# Comparison of Coal Based Hydrogen and Electricity Co-Generation Processes under a Carbon Constrained Scenario

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*Abstract*

Hydrogen and electricity produced from coal will represent a significant share in the energy mix within the foreseeable future. Various novel processes are developed or currently under development for hydrogen and electricity production from coal derived syngas. The commercial coal to hydrogen and coal to electricity processes include the coal gasification-water gas shift process and integrated gasification combined cycle (IGCC) process. More advanced approaches include enhanced water-gas-shift membrane technology and chemical looping technology.

This paper compares these technologies on the same baseline via Aspen Plus simulation with common assumptions. Firstly, performance of the key reactors, e.g. the reducer/oxidizer of the chemical looping system and the hydrogen-/carbon dioxide-selective water-gas-shift membrane reactor of the membrane system, are investigated and modeled based on thermodynamic principles. Operating conditions such as feed rate, operating temperature and pressure are then optimized. The optimized reactor models are integrated into a common coal gasification system to obtain the overall performance and energy conversion efficiencies of different process configurations. The results are helpful in opting and optimizing the design of future coal to hydrogen/electricity processes.

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## 1. Introduction

In view of the volatile crude oil and natural gas prices, coal, which accounts for 40% of the electricity generated world wide at present, is expected to remain as an important fossil energy resource within the foreseeable future [1].

The green house effect of $CO_2$ has led to increased concerns over $CO_2$ emissions from coal conversion plants. To mitigate such emissions, future coal conversion plants should have the capability to convert coal into carbon free energy carriers such as hydrogen and electricity while sequestrating at least 90% of the $CO_2$ generated during the energy conversion scheme.

Traditional pulverized coal combustion (PCC) technology converts approximately a third of the energy in coal into electricity. Such an energy conversion efficiency can be further reduced by up to 40% when the envisaged $CO_2$ regulation is implemented [2]. Coal gasification techniques such as integrated gasification combined cycle (IGCC) and gasification – water gas shift (WGS) processes can potentially increase the energy conversion efficiency with reduced $CO_2$ capture penalty; however, $CO_2$ capture in coal gasification plants will nevertheless reduce the plant efficiency by up to 24%. More advanced approaches such as enhanced WGS membrane technology and chemical looping technology has the potential to further improve the performance of the gasification based coal conversion processes. The enhanced WGS membrane technology integrates membrane into a regular WGS reactor to break the equilibrium by simultaneous removal of the WGS reaction product. Chemical looping technology, on the other hand, utilizes a chemical looping medium such as iron oxide to convert syngas into a concentrated hydrogen stream, avoiding the $CO_2$ separation step. In order to evaluate the potential of the various coal gasification schemes, process simulations using common assumptions are highly desirable.

## 2. Thermodynamic Analysis

Thermodynamic model can predict the conversion of reactants when thermodynamic equilibrium is achieved under certain conditions. Although the conversions predicted by thermodynamic modeling may not be identical to that obtained in actual reactor operations, it can be used as a good indicator to evaluate the potential of a process configuration. In the following sections, ASPEN plus® software is used to evaluate three key components of gasification based coal conversion processes. These components include water gas shift reactor in conventional gasification-WGS process, membrane enhanced WGS reactor in the membrane based coal gasification process, and the reducer and the oxidizer in the SCL process.

### 2.1 water gas shift reaction

Using Aspen Plus, a thermodynamic model for water gas shift reaction can be constructed with ease using one RGibbs block. Throughout this section, the feedstock is

limited in $H_2$, CO and steam. The ratio between $H_2$ and CO is fixed at 1:2, which is similar to that from a dry feed, oxygen blown gasifier. The property method is set to be PR-BM, which is used in all the models in this paper. The variables of interest in this case study include the operating temperature and steam to CO ratio since pressure will not have significant effect on the equal molar WGS reaction.

