Chemical Looping Combustion of Coal

Puneet Gupta, Luis G. Velazquez-Vargas, Fanxing Li and L.-S. Fan
Department of Chemical Engineering
The Ohio State University
Columbus OH, 43210

INTRODUCTION

Coal is commonly processed by combustion/gasification using oxygen to produce electricity. Coal, however, can be processed using an oxygen carrier instead of oxygen. Metal oxides such as Fe_2O_3 can act as suitable oxygen carriers. However, unlike combustion of coal with oxygen, there is a relatively pure sequestration ready CO_2 stream produced on combustion with metal oxide carriers. The reduced form of metal oxide can then be reacted with air to liberate heat to produce electricity or reacted with steam to form a relatively pure stream of hydrogen, which can then be used for a variety of purposes.

In this work, a process has been developed for the combustion of coal using metal oxides as oxygen carriers. Studies were focused on the development of oxygen carrier particles that can be reduced and oxidized over several cycles. Particle pelletization was investigated. Energy efficiency calculations were also performed in order to compare and evaluate the process against current and future combustion technologies.

PROCESS DESCRIPTION

The chemical looping combustion (CLC) of coal is a process in which coal is combusted using the oxygen contained in a metal oxide (oxygen carrier). The gaseous products formed (CO_2 & H_2O) are similar to conventional combustion processes. When the coal is being combusted, the metal oxide is reduced to the metallic form that is then separated from the ash and circulated to a second reactor where it is regenerated to give back the original metal oxide. The regeneration process is performed using steam, which generates hydrogen in the process. The process requires two reactors, one for combustion of coal and the other for regeneration of the used metal oxide. Figure 1 shows a simplified schematic diagram of the CLC process. Unlike conventional combustion, CLC provides, after an isobaric water condensation, a readily sequestrable CO_2 stream.

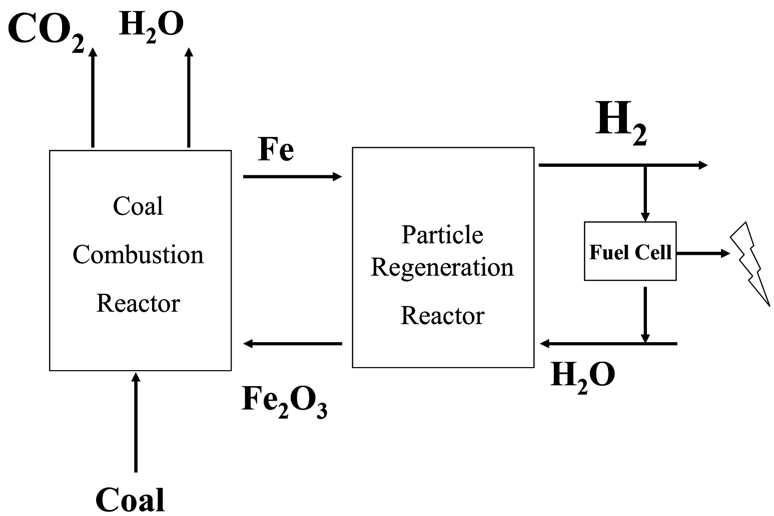

Figure 1. Simplified block diagram of the Chemical Looping Combustion of coal process.

To increase the conversions of coal/char, CO_2 is also passed into the coal combustion reactor. CO_2 reacts with char using the reverse Boudard reaction to form CO which then reduces the metal oxide. The ash is separated from the reaction products through size separation followed by magnetic separation.

RESULTS AND DISCUSSION

Reaction of coal with Fe_2O_3

Reaction of coal with Fe_2O_3 was carried out in a TGA setup. Coal and Fe_2O_3 were ground together using a mortar and pestle to provide for high dispersion into each other. Coal was taken in greater than stoichiometric quantity to ensure that the Fe_2O_3 reaction goes as far towards completion as possible given the batch conditions in the TGA. The weight of the mixture was analyzed as a function of time and temperature in an inert environment of nitrogen. Experiments were also carried out with only coal to separate the transitions that would take place in coal from the transitions that would take place in the coal + Fe_2O_3 mixture. Figure 1 shows the TGA results. It is seen that coal starts devolatalizing around 300-400 ^oC. However, reaction with Fe_2O_3 begins only around 750 ^oC, where a rapid fall in weight is observed. The experiment provided information about the minimum temperature of operation without the use of a gasifying agent to react coal and Fe_2O_3.

