Chemical Looping Process for Direct Conversion of Solid Fuels In-Situ CO$_2$ Capture

Thesis

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By

Hyung Rae Kim, B.S.

Graduate Program in Chemical Engineering

The Ohio State University

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Thesis Committee:

Liang-Shih Fan, Advisor

David Tomasko
Abstract

With the ever escalating demand for power generation, CO₂ emission from coal-fired power plants is becoming a growing environmental concern. In order to reduce the CO₂ emissions from the energy conversion processes, carbon capture techniques have been developed, such as a chemical absorption process for CO₂ capture using MEA solvent, Integrated Gasification Combined Cycle (IGCC) and oxy-combustion capture. However, the parasitic energy required for these methods to produce a concentrated, sequesterable CO₂ stream significantly mitigates their economic feasibility.

Currently, most chemical looping processes being developed have focused on the converting gaseous fuels, such as syngas and natural gas. However, due to the unstable natural gas prices and the capital intensive gasifier required for the syngas generation, a chemical looping scheme that utilizes the direct conversion of solid fuels such as coal and biomass can potentially be economically attractive. The Sold Fuel Direct Chemical Looping (SDCL) technology developed at the Ohio State University is a potentially attractive alternative to the conventional carbon separation techniques. In the SDCL process, an iron-based composite particle is used to serve as a chemical intermediate to produce heat for power generation from solid fuels via an iron reduction/oxidation reaction scheme. A sequestration-ready stream of CO₂ is produced in this system without an elaborate separation step.

The iron-based oxygen carrier in the SDCL process directly converts the coal and biomass with the effective CO₂ capture. The process consists of two main reactors, i.e. a reducer, and
combustor. In the reducer, the solid fuels are converted to CO$_2$ and H$_2$O using the oxygen liberated in the conversion of Fe$_2$O$_3$ to a mixture of Fe and FeO. However, the reaction between the oxygen carrier and char is fundamentally slow solid state reaction. In order to overcome the slow kinetics, a small portion of the CO$_2$/$H_2$O exhaust stream from the reducer is recycled to enhance the solid-solid reaction. The reduced iron particles are then transferred to the combustor, where they are fully oxidized to Fe$_2$O$_3$ and pneumatically conveyed to the reducer completing the cycle.

The experimental study of the SDCL process in a thermogravimetric analyzer (TGA) and fixed bed apparatus show that the oxygen carrier particle remains highly reactive after several reduction/oxidation cycles at 900°C. Both the volatiles and chars from coal and woody biomass are effectively converted to CO$_2$ and H$_2$O with minimal side reactions using the oxygen carrier particle. Additionally, the char conversion rate is enhanced when the oxygen carrier is coupled with reducer exhaust stream. During the oxidation of the particle, an exothermic behavior is observed and their reactivity is maintained.
Dedication

To the World
Acknowledgements

First of all, I would like to thank my family who has supported me from far away for a long time. My father always motivates and encourages me to pursue my education. He has been a great advisor, role model and friend for me. My mother has shown me her unconditional love. She made countless trips to see her son without hesitation all the time. Throughout my undergraduate years, my sister always provided me great meals and had so much fun together. I always miss her. Lastly, I truly appreciate my grandparents for their patience and love. I love them.

Addition to my family, I would like to acknowledge and special-thank to my advisor, Professor Liang-Shih Fan. His intellectual guidance, knowledge, enthusiasm, patience, motivation, encouragement, praise, expectation and belief in myself, and lecture surely made me become a better researcher and person during my graduate studies. I have learned many valuable lessons for life and research from him in many different ways. Being his research associate was something that I can be proud of for the rest of my life.

I am very thankful for my committee member, Professor David Tomasko. Since my freshman year of college, he attracted my interests in engineering during his classes. Great time with him in the softball team was unforgettable. I would like to thank Professor Alissa Park, who introduced me to the world of research and graduate school. I appreciate her for recognizing my potential. I will never forget her help and advice.
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I also appreciate for all the help from administrative members. Most of all, I appreciate Paul Green, Leigh Evard and Lynn Flanagan for their hard efforts for me and our group. At the same time I want to apologize for excessive and disorder works caused by me.

Lastly, I want to thank all my friends in Korea and the U.S, especially, my best of best friend Joyce Kwong for bringing happiness to my life. I thank my friends, Sungha Kim, Jae-wook Jung, Minkook Kim and Karam Kim for being my great friends. Also, I thank my old friends whom I always miss, Ki-Sun Park, Jae-Ho Ha, Hyung-Jin Choi, Jin-Keol Park and Francis J. Kim. My memorable childhood and youth with them was something that I can always keep in my heart. I wish their success in the future for whatever they do.
Vita

January 1985……………………………………………………….Born, Dae-Jeon, South Korea

June 2007………………………B.S. Chemical Engineering , The Ohio State University

September 2007 – Present………Graduate Research Associate, The Ohio State University

Field of Study

Major Field: Chemical Engineering
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Chapter 1: Introduction of Chemical Looping Combustion

1.1. CO₂ Capture Technologies

Power plants by fossil fuel combustion, especially coal combustion processes for electricity generation are the major sources for the CO₂ emissions. For instance, the Pulverized Coal (PC) power plants account for 1946.7 million tons of CO₂ emission, 32.7% anthropogenic CO₂ emissions in the United States in 2006. Due to the increasing concerns of global warming caused by CO₂ emission, the development of carbon capture and storage (CCS) strategies for the coal combustion power plants becomes more important. The control of CO₂ in the fossil fuel conversion plants generally associates with considerable decrease in plant efficiency and increase in costs of installation and operation. The cost breakdown of CCS technologies for a PC power plant using available technologies is shown in Table 1.1. As can be seen, the cost for carbon capture, which includes CO₂ separation and compression, is significantly higher than the costs for CO₂ transportation and storage. Therefore, the development of cost-effective CO₂ capture technologies from the conventional PC power plants is the key to the affordable CO₂ management.

Various carbon capture technologies for PC power plants have been suggested and developed, in order to reduce the carbon capture penalty in terms of plant efficiency and economic. Existing CO₂ capture technologies for fossil fuels-based power plants can be categorized into one or more of the following three categories depending on how the carbon is separated in the process: post-combustion capture, pre-combustion capture, and oxy-combustion capture.
The post-combustion carbon capture directly removes the CO₂ from the flue gas, resulted from the combustion. The pre-combustion capture system separates CO₂ from the fuel gas prior to the combustion using the gasification technology. Lastly, oxy-combustion capture system combusts coal with the high purity of oxygen separated from air, generating a highly concentrated CO₂ stream from the combustor.

1.1.1. Post-combustion Capture

Since the post-combustion CO₂ capture technologies separate CO₂ from the flue gas after combustion, they are most readily retrofitted to the existing PC power plants. Figure 1.1 (a) shows the schematic flow diagram of post-combustion capture. The combustor generates the heat for the steam from the fossil fuel combustion. After the flue gas is used for the steam generation, the CO₂ in the flue gas at ambient pressure is separated. Once concentrated CO₂ is obtained, it is compressed for transportation and sequestration.

Various technologies have been proposed for post-combustion carbon capture. These include chemical/physical absorption solvents, high temperature solid carbonate sorbents, CO₂ separation membranes, metal organic frameworks, enzyme systems, ionic liquids, molecular filtration, and enzyme-based system. Among these post-combustion CO₂ capture technologies, the chemical absorption process using monoethanolamine (MEA) solvent is most widely studied and applied to CO₂ separation in the power plants.

The schematic of the MEA system is given in Figure 1.2. The MEA solvent segregates the low partial pressure CO₂ in the flue gas using relatively strong chemical interaction between the MEA solvent and gaseous CO₂. The MEA solvent is suitable for CO₂ separation from the PC power
plant flue gas which has a CO₂ concentration of 10 ~ 15 volume %. The MEA solvent separates CO₂ with the following reaction.

\[
C_2H_4OHNH_2 + H_2O + CO_2 \leftrightarrow C_2H_4OHNH_3^+ + HCO_3^- \quad (1.1)
\]

In the absorber, the CO₂ in the flue gas reacts with MEA solvent to form water soluble ions. Because low temperature favors the absorption of CO₂, this separation step is carried out at around 40°C. After the absorption, the CO₂ rich solvent is introduced to the desorber, which is operated at 100 ~ 120°C, in order to regenerate the MEA solvent by releasing the CO₂. For the regeneration step, steam is used to heat up the spent solvent to the desired temperature. In the desorber, the solvent-CO₂ compound decomposes resulting regenerated MEA solvent and a concentrated CO₂ stream. The industrial demonstration by Mitsubishi Heavy Industries in Japan has proven that the MEA system is capable to separate around 90% of the CO₂ in the flue gas stream, producing a concentrated CO₂ stream that contains up to 99.8 wt. % CO₂. Such a CO₂ stream is suitable for further transportation, and sequestration.

However, the MEA system has shown disadvantages in the heat integration. The regeneration of the spent MEA solvent in the desorber requires significant amount of heat. Thus, it reduces the overall power output and the efficiency of the power plants. In addition to the heating requirement for the MEA regeneration, the large amount of cooling water is required for the MEA solvents, because the regenerated MEA solvent from the desorber needs to be cooled to absorption temperature for CO₂ capture before entering the absorber. Mitsubishi Heavy Industries and Kasai Power Co. in Japan have synthesized a new amine-based solvent, which increased the CO₂ loading capacity by 67% and reduced 20% of heat for the regeneration.
Another challenge to the carbon capture by the MEA process is a tendency of MEA solvent fouling with other pollutants in the flue gas such as NO\textsubscript{x} and sulfur. For example, NO\textsubscript{x} and SO\textsubscript{2} in the flue gas react with MEA solvent to form heat-stable salt that reduces the CO\textsubscript{2} absorption capacity of the solvent \textsuperscript{5}. These salts are very difficult to be regenerated, since they are in the thermodynamically stable form. It is estimated that each mole of NO\textsubscript{x} and SO\textsubscript{2} in the flue gas will lead to a loss of two moles of MEA solvent. With the price of the MEA solvent close to $1,000/ton \textsuperscript{6}, the presence of SO\textsubscript{2} and NO\textsubscript{x} in the flue gas can significantly increase the operating cost of the MEA system. Also, SO\textsubscript{2} can cause the corrosion in the process \textsuperscript{5}. Therefore, SO\textsubscript{2} and NO\textsubscript{x} need to be removed prior to the MEA system. The preferred levels of SO\textsubscript{2} and NO\textsubscript{x} are 10 ppm and 20 ppm by volume in the MEA system, respectively \textsuperscript{5, 7}. Such a stringent requirement can lead to increase in SO\textsubscript{2} and NO\textsubscript{x} removal costs.

The energy intensive nature of the MEA system results in a large energy penalty for CO\textsubscript{2} capture in a PC power plant. When retrofitted to an existing PC power plant, the MEA system reduces the overall plant efficiency by 21 ~ 42\% \textsuperscript{8, 9, 10, 11, 12, 13, 14}. Table 1.2 generalizes the energy penalties assuming 90\% CO\textsubscript{2} capture on various PC power plants using the MEA system. The reduction in plant efficiency is accompanied with increase in cost of electricity. Various studies indicate that a 90\% CO\textsubscript{2} capture with MEA will lead to an increase in the cost of electricity of 40 ~ 70\% \textsuperscript{12, 15, 16}. Table 1.3 summarizes the change in the cost of electricity using the MEA system.