In order to determine the effect of temperature, steam and CO molar ratios of 1, 1.5, 2 and 2.5 are investigated in the sensitivity analysis. As shown in Figure 1, at temperature below 250 ºC, most CO can be converted into $H_2$ in all cases. The CO conversion decreases with increased water gas shift reactor temperature. Moreover, higher steam to CO ratio leads to higher CO conversion. To ensure a high CO conversion, steam to CO ratio should exceed 2 and the WGS reactor operating temperature should be less than 250 ºC.
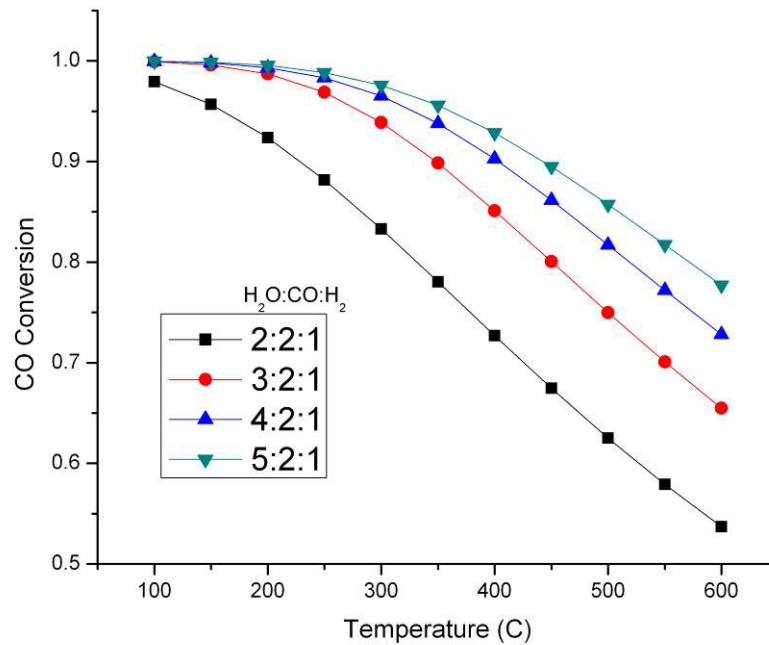


Figure 1 Temperature influence on CO conversion in WGS at 30 bar

*2.2 Enhanced WGS Membrane Reactor*

The basic thermodynamic principles dictate that simultaneous removal of reaction products enhances the conversion of the reactants. Since the products include both $CO_2$ and $H_2$, removal of either specie can enhance the reaction. Therefore, both $H_2$-slective and $CO_2$-selective membranes can be used in the enhanced WGS reactor. In the simplified thermodynamic simulation, the selectivity and permeation flux for both types of membranes are assumed to be infinity, which leads to similar performance of the two types of membranes. Therefore, only $H_2$-selective membrane is investigated.

Although there is no built-in model for membrane reactor in Aspen Plus, a series of RGibbs and Sep blocks can be stringed to represent permeate side and retentate side respectively. Similar model has been reported in previous study on steam reforming of methane [3-5]. As mentioned previously, two configurations for the flow direction between permeate side and retentate side, i.e. co-current and counter-current, will be investigated. The models for both co-current and counter-current design are illustrated in Figure 2.
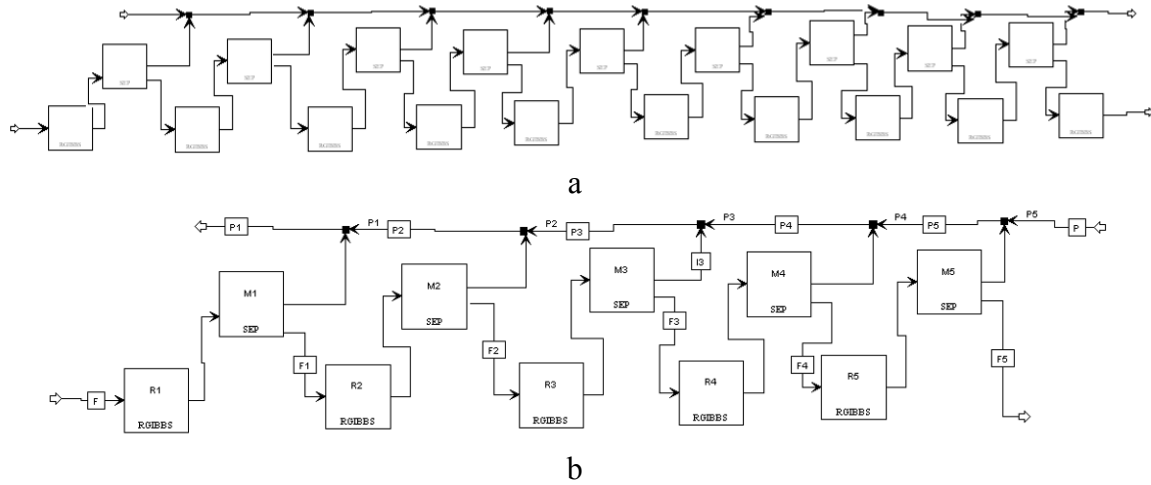


a



b

Figure 2 a. Cocurrent layout with 9 stages b. Countercurrent layout with 5 stages

