Multiscale Study of Chemical Looping Technology and Its Applications for Low Carbon Energy Conversions

DISSERTATION

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Abstract

The chemical looping strategy for fossil energy applications promises to achieve an efficient energy conversion system for electricity, liquid fuels, hydrogen and/or chemicals generation, while economically separate CO\textsubscript{2} by looping reaction design in the process. Chemical looping particle performance, looping reactor engineering, and process design and applications are the key drivers to the success of chemical looping process development. To better understand and to further scale up the chemical looping process, issues such as cost, time, measurement, safety, and other uncertainties need to be examined. To address these uncertainties, advanced reaction/reactor modeling and process simulation are highly desired, and the modeling efforts can accelerate the chemical looping technology development, reduce the pilot-scale facility design time and operating campaigns, as well as the cost and technical risks. The purpose of this work is to conduct modeling and simulations on the key aspects of chemical looping technology, including particle reaction kinetics, reactor design and operation, and process synthesis and optimization.

Understanding the reaction mechanism associated with looping intermediates is important to the rate process of reactions, in turn affecting the design of the looping particles. Extensive kinetic study was conducted using both the unreacted shrinking core model and ionic diffusion grain model, and the simulation results were validated.
experimentally. The unreacted shrinking core model considered various resistances, including intraparticle diffusion, external mass transfer, and surface chemical reaction. The simulation results were compared with experimental data, which showed a good agreement. A novel grain model considering ionic diffusion control is proposed to represent the reaction between iron oxide pellets and the reducing gases. The limiting cases of the model are discussed when one or two resistances are dominant. Numerical solutions were used to validate the proposed model by means of fitting available experimental data. This model is found satisfactory for the interpretation of experimental results.

Chemical looping reactors usually handle a number of interrelated gas-solid and/or solid-solid reactions, and the reactor design and operation requires comprehensive understanding of the complex reaction system, including the thermodynamics, the kinetics, and the fluid dynamics. Reactor models were developed to simulate the oxygen carrier reduction process in a countercurrent gas-solid moving bed reducer and particle regeneration step in a bubbling fluidized bed combustor. The moving bed code was validated by comparing the results from bench-scale experiments reported earlier. Both the steady state and dynamic composition profiles were obtained to help understand the reaction behaviors in the moving bed reducer. Numerical simulation on the effects of reducer length was also conducted. It was found that minor variations in the feed-rate ratio near a critical point that was represented by the metal oxide and reacting gas equilibrium condition could yield a significant difference in the simulation converging
time. This converging time difference also had an important practical implication in that the design and steady state operation of the moving bed reducer should be carried out to circumvent the condition of such a critical point.

Chemical looping systems are capable of processing multiple carbonaceous fuels into diversified products at a high efficiency and a low cost. A number of chemical looping process designs and configurations were studied, illustrating the flexibility of chemical looping system in different energy carrier conversion schemes. Process simulation and analysis were performed to estimate the performance of the chemical looping process under various mass and energy management schemes. The fates of pollutants and the effects of various process operating parameters, such as carbon and iron oxide conversions, were also evaluated. The simulation results demonstrated that chemical looping processes have great potentials for flexible and efficient production of electricity, hydrogen, and liquid fuels.
Dedicated to my family and friends for their love and support.
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1.1 Background

A clean, cheap, and abundant energy supply is a prerequisite for the sustainable economic and environmental prosperity of modern society. With the significant economic growth in the Asian Pacific region and the expected development in Africa, the total world energy demands are projected to increase from 462.4 quadrillion British thermal units (BTU) in 2005 to well over 690 quadrillion BTU by 2030. The projected energy supply through 2030 will be drawn from fossil fuels (i.e., oil, coal, and natural gas), renewable forms of energy (i.e., hydro, wind, solar, biomass, and geothermal), and nuclear energy, in that order.

The impact of the global warming induced by CO₂ emissions from fossil energy conversion processes has become an issue of international concern. An energy solution prompted by the combination of ever-increasing energy consumption and rising environmental concerns, thus, requires a coupling fossil energy conversion systems with economical capture, transportation, and safe sequestration schemes for CO₂. A long-term energy strategy for low or zero carbon emission technologies would also include nuclear energy and renewable energy. Nuclear power is capable of generating electricity at a cost comparable to the electricity generated from fossil fuels. A variety of social and political
issues related to operational safety and permanent waste disposal concerns, however, could limit nuclear energy’s widespread utilization in overall energy production.\textsuperscript{1, 2} Renewable energy sources, although attractive from the environmental viewpoint, face complex constraints for large-scale application. Even when both the decrease in renewable energy costs and the increase in fossil fuel prices are taken into account, it is projected that only about 8.5% of the total energy demands in 2030 will be from renewable sources.\textsuperscript{1} For primarily economic reasons, fossil fuels, including crude oil, natural gas, and coal, will continue to play a dominant role in the world’s energy supply for the foreseeable future.

Processing of fossil fuels, such as coal and natural gas, generates a flue gas stream that contains a number of by-products harmful to both human health and the environment. The control strategies for traditional pollutants such as sulfur oxides, nitrogen oxides, fine particulates, and mercury have been extensively studied. Carbon dioxide (CO\textsubscript{2}) control strategies in fossil fuel based power plants, however, are relatively new and challenging. The CO\textsubscript{2} control strategy in a fossil fuel power plant involves three steps, \textit{i.e.}, capture (separation and compression), transportation, and storage (geological sequestration). The cost for CO\textsubscript{2} capture is significantly higher, estimated at $15 - $75 for one ton of CO\textsubscript{2} processed, compared to that for transportation, $1 - $8, and for geological storage, $0.5 - $8.\textsuperscript{3} Thus, the development of cost-effective capture technologies is the key to affordable CO\textsubscript{2} emission control in fossil fuel based power plants.
There are a number of carbon capture techniques that could potentially be used in fossil fuel based power plants. These are generally categorized as post-combustion, pre-combustion, or oxy-combustion capture. Post-combustion capture separates CO$_2$ from the combustion flue gas. In pre-combustion capture, carbon is removed in a fuel conversion process prior to combustion. In oxy-combustion capture, oxygen replaces air as the oxidant during fuel combustion, which generates a concentrated CO$_2$ stream. The U.S. Department of Energy’s (US DOE) road map for CO$_2$ capture technologies is shown in Figure 1.1. This is given in terms of cost reduction benefits for various current techniques and future techniques that are being developed. The current techniques include those using amine solvents, physical solvents, and oxygen separation from air using cryogenic methods. The future techniques in the order of readiness, are represented by advanced physical solvents, advanced chemical solvents, ammonia, polybenzimidazole (PBI) membranes, solid sorbents, membrane systems, Ion Transport Membrane (ITM), biomass co-firing, ionic liquids, metal organic frameworks, enzymatic membranes, chemical looping, oxygen transport membrane, and biological processes. The cost reduction benefits increase with the time of development of these technologies.

### 1.2 Chemical Looping Technology

Chemical looping technology for fossil fuel conversion is an increasing field of interest as global concerns for CO$_2$ emissions escalate. The unique feature of this novel technology is in its near zero energy penalty for gas product separation.
Specifically, two or more interconnected reactors are involved in chemical looping processes to conduct the reduction-oxidation (redox) cycles of solid metal oxide composites, termed oxygen carrier particles. In the oxygen carrier reduction step, fuel is fully converted to CO₂ and H₂O in a separate reactor. H₂O can be easily condensed out of the flue gas stream from this reactor, resulting in a high purity CO₂ stream ready for geological sequestration or enhanced oil recovery. This reactor is termed the reducer or fuel reactor. In the oxidation step, the oxygen carrier particles are moved to a separate reactor and regenerated by steam/air while producing H₂/heat. This reactor is called the oxidizer/combustor or steam/air reactor. As shown in Figure 1.2, the chemical looping scheme avoids the mixing of the carbonaceous fuel with air, which renders the unnecessary costly separation of a gaseous mixture of CO₂ and H₂O from N₂. For conventional combustion and gasification approaches, CO₂ separation and compression will inevitably impose a 20~30% parasitic energy penalty relative to plants without carbon emission control. In comparison, the chemical looping process only has a 3~5% energy penalty, which translates into a significant potential cost advantage when compared to conventional CO₂ capture technologies. Additionally, chemical looping technology can be adopted to produce electricity, hydrogen, and/or syngas for liquid fuel and chemical synthesis.

The chemical looping approach for fossil fuel conversion applications has been recognized for over 100 years, yet no chemical looping process using fossil fuels has been commercialized. The reactivity and recyclability of the looping carrier particles
have hampered the conversion efficiencies and economics of these early processes. Table 1.1 summarizes several representative chemical looping processes studied in the 20th century.\textsuperscript{28-33} In recent years, with the pressing need for efficient and economical energy conversion systems coupled with growing concerns over carbon dioxide emission controls, the process development of the chemical looping concept has reemerged as an important strategy for fossil fuel conversion.\textsuperscript{34} With renewed research since the early 1980s, many earlier shortcomings have been alleviated. The chemical looping process has evolved into a promising technique which is competitive with the traditional fossil fuel conversion technologies.\textsuperscript{35}

### 1.2.1 Chemical Looping Material

In chemical looping systems, oxygen carriers, generally metal oxide particles, are cyclically utilized to deliver oxygen from the oxidant to the fuel. The oxygen donation to the fuel reduces the oxygen carriers. These reduced oxygen carriers are then returned to the combustor or air reactor and treated with the oxidant to regenerate them for the next loop. This cyclic oxygen delivery pattern avoids the direct contact between air and fuel streams resulting in an undiluted CO\textsubscript{2}/H\textsubscript{2}O exhaust stream from the reducer or fuel reactor, ready for sequestration. Therefore, the functioning of the oxygen carriers dictates the efficiency of CO\textsubscript{2} separation and, thus, its performance is a key factor that influences the success of chemical looping systems. The extensive research reported in the literature, focusing on synthesizing and testing different metal oxide compositions as oxygen
carriers that can perform the desired functions, is an indication of the vital role played by oxygen carriers in chemical looping systems.

One of the earliest studies of oxygen carriers dates back to the late 19th century. The steam-iron process developed by Lane and Messerschmidt used iron-based oxygen carriers for the generation of hydrogen. This process involved the reduction of the oxygen carriers using gaseous fuels and their re-oxidation with steam to generate hydrogen in fixed bed reactors. It was widely utilized until the 1920s. In the 1950s, Lewis and Gilliland proposed a circulating fluidized bed chemical looping system, using a copper-based oxygen carrier, for pure CO\textsubscript{2} generation. Only certain sporadic chemical looping concepts were postulated until the 1980s when Richter and Knoche and Ishida, & Jin revealed further energy and environmental benefits of these concepts. Reasons for little prior recognition include the availability of alternative cheaper and more efficient technologies for fuel utilization to generate required products and the lack of global awareness of the greenhouse effect of CO\textsubscript{2} emissions. The chemical looping systems saw progressive activities in the 1990s with emphasis on the potential for reducing CO\textsubscript{2} capture costs. Multiple metal oxides were tested to determine the suitable oxygen carriers for chemical looping systems. The most commonly tested oxygen carriers were iron-, nickel-, and copper-based particles.

The current approach for oxygen carrier selection is through the trial and error method. This is accomplished by screening large numbers of chemical looping carrier
candidates composed of various active metal oxides and supports. Advancement in analytical techniques and in data acquisition methods allowed the rapid screening of oxygen carriers for chemical looping systems. By 2010 more than 600 different types of oxygen carriers were tested. This large number of metal oxides tested highlights the importance of developing certain properties in the oxygen carrier for optimal performance in the chemical looping systems. The focus of Chapter 2 is to provide a perspective on the desirable properties of the oxygen carrier and their influence on the performance of chemical looping systems. Detailed discussions on the reaction kinetics and modeling of the iron based oxygen carriers are provided.

1.2.2 Chemical Looping Reactor

In addition to the metal oxide particle properties and performances discussed in the previous chapter, reactor design is another important factor governing the success of chemical looping systems. Chemical looping reactors usually handle a number of interrelated homogeneous and heterogeneous (gas-solid) reactions, and the reactor design requires comprehensive understanding of this complex reaction system, including the thermodynamics, kinetics, and fluid dynamics. Further, the individual reactor design and optimization should also be evaluated from the standpoint of the overall process. Chapter 3 discusses the chemical looping reactor design and modeling.

The chemical looping system either consists of a reducer and a combustor, when applied in the chemical looping combustion (CLC) process for heat and power
generation, or includes an additional oxidizer between the reducer and the combustor for hydrogen production when applied in the chemical looping gasification (CLG) process. The combustor usually involves a dense fluidized bed, to regenerate the oxygen carriers using air, above which a riser is placed to pneumatically convey the particles to the reducer. A cyclone is usually used for separation of the regenerated particles from the spent air stream. The global solids movement in the chemical looping system thus resembles the circulating fluidized bed (CFB) system, which has already been widely used for fluidized bed combustion (FBC) and fluidized catalytic cracking (FCC) applications. However, a number of designs have been proposed for the reducer. Despite the many variations in the reducer designs, they can be characterized by two fundamental modes based on the different gas-solid contact patterns, as given in Figure 1.3. Mode 1 is characterized by the mixed flow of gas and solid in a typical fluidized bed, operating in the bubbling, turbulent, fast fluidized-bed, or sprouted bed regime. The mode 1 reducer and the fluidized combustor jointly form a circulating fluidized bed (CFB) system. Most of the CLC processes are developed on the basis of such interconnected fluidized bed mode 1 systems. Mode 1 is typically represented by the bubbling/turbulent fluidized bed reducer system developed at the Chalmers University \(^{39}\) and by the circulating fluidized bed reducer system developed at the Vienna University of Technology, \(^{40}\) as given in Figure 1.3A. Mode 2, on the other hand, is represented by the gas-solid countercurrent contact pattern in a moving dense bed or a multistage fluidized bed. Fan and his team are developing both CLC and CLG processes based on the mode 2 reducer design at the Ohio State University.\(^ {41}\) The typical mode 2 system for CLC applications is given in Figure
1.3B. The mode of operation employed in the reducer significantly affects the type of reaction products generated and the oxygen carrier conversion achieved from the chemical looping reactions. Further, the mode of operation selected for a process system dictates the solids flux requirement to achieve a given process operating capacity and hence, the scalability of the processes to commercial usage.

1.2.3 Chemical Looping Process

Chemical looping systems are capable of processing multiple carbonaceous fuels into diversified products at a high efficiency and low cost. Figure 1.4 outlines such flexible chemical looping conversion pathways. From the front end, a chemical looping system could be fueled with various feedstocks, like natural gas, coal or biomass. It can also convert municipal waste or upgrade process waste such as light hydrocarbons from the Fischer-Tropsch (F-T) system tail gas into valuable products. The flexibility in fuel sources makes the technology deployment more competitive in the energy market. At the application end, the direct products from the chemical looping system are of high purity and quality, which makes the technology more compatible for process integration and intensification. For example, a chemical looping system renders an efficient \textit{in situ} CO$_2$ separation and, consequently, a low-cost CO$_2$ stream suitable for sequestration or utilization, such as enhanced oil recovery. It also opens the door for high-purity hydrogen production. The hydrogen can then be either burnt in a turbine system or a fuel cell system for high-efficiency power generation, or used for liquid fuel or chemical synthesis. Chapter 4-6 will review and discuss a number of chemical looping process
designs and configurations, and illustrate the flexibility of the chemical looping system in different energy carrier conversion schemes.
Figure 1.1 CO₂ capture techniques from fossil energy – technological solutions
Figure 1.2 General chemical looping scheme
Figure 1.3 Chemical looping reactor systems: (A) Mode 1 reactor schematic diagrams with fluidized bed or co-current gas-solid (OC) flow reducer and (B) Mode 2 reactor schematic diagram with gas-solid (OC) counter-current dense phase/moving bed reducer system.
Figure 1.4 Chemical looping conversion pathways
Table 1.1 Historical development of chemical looping for fossil fuel conversion

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Chapter 2

Chemical Looping Material Development and Reaction Kinetics Study

2.1 Oxygen Carrier Development

2.1.1 Primary Material Selection

The reduction-oxidation (redox) behavior of the oxygen carrier largely depends on the thermochemical properties of its principal metal oxides and can significantly affect the system performance. Thus, the oxygen carrier material selection first focuses on the metal oxides that have favorable equilibria with both solid-fuel and air, which can be conducted with the assistance of a consolidated Ellingham diagram, as shown in Figure 2.1.\textsuperscript{42,43} The Ellingham diagram illustrates the dependency of the change in Gibbs free energy (ΔG) of the redox reactions on temperature. The position of lines in the diagram indicates the relative reduction and oxidation potentials of oxygen carrier materials.

For the reducer operation, to effectively convert solid carbonaceous fuels, the CO\textsubscript{2} line should be positioned below the primary material lines in Figure 2.1. Based on this criterion, metal oxides such as CuO, NiO and Fe\textsubscript{2}O\textsubscript{3}, and metal sulfates such as CaSO\textsubscript{4} are normally selected for chemical looping applications.\textsuperscript{44-46} In addition, the candidate lines must be higher than the P\textsubscript{CO}/P\textsubscript{CO2}=1:999 line, which represents a 99.9\% fuel conversion, in order to obtain pure CO\textsubscript{2} and H\textsubscript{2}O at the reducer gas outlet. Similarly, the P\textsubscript{CO}/P\textsubscript{CO2}=5:995 line represents 99.5\% fuel conversion, and Figure 2.1 reveals that NiO
and CaSO₄ cannot achieve >99.5% fuel conversions. Furthermore, the cost and high toxicity of NiO materials are generally considered disadvantages for large-scale industrial applications. Although CaSO₄ has a high theoretical oxygen carrying capacity and low cost, it is plagued by CaO formation and sulfur emissions during the redox process.⁴⁷

For the combustor operation, the material lines need to be below the $P_{O₂}=0.01$ atm line in order to achieve full air conversion. The materials near this line can also release free oxygen to boost solid fuel conversion in the reducer, a process called Chemical Looping with Oxygen Uncoupling (CLOU).⁴⁸⁻⁵³ Figure 2.1 indicates that the CLOU materials have a very narrow operation range for the oxidation step, which usually requires a long residence time and high excess air flow. For example, the Mn₂O₃ line is above the line which corresponds to an oxygen partial pressure of 0.21 atm. Thus, it is difficult to regenerate Mn₂O₃ using ambient air. As a result, the Mn₃O₄-MnO cycle is usually considered for chemical looping application, and its theoretical oxygen carrying capacity is only 7%. The low melting point of Cu, low strength, high percentage of support materials required, high amount of excess air and long regeneration times may pose serious challenges for CuO material development.⁵³

From Figure 2.1, iron oxides exhibit favorable thermodynamic properties with complete conversions for both fuel and air in the redox cycles. Furthermore, iron oxide is advantageous for chemical looping as Fe-based oxygen carriers possess low raw material
cost, high melting points, high mechanical strength and few environmental and health concerns. The following section, thus, focuses on iron based material study.