1.1.2. Pre-combustion Capture

Pre-combustion capture separates the carbon in the fuel before combustion. Such a technique can be exemplified by the coal-based Integrated Gasification Combined Cycles (IGCC) process, which is illustrated in Figure 1.1 (b). In the IGCC process, coal first reacts with oxidant gases such as oxygen (and steam) to produce synthetic gas (syngas), which is comprised mainly of CO
and H₂. In order to capture carbon from the syngas prior to combustion, the syngas stream is further converted to H₂ through the water-gas shift (WGS) reaction.

\[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \quad (1.2) \]

Thus, the resulting gas stream from the WGS reaction contains high CO₂ concentration (up to ~40% by volume on the dry basis). The CO₂ can be captured using either chemical absorption-based acid gas removal processes such as MEA or methyl-diethanolamine (MDEA) or physical absorption based processes such as Selexol and Rectisol, yielding concentrated H₂. Then, the H₂ is used to generate electricity through a combined cycle system with minimal carbon emissions. Compared to the PC combustion processes, which fully oxidize carbonaceous fuels using air to generate heat, the modern coal gasifiers in the IGCC process convert coal into syngas via partial oxidation reactions with oxygen and/or steam under elevated pressures. The high pressure syngas stream has a much lower volumetric flow rate than the flue gas from coal-fired power plants. Therefore, the partial pressure of the contaminants is significantly increased. For instance, the volumetric flow rate of syngas generated from a dry feed, oxygen blown gasifier can be two orders of magnitudes lower than that from a PC boiler with similar coal processing capacity (dry basis). Meanwhile, the partial pressure of CO₂ in the syngas after water gas shift (WGS) reaction can be 80 times higher than that in the PC boiler flue gas (dry basis). As it has been mentioned in the earlier section, the coal combustor contains only 10 ~ 15 vol.% of CO₂ in the flue gas. The significantly reduced gas flow rate and increased gas partial pressures make the pollutant and CO₂ control an easier task for gasification processes when compared to coal combustion processes.
Despite the advantages in product versatility and pollutant controllability compared to combustion, gasification is more capital intensive process than combustion. It is estimated that an IGCC system requires 6 ~ 10% more capital investment than an ultra-supercritical PC plant 20. Although the CO₂ capture from the gasification process is easier compared to the PC plant, the CO₂ capture represents an energy and capital intensive step of the process. The CO₂ capture can lower the energy conversion efficiency of the IGCC system by 13 ~ 24%, increasing the cost of electricity by 25% ~ 45% 9, 13, 21, 22, 23. The efficiency loss mainly result from the large steam consumption for water gas shift reaction, heating and cooling of the CO₂ separation solvent, and power consumption for CO₂ compression.

1.1.3. Oxy-combustion Capture

The oxy-combustion capture was first proposed by Horn and Steinberg in 1982 24. In the oxy-combustion scheme, coal is combusted with almost pure oxygen (~95%) instead of air and a fraction of the flue gas is recycled to the coal boiler to moderate the combustion temperature. This is due to the current materials that are not capable to withstand the high temperature combustion with pure oxygen 3. Unlike the conventional PC power plant where CO₂ is diluted by N₂ in the air, the flue gas from oxygen-combustion contains mainly CO₂ and steam. The latter can easily be condensed out, resulting in concentrated CO₂ stream. Figure 1.1 (c) shows the oxy-combustion capture process. In the oxy-combustion technology for CO₂ capture, Air Separation Unit (ASU) is one of the key factors for efficiency loss and capital investment. For instance, about 230 kWh of electricity is consumed in order to produce 1 ton of oxygen when a cryogenic air separation unit is used 25.

Compared to the conventional PC boiler, the oxy-combustion boiler is more efficient due to the usage of pure oxygen in the combustion. Because of the decreased the concentration of inert gas
(N\textsubscript{2}) in the boiler, the combustion temperature enhanced and leads to more efficient combustion. However, the overall efficiency loss for oxy-combustion capture is estimated to be 20 – 35\%\textsuperscript{11,12}. Nearly, three quarters of energy loss comes from the operation of ASU for oxygen generation, and the increase of cost of electricity is nearly 46\%\textsuperscript{12}. The first oxy-fuel demonstration plant (30 MW) has been open in Schwarze Pumpe, Germany. A larger scale demonstration (200-300 MW) is planned by 2015\textsuperscript{25}. However, the needs to increase the ASU efficiency and reduce the ASU cost pose main challenge for the commercialization of oxy-combustion system. Moreover, improvement in furnace material and temperature control and safe oxygen handling are also important for reliable oxy-combustion plant operation. Novel oxygen production technologies are being developed to reduce the capital and operating cost for oxygen production. These technologies include ionic transport membrane (ITM) and ceramic autothermal recovery (CAR)\textsuperscript{3}.

1.2. Chemical Looping Combustion Process for CO\textsubscript{2} Capture

The chemical looping process is a novel concept that separates CO\textsubscript{2} in a more efficient way during the energy conversion process using metal oxide as an oxygen carrier. The metal oxides are reduced, while oxidizing the carboneous fuels like natural gas, syngas, biomass or coal, and then transported to another reactor to perform the combustion reaction with air as the reduced metal regains the oxygen to regenerate the metal oxide. The combustion reaction of metal with air is an exothermic reaction, resulting in a hot flue gas, which can be used for the power generation. Throughout the reactions in two different reactors of chemical looping combustion, the separation of high purity CO\textsubscript{2} and energy conversion are achieved, simultaneously in two different reactors. Thus, no energy is required for the separation of CO\textsubscript{2} since it is inherently separated from the flue gases. Equations 1.3 and 1.4 represent the schematic reactions in the first and second reactors of chemical looping process, respectively. Figure 1.3 shows the process diagram of chemical looping process.
MeO + C\textsubscript{x}H\textsubscript{y} \rightarrow CO\textsubscript{2} + H\textsubscript{2}O + Me \quad (1.3)

Me + Air/O\textsubscript{2} \rightarrow MeO + Heat \quad (1.4)

When the chemical looping process is analyzed using previous carbon capture technological views discussed in the previous section - post, pre, and oxy-combustion, it would be categorized into both pre-combustion and oxy-combustion captures. In the chemical looping process, the carbon in the fuel is completely segregated and purged out from the system prior to the air combustion of metal in the second reactor. Then, the most of carbon in the fuel is released as highly concentrated CO\textsubscript{2} form from the first reactor. The separation of carbon before the combustion with air represents a similar strategy as the pre-combustion separation technology using gasification. However, the chemical looping process achieves the pre-combustion separation of carbon without a water-gas shift reactor used in the pre-combustion technology. As it has been mentioned in the earlier section, this unit in the gasification process is known to be highly energy intensive and require large capital investment\textsuperscript{12}. In addition, the chemical looping process requires no gas-gas separation step comparing to the post-combustion, since the combustion and CO\textsubscript{2} emission occur in different reactors.

Furthermore, the oxidation of carboneous fuels occurs through the oxygen obtained from the metal oxides at high temperature in the chemical looping process, instead of using combustion air or pure O\textsubscript{2} from the ASU. Because the carboneous fuel is not exposed to air at high temperature, the thermal NO\textsubscript{x} in the resultant gases is almost suppressed\textsuperscript{27}. Comparing to the oxy-combustion technology for CO\textsubscript{2} capture, the fuel oxidation with oxygen provided by the metal oxide yields high concentration of CO\textsubscript{2} (~99%) with eliminating the additional CO\textsubscript{2} separation step and an expensive ASU.
1.3. Thesis Overview

As an alternative way of capturing CO$_2$, the chemical looping combustion technology for the solid fuels, such as coal and biomass conversion using Fe-based oxygen carrier particle is introduced in this thesis. The details of reaction scheme and the particle performance experiments are discussed. Chapter 2 overviews the chemical looping process and introduces the Solid Fuel Direct Chemical Looping (SDCL) process with the strategy of efficient conversion solid fuels. Chapter 3 focuses on the experimental work to test the capability of oxygen carrier particle in the various conditions. Chapter 4 further discusses the reactor designs along with future demonstration project. Lastly, Chapter 5 concludes the thesis with future plan.
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<tr>
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<td>$/tCO₂ Transported</td>
</tr>
<tr>
<td>CO₂ Storage</td>
<td>0.1 - 0.3</td>
<td>$/tCO₂ Injected</td>
</tr>
<tr>
<td>(Geological Sequestration)</td>
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Table 1.1. Cost of CCS Technology.
<table>
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<th>USCPC</th>
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<td>Base Case Efficiency (%) HHV</td>
<td>33 ~ 37</td>
<td>37 ~ 40</td>
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Table 1.2. Energy Conversion Efficiencies (HHV) of Various Pulverized Coal Combustion Power Plants and Energy Penalty for CO₂ Capture using MEA. ⁸ ⁹ ¹⁰ ¹¹ ¹² ¹³ ¹⁴.
<table>
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<tr>
<td>Cost of Electricity Increase (%)</td>
<td>66.45</td>
<td>42.15</td>
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Table 1.3. Increase in cost of electricity for CO$_2$ capture using MEA.
Figure 1.1. Existing Carbon Capture Processes A. Post-Combustion, B. Pre-Combustion and C. Oxy-Combustion.
Figure 1.2. MEA System for CO₂ Capture.
Figure 1.3. Schematic Diagram of Chemical Looping Combustion Process.
Chapter 2: Process Development of Solid-Fuel Direct Chemical Looping

2.1. Literature Review

2.1.1. History of Chemical Looping

As an alternative method of carbon capture from the fossil fuel combustion, the chemical looping combustion process has been developed. The principles of chemical looping were first introduced between the late 19th century and the early 20th century as a route of H\textsubscript{2} production. Howard Lane from England was one of the first researchers who conceived the chemical looping concept\textsuperscript{28}. He initialized the strategy of steam-iron process to produce large volume of cheap H\textsubscript{2} in 1903 for aerial operations\textsuperscript{28,29}. The steam-iron process generated H\textsubscript{2} with an aid of chemical intermediates, Fe\textsubscript{3}O\textsubscript{4} and FeO through a series of reaction schemes including steam. Equations 2.1 and 2.2 represent the steam-iron process proposed by Lane.

\begin{align*}
\text{Fe}_3\text{O}_4 + \text{CH}_4 & \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{FeO} \quad (2.1) \\
\text{FeO} + \text{H}_2\text{O} & \rightarrow \text{H}_2 + \text{Fe}_3\text{O}_4 \quad (2.2)
\end{align*}

His first commercial unit was constructed in 1904 and his plants throughout in the Europe and the United States were capable to annually produce 850 million cubic feet of H\textsubscript{2} by 1913\textsuperscript{28}. Followed by the Lane’s invention, German scientist, Messerschmitt introduced the simplified version of H\textsubscript{2} generation\textsuperscript{29}. Later, in 1960’s and 1970’s, the further researches on the steam-iron process had been performed with the government supports in the United States. These researches generally focused on the process integration, oxygen carrier development and the reactor design for the
The steam-iron process only partially converts the reducing gas and oxygen carriers. Moreover, the iron based looping medium shows poor recyclability, especially with the presence of sulfur from the fuel \(^{28,30,31,32}\). With the introduction of less costly hydrogen production techniques later in the 1940’s, the steam-iron process became less competitive and was discontinued.

