Chemical Looping Reforming – an Efficient Process for the Production of Hydrogen from Coal

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ABSTRACT

A novel Chemical Looping Reforming (CLR) process is proposed in which a highly recyclable iron oxide composite particle is reduced with coal and then oxidized back with steam to generate hydrogen. The reduction of iron oxide with coal results in a mixture of CO_2 and H_2O in the exhaust stream which after water condensation provides a ready to sequester relatively pure CO_2 stream. This eliminates the need for energy intensive CO_2 separation process which will be required in traditional air fired coal combustion processes. In oxidation part of the process, the reduced particle is oxidized with steam in a second reactor producing hydrogen and regenerating the iron oxide.

This paper describes the contacting pattern necessary for achieving high coal conversions in the first reactor. Detailed ASPEN simulations were carried out to simulate the workings of the reactor. It was found that a high H_2 production rate (0.183kg H_2/kg coal) is possible with complete conversion of carbon. The material balances and concentrations for various gaseous and solid streams are reported. The exit flue gas contained mainly CO_2. The sulfur in the coal was captured by introducing lime into the reactor which prevented FeS formation. FeS formation may potentially decrease the recyclability of the Fe_2O_3 containing particles as well as lead to contamination of the hydrogen produced by H_2S. The simulations showed that NOx will be produced at below detectable limits. Chlorine was found to form HCl and exit along with the CO_2 gas. It was found that a high Fe_2O_3 flow rate and temperature and a low oxygen demand are ideal for achieving high H_2 production rates, high carbon conversions and high CO_2 exit purity. Combining with a low cost of hydrogen production of \$0.83/kg, which is very competitive with respect to the \$1.2/kg H_2 as obtained from SMR of natural gas (\$7/M BTU) the CLR process is at the leading edge of clean coal conversion technologies.

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1. INTRODUCTION

Though a number of energy sources exist, fossil fuels, namely, petroleum, natural gas and coal provide more than 85% of US energy needs. Coal is both cheap and abundantly available in the US as compared to oil and natural gas which has to be imported from foreign countries. Burning of all fossil fuels lead to the production of CO_2 which is considered the most important green house gas. Conventional amine scrubbing technologies to separate CO_2 from the flue gas mixtures containing nitrogen may account for up to 75% of all carbon management costs. A technology that eliminates the need for costly CO_2 separation will be of significant value for future carbon management policy. There is a need for a better process that is cheaper, more efficient and eliminates CO_2 separations if possible.

Extensive research has been carried out on coal gasification to produce hydrogen and electricity. A number of demonstration plants have been setup in the US which have led to better understanding and reliable operations of coal gasification systems [Stiegel et al. 2006] The process starts with gasification of coal to syngas ($CO + H_2$) in a gasifier using pure O_2 obtained from an air separation unit (ASU). The syngas produced is cleaned up for sulfur and CO_2 and sent to water gas shift (WGS) reactors where the CO is converted to H_2 in a two step catalytic process using the WGS reaction:
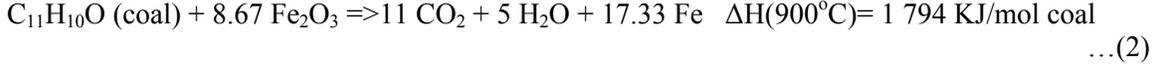
$$CO + H_2O <=> CO_2 + H_2 \qquad (1)$$

Lower temperatures favor the formation of H_2 and hence the second stage is carried out at lower temperature to drive the reaction toward H_2. The CO_2 produced is then removed using ambient temperature amine scrubbing technologies which tend to be highly energy extensive due to the high heat demand to regenerate the amine solvent and costly due to the high cost and make up rate of the solvent [Desideri et al. 1999]. The gases coming out of the CO_2 removal unit still contain some CO and hydrocarbons that need to be removed to obtain high purity H_2. This is achieved in a pressure swing adsorption unit (PSA). The tail gases from this unit are combusted in a gas turbine to generate electricity. The low pressure CO_2 produced in the CO_2 separation unit would require compression to obtain a high pressure sequestration ready CO_2 stream. Due to the large number of units that are required with their associated energy losses, the efficiency of the process is projected to be about 64% (HHV H_2 produced/ HHV coal introduced) [Simbeck et al. 2002]. Further, due to the presence of a number of reactor systems, the plant heat integration is relatively difficult.

A two-step coal gasification system (Chemical Looping Reforming CLR) [Gupta et al. 2004, 2005, 2006; Thomas et al. 2005] that is capable of delivering a sequestration ready CO_2 stream without associated separation costs has been developed. In this process, a hydrogen rich syngas stream can be achieved where the H_2/CO ratio can be readily tailored as per downstream requirements. The process is based on reaction of coal with iron oxide containing particles, which has superior heat integration than conventional gasification systems and combines the gasifier, the water gas shift reactors and the CO_2 separation systems into a set of two moving bed reactors.

