipment and a large portion of the energy penalty associated with the CLP. Hence, the successful commercialization of advanced air separation technologies such as ion transport membranes, which show potential for reducing both the capital cost and parasitic power requirement for air separation, would widen the advantage afforded by the CLP over conventional pre-combustion CO₂ capture technologies.
- Several additional process configurations should be evaluated to better understand the potential benefits afforded by the Calcium Looping Process.** These configurations, which include an air-blown IGCC plant equipped with the CLP and an SMR plant that integrates the reformer and carbonator into a single reactor vessel, appear to offer

opportunities for further process intensification and potential cost savings. However, detailed evaluations of these configurations were beyond the scope of this project.

REFERENCES

1. U.S. Department of Energy, National Energy Technology Laboratory; *Assessment of Hydrogen Production with CO₂ Capture Volume 1: Baseline State-of-the-Art Plants*; DOE/NETL-2010/1434, August 30, 2010. Available: http://www.netl.doe.gov/energy-analyses/pubs/H2_Prod_Vol1_2010.pdf.
2. U.S. Department of Energy, National Energy Technology Laboratory; *Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity*; DOE/NETL-2010/1397 (Revision 2), November 2010. Available: http://www.netl.doe.gov/energy-analyses/pubs/BitBase_FinRep_Rev2.pdf.
3. Ramkumar, S.; Phalak, N.; Statnick, R.M.; Fan, L.S. Calcium Looping Process (CLP) for Clean Hydrogen and Electricity Production from Coal; In Proceedings of the 35th International Technical Conference on Clean Coal and Fuel Systems, Clearwater, FL, June 6-10, 2010.
4. Wang, W.; Ramkumar, S.; Li, S.; Wong, D.; Iyer, M.; Sakadjian, B.; Statnick, R.M.; Fan, L.S. Subpilot Demonstration of the Carbonation-Calination Reaction (CCR) Process: High-Temperature CO₂ and Sulfur Capture from Coal-Fired Power Plants; *Ind. Eng. Chem. Res.* **2010**, *49*, 5094-5101.
5. Liss, W.H., et al.; *Variability of Natural Gas Composition in Select Major Metropolitan Areas of the United States*; Gas Research Institute Report GRI-92/0123, March 1992.
6. U.S. Department of Energy, National Energy Technology Laboratory; *Pulverized Coal Oxycombustion Power Plants Volume 1: Bituminous Coal to Electricity*; DOE/NETL-2007/1291 (Revision 2), August 2008. Available: <http://www.netl.doe.gov/energy-analyses/pubs/PC%20Oxyfuel%20Combustion%20Revised%20Report%202008.pdf>.
7. "Chemical Engineering Plant Cost Index;" <http://www.che.com/pci/>
8. NETL Power Systems Financial Model Version 5.0, December 2008. User Guide available at: <http://www.netl.doe.gov/business/solicitations/ssc2008/references/PSFM%20User%20Guide.pdf>
9. U.S. Department of Energy, National Energy Technology Laboratory; *Recommended Project Finance Structures for the Economic Analysis of Fossil-Based Energy Projects*; DOE/NETL-401/090808, September 8, 2008. Available: http://www.netl.doe.gov/energy-analyses/pubs/Project%20Finance%20Parameters%20-%20Final%20Report%20-%20Sept%202008_1.pdf
10. Song, Q.; Xiao, R.; Deng, Z.; Shen, L.; Zhang, M. Reactivity of a CaSO₄-Oxygen Carrier in Chemical-Looping Combustion of Methane in a Fixed Bed Reactor; *Korean J. Chem. Eng.* **2009**, *26*, 592-602.
11. Song, Z.; Zhang, M.; Ma, C. Study on the Oxidation of Calcium Sulfide using TGA and FTIR; *Fuel Processing Technology* **2007**, *88*, 569-575.

12. Anthony, E.J.; Jia, L.; Qiu, K. CaS Oxidation by Reaction with CO₂ and H₂O; *Energy & Fuels* **2003**, 17, 363-368.
13. Qiu, K.; Mattisson, T.; Steenari, B.-M.; Lindqvist, O. Thermogravimetric Combined with Mass Spectrometric Studies on the Oxidation of Calcium Sulfide; *Thermochimica Acta* **1997**, 298, 87-93.
14. "Air Separation Technology – Ion Transport Membrane (ITM);" Air Products and Chemicals, Inc., 2008. Available: http://www.airproducts.com/~media/Downloads/Article/Literature_Cryogenic-Air-Separation-ITM-28007017GLB.ashx
15. Ramkumar, S.; Phalak, N.; Fan, L.-S. Calcium Looping Process Enhanced Coal-to-Liquids Technology; In Proceedings of the 35th International Technical Conference on Clean Coal and Fuel Systems, Clearwater, FL, June 6-10, 2010.
16. Rogers, L.H.; Booras, G.S.; Breault, R.W.; Salazar, N. Power Systems Development Facility Update on Six TRIG Studies; In Proceedings of the 23rd Annual International Pittsburgh Coal Conference, Pittsburgh, PA, September 25-28, 2006.

ACRONYMS AND ABBREVIATIONS

°C	-	degrees Celsius
°F	-	degrees Fahrenheit
$\Delta H^\circ_{\text{rxn}}$	-	standard heat of reaction
ASME	-	American Society of Mechanical Engineers
ASU	-	air separation unit
BEC	-	bare erected cost
BOP	-	balance of plant
Btu	-	British thermal unit
CCF	-	capital charge factor
CCR	-	Carbonation-Calcination Reaction
CF	-	capacity factor
CGE	-	cold gas efficiency
CLP	-	Calcium Looping Process
COE	-	cost of electricity
COH	-	cost of hydrogen
CONSOL	-	CONSOL Energy Inc.
DOE	-	U.S. Department of Energy
ETE	-	effective thermal efficiency
ft ³	-	cubic foot
(g)	-	gas phase
gal	-	gallon
GE	-	General Electric Company
GJ	-	gigajoule
gpm	-	gallon per minute
h	-	hour
HGCU	-	hot gas cleanup
HHV	-	higher heating value
HRSG	-	heat recovery steam generator
IGCC	-	integrated gasification-combined cycle
kg	-	kilogram

KG	- total kilograms of hydrogen that would be generated over a 1-year period at 100 percent capacity factor
kJ	- kilojoule
kW	- kilowatt
kW _e	- kilowatt of electricity
kW _{net}	- kilowatt of net electricity
kW _t	- kilowatt of thermal energy
lb	- pound
LHV	- lower heating value
m ³	- cubic meter
MDEA	- methyldiethanolamine
MEA	- monoethanolamine
MJ	- megajoule
mmBtu	- million British thermal units
mol	- mole
MW _e	- megawatt of electricity
MWh	- megawatt hour
MWH	- total net megawatt-hours of electric power that would be generated over a 1-year period at 100 percent capacity factor
NETL	- National Energy Technology Laboratory
Nm ³	- normal cubic meter
No.	- number
O&M	- operating and maintenance
OC _{FIX}	- sum of all fixed O&M costs over a 1-year period
OC _{VAR}	- sum of all variable O&M costs over a 1-year period at 100 percent capacity factor
OSU	- The Ohio State University
PC	- pulverized coal
PFD	- process flow diagram
PSA	- pressure swing adsorber
psia	- pound per square inch, absolute pressure
(s)	- solid phase

scf	-	standard cubic foot
SMR	-	steam methane reformer
TG	-	turbine-generator
TOC	-	total overnight cost
ton	-	short ton
tonne	-	metric ton
TPC	-	total plant cost
U.S.	-	United States
v/v	-	by volume
w/w	-	by weight
WGS	-	water-gas shift
y	-	year

CHEMICAL SYMBOLS

Al_2O_3	-	aluminum oxide
Ar	-	argon
CaCl_2	-	calcium chloride
CaCO_3	-	calcium carbonate
CaO	-	calcium oxide
Ca(OH)_2	-	calcium hydroxide
CaS	-	calcium sulfide
CaSO_4	-	calcium sulfate
CH_4	-	methane
C_2H_6	-	ethane
C_3H_8	-	propane
C_4H_{10}	-	butane
CO	-	carbon monoxide
CO_2	-	carbon dioxide
COS	-	carbonyl sulfide
Fe_2O_3	-	iron (III) oxide (or ferric oxide)
H_2	-	molecular hydrogen
HCl	-	hydrogen chloride
HF	-	hydrogen fluoride
H_2O	-	water
H_2S	-	hydrogen sulfide
MgCO_3	-	magnesium carbonate
N_2	-	molecular nitrogen
NH_3	-	ammonia
O_2	-	molecular oxygen
SiO_2	-	silicon dioxide
SO_2	-	sulfur dioxide
SO_3	-	sulfur trioxide

APPENDIX

The work detailed here has not been performed as a part of this DOE contract. Nonetheless, it complements the work performed with respect to the CLP development.