2.1.2 Iron Oxide Based Oxygen Carrier

Based on the Ellingham diagram$^{42, 43}$, Fe$_2$O$_3$ can convert 100% of carbonaceous fuels to CO$_2$ and H$_2$O. However, the Fe$_3$O$_4$ and FeO lines are close to the H$_2$O and CO$_2$ lines; thus, incomplete fuel conversion occurs when Fe$_3$O$_4$ or FeO are at the last stage of contact with the fuel. Several counter examples have been reported, $^{54}$ which are not in compliance with the thermodynamic constraints. Because of iron’s multiple oxidation states, the gas-solid contacting patterns in the reducer dominate both the fuel and the oxygen carrier conversion. In a mixed flow pattern, or Mode 1, in order to achieve 100% CO$_2$ at the reducer gas outlet, only the Fe$_2$O$_3$-Fe$_3$O$_4$ redox pair can be used. In comparison, a countercurrent flow pattern, or Mode 2, could create multistage equilibrium states through the reducer. At the top of the reducer, Fe$_2$O$_3$ fully oxidizes fuel into CO$_2$ and H$_2$O; at the bottom, the solid fuel is gasified but the gasification products are only partially oxidized, and the oxygen carrier is reduced to FeO and Fe. Both experimental and simulation results show that the maximum iron oxide conversions, while ensuring 100% fuel conversion, are 11.1% and >50% for a well-mixed mode and for a countercurrent mode, respectively. $^{55}$ The Mode 2 design thus results in a much lower oxygen carrier circulation rate in the iron-based chemical looping system. Figure 2.1 also illustrates that FeO, Fe$_3$O$_4$ and H$_2$O lines are close to each other, which indicates the possibilities for hydrogen production application.
Naturally-occurring ores, such as ilmenite (FeTiO$_3$) have been considered for chemical looping applications in light of its low cost and one step reduction from Fe$_2$TiO$_5$ to FeTiO$_3$.\textsuperscript{56,57} However, phase separation and segregation occur during the redox cycles, which results in a separate iron oxide phase and titania phase.\textsuperscript{58} The iron phase migrates to the surface during the oxidation of FeTiO$_3$, while the TiO$_2$ crystals increase over the redox cycles, which could fracture the ilmenite particle. This mechanism could lower the particle strength, an effect which has been exploited in the Becher process for TiO$_2$ production.\textsuperscript{59} Figure 2.1 also shows that the FeTiO$_3$ line is far away from the H$_2$O line, meaning that steam oxidation of FeTiO$_3$ for hydrogen production is not favored.

Pure iron oxide quickly loses its reactivity in the first several redox cycles. When inert support materials are added, the strength, reactivity and recyclability of oxygen carrier particles can be drastically improved.\textsuperscript{60} The lack of understanding of the complex solid-solid interaction between the primary metal and the support material does not allow the prediction of the influence of support/active metal oxide interaction on oxygen carrier performance; thus, most of the oxygen carrier studies are by trial-and-error. A recent study on the ionic transfer mechanism opens a new direction for oxygen carrier design and synthesis.\textsuperscript{61,62}

\textbf{2.1.3 Reaction Mechanism Study}
Hematite ($\alpha$-Fe$_2$O$_3$) has a corundum-type structure. $O^{2-}$ forms a slightly distorted, hexagonal close-packed pattern, and $Fe^{3+}$ occupies two-thirds of the octahedral positions. The structure of magnetite ($Fe_3O_4$) is an inverse spinel type. It can be viewed as fitting iron cations in the interstices of a close-packed cubic oxygen lattice. Half of the $Fe^{3+}$ ions occupy the tetrahedral interstices, and the other half occupies the octahedral interstices. The $Fe^{2+}$ ions are only situated in the octahedral interstices. The lattice structure of wüstite ($Fe_xO$) is that of a rock salt. Iron cations can be considered to occupy all the octahedral interstices formed in the closed-packed cubic oxygen lattice. The Fe to O molar ratio is 1 in the perfect case. However, significant iron vacancies exist in wüstite. As a result, the Fe to O molar ratio in a typical wüstite sample ranges between 0.83 and 0.95.$^{63}$

The redox reaction mechanisms for pure iron and its oxides have been extensively studied and is well understood. Hauffe summarized the solid state diffusion patterns in the oxidation of metallic iron to iron (III) oxide, as listed below.$^{64}$ In all the solid phases, neutrality is maintained by electron flux.

1. Oxygen molecules dissociate on the hematite-gas interface.

2. Oxygen anions diffuse through the hematite layer to the hematite-magnetite interface via oxygen vacancies.
3. The inward diffusing oxygen anions and the outward diffusing iron cations contact and form magnetite.

4. Iron cations diffuse through the magnetite layer to the magnetite-hematite interface via iron vacancies.

5. Iron cations diffuse through the wüstite layer to the wüstite-magnetite interface via iron vacancies.


Edstrom systematically investigated the reaction of hematite to magnetite and wüstite. The mass transport was opposite in direction but the diffusion pattern was the same as described above. The concentration gradient is the driving force for the diffusion. In addition to the study on oxidation and reduction separately, Sakata et al. investigated the mechanism for the redox cycle of pure Fe₂O₃ at 300°C with the oxygen capacity varying between 98.9% and 100%. Using oxygen isotopes, they determined that bulk oxygen did not take part in the redox reactions. This demonstrated the low diffusivity of the oxygen ions to the surface. A mechanism involving the diffusion of iron ions, instead of oxygen ions, was proposed because iron ions are much smaller than oxygen ions. The relative diffusivities of iron ions and oxygen ions are not expected to change at higher temperatures. However, at higher temperatures, the metallic iron will also diffuse and sinter, leading to decreased reactivity over redox cycles.
However, since the practical importance of the iron making process and understand corrosion were the primary incentives for the early research, two other central aspects of chemical looping processes—recyclability and effects of support—received little attention. It has been confirmed that the commercial iron oxide particles lose their reactivity in first few redox cycles; the addition of support materials is considered one promising solution to this problem. Mattisson et al. carried out partial reduction and oxidation of Fe$_2$O$_3$ to Fe$_3$O$_4$ and found that reaction rates for various metal-oxide particles depended on the support used. Similar findings on the reduction of Fe$_2$O$_3$ with various supports and sintering temperatures have been reported in other studies. Mattisson et al. carried out partial reduction and oxidation of Fe$_2$O$_3$ to Fe$_3$O$_4$ and found that reaction rates for various metal-oxide particles depended on the support used. Similar findings on the reduction of Fe$_2$O$_3$ with various supports and sintering temperatures have been reported in other studies.

Urasaki, Tanimoto, et al. reported cyclic redox experiments conducted on Fe$_2$O$_3$ doped with 0–0.4% ZrO$_2$. The oxygen capacity varied by 30% to 50% at 450°C when H$_2$/He and H$_2$O/He gas mixtures were used. The presence of ZrO$_2$ led to improved oxidation rates compared with pure Fe$_2$O$_3$ and helped stabilize the surface area of the particle. They stated that the oxidation rates depended solely on the surface area, which decreased over several cycles, leading to decreased reactivity. Similar results were reported when Pd was the dopant. The studies indicated that a stable pore structure was important for the recyclability of pure Fe$_2$O$_3$ at lower temperatures. This behavior can be explained by the low ionic diffusivity of Fe$_2$O$_3$ at low temperatures. At high temperatures, however, the enhancement of oxygen ion diffusion becomes an important factor in the development of optimal oxygen carrier particles for chemical looping processes. Urasaki, Sekine, et al. found an approximately 22% increase in the steam oxidation rate of reaction upon adding a trace quantity (0.23 mol%) of zirconium to the Fe$_2$O$_3$. The increase was explained on
the basis of reduced sintering at 500°C. Takenaka et al. studied the effect of Mo and Rh on the recyclability of Fe₃O₄-based particles. Rhodium addition was found to initially increase the reaction rates of reduced particles with steam, attributed to the lowering of the activation energy of the reaction, but increased sintering was observed leading to decreased reactivity in the long term. ⁷¹ The addition of Mo helped prevent sintering by the formation of ferrites (MoₓFe₃₋ₓO₄) that inhibited the contact between metallic iron particles.

As seen in studies of nickel and other metal-based oxygen carrier particles, the improvements in performance of Fe-based carriers after support addition were often attributed to the increase in pore size and sintering resistance. These changes would lead to enhanced intraparticle gaseous diffusivity. ⁷² However, Li et al. found that the significant decrease in pore volume that was observed after the first redox cycle did not affect the reactivity of the Fe-Ti-O particle. ⁶⁰ Both the reactivity and morphological properties of pure iron oxides deteriorate rapidly over multiple redox cycles. When support materials, such as TiO₂ or Al₂O₃, were added, the reactivity and recyclability of oxygen carrier particles could be drastically improved. ⁴⁵, ⁶⁰ The excellent recyclability of the Fe-Ti-O particles may be attributed to the increased ionic diffusivities of both the oxygen anion and the iron cation. Ionic diffusion occurred due to the defects formed in the TiO₂ crystal structure in the presence of Fe³⁺ and Fe²⁺ ions. The introduction of Fe₂O₃ into the TiO₂ can cause either lattice substitution defects or interstitial addition defects in the TiO₂ crystal structure. The atomic radius of Ti⁴⁺ ions is 61 pm, and for Fe³⁺ it is 65 pm.
Because of the similarities in the atomic radii and the close packing structure of the lattice usually encountered for larger ions such as Ti$^{4+}$ and Fe$^{3+}$, it is reasonable to assume that cationic lattice substitution occurs rather than interstitial addition. To maintain electrical neutrality in the crystal structure, one oxygen ion (O$^{2-}$) will be vacated for every two Ti$^{4+}$ ions substituted by two Fe$^{3+}$ ions. The resulting oxygen ion vacancies will create point defects in the crystal structure if the vacancy concentration is lower than a critical concentration. When the vacancy concentration is higher than the critical concentration, other defects such as shear planes will occur. The presence of such vacancies in Fe-Ti-O particles has been confirmed by various studies. These vacancies are related closely to improved ionic diffusivity. Wang et al. determined that the critical atomic concentration is 2% Fe$^{3+}$ in TiO$_2$. Because of the presence of these oxygen vacancies, an oxygen ion will be able to diffuse through the crystal structure. Such diffusion will be limited severely in pure Fe$_2$O$_3$ where such vacancies in the crystal lattice are absent. In pure Fe$_2$O$_3$, alternative mechanisms for oxygen to diffuse out of the particle include anionic substitution and interstitial migration. The activation energy for these diffusion mechanisms, however, will always be higher as compared with Fe-Ti-O where an oxygen diffusion path may readily exist. Pure iron oxidation follows outward iron cation diffusion mechanism; supported iron obeys an inward oxygen anion diffusion pathway. Zhao and Shadman identified the diffusion of both atomic iron and oxygen through the ilmenite (FeTiO$_3$) structure during the reduction of ilmenite with carbon monoxide and hydrogen. Fe crystals were reported to be formed as a result of diffusion of the iron ions and coalescence of iron during the reduction. The formation of a 1 to 2
atomic percent iron containing TiO$_2$, in between the ilmenite crystals and the iron crystals, also was identified as the cause for enhanced diffusivity of the atomic iron, as well as of the oxygen. Moreover, 1 to 5.5 atomic percent titanium was found in the iron crystals.

To further understand the possible reasons behind this phenomenon, Li et al. extended the mechanism study to an atomic level. They found that TiO$_2$ is likely to increase the oxygen ion conductivity within the bulk phase rather than to decrease the energy barrier for the surface reduction reactions of iron oxides. The activation energy for the reduction reaction and the oxygen anion diffusivity within the dense solid phase has been calculated for wüstite and ilmenite (FeTiO$_3$) systems using the Density Functional Theory (DFT). Wüstite and ilmenite were chosen for the following reasons: (a) ilmenite is widely used as a supported oxygen carrier for chemical looping processes and wüstite is a pure form of iron oxide; (b) the valence states of iron in both compounds are directly comparable; and (c) they both have well-defined crystal structures. Since notable amounts of iron vacancies usually exist in wüstite, both perfect FeO and cation defected-Fe$_{0.96}$O were investigated. They found that the DFT calculation results are notably higher than experimental values for the activation energy of the reduction reaction, but they are in qualitative agreement. The activation energy for the defected Fe$_{1-x}$O (111) surface is lower than that for FeTiO$_3$ (001) surface. It indicates that the addition of TiO$_2$ is unlikely to significantly reduce the activation energy for the reduction of the oxides of iron. The results show that the energy barrier for oxygen anion migration in FeTiO$_3$ is only half of
that in the perfect FeO structure. Although the mobility of oxygen anions can be enhanced due to the presence of iron defects in Fe$_{0.96}$O, the energy barrier for oxygen anion diffusion in FeTiO$_3$ is still significantly lower. The cation to anion ratio is deemed to be the reason for increased oxygen anion diffusivity. Oxygen forms a close-packed lattice in both structures. In wüstite, nearly all the octahedral interstices are filled while only two-thirds are occupied in ilmenite and this may contribute to the ease of oxygen anion migration. Furthermore, since there are rare oxygen defects in ilmenite, the TiO$_2$-supported iron oxide particles should possess an even higher diffusivity because of the significant number of oxygen defects. This conclusion is consistent with the previous mentioned inert marker experiment that TiO$_2$ support can notably improve the ionic diffusivity of oxygen anion.  

Hydrogen ion diffusivity also could contribute to the reaction mechanism. Steinsvik et al. studied the conductivity of hydrogen ions through defect-containing crystal lattices of the Sr-Fe-Ti-O system and found that hydrogen ionic conductivity was an order of magnitude smaller than oxygen ion conductivity at temperatures above 700°C.  

Similar values were reported when steam was present. The contribution of hydrogen ion diffusion was found to increase with a decrease in temperature, reaching almost 50% of the total ionic conduction at 500°C. These findings from the present study can help elucidate the role of support in the performance of oxygen carrier materials and guide the rational design of high performance oxygen carrier for chemical looping applications.
2.2 Unreacted Shrinking Core Model

2.2.1 Model Setup

Turkdogan et al. systematically studied the reduction of iron ores of different sized particles at various temperatures and gas compositions. They found that the rate-limiting step varies from reaction control for Fe$_2$O$_3$-Fe$_3$O$_4$ reduction to diffusion control for Fe$_3$O$_4$-Fe$_x$O-Fe reduction. To study iron oxide reduction kinetics, various models have been developed in the literature such as the shrinking core model, cracking core model, particle-pellet (grain) model, and nucleation and growth model. De Lasa briefly reviewed these models and their applications in chemical looping reaction systems.