Besides \(\text{H}_2\) and power, the idea of chemical looping was adapted to produce different types of product. Lewis and Gilliland used the chemical looping process to obtain pure \(\text{CO}_2\) for the beverage industries. According to their patent filed in 1954, carbon based fuels such as coal and natural gas were burned with copper oxides to produce carbon dioxide \(^{33}\).

**2.1.2. Recent Study of Chemical Looping**

The chemical looping process started to regain its attention with efficient energy conversion and low carbon capture penalties prompted in 1980’s. Starting with the studies done by Richter and Ishida in 1980’s, researchers began to consider the chemical looping process for the power generation using natural gas as a feedstock \(^{34,35}\). Heat released from the combustion of natural gas with metal oxide particle was utilized to operate the turbine. Ishida and et al., Andedenen et al. and McGlashan perform the thermodynamic analysis on the chemical looping process concluding that it achieves higher efficiencies compared to other novel power generation systems such as IGCC and \(\text{H}_2/\text{O}_2\) fired high temperature steam cycle system \(^{35,36,37}\). Especially, McGlashan points out that the conventional internal combustion engine is operated at unusually high temperature, which causes the departure from the equilibrium, but the chemical looping combustion occurs without excessive temperature.
The initial laboratory scale work mostly focused on the development of oxygen carriers, since the performance of an oxygen carrier is a very critical factor in the chemical looping process. As the oxygen carrier metal oxide, many researchers studied Co, Ni, Cu, and Fe-based metal oxides and Al₂O₃, MgO, TiO₂, SiO₂, YSZ, clays and spinel structure metals like NiAl₂O₄ and MgAl₂O₄ are explored as supporting metals. For example, Adanez and et. al. prepared total of 240 samples using various metal oxides to determine the optimum particle. The particles were analyzed based on the oxygen capacity, kinetics, and strength. However, the most of these particle studies have been done in a small scale using a thermogravimetric analyzer (TGA) or fixed bed to alter the method of preparation, kinetics and recyclability of particle with gaseous fuels, not considering long-term operation. In order for particle to be used in the process, one must additionally consider the attrition rates during the redox loops, the actual oxygen carrying capacity and the economics of particle, effects of side reactions and pollutants such as carbon deposition, sulfur and ash poisoning.

For the last decade, the chemical looping technology has shown significant advancement from the proof concept to the large scale of process demonstrations. Many research groups all over the world have reported their demonstration unit construction and results. Chalmers University in Sweden operated 10kWth prototype reactor for more than 100 hours using circulating fluidized bed. Lyngfelt and et. al. utilized Ni-based oxygen carrier particle with NiAl₂O₄ supporter. The demonstration result shows that the CH₄ fuel conversion is 99.5% and the outlet stream of reducer achieves greater than 99% CO₂ purity. Additionally, the Korea Institute of Energy Research (KIER) has demonstrated 50kWth chemical looping unit using NiO/Bentonite as an oxygen carrier in 2004. The demonstration results of NiO/bentonite oxygen carrier showed that the system was capable to convert 99.7% of CH₄ with
the presence low concentration of CO and H₂ in the reducer. However, the system was suffered by high attrition rate of oxygen carrier particle. With the replacement of oxygen carriers by Co₃O₄/CoAl₂O₄, the system was operated for more than 25 hours with high fuel conversion (99.6%), and it was observed that the emission of NOₓ was negligible during the oxidation of particle with air in the riser ⁴².

2.1.3. Application of Solid Fuels in Chemical Looping

The recent study of chemical looping process discusses about direct application of solid fuels such as coal and biomass in the reducer instead using gaseous fuels ⁴³, ⁴⁴, ⁴⁵, ⁴⁶, ⁴⁷, ⁴⁸, ⁴⁹, ⁵⁰, ⁵¹. Because of low cost and abundant source of solid fuels, the process is expected to be more economically feasible.

Sold-fuel Direct Chemical Looping (SDCL) has been proposed using an iron-based composite particle to directly convert the solid fuels into valuable energy carriers, like H₂ and electricity through an iron reduction/oxidation reaction scheme. In this thesis, the study will focus on the heat generation rather than H₂. As it has been discussed so far, most of the process development of chemical looping processes has focused on the conversion of gaseous fuels, such as syngas and natural gas. However, due to the unstable natural gas prices and the large capital requirements of gasifier for the syngas generation, a system that utilizes the chemical looping scheme to directly convert solid fuels provides the prospective of more economical attractiveness. Abundant reserve of coal in the United States and utilization of unrealized biomass would make SDCL process be more promising technology in the near future. Compared to fossil fuel, biomass conversion is less carbon and pollutant intensive. Moreover, it is widely distributed and abundantly available. For instance, the annual biomass potential from forest and agricultural resources alone is over 1.3 billion dry tonnes in the United States, which is sufficient to displace nearly 40% of the
petroleum consumed in the nation. Therefore, biomass has the potential to be a favorable energy source to, at least partially, address the increasing environmental and energy sustainability concerns. The proposed SDCL is configured to directly convert the coal and biomass for H2/power generation with effective CO2 capture. The process consists of three main reactors, i.e. a reducer, oxidizer and combustor. Figure 2.1 shows the schematic process diagram of SDCL. The reducer converts the solid fuels into CO2 and H2O, while reducing the Fe2O3 oxygen carriers to a mixture of Fe and FeO. Then, the reduced iron particles are transferred to the combustor to produce heat as they react with air and are oxidized back to Fe2O3. The combustor serves to fully oxidize the composite particles to Fe2O3, which are pneumatically conveyed back to the reducer to complete the cycle of the particles. The reducer is a moving bed reactors with a countercurrent gas-solid contacting pattern whereas the combustor is an entrained riser. Equation 2.3 and 2.4 shows the reaction occurring in the reducer and combustor, respectively.

\[
\text{C}_x\text{H}_y \text{ (Solid fuels)} + \text{Fe}_2\text{O}_3 \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{Fe}/\text{FeO} \quad (2.3)
\]

\[
\text{Fe}/\text{FeO} + \text{Air}/\text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 \quad (2.4)
\]

As it is seen Figure 2.2, the reactions in the reducer can be separated into three sections; 1. devolatilization of solid fuel near the entrance, 2. particle reduction by volatiles in the upper section and 3. char gasification followed by the particle reduction in the lower section. When the solid fuel enters the reactor at high temperature, the solid fuel is quickly devolatilized, releasing the gaseous volatiles and forming carbon-rich char. The gaseous volatiles are generally hydrocarbons that can be used to reduce the oxygen carriers in the Section 1 in Figure 2.2. On the other hand, the carbon-rich char is carried down to the Section 2 in Figure 2.2 along with the oxygen carriers coming from the Section 1. Then, the oxygen carriers are further reduced by the char in the Section 2. However, the reaction between Fe2O3 and the char is a fundamentally
slow solid-solid reaction, which can be the rate-determining step of the process. There are three different strategies proposed to enhance the oxidation of solid fuel and the reduction of metal oxygen carrier.

Firstly, in order to overcome the slow kinetics of char conversion, it is proposed that a small portion (<5% of stoichiometric ratio based on the carbon flow) of the CO₂ and H₂O from the exhaust stream of reducer can be used as a char gasification enhancer. Once the gasification enhancers are introduced along with the solid fuels to the reducer, reactive reducing gases are formed and they reduce the oxygen carrier in more effective way. Figure 2.3 represents the chain reaction of CO₂ increment initiated by the injection of CO₂ and H₂O in the reducer reactor. The following chemical reactions represent the mechanism of reactions in the reducer. Equations 2.5 and 2.6 are char gasification and Equation 2.7 is the reaction of particle reduction, derived from the char gasification.

\[
\begin{align*}
\text{CO}_2 + \text{C (Char)} & \rightarrow 2\text{CO} & (2.5) \\
\text{H}_2\text{O} + \text{C (Char)} & \rightarrow \text{CO} + \text{H}_2 & (2.6) \\
\text{CO} + \text{H}_2\text{O} + \text{MeO}_x & \rightarrow \text{MeO}_{x-2} + \text{CO}_2 + \text{H}_2\text{O} & (2.7)
\end{align*}
\]

The second strategy is to use the indirect gasification enhancer, such as H₂. As the small amount of H₂ is introduced into the reactor, the chain reaction is initiated. The chain reaction scheme by indirect enhancer is shown in Figure 2.4. The metal oxide particle is reduced to produce H₂O as it reacts with H₂, then, H₂O gasifies the char resulting more reducing gases. The disadvantage of indirect gasifier is that possible valuable product, H₂ is used as an oxygen carrier.

\[
\text{H}_2 + \text{MeO} \rightarrow \text{Me} + \text{H}_2\text{O} & (2.8)
\]
\[ \text{H}_2\text{O} + \text{C} \rightarrow \text{CO} + \text{H}_2 \quad (2.9) \]

Last strategy of solid fuel application in the chemical looping process is “oxygen uncoupling”, two-staged oxidation process of solid fuel, proposed by Lyngfelt and Mattioson and Cao \(^{44, 45}\). The oxygen carrier with metal oxide releases gaseous oxygen at high temperature and the solid fuel reacts with the oxygen to produce CO\(_2\) and H\(_2\)O.

\[ \text{Me}_x\text{O}_y \rightarrow \text{Me}_x\text{O}_{y-2} + \text{O}_2 \quad (2.10) \]
\[ \text{C}_x\text{H}_y + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad (2.11) \]

Thermodynamic and experimental studies show that Mn\(_2\)O\(_3\)/Mn\(_3\)O\(_4\) and CuO/Cu\(_2\)O are the most promising candidates for the oxygen uncoupling process \(^{45}\). However, these metals that are active in the oxygen uncoupling obtains very low oxygen carrying capacity. Also, the low partial pressure of O\(_2\) in the system brings the kinetic limitation compared to the direct gasification process using CO\(_2\) and H\(_2\)O.

2.2. SDCL Process Development

2.2.1. Particle Selection Criteria

An ideal oxygen carrier particle in the SDCL process must possess 1. high oxygen transfer capacity with high melting points, 2. strong physical strength causing low attrition rate, 3. good reactivity with solid fuels, 4. good recyclability, 5. high tolerance toward contaminants such as ash, sulfur and mercury, 6. good chemical properties (minimum side reactions, i.e. carbon deposition, and CO and H\(_2\) formation), 7. efficient and easy energy management, 8. manageable solid loading and handling rates, and 9. economical prices for the mass production. Fe-based
metal oxide is chosen as the most suitable oxygen carrier for the conversion of solid fuels among other potential candidates.