A. Investigation of high temperature steam hydration of CaO for improved CO₂ capture capacity over multiple cycles

Introduction

It is well known that the CO₂ capture capacity of CaO decreases over multiple cycles of carbonation and calcination due to sintering at high temperatures during the calcination step (Curran et.al., 1967). As the sorbent is used over multiple cycles, repeated sintering worsens its performance resulting in high solids circulation rate and makeup and purge rate to achieve the desired CO₂ removal. To overcome this decay in reactivity, pretreatment methods like thermal activation of sorbents and synthesis of novel sorbents by physical and chemical modifications have been suggested. An alternative to this approach is the addition of an intermediate reactivation step – hydration of CaO (Manovic and Anthony, 2008; Lu et.al., 2006; Li et.al., 2008; Fan et.al., 2008). In this scheme, CaO exiting the calciner is hydrated in a ‘hydrator’ before being charged to the carbonator. Hydration of CaO results in the formation of Ca(OH)₂ according to the reaction –

The reactivation of CaO using steam hydration has been widely reported in the literature and there seems to be a unanimous agreement on the fact that the positive effect of hydration is due to the improved morphology of the sorbent (Zeman, 2008; Hughes et.al., 2004). It is suggested that the hydration causes cracks to be formed in the CaO particles, creating channels extending to the interior of the particles and thus improving CO₂ capture. Formation of larger pores due to hydration also improves performance of the sorbents as they become less susceptible to pore pluggage.

More recently, Wang et.al. (2011) reported process analysis of the OSU CCR Process with intermediate hydration. In this work, computer simulations for integrating the CCR Process into a coal-fired power plant were conducted using Aspen Plus software. It was found that if the hydrator was operated at high temperatures (> 350 °C), the exothermic heat of reaction could be utilized in the steam turbine cycle of the power plant. Commercially, hydration of lime is performed using excess water at ambient temperatures and pressures and this technique is known to produce a highly reactive sorbent for CO₂ capture. However, integration of low temperature hydration in a calcium-based CO₂ capture process will not generate useful heat and impose greater energy penalty on the process. Using a hydrator operated at 500 °C and 1 atm, Wang et.al. report that 90% CO₂ removal and complete SO₂ removal can be achieved with a 28% increase in thermal energy necessary to maintain a constant electrical output from the power plant.

Its advantages notwithstanding, hydration at conditions (500 °C and 1 atm) has not been reported in literature and as a result there is a lack of experimental evidence that it will maintain the

reactivity of CaO toward CO₂, over many cycles. Hence, the purpose of this study is to investigate such hydration of CaO in multicyclic CO₂ capture.

Experimental Methods

Limestones

The limestones investigated in this study were obtained from Graymont Inc. and Carmeuse Lime and Stone. Two limestone samples were obtained from each supplier. The Graymont samples came from the quarries at Pleasant Gap - Pennsylvania (PG), and Townsend – Montana (TS); the Carmeuse samples came from the quarries at Maysville – Kentucky (MV) and Blackriver – Kentucky (BR). The limestone compositions, as given by the suppliers, are provided in Table A1.

Table A1. Characteristics and composition of the limestones investigated.

Property / Composition	Unit	Limestone			
		Carmeuse		Graymont	
		BR	MV	PG	TS
Loss on Ignition (LOI)	%	43.3	43.2	43.2	43.7
Sulfur (S)	%	0.03	0.078	0.05	0.01
Silica (SiO ₂)	%	1.13	2.06	0.8	0.5
Ferric Oxide (Fe ₂ O ₃)	%	0.14	0.15	0.1	0.1
Alumina (Al ₂ O ₃)	%	0.28	0.41	0.3	0.1
Calcium Carbonate (CaCO ₃)	%	94.6	89.6	97.8	96.5
Magnesium Carbonate (MgCO ₃)	%	2.97	8.2	1.2	2.4
Free moisture	%	2.3	1.9	*	*
Loose Bulk Density	kg/m ³	1377	1537	1377	1761
Packed Bulk Density	kg/m ³	*	*	1697	1921

*data not available.

Experimental Setup

Calcination - The limestone samples were calcined in an oven (Fisher Scientific – Isotemp Muffle Furnace) capable of going up to a temperature of 1100 °C. Samples were placed in an alumina crucible for calcination.

Carbonation and Hydration - The hydration and carbonation of the samples was conducted in a bench-scale fixed-bed reactor. A diagrammatic representation of the setup has been provided earlier.

Thermogravimetric analysis – A thermogravimetric analyzer (Perkin Elmer Pyris1 TGA) was used to determine the extent of calcination and hydration and the CO₂ capture capacity of the sorbent.

Experimental Procedure

Preliminary screening of the limestone samples – All the limestones were tested in the TGA for their CO₂ capture capacity. A small sample of the limestone (15-20 mg) was used for these tests. The samples were subjected to the following three steps in the TGA:

- The sample was heated from 25 °C to 700 °C in N₂ and held isothermally at 700 °C for 30 min (calcination).
- The temperature was reduced from 700 °C to 650 °C and then the sample was held isothermally in 10% CO₂ (balance N₂) for 30 min. (carbonation).
- The sample was cooled down to 25 °C.

All heating and cooling steps were performed at a rate of 25 °C/min. The instrument recorded the increase in sample weight with respect to time, which indicates CO₂ capture by the sorbent.

Multicyclic tests – Following the initial screening, multicyclic tests were conducted for each limestone. Each cycle consisted of the following steps:

- Calcination was performed at 950 °C in the muffle furnace for 120 min. (including the time for ramping up the temperature). The furnace reached the said temperature in ~60 min.
- Hydration was performed using 90% steam and balance N₂ for 30 min. in the fixed bed reactor at 500 °C. The 10% N₂ acted as a carrier gas to convey the steam to the reactor.
- Carbonation was performed at 650 °C in the fixed bed reactor for 120 min using 10-12% CO₂ (balance N₂) stream.

A set of 5 cycles (calcination-hydration-carbonation) was performed for each stone. After every step, a small amount of sample was tested in the TGA. The TGA testing consisted of the same steps as outlined above. The focus of these tests is the CO₂ capacity of the sorbent post-calcination and post-hydration in each cycle. The evaluation of both the capacities was performed using the TGA as discussed earlier.

Multicyclic tests for more cycles on a selected limestone – Based on the initial screening and the 5-cycle experiments, the best performing limestone – PG – was selected for long term multicyclic testing. This testing extended the experiment to 15 cycles.

Results and Discussion

Preliminary screening of the limestone samples

The CO₂ capture capacity of the sorbent, calculated as ‘weight % CO₂ capture capacity’ and hereafter simply referred to as ‘capture capacity’, is defined as follows

$$\text{Weight \% CO}_2 \text{ Capture Capacity} = \frac{W_t - W_o}{W_o} \times 100 (\%)$$

where W_o is the sample weight after complete calcination (gm),
 W_t is the sample weight at a given time t (gm), and
 t is the time (min).

The values listed in Table A2 correspond to the carbonation time of 30 min in the TGA, as discussed earlier.