As shown in the Figure 2, the inferior retentate gas goes through all the RGibbs blocks one by one, and permeating gas ($H_2$) together with sweeping gas (steam or $N_2$) goes through all the Mix blocks. After each stage of reaction equilibrium, the hydrogen is separated by a Sep block to ensure that the partial pressures of hydrogen at both sides are equal:

$$P_{H_2}^{Fn} = P_{H_2}^{Pn} \qquad\qquad 1$$

Where $P_{H2}$ represent the partial pressure of hydrogen, and Fn is for retentate side while Pn is for the permeate side

The separation step that satisfies equation 1 can be carried out using the Design Spec function in Aspen Plus. After the separation, the hydrogen is mixed with the permeating stream. The remaining gas in the retentate side will enter the next stage for further conversions. The simulation result converges to the thermodynamic equilibrium as the number of blocks increases. Primary analysis is discussed in the following section which evaluates the key variables for membrane reactors.

2.2.1 Cocurrent Design

In this case, both the streams flow in the same direction. For simplicity, the membrane reactor is assumed to operate isothermally at 400 °C. The total pressure of the permeate side is assumed to be 1 bar.

In one case, with steam: CO equal to 1 in the feedstock at 30 bar and same amount of steam injected as sweeping gas, a 9-stage membrane reactor can convert nearly 95.9% of the CO into $H_2$. The corresponding $H_2$ recovery ratio, which is defined as the percentage of hydrogen recovered at permeate side relative to the total amount of hydrogen after fulfilling the reaction, is 98.6%. The trends of $H_2$ partial pressure and CO conversion along with these stages can be examined in Figure 3. The limitation can be also calculated from a black box model [6] based on overall hydrogen balance and chemical reaction equilibrium.
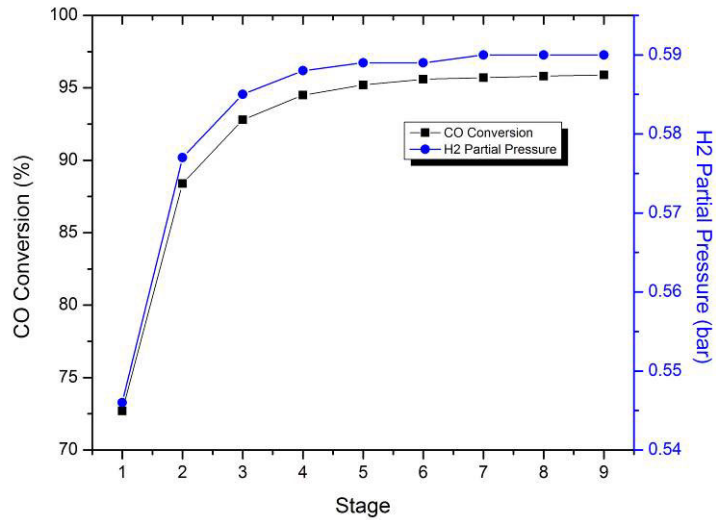


Figure 3    CO Conversion and $H_2$ partial pressure in a 9-stage cocurrent membrane reactor with a steam: CO ratio of 1.
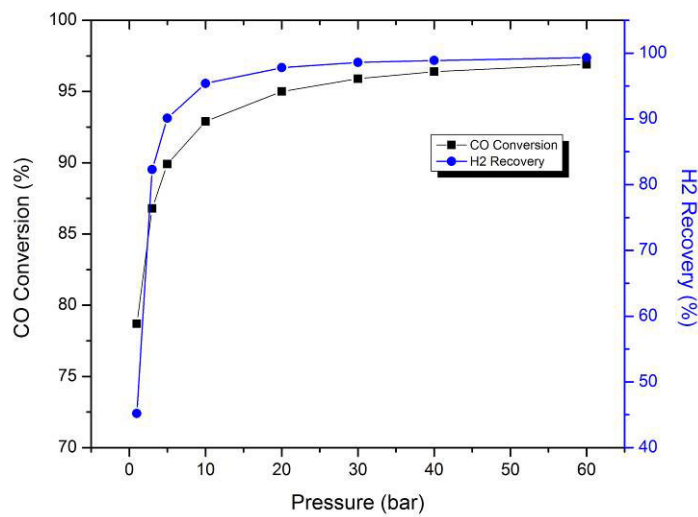