The shrinking core model is used in this study to consider the oxygen carrier reaction kinetics. The unreacted shrinking core model (USCM) is commonly used to describe the reaction of gas-solid systems. It considers three major factors that affect the overall reaction rate, i.e., diffusion through the gas film, intra-particle diffusion, and surface chemical reaction at a reaction interface. The USCM model assumes: first, the interfacial chemical reaction is a first order reversible chemical reaction; second, isothermal and isobaric conditions exist throughout the particle; and third, the volume of a pellet is unchanged by the progress of the reaction. In order to determine the reaction rate and the time for complete conversion, a three-interface USCM is adopted to represent the reactions listed in Table 2.1. It is noted that Fe$_{0.952}$O in the current model
is used to represent the wustite phase. The three-interface USCM is illustrated in Figure 2.2, and reaction rates in each reaction step are obtained through the following expressions

\[ V_1 = \lim_{i} P \left\{ A_i (A_i + B_i + B_i + F) + (A_i + B_i)(B_i + F)(y - y_i^*) \right\} \]

\[ V_2 = \lim_{i} P \left\{ [(A_i + B_i + B_i)(A_i + B_i + F) + A_i (B_i + F)](y - y_i^* - A_i (B_i + F)(y - y_i^*) \right\} \]

\[ V_3 = \lim_{i} P \left\{ [(A_i + B_i)(A_i + B_i + B_i + F) + A_i (B_i + F)](y - y_i^* - A_i (B_i + F)(y - y_i^*) \right\} \]

where

\[ A_i = \frac{1}{(1 - R_M)^{2/3} k_i (1 + 1/K_i)} \]

\[ A_2 = \frac{1}{(1 - R_W)^{2/3} k_2 (1 + 1/K_2)} \]

\[ A_3 = \frac{1}{(1 - R_F)^{2/3} k_3 (1 + 1/K_3)} \]

\[ B_i = \frac{(1 - R_W)^{1/3} - (1 - R_M)^{1/3}}{(1 - R_M)^{1/3} (1 - R_W)^{1/3}} \frac{d_p}{2D_i} \]

\[ B_2 = \frac{(1 - R_F)^{1/3} - (1 - R_W)^{1/3}}{(1 - R_W)^{1/3} (1 - R_F)^{1/3}} \frac{d_p}{2D_2} \]

\[ B_3 = \frac{1 - (1 - R_F)^{1/3}}{(1 - R_F)^{1/3}} \frac{d_p}{2D_3} \]

\[ F = 1/k_f \]
\[ \omega = (A_1 + B_1)[A_1(A_2 + B_2 + B_3 + F) + (A_2 + B_2)(B_3 + F)] + A_2[A_1(B_2 + B_3 + F) + B_2(B_3 + F)] \quad (17) \]

It is noted that, in the reducer, all the three reactions might not take place concurrently. There may be only one or two reactions proceeding at a specific time. Under these circumstances, the reaction rate must be calculated through formula for the states of two interfaces or single interface. The overall fractional reduction of iron oxide particles or reaction progress can be expressed as follows, based on the chemical formula of reduction products

\[ R = 0.1111R_M + 0.1889R_W + 0.7R_F \quad (18) \]

where \( R_M \), \( R_W \), \( R_F \) correspond to the conversions from \( \text{Fe}_2\text{O}_3 \) to \( \text{Fe}_3\text{O}_4 \), \( \text{Fe}_2\text{O}_4 \) to \( \text{Fe}_3\text{O}_4 \), and \( \text{Fe}_3\text{O}_4 \) to Fe, respectively. In addition, the water gas shift reaction in the gas phase is considered in this work. The reaction rate and equilibrium constant of the water gas shift reaction is based on the formulae in the literature.\(^{82,83}\)

### 2.2.2 Experimental Setup for Model Validation

A set of TGA tests were conducted for validating this particle kinetics model. The composite \( \text{Fe}_2\text{O}_3 \) particles were prepared and synthesized in a similar manner as in the previous work.\(^6\) The particle size was between 1.4-1.7 mm, which is suitable for solid flow in a moving bed reactor. A 50-mg batch of particles was placed in the TGA, and was reduced by 200 mL/min \( \text{H}_2 \) at 900 °C. The initial mass fraction of \( \text{Fe}_2\text{O}_3 \) in the solids was 60%, and the density of the particle was 2.5g/cm\(^3\). The particle porosity, \( \varepsilon' \), is 0.005,
which is an average value measured from BET. The property values for H$_2$ used in the
calculation are given below in Eqs. (19-22), most of which had been used by Hara et al.
in their investigation of the effect of temperature on iron oxide pellet reduction. The
properties used here for CO are the same as those of H$_2$, except that all three reaction-rate
constants are only 1/5 of those of H$_2$. It is noted that reaction-rate constants can be
different for pellets with different compositions and different micro-structures.

\[ k_{H_2} = 0.3 \text{m/s} \quad (19) \]

\[ K_{1H_2} = \exp(362 / T + 10.32) \]
\[ K_{2H_2} = \exp(-8580 / T + 8.98) \quad (20) \]
\[ K_{3H_2} = \exp(-2070 / T + 1.3) \]

\[ D_{1H_2} = 0.13 \times 0.7516 \varepsilon'(T/273)^{1.83}/10000 \]
\[ D_{2H_2} = 0.20 \times 0.7516 \varepsilon'(T/273)^{1.83}/10000 \quad \text{m}^2/\text{s} \quad (21) \]
\[ D_{3H_2} = 0.35 \times 0.7516 \varepsilon'(T/273)^{1.83}/10000 \]

\[ k_{1H_2} = 40 \exp(-6650 / T) \]
\[ k_{2H_2} = 80 \exp(-8000 / T) \quad \text{m/s} \quad (22) \]
\[ k_{3H_2} = 6800 \exp(-14000 / T) \]

where \( T \) is the temperature, K.

2.2.3 Results and Discussion

The three-interface USCM gives insight into the overall reaction as well as how
the interfaces between Fe$_2$O$_3$, Fe$_3$O$_4$, Fe$_x$O and Fe migrate through the particle during the
reduction process. The current model assumes that the iron oxide particle is surrounded
by pure reducing gas. This is because, in the TGA test, the solid is stationary in a small
crucible, while reducing gas rapidly flows through the system and takes out the product gas. Figure 2.3 compares results between the oxygen carrier particle modeling and TGA experiments. Dashed lines represent the conversions of individual species, while the solid line is the sum of the overall iron oxide conversion. The results show that the overall reaction progress predicted by the model is in favorable agreement with experimental data. Among all the three reduction reactions, Fe$_2$O$_3$ reduction is the fastest, which is closely followed by Fe$_3$O$_4$ reduction. Under given testing condition, near 22 minutes into the experiment, both reactions achieve full conversion, i.e., $R_M=R_W=100\%$. The slowest reaction is wustite reduction to metallic iron, which only achieves 70\% conversion ($R_F=70\%$) at 22 mins. Based on previous thermodynamic calculations, an iron oxide reduction conversion of 50\% could be achieved in a countercurrent moving bed conversion. Under the TGA testing condition, it’s seen that 7 mins are sufficient for a 50\% reduction conversion.

The USCM considers three factors influencing the reaction rate including external diffusion through gaseous film, intraparticle diffusion, and the surface chemical reaction. Reflected in the equations, $k_f$ is the mass-transfer coefficient through gaseous film (cm/sec) and $D$ is internal diffusivity in different iron oxide phases (cm$^2$/sec). For each surface reaction, $k$ represents the reaction rate constant while $K$ is the equilibrium constant. As shown in Figure 2.4, the USCM can help calculate the reaction time required by each step, and evaluate the importance of the three factors. The results show that the iron oxide particle reduction by hydrogen in this TGA study is dominated by intraparticle
diffusion. It is noted that the gas environment in the TGA can be assumed to be pure hydrogen, which is different from the gas concentration and profile in the moving bed reducer. Thus, the intraparticle diffusion might not be the only rate controlling step in the moving bed operation. This will be further discussed in the following section. In general, the USCM can well represent the oxygen carrier reaction kinetics and thus will be embedded in the following 1-D reducer model.

2.3 Grain Model

2.3.1 Model Step

A number of gas-solid reaction kinetic models have been developed for practical use during the last several decades. The majority of the models have been based on the assumption of a nonporous solid reactant. A typical representative is the shrinking core model. 82, 84 This type of model assumes sharp interfaces between the reacted zone and unreacted zone in the solids. However, in reality, the solid is porous and there is a gradual change in the gas profile throughout the pellets. The concept of a grain structure inside pellets has been investigated over several decades. For the detailed micro-structure, one can refer to the images captured by scanning electron microscopy (SEM). 78 The concept of grain structure has been taken into account by some previous models. 85-91 The ion diffusion mechanism inside grains has been studied recently and found to be influential for gas solid reaction kinetics. 92,93 Vargas has developed an oxygen carrier reaction model, in which the ion diffusion mechanism was applied to entire pellets, not individual
grains. The continuum assumption is used for pellets, which actually ignores the grain structures inside pellets and thus is not physically sound.

In the following section, a novel grain model considering ionic diffusion control will be developed and applied to the specific reaction of iron oxide reduction with hydrogen and/or carbon monoxide, which is of special interest in chemical looping applications. The assumptions for the ionic diffusion grain model, illustrated in Figure 2.5, are as follows:

1. The reduction is an isothermal process
2. The pellet is composed of spherical micro-grains having a small constant radius
3. Iron atoms form the grain lattice, which allows oxygen ions to diffuse out.
4. There is no structural change of the pellet during the reduction.
5. Reversible, first-order chemical reactions with the gaseous reactants take place at the outermost surface of each grain.
6. The concentrations in the bulk flow do not change due to diffusion through the pellet
7. The resistance of the reaction due to the gas film around the pellet is negligible.

Generally, consider a solid-gas reaction represented by

\[ v_a A_{(g)} + B_{(s)} \rightarrow v_c C_{(g)} + D_{(s)} \]

A material balance for gaseous reactant A gives
Similarly, for gaseous reactant $C$, we have
\[
\varepsilon \frac{\partial C^*_C}{\partial t^*} = \nabla^* \cdot (-D^C \nabla^* C^*_C) - \nu_a \frac{\partial C^*_B}{\partial t^*} \tag{24}
\]

The boundary conditions are
\[
\nabla^* C^*_A = \nabla^* C^*_C = 0 \quad (r^* = 0)
\]
\[
C^*_A = C_{A0}^*, \quad C^*_C = C_{C0}^* \quad (r^* = 1)
\]

The initial conditions for the gases are
\[
C^*_A = 0, \quad C^*_C = 0 \quad (0 \leq r^* < 1 \quad t^* = 0)
\]

The initial condition for the solid is
\[
C^*_B = C_{B0}^* \quad (t^* = 0)
\]

Assuming the solid particle is composed of small but highly dense grains each of which reacts according to the ionic diffusion model proposed by Vargas, we have
\[
\frac{\partial C^*_o}{\partial t^*} = \alpha^*_o \nabla^* \cdot (-D^o \nabla^* C^*_o) \tag{25}
\]

The corresponding boundary conditions for each grain are given as
\[
\nabla^*_o C^*_o = 0 \quad (r^*_o = 0)
\]
\[
-D^o \nabla^*_o C^*_o = k_o^\beta C^*_o \left( f^{(A)}_o - f^{(C)}_o / K_e \right) \alpha^*_o / \alpha^*_L \quad (r^*_o = 1)
\]

The initial condition for each grain is
\[
C^*_o = 1 \quad (t^* = 0)
\]
All the quantities with an asterisk are dimensionless. Gas concentrations are dimensionalized by $C_{gT}$, the overall gas concentration under the specified operating conditions of temperature and pressure. Solid concentrations and ion concentrations are normalized by the unreacted concentration of the diffusing ion in solid B, which can be denoted by $C_{o,B}$. For the iron oxide reduction, $B$ denotes Fe$_2$O$_3$ and thus $C_{o,B}$ becomes $C_{o,Fe_2O_3}$. The effective pore diffusion coefficients are normalized by $D_{eA}$, the pore diffusion coefficient of gas $A$, making $D_{eA}^* = 1$. Assuming gas $C$ has the same pore diffusion coefficients, we have $D_{eC}^* = 1$. Some important dimensionless variables are defined as follows:

$$\alpha_L = R / R_o$$

$$\alpha_C = C_{gT} / C_{o,B}$$

$$t^* = tD_{eA} / R^2$$

$$k_s^* = k_s R C_{o,B}^\beta / D_{eA}$$

$$C_o^* = C_o / C_{o,B}$$

When the ionic diffusion grain model is adopted for each grain, we have

$$-\frac{\partial C_B^*}{\partial t} = 3(1 - \varepsilon)\alpha_L k_s C_o^* C_g^* \left( f_A^{(v_s)} - f_C^{(v)} / K_c \right) / d_o R_o^*$$  \(26\)

$$\varepsilon \frac{\partial C_A^*}{\partial t^*} = \nabla \cdot \left[ \sum_{i=1}^{m} \left( \frac{\partial j_i^*}{\partial n} \right) \right] - 3(1 - \varepsilon)\nu \alpha_L k_s^* C_o^* C_g^* \left( f_A^{(v_s)} - f_C^{(v)} / K_c \right) / d_o R_o^*$$  \(27\)

$$\varepsilon \frac{\partial C_C^*}{\partial t^*} = \nabla \cdot \left[ \sum_{i=1}^{m} \left( \frac{\partial j_i^*}{\partial n} \right) \right] + 3(1 - \varepsilon)\nu \alpha_L k_s^* C_o^* C_g^* \left( f_A^{(v_s)} - f_C^{(v)} / K_c \right) / d_o R_o^*$$  \(28\)
2.3.2 Model Analysis

An important dimensionless number can be defined as

$$\theta = \frac{\alpha_L k_i}{D_e} = \frac{\alpha_L k_i R C_{o,b}}{D_e}$$

This parameter, the ratio between chemical reaction rate constant and the gas diffusion coefficient in the pellets, determines the behavior of the overall reaction front in the pellet. Generally, if $\theta >> 1$, the reaction is controlled by pore diffusion. If $\theta << 1$, the reaction is controlled by the chemical reaction. If $\theta \approx 1$, the reaction mechanism is mixed, controlled by both pore diffusion and the chemical reaction.

For the reaction on the outmost surface of each grain, we define

$$\psi = \frac{k_s^* \alpha_C}{\alpha_L D_e^*} = \frac{k_s R C_{o,b} \alpha_C}{\alpha_L D_o}.$$ 

This parameter is the ratio between the chemical reaction rate constant and the diffusion coefficient of the diffusing ions. Generally, if $\psi >> 1$, the reaction is controlled by ion diffusion. If $\psi << 1$, the reaction is controlled by the chemical reaction. If $\psi \approx 1$, the reaction control is mixed, ion diffusion and the chemical reaction.

Considering both the effects of the parameters $\theta$ and $\psi$, we have four limiting cases:

1) $\theta >> 1, \psi >> 1$, the reaction is controlled by both pore diffusion in pellets and ion diffusion in grains, the typical reaction state under this condition can be illustrated by Figure 2.5(a). In this case, a sharp interface exists between the reacted and the unreacted
zones. Also, the grains in the reacted zones are not fully reacted since the ion diffusion is too slow to supply enough ions on the outmost surfaces of the grains. The core zone of each grain actually is still not reacted. For this case, the equations for ion concentrations in the grains, (25), and the equations for the gases, (26) and (27), should be solved simultaneously using numerical methods since there is no ready analytical solution for them.

2) $\theta \gg 1$, $\psi \ll 1$, the reaction is controlled by both pore diffusion in pellets and the chemical reaction on grain surfaces, the typical reaction state under this condition is illustrated by Figure 2.5(b). There is a sharp interface between the reacted and unreacted zones. In the reacted zone, the grains are fully converted from the surface to the innermost core. This is because the ion diffusion is so fast that it not only can supply the surface reaction but also can maintain a uniform concentration of ions throughout the grain. This scenario is very similar to that of the unreacted shrinking core model. The numerical methods for this case will be described in detail in the following section.

3) $\theta \ll 1$, $\psi \gg 1$, the reaction is controlled by both the chemical reaction on grain surfaces and ion diffusion in grains, as illustrated by Figure 2.5(c). $\theta \ll 1$ implies that the pore diffusion is a relatively fast process. This makes the concentration of the reducing gases uniform throughout the pellet. Therefore, there will be no reaction front inside the pellet. In this case, the size of the pellet does not affect the reaction process at all. What really matters is only the size of the grain and the ion diffusion coefficient. In effect, the
concept that each pellet is composed of great number of grains breaks down here. This means every grain can be treated as a part of a continuum pellet. To get the solution of this case, only equation (25) needs to be solved and analytical solutions can be obtained under some particular condition, e.g., if the reaction is first order with respect to the solid reactant concentration, i.e., \( \beta = 1 \). For the details of the derivation of analytical solutions, one can refer to previous work. 92

4) \( \theta << 1, \psi << 1 \), the reaction is controlled only by the chemical reaction on grain surfaces, the typical reaction state under this condition can be illustrated by Figure 2.5(d). This case is very similar to case 3). The only difference is that ion diffusion is also a fast process. The concentration of the diffusing ions in grains will be uniform throughout every grain, making the solution of the gas-solid reaction equations even simpler. Each grain can be treated as a continuum pellet. The chemical reaction rate will be the only parameter that matters since the concentration of the diffusing ions is always uniform. Szekely et al classified this case as the “volumetric reaction of highly porous solid”. 89

For, other combination of \( \theta \) and \( \psi \), with at least one of the two parameter being around unity, the reaction is under mixed controlled. This is the most general case of the gas-solid reaction problem. To obtain the solution of this case, the equations for the ion concentration in grains, (25), and the equations for gases, (26) and (27), should be solved simultaneously. Numerical methods are required since an analytical solution is not known. However, through our analysis of the experimental data of the iron oxide
reduction from both our group and other investigators, we found that the inequality of \( \psi << 1 \) always holds. From the definition, \( \psi = k_4 R C^{\beta}_{o,b} \alpha_c / \alpha_L D_o \), it can be seen that only \( \alpha_L \) can be affected by the grain structure of a pellet: the other parameters are determined by more fundamental physics. Clearly, a large value of \( \alpha_L \) gives a small value of \( \psi \). This indicates that a very small grain size helps ensure that \( \psi << 1 \). From the SEM images, the grain size is around 1-5 \( \mu \)m. Considering that the size of pellets is usually around 1-5 mm, the value of \( \alpha_L \) would be around \( 10^3 \). This is significant since the choice of \( \psi = 1 \)–100 gives an unfavorable fit of the model to the experimental data while \( \psi = 0.01 \) gives a satisfactory fitting.

The condition of \( \psi << 1 \) can also be used to simplify our ionic diffusion grain model and, therefore, allow a more efficient numerical solution method. A direct consequence of \( \psi << 1 \) is that the concentration of the diffusing ions is uniform throughout every grain. Thus, the ionic diffusion equation can be simplified to

\[
\frac{dC^*_{o}}{dt} = -3k_s C^*_{o} C^*_{g} (f^{(e)}_{A} - f^{(e)}_{C}) / K_e \alpha_c \alpha_L / R^*_o
\]

This simplification significantly reduces the computational complexity of the present ionic diffusion grain model since resolving the solution inside every grain is avoided.

**2.3.3 Results and Discussion**

The present ionic diffusion grain model was used to fit two sets of experimental data. The experiment tests were conducted in a similar way as described in section 2.2
with different sized particles. It was found that \( \beta = 1.5 \) gave the best fit. In the fitting procedure, the chemical reaction rate constant \( k \) was determined and fixed by the case with the smallest pellet radius. The grain size was assumed to remain unchanged as the pellet size varied. This assumption gives \( \alpha \propto R \). The pore diffusion was allowed to change when the pellet radius increased.

The newly developed ionic diffusion grain model was used to fit the experimental results obtained by our group. It can be see the model results are in good agreement with the experiments (see Figure 2.7). The pore diffusion coefficient of hydrogen found for the pellets of different sizes are listed in Table 2.2. Clearly, the results indicate that the pore diffusion coefficient of hydrogen increases as the pellet size increases. This overall reduction trend is consistent with the measurements performed by Turkdogan & Vinters.