Table A2. Properties for different limestones

Limestone	Wt % CO ₂ capture capacity	Inerts (%)
MV	47.98	4.07
BR	52.63	4.26
TS	54.08	5.28
PG	56.46	3.44

Quite clearly, PG is the best performer followed by TS and BR. Although the theoretical maximum wt capture capacity of pure CaO is 78.5, it is not achieved in actual testing. This phenomenon has been widely reported in literature and is attributed to the formation of the product (CaCO₃) layer formation which hampers the carbonation rates (Alvarez and Abanades, 2005; Bhatia and Perlmutter, 1983). The increase in molar volume during conversion of CaO to CaCO₃ also leads to diffusion resistance due to pore pluggage limiting the conversion (Abanades and Alvarez, 2003). Since the limestones have been obtained from quarries, they do not consist of 100% CaCO₃ and contain appreciable amount of inerts. The presence of inerts reduces the CaO available, further limiting CO₂ capture per unit mass of the calcined sample. The estimated amount of inerts present in each limestone is also provided in Table A2. The fraction of inerts in the limestone was calculated from data obtained from the TGA according to the following formula:

$$\text{Inerts \%} = (1 - f_{\text{CaCO}_3}) \times 100$$

$$\text{where } f_{\text{CaCO}_3} = \frac{W_{\text{CO}_2} \times 100}{44 \times W_o}$$

f_{CaCO_3} = fraction of limestone present as CaCO₃

W_{CO_2} = CO₂ evolved from sample (gm)

W_o = weight of original sample (gm)

Small differences were found to exist between the limestone supplier data (Table A1) and calculated values (Table A2).

Multicyclic tests

A multicyclic test consisting of 5 cycles was performed using each limestone according to the procedure detailed earlier and the results are shown in Figures A1-A3. From Figure A1, it can be seen that the capture capacity is lower as compared to the values listed in Table A2. The higher temperature of calcination used in the multicyclic tests compared to the TGA (950 °C vs. 700 °C) results in greater sintering of the sorbent, which has a negative impact on the surface area ultimately affecting the gas-solid reaction conversion. During these tests, the calcined samples were removed immediately from the muffle furnace after the furnace cooled down to room temperature. However, cycle 3 sample of BR was left overnight in the furnace at room temperature. The longer time allowed this sample to atmospherically hydrate in the furnace due to which it exhibited improved capture capacity in that cycle.

Figure A1. $\text{CaCO}_3\text{-CaO-Ca(OH)}_2$ cycle – post-calcination capture capacity.

Figure A2. $\text{CaCO}_3\text{-CaO-Ca(OH)}_2$ cycle – post-hydration capture capacity.

The post-hydration capture capacity is shown in Figure A2. Comparing Figures A1 and A2, it can be seen that for a given cycle, the capture capacity post-hydration is higher than post-calcination. Hydration helps to reverse the effect of sintering and this helps in restoring the capture capacity. To illustrate that the capture capacity of CaO in a $\text{CaCO}_3\text{-CaO-Ca(OH)}_2$ cycle exhibits a different trend from CaO in a $\text{CaCO}_3\text{-CaO}$ cycle, PG was subjected to the $\text{CaCO}_3\text{-CaO}$ cycles. Figure A3 shows the comparison between the capture capacity of CaO in $\text{CaCO}_3\text{-CaO}$ and $\text{CaCO}_3\text{-CaO-Ca(OH)}_2$ cycles. It can be hypothesized that the hydration history remains in the sorbent when it is cycled, which affects the capture capacity of CaO. However, this effect seems to be the characteristic of the limestone because no general conclusions can be drawn across the different stones, from Figure A2.

Figure A3. Comparison of post-calcination capture capacity of PG in CaCO₃-CaO-Ca(OH)₂ and CaCO₃-CaO cycles.

The different wt% CO₂ capture capacities observed for CaO obtained from different limestones could be likely due to certain stone characteristics. In particular, the CO₂ capacity is affected by two factors – the calcium content of the limestone and the extent of hydration of derived CaO in the fixed hydration time employed during the investigations. Hence it is important to consider these parameters in the calculations. Thus, the capture capacities for the hydrated samples were re-evaluated taking these two factors into consideration.

The weight of inerts in the original stone (obtained using TGA data) is defined as weight of all species excluding CaCO₃. This weight is assumed to be constant, i.e. unreactive and inert with respect to temperature. This assumption is an approximation, since the limestone contains other species which, though being non-reactive toward CO₂ capture at high temperatures of operation, can undergo chemical transformation in the TGA. For the calcitic stones, this assumption is valid since the fraction of inerts present in the original stone is very low. It was found that unexpected change in sample weight was insignificant in the TGA for these stones.

$$\text{Capture capacity (calcium basis)} = \frac{\text{CO}_2 \text{ captured (gm)}}{\text{weight of active sorbent (gm)}} \times 100$$

$$\text{wt\% CO}_2 \text{ capture on calcium basis} = \frac{\text{the weight of CO}_2 \text{ captured}}{\text{the active weight of calcined (dehydrated) sorbent } \square \text{ in TGA}} * 100$$

Active sorbent is defined as weight of the sample present in the form of CaO, free of inerts and therefore capable of capturing CO₂. It is calculated as follows:

$$W_{\text{active}} = W_{\text{calcined}} \times (1 - f_i)$$

where,

$$f_i = \frac{w_i}{w_{\text{CaO}} + w_i} \times 100$$

$$w_i = \frac{f_{\text{CaCO}_3} \times W_o \times 56}{100}$$

$$\text{and } w_{\text{CaO}} = (1 - f_{\text{CaCO}_3}) \times W_o \quad w_i = (1 - f_{\text{CaCO}_3}) \cdot W_o$$

W_{active} = active sorbent in the sample (gm)

W_{calcined} = sample weight after calcination and before carbonation (gm)

f_i = weight fraction of inerts in the calcined sample

w_i = weight of inerts in original sample (gm)

w_{CaO} = weight of CaO in calcined sample (gm)

The 5-cycle average wt% CO₂ capture capacity on the basis of calcium content is shown in Figure A4. The numbers are in fair agreement with the data presented in Table A1. PG, which has the highest CaCO₃ (or calcium) content shows the greatest wt% CO₂ capture capacity and MV shows the lowest capacity.

Figure A4. CaCO₃-CaO-Ca(OH)₂ cycle – 5-cycle average post-hydration capture capacity (calcium basis).

For the second calculation, the estimation of the degree of hydration was required. It was assumed that the amount of water evolved during dehydration/calcination (prior to carbonation) in the TGA is indicative of the degree of hydration of sorbent.

$$\text{Capture capacity (hydrate basis)} = \frac{W_{\text{CO}_2, \text{hydrated sorbent}}}{W_{\text{hydrated}}} \times 100$$

where

$$W_{\text{CO}_2, \text{hydrated sorbent}} = W_{\text{CO}_2, \text{total}} - W_{\text{CO}_2, \text{unhydrated sorbent}}$$

$$W_{\text{hydrated}} = \frac{W_{\text{H}_2\text{O}}}{18} \times 56$$

$$W_{\text{CO}_2, \text{hydrated sorbent}} = W_{\text{CO}_2, \text{total}} - W_{\text{CO}_2, \text{unhydrated sorbent}}$$

$$W_{\text{unhydrated}} = W_{\text{active}} - W_{\text{hydrated}} \quad W_{\text{hydrated}} = \frac{W_{\text{H}_2\text{O}}}{18} \times 56$$

x_{calcined} $W_{\text{unhydrated}} = W_{\text{active}} - W_{\text{hydrated}}$ = weight % CO₂ capture by the calcined sorbent in the corresponding cycle

$$W_{\text{CO}_2, \text{unhydrated sorbent}} = \frac{x_{\text{calcined}}}{100} \times W_{\text{unhydrated}}$$

$$W_{\text{CO}_2, \text{total}} = W_{\text{CO}_2, \text{unhydrated sorbent}} = \frac{x_{\text{calcined}}}{100} * W_{\text{unhydrated}} \text{ total CO}_2 \text{ captured (gm)}$$

$$W_{\text{CO}_2, \text{unhydrated sorbent}} = \text{CO}_2 \text{ captured by unhydrated sorbent (gm)}$$

$$W_{\text{hydrated}} = \text{hydrated sorbent, in the form of CaO (gm)}$$

$$W_{\text{unhydrated}} = \text{unhydrated sorbent, in the form of CaO (gm)}$$

As can be seen from Figure A5, the difference among the limestones is not as significant as in Figure A4. Thus, it can be concluded that the degree of hydration of CaO is a strong function of the precursor. A fixed hydration time (30 min) was used in this work and the results clearly show that this time is not good enough to hydrate CaO obtained from different precursors to the same extent. While designing calcium-based CO₂ capture systems to achieve the same performance using different precursors, this factor will assume greater importance.