Figure 4    CO conversion and $H_2$ recovery ratio at different feed pressures

Unlike previous WGS reaction, pressure becomes a factor in the thermodynamic equilibrium. By changing the pressure in feedstock within last case, the CO conversion and $H_2$ yield vary significantly. As shown in Figure 4, higher pressure in reactant stream will increase the partial pressure of hydrogen at the same side. Therefore, more hydrogen will be driven to the permeate side, which enhances $H_2$ production. At above 20 bar, the influence of feed pressure becomes minor. Similar results can be expected for the sweeping gas flow rate. Higher sweeping gas flow rate leads to lower hydrogen partial pressure in the permeate side, resulting in increased hydrogen yield.
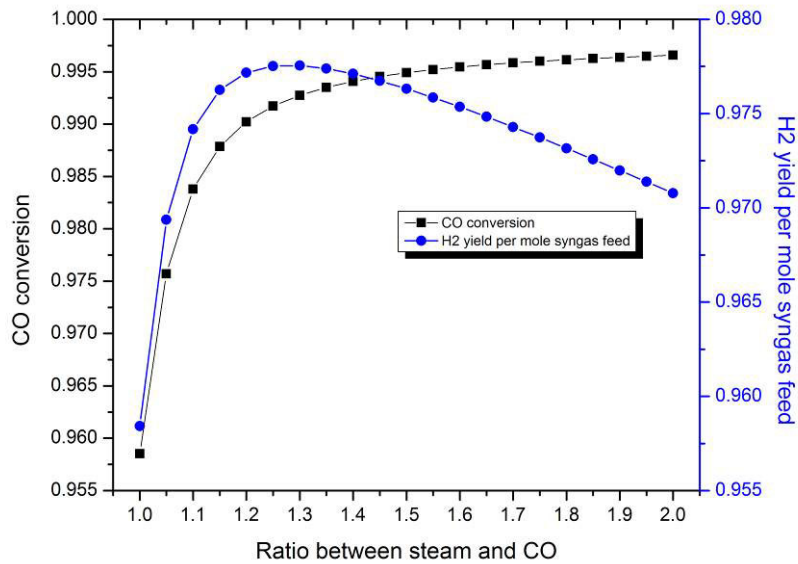


Figure 5          Effect of steam ratio in feedstock

The steam to CO ratio in the reactant stream can also affect hydrogen yield. As shown in Figure 5, on one hand, high steam ratio can promote the WGS reaction. On the other hand, high steam ratio decreases the partial pressure of hydrogen in the reaction side, which limits the hydrogen permeation via membrane. Therefore, there is a peak value in the trend of hydrogen yield. In this case, the highest hydrogen yield appears at a ratio between 1.2 and 1.3.

2.2.2 Countercurrent Design

In this configuration, sweeping gas (steam or nitrogen) together with permeated hydrogen will flow in an opposite direction to the flow of reactant gas. Figure 6 shows the simulation results from a 10-stage membrane reactor model, with steam: CO = 1:1 in the feedstock at variational pressure and sweep gas (1 bar): CO = 1:1. The reaction is also kept at 400 °C.
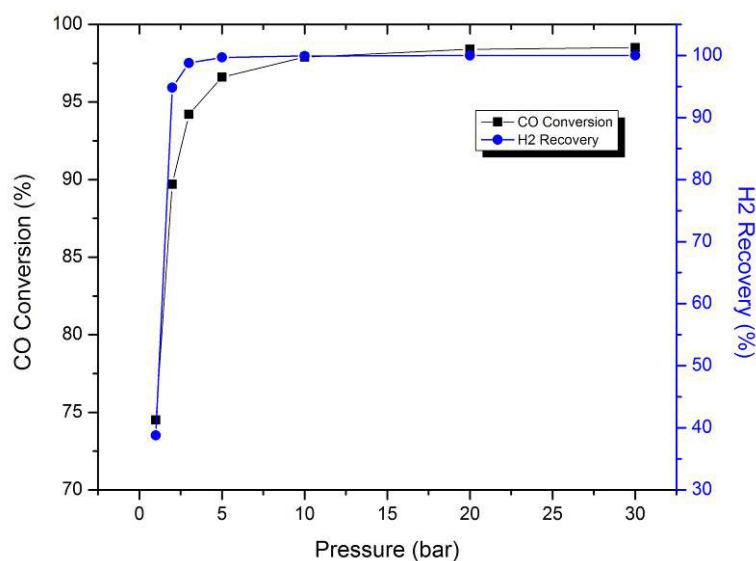
Figure 6    CO conversion and $H_2$ recovery ratio at different feed pressure

In this configuration and interested operating condition (pressure>3 bar), CO can almost be fully converted to $H_2$ and transferred to the permeate side. However, the full conversion may require huge membrane surface area and reliable membrane performance.

