

# COAL DIRECT CHEMICAL LOOPING (CDCL) PROCESS FOR HYDROGEN AND POWER GENERATION

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## ABSTRACT

Coal Direct Chemical Looping (CDCL) process is introduced and discussed. Utilizing iron oxide as the oxygen carrier, the CDCL process produces hydrogen and electricity from solid carbonaceous fuels such as coal and biomass with 100% CO<sub>2</sub> capture. The operations of the key CDCL units are tested in a bench scale moving bed reactor using various types of solid fuels. Thermodynamic models are also developed using ASPEN Plus<sup>®</sup> software to analyze individual CDCL reactor. Based on these results, process simulations are performed to illustrate the energy management scheme of the CDCL process. The experiment and simulation results show that the CDCL concept is feasible. Moreover, around 75% process efficiency (HHV basis) can be achieved with 100% CO<sub>2</sub> capture. The high energy conversion efficiency of the CDCL process results from the process intensification coupled with energy management optimization.

## 1. INTRODUCTION

Coal is a cheap and relatively abundant fossil fuel. However, it is carbon intensive. Coal combustion power plants alone account for a third of the total CO<sub>2</sub> emission in the United States [1]. CO<sub>2</sub> capture in existing coal conversion plants can be costly and ineffective. For instance, CO<sub>2</sub> capture can reduce the energy conversion efficiency of a coal combustion power plant by up to 40%. Further, the efficiencies of traditional coal gasification technologies are far from being optimized. The energy conversion efficiency for hydrogen production in a conventional coal to hydrogen plant is reported to be at 64% (HHV) without the CO<sub>2</sub> capture [2]. This efficiency is much lower than that for a steam methane reforming process, which is at 70% - 80% [3]. Clearly, the coal conversion processes could be more streamlined with consideration of process intensification incorporating carbon capture in order to reduce the capital and operating costs, reduce carbon dioxide emission and increase the energy conversion efficiency of the processes. Chemical-looping process, which integrates CO<sub>2</sub> capture in the fuel conversion scheme, is a promising approach for clean and efficient coal conversions [4]. In this paper, a novel coal direct chemical looping (CDCL) process which directly converts coal into hydrogen and/or electricity is discussed. Experimental results obtained from a bench scale moving bed unit are provided. An ASPEN Plus<sup>®</sup> model that simulates the CDCL process is also presented.

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## 2. PROCESS OVERVIEW

### 2.1 Coal Direct Chemical Looping Process - Configuration I

There are many potential configurations for the CDCL process. Figure 1 shows the simplified flow diagram of Configuration I for the CDCL process [5-8]. Similar to the SCL process, the CDCL process is also comprised of three reactors, i.e., the reducer, the oxidizer, and the combustor. The reducer converts carbonaceous fuels to CO<sub>2</sub> while reducing Fe<sub>2</sub>O<sub>3</sub> to a mixture of Fe and FeO; the oxidizer oxidizes the reduced Fe/FeO particles to Fe<sub>3</sub>O<sub>4</sub> using steam, producing a H<sub>2</sub> rich gas stream; the combustor pneumatically transports the Fe<sub>3</sub>O<sub>4</sub> particles from the H<sub>2</sub> reactor outlet to the reducer inlet using air. The Fe<sub>3</sub>O<sub>4</sub> particles are re-oxidized to Fe<sub>2</sub>O<sub>3</sub> during the conveying process.

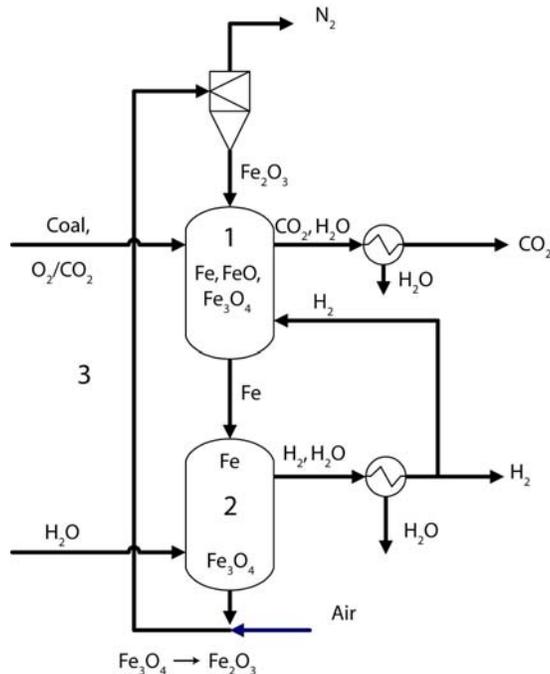
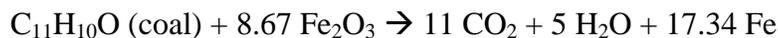


