Syngas Chemical Looping Process for Hydrogen Production: Bench Scale Demonstration and Process Simulation

Fanxing Li, Deepak Sridhar, Hyung Kim, Liang Zeng, Fei Wang, L. -S. Fan[1]
Department of Chemical and Biomolecular Engineering
The Ohio State University
Columbus, OH, USA

Abstract

The Syngas Chemical Looping (SCL) process converts gaseous fuels such as syngas and hydrocarbons into hydrogen and electricity while capturing 100% of the CO_2 generated [1,2]. The SCL process simplifies the overall fuel conversion scheme while reducing pollutants in an indirect but highly effective manner. This is achieved via a specially tailored Fe_2O_3 based composite particle. As a result, hydrogen production cost is substantially reduced. Extensive demonstrations of the SCL process have been carried out under a bench scale (2.5 KWt) unit using coal-derived syngas, natural gas, and other light hydrocarbons as feedstock. Hydrogen with an average purity higher than 99.95% was produced.

In this paper, the SCL process demonstrations are discussed. ASPEN® simulation based on the bench scale demonstration results was used to analyze the SCL process.

1. Introduction

The sustainable development of the modern society demands efficient and environmentally friendly energy conversion techniques. Through the aid of an iron based reaction medium, the syngas chemical looping (SCL) process converts syngas into hydrogen and/or electricity while generating a sequestrable CO_2 stream.

In this paper, comprehensive ASPEN simulation models are developed to simulate both the traditional coal to hydrogen process and the SCL process based on common assumptions. The ASPEN simulation on the SCL process, which is supported by the bench scale demonstration results on the major chemical looping units, show that the SCL process is 5 – 7% more efficient when compared to the traditional coal-to-hydrogen process. The results from the bench scale demonstration and the process simulation suggest that the SCL process can be a technically attractive process to efficiently produce hydrogen and/or electricity from coal.

---

[1] Corresponding Author

2. Traditional Coal-to-Hydrogen Process and the Syngas Chemical Looping Process

Hydrogen is mainly produced from steam reforming of methane. With soaring crude and natural gas prices, coal is emerging as a viable choice for hydrogen generation. Coal is used for hydrogen production through the well known gasification process. Figure 1 shows the schematic of a specific configuration of a conventional coal to hydrogen process.
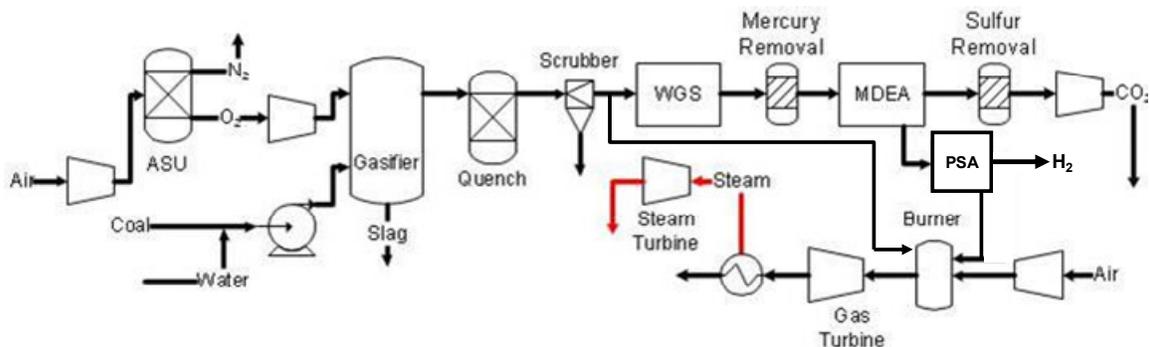