*2.3 Syngas Chemical Looping System*

Syngas chemical looping (SCL) system can convert syngas into hydrogen via an oxygen intermediate – iron oxides. The conversion can be completed within a loop of three reactors: the reducer, the oxidizer and the combustor. The reducer utilizes iron oxides to fully oxidize syngas into steam and $CO_2$. Consequently, $CO_2$ can be extracted by condensing all the steam without extra energy penalty. The solid product, reduced iron oxide, can be reoxidized to $Fe_3O_4$ by low temperature steam in oxidizer together with hydrogen production. The regeneration of iron oxides from $Fe_3O_4$ can be achieved in combustor by direct oxidation using air. The heat released in this step can be used to compensate the heat required in the reducer or to generate steam or power.

Analogously to membrane reactor designs, there are mainly two solid gas contacting patterns, i.e. cocurrent and countercurrent. For cocurrent design, one block of Rgibbs can be used to mimic the thermodynamic situation. However, to fully convert syngas in reducer, the result shows that huge amount of iron oxides are in need, which leads the effluent solids are $Fe_3O_4$. Due to thermodynamic restrictions, the consequence is that no hydrogen can be generated by steam in oxidizer. Thus, cocurrent fluidized bed reactor design is excluded for hydrogen production.

For countercurrent moving bed reactor design, novel multistage models for both reducer and oxidizer have been developed. As shown in Figure 7, Solid reactants are introduced from the top down, whereas gas stream flows antrorsely through the reactor,

represented as a series of Rgibbs reactors. Oxygen transfers between gas and solid streams during each stage by chemical reaction. The opposite operating flow direction ensures that reductive stream and oxidative stream get in touch and react to the largest extent.
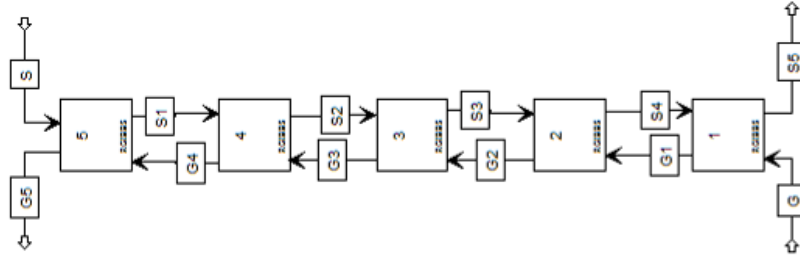


Figure 7          5-stage moving bed reactor model for SCL system

Figure 8 illustrates both gas (CO: $H_2$ = 2:1) and solid (pure $Fe_2O_3$) conversions in a reducer working at 900 °C, 30 bar by varying the molar ratio between solid and gas. As shown in Figure 8, to fully convert syngas, the minimum solid gas molar ratio is 0.913, which corresponds to a mixture of 90.7% FeO and 9.3% Fe. These reduced particles can then react with steam to produce hydrogen. Figure 9 concludes the minimum steam consumption per mole CO input for completed hydrogen production at different temperatures. The results suggest that hydrogen production favors low temperature, which is consistent to the exothermic nature of steam iron reaction.
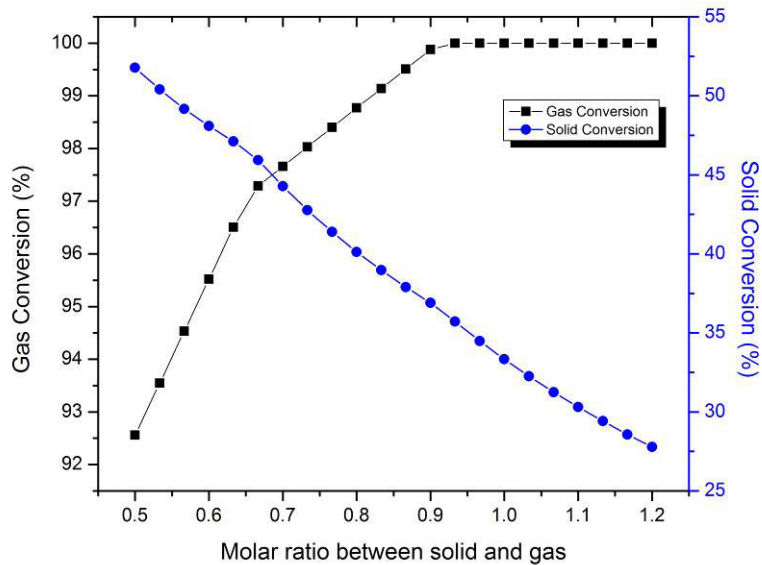