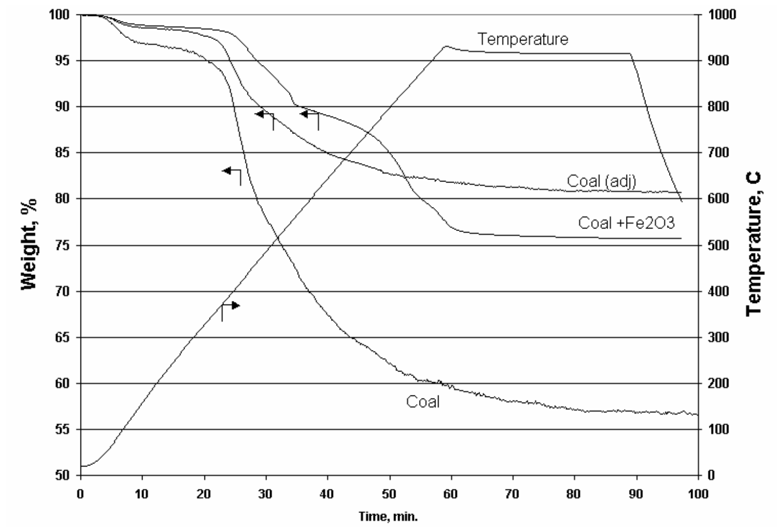

Figure 1: Weight v/s Temperature data for reaction between coal and Fe_2O_3 and coal devolatalization

The final product mixture was analyzed using X-ray diffraction (XRD) to identify the phases present. The XRD pattern is shown in Figure 2. It was found that the final mixture consisted of all forms of iron oxides in varying amounts. Also a peak corresponding to pure iron was observed confirming that the reducing reaction with coal had taken place. Though the results were not quantitative, they did provide proof of concept that Fe_2O_3 can act as an oxygen carrier for coal combustion.

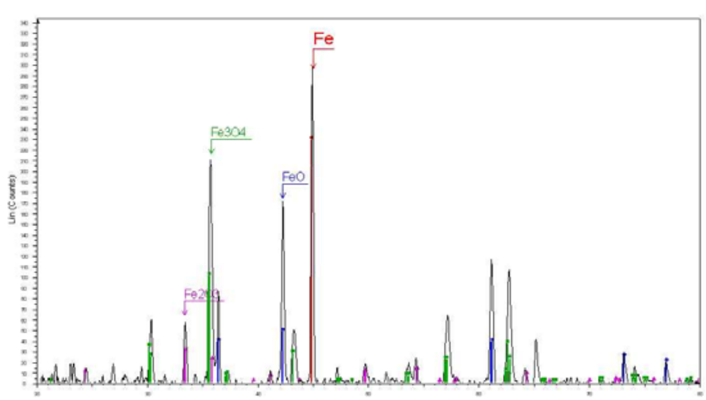

Figure 2: XRD pattern of the coal+Fe2O3 mixture after undergoing reaction in a TGA showing all forms of iron oxide present in addition to a large amount of elemental iron.

Particle recyclability

Cyclic reduction/oxidation studies were conducted on various oxygen carrier particles in order to understand their recyclability over many cycles. Particle recyclability is important in order for the process to be economic. Reduction and oxidation cyclic studies were performed in a TGA apparatus at 900 ^oC. Reduction was performed using a mixture of 33 % H_2 in nitrogen. Oxidation was performed with a mixture of 7 % O_2 in nitrogen. Experiments showed that pure Fe_2O_3 particles lost their reaction capacity after a few cycles. In order to add immunity towards sintering at high temperatures, special particles were synthesized to provide better recyclability. Figure 3 shows the cyclic performance of the synthesized partricles. Particles were recyclable for several cycles without any drop in activity. It can also be observed from figure 3 that during the first cycle, there is a change in the reaction rate during reduction. It is believed that this change is due to the adjustment in the pore structure of the particles due to the difference in molar volume between the reaction products and the reactants along with sintering at high temperatures.