Figure A5. CaCO₃-CaO-Ca(OH)₂ cycle – 5-cycle average post-hydration capture capacity (hydrate basis).

Multicyclic test for more cycles using PG limestone

On the basis of the results obtained in 3.1 and 3.2, PG was selected for prolonged multicyclic testing. The same experimental conditions that were used in 3.2 were employed here. However, the series of calcination-hydration-carbonation was extended to 15 cycles. The results are presented in Figure A6. While the overall capture capacity decayed by approximately 10% over the 15 cycles tested, it was found that the capacity was 45% or higher in all cycles. Thus hydration can help to substantially reduce the calcium loading in the process.

Figure A6. $\text{CaCO}_3\text{-CaO-Ca(OH)}_2$ cycle – 15-cycle investigation conducted for PG.

Conclusions

This work demonstrates that high-temperature steam hydration conducted in a fixed bed reactor successfully maintains reactivity of CaO toward CO_2 over many carbonation-calcination-hydration cycles. **The ability to sustain high CO_2 capture capacity will further enhance the economic viability of calcium-sorbent based CO_2 capture processes like the CLP.** CaO obtained from commercially available precursors was tested and it was found that the extent of hydration of CaO is a function of the precursor.

B. Reactivation of Calcium-Based Sorbents through Hydration with Water

Introduction

Prior studies by several researchers have found that the physical and chemical properties of calcium-based sorbents undergo changes upon intermediate hydration. However, these studies only show the effect of hydration in terms of an improvement in CO₂ capture capacity. The detailed reactivation mechanism is still sketchy to date. The purpose of this study is to conduct a systematic investigation of the characteristics of the spent sorbents before and after the hydration employing experimental techniques like TGA, SEM, BET and XRD.

Experimental Procedures

Materials

Among various calcium-based materials, naturally-occurred limestone offers several advantages including low cost and widespread availability. In order to minimize the uncertainty factors from the precursors, Graymont limestone is used throughout the study. This is same as the limestone PG used in the previous study detailed under part A above. The composition of Graymont limestone is listed in Table B1. As can be seen, the Graymont limestone contains high purity of calcium carbonate (97.8%). In addition, CO₂ and N₂ used for carbonation and calcination reaction are 99.99 % and 99.999 % pure, respectively.

Table B1. Compositions of Graymont Limestone.

Component (%)	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Total Sulfur	MgCO ₃	Mg	CaCO ₃	Ca	LOF ^a
	0.8	0.3	0.1	0.05	1.2	0.3	97.8	39.1	43.2

(^a Loss on Fusion)

Particle Preparation

Graymont limestone is calcined at different temperatures from 800 °C to 1100 °C for different time durations, 1, 4, and 16 hours, respectively, to produce samples under various levels of sintering (denoted as sintered_CaO sorbents) under N₂ environment. Then, the sintered_CaO sorbents are reactivated through hydration by excess water at room temperature with a fixed amount of reaction time to form calcium hydroxide. Once the hydration reaction is complete, the samples are heated to 200 °C to remove excess water. After that, calcium hydroxide is dehydrated at a milder temperature of 700 °C under N₂ environment to form reactivated samples (denoted as hydrated_CaO sorbents). The experimental procedures are shown in Figure B1 and the corresponding reactions are listed as follows:

Calcination: $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$

Hydration: $\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2$

Dehydration: $\text{Ca(OH)}_2 \rightarrow \text{CaO} + \text{H}_2\text{O}$

Figure B1. Experimental procedures.

Chemical Characterization of Samples

The performance of calcium-based sorbents obtained from assorted conditions before and after the hydration towards carbonation reaction is tested in Perkin Elmer Thermogravimetric Analyzer (Pyris TGA 1).

Physical Characterization of Samples

The characterization of morphological properties such as the surface area, the pore volume and the pore size distribution would be determined by the Brunauer-Emmett-Teller (BET) methods based on the adsorption and/or desorption curve. Those properties of calcium-based sorbents are tested in a NOVA 4200e analyzer (Quantachrome Company). BET analysis is a non-destructive measurement of pore properties and only require small amounts ($\sim 0.2\text{g}$) of well-mixed samples. The BET surface area, pore volume and pore size distribution are measured at -196°C using nitrogen as the adsorbent. All samples are vacuum degassed at 300°C for 4 hours prior BET analysis. The surface morphologies of the sorbents before and after the hydration are examined by XL-30 ESEM. Further, to associate the crystal structures of the calcium-based sorbents obtained from various conditions to the CO_2 capture capacity, XRD patterns are identified and quantitatively analyzed using Scintag XDS2000.

Results and Discussions

Physical and chemical characterization of various calcium-based sorbents precursors

The physical properties of different calcium-based sorbents precursors, including Graymont lime (CaO), Graymont limestone (CaCO_3) and Graymont quick lime (Ca(OH)_2), are listed in Table B2. It is shown that CaO and Ca(OH)_2 contain only one crystal structure, i.e. a cubic crystal structure and a hexagonal crystal structure, respectively, but CaCO_3 has three different crystal structures, including a trigonal crystal structure (calcite), an orthorhombic crystal structure

(aragonite), and a hexagonal crystal structure (vaterite). It can be seen from the Table B2 that the calcium oxide (CaO) is composed of the densest packing structure with the highest bulk density (3.29 g/cm³) among all.

Table B2. Physical parameters comparison of various calcium compounds.

	CaO	Ca(OH) ₂	CaCO ₃
Molar Mass (g/mol)	56	74	100
Density (g/cm ³)	3.29	2.24	2.71 (Calcite) 2.947 (Aragonite) 2.645 (Vaterite)
Crystal Structure	Cubic	Hexagonal	Calcite (trigonal) Aragonite (orthorhombic) Vaterite (hexagonal)

The surface area and the pore volume of those precursors and their derived calcium oxides are listed in Table B3. As can be seen from the table, lime exhibits relative low reactivity compared to limestone_CaO and Ca(OH)₂_CaO. It is likely that the surface area and pore volume of limestone_CaO and Ca(OH)₂_CaO is three to four times as much as lime and hence they show better CO₂ capture capability. The pore size distributions of various calcium compounds are given in Figure B2. As can be seen, lime, limestone and calcium hydroxide are of a microporous structure in nature but limestone and calcium hydroxide become of mesoporous structure after calcined. The mesopores (5-20nm) has been proved to be less susceptible to pore closure and sintering, leading to better CO₂ capture capacity. The detailed effect of surface area, pore volume and pore size distribution on the CO₂ capture capacity of calcium-based sorbents will be discussed in the following sections.

Table B3. The surface area, pore volume and CO₂ capture capacity.

	Lime ^a	Limestone ^b	Ca(OH) ₂ ^c	Limestone_CaO ^d	Ca(OH) ₂ _CaO ^d
Surface area (m ² /g)	6.72	0.9	10.16	20.21	25.90
Pore volume (cc/g)	0.03	0.003	0.047	0.152	0.159
Reactivity (wt capture %)	22.37	-	-	57.36	51.80

^a Graymont quick lime

^b Graymont limestone

^c Graymont calcium hydroxide

^d Obtained by calcining its precursor at 700 °C

Figure B2. Pore size distributions of different calcium-based sorbents before and after calcined.