Figure 1 shows a simplified diagram of the CLR process. The process has two reactors. In reactor 1 (also called the fuel reactor), coal is reacted with iron oxide (Fe_2O_3) containing particles to form gaseous combustion products CO_2 and H_2O and the iron oxide is reduced to Fe. A pittsburg #8 coal composition may be written as $C_{11}H_{10}O$ given the elemental composition [Stultz

et al. 1992]. Then the reaction in reactor 1 may be written as:

$$C_{11}H_{10}O \text{ (coal)} + 8.67 \text{ Fe}_2O_3 => 11 \text{ CO}_2 + 5 \text{ H}_2O + 17.33 \text{ Fe}   \Delta H(900^oC)= 1\ 794 \text{ KJ/mol coal}$$
…(2)

   H$_2$O can be separated from gaseous products leading to a ready-to-sequester CO$_2$ stream without the inherent separation costs associated with traditional coal gasification systems. Since this reaction is endothermic, pure oxygen is introduced into this reactor to partially combust the coal and provide the heat of reaction. The addition of oxygen does not allow for all coal to react with Fe$_2$O$_3$, thereby limiting the quantity of Fe. However it is important to note that reaction (2) is an energy conversion process where the calorific value of coal is transferred to Fe. The reaction being endothermic, the calorific value of Fe if it were to be oxidized would be more than the coal that was used to make it. Hence combustion of some of the coal to provide for the heat of reaction (2) would lead to an overall energy balance between coal going into reactor and Fe coming out of the reactor. Ash in the coal may be separated from Fe exiting Reactor 1using methods based on particle size difference. Magnetic separation of Fe can also be used.
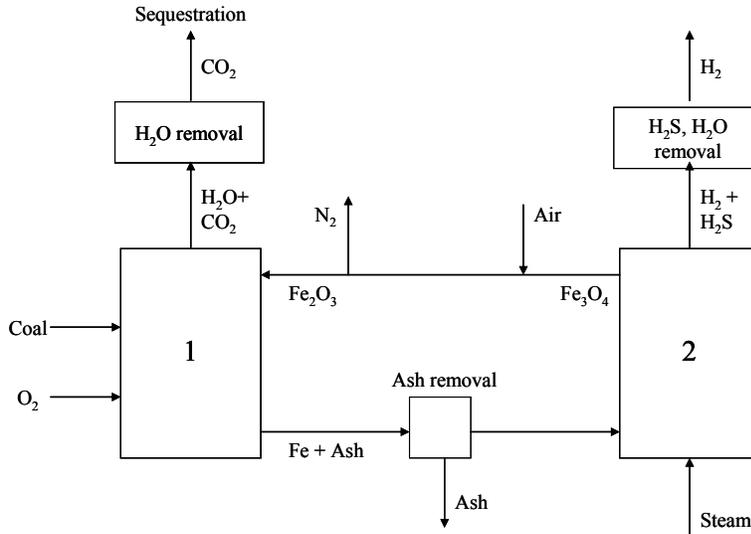

Figure 1 Simplified schematic of the Chemical Looping Reforming (CLR) system

   The regeneration of Fe back to Fe$_2$O$_3$ may be done in a number of ways. It is possible to react the Fe with air or oxygen generating heat in the process, the oxidation of different metals, including iron, have been extensively investigated in previous studies [Lyngfelt et al. 2001; Jin et al. 2004; Cho et al. 2004; Ishida et al. 2005; Corbella et al. 2006; Mattisson et al. 2006]. This heat carried out of the reactor by unreacted air may be used to generate steam for power generation.

   To generate hydrogen, the Fe is regenerated with steam in reactor 2 (hydrogen production reactor). This leads to the formation of Fe$_3$O$_4$.

$$3 \text{ Fe} + 4 \text{ H}_2O <=> \text{Fe}_3O_4 + 4H_2 \tag{3}$$

This reaction leads to the formation of H$_2$ which is obtained in high purity after condensation of unreacted water. Next the Fe$_3$O$_4$ formed is reacted with air to form Fe$_2$O$_3$ to be reused for reaction with coal. The heat generated heats up the particles which then help compensate the endothermic heat of reaction (2).

The sulfur present in coal is expected to react with Fe and form FeS. This species will be carried over to reactor 2 where it will react with steam to form H_2S which will exit along with the hydrogen stream. Hence H_2S cleanup will be necessary. This may be achieved using amine absorption techniques or high temperature regenerable metal oxide sorbents.

For the process to be economically viable, it is important that the Fe_2O_3 particles maintain reaction rate and oxygen transfer capacity over numerous reaction/regeneration cycles. This has been achieved through suitable particle development as reported earlier [Gupta et al. 2004, 2005].

Earlier studies [Gupta et al, 2006] showed that a maximum of about 86% coal to hydrogen conversion efficiency (or 0.18 kg H_2/ kg coal) may be achieved in the CLR process. The studies also showed that a hydrogen production cost of $0.83 /kg of hydrogen is possible which is very competitive with respect to the $1.2/kg H_2 as obtained from SMR of natural gas ($7/M BTU).