Figure 1.　　Simplified schematic of the traditional Coal-to-Hydrogen process

In this process, coal is first pulverized and mixed with water to form coal slurry. The coal slurry is then pressurized and introduced to the gasifier to be partially oxidized at 1500 °C and 30 atm. The high temperature raw syngas after gasification is then quenched to 250 °C with water. The quenching step solidifies the ash. Moreover, most of the NH_3 and HCl in the syngas are removed during this step. After quenching, the syngas is sent to a Venturi scrubber for further particulate removal. The particulate-free syngas, saturated with steam, is then introduced to the raw syngas water gas shift (WGS) unit. The syngas exiting the WGS unit contains mainly of H_2 and CO_2 with small amount of CO, H_2S, and mercury. This gas stream is then cooled down to around 40 °C for mercury removal using an activated carbon bed. The CO_2 and H_2S in the syngas are then removed using an MDEA unit, resulting in a concentrated hydrogen stream with small amounts of CO_2 and unconverted CO. The hydrogen rich gas stream is then passed through a pressure swing adsorption unit (PSA) to obtain a purified hydrogen stream with a purity of above 99.99%. The tail gas from the PSA, which is a mixture of H_2, CO, and CO_2, will be re-compressed and sent to a combined cycle system for power generation to compensate the parasitic energy requirements. The combined cycle system consists of a gas turbine with an inlet firing temperature of 1430 °C and a two stage steam turbine working at 550 °C and 35 atm. The CO_2 obtained from the MDEA unit is compressed to 150 atm for sequestration.

As can be seen in Figure 1, the conventional coal to hydrogen process involves elaborate unit operations including air separation, coal gasification, syngas cleanup, conditioning, and separation and CO_2 compression. As a result, the capital investment for conventional coal to hydrogen process is much higher than a steam methane reforming plant with a similar hydrogen production capacity. In order for the gasification based coal

to hydrogen process to be economically attractive, process intensification that can reduce the capital investment while improving the energy conversion efficiency of the traditional coal to hydrogen process is required. The SCL process simplifies the syngas conversion and product gas separation scheme through the assistance of an iron oxide based oxygen carrier particle. The simplified schematic flow diagram of the SCL process is shown in Figure 2.
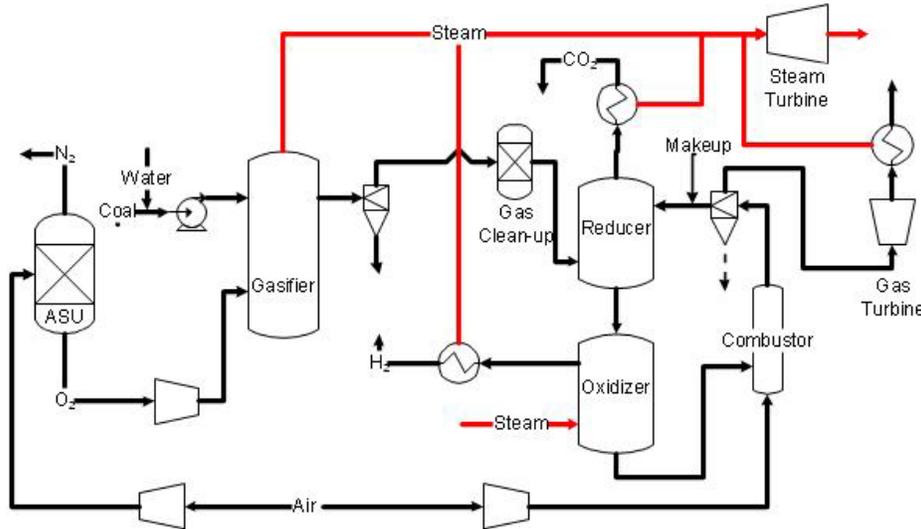

Figure 2.   Simplified schematic of the Syngas Chemical Looping process

The SCL process has air separation and coal gasification units similar to that in the conventional coal to hydrogen process. The difference lies in the syngas cleaning, conversion, and separation steps. In the SCL process, a candle filter is used to remove the particulates in the syngas stream. This is followed by a hot gas cleaning step at 400 ºC for bulk sulfur removal. The particulate free raw syngas after the hot gas clean up unit, which has a H2S concentration of lower than 20 ppm, is then introduced to a reducer operated at 900 ºC and 30 atm. The reducer is a countercurrent moving bed reactor with Fe_2O_3 fed from the top and syngas fed from the bottom. The main reactions in the reducer include:

$$Fe_2O_3 + CO/H_2 \rightarrow 2FeO + CO_2/H_2O$$
$$FeO + CO/H_2 \rightarrow Fe + CO_2/H_2O$$
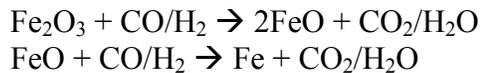
The impurities in the syngas stream such as sulfur compounds and elemental mercury will not react with the iron oxide. Therefore, these pollutants will leave the reducer along with the CO_2 and steam resulted from the oxidation of the syngas stream. After condensing out steam, the concentrated CO_2 stream can be further compressed and sequestrated.

The reducer is slightly endothermic. The heat required in the reducer is fully compensated by the sensible heat carried by the hot iron oxide particles introduced from the combustor.

The iron oxide exiting from the bottom of the reducer is comprised mainly of FeO and Fe. Such a solid stream is then introduced to the oxidizer, which is also a countercurrent moving bed operated at 900 ºC and 30 atm. The oxidizer converts steam into hydrogen while regenerates the FeO and Fe introduced from the reducer into Fe_3O_4. The main reactions in the oxidizer are:

$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$
$3FeO + H_2O \rightarrow Fe_3O_4 + H_2$
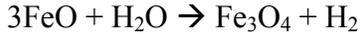
The above reactions are slightly exothermic. The reducer is adjusted to be heat neutral by introducing low temperature steam. The gaseous product from the reducer is a mixture of hydrogen and steam. Steam can be easily condensed out to obtain a concentrated hydrogen stream.

The partially regenerated Fe_3O_4 from the oxidizer is further combusted in the combustor using air. The combustor is an entrained bed reactor operated at adiabatic conditions. The hot oxygen depleted air generated in the combustor can be used for power generation while the hot Fe_2O_3 particle is recycled back to the reducer.

As can be seen, the hydrogen product is generated from the oxidizer whereas CO_2 and other contaminants are generated in the reducer. Therefore, the energy required for CO_2 separation and contaminant removal is reduced. In the following sections, moving bed test results on the SCL reducer is reported. A detailed ASPEN simulation is then provided.

3. Bench Scale Tests of the SCL Process

3.1 Reactor Setup

A bench scale moving bed reactor was used to demonstrate the SCL process[3]. The bench scale reactor setup is illustrated in Figure 3. In a typical demonstration, solid reactants such as 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 bed height is maintained by the bed height sensor system. Reactant gas is introduced from the gas inlet located at the bottom of the moving bed to react with the solids in a counter current manner. The gas composition along the reactor is constantly monitored using a Varian CP-4900 micro GC. The solid samples can be taken from the solid sampling ports after the experiment for further characterization. The moving bed setup mimics the actual gas-solid contacting pattern in the proposed reducer and oxidizer design. More detailed information regarding the reactor setup can be found in Gupta et al. [3].
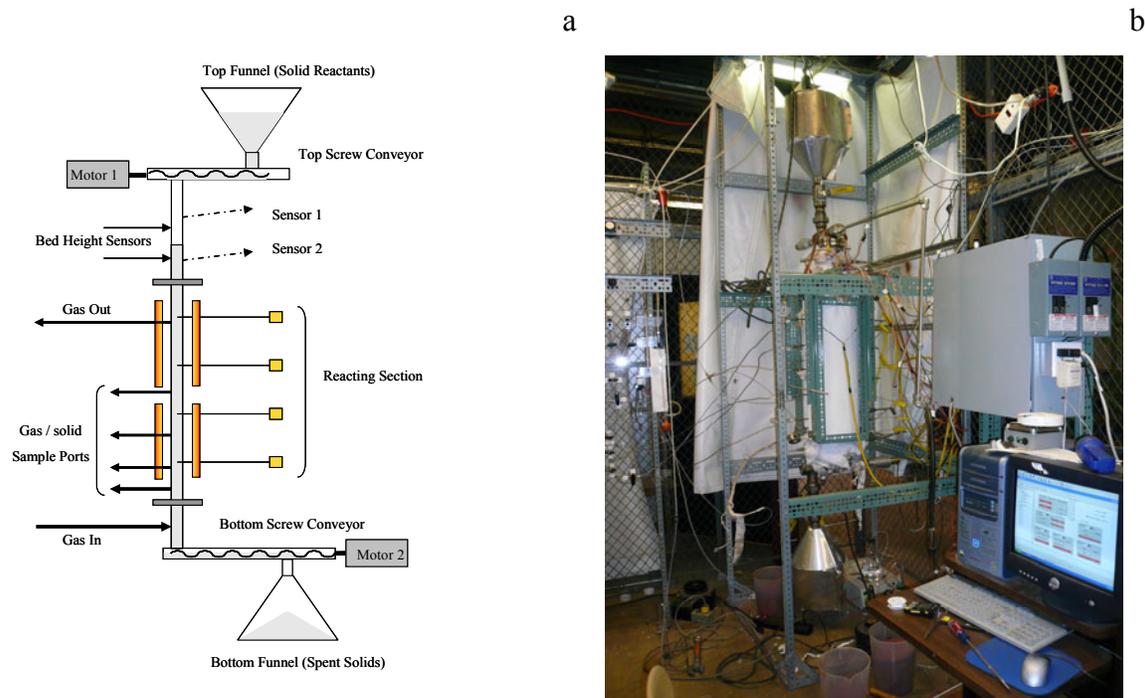
a   b