As an oxygen carrier in the SDCL, many metal oxides such as Fe, Ni, Cu, Co, Mn, W, Mo, Cr, V, Ce, In, and Sn-based oxides can be explored. First of all, the melting points of these metals are considered. Among these metals, Mo, Cr, V, Ce, In and Sn have relatively low melting points and they are most likely to be sintered or agglomerated during the redox reactions, which causes the difficult solid handling at high temperature. Therefore, these metals are eliminated from the consideration. Also, the prices of metal are considered. Table 2.1 summarizes the price of various metals.

Next, the oxygen carrying capacities of metals are studied. Figure 2.5 compares the oxygen capacities of various metals, and Fe has the highest oxygen contents, when Fe₂O₃ is converted to Fe. As it is seen in Figure 2.5, because Mn has higher molecular weight than other metals, they require higher solid flow circulations. The oxygen transfer capacity represents the maximum available oxygen in the metal oxide. For example, in terms of weight change of Fe₂O₃ to Fe, the maximum conversion is 30.06%. In other words, when Fe₂O₃ is reduced, the solid weight is decreased by 30.06%. As the inert supports are added, the oxygen capacity linearly decreases. A higher oxygen transfer capacity of the particle yields a lower particle holdup in the reactors and hence, reduces the reactor size. Moreover, H₂ or heat production rate can be maximized with the high oxygen capacity of particle. It is determined mainly by the choice of the primary metal oxide and its reduced form. Addition of supporting metals as inert such as Al₂O₃, TiO₂, SiO, YSZ and etc. used in preparation of oxygen carrier also helps maximize the oxygen transfer capacity. Based on the consideration of oxygen carrying capacity, Fe, Ni, Co and Cu were selected as candidates of oxygen carriers for the SDCL.
Among these final candidates, NiO is widely used in the chemical looping process by many researchers and often referred to as the ideal oxygen carrier since it has high melting points and acceptable oxygen carrying capacity. Also, it shows good kinetics with CO or H₂, 49, when compared to Fe₂O₃. The use of NiO as an oxygen carrier in the chemical looping combustion process with gaseous fuels can reduce the size of reducer. However, SDCL is limited by the rate of char gasification with the oxygen carrier. As mentioned, the rate-determining step of SDCL is the solid-solid reaction between char from the solid fuels and metal oxide. The reduction rate of metal oxide becomes insignificant factor in the process development 51. Therefore, the oxygen carrier and the char are mainly converted via the following reactions with the presence of CO₂ or H₂O similar to Equation 2.5 ~ 2.7.

\[ \text{H}_2\text{O}/\text{CO}_2 + \text{C} \rightarrow \text{CO} + \text{H}_2/\text{CO} \]  \hspace{1cm} (2.12)  

\[ \text{MeO} + \text{H}_2/\text{CO} \rightarrow \text{Me} + \text{H}_2\text{O}/\text{CO}_2 \]  \hspace{1cm} (2.13)  

For metal oxides such as NiO and Fe₂O₃ reaction 2.13 is much faster than reaction 2.12. As it has been mentioned earlier, CO₂ or H₂O enhances the solid-solid reaction rate. Therefore, with the presence of CO₂ and H₂O, the reaction rate between NiO and char is similar to that between Fe₂O₃ and char although NiO reacts faster with CO and H₂ than Fe₂O₃. In the SDCL, the advantage of NiO in reactivity with reducing gases is ignored when applied to the chemical looping combustion of solid fuels, because the overall reaction is strongly controlled by the char gasification.
2.2.2. Reactor Configuration

The SDCL process maximizes the competence of the chemical looping combustion process via improvements in the particle performance, reactor design, and energy management. The SDCL system consists of two main reactors; a reducer and a combustor. A counter-current moving bed design is adapted for the reducer. In the moving bed, the solids travel downwards by gravity, whereas the gases flow upwards against solid flows in the reactor. The purpose of using a moving bed system over the fluidized reactor system or fixed bed, which is the most popular reactor system used in the industries is that it provides a condensed reactor size along with greatly improved particle conversion. In a fluidized bed system, thermodynamic and kinetic limits constraint reducibility of Fe₂O₃ to only Fe₃O₄, but the moving bed configuration yields the most reduced metallic iron, Fe.

Thermodynamic analysis evaluates the optimum performance of a given reactor design. With the ASPEN® plus model based on Gibbs free energy calculation, the optimum performances of two different reducer configurations (counter-current moving bed and fluidized bed) are obtained and are listed in Table 2.2. A counter-current moving bed is represented as a counter-current PFR reactor and CSTR reactor represents a single stage fluidized bed.

Figure 2.6 illustrates the equilibrium iron-gas-carbon system as a function of gas compositions and temperature. For example, the wustite (FeO) is the most stable form when the compositions of CO and CO₂ are 60% and 40%, respectively at 900°C. In this environment, magnetite (Fe₃O₄) and hematite (Fe₂O₃) will be reduced to wustite and metallic iron (Fe) will be oxidized to wusitite. In order for wustite to be reduced to metallic iron, the temperature must be reduced at the same gas composition, moving the equilibrium system to the parallel left or increase the CO
concentration (decrease the CO₂ concentration), forcing the system upward. The composition of H₂ and H₂O also affects the iron oxidation state in the similar manner as CO-CO₂. Similarly, the equilibrium line of CO-CO₂ composition represents the status of carbon in the system. At low temperature, CO₂ becomes more stable gas species than CO, thus, the carbon soot is formed by the Boudouard reaction. With the consideration of carbon equilibrium, the SDCL must be operated on the right side of carbon equilibrium line.

Based on the thermodynamic analysis using Figure 2.6, it shows that the counter-current moving bed reactor system is capable to achieve higher concentration of CO₂ and H₂O at the exit with high conversion (reduction) of iron particle. If the system is operated at 900°C, the hematite can be reduced to metallic iron in the counter-current moving bed. Since the counter-current moving bed is considered as PFR reactor, and gases flow in the opposite direction of solid, the relation between gas composition and iron status is considered independent. Thus, the hematite from the solid inlet would travel the equilibrium graph vertically in Figure 2.6 at any given temperature independently from the gas compositions. At the same time, the gas composition will reach the bottom of equilibrium in Figure 2.6, resulting high concentration of CO₂ and H₂O. However, in case of fluidized bed, the system would reduce the hematite to magnetite and produce lower concentration of CO₂ and H₂O. Because the fluidized bed is considered as CSTR reactor, solid iron particle and reactant and product gases are well-mixed in the system. For the high concentration of CO₂ and H₂O, the hematite particle reaches only magnetite state. If the higher particle reduction is required, then the system causes the significant decrease of CO₂ composition or temperature increase to the unreasonable range. At 900°C of fluidized bed, wusitite is produced in 80% CO₂ and 20% CO, which requires excessive fuel use.
The simulation results confirm that Fe₂O₃ composite particle under counter-current moving bed configuration delivers better overall reducer performance due to high oxygen carrier capacity and low CO and H₂ formation. Unlike the maximum oxygen carrying capacity discussed in Table 2.1, the effective oxygen carrying capacity shown in Table 2.3 takes into account the metal oxide loading as well as the maximum achievable oxygen carrier conversions due to the thermodynamic limitations. Therefore, it is a better indicator of the actual oxygen carrying capacity of the particle. However, the effective oxygen carrying capacity is a complicated parameter affected by particle type, reactor design, type of fuel to be converted, metal oxide loading etc.

2.2.3. Fate of Pollutants

Although the direct oxidation of solid fuels by oxygen carriers in the SDCL provides advantages in terms of plant efficiency and economics by simplifying the reaction scheme, the SDCL must deal with pollutants such as sulfur, ash and mercury in the solid fuels, because the particle is directly exposed to the pollutants in the solid fuels, especially coal. A simulation was conducted using ASPEN® to study the cycle of sulfur in the SDCL. The ASPEN® simulation predicts that sulfur contained in the coal will react with Fe₂O₃ in the reducer to form FeS the solid phase and H₂S and SO₂ in the gas phase. FeS will be carried over to the combustor. The sulfur in the FeS particle is emitted as SO₂ from the combustor, as it reacts with air. Figure 2.8 below summarize the sulfur distribution in the gas and solid products at 900°C and 1 bar. The results show how sulfur in coal is distributed in the products including the oxygen carrier and resultant gases, as the molar flow rate ratio of Fe₂O₃ in the oxygen carrier and carbon in the coal feedstock (m) varies. Generally, the major products are H₂S, SO₂ and SO₃ in the gas streams and FeS in the solids. At the low oxygen carrier flow rate (m<1), the reducer produces CO and H₂ instead of CO₂ and H₂O and this reductive environment in the reducer results in 54.4% of the sulfur content from the coal forming FeS, whereas most of the remaining sulfur exits the reducer as H₂S as well as a small
amount of SO₂. As m approaches 1.27, the coal is fully converted, the amount of H₂S drops, and more SO₂ starts to appear. The sulfur distribution in the gas products gradually changes from 45.6% of H₂S to 45.6% of SO₂/SO₃. This transition is mainly due to the more oxidative environment in the reducer caused by the full conversion of carbon. Continuing to increase oxygen carrier flow rate shifts the sulfur distribution from the solid phase to the gas phase. For example, when m reaches 2.53 producing FeO as a reduced oxygen carrier, the sulfur distribution in Fe₀.₈₇₇S decreases from 54.4% to 20.14%, and the share of SO₂ significantly increases. Furthermore, no FeS is produced at extremely high values of m (m>6.81), because all the sulfur is gasified with the excessive oxygen carrier. During these stages, 99.98% of sulfur comes out as SO₂ and 0.02% as SO₃. For the sensitivity test, the sulfur distribution in the gas phase changes from 45.58% SO₂/0.01% SO₃ to 79.85% SO₂/0.01% SO₃ and then to 99.98% SO₂/0.02% SO₃. Those transition points are highlighted in the Figure 2.8.