This paper describes the reactor designs and operational conditions that allow for high conversions of coal to hydrogen. The process can be heat integrated in a number of ways depending upon configuration. The studies reported in this paper are related to developing one such set of operational conditions based on thermodynamic equilibrium analysis. Studies were also carried out to understand the fate of trace elements chlorine and sulfur from a thermodynamic standpoint.
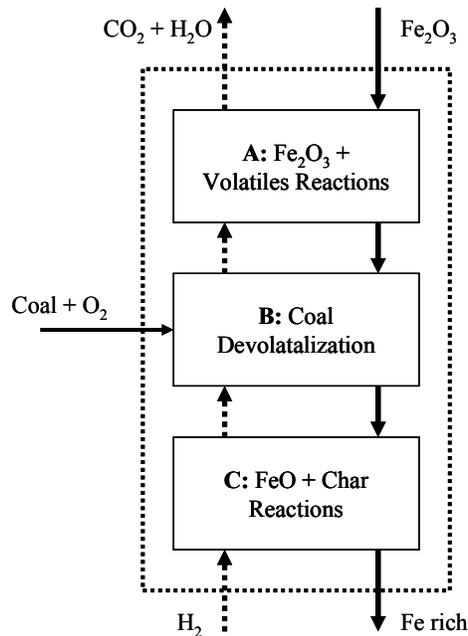

Figure 2: Contacting pattern in Reactor 1

2. Reactor Design

As shown in figure 1, prior to entry into Reactor 1 the iron oxide containing particles are combusted with air. This leads to a temperature rise that provides for some of the reaction heat required for reaction 2. The coal entering reactor 1 would readily absorb heat from such particles and devolatilize. Such volatiles if not suitably treated, will exit reactor 1 in the gaseous form and

contaminate the CO_2 stream. This will lead to a decrease in hydrogen production since a large part of the coal energy is exhausted as volatiles as well as would not allow for the production of a relatively pure ready-to-sequester CO_2 stream. Hence it is necessary that coal be introduced at a position below where the iron oxide particles are fed so that the volatiles react with Fe_2O_3 and reduce it while themselves converting to CO_2 and H_2O. The remaining char then needs to be mixed well with the iron oxide particles to reduce them to iron phase. This is easily achieved by suitable reactor designs that allow for coal mixing with the iron oxide containing particles in the middle. The reactor is envisaged to be of a moving bed design. Figure 2 shows a schematic of the contacting pattern. A small quantity of hydrogen (less than 5 % of hydrogen produced in reactor 2) is added at the bottom of the reactor to help convert the char particles by partially gasifying them.
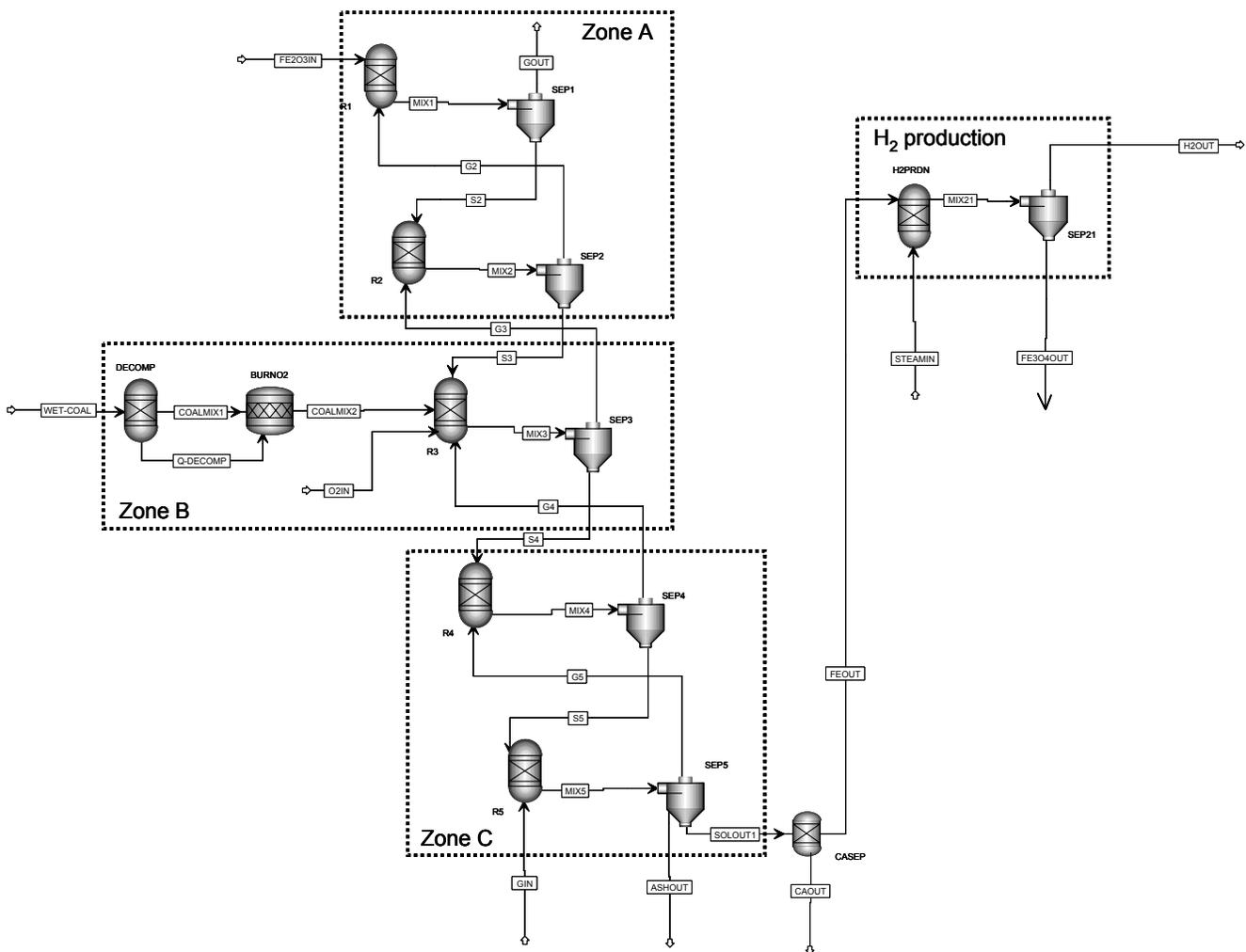

Figure 3: ASPEN process simulation of the fuel reactor of Chemical Looping Reforming (CLR) process to produce hydrogen from coal.