As a reference, three different calcium-based sorbents from Graymont were tested in the XRD. In Figure B3, all three calcium-based sorbents show similar XRD spectra in the form of calcium oxide. As can be seen, there is no difference in terms of position of each peak. However, the changes in the intensity and peak breadth of XRD spectra for CaO before and after the hydration with respect to CO₂ capture reactivity will be investigated in the following sections.

Figure B3. XRD spectra of calcium oxides from various precursors (a) Lime (b) Limestone_CaO (c) Ca(OH)₂_CaO.

Chemical characterization of sintered_CaO sorbents and hydrated_CaO sorbents

The performance of sintered_CaO sorbents and hydrated_CaO sorbents are first tested in the TGA. It is indicated in Figure B4 that the reactivity of sintered_CaO sorbents decreases with increasing calcination temperatures and/or calcination times but it can be recovered to the original state through hydration. At a given calcination temperature, the sintered_CaO sorbents have higher reactivity at a short calcination time and their reactivity decreases with increasing times. For the calcination temperature of 800 °C, the reactivity decreases from 43.81% to 23.78% when the calcination time increases from 1 hour to 16 hours. When the calcination temperature further increases to 1100 °C and hold for 16 hours, the reactivity becomes less than 5%. Despite the reactivity of as low as only 3.08 % from severe sintering, the sorbents still can be effectively reactivated through hydration with excess water at room temperature. It should be noted that there is no obvious difference in the reactivity for various hydrated_CaO sorbents from different

deactivated sorbents as shown in Figure B4. The average reactivity of twelve samples is 54.20% close to the original value of 57.36%. Hence, it can be stated that hydration can effectively reactivate the spent sorbent to its original state under various degrees of sintering.

Figure B4. The reactivity of various calcium oxides towards carbonation at 650 °C: (a) 800 °C (b) 900 °C (c) 1000 °C (d) 1100 °C. (H: hydrated_CaO sorbents)

Numerous studies show that the utilization of the calcium-based sorbents is governed by the surface morphology and the texture of the calcium-based sorbents²⁶⁻²⁹. For the carbonation reaction, the effective surface area and pore volume are necessary to allow for the CO₂ molecules to adsorb on the surface and react with the sorbents to form calcium carbonate. Once the CO₂ is attached on the CaO surface, the reaction starts to take place and the calcium carbonate layer then forms. The surface area and pore volume of various calcium-based sorbents before and after hydration are given in Figure B5 and Figure B6. It is seen, as expected, that sintered_CaO sorbents do not have much surface area and pore volume. The figure shows that the surface area and the pore volume decrease with an increase in sintering times and/or sintering temperatures. In addition, a higher calcination temperature increases the reduction rate of the surface area and the pore volume. The original sorbent contains the surface area of 20.21 m²/g and the pore volume of 0.152 cm³/g. Using the calcination temperature of 800 °C as an example, the surface area decreases from 7.807 m²/g to 4.104 m²/g and the pore volume decreases from 0.0465 cm³/g to 0.0106 cm³/g when the sintering time increases from 1 hour to 16 hours. However, the step of hydration can recover the surface area and the pore volume of sintered_CaO sorbents. As can be seen from Figure B5 and Figure B6, hydrated_CaO sorbents from various deactivated samples can retain high surface area and pore volume. Further, these sorbents can even maintain higher

surface area and pore volume than the original sorbent as shown in the figure. The averaged surface area and pore volume of twelve hydrated_CaO sorbents are $34.22 \text{ m}^2/\text{g}$ and $0.253 \text{ cm}^3/\text{g}$, respectively. Both properties are 1.7 times larger than the original sorbent. Thus, the hydration has a notable effect on the deactivated sorbents in that it not only increases the surface area but also the pore volume. The surface area, pore volume and reactivity of sintered_CaO sorbents and hydrated_CaO sorbents are summarized in the **Error! Reference source not found.**

Figure B5. Effect of calcination temperature and time on the surface area of sintered_CaO and hydrated_CaO sorbents: (a) 800 °C (b) 900 °C (c) 1000 °C (d) 1100 °C

Figure B6. Effect of calcination temperature and time on the pore volume of sintered_CaO and hydrated_CaO sorbents: (a) 800 °C (b) 900 °C (c) 1000 °C (d) 1100 °C

Table B4. Effect of calcination temperature and time on the morphological properties of sintered_CaO sorbents and hydrated_CaO sorbents.

800 °C				Sintered_CaO			Hydrated_CaO		
Time (hr)	Reactivity (g-CO ₂ /g-sorbent)	Surface area (m ² /g)	Pore volume (cc/g)	Reactivity (g-CO ₂ /g-sorbent)	Surface area (m ² /g)	Pore volume (cc/g)	Reactivity (g-CO ₂ /g-sorbent)	Surface area (m ² /g)	Pore volume (cc/g)
1	43.81	7.807	0.0465			0.2463	55.95	29.55	0.2463
4	37.86	7.163	0.0374			0.2206	54.23	33.007	0.2206
16	23.78	4.106	0.0106			0.1815	53.56	34.002	0.1815
900 °C				Sintered_CaO			Hydrated_CaO		
Time (hr)	Reactivity (g-CO ₂ /g-sorbent)	Surface area (m ² /g)	Pore volume (cc/g)	Reactivity (g-CO ₂ /g-sorbent)	Surface area (m ² /g)	Pore volume (cc/g)	Reactivity (g-CO ₂ /g-sorbent)	Surface area (m ² /g)	Pore volume (cc/g)
1	23.51	4.181	0.0234			0.3126	53.10	33.982	0.3126
4	14.22	3.042	0.0103			0.2521	55.82	33.801	0.2521
16	9.70	2.283	0.0074			0.2326	52.67	35.728	0.2326
1000 °C				Sintered_CaO			Hydrated_CaO		
Time (hr)	Reactivity (g-CO ₂ /g-sorbent)	Surface area (m ² /g)	Pore volume (cc/g)	Reactivity (g-CO ₂ /g-sorbent)	Surface area (m ² /g)	Pore volume (cc/g)	Reactivity (g-CO ₂ /g-sorbent)	Surface area (m ² /g)	Pore volume (cc/g)
1	11.63	2.554	0.0108			0.3008	54.89	35.092	0.3008
4	9.58	1.94	0.0081			0.2467	54.22	33.821	0.2467
16	6.79	0.869	0.0039			0.2871	55.34	36.534	0.2871
1100 °C				Sintered_CaO			Hydrated_CaO		
Time (hr)	Reactivity (g-CO ₂ /g-sorbent)	Surface area (m ² /g)	Pore volume (cc/g)	Reactivity (g-CO ₂ /g-sorbent)	Surface area (m ² /g)	Pore volume (cc/g)	Reactivity (g-CO ₂ /g-sorbent)	Surface area (m ² /g)	Pore volume (cc/g)
1	7.01	1.832	0.0094			0.2918	54.86	34.731	0.2918
4	4.82	1.298	0.0036			0.2394	54.29	35.437	0.2394
16	3.08	0.827	0.0033			0.2186	55.09	35.165	0.2186

The surface area and the pore volume as well as the pore size distribution of various calcium-based sorbents are obtained in the BET analysis. The effects of the varying calcination times and temperatures on pore size distribution are shown in **Error! Reference source not found..** In all sintered_CaO sorbents, the mesoporosity is reduced with an increase in calcination times at a given calcination temperature. The pore size distribution for deactivated sorbents peaks at the diameter of 5 nm. However, the hydrated_CaO sorbents exhibit a bimodal distribution which peaks at 5 nm and 20 nm corresponding to microporous and mesoporous regimes respectively. A strong presence of the 20 nm pores for the hydrated CaO is clearly visible in Figure B7, which is believed to govern the performance of calcium-based sorbents with respect to CO₂ capture capacity. It can thus be inferred that the hydration results in a predominately mesoporous structure and an increase in surface area and pore volume.