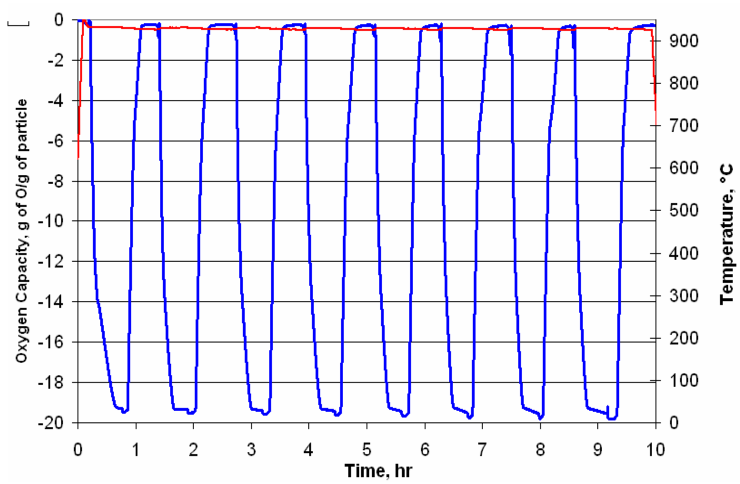

Figure 3. Reduction and oxidation cyclic studies of a synthetic Fe_2O_3 particle

Particle pelletization

In order to carry out the CLC process in commercial scale reactors and avoid high-pressure drops inside, particles should be pelletized to bigger sizes. Particle pelletization was performed using a bench scale table press machine. A maximum force of 600 lb was applied to each pellet. Pellets of different sizes were prepared ranging from 1 to 5 mm.

Recyclability of the pellets was tested in a TGA apparatus at 900 ^oC. Reduction was performed using a mixture of 33 % H_2 in Nitrogen. Oxidation was performed with a mixture of 7 % O_2 in nitrogen. Figure 4 shows a reduction and oxidation cyclic study of a 3 mm pellet. In figure 4 it can be observed that the pelletization process did not affect the recyclability properties of the particle. At the start of the third cycle, the reaction time was reduced by the operator. This caused the particles to go through an adjustment in their reaction rate as it can be seen in figure 4. However, particle recyclability was still found to be excellent.

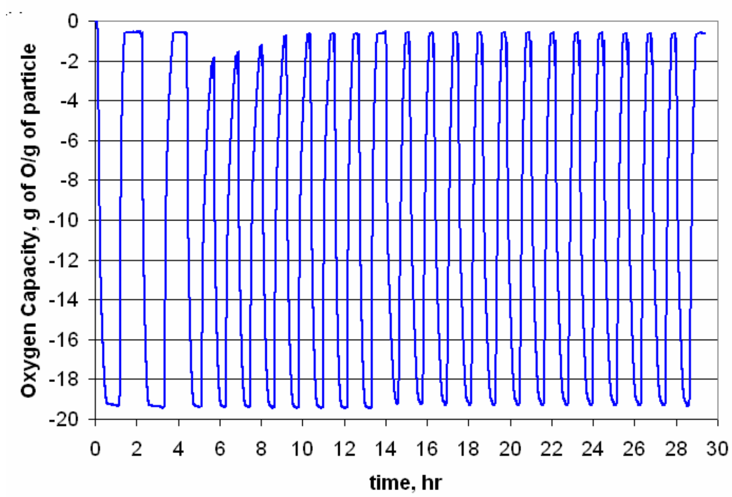

Figure 4. Reduction and oxidation cyclic study of a 3 mm pellet of a supported Fe_2O_3 particle.

Process simulation

Process simulations were performed using ASPEN PLUS ® to heat integrate the system and to determine the efficiency of hydrogen production. This efficiency is defined as the HHV of the hydrogen produced divided by the HHV of raw coal input. All "hot" streams were used to generate steam, which was used in the oxidation reactor to make hydrogen. Simulations were run for Pittsburgh #8 coal. The hydrogen production efficiency was calculated to be close to 90%. Assuming heat losses and parasitic energy consumption to be of the order of 5%, the efficiency can be assumed to be in the range of 85%. In comparison, the hydrogen production efficiency for a coal gasification-WGS process is reported around 64% [4]. The CLC process is a major advancement over the traditional route.

CONCLUSIONS

It was shown that the reaction of Fe_2O_3 with coal is feaseable at temperatures greater than 750 ^oC. The reactions of coal with iron oxide reduce the metal oxide to its metallic form. The reduce metal has the potential to be oxidized with steam to produce hydrogen. Cyclic looping studies revealed that the composite particles retain their activity over multiple reduction/oxidation cycles. The pelletization process did not adversely affect the recyclability properties of the particles. The developed CLC process is capable of transforming close to 85% of the thermal energy of coal into hydrogen. This is much higher than the 64% envisaged for coal gasification technologies. The high efficiencies and flexibility to produce desired products, coupled with the integrated environmental benefits in terms of a readily sequestrable CO_2 stream make chemical looping combustion of coal an attractive technology for the energy management

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