3. Reactor simulations

Simulations were carried out in ASPEN PLUS 12.1 process simulator to identify the operational conditions and conversions achieved in the contacting pattern shown in figure 2. Figure 3 shows the chemical flowsheet developed. Characteristics of Pittsburg #8 coal (table 1) were used in the simulations. The coal was defined as a non-conventional solid and decomposed into constituent elements (C, O_2, N_2, H_2, Cl_2, H_2O, S and Ash) in a Yield reactor (DECOMP). All the oxygen formed was reacted with carbon to form CO in a second stoichiometric reactor (BURNO2). These transformations allowed coal to be converted from a non conventional component to regular elements that could be easily reacted with iron oxide using existing property models in ASPEN. No external energy was added or subtracted from the surroundings for this transformation. The energy requirements were met by the sensible heat change of the product stream out of this transformation.

Zones A and C of the reactor as shown in figure 2 were each simulated using two RGIBBS reactors (R1, R2 and R4,R5) in series simulating counter current operation of gas and solid. Zone B was simulated using another RGIBBS reactor (R3) where the simulated coal reacts with iron oxide particles coming down the Zone A and going into Zone C. The RGIBBS reactors use free energy minimization principles in order to determine the composition of the product scheme given a list of possible products. For the purposes of this simulation the list of possible products in the gaseous and solid phases are provided in Table 2. The calculations allow for the finding the fate of trace elements like sulfur, chlorine and nitrogen present in coal.

The reduced particles exiting Zone C were oxidized in another RGIBBS reactor (H2PRDN) with steam in order to produce hydrogen. Ideally, the hydrogen production reactor can be simulated as a countercurrent moving bed also. However this was avoided for ease of computation by passing excess amount of steam into a single RGIBBS reactor (H2PRDN) to calculate the hydrogen production rate.

All flow streams were normalized for 1kg/hr of coal flow. The simulations allowed for change in oxygen and Fe_2O_3 flow rate into the reactor and the temperature of the Fe_2O_3 stream to maximize hydrogen production as well as convert most of the coal put into the reactor. The associated temperature profile in the reactor can be obtained from the outlet of the RGIBBS reactors for zones A, B and C.

Table 1: Characteristics of Pittsburg #8 coal used in reactor simulations

Proximate Analysis (%)		Ultimate Analysis (%)		Heating Value (Btu/lb)	
Moisture	5.2	Carbon	74.0	As-received	12,540
Volatile Matter (dry)	40.2	Hydrogen	5.1	Dry	13,230
Fixed Carbon (dry)	50.7	Nitrogen	1.6		
Ash (dry)	9.1	Sulfur	2.3		
		Ash	9.1		
		Oxygen	7.9		

4. Results and Discussions

A number of simulations were run to assess the conversions taking place in the fuel reactor. The Fe_2O_3 inlet temperature, Fe_2O_3 to coal stoichiometry and oxygen to coal stoichiometry was varied. These effects were varied in order to maximize hydrogen production, maximize coal

conversion and maximize CO_2/CO outlet ratio from the top of the reactor. A number of such combinations of parameters were obtained which satisfied a coal conversion of more than 99% and CO_2/CO ratio greater than 10. One such combination is reported in this paper. Table 3 shows the values of the variables tested and the corresponding values for H_2 production, coal conversion and the exit CO_2/CO ratio. The hydrogen production rate of 0.183kg/kg of coal consumed is equivalent to 86% energy conversion efficiency on a HHV basis. The coal introduced into the reactor is nearly completely reacted leaving little or no trace of carbon in the solid exit stream. The CO_2/CO ratio of 37.7 is high enough such that the presence of CO in this stream may be neglected.

Table 2: Possible products considered for simulation with RGIBBS reactors.

Solid Products Possible		Gaseous Products Possible	
Fe	C	H_2	N_2
FeO	CaO	H_2O	NH_3
Fe_3O_4	$Ca(OH)_2$	CO	N_2O
Fe_2O_3	$CaCO_3$	CO_2	NO
FeS	$CaCl_2$	H_2S	NO_2
FeS_2,	CaS	COS	HCN
FeSO4	$CaSO_4$	CS_2	Cl_2
$FeCl_2$	$CaSO_3$	SO_2	HCl
$FeCl_3$	Inerts	SO_3	CH_4
S		O_2	

Table 3: Simulation conditions for obtaining high production rates of H_2 for 1kg/hr coal flow basis.

Fe_2O_3 Temp ^oC	Fe_2O_3 flow (kg/hr)	Oxygen flow (kg/hr)
1000	10	0.35
H_2 Production (kg/hr)	Coal conversion	CO_2/CO outlet ratio
0.183	> 99.99%	37.7

Table 4: The composition of the GOUT stream as depicted in figure 3.