(a)

(b)

Figure B7. Pore size distributions for sintered_CaO and hydrated_CaO Sorbents: (a) 800 °C (b) 900 °C (c) 1000 °C (d) 1100 °C (S: sintered, H: hydrated)

Enhancement in the surface area, the pore volume and the pore structure through the hydration path is clearly evidenced; so is its close linkage to a high performance of hydrated CaO on the CO₂ capture capacity. In order to further understand the effect of hydration on CO₂ capture capacity, the reactivity data for the original sorbent, sintered_CaO sorbents and hydrated_CaO sorbents with respect to the variation of the surface area or the pore volume is given in **Error! Reference source not found.** Surprisingly, the reactivity is varied in proportion to the surface area or the pore volume only at lower values but there is little reactivity variation, with surface area or pore volume at higher values. That is, the hydrated_CaO sorbents have considerably higher surface area and pore volume than the original sorbent; however, the reactivity of the hydrated CaO is not further increased. For example, comparing the deactivated sorbent calcined at 800°C for 1 hour, its reactivated sorbent and the original sorbent, the surface area is 7.807 m²/g, 29.55 m²/g and 20.21 m²/g, respectively. The surface areas are quite different but their reactivities are similar which are 43.81%, 55.95% and 57.36 %, respectively.

Figure B8. Effect of surface area (left) and pore volume (right) on the reactivity of various calcium-based sorbents

The hydration reaction is a highly exothermic reaction, likely resulting in inner-pore expansion and intra-particle attrition. It will also release considerable heat once the water reacts with calcium oxide and hence creating cracks and forming a porous structure on the outer surface. Those cracks are able to create channels extending toward the interior of the particle. In the BET analysis, the nitrogen is used as an adsorbent to measure the surface area and the pore volume and can easily penetrate the interior of particles. However, during the carbonation, the calcium layer is formed simultaneously while the CO_2 molecules react with CaO . The formation of carbonate layer prohibits the diffusion of CO_2 molecules into the interior of sorbents. That is, the high surface area of locally available pores due to the hydration is not accessible once the calcium carbonate layer is formed on the outer surface. The simplified scheme is illustrated in Figure B9.

Figure B9. Illustration of hydrated_CaO sorbents.

Surface morphologies of sorbents before and after the hydration are examined using SEM technique. In the course of sintering, particles lose their individual identity and agglomerate together as shown in Figure B10. In addition, it can be seen that the particles break into smaller particles and large cracks are found on the surface. Hydration results in the superior macro-structure, including a high surface area, a high pore volume and a predominately mesoporous structure; however, during the hydration, massive microstructural changes occur simultaneously with macrostructural changes as a result of a complex interplay of the carbonation reaction. In the following sections, the changes in microscopic level before and after the hydration are also investigated.

Figure B10. SEM images for limestone sintered at 800°C for an hour (a) sintered_CaO sorbents (b) hydrated_CaO sorbents.

The crystal structure is a unique arrangement of atoms in a crystalline solid and able to govern many of its physical properties. Calcium oxide, calcium carbonate and calcium hydroxide are composed of different crystal structures as shown in Figure B11.

Figure B11. Crystal structure of different calcium-based sorbent (a) calcium oxide (CaO) (b) calcium hydroxide (Ca(OH)₂) (c) calcite (CaCO₃) (d) Aragonite (CaCO₃) (e) Vaterite (CaCO₃)

Due to the nature of calcium carbonate, it contains three different kinds of crystal structures. The crystal structures of derived calcium carbonates obtained from the carbonation reaction with the sintered_CaO sorbents and the hydrated_CaO sorbents are detected using X-Ray diffraction. As can be seen from the Figure, the spectra of those calcium carbonates are similar with the characteristics of calcite. No vaterite or aragonite is found from the spectra. Despite different sources of calcium oxide, including sintered_CaO sorbents and hydrated_CaO sorbents, it can only produce the calcium

carbonated in the form of calcite. This is predictable since the calcite is the most stable polymorph of calcium carbonate. The other two are in the metastable phase of calcium carbonate at ambient conditions and vaterite is even more unstable. Aragonite would change to calcite at 470 °C and vaterite would convert to calcite at low temperature or aragonite at high temperature (~ 60 °C) once it is exposed to water.

Figure B12. XRD spectra of calcium carbonate carbonated from sintered_CaO sorbent (Top) and hydrated_CaO sorbent (bottom)

Eliminating the possibility of different polymorph results from the carbonation reaction, X-Ray Diffraction is performed on different sintered_CaO sorbents and hydrated_CaO sorbents. The samples were prepared by homogenizing powders on the holder with non-diffraction pattern and the spectrum is detected over the angular range 25° - 70° (2θ) in 0.03° and 1.8 s per step. These results are shown in Figure to Figure . As can be seen, there is no distinguishing difference in terms of peak positions between the sintered_CaO sorbents and the hydrated_CaO sorbents at a given calcination temperature and/or calcination time. This implies that the CaO structure is not changed before and after the hydration. It is obvious in the nature of the calcium oxide since calcium oxide only shows one crystal structure, i.e. a cubic structure. Hence, it is stated that the crystal structure does not play a chemical role in the capture of CO_2 .

Figure B13. X-Ray Diffraction Spectra for limestone sintered at 800°C of sintered_CaO sorbents (Left) and hydrated_CaO sorbents (Right)

Figure B14. X-Ray Diffraction Spectra for limestone sintered at 900°C sintered_CaO sorbents (Left) and hydrated_CaO sorbents (Right)

Figure B15. X-Ray Diffraction Spectra for limestone sintered at 1000°C sintered_CaO sorbents (Left) and hydrated_CaO sorbents (Right)

Figure B16. X-Ray Diffraction Spectra for limestone sintered at 1100°C sintered_CaO sorbents (Left) and hydrated_CaO sorbents (Right)

However, most crystals are composed of many sets of planes. Each set of planes has a specific interplanar distance and will give rise to a characteristic angle of diffracted X-rays. The relationship between wavelengths (λ), atomic space (d) and angle (θ) can be expressed by Bragg's Law as follows:

$$n\lambda = 2d\sin\theta$$

Where

- n: An integer
- λ : The wavelength (cm)
- d: The spacing between the planes in the atomic lattice (cm)
- θ : The angle between the incident ray and the scattering planes

On the other hand, each peak in the XRD pattern can represent as a specific crystallographic plane. The first five planes in the CaO surface are (111), (200), (220), (311) and (222). It is observed that the sintered sorbent and the hydrated sorbents have the same peaks which are the characteristic values of CaO. However, the intensity and peak breadth of XRD spectra for CaO before and after the hydration are different, possibly leading to their distinct performance on the CO₂ capture capacity. The intensity of each crystal surface of sorbents obtained from different conditions is summarized in Table B5. It can be seen from the table that the intensity of (111) and (200) increases and rest of three decreases once hydration is applied. That is, the concentrations of (111) and (200) on hydrated_CaO sorbents surface are higher compared to that on their corresponding sintered_CaO sorbents surface. For example, in Table B5, the hydrated_CaO sorbent sintered at 1100 °C for 16 hour has 19.9% of (111) and 49.1% of (200) but the sintered_CaO sorbent only has 16.9% of (111) and 46.9% of (200). Their reactivity is 55.1% and 3.1 %, respectively. This trend can be observed in each set of the sintered_CaO sorbent and the hydrated_CaO sorbent at a given calcination temperature or calcination time as shown in Table B5.

Table B5. The intensity of each crystallographic plane for various calcium oxides.