2.4 Conclusions

The development of an ideal looping carrier requires thorough consideration of many intertwining factors, including thermodynamic properties of the particle, reaction kinetics, cost, recyclability, physical strength, ease in heat integration, resistance to contaminants, and environmental and health effects. For the chemical looping system, the system is characterized by metal (metal oxide) oxidation (reduction) reactions. Four metals, namely, Ni, Cu, Mn, and Fe, have been considered as the primary active metals that can be embedded onto an inert solid support to participate in the reduction and
oxidation reactions. Among these metals, nickel-based particles exhibit superior thermal stability and reactivity with gaseous fuels, but they are costly and have toxic properties. Copper-based particles also possess good reactivity and allow oxygen uncoupling reactions. Copper, however, is also costly and has a high tendency to sinter and agglomerate. Iron-based particles are cheap and are suitable for hydrogen production, but iron’s reactivity with gaseous fuels is relatively low. The understanding of these looping particles is mostly limited to the macroscopic properties. More fundamental studies of the reaction mechanism, based on marker experiments and Density Functional Theory (DFT) calculations, reveal the significance of ionic diffusion patterns enhanced by support materials.

A three-interface unreacted shrinking core model was applied to describe the reaction of the gas and solid flows within the reactor. The kinetic model assumes three major reaction steps: external gas diffusion, intraparticle diffusion and surface reaction. Both kinetics and thermodynamics are considered in the model. The code was validated through comparing the simulations with experimental data. The results indicate that intraparticle diffusion is the controlling step for test condition considered, and also give insights of the reaction progress for individual iron oxide particles.

An ion diffusion grain model is developed based on a fundamental understanding of gas-solid reactions. The fact of grain structure inside pellets has been revealed over the decades and has been taken into account by some previous models. The ion diffusion
mechanism inside grains has just been exploited recently. This fundamental mechanism is incorporated into a grain model for the first time. In this model, iron oxide pellets are assumed to be composed of spherical micro-grains having a small constant radius. Structural changes of individual pellets during the reduction are negligible. The diffusion of oxygen ions is allowed within the grain lattice defined by the iron atoms. Chemical reaction is considered to take place only at the outermost surface of each grain. Three resistances to the overall progress of reaction are considered in this model: pore diffusion of gases in pellets, oxygen ion diffusion in grains, and chemical reaction on grain surfaces. Four limiting cases are discussed thoroughly when one or two resistances are dominant. When the ratio between chemical reaction rate constant and the diffusion coefficient of the diffusing ions is very small, the governing equations for the present model can be significantly simplified. Much computational effort can be saved when the numerical solutions are pursued. The numerical results were used to validate the proposed model by fitting available experimental data.
Figure 2.1 Ellingham diagram calculated from HSC Chemistry, showing the variation of oxidation Gibbs free energy with temperature for various compounds.
Figure 2.2 Schematic diagram of the unreacted shrinking core model for the reduction of hematite.
Figure 2.3 Comparison between TGA experimental results and USCM results for individual oxygen carrier particles reduction by hydrogen at 900 °C.
Figure 2.4 Reaction time for different controlling steps.
Figure 2.5 Representation of the ionic diffusion grain model for the reaction of a porous solid with a gas.
Figure 2.6 Four limiting cases of the ionic diffusion grain model for the reaction of a porous solid with a gas. (a) $\theta >> 1$, $\psi >> 1$, the reaction is controlled by both pore diffusion in pellets and ion diffusion in grains; (b) $\theta >> 1$, $\psi << 1$, the reaction is controlled by both pore diffusion in pellets and the chemical reaction on grain surfaces; (c) $\theta << 1$, $\psi >> 1$, the reaction is controlled by both the chemical reaction on grain surfaces and ion diffusion in grains; (d) $\theta << 1$, $\psi << 1$, the reaction is controlled only by the chemical reaction on grain surfaces.
Figure 2.7 The comparison between results from the present ionic diffusion grain model and the experimental data.
Figure 2.8 The comparison between results from the present ionic diffusion grain model and the experimental data.
Table 2.1 Key reactions in the syngas chemical looping process for an Fe-based carrier

<table>
<thead>
<tr>
<th>Reactor</th>
<th>Reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reducer</td>
<td>3Fe₂O₃+CO/H₂=2Fe₃O₄+CO₂/H₂O</td>
</tr>
<tr>
<td></td>
<td>((x/(4x-3))Fe₃O₄+CO/H₂=(3/(4x-3))Fe₆O+CO₂/H₂O)</td>
</tr>
<tr>
<td></td>
<td>Fe₆O+CO/H₂=xFe+CO₂/H₂O</td>
</tr>
<tr>
<td>Oxidizer</td>
<td>xFe+H₂O=Fe₆O+H₂</td>
</tr>
<tr>
<td></td>
<td>((3/(4x-3))Fe₆O+H₂O=(x/(4x-3))Fe₃O₄+H₂)</td>
</tr>
<tr>
<td>Combustor</td>
<td>4Fe₅O₄+O₂=6Fe₃O₃</td>
</tr>
</tbody>
</table>
Table 2.2 The diffusion coefficients of hydrogen in pellets in the experiments performed by Turkdogan & Vinters.

<table>
<thead>
<tr>
<th>d (mm)</th>
<th>(D_{eA})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>1.1×10^{-4}</td>
</tr>
<tr>
<td>1.8</td>
<td>4.3×10^{-5}</td>
</tr>
<tr>
<td>3.6</td>
<td>5.8×10^{-5}</td>
</tr>
<tr>
<td>8.0</td>
<td>7.1×10^{-5}</td>
</tr>
</tbody>
</table>
Table 2.3 The diffusion coefficients of hydrogen in pellets in the experiments performed by our group.

<table>
<thead>
<tr>
<th></th>
<th>0mm&lt;d&lt;0.5mm</th>
<th>1.2mm&lt;d&lt;1.6mm</th>
<th>2.0mm&lt;d&lt;2.8mm</th>
<th>2.8mm&lt;d&lt;3.4mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{ea}$</td>
<td>$3.5 \times 10^{-7}$</td>
<td>$5.1 \times 10^{-7}$</td>
<td>$1.1 \times 10^{-6}$</td>
<td>$1.4 \times 10^{-6}$</td>
</tr>
</tbody>
</table>
Chapter 3

Chemical Looping Reactor Design and Equipment Modeling

3.1 Introduction

A chemical looping reactor system consists of a reducer, a combustor, a non-mechanical valve, a fine removal device, gas-solid separators, and other auxiliaries, where the reducer is the key component for fuel conversion. As discussed in the previous section, there are two fundamentally different reducer modes that classify the chemical looping systems. Figure 3.1 illustrates that Mode 1 reducer design is generally characterized by mixed fluidized beds, while Mode 2 is characterized by gas-solid countercurrent moving/dense beds. Table 3.1 further compares the two modes in the context of iron-based chemical looping applications. The channeling flow and back mixing in the Mode 1 reducer usually results in poor fuel and oxygen carrier conversions. The Mode 2 reducer design has the distinct advantage of enhancing chemical looping the iron oxide conversion while enabling full fuel conversion. Thus Mode 2 reactor requires for a significantly lower circulation rate of Fe₂O₃ particles than Mode 1. The small circulation rate together with the mitigating circumstances in the moving bed reactor reduces the particle attrition rate and oxygen carrier loss. Furthermore, in the Mode 1 system, it is inevitable that the sizes of the oxygen carrier particles, attrited fines, the solid fuel, and ash, are similar, which complicates the ash removal and reactor design. Additional compartments, such as bubbling beds, are usually used for ash and unreacted
fuel segregation and separation in the Mode 1 system. A Mode 2 moving bed reactor allows for a larger particle size of oxygen carriers, which eases the ash separation and requires a much smaller reactor diameter as higher gas velocity in the reactor is possible.

Based on the concept discussed above, a syngas chemical looping (SCL) process has been developed. The SCL process circulates iron-based oxygen carrier particles through three reactors for hydrogen and electricity coproduction while using syngas as a fuel and capturing CO$_2$. The syngas is mainly composed of CO and H$_2$ and is derived from a typical coal or biomass gasifier. The SCL reducer is a good example of a countercurrent moving bed operation, which ensures the full conversion of fuels while enhancing the extent of iron based oxygen carrier conversion. The high extent of conversion of the iron based oxygen carrier facilitates the generation of hydrogen from steam-iron reaction in the oxidizer. The combustor fully regenerates the oxygen carrier particles, which are then circulated back to the reducer via a riser. Table 3.2 summarizes all the key reactions involved in the SCL process.

The countercurrent moving bed operation is seen in many industrial applications such as blast furnaces, kiln heaters, and adsorptions. The SCL moving bed reducer concept and application has been proven in a bench scale unit, and the SCL integrated process has been tested under a 25kWth sub-pilot scale continuous operation for more than 300 hours. In order to further scale up the chemical looping process, issues such as cost, time, measurement, safety, and other uncertainties in larger unit operations need
to be examined. To address these uncertainties, advanced reactor modeling is highly desired and the modeling efforts can accelerate the SCL technology development, reduce the pilot-scale facility design time and operating campaigns, as well as reduce the cost and technical risks.

Previous computational efforts on chemical looping process development have heavily focused on mode 1 fluidized bed reducer modeling and analysis, which was recently reviewed by Adanez et al. Kang et al. developed a steady-state model for a countercurrent moving bed reducer. A one-step reduction from Fe$_2$O$_3$ to Fe$_x$O was assumed in their model, which is unrealistic and thus does not represent the complex rate process of this reaction system. Additionally, many of the earlier modeling work lacks first-hand experimental data for comparisons and validation. In this chapter, both a one-dimensional (1-D) dynamic reactive flow model and a two-dimensional (2-D) computational fluid dynamics (CFD) model were developed to simulate the countercurrent gas-solid interaction within a moving bed reducer in the SCL process. A three-interface shrinking core model was used to represent the overall reaction thermodynamics and kinetics of individual iron based oxygen carrier particles. The individual particle model was validated by experimental TGA data. The moving bed code was validated by comparing the modeling results with the experimental data from a 2.5 kW$_{th}$ bench-scale reactor that the authors obtained earlier. The model was used to investigate the flow and reaction progress and assist in the design and optimization of the
SCL reducer. A 2-D CFD model is also developed for the combustor to assist understanding the reaction and flow behavior inside the fluidized bed reactor.

3.2 1-D Reducer Modeling

In order to simulate the moving bed reducer in the SCL process accurately, a suitable flow model is highly needed to describe the gas and solid flow pattern within the reactor. There are various flow models that can be employed. In this section, a one-dimensional flow model was developed to simulate the countercurrent gas-solid flow pattern within the moving bed reactor. Compared to multi-dimensional models, the 1-D model is simple and serves a practical purpose.

3.2.1 Mathematical Mode

The three-interface shrinking core model was adapted in the present reactive flow model to describe the overall conversion in the reactor. The assumptions in this model are given as follows:

(a) uniform temperature within the solid particles.
(b) both gas and solid streams in plug flow.
(c) three-interface unreacted shirking core model representing reaction kinetics.
(d) ignoring the temperature difference between gas and solid.

The 1-D model describes the unsteady generation of gases, the changing flow patterns, and the reaction kinetics in the system, which is different from the previous
work of using a steady state assumption. 97 The mass balance equations for the gas phase and the solid phase in the reducer can be expressed as follows in the Lagrangian framework.

\[
\frac{De_i}{Dt} = \sum_l \nu_{li} \frac{3(1-\varepsilon)V_i}{r_p}, \quad (1)
\]

\[
\frac{DE_i}{Dt} = \sum_l \nu_{li} \frac{3(1-\varepsilon)V_i}{r_p}, \quad (2)
\]

where \( C_i \) stands for the concentrations of gas species, such as \( \text{H}_2, \text{CO}, \text{H}_2\text{O}, \text{CO}_2 \), and \( E_i \) stands for the concentration of solids, such as \( \text{Fe}_2\text{O}_3, \text{Fe}_3\text{O}_4, \text{Fe}_x\text{O} \) (\( x=0.952 \)) and \( \text{Fe} \). The right hand side terms of Eqs. (1) and (2) denote the rates of change of the concentrations from the chemical reactions between the gases and the solids. \( \nu_{li} \) is the stoichiometric coefficient for species \( i \) appearing in the \( l \)th reaction. For the reactant species, the stoichiometric coefficient has a negative value, \( \nu_{li} < 0 \). On the other hand, for the products, the stoichiometric coefficient has a positive value, \( \nu_{li} > 0 \). Here, the chemical reaction is the only factor that changes the concentrations of every species, which establishes the relationship that the substantial derivatives equal the right hand side terms. Since both the gas and solid streams are in plug flow (assumption (b)), Eqs. (1) and (2) in the 1-D Eulerian framework can be rewritten as

\[
\frac{\partial e C_i}{\partial t} = -U_i \frac{\partial e C_i}{\partial z} + \sum_l \nu_{li} \frac{3(1-\varepsilon)V_i}{r_p}, \quad (3)
\]

\[
\frac{\partial E_i}{\partial t} = -U_{S_i} \frac{\partial E_i}{\partial z} + \sum_l \nu_{li} \frac{3(1-\varepsilon)V_i}{r_p}, \quad (4)
\]
where $U_i$ and $U_s$ are velocities of the gases and solids respectively, and $z$ is the spatial coordinate that begins at the bottom of the reducer and ends at the top of the reducer. The mathematical model developed here includes both time derivative terms and convective terms. This can help obtain the whole evolution process of the reactive flow in the 1-D moving bed reducer. It should be noted that $D(\cdot)/Dt$ in Eqs. (1) and (2) are substantial derivatives, indicating the change rate of the concentration of every species as the species move in the reducer. In Eqs. (3) and (4), the substantial derivatives have been split into local time derivative terms and spatially convective terms in the 1-D Eulerian framework.

A FORTRAN90 program is coded based on the governing Eqs. (3) and (4), and the unreacted shrinking core kinetic model. For the temporal terms, a third-order TVD Runge-Kutta scheme is used for discretization. $^98$ For the spatial terms, a fifth-order WENO scheme is used. $^99$ The entire calculation procedure for reaction rates can be found in the work from Hara et al. $^82$ The initial conditions for the 1-D reducer modeling are that the bed is filled with Fe$_2$O$_3$ particles and the voidage is filled with syngas.

3.2.2 Steady State Results and Model Validation

A 2.5 kW$_{th}$ bench scale moving bed reactor for conducting gas-solid reactions was constructed and operated in order to obtain the reactor performance data for modeling and scaling up analysis of the SCL process.$^55$ The length of the moving bed reactor is 0.9m with an inner diameter of 4.06 cm, as shown in Figure 3.2. There are a number of
gas and solid sampling ports along the reactor so that the fuel gas and oxygen carrier 
particle composition profiles in the reactor can be measured. Data from the bench scale 
reducer study reported earlier by the authors were used to verify the 1-D reducer model. 

55 The Fe$_2$O$_3$ particles, with similar properties as tested in the TGA experiments discussed 
in Chapter 2, were introduced at the top of the reducer at a feed-rate of 12.87g/min. The 
diameter of the solids is 4.0 mm, and the bed voidage of the reducer is 0.4. The pressure 
and the temperature of the system were 1 atm and 900 °C, respectively. A simulated 
syngas was introduced from the bottom; the fractions of H$_2$, CO, CO$_2$, N$_2$ were 29.19%, 
43.768%, 5.02% and 22.022% respectively. The gas feed-rate is 0.002262Nm$^3$/min.

In the SCL system, the moving bed reducer is designed to fully convert the syngas 
to CO$_2$ and H$_2$O at the top of the moving bed reducer. At the same time, a maximum 
oxygen carrier conversion should be obtained at the bottom of the reducer. In order to 
verify the 1-D reducer model, the previous bench scale reducer testing is used to specify 
the model input and output. Figure 3.3 illustrates the numerical results of the 1-D moving 
bed reducer when steady state is reached. The steady state results show that the syngas 
conversion at top of the reducer is 97.5% at the top, while the oxygen carrier conversion 
is 49.2% at the bottom. In the bench scale experiment, a syngas conversion in excess of 
99.5% and an oxygen carrier conversion of nearly 50% were obtained. It can be seen that 
the present numerical results agree favorably with those from the previous experiments, 
which further validates the 1-D mathematical model. Therefore, this 1-D model can be 
used for further investigations of the reducer in the SCL system.
The 1-D reducer model can not only calculate the overall gas and solid conversions at the reactor outlets, but can also provide dynamic gas and solid conversion profiles inside the reactor, which is helpful for understanding the reaction behavior. As shown in Figure 3.3, the calculated syngas and oxygen carrier conversion profiles along the axial locations of the reactor at steady state conditions match well with the previous profiles measured from sampling ports. Both experimental and modeling results show that the gas and solid conversion profiles have opposite trends because of the countercurrent contact pattern. The results also indicate that the conversion rates at both ends are much faster than the conversion rates in the middle section of the reducer. The syngas and Fe$_2$O$_3$ particles are introduced at the bottom and the top of the reducer, respectively, which creates a large driving force for reduction reaction going forward. In the middle section, however, the gas and solid compositions are close to an equilibrium state, and thus nearly no reaction is observed. Specifically, the modeling results show that the equilibrium state is maintained when the gas and solid conversions are 38% and 30% (pure Fe$_{0.952}$O), respectively. Such an intermediate equilibrium stage and overall gas and solid conversions can be also predicted by a multistage equilibrium model developed in a preceding work. Both the equilibrium model and the kinetic model have been validated by experimental data, and both modeling results show that the countercurrent moving bed reducer design is capable of ensuring a full syngas conversion while enhancing oxygen carrier conversion.
As shown in Figure 3.3, under the current operation condition and reducer design, an individual particle quickly completes the reduction from Fe$_2$O$_3$ to Fe$_3$O$_4$ and then to Fe$_3$O at the top. The reduction from Fe$_3$O to Fe is then limited by thermodynamic equilibrium before the gas profile is changed at the bottom where fresh syngas is introduced. Compared with the previous oxygen carrier kinetic studies in the TGA where only intraparticle diffusion dominates the reduction process, the oxygen carrier particle reduction in the moving bed reducer is restricted by the reaction thermodynamics. It is also noted in Figure 3.3 that there is a minor difference between the modeling results and experimental data. Such deviation may result from the flow and temperature maldistribution across the bed, and from the randomness of the gas and solid sampling in the experiments. The unsaturation degree x in the wustite (Fe$_x$O) phase varies from 0.830<x<0.952, which could also affect the equilibrium conditions and thus compositions of the system.