CO_2 (%)	62.804	O_2 (ppb)	0.5627
H_2O (%)	34.124	SO_3 (ppb)	0.0902
CO (%)	1.864	HCN (ppb)	0.0029
N_2 (%)	0.685	CL_2 (ppb)	0.0004
H_2 (%)	0.485	CH_4 (ppb)	0.0001
HCL (ppm)	338	N_2O (ppb)	1.80E-05
SO_2 (ppm)	53.3	NO_2 (ppb)	1.35E-06
H_2S (ppm)	0.44	CS_2 (ppb)	1.13E-06
COS (ppm)	0.075		
NO (ppm)	0.0034	Temperature (^oC)	1108
NH_3 (ppm)	0.0026	Pressure (atm)	1

Table 4 shows the compositions the GOUT stream depicted in figure 3. It is readily seen that the stream consists of primarily CO_2 and steam, the combustion products of coal. Upon condensation of H_2O a relatively pure CO_2 stream will be obtained. If it is desired that the trace quantities of CO and H_2 be converted to CO_2 and H_2O, then the gas stream can be passed over a NiO/CuO bed or a small quantity of air be introduced. Since the temperatures are high enough (1108^oC), such conversion will readily take place.

The outlet gas also contains the reaction products originating from the trace elements in coal. It is seen that NO and NH_3 formation will be limited to ppb levels, with N_2 being the dominant phase. N_2O and NO_2 will be present in below traceable limits. The primary reason for such low NOX production is the lower reaction temperatures ($<1000^oC$) and the absence of N_2 entering the reactor along with combustion oxygen. As a result only the nitrogen from the coal is present for NOx formation. The sulfur exits the reactor in the gaseous phase mainly as SO_2 with trace quantities of H_2S and COS. SO_3 and CS_2 are found at below detectable limits. SO_2 concentration of 53.3 ppm is lower than that emitted by conventional PCC boilers after lime scrubbing (200ppm). As a result such a gas may be emitted to the atmosphere under the current sulfur regulations for flue gas. The chlorine is present mainly as HCl and at a high concentration of 338 ppm. In case GOUT needs to be emitted to the atmosphere, a scrubber may be required to get rid of this species. In case the CO_2 in this gas stream needs to be sequestered, then separation of these species may not be important since they can be sequestered along with the CO_2.

Table 5: Selected solid stream flowrates as depicted in figure 3 for 1kg/hr coal flow basis.

Mass Flow (kg/hr)	FE2O3IN	FEOUT	FE3O4OUT	CAOUT
Fe_2O_3	10.00	0	2.9E-03	0
Fe_3O_4	0	0	9.663	0
FeO	0	5.43	0	0
Fe	0	2.77	0	0
S	0	0	0	0
C	0	0	0	0
FeS	0	0	0	0
FeS2	0	0	0	0
$FeSO_4$	0	0	0	0
$FeCl_3$	0	0	0	0
$FeCl_2$	0	0	0	0
CaO	0.4515	0	0	6.49E-03
CaS	0	0	0	0.0466
$CaSO_3$	0	0	0	0
$CaSO_4$	0	0	0	0
$CaCO_3$	0	0	0	0.7296
$Ca(OH)_2$	0	0	0	0
$CaCl_2$	0	0	0	0
Inert	2.20	2.20	2.20	0
Temperature (^oC)	1000	725.5342	584.2385	725.5342
Pressure (atm)	1	1	1	1

Table 5 shows the flow rates of various components in selected solid streams as depicted in Figure 3. The FE2O3IN stream consists of only Fe_2O_3 and CaO. The CaO is added to react with sulfur present in coal and hence prevent the reaction of sulfur and iron oxide. Inert materials are also present in this stream which helps transfer the heat between the different reactors in the process. Simulations were run for atmospheric pressure operation. The stream enters the reactor zone A at a 1000^oC after the Fe_3O_4 component in oxidized with air. The exit solid stream from zone C of the reactor is then processed to separate the ash (stream ASHOUT) and calcium compounds (CAOUT) from the Fe bearing particles. This is done on the basis of size separation since ash and Ca bearing particles are designed to be much smaller in size as compared to Fe containing pellets. The resultant iron containing stream (FEOUT) contains mainly FeO, Fe and

inerts. Since excess amount of Fe_2O_3 is added to the reactor it is expected that not all of it will be converted to Fe. The FeO/Fe molar ratio for this set of conditions was found to be 1.51. This corresponds to about 60% consumption of the oxygen entering the reactor as Fe_2O_3.

The CAOUT stream shows the fate of the CaO injected in zone A. It is seen that most of the CaO is converted to $CaCO_3$ while some became CaS. It is notable that no FeS formation was seen in stream FEOUT on addition of CaO to zone A. As a result the hydrogen produced by oxidation with steam did not contain any sulfur species. Similarly, the FEOUT stream did not contain any unconverted carbon from coal or any chlorine species. This results in a near pure H_2 stream with all trace impurities in coal moving to the GOUT stream or in the CAOUT stream.