Figure 1. A Simplified Flow Diagram for Coal Direct Chemical Looping Process – Configuration I

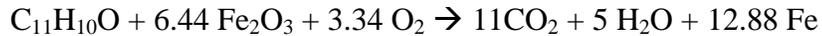
#### *Reducer*

The reducer is a countercurrent gas-solid reactor operated at 750 – 950 °C and 1 – 30 atm. The countercurrent operational mode is intended to maximize the solids and gas conversions. The solids flow can be in a moving bed or in a series of fluidized beds. It is noted that the moving bed contact mode is highlighted in this design as it represents the fundamental countercurrent solids contact pattern with gases that is preferred in this reactor system. The desirable reaction in the reducer is:



The coal exemplified here is Pittsburgh #8 and is represented as  $C_{11}H_{10}O$  given the elemental composition. The reaction is highly endothermic with the heat of reaction equal to 1,794 kJ/mol at 900 °C. Therefore, a significant amount of heat needs to be provided to the reducer.

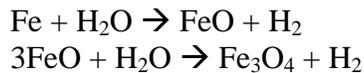
One option for balancing the heat is to partially combust coal in-situ by sending a sub-stoichiometric amount of  $O_2$  into the reducer. The overall reaction would then be:



This reaction takes place with zero heat of reaction at 900 °C. Since the amount of oxygen required for the above reaction is significantly less than that for the coal gasification reactions, the size of the air separation unit (ASU) is smaller than those in traditional gasification processes. The reduction in oxygen demand leads to savings in both operating cost and capital investment of the coal to hydrogen plant. Another option for the heat balance in the reducer is to combust a portion of reduced particles and uses them as the heat source. This option is similar to the steam methane reforming process where heat is provided by combusting a portion of the methane outside the reforming tubular reactors.

#### *Oxidizer*

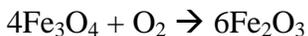
The oxidizer is a moving bed reactor operating at 500 – 850 °C and 1 – 30 atm. In the oxidizer, the Fe and FeO mixture from the reducer reacts with steam countercurrently. The reactions in the oxidizer are as follows:



This reaction is slightly exothermic. To maintain adiabatic operation, steam at a moderately low temperature is introduced into the oxidizer to modulate the reactor temperature.

#### *Combustor*

$Fe_3O_4$  from the oxidizer is fully regenerated in the combustor. The combustor is an adiabatic entrained bed reactor operated at a pressure similar to the reducer and the oxidizer. Air is used to pneumatically convey the  $Fe_3O_4$  particles from the oxidizer outlet to the reducer inlet while fully regenerating the particles by the following reaction:



This exothermic reaction heats up the solids as well as the gas. The hot solids are subsequently fed into the reducer to partially compensate for the heat needed for the coal conversion. The hot gas is then be used for power generation. The coal ash, which is significantly smaller in size than the  $Fe_2O_3$  composite particles, is separated out along with the fine particles using a cyclone on the top of the reducer. Fresh makeup particles are also introduced to the reducer to maintain reactivity.

## 2.2 Coal Direct Chemical Looping Process - Configuration II

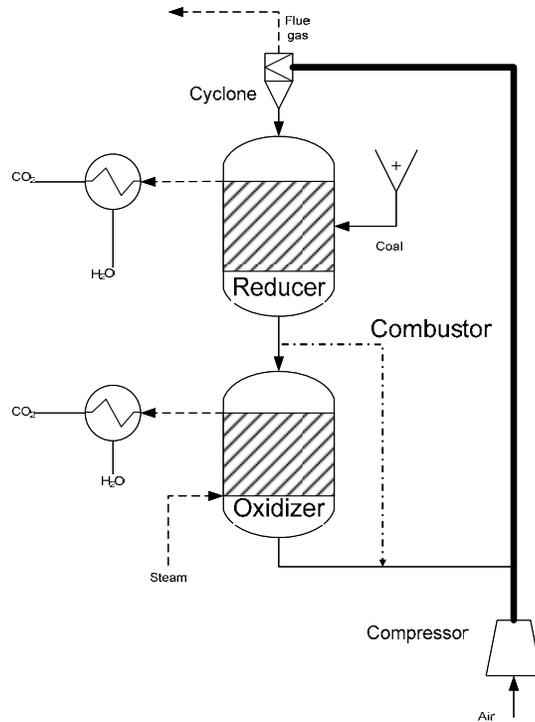


Figure 2 A Simplified Flow Diagram for Coal Direct Chemical Looping Process – Configuration II

There are also three major units involved in CDCL Configuration II, i.e. the reducer, the oxidizer, and the combustor. A simplified diagram for Configuration II of the CDCL process is shown in Figure 2. The key difference between Configurations I and II lies in the heat integration strategy. As indicated in Section 2.1, the reaction between coal and iron oxide in the reducer is highly endothermic. Unlike Configuration I where the heat requirement of the reducer is met by partial oxidation of coal, in Configuration II, reduced iron oxide particles are combusted to compensate for the heat deficit of the reducer.