3.2.3 Unsteady State Results

As stated in the model setup, the temporal terms are considered in the governing equations of the reducer system. This means that not only can the steady state of the reducer be revealed by the simulation, but the dynamic conversion profiles can also be modeled. Figure 3.4 displays the conversion profiles of both the solids and the gases at different times under unsteady state conditions. During the early stages, the conversion profiles change rapidly (see the results at t=1,000s in Figure 3.4a). The major pattern of the conversion profiles has formed at the bottom of the reducer when t=5,000s (see
Figure 3.4b). Subsequently, as shown in Figure 3.4c and 3.4d, the rightmost segments correspond to the first two reduction reactions (\(\text{Fe}_2\text{O}_3-\text{Fe}_3\text{O}_4-\text{Fe}_x\text{O}\)), and move towards the top of the reducer without significant shape change, while the leftmost segments correspond to the third reaction (\(\text{Fe}_x\text{O}-\text{Fe}\)) and stay at the bottom of the reducer. The equilibrium stage emerges between the left and right segments, and extends as reaction progress. The system reaches its steady state at around 150,000s (see Figure 3.4e), which is caused by the slow translational movement of the profiles towards the top of the reducer.

From the observation of the numerical results, two aspects arise and will be discussed later. The first aspect is that since the conversion profile is mostly flat in the middle part of the reducer, the reducer may be shortened without affecting the reactions inside. The second aspect is that the efficiency of the current case is relatively low. The system takes too long a time to reach the steady state because of the thermodynamic equilibrium stage formation in the middle part of the reducer. Adjustment of the feed-rate ratio between the gases and solids may be a simple and straightforward way to decrease the converging time.

**3.2.4 Reducer Design: Effective Reducer Length**

The reducer length can be optimized using the 1-D moving bed model. The reducers with the lengths of 0.5m, 0.4m and 0.2m are simulated under the same initial and boundary conditions. The steady-state simulation results are shown in Figure 3.5,
from which it can be seen that the conversion profiles of the reducers with the length of 0.5m and 0.4m have approximately the same conversion profiles as the reducer of length 0.9m. The main difference is that the flat parts or the equilibrium state of the profiles in the shorter reducers are shortened. However, the reducer with 0.2m length seems to be too short to complete the reactions, unlike the other cases. The flat parts of the profiles in the reducer of 0.2m have almost completely disappeared. As a result, the syngas conversion in this case is not as high as the conversion in the reducers with longer lengths. A reducer of 0.4m can achieve exactly the same results as a reducer of 0.9m, indicating that the design of the current reducer is conservative and the reducer can be shortened without changing the reaction processes.

It is noted that no matter how long the reducer is designed, the segments with solid conversion higher than 30% are always present at the bottom of the reducer. Under the given syngas to oxygen carrier flow rate ratio, the reducing gas is almost completely converted at the top, and the reducing gas concentration at the middle and top sections is not enough to drive the reaction equilibrium towards wustite reduction to metallic iron. Under this circumstance, the high reducing gas concentration can only be reached near the bottom of the reducer where the new reducing gases are just injected in.

3.2.5 Reducer Operation: Gas-Solid Feed-Rate Ratio Effect

The gas-solid feed-rate ratio is an important variable in the moving bed reducer operation. Since the time for the system to reach the steady state is considerable in the
previous scenario, it is desired to determine how the converging time varies with the feed-rate ratio. Before the related numerical simulations are conducted, an analysis based on the equilibrium constants of the three reduction reactions is performed. The equilibrium constant of the third reaction is $K_3=0.6283$ at 900 °C. When the syngas can be fully converted in the reducer, the ideal percentage of the syngas consumed in the first and second reactions would be $1/(K_3+1)=61.414\%$ with the rest of the syngas (38.586\%) being consumed in the third reaction. As illustrated above, Fe$_2$O$_3$ in the solids can be converted completely into Fe$_x$O by the first and second reactions. The generated Fe$_x$O can only be partially converted into Fe from the lack of reducing gas. The total amount of Fe$_2$O$_3$ is determined by the 61.414\% of the reducing gases. The amount of converted Fe$_x$O corresponds the 38.586\% of the reducing gases. Through the combination of the first two reactions

$$\frac{x}{3x-2}Fe_2O_3 + H_2/CO \leftrightarrow H_2O/CO_2 + \frac{2}{3x-2}Fe_xO$$

and the third reaction

$$Fe_xO + H_2/CO \leftrightarrow H_2O/CO_2 + xFe,$$

the feed-rate ratio between gas and solids can be determined to be 1.4647 when the reducing gases are critically and fully converted. At this critical ratio of 1.4647, a maximized solids conversion of 48.823\% can be obtained to ensure a full syngas conversion at the top of the reducer.
From the data of previous experiments, the feed-rate ratio between gas and solids is found to be 1.5265, which is slightly higher than the critical ratio of 1.4647. In the following numerical investigation, the gas feed-rate remains unchanged, and the solids feed-rate is changed to adjust the feed-rate ratio between gas and solids. The situation with a ratio lower than the critical value is first examined. The solids feed-rate is increased by 5%, making the feed-rate ratio decrease to 1.4538. The results of this case are shown in Figure 3.6, and the steady state conversion profiles are significantly different from the previous results. All the profiles appear near the bottom of the reducer with an unreacted zone at the top. The converging time of this case is about 20,000s, which is much less than that of the case with a feed-rate ratio of 1.5265. This profound difference can be understood easily as follows. After the case with the ratio of 1.4538 reaches the steady state, imagine how the conversion profiles would change if the feed-rate ratio is increased to 1.5265. Because the system can only fully convert the gases when the feed-rate ratio is lower than the critical value 1.4647, the system now cannot fully convert all of the fuel gases. Therefore, the excessive reducing gases will keep going upwards beyond the position of $z=0.35$ (see Figure 3.6) and will react with the unreacted Fe$_2$O$_3$ in the upper positions, making the entire profiles except the bottom segment moving slowly towards the top of the reducer. The moving speed of the profiles is determined by the amount of the excessive reducing gases and is thus essentially determined by the feed-rate ratio. The salient changes of the profiles during this movement are that the middle segments of the profiles keep expanding (one can refer to Figure 3.4b-3.4e for better understanding). The expansion of the middle segments is
because an equilibrium stage is reached in that area. It can be conjectured that when the 
feed-ratio is only slightly higher than the critical ratio, the converging time would be 
extremely long since the unsteady movement of the profile are very slow. As the result, 
such gas to solid feed-rate ratio should be avoided in a practical reducer operation.

Generally, the converging time can be shortened in two ways. One is to make the 
feed-rate ratio slightly smaller than the critical ratio. The other is to shorten the reducer to 
a proper size without affecting the reactions inside. A series of numerical simulations 
with different feed-rate ratios and reducer lengths is performed. Figure 3.7 shows that the 
converging time varies as the feed-rate ratio between the gas and solids is changed. The 
converging time is prohibitively long when the feed-ratio is close to but higher than the 
critical ratio. For the actual moving bed operation, a ratio slightly below the critical ratio 
is recommended. However, if the ratio is too small, this operation is not favorable since 
the conversion of the solids becomes low, which requires a large oxygen carrier 
circulation rate. It is also noticed from Figure 3.7 that a shorter reducer needs less time to 
reach the steady state. Figure 3.8 displays the evolution of the gas and solids conversion 
profiles as the feed-rate ratio varies. On one hand, the gas conversion cannot reach 100% 
after the feed-rate ratio goes beyond the critical value. On the other hand, the reducer 
with a length of 0.2m is not long enough to function as well as the other longer reducers 
since the gas conversion is appreciably lower than 100% even when the feed-ratio is 
lower than the critical value. Nevertheless, the reducer of 0.38m actually functions as
well as the one of 0.9m, indicating the shorter reducer can be considered in practical reducer design.

3.3 2-D Reducer Modeling

Previously, a 1-D dynamic model was adopted to address the reactions occurring in the reducer without consideration of the heat of reaction and heat transfer. In this section, the heat and mass transfer inside the reducer are modeled and analyzed in a 2-D CFD model. In order to make the simulation adhere to the real situation, a 2-D axisymmetric geometry is used.

3.3.1 CFD Model Setup

The reducer is sized based on the bench scale test facility, with a length of 0.9 m and a radius of 0.0203m, as shown in Figure 3.9. Both the gas inlet and outlet are 0.0203m wide. They are located at a radial position with a distance of 0.0406m away from the axis line. The solids move from the top of the reducer to the bottom, and the gas goes on an opposite direction, which results in a countercurrent two-phase flow system in the reducer. As the gas moves to the top of the reducer, it reacts with the solids and reduces them from hematite to magnetite, then to wustite. Under certain operating conditions, the reduction can go along down to metallic iron. The mesh in the main part of the reducer is 10X440, while both of the gas inlet and gas outlet domain are 10X10 cells.
Similar to previous kinetic modeling, there are totally three reactions assumed in the reducer, including

\[ 3\text{Fe}_2\text{O}_3 + H_2 \leftrightarrow H_2\text{O} + 2\text{Fe}_3\text{O}_4 \]

\[ \frac{x}{4x-3} \text{Fe}_3\text{O}_4 + H_2 \leftrightarrow H_2\text{O} + \frac{3}{4x-3} \text{Fe}_3\text{O} \]

\[ \text{Fe}_x\text{O} + H_2 \leftrightarrow H_2\text{O} + x\text{Fe} \]

where \( x = 0.952 \). Their reaction rates are calculated by an user-defined function which is based on the unreacted shrinking model. For the sake of simplicity, the three reactions will be denoted by M, W and F respectively.

The solids in the whole domain of the moving bed will be given a fixed constant velocity. The 2-D space is axisymmetric. The physical property data are from either default value in Fluent or literature. User defined functions (UDFs) are used to conduct calculation based on the shrinking core model. It is also noticed that the densities of different species varies with their molecular weights, in order to ensure that the volume of the solids mixture would keep unchanged throughout the reduction process. The unchanged volume of solids gives an unchanged voidage for the gas to go through. This will result in a near uniform flow structure of the gas along the axial direction, which is adhere to the real situation. The packing limit is 0.6. The heat transfer coefficient is chosen to follow the law of gunn. This choice gives a better result when the fluids and granular solids are mixed together in two-phase flow.
In this simulation, the initial and boundary conditions are the same with the bench scale moving bed reducer experiments. The voidage: 0.4
The density of the particle: 2500 kg/cm³
Mass fraction of Fe₂O₃ in pellets: 0.60
The federate of pellets: 12.87 g/min
The diameter of the iron pellet: 0.004m
The gas injection: 16.831*0.0001 Nm³/s
Initial molar fraction of H₂: 0.72958

3.3.2 Model Validation and Results Analysis

Three cases have been simulated using the 2-D CFD model. The first one is simulated with a forced constant temperature of 1173K for the whole system. This is achieved by setting a fixed temperature to both phase-1 and phase-2 in the bed zone. For the second case, there is no fixed temperature. The heat will be released or absorbed according to the specific attributes of the reactions. Also, the reducer is operated under adiabatic condition in this case, which means there is no heat flux coming through the wall. The third case is similar to the second one except that a heat flux of 300 w/m² is add to the wall, which means the whole system are continuously heated by external devices. This operation actually follows the facts in the previous experiments, where a PID control loop is used to ensure that the temperature of the system is always close to 1173K.
During all the three simulations, a big time-step of 2 second was set at the beginning to make simulation approach the converged solution faster. Then the time-step was decreased to a smaller value of 0.2 second to enhance the resolution of the final steady results. So the final time when the solution reached their steady state is actually not so reliable since the bigger time-step adopted first might incur too much numerical errors to the simulation. Usually this time would be bigger than the converged time in the real word. It indeed doesn't matter since only the final steady state is what the most interested. However, if the whole evolution process of the simulation is more desired, it is suggested to stick to the small time-step from the very beginning to the end. The disadvantage of such operation is that the simulation would be computationally expensive.

In the bench scale experiment\(^2\), the solid conversion at the bottom of the reducer reached around 50% and the gas conversion became very close to 100% at the top of the reducer. Figure 3.10 shows that the reactions proceed very fast at both ends of the reducer, and the first two reactions have finished in the top part of the reducer while the third reaction only starts near the bottom part. During the experiment, the temperature is kept around 1173K by using external heating devices.

The first case simulated the scenario that the temperature in the whole system is fixed at 1173K. The gas conversion, the fractional solids conversion and also the overall solids conversion are illustrated in Figure 3.11. The results show that both the gas
conversion and solids conversion are in favorable agreement with those obtained in the experiments. This indeed validates the 2-D axisymmetric simulation of the reducer system. The results also indicate that the first reaction proceeds very fast near the top of the reducer while the third reaction only occurs near the bottom part. These two phenomena are very consistent with the experimental results. From Figure 3.11(c), it can be seen that the second reaction is finished in a position close to the bottom. This means the reaction rate predicted by the simulation is somewhat slower than that in the experiment. The velocity magnitude of the gases for the first case is displayed in Figure 3.12, which shows that the gas moves to the top of the reducer at a uniform velocity of around 0.313 m/s, close to the theoretical value of 0.3128 m/s. At both ends of the reducer, the velocity decreases dramatically due to space expansion caused by the existence of the inlet and outlet for gases. The volume fraction of the solids in the moving bed is kept basically unchanged during the simulation as shown in Figure 3.13. This is in accordance with the real situation and should be attributed to the uniformity of the gas velocity.

In order to display the results clearly, we extracted some data from the center line of the reducer and showed them in Figure 3.14, from which we can see that the reactions were fast at the top part of the reducer where the new-fed pellets were just running into the reducing gas. After this fast reaction zone, the reaction rate became very slow in the middle part of the reducer. The third reaction F started only near the bottom of reducer
where the fraction of FeO and H$_2$ are both relatively high. This scenario is comparable with that appeared in the experimental data shown in Figure 3.10. 55

The second case activates the heat transfer sub-model in the whole system, and the wall is treated as adiabatic. In this case, both the gas conversion and overall solids conversion are visibly lower than those in the first case (see Figure 3.15). This is because both the second and the third reaction are endothermic. The first reaction is exothermal, but still it can’t offset the heat absorbed by the last two reactions. It can be seen clearly in Figure 3.16 that the temperature in the bottom and also the middle part of the reducer decreases to a temperature around 880K. Evidently, this scenario is caused by the heat absorption of the second and the third reactions. At the top of the reducer, the temperature is around 1200K is just due to the heat release of the first reaction. It should also be noted that, flow dynamics is also affected by the decrease of the temperature near the bottom part. Figure 3.17 illustrates that the gas velocity becomes smaller than that in the first case. As the gas goes upwards it keeps accelerating because the temperature is recovered at the top part. This acceleration of the gas actually influences a lot the distribution of the solids particle. Figure 3.18 shows that the volume fraction of the solids becomes obviously smaller in the bottom part of the reducer and larger in the top part. The second case indicates that the heat change due to the reactions and its transfer in the system do matter a lot in such kind of reducer system. It would be difficult to design a system like this without considering its heat transfer mechanism.
The third case describes the situation when an extra heat flux from external heating device is added. Figure 19 gives the temperature distribution of the heated system. The simulation results indicate that the overall temperature was increased by the extra heating. The lowest temperature is about 1100K now, which is 220K higher than that in the second case without heating. It should be noted that the lowest temperature is near the axis line of the bottom and middle part of the system. This means the innermost part of the bed is difficult to be heated since it’s far away from the heated wall. Figure 3.20 shows that, in this case, the heat actually help the gas conversion and solids conversion go back to the values close to those in the experiments, which are also determined by the thermodynamic properties of these reactions. Since the temperature distribution in this system is much better than that in the second case, Figure 3.21 and 3.22 show that the uniformity of the gas velocity is recovered, and the volume fraction of the solids becomes basically unchanged as when it was initialized, respectively.

3.4 2-D Combustor Modeling

3.4.1 Reaction Kinetics in Combustor

The combustor mainly consists of a frustum and a riser. The frustum fully regenerates the reduced iron oxide particles via the following reaction, and the riser conveys the regenerated particles to the top of the reducer.

$$4\text{Fe}_3\text{O}_4 + \text{O}_2 \rightleftharpoons 6\text{Fe}_2\text{O}_3$$
A one-interface unreacted shrinking core model is adopted to represent the oxidation kinetics occurring in the frustum. The oxidation is considered as diffusion-controlled, and the intrapartical diffusivity is given below.\textsuperscript{101}

\[ D_e = 6.1 \exp(-17000/RT) \]

The oxidation process for a single pellet was calculated by adopting the aforementioned one-interface model. The result is shown in Figure 3.23, from which we can learn that the combustion process of a magnetite pellet is very fast. It only takes about 0.5 minute to fully convert magnetite to hematite in one pellet under pure oxygen environment. The oxidation kinetics is parabolic, which is consistent with TGA experiment results. It is noted that the real oxidation process usually slows down due to the low oxygen partial pressure.

3.4.2 CFD Model Setup

By assuming the gas and solids phases are uniformly introduced from the bottom of the combustor, the computational domain can be treated as axisymmetric. The reason of using axisymmetric simulation instead of 2-D planar simulation is to consider the transition from frustum to riser, which has a significant impact on the performance of combustor. The gravitational force is along negative \( x \)-axis direction. Figure 3.24 shows that the combustor contains a frustum, a transition region and a riser from left to right. The width of the frustum is 0.1m, while its length is 1m. The length of the transition part is 0.37m. The width of the riser is 0.038m. It should be noticed that a long riser is
adopted in the simulation, which is 0.93m. This is because a long riser will make the outflow condition of the outlet of the riser much more physically sound and make the calculation converge faster.