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

3.2 Reducer/Oxidizer Test Procedure and Results

The experiment to demonstrate continuous reducer operation was carried out first.
Before the experiment, around 12 kg composite pellets with 60% Fe_2O_3 and 40% inert
support was loaded to the top funnel. The reactor was then sealed and flushed overnight
using N_2 at a flow rate of 500 ml/min.

Prior to the experiment, the solid transport system was activated to continuously
move the particles through the reacting section. Meanwhile, the reactor was gradually
heated up to around 900 °C. Once the desired reacting temperature was achieved,
simulated syngas that consists of CO, H_2, and CO_2, was introduced into the bottom of the
reactor. N_2 was also introduced along with the simulated syngas as an internal standard.

After the injection of the reactant gas, the gas compositions at the various
positions of the reactor were constantly monitored and sampled using the MicroGC. The
steady flow of both solid and gas was maintained for at least three solid residence time to
ensure the achievement of steady state operation. After the experiment was finished, the
reactant gas, the solid transport system, and the heating elements were simultaneously
switched off. Nitrogen was introduced to the system to prevent re-oxidation of the solid
samples. The solid samples at various positions of the reactor were taken from the reactor
once it is cooled down to room temperature. These samples were than characterized using
a CM-120 total carbon analyzer (UIC Inc.) for carbon content. The same samples were
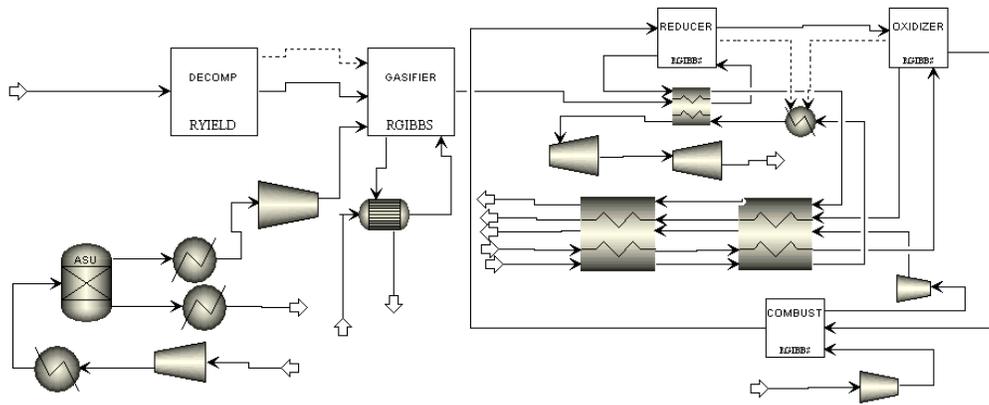
oxidized in a TGA using air. The solid conversions were then determined using the weight change obtained in the TGA and the carbon content characterized in the carbon analyzer.