Upon oxidation with steam to produce hydrogen in the H2PRDN reactor, the Fe and FeO in stream FEOUT are converted to Fe_3O_4. The temperature as shown in table 5 for Fe3O4OUT stream of 584 ^{o}C is lower than that expected in the real reactor. For the purpose of this simulation, a large excess of steam was added to the H2PRDN reactor to completely convert the iron to Fe_3O_4. In reality the steam flow will be lower and hence the reaction heat will lead to a higher temperature of the exit gas streams,

Table 6 shows the mass balance of the sulfur species on the fuel reactor on a mole basis. It is readily observed that most of the sulfur entering the reactor is taken out as CaS. This constitutes about 99.4 % sulfur capture into the calcium. Rest 0.6% sulfur exists in the gaseous phase in the stream GOUT. As reported earlier, in the absence of CaO injection into the reactor, most of the sulfur exits the reactor in the form of FeS leading to contamination of the H_2 produced. Table 7 shown the mole balance on chlorine species. The chlorine is found to exit only in the gaseous stream GOUT predominantly as HCl and no corresponding chlorides of Ca and Fe were found in the solid exit streams. Table 8 shows the mole balance for nitrogen species. Similar to chlorine most of the nitrogen exits the reactor in the gaseous phase as N_2 with minimal NO_X formation.

Table 6: Sulfur balance in the CLR process for a 1kg/hr flow basis

IN (mol/hr)			OUT (mol/hr)		
COALMIX2	S	0.6504	GOUT	SO_2	0.004211
				SO_3	7.13E-09
				H_2S	3.46E-05
				COS	5.93E-06
			CAOUT	CaS	0.64615
Total		0.6504			0.6504

Table 7: Chlorine balance in the CLR process for a 1kg/hr flow basis

IN (mmol/hr)			OUT (mmol/hr)		
COALMIX2	Cl_2	13.37	GOUT	Cl_2	2.98E-08
				HCl	26.74
TOTAL Cl		26.74			26.74

Table 8: Nitrogen balance in the CLR process for a 1kg/hr flow basis

IN (mmol/hr)			OUT (mmol/hr)		
COALMIX2	N_2	541.45	GOUT	N_2	541.45
				NH_4	2.06E-04
				NO	2.71E-04
				NO_2	1.07E-10
				N_2O	1.42E-09
				HCN	2.25E-07
Total N_2		541.45			541.45

Effect of Fe$_2$O$_3$ Flowrate

Figure 4 (a) and (b) show the effect of increasing Fe_2O_3 flow rate on the behavior of the process. In particular, the effect on H_2 production rate, unconverted carbon, exit CO_2/CO molar ratio and exit FeO/Fe ratio was evaluated. Only inlet Fe_2O_3 flow rate was changed keeping the inlet oxygen flow rate (0.35kg/kg coal) and Fe_2O_3 temperature (900 ^oC) constant. From figure 4(a) it is readily seen that a higher Fe_2O_3/Coal ratio leads to higher H_2 production rate as well as there is less unconverted carbon exiting the reactor. Both these factors are desirable. From figure 4(b) with higher Fe_2O_3/coal ratio, the outlet CO_2/CO ratio also improves. The FeO/Fe ratio also increases which will result in reduction in the oxygen transferred per particle. Increasing the Fe_2O_3 flow would lead to an increase in the reactor size which will lead to an increase in the costs. As a result, an optimum value for Fe_2O_3/coal ratio based on process economics will need to be selected.
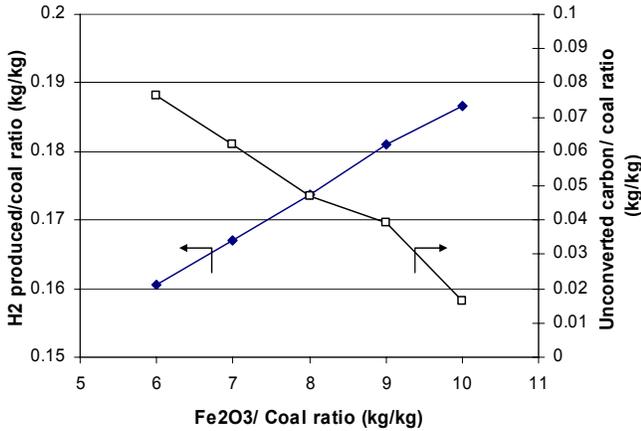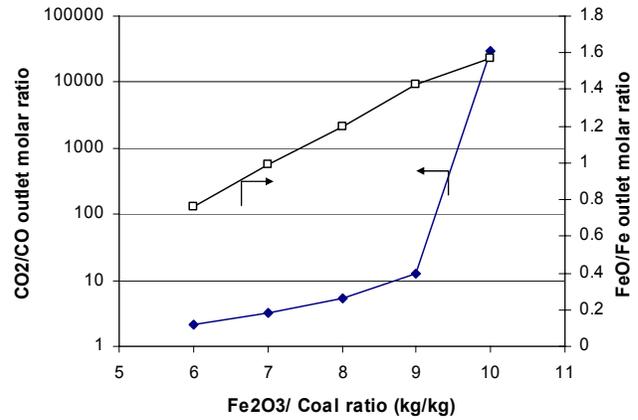
(a)   (b)