Additionally, ash from the solid fuels can be fatal factor for the SDCL process. At high temperature, ash becomes sticky and attaches to the oxygen carrier particles. Qiu and et. al reports that the softening temperature of coal ash varies depending on the types of coal, but generally the softening of ash is observed around 1000°C ~ 1300°C. The fusion temperature can be altered by mixing different types of coal in the process. Once the ash is attached, the porosity of oxygen carrier may be significantly reduced, causing the deactivation. Since the particles size (>0.71 mm) in the SDCL process is much larger than the size of pulverized coal (50–250 µm), ash is proposed to be separated from the composite particles based on size difference using a cyclone.
<table>
<thead>
<tr>
<th>Metal</th>
<th>Price</th>
<th>Unit (2007)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cobalt</td>
<td>54,600</td>
<td>US $/ton</td>
</tr>
<tr>
<td>Zinc</td>
<td>3,400</td>
<td>US $/ton</td>
</tr>
<tr>
<td>Nickel</td>
<td>37,200</td>
<td>US $/ton</td>
</tr>
<tr>
<td>Magnesium</td>
<td>4,960</td>
<td>US $/ton</td>
</tr>
<tr>
<td>Iron Ore</td>
<td>59.6</td>
<td>US $/ton</td>
</tr>
<tr>
<td>Copper</td>
<td>7,231</td>
<td>US $/ton</td>
</tr>
<tr>
<td>Manganese</td>
<td>1,190</td>
<td>US $/ton</td>
</tr>
</tbody>
</table>

Table 2.1. Price of Various Metals. \(^{59}\)

---

29
Table 2.2. Reducer performances using different reactor design and oxygen carrier particles

<table>
<thead>
<tr>
<th>Reactor Type</th>
<th>Counter-current RFR</th>
<th>CSTR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen carrier</td>
<td>Fe$_3$O$_4$</td>
<td>Fe$_3$O$_4$</td>
</tr>
<tr>
<td>CO$_2$ enhancer percentage(^*) (mol %)</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Maximum metal oxide conversion(^#) (%)</td>
<td>68.11</td>
<td>11.27</td>
</tr>
<tr>
<td>Effective oxygen capacity(^!) (wt %)</td>
<td>14.30</td>
<td>2.37</td>
</tr>
<tr>
<td>CO+H$_2$ in gas exhaust (%)</td>
<td>0.005</td>
<td>0.005</td>
</tr>
</tbody>
</table>

\(^*\)-Molar flow rate of char gasification enhancer (CO$_2$)/Molar flow rate of carbon in the coal $\times$ 100%;
\(^#\)-Maximum metal oxide reduction at 900 °C with 100% coal is converted (based on Illinois #6 coal);
\(^!\)-Effective oxygen carrying capacity = Maximum oxygen carrying capacity of the pure metal oxide $\times$ Metal oxide loading $\times$ Maximum theoretical metal oxide conversion.
Figure 2.1. Schematic Process Diagram of SDCL Process.
Figure 2.2. Reaction Mechanism in Reducer.
Figure 2.3. Chain Reaction Scheme by Direct Gasification Enhancer.

\[
\begin{align*}
H_2O + C & \rightarrow H_2 + CO \\
CO_2 + C & \rightarrow 2CO \\
3CO + H_2 + FeO_x & \rightarrow 3CO_2 + H_2O + FeO_{x-4} \\
H_2O + C & \rightarrow H_2 + CO \\
3CO_2 + 3C & \rightarrow 6CO \\
7CO + H_2 + FeO_x & \rightarrow 7CO_2 + H_2O + FeO_{x-7} \\
\vdots
\end{align*}
\]
Figure 2.4. Chain Reaction Scheme by Indirect Gasification Enhancer.
Figure 2.5. Oxygen Carrying Capacity of Various Metal Oxides
Figure 2.6. Thermodynamic Limits of Fe/FeO/Fe$_3$O$_4$/Fe$_2$O$_3$ as a Function of Temperature and Gas Partial Pressures.
Figure 2.7. Fate of Sulfur in the SDCL Process.
Figure 2.8. Sulfur Distribution at 900°C and 1 bar.
Chapter 3: Feasibility Tests of Solid Fuel Direct Chemical Looping

3.1. Preliminary Oxygen Carrier Test

Fe$_2$O$_3$-based composite particle is prepared in both pellet and particle forms for the similar to that described in Li et al. and Gupta et al. 63, 65. The composite particle contains 60 wt. % of Fe$_2$O$_3$ and 40 wt. % of supporters (TiO$_2$ and Al$_2$O$_3$). The pellets are cylindrical shape with 5 mm diameter and ~2 mm height, pelletized from ~100µm powder.

As the preliminary tests to observe the particle’s physical and chemical capabilities, three tests are performed. Firstly, Fe$_2$O$_3$-based composite particle is tested in a thermogravimetric analyzer (TGA) to measure the reducibility using different reducing gases such as H$_2$, CO, CH$_4$ and C$_3$H$_8$. The second TGA experiment tests the recyclability of oxygen carrier in the redox reaction using H$_2$ and air. The particle undergoes five redox cycles. Lastly, the pellets are prepared and its crushing strength is measured to estimate the attrition rate of particle in the system.

3.1.1. Oxygen Carrier Reduction

Experimental Procedures

A Setsys System TGA by Setaram is used to characterize the reducibility of Fe-based oxygen carrier. The schematic diagram of TGA system is described in Figure 3.1. Powder samples are used and the reductions by H$_2$, CO, CH$_4$ and C$_3$H$_8$ are compared for these tests. Approximately 50 mg of particle is loaded in the crucible and the gas flow rates are set to be 35 mL/min and 50 mL/min for He carrier gas and reducing gas, respectively. The TGA is then heated to 900°C and
recorded the weight change of particle. Because the weight loss of Fe$_2$O$_3$-based oxygen carrier is nearly proportional to the level of its reduction, the reactivity of particle can be quantified. Figure 3.1 shows the diagram of TGA set-up.

Results and Discussions

Figure 3.2 shows the reactivity of particle in the various reducing gases. As can be seen, H$_2$ poses the fastest reactivity among these reducing gases whereas CO shows very slow reduction rate. In Figure 3.2, H$_2$ almost fully reduces the Fe$_2$O$_3$ within 5 minutes and stabilized around 82 weight %, which represents metallic iron. The weight loss of CO reduction indicates only 12 wt. % decrease after 30 minutes of reaction. The weight change of Fe$_2$O$_3$-based composite particle can be calculated using Equation 3.1 and Equation 3.2.

\[
weight \% = \frac{x + y}{x_i + y} \quad (3.1)
\]

\[
y = \frac{x_i}{0.6} \times 0.4 \quad (3.2)
\]

Here, y is the weight of supporting metals, which is 40 wt. % of total initial weight, and $x_i$ represents the initial weight of Fe$_2$O$_3$ and x is the final weight of sample. Using these equations, when the composite particle with 40 wt. % supporters is fully reduced to Fe from Fe$_2$O$_3$, the weight change should be 81.8%.

On the other hand, the particle reduction using hydrocarbons such as CH$_4$ and C$_3$H$_8$ indicates unusual behavior showing weight increase after a certain point. The weight gain of iron sample is due to the carbon deposition on the surface of particle. The equation for carbon deposition by CH$_4$ is shown in Equations 3.3. Metallic characteristics of oxygen carrier can accelerate the
carbon deposition. The strategy to reduce the carbon deposition has been discussed in literatures. The presence of CO₂ or H₂O in the system reduces the rate of carbon deposition by it gasifies the carbon.

\[ \text{CH}_4 \rightarrow \text{C} + \text{H}_2 \]  (3.3)

3.1.2. Oxygen Carrier Recyclability

*Experimental Procedures*

A Perkin Elmer (Model: Pyris 1) TGA is used to carry out the recyclability tests of Fe-based oxygen carrier. The schematic diagram of TGA system is described in Figure 3.4. Powder samples are used for the recyclability test with H₂ and air. Approximately 40mg of particle is loaded in the crucible and the gas flow rates are set to be 50 mL/min and 80 mL/min for H₂ and air, respectively. Flow rate of N₂ is 110 mL/min and the N₂ flows into the TGA all the time to flush the system between reductions and oxidations. The TGA is then heated to 900°C and records the weight change of particle for 5 redox cycles.

*Results and Discussions*

An ideal oxygen carrier particle for the SDCL process possesses good reactivity and recyclability. Good kinetic reduces the residence time of particle in the moving bed while increased recyclability minimizes the particle make-up rate. As can be seen in Figure 3.3, the oxygen carrier is capable to be fully reduced and oxidized during 5 cycles.

After 15 minutes of reaction, the final conversion is read from Figure 3.3. The conversion of the particle after each reduction or oxidation step, which can be derived from Figure 3.3, is used to
characterize its reactivity. Figure 3.4 illustrates the reactivity change of the particle. The conversion \( y \) is calculated using the following equation.

\[
y = \frac{x_i - x}{x_i - x_f}
\]  

(3.4)

Here, \( x_i \) represents the initial weight of fully oxidized sample, \( x \) is final weight and \( x_f \) is the weight of fully reduced particle.

According to Figure 3.4, the particle reactivity is relatively low during the first and second reduction cycles; however, it is stabilized at near 99% after the third cycle. On the other hand, the oxidation rates are relatively steady throughout the 5 cycles. With the superior recyclability and reactivity of particle with \( H_2 \), the Fe-based oxygen carrier particle can be suitable in the SDCL process.

Figure 3.5 shows the recyclability test of commercial-grade \( Fe_2O_3 \) in the same experimental condition. The pure \( Fe_2O_3 \) is fully reduced at the first cycle, but it looses the recyclability afterwards. This phenomenon occurs, because the pure \( Fe_2O_3 \) is sintered and the pore size is reduced resulting failure of oxygen diffusion.

3.1.3. Physical Strength

*Experimental Procedures*

The crushing strength of the cylindrical shaped particles/pellets is determined according to the ASTM D4179 standard using a motorized press stand with a digital pressure transducer (Shimpo FGV-100X). During testing preparation, a pellet was loaded into the press. Next, the
motorized press gradually compresses the pellet in an axial direction. Then, the digital pressure transducer records the pressure at which the pellet is crushed. Figure 3.6 shows the crushing direction of pellet. In order to obtain a reliable mean crushing strength and distribution of the pellet crushing strength, more than 11 pellets were tested.

**Results and Discussions**

Particle needs to be processed in pellet form in order to be used in the SDCL process. Compression based pelletization technique is used to pelletize the particle. Strength of particle is varied from about 100 N/mm to 155 N/mm. After 11 measurements, the average strength is calculated to be 132.2 N/mm. Figure 3.7 shows the pellet strength test result.

3.2. Reaction with Volatiles

For the reaction with volatiles and chars, there are three different solid fuels used, lignite coal obtained from Carbon County, Utah, sub-bituminous Powder River Basin (PRB) coal obtained from Converse County, West Virginia and Japanese pulverized woody biomass prepared from Nagoya University. Table 3.1 summarizes the composition of these solid fuels. Lignite coal from Utah is low rank coal, which contains low carbon and high ash contents. Woody biomass shows the high volatile content (>80%) with very low fixed carbon (<20%) and ash (<1%). The TGA analysis on lignite coal and woody biomass in Figure 3.8 confirms the contents of volatiles. The lignite coal and woody biomass rapidly release the volatile matters around 400°C and 200°C, respectively. All solid fuels are grounded and sieved under ~150 µm

**Experimental Procedures**

For the reactivity test of particles with coal and woody biomass volatiles, a fixed bed with pre-heating function is designed and built. The fixed bed requires pre-heating section for the oxygen
carrier particles, because the Fe-based oxygen carrier particle is more reactive at high temperature (900°C), but coal and woody biomass devolatilization starts to occur at 400°C and 200°C, respectively according to Figure 3.8. In this fixed bed set-up, approximately 30 g of fresh oxygen carrier particle is loaded in the 5/8” quartz tube and pre-heated to the desired reaction temperature (900°C) in N₂ atmosphere. At the same time, the dry coal/woody biomass is loaded on the top section of the quartz tube, which is enclosed by a ball valve and purged with N₂ all the time. Once the reactor reaches the desired reaction temperature, 900°C, the ball valve is open, and coal/woody biomass falls into the quartz tube driven by purged N₂. As soon as the coal/biomass enters the pre-heated section, it is quickly volatilized and the volatile matters are carried by N₂ to react with particle. This experiment mimics the solid fuel injection in the SDCL actual process in Figure 2.1. After the outlet gas passes through the desiccants and cooler to condense out the moisture, the outlet gas is collected in a gas sampling bag (Zefon, Tedlar Sampling bag) during the recorded time for the analysis using the gas chromatography (Varian, Micro CP 4900). Figure 3.9 shows the schematic diagram of fixed bed set-up. The flow rate of N₂ is set to be around 50 ml/min corresponding to approximately 30 seconds of gas residence time within the reaction zone.