The details of the setup for the simulation are given as follows. It should be noted that this model is axisymmetric and the gravitational acceleration should be added in the negative x direction. The Eulerian multiphase model is chosen, and the number of Eulerian phases is set to be 2. The energy equation is included in the simulation. The species model adopted is species transport. The phase-1 is mixture-fluid and the phase-2 is mixture-solid. The setups for each component are basically the same with that in the two-dimensional reducer model. After the parameters of the materials are defined, the mixture-fluid is chosen as phase-1 while the mixture-solid is chosen as phase-2. For the phase-2, we also should check the Granular box and define the diameter as 0.0015m. The packing limit should also be given here, which we set to be 0.63.

The chemical reaction kinetics was coupled into the simulation with several udf files. For the interaction between the two phases, the drag coefficient should come from the gidaspow drag law. The restitution coefficient of collisions is set to be a constant of 0.9. There are totally three zones in the model, including fluidized bed, riser and transition part. The temperatures for all the three zones are set as 1323 K. The boundary condition of the inlet is velocity inlet. The velocity of phase 1 is 0.9144 while that of
phase 2 is 0.00635. The volumetric for phase-2 is 0.5. The temperature here is also 1323K. The fraction of O\textsubscript{2} in phase-1 is 21% since phase-1 is actual air.

In order to make the simulation converge easily all the default lower-accuracy schemes are adopted. Some under-relaxation factors are made a little bit smaller than the default values which can help the program become relatively stable. For initialization, the phase-2 volume fraction was changed to 0. After that, the frustum (fluidized bed) was patched with a value of 0.5 for phase-2 volume fraction. The initial bed was confined only in the frustum, which can also help the simulation converge faster since the bed is actually only appearing in the frustum at the end of the simulation.

### 3.4.3 Results and Discussion

In order to study the fluid dynamics in the combustor, no reactions are considered in the CFD model at the beginning. The key parameters for this simulation are actually from the experiment performed by PSRI. So, the results of the simulation need to be compared with the experiments. Figure 3.25 displays the contours of the volume fraction of solids. It can be seen that the highest volume fraction is close to the packing limit value 0.63 in the frustum. The figure also shows that there are lots of small regions in which the volume fraction is relatively low. It means the solids are in the status of fluidization. They are not mixed uniformly with the gas. Actually there are plenty of small structures in the bed which is in good agreement with the real situation found in experiments. It is noted that in the transition part between the frustum and the riser, the volume fraction decreases fast. This is because the gas is accelerating quickly in this region and hence the forces exerted on the solids become larger. In the riser, the volume
fraction becomes very small since the gas velocity is very large there, most of solids which enter into the riser will be blew away through the outlet.

Figure 3.26 gives an illustration of the static pressure in the system. It can be seen that the total pressure loss in the frustum is around $1.0 \times 10^4$ Pa. For the situation in which the solids are in the status of fluidization, it is expected that the pressure loss multiplied by the cross-section area should just have the capacity to support the weight of the bed. The volume-weighted average of the volume fraction of phase-2 is around 0.42, and thus the total pressure loss should be $1.05 \times 10^4$ Pa. This means the pressure gradient obtained from the simulation is reasonable.

Different flow regimes have been simulated based on the combustor model. By using small advancing time step, it is believed that the flow structure is captured with high fidelity. Figure 3.27 displays a time series of the volume fraction of phase-2 in the combustor. It was illustrated that the two-phase flow gave a classical quasi-periodic turbulent scenario. At $t=116.15$s, the results shows that the flow field seems peaceful, no visible violent incident occurring. The frustum is actually a moving bed at this time since most part of the bed has reached its packing limit. The top part of the bed is the only region where the packing is relatively loose since that is the freeboard zone. As time goes on, it is seen that the bottom part of the moving bed loses it stability and start to produce several small bubbles in the bed. This phenomenon begins at $t=116.16$ s, and spreads very quickly. Figure 3.27 shows clearly that the whole bed has been full of small bubbles at $t=116.17$ s. Now, the flow structure has changed utterly, the present state of the bed is
the typical bubbling fluidization. The transition from moving bed to bubbling fluidization can be very fast according to the simulation. After the flow reaches the state of bubbling fluidization, the small bubbles in the bed start to coalesce with each other, making the bubbles lesser and bigger (see Figure 37 from t=116.17 to 116.80 s). It has been well recognized that coalescence is the dominating phenomenon in bubbling fluidization. The coalescence process can proceed for a while from t=116.17 to 116.80 s. It’s noted that there is only one large bubble left in the bed at t=116.80 s. This means in the present setup the state of bubbling fluidization can’t sustain for a long time. Finally it calms down and goes back the state of moving bed, see the plot at t=117.00 s. The system can maintain the cyclic behavior from moving bed to bubbling state and then back to moving bed. The moving packed bed can last for 3-10 seconds and then it will go to next bubbling fluidization status. It seems that the gas velocity in this case is not big enough to support the all-time bubbling fluidization status, and hence, the flow regime kept changing it status.

The experiment shows that the expansion ratio of the bed, which is defined as the height of the fluidized bed to that of the packed bed is around 1.2-1.3. The information can be obtained by comparing the height of the bed at two different time from Figure 3.27, say t=116.15 s and 116.20 s. It’s easy to know that the height of t=116.20 is about 20% larger than that of t=116.15. This is in good agreement with the experimental results.
Figure 3.28 gives a comparison of both gas conversion and solid conversion at two different flow regimes. The results indicate that both the conversions are not influenced by the change of flow structure. It might be because the reaction rate is so fast that all the reaction can be almost done at the bottom of the bed. Figure 3.28 shows that the solid conversion is close enough to 100%, which means the oxygen is sufficient to oxidize all the pellets.

The axial velocities are compared at the two different flow regimes in Figure 3.29. The detail distribution of the axial velocity is significantly different, however, there is still an apparent common property possessed by the two different flow regimes. The axial velocity near the axis in the frustum is negative or smaller than that near the wall. This phenomenon is actually very typical and has been recognized by previous researchers. In the riser, the pellets are prone to fall down near the axis line when the bed is in fixed bed state, while the pellets probably goes upward when the bed is in the state of bubbling fluidization.

Figure 3.30 gives an illustration of the static pressure in the system. It can be seen that the total pressure loss in the frustum is around 1.0X10^4 Pa when the bed is in the state of fixed bed. This value is just enough to support the weight of the bed. This evaluation further validates the CFD simulation. It is also noted that the pressure loss is much larger when the bed in the flow regime of bubbling fluidization. This is also reasonable, since the interaction between the bubbles and the pellets will consume more
static pressure. This phenomenon can also be understood by referring to previous works.\textsuperscript{102}

3.5 Conclusions

The design of iron-based CLC systems can be classified on the basis of the fuel-OC contacting pattern in the reducer. Mode 1 contacting pattern refers to a mixed flow mode, typical of a fluidized bed reactor system. One equilibrium stage can be achieved in the Mode 1 operation, which yields an iron oxide conversion of 11.1\%. Mode 2 refers to the fuel-OC countercurrent contacting pattern. This is represented in cases where the reactor is operated in a dense moving-bed or a multistage fluidized bed simulating multiple equilibrium stages. Compared with Mode 1, Mode 2 operation is possible to have higher OC conversion that can reduce the solids circulation rate, increasing the system efficiency. The main considerations in designing a reducer for a solid fuel CLC application are sufficient fuel residence time and kinetics of the solid-fuel gasification with enhancing gas if required. Additional considerations are necessary for contaminants (such as ash and sulfur) removal from the reactor system.

The SCL process circulates iron-based oxygen carrier particles through 3 reactors, namely the reducer, the oxidizer, and the combustor, to perform reduction-oxidation reaction cycles for carbon dioxide capture and hydrogen production from coal or biomass derived syngas. The countercurrent moving-bed operation of the reducer highlights the SCL technology. This paper presents a one-dimensional flow model for moving bed
reducer in SCL system. The three-interface unreacted shrinking core model is applied to
describe the reaction of the gas and solid flows within the reactor. The code is validated
through comparing the simulated results with experimental data. The 1-D model assists in
better understanding of the actual reaction properties in the moving bed reducer. In the 1-
D modeling work, first of all, the entire progress of the composition evolution in the
moving bed reducer is obtained through explicit temporal integration. Second, a shorter
reducer is suggested based on the numerical simulations on reducers with different
lengths. Third, the converging time before the reducer reaches the steady state is analyzed
by varying the ratio between gas and solids feed rates. In conclusion, the results show a
minor change of the feed-rate ratio could cause significant differences in the converging
time. Generally, for the system to reach the steady state can be shorten in two different
ways: one is to make the feed-ratio slightly smaller than the critical ratio, and the other is
to shorten the reducer to a proper size without affecting the reactions inside. Thus, 1-D
moving bed reactor model provides a practical strategy in optimizing the reducer design
and operation in the SCL process.

A two-dimensional moving bed reducer CFD model has been built and executed.
The three-interface reaction kinetic model for the overall reacting rate of the pellet was
adopted. Several user-defined function (udf) files were coded and used to give the
reaction rates for the simulations. Both the results of two-dimensional Fluent simulations
and those of one-dimensional Matlab codes developed in last quarter were compared with
related experiments. It was found that the results of two-dimensional Fluent simulations
were more physically sound through some comparison with experiments. The results also indicated that intra-particle diffusion coefficient of reducing gas is an important parameter for the reactions.

Fluent simulations for an axis-symmetric combustor with chemical reaction were executed. Both chemical reaction and flow dynamics were delineated in detail. It was found that the combustion of magnetite could proceed completely in the current setup and most of the reaction happened in the bottom of the combustor due to the fast reaction rate. By using small advancing timestep, the flow structure was captured with high fidelity. It was demonstrated that the two-phase flow gave a classical quasi-periodic scenario. The flow regime kept changing from two different flow regimes. The transition of the regime from moving bed to bubbling fluidization was very quick and remarkable. In the state of bubbling fluidization, the originally generated small bubbles would experience successive coalescences and became large in size and less in quantity. The bubbling fluidization bed would calm down to a new fixed bed eventually after the last big bubble was blown away. The simulation shows that the magnetite can be fully oxidized in the combustor in the present setup. The static pressure loss is just enough to support the bed when the flow regime is fixed bed. The expansion ratio of the bubbling fluidization is about 1.2, which is in good agreement with experiments.
Figure 3.1 (a) Mode 1 reducer: fluidized bed gas-solid flows; (b) Mode 2 reducer: gas-solid dense phase/moving bed flows.
Figure 3.2 The schematic diagram of the moving bed reducer.
Figure 3.3 The comparison of the gases and solids conversions between the numerical results and the previous experimental data in the moving bed reducer.
Figure 3.4 The conversion profiles of both gases and solids at different times in the reducer.
Figure 3.5 The steady overall conversion profiles of syngas and solids when the reducer is shortened.
Figure 3.6 The conversion profiles when the solids feed-rate increases by 5%. This lower solids feed-rate makes the feed-rate ratio between gases and solids decrease to 1.4538, lower than the critical ratio 1.4647.
Figure 3.7 The converging time verse the feed-rate ratio between gases and solids.
Figure 3.8 The gases and solids conversions verse the feed-rate ratio between gases and solids.
Figure 3.9 The geometry of the reducer
Figure 3.10 The gases and solids conversion in the bench scale moving bed experiment.
Figure 3.11 Illustration of gas and solid conversion for the first case (Temperature is fixed at 1173K). (a) gas conversion; (b) conversion from Fe\textsubscript{2}O\textsubscript{3} to Fe\textsubscript{3}O\textsubscript{4}; (c) conversion from Fe\textsubscript{3}O\textsubscript{4} to Fe\textsubscript{x}O; (d) conversion from Fe\textsubscript{x}O to Fe; (e) overall solids conversion
Figure 3.12 Velocity magnitude of gases for the first case (Temperature is fixed at 1173K).
Figure 3.13 Volume fraction of phase-2 for the first case (Temperature is fixed at 1173K).
Figure 3.14 Gas conversion, solid conversion and the conversion of three reactions: rf, rm and rw.
Figure 3.15 Illustration of gas and solid conversion for the second case with adiabatic wall. (a) gas conversion; (b) conversion from Fe$_2$O$_3$ to Fe$_3$O$_4$; (c) conversion from Fe$_3$O$_4$ to FexO; (d) conversion from FexO to Fe; (e) overall solids conversion.
Figure 3.16 Temperature distribution in the reducer for the second case with adiabatic wall.
Figure 3.17 Velocity magnitude of gases for the second case with adiabatic wall.
Figure 3.18 Volume fraction of phase-2 for the second case with adiabatic wall.
Figure 3.19 Temperature distribution in the reducer for the third case with heat flux.
Figure 3.20 Illustration of gas and solid conversion for the third case with heat flux. (a) gas conversion; (b) conversion from Fe$_2$O$_3$ to Fe$_3$O$_4$; (c) conversion from Fe$_3$O$_4$ to Fe$_x$O; (d) conversion from Fe$_x$O to Fe; (e) overall solids conversion.
Figure 3.21 Velocity magnitude of gases for the third case with heat flux.
Figure 3.22 Volume fraction of phase-2 for the third case with heat flux.
Figure 3.23 The reaction time for oxidization of a single pellet.
Figure 3.24 Geometry of the combustor, including frustum, transition area and riser from left to right.
Figure 3.25 The volume fraction of phase-2 in the combustor
Figure 3.26 The static pressure in the combustor
Figure 3.27 The volume fraction of phase-2 in the combustor, the corresponding time is shown in the bottom of each plot.
Figure 3.28 Comparison of the conversion at two different flow regimes.
Figure 3.29 Comparison of axial velocities at two different flow regimes.
Figure 3.30 Comparison of the static pressure at two different flow regimes.
Table 3.1 Reducer design comparison: Mode 1 versus Mode 2

<table>
<thead>
<tr>
<th>Reducer Modes</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Operation Regime</strong></td>
<td>Bubbling, turbulent, fast fluidized, or spouted bed</td>
<td>Moving packed, or multistage fluidized bed</td>
</tr>
<tr>
<td><strong>Gas Solid Contacting Pattern</strong></td>
<td>Mixed</td>
<td>Countercurrent</td>
</tr>
<tr>
<td><strong>Controllability on Fuel and OC Conversions</strong></td>
<td>Poor, due to back mixing and gas channeling</td>
<td>High</td>
</tr>
<tr>
<td><strong>Maximum Iron oxide Conversion</strong></td>
<td>11.1% (to Fe$_3$O$_4$)</td>
<td>&gt;50% (to Fe &amp; FeO)</td>
</tr>
<tr>
<td><strong>Solids circulation rate</strong></td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td><strong>Subsequent Hydrogen Production</strong></td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td><strong>Particle size, μm</strong></td>
<td>100-600 [40,41]</td>
<td>1000-3000 [9,37]</td>
</tr>
<tr>
<td><em><em>Reducer gas velocity</em>, m/s</em>*</td>
<td>&lt;0.4</td>
<td>&gt;1.0</td>
</tr>
<tr>
<td><strong>Reactor size for the same fuel processing capacity</strong></td>
<td>Large</td>
<td>Small</td>
</tr>
<tr>
<td><strong>Hydrodynamics effects on scaling up</strong></td>
<td>Large</td>
<td>Small</td>
</tr>
</tbody>
</table>

*RReducer gas velocity calculated at 900 °C, 1 atm*
Table 3.2 Key reactions in the SCL process

<table>
<thead>
<tr>
<th>Reactor</th>
<th>Reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reducer</td>
<td>$3\text{Fe}_2\text{O}_3+\text{CO}/\text{H}_2=2\text{Fe}_3\text{O}_4+\text{CO}_2/\text{H}_2\text{O}$ (1)</td>
</tr>
<tr>
<td></td>
<td>$(x/4x-3)\text{Fe}_3\text{O}_4+\text{CO}/\text{H}_2=(3/4x-3)\text{Fe}_x\text{O}+\text{CO}_2/\text{H}_2\text{O}$ (2)</td>
</tr>
<tr>
<td></td>
<td>$\text{Fe}_x\text{O}+\text{CO}/\text{H}_2=x\text{Fe}+\text{CO}_2/\text{H}_2\text{O}$ (3)</td>
</tr>
<tr>
<td>Oxidizer</td>
<td>$x\text{Fe}+\text{H}_2\text{O}=x\text{Fe}_x\text{O}+\text{H}_2$ (4)</td>
</tr>
<tr>
<td></td>
<td>$(3/4x-3)\text{Fe}_x\text{O}+\text{H}_2\text{O}=(x/4x-3)\text{Fe}_3\text{O}_4+\text{H}_2$ (5)</td>
</tr>
<tr>
<td>Combustor</td>
<td>$4\text{Fe}_3\text{O}_4+\text{O}_2=6\text{Fe}_2\text{O}_3$ (6)</td>
</tr>
</tbody>
</table>
Chapter 4

Chemical Looping Process for Electricity Generation

4.1 Introduction

Electric power is the most important and common energy carrier in the current energy market. Efficient, clean, and cost-effective electricity generation from various primary sources, especially coal and natural gas, is crucial for sustainable development. However, under the scenario of greenhouse gas regulation, CO\textsubscript{2} capture and compression will impose a considerable energy penalty for power generation process such as conventional pulverized coal (PC) combustion and integrated gasification combined cycle. For example, the post-combustion capture for a conventional PC plant via MEA will reduce the net power output by nearly 30%, and increase capital cost by about 80%.\textsuperscript{104} A lower energy penalty, between 8 and 12%, is expected in the IGCC electricity production process with pre-combustion CO\textsubscript{2} capture. However, the IGCC process is highly capital intensive, up to ~$3,600/kW, which has hindered its commercial development. As an advanced oxy-combustion technology, chemical looping enables efficient power generation with near 100% CO\textsubscript{2} capture, which can be attributed to its capability of in-situ air and CO\textsubscript{2} separation and flexibility for integration with other technologies. Several chemical looping processes will be illustrated below for power generation.
4.2 Mode 1 Chemical Looping Combustion Process

Figure 4.1 illustrates a typical chemical looping combustion process flow diagram. In this process, two separate high temperature gas streams are produced from different chemical looping compartments, i.e. the CO$_2$ rich gas from the reducer and the flue gas from the combustor. After heat recovery, the flue gas goes through cleanup units to further remove particulate matter and other possible pollutants such as SO$_x$, before its emission from the stack; the effluent gas from the reducer goes to the CO$_2$ purification and compression unit (CPU) before transportation and sequestration. Heat is recovered to raise high pressure steam for power generation. A Mode 1 fluidized bed reducer design has been extensively considered for such CLC application. The following section discusses two Mode 1 CLC process configurations from Vienna University of Technology (VUT) and Chalmers University.\textsuperscript{40}

The VUT CLC process adopts a dual circulating fluidized bed (DCFB) design for gaseous fuel conversion. As shown in Figure 4.2, the primary components of the DCFB system are a reducer, a combustor, three loop seals, and two cyclones. The system forms two particle circulation loops, the global particle circulation loop and the local particle circulation loop. The cyclone and internal loop seal placed around the reducer allow for local particles circulation within the reducer, independent of the global particles circulation between the reducer and the combustor. The reducer is operated near the turbulent regime and the combustor is operated in either the dilute or dense transport regime. The fluidization agents for the reducer and the oxidizer are gaseous fuel and air,
respectively. Gaseous fuel is injected at the bottom of the reducer, and air is injected at both the bottom (primary air inlet) and the middle portion (secondary air inlet) of the oxidizer. The staged injection of air enables effective control over the global solids circulation rate. At a fixed overall air injection rate, a larger primary air injection rate leads to a higher global solids circulation rate. As it is compatible with the operation of both the combustor and the reducer, steam is used as the fluidization gas in all of the loop seals. Based on the DCFB design and operation at VUT, a 10 MW$_{th}$ CLC plant feasibility study was conducted. In this study, NiO based oxygen carrier particles are used to convert natural gas feedstock at ambient pressure. Because the demonstration plant is a small scale design, only a single pressure steam cycle is considered. The results show that the net power generation efficiency ranges between 32.5–35.8% without CO$_2$ purification and compression.