In Configuration II, composite  $\text{Fe}_2\text{O}_3$  particles with an inert support are used to oxidize coal in the reducer while being reduced to a mixture of metallic iron and  $\text{FeO}$ . The gaseous product of this reactor is mainly  $\text{CO}_2$  mixed with a small amount of  $\text{H}_2\text{O}$ . The reduced  $\text{Fe}/\text{FeO}$  particles from the reducer are split into two streams. The first stream, comprising most of the reduced  $\text{Fe}/\text{FeO}$  particles, is sent to the oxidizer to perform the steam-iron reaction. The oxidizer produces  $\text{H}_2$  while oxidizing the reduced  $\text{Fe}$  particles to  $\text{Fe}_3\text{O}_4$  with steam. The rest of the reduced particles from the reducer, along with the  $\text{Fe}_3\text{O}_4$  particles discharged from the oxidizer, are burned in the combustor with air. As a result, high temperature solid and gas streams are generated from the combustor. The sensible heat carried by the high temperature solids is used to support the heat

requirement in the reducer. By increasing the amount of particles being combusted, the excess heat can also be produced from the combustor for electricity generation at the expense of the hydrogen yield.

### 3. EXPERIMENTAL AND MODEL SETUP

#### 3.1 Reactor Setup

A bench scale demonstration unit for CDCL demonstration was designed and constructed at the Ohio State University. Figure 3 illustrates the schematic diagram of the unit. The unit was designed to handle solid flow rates up to 1.36 g/s (4.9 kg/hr) with gas flow rates up to 200 ml/s (12 l/min). The reacting section of the reactor has an I.D. of 1.6 inches and a height of 40 inches. In a typical demonstration, solid reactants such as the oxygen carrier particle and/or coal char are first loaded to the top funnel and then moved downwards steadily by the screw conveyor system. The gas composition along the axial positions of the reactor is constantly monitored using a Varian CP-4900 micro GC and the solid can be taken from the solid sampling ports for further characterization. Detailed information regarding the reactor setup is described in Gupta et al. [9].

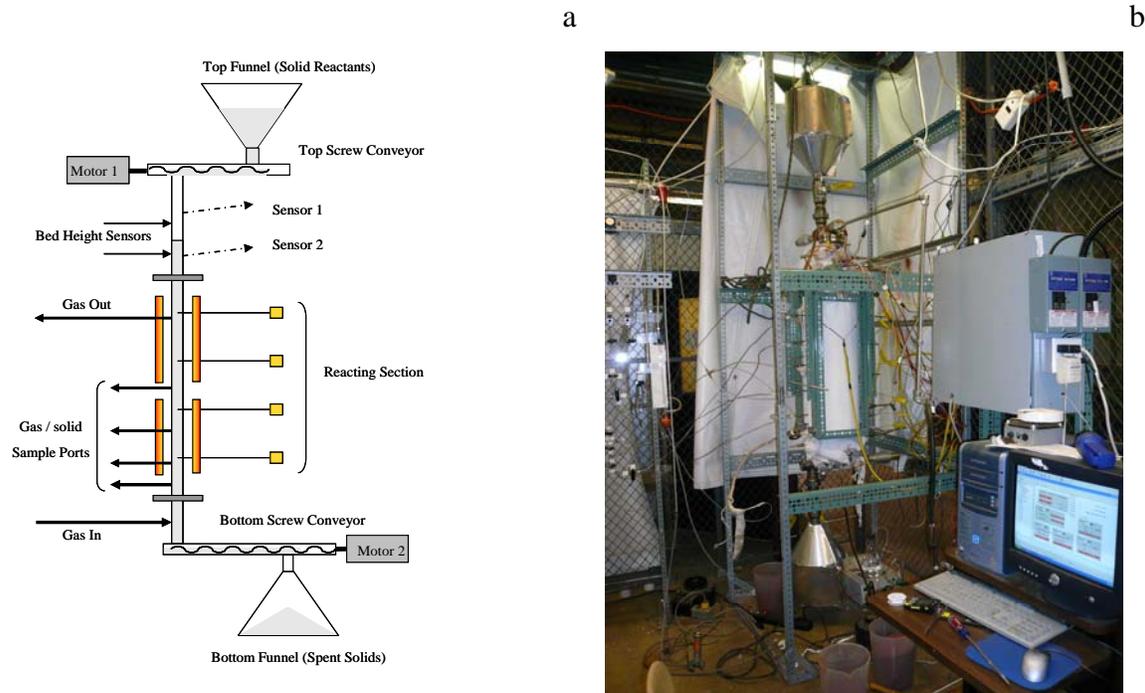


Figure 3. Bench Scale Demonstration Unit for SCL Process a. Schematic flow diagram of the unit; b. picture of the unit.