Results and Discussions

As a blank experiment, the reactor is heated to 900°C without oxygen carrier particle in the reaction zone, and the coal/woody biomass drops directly into the reactor. The outlet gas is analyzed by GC. The result in Figure 3.10 shows that significant peaks of hydrocarbons including CH₄, C₃ and other hydrocarbons.
The Figure 3.11 shows the coal volatile conversion by the particle. The peak representing CO$_2$ in Figure 3.10 (b) is relatively small compared to that with the presence of particle in Figure 3.11 (b) and hydrocarbon peaks in Figure 3.11 (b) are insignificant with the oxygen carriers.

Table 3.2 summarizes the gas composition of volatile conversions for lignite coal and woody biomass. The results show that most of hydrocarbons, H$_2$ and CO in the volatiles are converted to CO$_2$ and H$_2$O. Especially, most of volatiles from the woody biomass are converted to CO$_2$ showing minimal H$_2$, CH$_4$ and CO in the outlet gas.

Moreover, the iron particle from the fixed bed underwent sulfur analysis using three different methods to study the behavior of sulfur. X-Ray Defractory (XRD) analyzer (Sintag PAD-V), Inductively Coupled Plasma (ICP) analyzer (Teledyne-Leeman Labs, Prodigy) and combustion total sulfur (TS) analyzer (Thermo Scientific, TS 2000) were used for the sulfur detection on the iron particles. However, the XRD analysis indicated no evidence of sulfur formation such as the presence of FeS and elemental sulfur (S). The XRD analysis contained only significant peaks of Fe$_3$O$_4$ and Fe$_2$O$_3$, but, FeS and elemental S have no matched peaks from the XRD database. Many literatures report that the lower detection limit of XRD analysis is around 1~5% depending on the scan rates and models $^{70, 71}$. It is, therefore, likely that the peaks of the sulfur containing species did not show up in the XRD graph due to the relatively low sulfur level.

As a second method for sulfur analysis, ICP analysis is used. For the ICP analysis, the milled iron sample is digested into aqueous solution by adding acids, HNO$_3$ and HClO$_4$. The analysis shows that the sulfur concentration in the iron sample is 31.3 ppm. However, the digestion of iron sample process is difficult to achieve the full digestion because of its very low solubility of iron
The TS analysis using combustion with pure oxygen is applied to measure the sulfur on the particle. The combustion TS analysis represented average of 41.32 ppm level of sulfur on the particle. Three runs are made and the repeatability of analysis varied within +/- 4% error. Because of small sulfur presence is expected during the reduction of iron, the TS by combustion would be appropriate method for the sulfur analysis rather than XRD and ICP analysis. Figure 3.12 shows the combustion sulfur analysis results. As predicted by thermodynamic simulation, sulfur indeed reacts with Fe₂O₃ to form sulfur compounds.

3.3. Reaction with Chars

Experimental Procedures

In the SDCL, the reaction between two solids, oxygen carrier and char, is known to be fundamentally slow reaction. Therefore, the conversion of char acts as a rate-determining step in the SDCL process and it is important to overcome the slow kinetic of solid-solid reaction. There are two experiment set-ups to study the reaction of char and oxygen carrier. In the first experiment, a TGA is used to observe the behavior of solid samples and the fixed bed experiment determines the composition of outlet gas.

TGA Experiment

Firstly, coal/woody biomass char is prepared with the fixed bed in N₂ environment at 800°C. Raw solid fuel is packed in the fixed bed with ~500 mL/min of N₂ and heated to 150°C for drying, then heated to 800°C for 6 hours. After tars and volatile matters are completely removed in the inert environment, the remained char is recovered. Then, the char is dry-mixed with the Fe-based
oxygen carrier particle at six different ratios (i.e. 1:9, 3:7, 5:5, 7:3, 9:1, and 0:10 = Particle:Char). Approximately 50–80 mg of mixture is loaded in a quartz crucible. The TGA (Setaram, Setsys) is flushed with 100 mL/min of inert gas, He and heated to 900°C at the rate of 99°C/min, and kept at 900°C for 60 minutes. The weight change of mixture is recorded. The TGA experiment in the He atmosphere determines the optimum mixing ratio of char powder and oxygen carrier. Then, the optimum sample is compared in the CO₂ atmosphere along with 100% char sample.

**Fixed Bed Experiment**

The fixed bed experiment set-up for the char gasification is shown in Figure 3.15. About 1:2 ratio of char and oxygen carrier is placed on the top of 3–5 g of the oxygen carrier particle packed at the bottom of fixed bed reactor. The purpose of bottom oxygen carrier is to ensure the complete conversion to CO₂. As an inlet gas, ~20 vol.% of CO₂ is introduced along with the balanced N₂ and the outlet gas is constantly monitored with GC (Varian, Micron GC 4900). In order to compare the effect of oxygen carrier on the gasification rate, only char is packed in the same gas flow and the outlet gas is monitored as well. After the experiments, the fixed bed reactor is cooled to room temperature with N₂. Solid samples are taken and characterized in the TGA. The iron particle is oxidized with air and the weight increase is recorded.

**Results and Discussions**

**TGA Experiment**

Figure 3.16, 3.17 and 3.18 show the weight loss of coal/woody biomass char and oxygen carrier mixtures at the elevated temperature in the inert atmosphere. Before analyzing the reaction between oxygen carrier and chars, 100% chars are loaded in the TGA for the blank tests. The TGA experiment shows that 100% char samples also have weight losses. For example, the weight losses recorded are 2%, 5% and 6% for the lignite, PRB and woody biomass chars, respectively.
The weight loss of 100% chars is due to the moisture and a small amount of unconverted volatiles from the preparation in the fixed bed.

As it is seen in Figure 3.16, the mixture of lignite coal char and oxygen carrier achieves the maximum weight loss when the mixing ration of oxygen carrier and char is 7:3. The weight loss starts to be seen when the temperature is around 400°C and the weight loss becomes faster as the temperature increases. After nearly one hour of reaction, the weight of mixture reaches around 90 wt.% of original sample. In Figure 3.17, the PRB coal char samples are analyzed. The PRB coal char obtain the maximum reaction rate, when the mixing ratio of oxygen carrier and char is 5:5. The TGA records the final weight loss of 5:5 sample as approximately 88 wt. %. Lastly, the mixture of woody biomass char and oxygen carrier is analyzed in Figure 3.19. The mixtures with woody biomass show similar behavior as the lignite coal char. The maximum weight loss occur with 7:3 mixing ratio of particle and char, and 5:5, 9:1 and 3:7 of particle:char mixing ratios appear in the same order as lignite coal char mixtures. Because the lignite coal is low-rank coal according to the proximate and ultimate analysis, which has low fixed carbon and high ash content, available carbon for gasification is much less than PRB coal. Also, woody biomass contains low fixed carbon compared to these two types of coal, but the fixed carbon can be more easily accessible than those in the lignite coal char, because much less contaminants that may interfere the interaction with particles are present in the biomass. The TGA experiment reveals that the reaction between oxygen carrier particle and coal char occurs at high temperature, but the reaction rate is extremely slow.

Figure 3.19 compares the weight changes of chars of lignite coal and PRB coal in CO₂ and He atmosphere. In this comparison, both of coal chars show obvious weight differences in different gas environments. The weight loss of solid sample in the CO₂ atmosphere corresponds to the char
gasification by CO₂ and oxygen carrier particle reduction. The lignite coal chars have 4% and 2% weight changes in CO₂ and He, respectively, and the weight loss PRB coal chars increased from 5% to 10% in CO₂ compared to He. The observation of coal chars in CO₂ atmosphere represents that the Boudard Reaction, discussed in Chapter 2, can be valid in the SDCL. The PRB sample with 5:5 mixing ratio, which obtained the maximum weight loss in Figure 3.17, is analyzed in CO₂ environment. The result in Figure 3.21 indicates that the weight loss of 5:5 mixture significantly increases due to the gasification enhancer, CO₂. The weight loss is mainly due to the gasification of coal char by CO₂ and the particle reduction by the resultant gases from the char gasification. The results of TGA experiment imply that the fixed carbon in the char is not fully gasified when it is heated in the inert gas environment, which results insufficient reducing gases for the oxygen carrier reduction. The gasification of char and the particle reduction can be improved by supplying CO₂ into the system, because it increases the local reducing gas concentrations.

**Fixed Bed Experiment**

The purpose of fixed bed experiment is to study the effects of gasification enhancer and oxygen carrier by analyzing the gas compositions from the fixed bed. In Figure 3.21 and 3.22, the CO₂ gasification rate of lignite coal char and PRB coal char is compared with the gasification rate by the oxygen carrier particle. With the oxygen carrier particle mixed with the lignite coal char, the increase of CO₂ concentration is accelerated. The concentration of CO₂ increases up to 32 vol % at 53 minutes into the reaction from the initial concentration 22 vol. %. After CO₂ is produced for about 40 minutes, the size of CO₂ peak decreases and its concentration goes back toward the initial concentration. However, the char gasification without the aid of oxygen carrier particle shows very slow gasification rate in Figure 3.21. The rate of CO₂ concentration increase shown in Figure 3.21 corresponds to 0.0031 min⁻¹. Even after 200 minutes gasification time, the conversion
of CO₂ appears to be very low. In comparison, when the CO₂ concentration reaches the maximum with the oxygen carrier particle, the rate of CO₂ concentration increase is approximately 1.04 min⁻¹.

In addition to the gasification of lignite coal char, the PRB coal char gasification result is shown in Figure 3.22. The PRB coal char is gasified by CO₂ and oxygen carrier with the similar manner as the lignite coal char, but the CO₂ gasification of PRB coal char occurs at faster rate (0.0182 min⁻¹). Similar to the lignite coal char, the CO₂ concentration has a peak and is reduced afterwards. The rate of CO₂ increase by the oxygen carrier is almost 10 times faster than one without the oxygen carrier. However, the char gasification becomes dependent on the gasification by CO₂, because of lack of driving force of gasification provided by oxygen carriers after around 40 minutes. As the char is gasified, the Fe₂O₃-based oxygen carrier supplies oxygen to the gasification resultant gases to produce CO₂ and H₂O. Once the particle is reduced to the certain level due to the char oxidation, the char conversion is not accelerated anymore by the oxygen carrier. Then, the char gasification is strongly dependent on the CO₂ inlet, resulting similar gasification rate as the case without the oxygen carriers. The fixed bed experiment indicates that the gaseous products from the char gasification by CO₂ are reducing agents for the Fe-based oxygen carriers. Also, the local CO₂ concentration increases because of the chain reaction with the particles, the gasification rate becomes faster.