Temperature	800 °C						900 °C					
	1_S	1_H	4_S	4_H	16_S	16_H	1_S	1_H	4_S	4_H	16_S	16_H
Time (hours)												
Reactivity	43.8	56.0	37.9	54.2	23.8	53.6	23.5	53.1	14.2	55.8	9.7	52.8
(111)	14.8	19.1	19.0	20.5	16.6	18.5	15.8	19.5	17.6	20.1	16.5	19.9
(200)	44.6	48.9	50.7	51.8	44.0	45.4	46.4	49.2	47.4	49.0	47.6	49.3
(220)	26.5	21.5	20.7	19.7	26.0	24.8	24.2	22.3	22.8	21.6	23.7	21.6
(311)	6.8	5.3	5.5	4.3	6.9	5.8	7.1	4.7	6.1	5.2	6.0	4.6
(222)	7.3	5.2	4.3	3.8	6.5	5.5	6.6	4.3	6.2	4.2	6.2	4.7

Temperature	1000 °C						1100 °C					
	1_S	1_H	4_S	4_H	16_S	16_H	1_S	1_H	4_S	4_H	16_S	16_H
Time (hours)												
Reactivity	11.6	54.9	9.6	54.2	6.8	55.3	7.0	54.9	4.8	54.3	3.1	55.1
(111)	16.9	19.7	17.3	19.0	14.7	17.8	17.0	20.0	16.8	17.7	16.9	19.9
(200)	46.9	48.7	47.3	51.2	44.4	48.2	46.5	48.3	47.0	46.5	46.9	49.1
(220)	23.3	21.0	23.1	21.1	26.6	23.5	24.1	22.0	23.4	24.9	23.4	22.1
(311)	6.5	5.5	5.9	4.5	7.2	5.3	6.0	5.2	6.8	5.3	7.4	4.8
(222)	6.4	5.0	6.3	4.4	7.0	5.2	6.3	4.5	6.1	5.6	5.4	4.2

(Reactivity: carbonated at 650°C with 10% CO₂ stream for 20mins)

(S: sintered_CaO sorbent; H: hydrated_CaO sorbent)

The crystallographic planes are the fictitious planes linking nodes. Each of them may have different atomic arrangement and can result in a higher density of nodes, leading to different behavior of the crystal such as optical properties, surface tension, cleavage, microstructure defects, adsorption and reactivity. Once CO₂ molecules diffuse to the surface, they tend to adsorb on the site with a lower energy barrier. In addition, a charge transferred from the oxygen anion (O²⁻) on CaO surface to the CO₂ molecule can lead to energetically favorable carbonate species (CO₃²⁻). Depending on the geometric difference of each crystallographic plane, the coordinated number of surface oxygen would not be the same and thus it may affect the CO₂ adsorption on the CaO surface. Due to the nature of calcium carbonate, the CO₂ would tend to interact more strongly with lower coordinated numbers of surface oxygen. The intensity of each plane on the CaO surface with respect to reactivity is plotted in the Figure . It can be seen that more (111) plane and (200) plane on the CaO surface can lead to better CO₂ capture capacity. Jensen et al. shows that CO₂ would adsorb as monodentate on both edge and corner site on regular (100) surface but no stable CO₂ adsorption is found on the terrace site ³⁰. That is, the energy barrier of CO₂ molecules on a given crystal plane may vary a lot and hence different preferred orientations on a CaO surface can lead to various performance on CO₂ capture capacity.

Figure B17. The effect of relative intensity of each crystallographic plane on the CO₂ capture reactivity

Once the hydration is applied to the deactivated sorbents, it improves not only the macroscopic structure such as the surface area, the pore volume and the pore size distribution but also the microscopic structure, i.e. the concentrations of crystallographic planes on the CaO surface. The latter could play a very significant role in the CO₂ capture capacity, leading to distinctly improved performance between deactivated sorbents and reactivated sorbents. More comprehensive study on the behavior of CO₂ adsorption on a given crystal surface of CaO will be investigated in the continuing work.

Conclusions

It is found that an increase in calcination temperatures and/or calcination times has a negative effect on CO₂ capture capacity, but sintered sorbents are effectively reactivated through hydration with water. The results show that hydrated sorbents have improved such morphology properties as the surface area, the pore volume and the pore size distribution, which enhances the CO₂ capture capacity. However, the CO₂ capture capacity is also improved by the hydration with the alteration of microstructural properties, such as the preferred orientation in the crystal structure. Specifically, the first two planes of the CaO sorbents, i.e. (111) and (200), are found to increase after the hydration. It is shown that the preferred crystallographic plane on a CaO surface has a significant effect on the CO₂ sorption capacity. That is, with more (111) plane and (200) plane in the CaO sorbents, the CO₂ capture capacity can further be enhanced.

C. CLP for Enhanced Reforming of Hydrocarbons

Introduction

The CLP enables high purity H₂ production from coal-gasified syngas with in-situ CO₂ and sulfur capture in a single step. Process overview and experimental results from the bench-scale and sub-pilot scale testing have been presented in this report. However, it is also possible to integrate the reforming of hydrocarbons along with CO₂ and sulfur capture in the CLP. This study provides details of such a process scheme. Experiments have been performed with CH₄ in a fixed-bed reactor and the results are presented here.

Process Overview and Thermodynamic Analysis

In the carbonator, hydrocarbon reforming, WGS and CO₂ removal occur simultaneously. The steam reforming of the hydrocarbons occurs in the presence of the reforming catalyst, and the CO₂ produced by the combined reforming and water gas shift reaction is removed by the CaO sorbent. The concomitant carbonation of the CaO, leading to the formation of the CaCO₃, incessantly drives the equilibrium-limited WGS and reforming reactions, according to Le Chatelier's principle.

The reactions occurring in the carbonator are as follows:

CaCO₃ is then decomposed by heating in the calciner, to obtain CaO and a pure CO₂ stream:

The regenerated CaO undergoes hydration to form Ca(OH)₂, according to the following reaction:

The CaO and H₂O participating in the carbonator reactions are obtained by the dehydration of the above product.

A major advantage of the CLP is the internal heat integration that it provides to the reforming of hydrocarbons. The exothermic carbonation and WGS reactions convert the highly endothermic reforming of hydrocarbons into a heat neutral process (slightly exothermic). An example of a system for the conversion of methane to hydrogen in the CLP carbonator is provided below:

Figure C1. Thermodynamic analyses of the reforming and WGS reactions in the presence and absence of a calcium-based CO_2 acceptor.

As seen from Figure C1, the equilibrium constant for the combined reforming and WGS reaction is very poor up to 700 °C, which explains the need to carry out these reactions at high temperatures (800-900 °C) and under pressure. However, due to the integration of CO_2 capture with these reactions, high equilibrium constants are obtained at comparatively lower temperature range of 500-750 °C. Operation at lower temperature is likely to result in cost-savings due to lower consumption of supplemental fuel. Moreover, since in-situ CO_2 removal drives the H_2 -producing reactions forward, excess steam requirement is reduced. Finally, WGS catalysts are eliminated resulting in further cost savings.

The three stages of the CLP have been investigated in this study with the focus on improving the overall efficiency of the hydrocarbons to H_2 conversion process.

Experimental Methods

Chemicals, Sorbents, and Gases

The reforming catalyst was obtained from Sud-Chemie Inc, KY, and consisted of Nickel oxide. The CaO was obtained from precipitated calcium carbonate (PCC) precursor. Detailed procedure of the synthesis of PCC is provided elsewhere. Pure CH_4 (mention purity) was used as the feed gas for all tests.

Bench-scale Experimental Setup

The combined steam methane reforming (SMR), WGS and carbonation reaction was investigated in a bench-scale fixed bed reactor, described earlier in Section 4 of this

document. Pure CH₄ was metered into the reactor by a mass flow controller (MFC). From the MFC, the CH₄ flows to the steam generating unit which also serves to preheat the CH₄ entering the reactor. The reactor, which is heated by a tube furnace, is provided with a pressure gauge and a thermocouple to monitor the pressure and temperature within. The reactor consists of two concentric sections. The inner section is filled with solid particles consisting of only catalyst or catalyst and sorbent mixture, depending on the type of investigation. The outer section provides a preheating zone for the gases before they come in contact with the bed of solids. The packed bed section of the reactor is detachable which enables easy removal and loading of the solid particles. The gases leaving the reactor enter a back pressure regulator. After exiting the back pressure regulator, the gases are cooled in a heat exchanger using chilled water to condense the unreacted steam. The product gas at the exit of the heat exchanger is dried in a desiccant bed and is sent to a set of continuous analyzers capable of determining the concentrations of CO, CO₂, CH₄ and H₂ in the gas stream.