Solid fuels such as coal, petroleum coke, and biomass are notably cheaper than gaseous fuels. Therefore, it is desirable to convert solid fuels directly in the CLC systems. The research group at Chalmers University and its collaborators are scaling up a solid fuel CLC process under the ÉCLAIR project. The setup is similar to the VUT DCFB design, except that a carbon stripper is added between the reducer and the combustor. In the reducer, the oxygen carrier and the solid fuel are fluidized by steam and recycled CO$_2$. The solid mixture captured from the reducer cyclone goes to the carbon stripper, where the unconverted solid fuel is separated and returned to the reducer while the oxygen carrier particles are selectively carried over to the combustor for regeneration. A
455 MW_{e} coal-fired CLC plant is designed based on this concept, and the techno-economic study shows that the proposed CLC process has only 2\% efficiency penalty, and the associated CO_{2} avoidance cost is about 10 euro/ton CO_{2}.\textsuperscript{106} 

VUT is also modifying its gaseous fuel system into a solid fuel system.\textsuperscript{107} The major changes occur in the reducer design, as shown in Figure 4.3. A set of ring-type flow obstacles are placed vertically in the reducer to divide it into several zones. The reducer design features a Mode 2 countercurrent gas-solid flow pattern and is a shift from the previous Mode 1 mixed/circulatory solid flow pattern. Each zone retains solids, intensifying the gas-solid mixing while establishing the countercurrent gas-solid flows. With this design, both char and volatile conversions could be enhanced. In addition, ash separation could be carried out on the basis of the difference in particle size distributions between ash and oxygen carrier particles.

4.3 Coal Direct Chemical Looping Combustion Process

4.3.1 Coal Direct Chemical Looping Process

The Coal Direct Chemical Looping process with a Mode 2 reducer design is a potentially disruptive technology that shows promise for significantly reducing the cost and energy penalty associated with capturing carbon dioxide from coal-fired power plants. The process, which is essentially an advanced form of oxycombustion, uses iron-based particles to carry oxygen from the combustion air to the coal. As such, it eliminates the need for a cryogenic air separation unit (ASU), which is responsible for
most of the energy penalty and incremental cost associated with the use of conventional oxycombustion for CO₂ capture.¹⁰⁴

In the CDCL process, the iron-based oxygen carrier particles are circulated between two reactors: the combustor (air reactor) and the reducer (fuel reactor). The dominant overall reactions in these reactors are given by Equations 1 and 2. In the combustor, the particles are oxidized from elemental iron (Fe) or ferrous oxide (FeO) to ferric oxide (Fe₂O₃) by reacting exothermically with the oxygen in air. The fully oxidized particles are then fed to the reducer, where they are reduced from Fe₂O₃ to Fe and FeO as they react endothermically with coal to form predominantly CO₂ and H₂O. The process results in the same overall net reaction (Equation 3) and generates the same net heat as coal combustion in air. Hence, it is ideally suited for replacing the pulverized coal boiler in a coal-fired power plant. Although the CDCL process does not produce a flame, both the combustor and the reducer operate at high temperatures (850-1,200°C), and the process provides heat of sufficient quality to support a supercritical steam cycle. Moreover, as a result of the chemical looping scheme, the CO₂ produced in the CDCL process (via Equation 2) is not diluted with spent combustion air. Thus, this CO₂ requires only simple purification, dehydration, and compression to prepare it for geologic storage.

**Combustor:** \[ \text{Air + Fe/FeO} \rightarrow \text{FeO}_3 + \text{Spent Air + Heat} \] \hspace{1cm} (1)

**Reducer:** \[ \text{Coal + FeO}_3 + \text{Heat} \rightarrow \text{Fe/FeO + CO}_2 + \text{H}_2\text{O} \] \hspace{1cm} (2)

**Overall:** \[ \text{Coal + Air} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{Spent Air + Heat} \] \hspace{1cm} (3)
Key aspects of the CDCL technology, which was developed by The Ohio State University (OSU), include its high-performance iron-based composite oxygen carrier particles and its innovative reducer design. The oxygen carrier particles used in the CDCL process have been developed by OSU during the past 10 years and consist of Fe$_2$O$_3$ plus one or more inert supporting materials. Iron was selected as the oxygen carrier over other candidate metals (e.g., Cu, Ni, Co) because of its relatively high oxygen carrying capacity, high equilibrium conversion of carbon to CO$_2$, low cost, high melting point, high strength, and low health and environmental risks. OSU has engineered the particles to include supporting materials that enhance oxygen diffusion and increase particle strength.$^{61,62}$ Experimental tests indicate that the resulting particles are ten times more reactive than pure Fe$_2$O$_3$, and are recyclable for more than 100 reduction-oxidation cycles without loss in reactivity.$^{35,60}$ The performance of the particles has been demonstrated at the 2.5 and 25 kW$_t$ scales, and will be demonstrated this year in 250 kW$_t$ pilot testing of OSU’s Syngas Chemical Looping (SCL) process. (The SCL process is similar to the CDCL process, but it does not provide for direct coal injection into the reducer. Rather, the coal is first gasified, and the resulting syngas is fed to the reducer).

The reducer in the CDCL process is uniquely configured to facilitate the overall solid-solid reaction between oxygen carrier particles and coal. As illustrated in Figure 4.4, the reducer employs a two-stage moving bed design, which provides for
countercurrent gas and solids flows and long solids residence times to enable high conversion efficiencies. The fully oxidized oxygen carrier particles (i.e., Fe$_2$O$_3$) are introduced at the top of the reducer and travel downward through both moving bed stages. The iron is reduced progressively from Fe$_2$O$_3$ to Fe$_3$O$_4$, FeO, and Fe along the length of the reactor as it reacts with fuel. Coal is introduced into the injection zone located in the middle of the reactor, between the two moving bed stages. The coal rapidly devolatilizes at the reactor operating temperature. The gaseous products of this devolatilization (i.e., CH$_4$, CO, H$_2$, tar, and other species) travel upward through the Stage I moving bed, where they are oxidized to CO$_2$ and H$_2$O by the countercurrently flowing oxygen carrier particles. Meanwhile, the coal char largely flows downward with the carrier particles into the Stage II moving bed. A portion of the CO$_2$ and H$_2$O leaving the top of the reducer is recycled and injected at the bottom of the Stage II bed to promote the solid-solid reaction between the coal char and the iron particles. This “enhancer gas” serves to gasify the char by reacting with it to form CO and H$_2$, as shown in Figure 4.4. The gaseous CO and H$_2$ then flow upward through the reducer, where they are oxidized by the countercurrently flowing oxygen carrier particles to form CO$_2$ and H$_2$O. The reduced oxygen carrier particles (i.e., Fe and FeO) exiting the bottom of Stage II are sent to the air reactor for reoxidation to Fe$_2$O$_3$. The Stage I and Stage II moving beds have been tested separately at bench scale (2.5 kW$_t$), and the integrated two-stage reducer is now being demonstrated at the sub-pilot (25 kW$_t$) scale. The bench-scale tests showed nearly 100% conversion of methane (used to represent coal volatiles) and ~95% conversion of coal char in the Stage I and Stage II beds, respectively, suggesting that the
integrated reducer can achieve >95% overall coal conversion to form a concentrated stream of CO₂ and H₂O. The sub-pilot tests are being conducted to confirm this result.

The viability of the CDCL process ultimately will depend upon its economic performance at commercial scale. Hence, a conceptual design was developed for a 550 MWₑ (net) supercritical CDCL power plant including >90% CO₂ capture and compression (the “CDCL Plant”), and a techno-economic analysis was completed to enable an initial assessment of its technical performance and cost. This paper summarizes the results of this analysis and compares them with results for a 550 MWₑ (net) supercritical PC power plant without CO₂ capture (the “Base Plant”) and a 550 MWₑ (net) supercritical PC power plant equipped with a monoethanolamine (MEA) scrubbing system for 90% CO₂ capture and compression (the “MEA Plant”). Because the CDCL process is at an early stage of development, the results presented here are preliminary. The primary purpose of this techno-economic analysis is to guide design improvements that will contribute to the development of a commercially viable technology. Nevertheless, these results provide an indication of the potential for the CDCL process to improve upon current approaches for capturing CO₂ from coal-fired power plants.

4.3.2 Process Design

The performance and cost results for the Base Plant and the MEA Plant were taken directly from Cases 11 and 12, respectively, in the U.S. Department of Energy
(DOE) report titled *Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity.*\(^{104}\) Hence, to ensure consistency among the cases being compared, the commercial-scale CDCL Plant was designed using the same design basis and assumptions (wherever possible) that are used in that report. Figure 4.5 presents a simplified process flow diagram (PFD) for the CDCL plant. This PFD provides the basis for the process simulation and economic results presented later in this paper. The CDCL plant is designed for a coal feed rate of \(207,072\) kg/h, which is the rate required to produce \(~550\) MW\(_e\) net electric output. The design coal is an Illinois No. 6 bituminous coal that has a higher heating value (HHV) of \(27,113\) kJ/kg and contains \(2.51\)% sulfur, \(9.70\)% ash, and \(11.12\)% moisture on an as-received basis.\(^{104}\) The plant is assumed to be sited on a 300-acre, greenfield site in the Midwestern U.S., with design ambient conditions of \(15\)°C and \(1.01325\) bar.\(^{104}\)

As shown in Figure 4.5, the CDCL process offers a relatively straightforward approach to CO\(_2\) capture. The reducer and combustor take the place of the conventional PC boiler. The reducer is designed as a two-stage moving bed, as described in the Introduction. The combustor is designed as a bubbling fluidized bed that discharges into an entrained riser section, which transports the oxidized carrier particles back to the top of the reducer. L-valves and zone seals are used to control the flow of particles between these two main reactors, which are both operated at nominally 1 bar total pressure. Heat transfer surface is located in the fluidized bed combustor to maintain its temperature at \(~1,200\)°C while raising steam for electricity generation. Heat is also recovered from the
spent air stream after it exits the combustor and from the CO₂ stream after it exits the reducer to raise steam, as indicated in the PFD.

The coal used in the CDCL process is pulverized and fed into the reducer through the coal injection zone located between its two moving bed stages. Hot oxygen carrier particles are introduced into the top of the reducer. For purposes of this design, the carrier particles are assumed to contain 40% Fe₂O₃ and 60% Al₂O₃ (inert supporting material) by weight. The actual composition of the proprietary carrier particles developed by OSU will differ somewhat from this assumed composition. The carrier particles oxidize the coal volatiles and gasified coal char as they travel downward through the reducer. In addition to carrying oxygen, the particles serve as a heat carrier, providing all of the energy required for the endothermic reactions in the reducer. Hence, the particles are cooled as they react along the length of the reducer. The temperature at the bottom of the reducer is maintained at ≥850°C to promote gasification of coal char, and the temperature at the top of the reducer is limited to ≤1,200°C to avoid fusion of the carrier particles. Given these temperature limits, it is the heat carrying capacity, rather than the oxygen carrying capacity, that determines the required carrier particle flow rate to the reducer. (For the current design, in order to meet the temperature restrictions, the carrier particle flow rate is about 74% greater than the flow rate that would be required to stoichiometrically oxidize the coal).
As shown in Figure 4.5, the hot CO₂ product stream exiting the top of the reducer is cooled to raise steam for electricity generation. This stream contains all of the HCl formed from the chlorine in the coal, as well as a portion of the coal ash (including unburned carbon) and some sulfur compounds. (In this design, it is assumed that half of the coal ash is entrained in the CO₂ stream, and the other half reports to the combustor with the spent carrier particles). Based on process simulations, a small amount (~16%) of the coal sulfur will react to form SO₂ in the reducer, but most (~84%) will react to form Fe₀.₈₇₇S. In addition to these impurities, the CO₂ stream contains a substantial amount of water vapor arising from the moisture and hydrogen in the coal. Hence, this stream must be purified to remove particulate matter and condensable acid gases and dehydrated before it is compressed for geologic storage. The conceptual commercial plant design shown in Figure 4.5 includes a baghouse, an acid gas scrubber, and a condenser for these purposes. An induced draft (ID) fan is located downstream of the scrubber to overcome the pressure drop created by the gas purification equipment and heat exchangers along the CO₂ stream. In addition, as illustrated in Figure 4.5, a portion of the “wet” CO₂ ahead of the condenser is recycled back to the bottom of the reducer for use as the char gasification enhancer. Per the discussion in the Introduction, both the CO₂ and the water vapor in this stream are effective gasification enhancers. The enhancer gas travels through a small compressor, which is used to overcome the pressure drop across the reducer, and a cross heat exchanger, which is used to reheat the enhancer gas stream (by exchange with the hot CO₂ product stream), before it is reintroduced into the reducer. The rest of the CO₂ stream passes through the condenser and is then compressed to 153
bar using a six-stage centrifugal compressor, which includes inter-stage cooling and a triethylene glycol unit for further dehydration.

The spent carrier particles and coal ash exiting the bottom of the reducer are transported to the combustor, where the Fe and FeO (actually, Fe$_{0.947}$O) in the spent particles are oxidized to Fe$_2$O$_3$ by the oxygen contained in air. Any unburned carbon in the coal ash also is oxidized to CO$_2$ in the combustor. The temperature in the combustor must be maintained close to 1200°C to maximize the temperature of the carrier particles while avoiding the risk of particle fusion. Because the carrier particles provide the heat required for the endothermic reactions in the reducer, a high particle temperature is desired to minimize the required particle circulation rate. The CDCL combustor is designed analogously to a fluidized bed coal combustor with in-bed heat exchange surface to maintain a uniform temperature profile. Air is supplied to the combustor using a forced draft (FD) fan; the total air requirement is determined based on stoichiometric and hydrodynamic considerations.

The hot product stream from the air reactor, which contains fully oxidized carrier particles and coal ash entrained in spent air, is sent to a series of cyclones for gas/solids separation. The first cyclone captures the carrier particles, which have a much larger diameter than the coal ash. The second cyclone captures much of the coal ash, as well as fines produced from carrier particle attrition. For purposes of this evaluation, losses due to attrition were assumed to be 0.02% of the carrier particle circulation rate. This is a
reasonable target, based on the attrition rates observed with fluid catalytic cracking catalysts.\textsuperscript{108} To compensate for these losses, fresh makeup carrier particles are added to the system ahead of the reducer.

The hot, spent air leaving the cyclones, which is the flue gas from the CDCL process, is cooled in a heat recovery steam generator (HRSG) to provide additional heat to the steam cycle. It then passes through a typical air pollution control train, including a baghouse for particulate matter removal and a limestone forced oxidation wet flue gas desulfurization (FGD) system for \( \text{SO}_2 \) removal, before being discharged through a stack. An ID fan is used to overcome the pressure drop created by the HRSG, baghouse, and FGD system. For purposes of this preliminary analysis, it is assumed that selective catalytic reduction is not required, given the low probability for \( \text{NO}_x \) formation in the combustor. The combustor does not produce a flame, does not involve combustion of nitrogen-containing fuel, and operates below the temperatures (i.e., \( >1,300^\circ\text{C} \)) that would promote thermal \( \text{NO}_x \) formation. Experimental testing will be required to determine the actual extent of \( \text{NO}_x \) formation.

As indicated in Figure 4.5 and discussed above, the heat recovered from the combustor, the spent air exhaust stream, and the \( \text{CO}_2 \) stream is used to raise steam, which is sent to a steam turbine-generator to produce electricity. The analysis presented here assumes a supercritical steam cycle with a main steam pressure of 242 bar and main and reheat steam temperatures of 593°C, consistent with Cases 11 and 12 in the DOE baseline.
It is anticipated that a supercritical steam cycle would be used in greenfield installations of the CDCL process to maximize net plant efficiency.