3.4. Oxidation of Oxygen Carrier

*Experimental Procedures*

After the reduction of pellets using H₂ in the fixed bed, air is injected into the reactor at a rate of 150 mL/min to oxidize the reduced pellets. Nitrogen is also introduced during the heating at a flow rate of 300 mL/min. The reaction is carried out at 891°C and 944°C, and the temperature
change of the particle is monitored by a type K thermocouple (Omega Engineering) until the temperature of particle decreased to the initial value. The thermocouple with 1/8 inch O.D. is embedded in the oxygen carrier particle.

Results and Discussions
The temperature change of oxidizing particle is shown in Figure 3.23. For the first experiment, the particle is fully reduced by H₂ and constantly maintained at 881°C until air is introduced. As it is seen in the Figure 3.23, the temperature of particle reaches the maximum of 1072°C. Similarly, the particle temperature goes up to 1079°C, when the initial temperature is 941°C. After the oxidation with air, the particle indicates no signs of agglomeration or sintering, which represents its good recyclability. The fixed bed experiment for the oxidation of particle implies the feasibility of oxygen carriers to produce heat without loosing its activity at high temperature. As the Fe-metallic particle is oxidized, the particle undergoes highly exothermic reaction, producing hot air, which can be utilized for power generation or heat carrier.

As it is seen in Figure 3.23, the combustion in the SDCL occurs around ~1100°C. Many literatures report that the combustion in the chemical looping process is within manageable temperature, unlike the fossil fuel combustion where the temperature reaches up to ~3000°C. Therefore, the chemical looping combustion minimizes the thermal NOₓ formation during the combustion. Figure 3.24 shows the calculated concentration of thermal NOₓ as a function of combustion temperature. The thermodynamic analysis of NOₓ formation shows that the combustion temperature in the chemical looping process produces only small amount of thermal NOₓ, since the combustion is at relatively low temperature. Around 1200~1300 K where the combustion of oxygen carrier occurs, the NOₓ formation is only 2~3% of thermal formation during the normal combustion.
For the calculation of thermal NO\textsubscript{x} formation, Equations 3.5 and 3.6 were considered. Then, the concentrations of NO\textsubscript{x} were calculated using Equations 3.7 and 3.8.

\[
\begin{align*}
\text{N}_2 + \text{O}_2 & \rightarrow 2\text{NO} \quad (k_1) \\
\text{NO} + \frac{1}{2}\text{O}_2 & \rightarrow \text{NO}_2 \quad (k_2) \\
[\text{NO}] & = (k_1[\text{N}_2][\text{O}_2])^{1/2} \quad (3.7) \\
[\text{NO}_2] & = k_2[\text{NO}][\text{O}_2]^{1/2} \quad (3.8)
\end{align*}
\]

Both of reactions in Equation 3.5 and 3.6 are reversible and the equilibrium was found using the minimum Gibbs free energy in Equation 3.9.

\[
k_i = \exp\left(-\frac{\Delta G_i}{RT}\right) \quad (3.9)
\]

3.5. Conclusion

The feasibility of Fe-based oxygen carrier for the SDCL process has been proved. The synthesized oxygen carrier particle is capable to convert the volatiles and char in an effective manner with almost complete CO\textsubscript{2} separation. The gas composition of resultant gases from the volatile and char oxidation by oxygen carrier shows the high concentration of CO\textsubscript{2} with minimal side products such as CO, CH\textsubscript{4} and H\textsubscript{2}. The char conversion can be considerably enhanced by adding gasification enhancing gas, CO\textsubscript{2}. The injection of CO\textsubscript{2} gasifies the char and speeds up the overall gasification rate by raising the local concentration of CO\textsubscript{2} around the char. Also, the experimental studies indicate that the volatile conversion is more significant step for the woody biomass, whereas the coal requires both extensive conversion of volatiles and chars. The combustion of oxygen carrier particle shows the exothermic behavior, which implies that heat from the combustion, can be utilized for the power generation. Because the combustion does not happen in the excessive temperature, thermal NO\textsubscript{x} formation can be minimized.
Table 3.1. Proximate and Ultimate Analysis of Coal and Biomass.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Volatile Matter</th>
<th>C (FC)</th>
<th>H</th>
<th>N</th>
<th>Hg(ppm)</th>
<th>S</th>
<th>Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignite Coal</td>
<td>26.39</td>
<td>41.79(30.13)</td>
<td>2.85</td>
<td>0.73</td>
<td>0.242</td>
<td>2.09</td>
<td>43.48</td>
</tr>
<tr>
<td>PRB Coal</td>
<td>44.15</td>
<td>70.50(49.66)</td>
<td>4.80</td>
<td>0.90</td>
<td>0.06</td>
<td>0.29</td>
<td>6.19</td>
</tr>
<tr>
<td>Biomass</td>
<td>82.77</td>
<td>49.04(16.60)</td>
<td>6.34</td>
<td>0.12</td>
<td>-</td>
<td>-</td>
<td>0.63</td>
</tr>
<tr>
<td>Fuel</td>
<td>Gas Collected (mL)</td>
<td>Initial</td>
<td>Final</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>--------------</td>
<td>-------------------</td>
<td>---------</td>
<td>-------</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>H₂</td>
<td>CH₄</td>
<td>CO</td>
<td>CO₂</td>
<td>N₂</td>
<td>Wt (g)</td>
<td>C (wt%)</td>
</tr>
<tr>
<td>Lignite</td>
<td>0.33</td>
<td>48.29</td>
<td>5.46</td>
<td>167.5</td>
<td>2250</td>
<td>3.0</td>
<td>30.25</td>
</tr>
<tr>
<td>Biomass</td>
<td>0</td>
<td>0.65</td>
<td>0.27</td>
<td>105</td>
<td>2345</td>
<td>0.46</td>
<td>31.12</td>
</tr>
</tbody>
</table>

Table 3.2. Volatile Conversion by Oxygen Carrier Particle.
Figure 3.1. Diagram of TGA Experiment Set-Up.
Figure 3.2. TGA Curve of Particle Reduction Using Various Reducing Gases.
Figure 3.3. Recyclability of Oxygen Carrier Particle.
Figure 3.4. Particle Conversion After 15 Minutes of Reduction/Oxidation Time.
Figure 3.5. Recyclability of Commercial-Grade Fe$_2$O$_3$.
Figure 3.6. ASTM D4179.
Figure 3.7. Particle Strength.
Figure 3.8. Volatilization of Lignite Coal and Woody Biomass in N₂ Environment.
Figure 3.9. Schematic Diagram of Fixed Bed Set-Up for the Volatile Reaction.
Figure 3.10. GC Results for the Blank Experiment.
Figure 3.11. GC Results of Volatile Conversion with Oxygen Carrier Particle.
Figure 3.12. Result of TS.
Figure 3.13. Fixed Bed Set-Up for the Reaction with Char.
Figure 3.14. Lignite Coal Char in Inert Atmosphere.
Figure 3.15. PRB Coal Char in Inert Atmosphere.
Figure 3.16. Woody Biomass Char in Inert Atmosphere.
Figure 3.17. Char Gasification with CO\textsubscript{2} and Comparison with He Atmosphere.
Figure 3.18. Comparison of PRB Coal Char and Oxygen Carrier Mixtures in Different Atmosphere (CO₂ and He).
Figure 3.19. Rates of Lignite Coal Char Gasification with Presence of Oxygen Carrier Particle in CO₂.
Figure 3.20. Rates of PRB Coal Char Gasification with Presence of Oxygen Carrier Particle in He.
Figure 3.21. Temperature Change of Particle During Oxidation with Air.
Figure 3.22. Calculated Thermal NO$_x$ Formation.
Chapter 4: Design of Reactor Models

4.1. Bench Scale Reactor

4.1.1. Reactor Modification

The current bench-scale reactor was modified in order to address the issues experienced during the demonstration of the SDCL process. These issues include the occasional plugging of the 1.5” ID reactor when large pellets (5 mm diameter and 2 mm height) are used and the segregation between the pellets and char particles inside the reactor. Figure 4.1 shows the new reactor design.

To ensure smooth flow of the pellets, the reactor inner diameter was increased from 1.5” to 1.939”. Since the SDCL process requires the iron oxide pellets and fine chars from the solid fuels to flow together, the homogenous flow of the iron oxide pellets and char particles without segregation is the key to consistent experimental results. It was found previously that a cylindrical reactor design with normal solid discharge port design leads to faster flow rate of coal char and relatively slow flow rate of the pellets due to the large particle size difference between pellets (~5 mm) and fine chars (~100 μm). In order to address this issue, a conical shaped solid discharge port was installed to the outlet of the cylindrical reactor. The cone, which has an angle of 58° from the base, ensures homogeneous discharge of both solids. As a result, the segregation between the two types of solids is minimized.

The sampling ports are connected with 3/8” stainless steel tubes. There are 6 sampling ports throughout the reactor and they are installed every 5”. Once gas sampling lines are removed after the experiment, solid samples are obtained using a 6 inch long and 1/4” OD stainless scoop. Also,
two pressure gauges are installed at the bottom and upper sections of the reactor. The pressures will be recorded during the experiment in order to ensure there is no pressure build-ups inside of the reactor. In addition to the former reactor heaters, two sets of new auxiliary heaters were added at the bottom and top of reactor. Figure 4.2 shows the design of bench scale reactor.

4.1.2. Bed height Control System

In the bench scale reactor demonstration, it is important to control the solid flows and bed height. Figure 4.3 shows the schematic diagram of bed height control system. Similar to the prior bench-scale reactor set-up, the modified reactor implemented the conductive characteristic of iron-based particle at high temperatures. The bed height control is operated over ~450°C, and it does not require moving parts. Because the conductivity of the particle increases with the temperature due to its ceramic composition, the sensor operates very stably at high temperature.

Bottom 1/16” metal bar is energized with 4.5 V signal. Once the particle is filled up to the sampling port being monitored, the circuit is completed and it sends the “on” signal to a computer, which is expressed as “1” by the computer. During this time, the top motor will be turned off to avoid overflowing of particles. On the other hand, the computer shows “0” or “off” signal, when the bed is empty and the circuit is not completed. The top motor will be turned on to fill up the bed during this period until the circuit is connected by particles. Figure 4.4 shows the preliminary test results of bed height control. The preliminary test shows that the top motor regularly operates the particle delivery almost every 10 minutes.

Addition to the bed height control system, a sight window (A.E. Ehrke, 3” sight window) is placed at the upper section of reactor, in order to ensure the level of solids in the reactor. The
diameter window is 3 inch and the window is made out of quartz. Transparent quartz window provides clear view of inside of reactor at high temperature without any gas leakages.