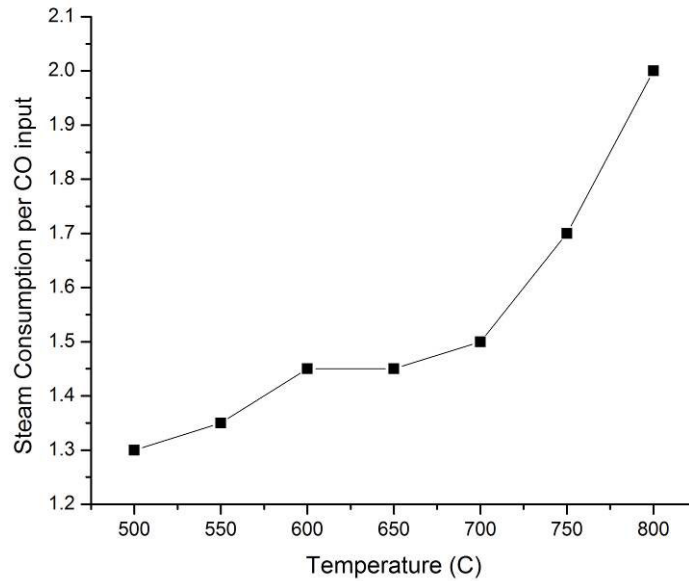Figure 8          Influence of feed ratio in reducer

Figure 9        Influence of temperature in oxidizer

### 3. Process Simulation for Advanced Hydrogen Production

To evaluate the performance of the conventional gasification-WGS process, the enhanced WGS membrane process, and the SCL process, a set of common coal gasification and syngas cleanup system is used for comparison based on identical assumptions.

All the process simulations are based on a Shell dry feed oxygen blown gasifier with 99% carbon conversion and 0.5% heat loss. The gasifier utilizes dried (5% moisture) Illinois #6 coal and pure oxygen (from Air Separation Unit, ASU) to generate syngas with a composition shown in Table 1. Syngas is cooled through gas quench to 500 °C, during which ash and fine particles have been cleaned off. Afterwards, the syngas is routed to high temperature cleanup units to remove sulfur. The clean syngas will then be introduced to the following systems for hydrogen and power production.

Table 1        Summary for Shell Gasifier

| Mass Flow   ton/hr | Feedstocks | Products |
|---|---|---|
| $H_2O$ | | 4.18 |
| $N_2$ | 4.75 | 6.42 |
| $O_2$ | 103.1 | 0 |
| S | | 4.81e-005 |
| $H_2$ | | 5.98 |
| HCL | | 0.40 |
| CO | | 190.8 |

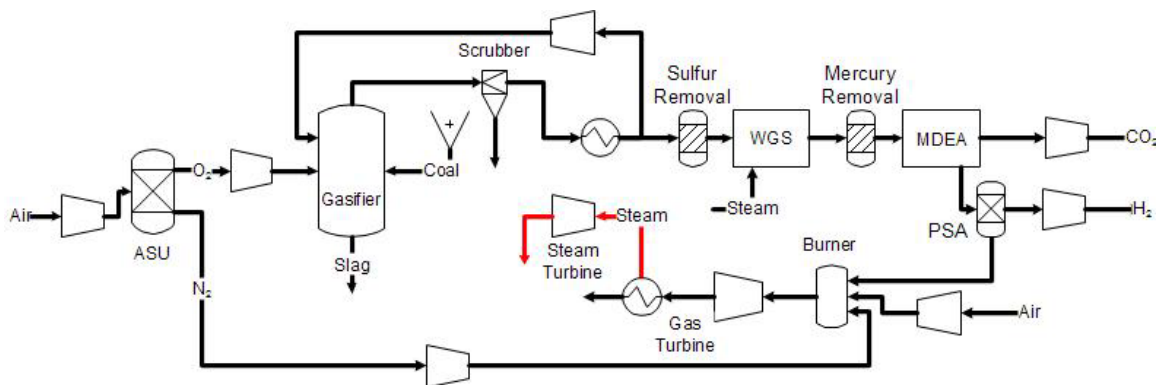| | | |
|---|---|---|
| $CO_2$ | | 6.80 |
| $NH_3$ | | 0.0048 |
| COS | | 0.438 |
| $H_2S$ | | 3.29 |
| $CH_4$ | | 0.069 |
| Illionis #6 COAL (5% moisture) | 124.3 | 0 |
| ASH | | 12.88 |
| C | | 0.847 |
| Temperature °C | 133 | 1233 |
| Pressure    bar | 35 | 30 |

## 3.1 Traditional WGS Process



Figure 10      Traditional WGS process for hydrogen production

As shown in Figure 10, clean syngas goes through WGS unit together with sufficient excessive steam (steam: CO = 2.1). The WGS unit is operated at 230 °C with 95% CO conversion. The effluent gas products are then cooled for mercury removal. MDEA unit is used to capture $CO_2$, and then pressure swing absorption (PSA) unit is used to purify $H_2$. The tailgas from PSA, including 23% of the total $H_2$ product and unconverted combustible gas, is to be burned in a gas turbine. For all the cases in this section, the pressure specifications for $CO_2$ and $H_2$ are 150 bar and 60 bar, respectively.