#### 3.2 Experimental Procedures

The key reactions in the reducer are relatively slow and are limited by thermodynamic equilibrium. Therefore, the reducer performance is the key to success for the CDCL process. Two sets of experiments are carried out to demonstrate the feasibility of the proposed reducer configuration. The first experiment validates the conversion of methane, which is a more stable form of coal volatile, using  $\text{Fe}_2\text{O}_3$  composite particles. The second set of experiments validates the conversion of coal char with the presence of oxygen and  $\text{Fe}_2\text{O}_3$  composite particles. Before the methane experiment, the  $\text{Fe}_2\text{O}_3$  composite particles are loaded in the top funnel. The particles are then moved downwards steadily by the screw conveyor system at a preset flow rate of 31.5 g/min. Meanwhile, the reactor is gradually heated up. After the desirable reaction temperature is attained, reactant gases are introduced into the gas inlet located at the bottom of reactor. In the char conversion experiments, coal char and  $\text{Fe}_2\text{O}_3$  particle mixture is loaded to the top funnel and then moved through the reaction zone to perform the reaction. Depending on the configuration,  $\text{O}_2$ ,  $\text{H}_2$ , and/or  $\text{CO}_2$  is introduced in the gas injection portions. After the moving bed operation, the solid samples are taken from the various sampling ports for further analysis using a carbon analyzer (UIC Inc., CM 120) and a thermogravimetric analyzer (TGA) (Perkin Elmer, TGA-7). The carbon analyzer determines the carbon deposition and coal char conversion while the TGA verifies the conversion of particles through the weight change of the particle during air oxidation.

### 3.3 Model Setup

Configuration II of the CDCL process is investigated. The overall thermal input for the process is set to be 1000 MW, which is equivalent to 132.9 ton/hr as-received Illinois #6 consumption. For the configuration using gas turbine after combustor, an air compressor will be used to elevate the pressure of air up to 18 atm. When steam generators are used to recover the combustor heat, an air blower will be used to a pressure of 2 atm. The composition of oxygen carrier (i.e. ratio between fresh  $\text{Fe}_2\text{O}_3$  and inert SiC) is adjusted by applicable temperature range in CDCL system. Lower inert contents can result in larger temperature difference among the three key reactors and vice versa, although the ratio will not affect the overall thermal balance. The given composition is calculated to be good for thermoregulation, as well as the inert can be a good support and dispersant for the particle. Finally, all the products will be cooled to ambient temperature. For delivery,  $\text{CO}_2$  and  $\text{H}_2$  will be compressed to 135 atm and 60 atm, respectively. Table 1 summarizes the main assumptions for working condition throughout the whole process. The reactor modeling and process simulation are mainly performed on the platform of ASPEN Plus<sup>®</sup>. Therefore a brief summary for the model setup is given in Table 2.

Table 1 Working Conditions for the CDCL Process Assumed in the Simulation Model

Environment Condition	T=25 C, P=1 atm
Reaction	All reaction reach equilibrium in high temperature
Exhaust Temperature	120 °C
Heat Loss in CDCL System	1% of total thermal input
Thermal Energy for Coal Preparation	0.3% of total thermal input
Other Auxiliaries Consumption Including Pumps	0.5% of total thermal input
Pressure Drop in Key Reactors	2 atm
All Pressure Changers	mechanical efficiency is 1
Gas Turbine	Isentropic efficiency is 0.9
Steam Turbine	Isentropic efficiency is 0.86
Compressor	4 stage with intercooler at 40C, Isentropic efficiency is 0.83
HRSB	Exhausting temperature is 120 °C

Table 2 Aspen Plus® Models Setup

<b>stream class</b>	MIXCINC
<b>databank</b>	COMBUST, INORGANIC, SOLIDS, PURE
<b>components</b>	Fe0.947O (Wuestite) is selected instead of FeO
<b>property method</b>	PR-BM, except STEAM-TA for steam cycle
<b>solution strategy</b>	Sequential Modular
<b>unit operations</b>	<b>Models</b>
Reactor	Ryield, Rgibbs
Pressure Changers	Pump, Compr, Mcompr
heat exchangers	Heater, MheatX
Mixers/Splitters/Separators	Mixer/Fsplit/Sep/Flash2

