Hydrogen Production from Syngas Using Metal Oxide Composite Particles

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INTRODUCTION

Hydrogen is a clean fuel source, which has many important applications such as in the transportation industry, power generation, chemical production and oil hydrogenation. It is believed that hydrogen will be the fuel for the future. In order to support the future hydrogen economy, efficient ways to produce hydrogen are being developed [4-7]. Reforming of methane has traditionally been used to produce hydrogen mostly for ammonia synthesis. However, due to the increase in natural gas prices, new energy sources that are accessible and more economical are needed. Since coal is the most easily available and abundant fuel source, technologies that generate hydrogen from coal hold great potential.

There is intense research ongoing on coal gasification related technologies in order to produce hydrogen [8]. The syn gas produced, which mainly consists of CO and H_2, undergo the water gas shift (WGS) reaction in order to convert most of the CO to CO_2 by reacting with steam and producing hydrogen in the process.

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (1)$$

Usually the WGS operation is performed in two temperature ranges; at moderate temperatures (350 – 450 ^oC) using iron based catalyst, and at low temperatures (200 – 300 ^oC) using copper based catalyst [1, 2]. The low temperature stage is highly sulfur sensitive. Thus, synthesis gas has to be purified before entering the catalytic bed. Even though a catalyst is used, the conversions achieved are well below the thermodynamic limit [3]. After the WGS reaction, the CO_2 is separated in order to obtain a pure CO_2 stream. After the CO_2 separation the hydrogen is purified in a PSA unit. The remaining gas is then burned in a gas turbine to produce electricity. Figure 1 shows a block diagram of the WGS approach for hydrogen production.

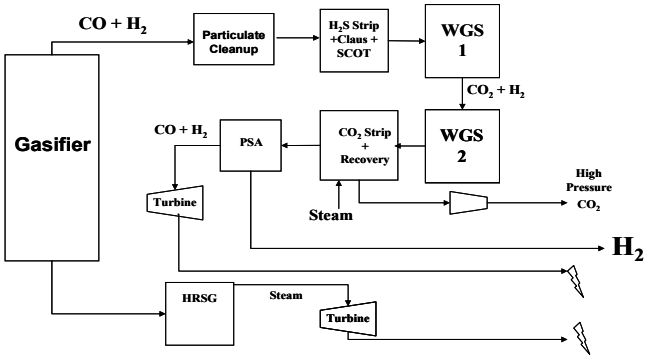


Figure 1. Simplified block diagram of the Syngas-WGS approach for the production of hydrogen.

Symbeck et al. (2002) reported that the efficiency of the system Syngas-WGS for hydrogen production was 64%. A system that can produce hydrogen more efficiently and reduce the cost of hydrogen is highly desirable. OSU has developed a concept based on the reduction and oxidation of metal oxide particles which replaces the WGS reactors and produces hydrogen more efficiently at a lower price.

RESULTS AND DISCUSSION

Process development

In this study, a Syn Gas Redox (SGR) process is developed to produce H_2 from synthesis gas at high temperatures with integrated high pressure CO_2 production. The SGR process involves two steps of operation: 1) syngas oxidation and 2) H_2 production. Figure 2 shows a simplified block diagram of the SGR process.

In the syngas oxidation stage, the syngas reacts with a metal oxide (MO) producing CO_2 and H_2O. After an isobaric water condensation, this process gives a sequestrable CO_2 stream. The main reactions occurring in the syngas oxidation stage can be written as:

$$CO + MO \rightarrow CO_2 + M \quad (2)$$

$$H_2 + MO \rightarrow H_2O + M \quad (3)$$

During the syngas oxidation, the metal oxide is reduced to its metallic form (M). This reduced metal, in the hydrogen production step, is then reacted with steam to generate hydrogen and regenerate the metal oxide. The reaction in the hydrogen production stage can be written as:

$$H_2O + M \rightarrow H_2 + MO \quad (4)$$

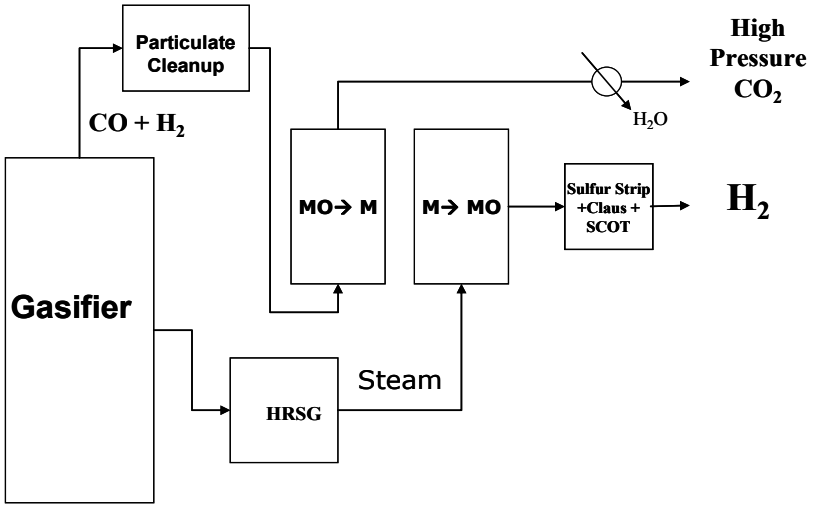


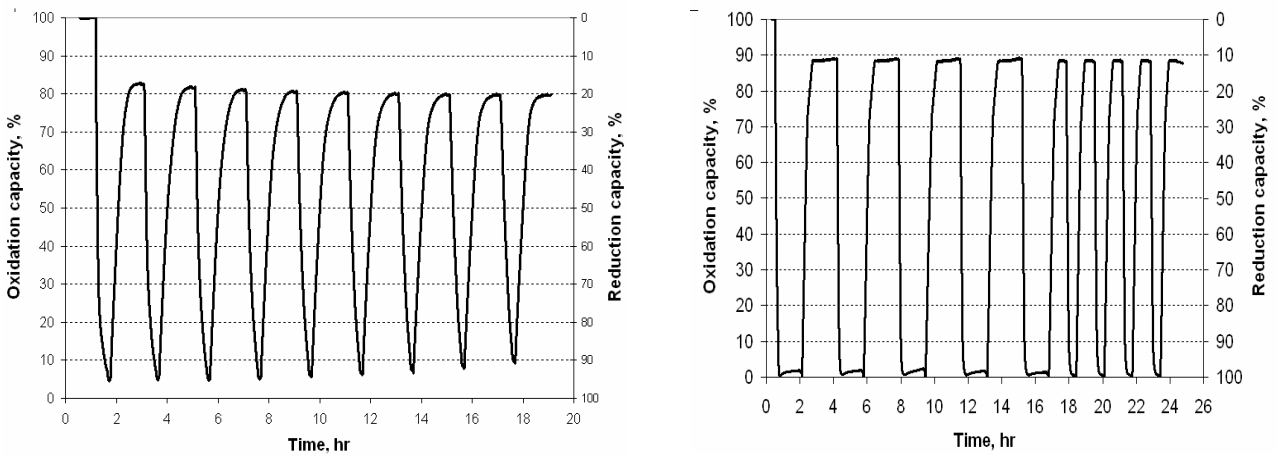
Figure 2. Simplified block diagram of the syn gas redox (SGR) process for the production of Hydrogen.

The process can be implemented at production scale using two similar packed bed reactors where one is in syngas oxidation mode and the other is in the H_2 production mode. Once breakthroughs are seen, the gases can just be switched from one reactor to the other in order to provide a continuous mode of operation. The advantage of the process proposed here, compared with the traditional WGS reaction, is that two separate high-pressure streams of CO_2 and H_2 can be produced at high temperatures.

The SGR process offers no additional cost associated to the CO_2 separation. Because close to 70-85% of the cost associated with carbon management lies in the CO_2 separation, the SGR process offers an attractive advantage for future CO_2 planning.

Particle development

In order to develop this technology for commercial applications, synthetic metal oxide particles were developed that are capable of reacting with syngas and steam for many cycles. These particles were tested under simulated syngas environment. Reduction and oxidation cyclic studies were performed at 900 ^oC using a TGA apparatus. Particles were reduced using a mixture of CO and H_2 in N_2 with a CO/H_2 ratio of 2. On the other hand, particles were oxidized using 10% H_2O in N_2. The sample weight and the particle size in all the experiments was 20 mg and 75-125 μm respectively. Figure 3 shows the cyclic studies of two different metal oxide composite particles.



a) b)

Figure 3: Reduction-oxidation cyclic studies for two types of synthesized particles at 900 ^oC.

In figure 3a, it can be observed that the particle redox capacity slowly diminishes after a few cycles. In the first cycle, the particles reached up to 96 % reduction and about 82% oxidation capacity. In the ninth cycle, however, the particle reached only 90% reduction and 80% oxidation. This small drop in capacity after few cycles indicates a continuous decrease in particle recyclability with time. Particle recyclability might be affected due to particle sintering at high temperatures. Another formulation was prepared that was able maintain its capacity at high temperatures. Figure 3b show the cyclic studies of a modified metal oxide composite

particle. This particle was found to be recyclable, achieving, after nine cycles, 100% reduction and close to 90 % oxidation capacity.

CONCLUSIONS

The SGR process developed here replaces the WGS reactors producing hydrogen more efficiently. This process can be carried out using two reactors, one working in the syngas oxidation mode and the other one working in the hydrogen production mode. Nearly pure CO_2 and H_2 streams can be obtained without need of further CO_2 separation. In this work, it was found that composite particles retain their activity over multiple redox cycles with high conversions. These particles were found to possess a high potential for hydrogen production from synthesis gas.

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