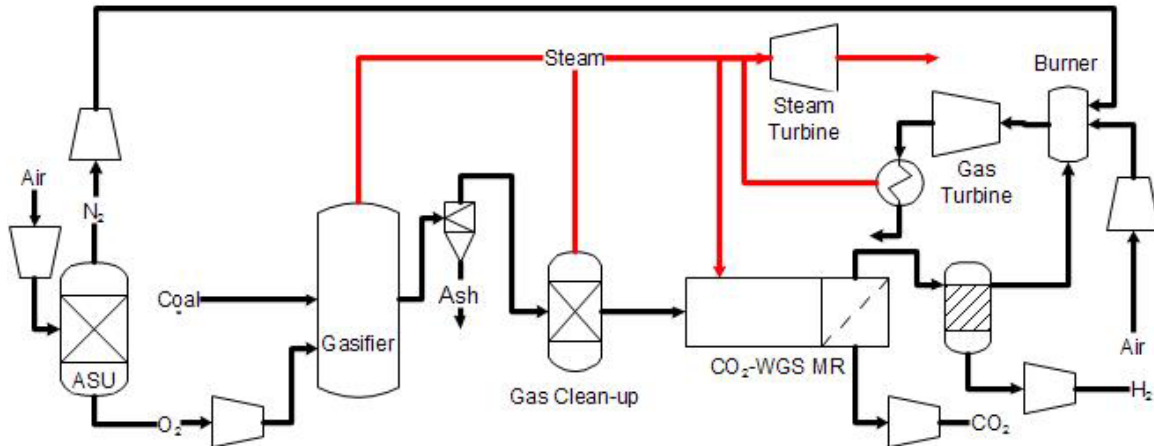## 3.2 $CO_2$ selective membrane reactor

Figure 11    Enhanced $CO_2$ selective membrane technology for hydrogen production

The $CO_2$ selective membrane reactor can be integrated into hydrogen production process as shown in Figure 11. For membrane reactor simulations both in 3.1 and 3.2, the ratio between steam and CO is adjusted to 1.3 to achieve full conversion of CO, and no sweeping steam is considered at present. Also, the pressure is set to be 1 bar at permeate side and the whole reactor is kept at 28 bar and 400 °C. To eliminate the impurities in raw hydrogen product, PSA is required for purification. 24% of the total $H_2$ product goes together with the tailgas for combustion.
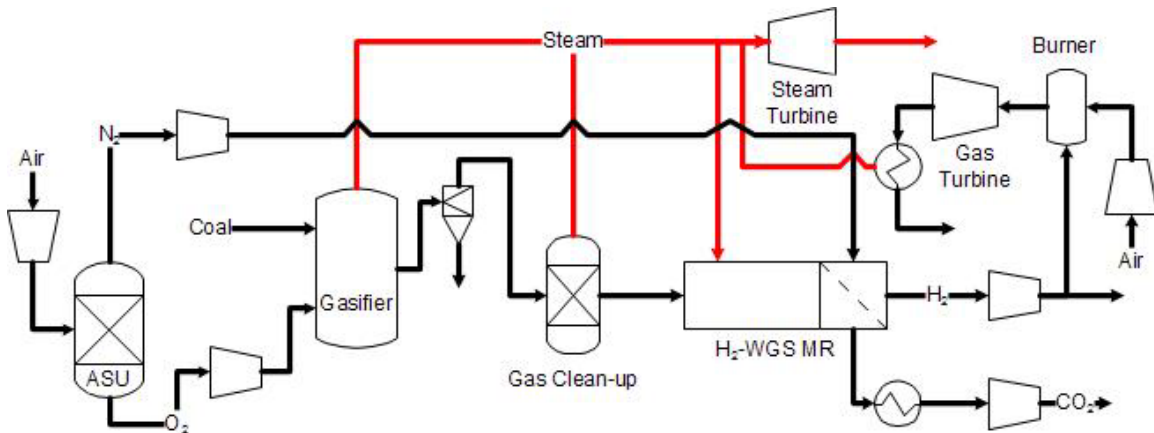
*3.3 $H_2$ selective membrane reactor*