Reforming Reaction in the Presence of Reforming Catalyst

The reforming of CH₄ was investigated in the presence of the Reforming catalyst obtained from Sud-Chemie Inc. For these tests, 5 g of finely powdered catalyst was loaded into the reactor. Quartz chips (inert) were added to reduce the pressure drop in the reactor. The dry gas compositions were monitored continuously using the CO, CO₂, CH₄ and H₂ gas analyzers. The CH₄ flowrate was maintained constant at 37 ml/min for all experiments.

Simultaneous Reforming, WGS and Carbonation

The combined reforming, WGS and carbonation reaction was investigated using a mixture of CaO sorbent and reforming catalyst. 2.5 g catalyst and 2.5 g PCC was fed into the reactor. Both catalyst and sorbent were finely powdered before feeding into the reactor. The sorbent was calcined at 700 °C in 1000 ml/min N₂ for 4 h. Following this, the mixture was exposed to pure H₂ (200 ml/min) at 650 °C to reduce and reactivate the catalyst. The combined reaction was then conducted using methane and steam and the effect of different parameters like temperature, pressure and steam to carbon (S:C) ratio is investigated.

Different Calcination conditions and Reactivation using Hydration

The combined reforming, WGS and carbonation reaction was investigated over multiple cycles using different calcination conditions. Calcination was either performed in pure N₂ or a 50:50 (by vol.) mixture of steam-CO₂ at 950 °C. The total flowrate of the calcining medium was 1000 ml/min in both cases. The higher calcination temperature resulted in sintering of the sorbent, which reduces the CO₂ capture capacity over multiple cycles. To reverse the effect of sintering, the sorbent was hydrated at 600 °C and 150 psig using a 80:20 (by vol.) mixture of steam-N₂ (total flowrate 400 ml/min) for 1 hour and multicyclic tests were conducted.

Results and Discussion

SMR using Ni-based Catalyst (no CaO sorbent)

Figure C2: Effect of temperature and S:C on (a) H₂ purity and (b) the amount of CO, CO₂ and CH₄ remaining in the product gas for the SMR reaction in the presence of Ni-based catalyst.

Baseline tests were conducted in the bench scale reactor to investigate SMR in the presence of a Ni-based reforming catalyst procured from Sud Chemie. The temperature and S:C were varied in these tests. The results have been provided in Figure C2. It can be seen in Figure C2(a) that for both S:C – 3:1 and 5:1 – the H₂ purity increases with the

increase in temperature till the temperature reaches 700 °C. Above 700 °C, the H₂ purity remains almost constant. With the increase in S:C from 3:1 to 5:1, it was found that the H₂ purity increases at all the temperatures as expected. Figure C2(b) depicts the composition of CO, CO₂ and CH₄ in the product gas at the outlet of the reactor on a steam- and nitrogen-free basis. The amount of CH₄ in the stream decreases with temperature and is in the ppm range at temperatures above 850 °C. It can also be seen that with the increase in the S:C, the conversion of CH₄ to CO, CO₂ and H₂ increases. CO in the product stream increases with the increase in temperature as the conversion of CH₄ to CO increases. This is because reforming is an endothermic reaction. In addition, the conversion of CO to CO₂ decreases with an increase in temperature due to the equilibrium limitation of the exothermic WGS reaction. This reduces CO₂ in the product. However, CO₂ increases with the increase in S:C due to the higher conversion of CO to CO₂ by the WGS reaction at higher steam addition rates.

Enhanced Reforming and WGS Reaction with CO₂ Capture

In order to study the improvement in CH₄ conversion and H₂ purity, SMR was conducted in the presence of the reforming catalyst and CaO sorbent, as per the procedure described earlier.

Figure C3 depicts the composition of the product gas of SMR conducted in the presence of reforming catalyst and CaO sorbent. A typical breakthrough curve is clearly visible. It was found that >99% pure hydrogen can be obtained in the prebreakthrough region of the curve when the CaO is active and captures CO₂. It was also found that CH₄ is almost completely converted and the concentration of CH₄, CO and CO₂ in the product stream is only a few ppm. The removal of CO₂ by CaO enhances the WGS reaction and the reforming reaction resulting in the production of very pure H₂. As the CaO sorbent gets consumed in the fixed bed, the concentration of CO₂, CH₄ and CO begins to increase in the product gas. This region of the curve is the breakthrough period. At the end of the breakthrough period, the CaO sorbent is completely converted to CaCO₃ and no further CO₂ capture is possible. The conversion of CH₄ to H₂ occurs only due to the reforming catalyst in the postbreakthrough period.

Figure C3 : Breakthrough curve in the composition of the product gases obtained during the simultaneous reforming, water gas shift and carbonation reaction at 650 °C and atmospheric pressure.

The effect of S:C and temperature was investigated on the above system. The purity of H₂ produced is greatly enhanced by the presence of the CaO sorbent as shown in Figure C4(a). Purity of H₂ increases from <80% in the presence of the catalyst alone to >90% in the presence of the catalyst and sorbent. Higher H₂ purity is obtained at 650 °C than at 700 °C due to the favorable thermodynamics of the CO₂ removal (carbonation reaction) and the WGS reaction at lower temperatures. In the presence of the catalyst and sorbent, the H₂ purity increases with the increase in S:C from 2:1 to 3:1. A further increase in S:C does not produce an appreciable increase in H₂ purity.

Figure C4(b) illustrates the effect of temperature and S:C on the conversion of CH₄. The presence of the sorbent enhances the CH₄ conversion to a large extent, especially at 650°C, where the conversion goes up from 83% to 94% at S:C of 3:1. But when the ratio approaches 5:1, the CH₄ conversion enhancement due to presence of the sorbent is not significant, because the conversion with or without the sorbent almost reaches 100%. The conversion in the presence of the sorbent and catalyst mixture is similar at both temperatures investigated.

Figure C4: Effect of temperature and S:C on (a) H₂ purity (b) CH₄ conversion.

The effect of pressure was also studied on the combined reaction at 650 °C and S:C = 3. Thermodynamics predicts a decrease in the H₂ purity with the increase in pressure, in the presence of a catalyst alone, according to the Le Chatlier's principle. On the contrary, Figure C5(a) shows that the H₂ purity remains almost constant when CaO is used along with the catalyst. A high H₂ purity of >95% is obtained at pressures ranging from 1 to 150 psig.

Figure C5: Effect of pressure on (a) H_2 purity and (b) CH_4 conversion. ($T = 650\text{ }^\circ\text{C}$, $\text{S:C} = 3$)

The effect of pressure on the concentration of CH_4 in the product stream is shown in Figure C5(b). With an increase in pressure there is a small increase in CH_4 concentration, from 3% at 0 psig to 5% at 150 psig, in the pre-breakthrough region of the curves. This negative effect of increasing pressure, though minor, is due to the thermodynamics of the combined reaction governed by the Le Chatlier's principle. In the post breakthrough region of the

curves, when the sorbent no longer captures CO_2 , the increase in pressure of 1 to 150 psig results in a larger increase (5% to 17%) of CH_4 in the product stream. Hence, it can be concluded that the presence of the sorbent results in a significant increase in CH_4 conversion even at high pressures.

Conclusions

The integration of the CLP in process of H_2 production using SMR was presented and various process conditions were investigated. It was observed that the conversion of CH_4 is improved to a large extent due to the presence of CaO , which captures CO_2 and simultaneously drives the equilibrium-limited reforming and WGS reactions in the forward direction. It is possible to carry out the combined reaction at a comparatively lower temperature of $650\text{ }^\circ\text{C}$ to produce high purity H_2 at low S:C of 3:1 for various pressures ranging from 0 to 150 psig.