After the experiment, it was found that nearly 99% syngas was converted to CO_2 and H_2O. Meanwhile, Fe_2O_3 was reduced by 49.5%. The carbon content in the reduced metal oxide was found to be lower than 0.1% (by weight).

Test on the oxidizer operation was carried out using the reduced composite Fe_2O_3 particle obtained from the previous test. The reduced particles were made to flow through the reactor in a manner similar to the previous test. The reacting gas comprised of steam balanced with inert gas (N_2). The same analysis method was used to monitor the H_2 production and extent of solid oxidation. It was observed that the reduced particles can be completely converted at 500 ºC or even lower. The average hydrogen product purity was found to be 99.95%.

4. Process Simulation

4.1 summary of interested system

The ASPEN flow sheets of the traditional coal to hydrogen process and the SCL process are shown in Figure 4 and Figure 5. The process configurations are identical to that described in Section 2.

Figure 4   ASPEN Flowsheet of Conventional Coal to Hydrogen Process

Figure 5   ASPEN Flowsheet of the SCL Process

4.2 Assumptions

To compare the differences between the SCL process and conventional process for hydrogen production from coal, two detailed models have been set up on ASPEN plus under the same assumptions, which are:

- 132.9 tonne/hr of Illinois #6 coal is fed into the system (1000 MW in HHV), the composition of the Illinois #6 coal is shown in Table 1;
- Energy consumed for units such as acid gas removal are simulated based on performance data of the commercial units;
- The GE slurry feed gasifier has a carbon conversion of 99%, heat loss in the gasifier is 0.6% of the HHV of coal, heat loss in all the other units are negligible [4];
- A GE 7H gas turbine combined cycle system is used, all the exhaust gas is cooled down to 130 °C before exiting the Heat Recovery Steam Generator (HRSG);
- At least 90% of the CO_2 generated needs to be captured and compressed to 15 Mpa for sequestration;
- The mechanical efficiency of pressure changers is 1, whereas the isentropic efficiency is 0.8~0.9;
- Solids circulating in SCL consist of 60% Fe_2O_3, and 40% inert support, by weight;
- The pressure of H_2 coming out of the system should be 3 Mpa ;
- steam is superheated to 680 ºC, 30 atm to recover heat and then drive steam turbine;
- Pressure drop in the combustor is 0.2 MPa; pressure drop both the reducer and the oxidizer is 0.1 MPa;
- The reactions in high temperature reactors such as gasifier can reach their thermodynamic equilibriums;
- Experimental results obtained from the SCL reducer test is used to simulate reducer performance;
- The CO_2 capture cost is about 100.6 kWh per tonne CO_2 for traditional case[5];

- All the compressors are designed as 4-stage type with intercooler outlet temperature at 40 ºC;
- The PSA unit can recover 77% hydrogen with 0.2 MPa pressure drop for the product gas and 2.5 MPa pressure drop for the tail gas;
- The air separation unit (ASU) consumes 367 kWh per ton of oxygen, mainly calculated based on gas compressions.

Table 1: Physical and Chemical Properties of Illinois #6 coal [6]

Proximate Analysis	Wt% (As-Received)	Wt%, dry	Ultimate	Wt% (As-Received)	Wt%, dry
Moisture	11.12		Moisture	11.12	
Fixed Carbon	44.19	49.72	ASH	9.7	10.91
Volatiles	34.99	39.37	CARBON	63.75	71.72
Ash	9.7	10.91	HYDROGEN	4.5	5.06
	100	100	NITROGEN	1.25	1.41
			CHLORINE	0.29	0.33
HHV (MJ/kg)	27.13511	30.53107	SULFUR	2.51	2.82
			OXYGEN	6.88	7.75

5. Results and Discussions

In order to co-produce of H_2 and electricity from coal, 551.4 tonne/hr of air is compressed into ASU to obtain a stream of 96% pure O_2 for the gasifier. The entrained bed GE/Texaco slurry feed gasifier can covert 132.9 ton/hr of coal into high temperature, high pressure raw syngas. The high temperature syngas from the gasifier is then cooled down using a radiant cooler. The syngas composition of this gasifier is shown in Table 2.