Figure 4: Effect of inlet Fe$_2$O3 flow rate on hydrogen production rate, unconverted carbon, CO$_2$/CO outlet ratio and FeO/Fe outlet ratio for O$_2$/Coal = 0.35 kg/kg, Inerts/coal = 5 kg/kg and inlet Fe$_2$O3 temperature of 900°C.
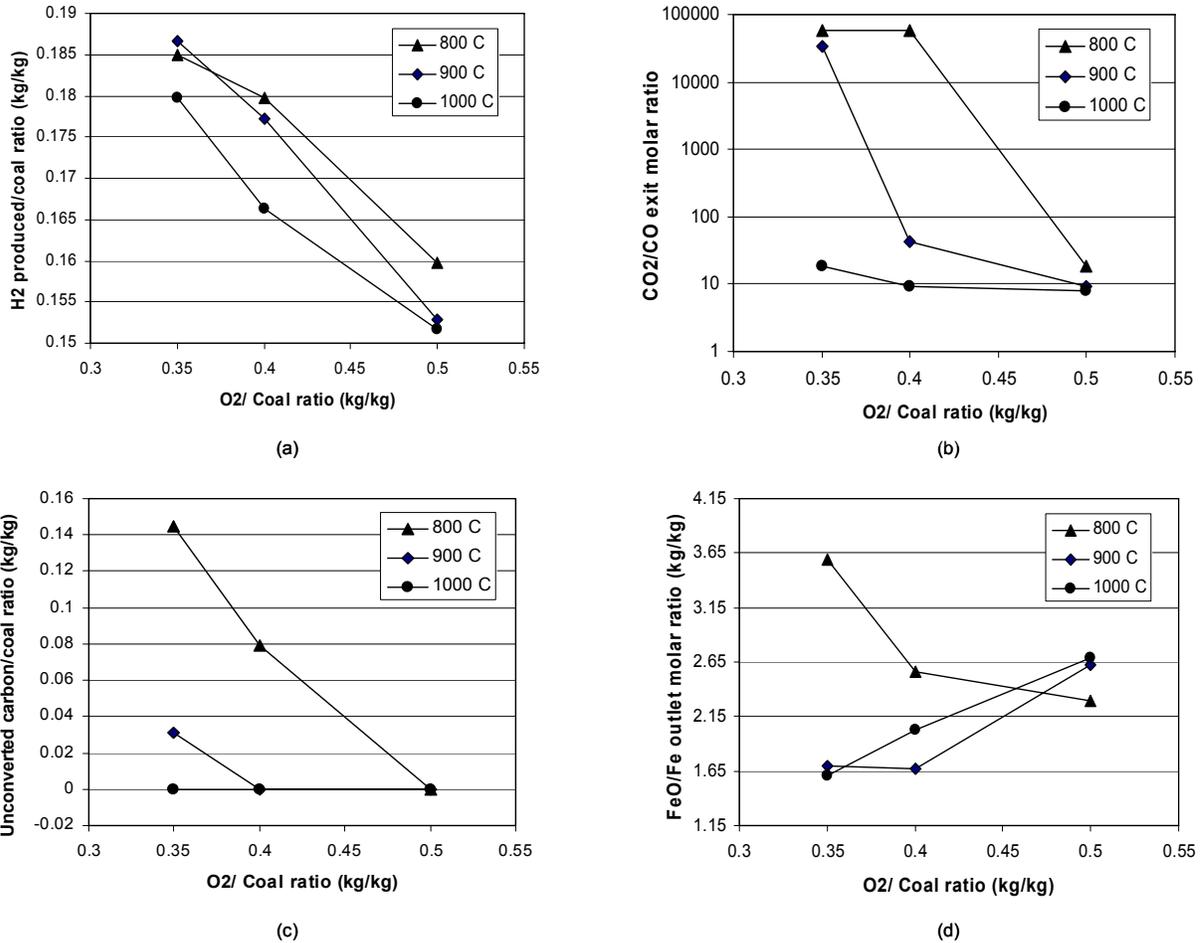
(a)

(b)

(c)

(d)

Figure 5: Effect of varying oxygen inlet flow and Fe_2O_3 inlet temperature on (a) hydrogen production rate, (b) CO_2/CO outlet ratio, (c) unconverted carbon, and (d) FeO/Fe outlet ratio for Fe_2O_3/Coal ratio = 10 kg/kg and Inerts/coal = 3.5 kg/kg

Effect of Inlet Oxygen Flowrate

Figure 5 shows the effect of increasing the oxygen flow into the reactor along with the inlet temperature of the Fe_2O_3 streams. For the purpose of these simulations, the Fe_2O_3/Coal ratio was kept at 10. Figure 5 (a) shows that, at all temperatures, the H_2 production rate decreases as the O_2 flowrate is increased. This is due to the fact that more coal is converted using oxygen rather than Fe_2O_3 as observed from figure 5(d). As a result lesser amounts of Fe are available for steam oxidation to H_2. It is also observed that at lower temperatures, H_2 production is enhanced. From Figures 5(b) and (c) it is observed that the CO_2/CO ratio and unconverted carbon decrease with increase in O_2 inlet flow. Only at 1000°C does the carbon gets completely converted for low (0.35kg/kg coal) oxygen flow rate. For low temperature (800°C) and low O_2 flow rate (0.35kg/kg coal), the unconverted carbon is very high (14%) as is the FeO/Fe ratio. The results imply that more than likely the reaction heat and temperature is not high enough to provide a high thermodynamic conversion. From this analysis it can be concluded that a low oxygen flow rate and a high Fe_2O_3 inlet temperature lead to better conversions of Fe_2O_3 and coal in the reactor.