4.1.3. Gas Delivery Panel

The previous gas mixing and delivery system uses manual upstream-referenced flow controller (VICI Valco Model 202). Although the manual gas flow controllers can accurately control the flow rates of the gases, it is inconvenient to adjust and calibrate, especially during the experiment. A new, fully automatic gas delivery system was designed and constructed. Figure 4.5 shows the design of the new gas panel. The gas delivery system is capable to supply reactant gases and inert gases such as N\textsubscript{2}, He and Ar to the fixed bed reactor, the TGA and the bench scale reactor. Moreover, the panel is connected to the gas chromatography (Varain, MicroGC CP 4900), which allows convenient calibration of the compositions from the panel. The reactant gases that can be delivered from the panel include reducing gases such as CO, H\textsubscript{2}, and CH\textsubscript{4} and oxidizing gases such as O\textsubscript{2}, air, and CO\textsubscript{2}. The current gas panel design prevents oxidizing gases from mixing with reducing gases with a 3-way valve to ensure safe operation.

Digital flow meters (Omega Engineering, FMA 4500 Series) were installed to regulate the flow rates of all gases from the cylinders. A USB-based measurement and automation device (Labjack, U3LV) was used to control the digital flowmeters. To be more specific, the computer sends analog signals between 0-5 V to the automation device on the mass flow controller. The automation device will then transform the analog signal to a signal recognizable to the mass flow meter to regulate the gas flow rate from the cylinder. Typically, 0 V signal from the computer corresponds to zero gas flow and 5 V corresponds to maximum gas flow. The mass flow meters were pre-calibrated by the vender prior to shipping. The accuracy of the mass flow controller is ±1.5% of actual flow with a linear relationship between the voltages and flows. A digital flow
reader (Varian FM100) was attached to the panel to independently measure/check the gas flow rates from the mass flow controllers up to 1 L/min. A manual bubble flow meter was also installed next to the digital flow meter for calibration of gas flows larger than 1 L/min. All the connections on the panel were made with 1/4” stainless steel tubes.

Besides gas delivery, the gas panel is also used to extract gaseous samples from the 8 gas sampling ports/outlet on the bench-scale moving bed reactor using a set of assembly independent from the gas delivery assembly. The gas sampling assembly essentially connects the gas sampling ports to the GC (Varian, Micro CP GC 4900) system with a transparent desiccant bed in between. The gas sampling assembly is designed so that each port can be individually monitored with ease. Exhaust gases will be vented to the building ventilation system via the gas panel vent.

4.2. Cold Model Test

4.2.1. Reactor Design

Before the SDCL sub-pilot scale design, the cold model reactor has been designed and constructed. The size of cold model unit is equivalent to the 25kWth sub-pilot scale SDCL design, which is 7 feet height and 5 inch inner diameter. Solids are loaded from the top of funnel flowing downward. A flow adjustor for the oxygen carriers is located at 5 feet from the bottom of the unit. Different designs of flow adjustor are shown in Figure 4.6 (b). The flow adjustor helps the oxygen carrier flowing in a plug flow reactor (PFR) without severe mixing in the radial and vertical directions. As a preliminary test of cold model, the flow of oxygen carrier in the PFR is studied. Using the tracer particle in the cold model, the level of mixing at different vertical positions is observed.
4.2.2. Preliminary Tests

Experimental Procedures

As a preliminary test, different shapes of flow adjustors were tried for the oxygen carrier particle flow in the PFR. The flow adjustor is a conic shape with 45 degree angle. The first adjustor model concentrates the particle into 1.5 inch diameter, which provides 2.5 inch of slope length. The second model has the same slope angle and 3 inch outlet diameter with 1.75 inch slope length. Spherical glass beads were used instead of Fe-based oxygen carrier pellets due to the excessive dust formation during the test. These glass beads have the same density (2.5 s.g.) and similar mean particle size (5 mm) as the oxygen carrier pellets. The bottom section of cold model was first filled with the colorless glass bead. Once the cold model was filled to the flow adjustor, red glass beads were placed on the top of colorless glass beads as a tracer. There were several layers of red glass beads placed up to the top section. The initial set-up of cold model unit is shown in Figure 4.7. The displacement of tracer was monitored during the experiment. When the ball valve at the bottom was open and the glass beads started to flow, the continuous pictures were taken and the particle flow was compared by the frames.

Results and Discussions

Figure 4.8 and 4.9 show the pictures of particle flow at different time. In Figure 4.8 and 4.9, particles are concentrated into smaller diameter from 5 inch. The panorama pictures of particle flow show that the particles near the wall flow much slower than ones in the middle. The mixing of particle quickly and severely starts to appear in Figure 4.8 (a). The vertical velocities are accelerated at the center and decelerated towards the sides causing the tracers to be mixed. On the other hand, the particle flow with the short slope flow adjustor experiences less particle mixing during the flow. Figure 4.9 (a) shows no significant signs of mixing yet comparing to Figure 4.8
(a). Starting from Figure 4.9 (b), the particles in the middle start to flow faster and there are stagnant zones near the walls. However, the magnitude of flow difference is visibly less than the first case. This can be explained by the travel distance of each particle in the unit. In Figure 4.10, the particle 1, which is located near the wall, must travel longer distance than particle 2 and 3 as they pass through the flow adjustor. When the slope of adjustor is shorter, the distance for the particle 1 to pass the adjustor is shorter as well. Therefore, the radial separation becomes minimal. Moreover, the angle of adjustor, $\Theta$, can be increased to preventing the deceleration of particle. As the angle, $\Theta$, increases, more gravity force can be applied to the particle, resulting less deceleration of particle on the adjustor slope. The flow number ($i$) that estimates the segregation of particle by the adjustor can be defined as the following:

$$i = \frac{r}{m \times \cos(\Theta)} \quad (4.1)$$

Here, $r$ is the diameter of bottom section of flow adjustor, $m$ is the length of slope and $\Theta$ is the angle of adjustor. Higher flow number, $i$, means smoother flow without minimal mixing. It shows that the particle flow is proportional to the bottom diameter and the angle of adjustor, but disproportional to the length of slope.

As the further demonstration of cold model reactor to fully understand the behavior of particle in PFR, the following tasks will be studied; 1. management of gas flows including the gasification enhancer and 2. solid mixing dynamics between solid fuels and oxygen carriers in the reducer unit. Because the reducer is operated with the counter-current moving bed manner, it is necessary to avoid the fluidization of oxygen carrier and solid fuel. Therefore, the flow rate of gasification enhancer must be kept below the minimum fluidization velocity of solid materials in the reducer,
while enough gasification enhancer is provided to initiate the reaction. The injection point of solid fuel is located around 5 feet from the bottom of reactor, but the location of solid fuel injection can be adjusted depending on the types of solid fuel used. Figure 4.6 shows the design of cold model of SDCL reducer unit. Also, as the oxygen carriers pass through the flow adjustor, they focus into the smaller surface area proving space for the solid fuel injection at point 2 in Figure 4.6 (a).

4.3. Design of Sub-Pilot Scale System

Based on the cold model reactor study, the 25 kW th sub-pilot scale system has been designed shown in Figure 4.11. This 25 kW th unit will be used to study the continuous operation of SDCL. There are four injection ports for pulverized solid fuels around the 5 inch diameter reactor body. The pulverized solid fuels will be carried by the high velocity of gasification enhancer, CO₂. The velocity of injection gas will be determined after considering the characteristics of solid fuels, such as mean particle size, density and shapes. The reducer unit in the designed sub-pilot scale has 5 inch ID and 10 feet height. Resultant gas will exit at the top of reducer as concentrated CO₂ and steam. After the resultant gas passes through the condenser, most of steam will be removed and the gas will be analyzed with a gas chromatography. Then, the reduced particles move to the combustor unit where they are re-generated back to Fe₂O₃ with air and pneumatically carried to the reducer. The height of combustor will be 15-20 feet height depending on the diameter and auxiliary system.
Figure 4.1. Schematic Diagram of Bench Scale Reactor.
Figure 4.2. Design of Bench Scale Reactor Body.
Figure 4.3. Bed Height Control System Located at Upper Part of Reactor.
Figure 4.4. Preliminary Data of Bed Height Control.
Figure 4.5. Design of Gas Delivery System.
Figure 4.6. Design of Cold Model Unit: A. Overall Design of Cold Model Unit. B. Design of Flow Adjustor.
Figure 4.7. Initial Set-Up of Cold Model Unit for Preliminary Test.
Figure 4.8. Flow of Particle, I=0.86.
Figure 4.9. Flow of Particle, I=3.0.
Figure 4.10. Analysis of Particle Flow with Flow Adjustor at Different Radial Position.
Figure 4.11. Design of Sub-Pilot Scale Reactor.
Chapter 5: Conclusion and Future Works

5.1. Conclusion

The solid fuel-direct chemical looping (SDCL) process that utilizes Fe-based oxide as a oxygen carrier is developed for the power generation from the carbonaceous solid fuels, such as coal and biomass with achieving in-situ CO₂ separation.

Since the capability of redox reactions of oxygen carrier particle determine the feasibility of process, the performance of the particle in the reducer and combustor is the key to the SDCL process. A novel iron oxide based composite particle is developed using the mechanical mixing and high temperature sintering with inert metal oxides as supporters. The physical and chemical properties of the particle including compressive strength, reactivity and recyclability are tested. The synthesized particle is reduced and easily regenerated with air. The experiments in the fixed bed for the reducer show the effective CO₂ capture and solid fuel conversions. The char conversion can be considerably enhanced by adding gasification enhancing gas, CO₂. The injection of CO₂ gasifies the char and accelerates the overall gasification rate by raising the local concentration of CO₂ around the char. Also, the experimental studies indicate that the volatile conversion is more significant step for the woody biomass, whereas the coal requires extensive conversion of volatiles and chars. During the combustion of oxygen carrier particle, the combustion of oxygen carrier particle shows the exothermic behavior, which implies that heat from the combustion can be utilized for the power generation. Because the combustion does not happen in the excessive temperature, thermal NOₓ formation can be minimized. Reduction and
regeneration of the particle in a fixed bed is performed. The feasibility of Fe-based oxygen carrier for the SDCL process has been proved and the particle is deemed suitable for the chemical looping gasification processes.

5.2. Future Works

For the next two years, the proposed SDCL process will be further advanced to bench scale (2.5kWth) and the sub-pilot scale (25 kWth). To be more specific, the following objectives will be attained for the next stage of research: 1. to further improve the oxygen carrying capacity as well as the sulfur/ash tolerance of the current oxygen carrier particle; 2. to demonstrate continuous SDCL operations in an integrated mode with > 99% solid fuels (coal - bituminous, sub-bituminous, and lignite and woody biomass) conversion as well as the production of high temperature exhaust gas stream that is suitable for steam generation in existing PC boilers; 3. to identify, via demonstrations, the fate of sulfur and NOx; 4. to conduct thorough techno-economic analysis that validates the technical and economical attractiveness of the SDCL system.


42. Ryu, H. Korea Institute of Energy Research. At Kick-off meeting of research project entitled “Development of Inherent CO₂ Separation Technology by Chemical Looping Combustion System” on November 13th, 2006. Daejeon, Korea