Table 2   Syngas from GE gasifier obtained from the ASPEN model

Gas Species in the Syngas Stream	Percentage (%)
H2O	25.32845
N2	1.46731
O2	6.61E-08
S	1.86E-04
SO2	3.05E-03
H2	23.59942
CO	39.31033
CO2	9.576
H3N	1.04E-03
COS	3.85E-02
H2S	0.676
CH4	1.75E-04
Total Flow kmol/hr	14483
Total Flow tonne/hr	303
Temperature ^oC	1631
Pressure atm	30

In the conventional case, syngas is split into two streams, 10% of the syngas is directly used for power generation and the rest of the syngas is sent to the hydrogen production units for low temperature (220 ºC) water gas shift reaction, CO_2 separation, and product upgradation in PSA. The tail gas including part of hydrogen product from PSA is also used for power generation. In this configuration, 90% of the feed carbon is ready for sequestration. Hydrogen production rate is estimated to be 13.30 tonne/hr along with 71.6 MW net electricity generation.

In the SCL case, all the syngas, after bulk sulfur removal, is introduced to the reducer. The syngas is fully oxidized in the reducer with 49.5% iron oxide reduction, which is consistent to the experimental results. Therefore, the solid product from the reducer is a mixture of metallic iron and Wuestite. The reduced iron oxide is then introduced to the Oxidizer (800 ºC, 30 atm) to perform the iron-steam reaction while being partially regenerated to Fe_3O_4. The combustor will further combust Fe_3O_4 (1128 ºC, 30 atm) from the oxidizer, forming Fe_2O_3. The high temperature exhaust gas streams from all three looping units are used for steam/power generation. After the compensation of parasitic power requirements, 74.8 MW of net power and 14.67 tonne/hr of H_2 are

produced with 100% CO_2 captured and compressed for sequestration. Table 3 compares the results between SCL process and conventional process. As can be seen in Table 3, significant efficiency improvement can be potentially realized through the utilization of the chemical looping strategy proposed in the SCL process.

Table 3: Summary of Hydrogen from Coal Cases

	Conventional Process	SCL Process
Coal feed(tonne/hr)	132.9	132.9
Carbon Capture(%)	90	100
Hydrogen(tonne/hr)	13.30	14.67
Net Power(MW)	71.6	74.8
Efficiency(%HHV)	59.7	65.3

6. Conclusions

A novel Syngas Chemical Looping process that converts coal derived syngas into hydrogen and electricity is discussed in this paper. Experimental results obtained from a bench scale unit indicated that the process is technically feasible. ASPEN simulation further confirmed that the SCL process has the potential to improve the energy conversion efficiency of the conventional coal to hydrogen process by over 6% while capturing all the carbon in coal.

7. Acknowledgement

8. References

1. Gupta P, Velazquez-Vargas LG, Fan LS. Syngas redox (SGR) process to produce hydrogen from coal derived syngas. *Energy & Fuels.* Sep-Oct 2007;21(5):2900-2908.
2. Velazquez-Vargas LG, Thomas T, Gupta P, Fan L-S. Hydrogen production via redox reaction of syngas with metal oxide composite particles. Paper presented at: Proceedings of AIChE Annual Technical Meeting, 2004.
3. Gupta P, Velazquez-Vargas LG, Valentine C, Fan LS. Moving bed reactor setup to study complex gas-solid reactions. *Review of Scientific Instruments.* Aug 2007;78(8):-.
4. Higman C. *Gasification.* 2ND ED. ed. Boston: GULF PROFESSIONAL; 2008.
5. Shah VA, Huurdeman TL. Synthesis gas treating with physical solvent process using Selexol process technology. *Ammonia Plant Saf. FIELD Full Journal Title:Ammonia Plant Safety & Related Facilities.* 1990;30:216-224.
6. NETL. Shell Gasifier IGCC Base Cases; 2000.