Figure 12    Enhanced $H_2$ selective membrane technology for hydrogen production

Figure 12 shows the process based on enhanced $H_2$ selective membrane technology. The pure hydrogen stream is separated after membrane reactor, with 23.5% for power generation and 76.5% for further compression. The $CO_2$ rich stream is to be cooled and cleaned before sequestration.
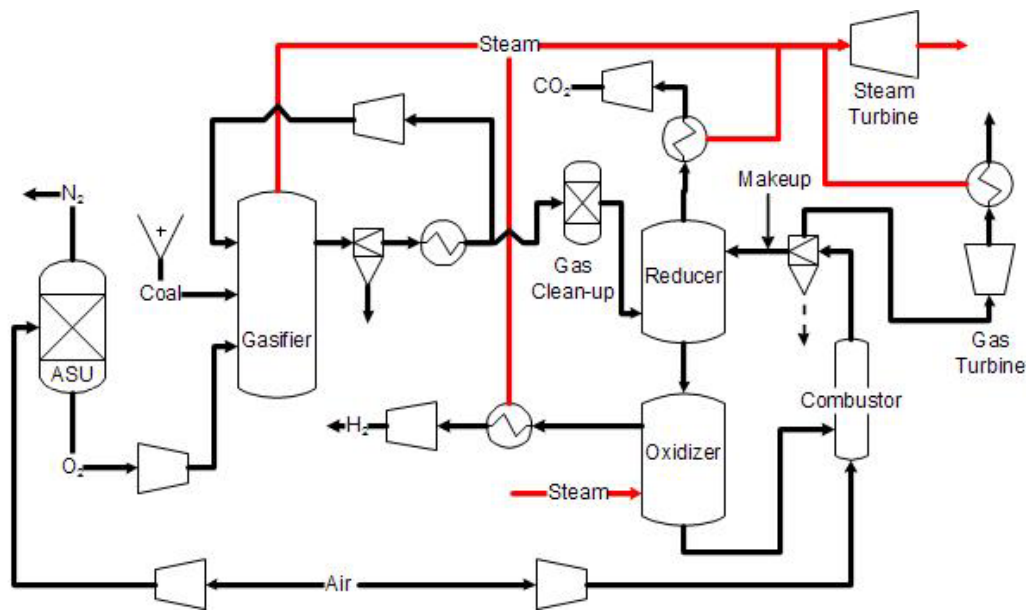
*3.4 SCL process*

Figure 13    SCL process for hydrogen production

SCL process (shown in Figure 13) adopts chemical looping strategy to produce $CO_2$ and $H_2$ in two different reactors. An iron oxide based looping medium is first reduced by syngas and then partially regenerated with steam to produce electricity. The partially regenerated iron oxide is then further combusted in the combustor with air. The heat generated in the combustor is used to generate electricity.

The results for all the four processes are summarized in Table 2. As shown in Table 2, the SCL process has the highest thermal efficiency for hydrogen production. There is little difference between two kinds of enhanced WGS membrane reactor. Conventional WGS process gets the lowest efficiency. However, it is better than most current coal gasification-WGS processes due to the incorporation of the hot/warm gas cleanup unit.

Table 2    Summary of process simulation results

|  | WGS | $CO_2$-WGS MR | $H_2$-WGS MR | SCL |
|---|---|---|---|---|
| Thermal Input (MW) | 1000 | 1000 | 1000 | 1000 |
| CO2 Capture (%) | 90 | 100 | 100 | 100 |
| Hydrogen production (kg/hr) | 14.65 | 15.0 | 15.1 | 15.3 |
| Net power (MW) | 59.7 | 62 | 59.8 | 61.2 |
| Overall Efficiency (%) | 63.71 | 65.32 | 65.42 | 66.58 |

## 4. Conclusions

Present work studies four advanced hydrogen production schemes using Aspen Plus for both thermodynamic analysis and process evaluation. Optimum operating conditions for water gas shift reaction have been decided based on thermodynamic restrictions. Novel models for both cocurrent and countercurrent design have been

developed membrane based WGS reactor and syngas chemical looping reactors. Sensitivity analyses have also been performed. Based on preliminary process simulations using thermodynamic modeling results, the SCL process can potentially deliver the highest thermal efficiency among the advanced hydrogen production technologies. Enhanced WGS membrane technology can also improve the overall efficiency of the coal to hydrogen process.

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