5. CONCLUSIONS

The chemical looping reforming (CLR) process is described which can be used to make hydrogen from coal using reaction with regenerable iron oxide based materials. The gas solid contacting pattern was developed for the fuel reactor to achieve high conversions of coal and obtain high purity CO_2 stream which is sequestration ready. Thermodynamic calculations carried out in ASPEN PLUS process simulator showed a high hydrogen production rate of 0.183kg/kgcoal. Greater than 99% of the coal was converted in the process. Addition of CaO to the Fe_2O_3 inlet let to the capture of more than 99% of the sulfur in the form of CaS. The rest of the sulfur escaped with the CO_2 stream mainly as SO_2. There was almost no contamination of H_2 stream found with sulfur or chlorine species. The NO_X formation was observed to be below detectable limits.

6. ACKNOWLEDGEMENTS

7. REFERENCES

Cho, Paul; Mattisson, Tobias; Lyngfelt, Anders. Comparison of iron-, nickel-, copper- and manganese-based oxygen carriers for chemical-looping combustion. Fuel (2004), 83(9), 1215-1225.

Corbella, Beatriz M.; de Diego, Luis F.; Garcia-Labiano, Francisco; Adanez, Juan; Palacios, Jose M. Performance in a Fixed-Bed Reactor of Titania-Supported Nickel Oxide as Oxygen Carriers for the Chemical-Looping Combustion of Methane in Multicycle Tests. Industrial & Engineering Chemistry Research (2006), 45(1), 157-165.

Desideri, Umbertoa; Paolucci, Alberto. Performance modelling of a carbon dioxide removal system for power plants. Energy Conversion and Management Vol: 40, Issue: 18, December, 1999

Ishida, Masaru; Takeshita, Kenji; Suzuki, Kumi; Ohba, Takeyasu. Application of Fe2O3-Al2O3 Composite Particles as Solid Looping Material of the Chemical-Loop Combustor. Energy & Fuels (2005), 19(6), 2514-2518.

Jin, Hongguang; Ishida, Masaru. A new type of coal gas fueled chemical-looping combustion. Fuel (2004), 83(17-18), 2411-2417.

Lyngfelt, A.; Leckner, B.; Mattisson, T.. A fluidized-bed combustion process with inherent CO2 separation; application of chemical-looping combustion. Chemical Engineering Science (2001), 56(10), 3101-3113.

Mattisson, Tobias; Johansson, Marcus; Lyngfelt, Anders. The use of NiO as an oxygen carrier in chemical-looping combustion. Department of Energy and Environment, Division of Energy Technology, Chalmers University of Technology, Goeteborg, Swed. Fuel (2006), 85(5-6), 736-747.

Gupta, Puneet, Velazquez-Vargas, Luis G.; Thomas, Theodore; Fan, L.-S. Hydrogen Production From Combustion Looping (Solids-Coal). Proceedings of the International Technical Conference on Coal. Utilization & Fuel Systems. 2004.

Gupta, Puneet, Velazquez-Vargas, Luis G.; Thomas, Theodore; Fan, L.-S. Chemical Looping Combustion of Coal to Produce hydrogen. Proceedings of the International Technical Conference on Coal Utilization & Fuel Systems. 2005.

Gupta, Puneet; Velazquez-Vargas, Luis G.; Li, Fanxing; Fan, L.-S. Chemical looping combustion of coal. AIChE Annual Meeting, Conference Proceedings, Cincinnati, OH, United States, Oct. 30-Nov. 4, 2005 (2005).

Gupta, Puneet; Velazquez-Vargas, Luis G.; Li, Fanxing; Fan, Liang.-Shih. Chemical looping refroming process for the production of hydrogen from coal.   Proceedings - Annual International Pittsburgh Coal Conference 23rd, Sept 25-28, (2006)

Gupta, Puneet; Velazquez-Vargas, Luis G.; Fan, Liang.-Shih. Methods for making hydrogen from gaseous and solid carbonaceous fuel. U.S. Prov. Pat. Appl. 2006; US 60/758,507.

Gupta, Puneet; Velazquez-Vargas, Luis G.; Fan, L.-S. Oxygen Carrying Particles for hydrogen via Reduction-Oxidation Reactions and its Synthesis Methods. U.S. Prov. Pat. Appl. 2006; US 60/758,424

Gupta, Puneet; Velazquez-Vargas, Luis G.; Li, F.; Fan, L.-S. Syngas chemical Looping Process for Synthesis of Chemicals and Fuels. U.S. Prov. Pat. Appl. 2006; US 60/808,928.

Peters M.S., K.D. Timmerhaus. Plant Design and Economics for Chemical Engineers, 4th Edition. New York: McGraw-Hill; 1991.

Simbeck, D., Chang, E. Hydrogen Supply: Cost Estimate for Hydrogen Pathways – Scoping Analysis, USDOE NREL/SR-540-32525. July, 2002.

Simell, P.A.; Leppälahti, J.K.; Bredenberg, J.B.S. Catalytic purification of tarry fuel gas with carbonate rocks and ferrous materials. Fuel 1992; 71(2): 211-218.

Stiegel G.J., Ramezan M. Hydrogen from Coal Gasification: An Economical Pathway to a Sustainable Energy Future. International Journal of Coal Geology 2006; 65: 173-190.

Stultz S.C., J.B. Kitto. Steam — Its Generation and Use. Barberton: Babcock & Wilcox Company; 1992.

Thomas, Theodore J., Fan, Liang-Shih, Gupta, Puneet, Velazquez-Vargas, Luis Gilberto. Combustion Looping Using Composite Oxygen Carriers. U.S. Pat. Appl. Publ. 2005; US 2005175533.