## 4. RESULTS AND DISCUSSIONS

### 4.1 Experimental Results

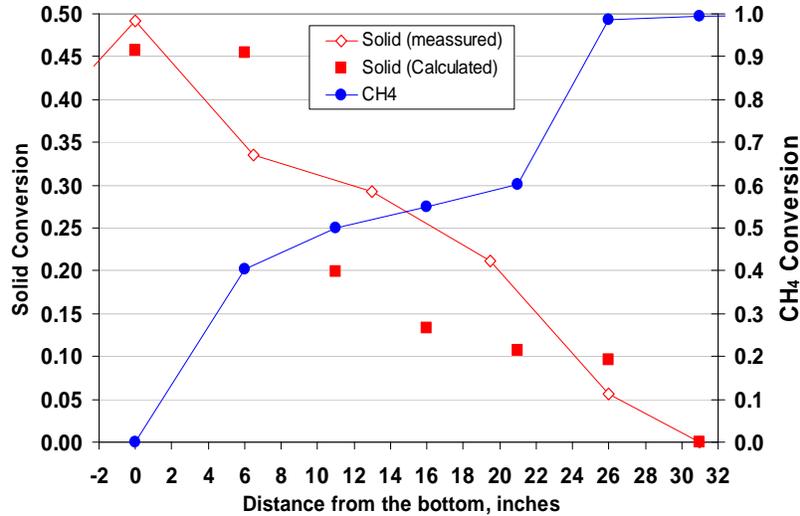


Figure 4. Reduction of  $\text{Fe}_2\text{O}_3$  Particles in the Bench Unit using Methane as Reducing Gas

Figure 4 shows the gas and solids conversions achieved in the methane conversion experiment. As can be seen, 45 – 50% conversion in solids and 99.8% conversion in gas are achieved. Various types of coal char have also been tested using the bench scale moving bed reactor. The key experimental results are presented in Table 3. As shown in Table 3, 90–95% of coal char can be converted into nearly pure  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Even better performance can be achieved through the optimizations in reactor design and operating conditions. To generalize, the proposed CDCL reducer concept is feasible.

Table 3 Summary of the Reducer Demonstration Results using Coal, Coal char, and Simulated Coal Volatile ( $\text{CH}_4$ )

Type of Fuel	Coal Volatile ( $\text{CH}_4$ )	Lignite Char	Bituminous Char	Anthracite Coal
Fuel Conversion (%)	99.8	94.9	90.5	95.5
$\text{CO}_2$ Concentration in Exhaust (% Dry Basis)	98.8	99.23	99.8	97.3

## 4.2 ASPEN Plus® Simulation Results

Table 4 Power balance in the CDCL Simulations

Unit Operations	Input			Output			Net power
	Air compressor	CO <sub>2</sub> compressor	H <sub>2</sub> compressor	HP steam turbine	IP steam turbine	LP steam turbine	
Power MW	22.7	8.9	11.1	-26.2	-46.6	-29.9	-60.0

According to the ASPEN Plus® simulation, 0.1317 tonnes of H<sub>2</sub> are obtained from each tones of coal. Moreover, excess power is generated from the CDCL process. The power balance of the process is shown in Table 4. The results indicate that almost 69.0% (HHV) heating value is transferred from coal to hydrogen and the overall efficiency of the process 75.0% (HHV) when the excess power is taken into account. It is noted that such efficiency is achieved with 100% CO<sub>2</sub> capture. To compare, the traditional process has an energy conversion efficiency of around 58% (HHV) with 90% CO<sub>2</sub> capture. Therefore, the CDCL process is potentially more efficient than the conventional coal to hydrogen processes.

## 5. CONCLUDING REMARKS

Coal direct chemical looping (CDCL) process that converts coal into hydrogen and/or electricity is discussed. The feasibility and performance of the CDCL process is investigated through both experiments and ASPEN Plus® simulations. Bench scale experiments show that the proposed reducer reactor is capable to convert 99.8% coal volatiles and more than 90% coal char into CO<sub>2</sub> and steam. ASPEN Plus® simulations indicate that the CDCL process is nearly 20% more efficient compared to conventional coal to hydrogen processes. To conclude, the CDCL process concept is feasible according to both the preliminary testing results obtained from a bench scale unit and the ASPEN Plus® process simulations.

## 6. ACKNOWLEDGMENT

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