4.3.3 Process Simulation

The technical performance of the commercial-scale CDCL plant design was simulated using Aspen Plus® software. The reducer and combustor were modeled by minimizing the Gibbs free energy of the reaction products (i.e., using RGIBBS blocks in Aspen Plus®). A single equilibrium stage (i.e., one RGIBBS block) was sufficient to model the fluidized bed combustor. For the moving bed reducer, a multistage equilibrium model, consisting of a set of four interconnected RGIBBS blocks, was used. (The addition of additional equilibrium stages did not significantly alter the results). Char conversion in the reducer was limited to 95% of the fixed carbon in the coal, per OSU’s bench-scale experimental results. The steam cycle in the CDCL plant was modeled using the STEAM-TA property method in Aspen Plus®; the acid gas scrubber was modeled using the ELECNRTL method, and all other process units were modeled using the PENG-ROB method. Performance assumptions for balance of plant (BOP) equipment items were consistent with those specified in the DOE report titled Quality Guidelines for Energy System Studies: Process Modeling Design Parameters. The FD and ID fans were modeled assuming a polytropic efficiency of 75%, and the enhancer gas recycle compressor was modeled assuming an isentropic efficiency of 75%. The CO₂ compressor was modeled assuming a polytropic stage efficiency of 86%, a mechanical stage efficiency of 98%, an inter-stage cooler approach temperature of 5.6°C, and an
inter-stage cooler pressure drop of 0.03 bar. The supercritical steam cycle was modeled using the assumptions detailed in the DOE quality guidelines.\textsuperscript{110}

Table 4.1 presents key performance results from the CDCL Plant process simulation and compares these with the performance of the Base Plant and the MEA Plant. As discussed above, all three plants were modeled using the same design basis, and all are designed to produce $\sim$550 MW\textsubscript{e} of net electric output. Both the CDCL Plant and the MEA Plant include CO\textsubscript{2} compression to 153 bar.

The CDCL Plant achieves 97.0\% CO\textsubscript{2} capture and compression with an energy penalty (i.e., percent reduction in net efficiency) of just 10.6\% relative to the Base supercritical PC plant without CO\textsubscript{2} capture. This represents a substantial improvement over the 27.6\% energy penalty associated with 90.2\% CO\textsubscript{2} capture and compression in the MEA Plant. In fact, the net efficiency of the supercritical CDCL Plant (35.2\%) is only 4\% less than the net efficiency of a conventional subcritical PC plant without CO\textsubscript{2} capture (36.8\%).\textsuperscript{104} The CDCL Plant efficiency might be further improved by operating the reducer and combustor at elevated pressure and using a combined cycle for electricity generation,\textsuperscript{111} as is done in pressurized fluidized bed combustion power plants. However, an analysis of this configuration is beyond the scope of this paper.

The greater net efficiency of the CDCL Plant compared to the MEA Plant arises largely because the CDCL Plant does not require steam extraction for solvent
regeneration. As shown in Table 4.1, this regeneration energy requirement significantly lowers the gross efficiency of the MEA Plant and accounts for about two-thirds (18.3%) of its 27.6% energy penalty. In contrast, the gross efficiency of the CDCL Plant (41.2%) is only slightly less than the gross efficiency of the Base Plant (41.5%); this slight decrease results from small inefficiencies in heat recovery and integration in the CDCL Plant and contributes a 0.8% energy penalty. CO₂ compression accounts for most (7.1%) of the 10.6% energy penalty associated with the CDCL process. The energy penalty for CO₂ compression is slightly greater in the CDCL Plant than in the MEA Plant, owing to the CDCL Plant’s greater CO₂ capture efficiency (97.0% vs. 90.2% in the MEA Plant) and lower compressor inlet pressure (1.0 bar vs. 1.6 bar in the MEA Plant). The rest of the CDCL Plant energy penalty is associated with the fans and compressors required to overcome the pressure drops associated with transporting carrier particles through the process (2.2%), the solids handling equipment required to transport makeup and spent carrier particles and feed coal into the reducer (0.3%), and the incremental cooling load required to condense water from the CO₂ stream (0.3%). Although the CDCL process is an advanced form of oxycombustion, it does not require a cryogenic air separation unit. Hence, the large auxiliary load typically associated with air separation is avoided, and the overall energy penalty associated with the CDCL process is substantially less than the 25-30% energy penalty associated with conventional oxycombustion.¹⁰⁴

As discussed above, the CO₂ removal performance of the CDCL Plant is superior to the performance of the MEA Plant. In the CDCL process, the CO₂ that is produced in
the reducer is captured essentially in its entirety, without reliance on an absorption or adsorption process to separate the CO₂ from a dilute gas stream. The small CO₂ emissions in the CDCL Plant arise from incomplete char conversion in the reducer, which results in the leakage of a small amount of fuel carbon to the combustor (where it is oxidized by air to form CO₂), and from the CO₂ that is liberated from the limestone reagent in the wet FGD. Both the CO₂ formed in the combustor and the CO₂ formed in the FGD are emitted through the stack with the spent air stream. In the MEA Plant, the FGD is located upstream of the post-combustion CO₂ capture process, so most of the CO₂ formed from the limestone reagent is captured. However, the MEA system captures only ~90% of the CO₂ in the incoming gas stream because of less-than-perfect separation efficiency. These differences in CO₂ capture performance, coupled with the difference in net efficiency between the plants, result in a 75% lower CO₂ emission rate for the CDCL Plant compared to the MEA Plant.

4.3.4 Economic Analysis

The process economics for the CDCL Plant were computed using the same methodology and assumptions that were used for the Base and MEA Plants, which are detailed in the DOE baseline report¹⁰⁴ and in DOE’s Quality Guidelines for Energy System Studies: Cost Estimation Methodology for NETL Assessments of Power Plant Performance.¹¹⁰ All three plants were assumed to be built in a Midwest U.S. location with access by rail, and all were assumed to operate at an 85% capacity factor. The capital costs and operating and maintenance (O&M) costs reported here are “overnight”
costs expressed in 2007 dollars. The costs for the MEA Plant and CDCL Plant include the costs associated with CO$_2$ capture and compression, but they do not include costs for CO$_2$ transport, storage, and monitoring.

Capital costs for the Base Plant and MEA Plant were taken from the DOE baseline report.$^{104}$ Capital costs for the CDCL Plant were factored from the baseline report, other U.S. DOE reports, literature sources, vendor quotes, and engineering cost estimating equations. The capital costs for the two main CDCL equipment items, the reducer and combustor, were developed from budgetary estimates provided by a commercial equipment vendor.

For each of the Base, MEA, and CDCL Plants, the total overnight cost (TOC) was derived by summing the total plant costs (TPC) of all individual equipment items and then adding owner’s costs (i.e., preproduction costs, inventory capital, initial costs for catalysts and chemicals, land, financing costs, and other owner’s costs). The TOC was the capital cost metric used in the COE calculation for each plant. The total plant costs of individual equipment items include bare erected costs, engineering and home office costs, and project and process contingencies. For Base Plant and MEA Plant equipment items, process and project contingencies were taken from the DOE baseline report.$^{104}$ The same contingencies were applied to corresponding equipment items in the CDCL Plant, and a 20% project contingency was applied to all equipment items that are unique to that plant. In addition, a 30% process contingency was applied to the reducer in the CDCL Plant to
account for uncertainties regarding its design. (The design and cost of the combustor in the CDCL Plant are based on commercially-proven fluidized bed combustion equipment; hence, no process contingency was applied to this item).

Fixed O&M costs (i.e., operating labor, maintenance labor and materials, administrative and support labor, property taxes, and insurance) were approximated using common cost estimating practices. Table 4.2 summarizes the unit prices that were used to calculate variable O&M costs. The assumed price for oxygen carrier particles is based on an estimate provided by a commercial catalyst vendor, and the other prices are taken from the DOE baseline report. In addition, to account for differences in CO$_2$ removal performance between the CDCL and MEA Plants, the incremental CO$_2$ emission reduction achieved by the CDCL Plant (over and above that achieved by the MEA Plant) was credited at a rate of $20/ton ($22.05/tonne). We believe this credit price is reasonable, because it is slightly less than the cost of CO$_2$ avoided for the CDCL Plant. Hence, the market price for CO$_2$ would likely need to be at least this high before the CDCL technology would deploy commercially.

The economic performance of the Base, MEA, and CDCL Plants is compared on the basis of the first-year cost of electricity, expressed in dollars per megawatt-hour of electricity produced. For the Base Plant, first-year capital charges were calculated using a capital charge factor (CCF) of 0.116, which is based on a typical financing structure for low-risk investor owned utility projects with a 5-year construction period. For the MEA
and CDCL Plants, which are higher-risk investments because of the early developmental status of CO$_2$ capture technology, a CCF of 0.124 was used. (This CCF results from the use of a financing structure with a lower debt-to-equity ratio and higher cost of debt to reflect the greater risk profile of these projects).\textsuperscript{104}

Table 4.3 summarizes the capital cost estimates for the Base Plant, MEA Plant, and CDCL Plant. The TOC for the CDCL Plant with CO$_2$ capture ($2,653$/kW$_{\text{net}}$) is 31\% greater than the TOC for the Base Plant without CO$_2$ capture ($2,024$/kW$_{\text{net}}$). This represents a substantial improvement over the 76\% increase in TOC associated with the use of MEA scrubbing to capture CO$_2$. The cost increment between the CDCL Plant and the Base Plant is mostly attributable to the reducer and combustor, which are 44\% more costly than the PC boiler that they replace, and to the CO$_2$ purification, dehydration, and compression equipment, which is not required in the Base Plant. Capital costs for many balance-of-plant equipment items are also slightly greater in the CDCL Plant than in the Base Plant, owing largely to the energy penalty associated with CO$_2$ capture and compression in the CDCL Plant. (As a result of this energy penalty, larger equipment is required to achieve the same net power output). However, the capital cost increases associated with CO$_2$ capture in the CDCL Plant are modest in comparison to the MEA Plant, which has a much greater energy penalty than the CDCL Plant and requires both a PC boiler and a high-cost post-combustion MEA scrubbing system. (These two items collectively cost 70\% more than the CDCL process equipment).
Table 4.4 presents the estimated first-year cost of electricity for the Base Plant, MEA Plant, and CDCL Plant. The estimated first-year COE for the CDCL Plant ($78.40/MWh) is 33% greater than the first-year COE for the Base Plant ($58.90/MWh) and 22% less than the first-year COE for the MEA Plant ($100.90/MWh). This result indicates that the CDCL process has the potential to significantly improve upon the economic performance of conventional CO₂ capture technologies and to achieve DOE’s goal of ≥90% CO₂ capture at no more than a 35% increase in COE.¹¹¹

The reduction in COE between the MEA Plant and the CDCL Plant is largely driven by the lower capital cost of the CDCL Plant. Hence, any inaccuracy in the capital cost estimate presented in Table 4.3 could significantly affect the results of this analysis. The greatest source of uncertainty in the CDCL Plant capital cost estimate is the cost of the reducer, combustor, and accessories. The reducer is a novel piece of equipment that has not been implemented at large scale, and the integrated solids loop has not yet undergone a detailed commercial design. To illustrate the effect of this uncertainty on the CDCL Plant economic analysis results, a 25% increase in the cost of the reducer, combustor, and accessories would result in a first-year COE of $83.30/MWh (representing a 41% increase over the Base Plant COE), and a 25% decrease in the cost of this equipment would result in a first-year COE of $73.50/MWh (representing a 25% increase over the Base Plant COE).
The oxygen carrier particle attrition rate is an even greater source of uncertainty in the economic analysis results. Although the target attrition rate (0.02% of the carrier particle circulation rate) appears to be small, attrition becomes economically significant because of the high anticipated unit cost of makeup particles ($2.20/kg) and the large particle circulation rate at commercial scale. (For the 550 MWₑ plant studied here, the particle circulation rate is ~6,000,000 kg/h). Hence, a seemingly small change in the assumed attrition rate can significantly affect the economic analysis results. For example, the first-year COE for the CDCL Plant increases to $86.00/MWh (representing a 46% increase over the Base Plant COE) if the assumed attrition rate is increased from 0.02% to 0.05%. As a result of this sensitivity, additional work is being conducted to better characterize attrition in the CDCL process and to develop carrier particles with improved attrition resistance.

The economic viability of the CDCL process also will depend on the ability to uniformly distribute coal in the reducer and on the operating and maintenance costs associated with handling large quantities of circulating particles at high temperature. These uncertainties will be best resolved by development and testing of the process at larger scale.

As discussed above, the economic analysis presented here imposes a risk premium on the MEA Plant and CDCL Plant, because MEA scrubbing and Coal Direct Chemical Looping are currently unproven technologies for coal-fired power plant
applications at commercial scale. However, once these technologies are successfully demonstrated and deployed, it is likely that the risk premium would not be required for an \(N\textsuperscript{th}\)-of-a-kind installation. This would improve the process economics. For example, if the CDCL plant is evaluated using the same low-risk financing structure that is used for the Base Plant, its estimated first-year COE decreases to $75.53/MWh, representing a 28% increase over the Base Plant COE.

Finally, because of its low energy penalty and its use of a number of conventional PC plant equipment items, the CDCL Process could be a good candidate for repowering an existing power plant with relatively little decrease in net generating capacity. (The low energy penalty is important, because it helps to minimize the disparity in equipment sizing between the existing PC plant and a CDCL plant with the same net capacity). The ability to reuse existing equipment and a developed site could further improve the economics of the process. We plan to study repowering options for the CDCL process as part of a future analysis.

4.4 Integration between Chemical Looping Gasification and Solid Oxide Fuel Cell

The solid oxide fuel cell (SOFC) is an electrochemical device that can directly convert chemical energy to electricity at high temperature without the restrictions that are placed on heat engines. In order to industrialize power generation through SOFC technology, viable gaseous fuel source and effective process design are of great importance. Hydrogen fueled SOFC is widely considered a viable future technology due
CDCL gasification is a novel technology that can efficiently convert solid fuels into hydrogen. Process integration between the CDCL system and SOFC system has the potential to construct a highly efficient process for electricity generation. The proposed CDCL-SOFC process has a number of configurations, either at high pressure or low pressure. Specifically, when integrating the chemical looping oxidizer and the SOFC anode within a closed loop of hydrogen and steam as shown in Figure 4.6, the power generation can be further enhanced.

The current design considers a CDCL-SOFC process with 1000 MW thermal input. In the CDCL system, a moving bed design is adopted for both the reducer and the oxidizer. In the moving bed reducer, solid flows downward while gas ascends upward. The countercurrent design can fully convert coal into CO\textsubscript{2} and H\textsubscript{2}O with iron oxide being reduced to the form of Fe, FeO, and a trace amount of Fe\textsubscript{0.877}S. 71.5% of the reduced iron particles are used for hydrogen generation in the oxidizer, and the other 28.5% is combusted in the combustor. The oxidizer operates at 850 °C, converting a gaseous mixture of 90.4% H\textsubscript{2}O and 9.6% H\textsubscript{2} mole fraction into a mixture of 35.9% H\textsubscript{2}O, 64.1% H\textsubscript{2}, and about 359 ppm of H\textsubscript{2}S. The gaseous mixture then goes to the anode of a sulfur tolerant SOFC for electricity generation. At the same time, Fe and FeO will be oxidized to Fe\textsubscript{3}O\textsubscript{4}, which flows to the combustor for Fe\textsubscript{2}O\textsubscript{3} regeneration.

The air is first preheated in the Heat Recovery Steam Generation (HRSG) section and is then delivered to the cathode of the SOFC device. 30% of the oxygen and 85% of
the hydrogen are consumed in the SOFC operating at 900 °C. The spent air then goes from the cathode to the combustor to regenerate Fe₂O₃. The spent hydrogen/steam mixture from the anode is then cooled to about 240 °C and delivered to a sulfur removal unit. Only a small amount of steam needs to be made up to the hydrogen/steam mixture before it is recycled back to the oxidizer.

During the CDCL-SOFC process, nearly all the CO₂ can be separated by simple condensation and compressed to 153 atm for transportation and sequestration, which consumes about 35.8 MWₑ work. The other pollutants such as Cl, S, and Hg can either be co-sequestered with CO₂ or removed by conventional techniques. For the given 0.36% sulfur contents in the bituminous coal feedstock, 43% of the sulfur is converted to SO₂ in the reducer, 40% goes to the hydrogen/steam mixture as H₂S, and the remaining 16.2% forms SO₂ during combustion. All the sulfur can be cleaned using commercially-available technology. Much less NOₓ is formed in the combustor than traditional coal combustion. Ash can be removed from the oxygen carrier by a cyclone positioned before the reducer.

When the CDCL and the SOFC system are properly integrated, 535 MW of net electricity can be produced by the CDCL-SOFC system, and 96 MW of electricity can be generated from the steam turbine system through the recovery of low grade heat. The overall process can produce electricity up to 631 MW without CO₂ compression, which equals a coal to power efficiency of 63% (HHV). In conclusion, the CDCL is an enabling
technology for clean coal conversion, and its unique integration with SOFC provides the opportunity for high efficiency electric production.

4.5 Conclusions

In summary, Coal Direct Chemical Looping is an emerging technology with the potential to enable significant reductions in the cost of capturing CO$_2$ during the production of electricity from coal. The main enabling feature of the technology is its use of iron-based oxygen carrier particles to essentially provide for oxycombustion of coal without the need for a cryogenic air separation unit. This allows substantial reductions in both the capital cost and the energy penalty associated with CO$_2$ capture. The CDCL process has been tested successfully at the 2.5 and 25 kW$_t$ scales, and further scale-up is being pursued.

The preliminary techno-economic analysis presented here suggests that the CDCL technology is capable of meeting DOE’s performance goal for CO$_2$ capture technologies of ≥90% capture at no more than a 35% increase in cost of electricity. However, this result is particularly sensitive to several critical factors, including the oxygen carrier particle attrition rate, the cost of makeup carrier particles, and the design and cost of the reducer and combustor at commercial scale, which require further definition given the relatively early developmental stage of the CDCL technology. The project team is working to reduce the uncertainty associated with these factors, and the techno-economic analysis will be updated as new data and refined design concepts become available.
Figure 4.1 Simplified process flow diagram for a chemical looping combustion process
Figure 4.2 Adapted Schematic Diagram of the Dual Circulating Fluidized Bed (DCFB) CLC System at The Vienna University of Technology.\textsuperscript{40}
Figure 4.3 Dispersed gas-solid counter-current contacting pattern in the modified Vienna University of Technology solid fuel reducer.  

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Figure 4.4 The gas-solid contacting pattern in the reducer.

Particle reduction:
\[ \text{CH}_4 + 4 \text{Fe}_2\text{O}_3 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 8\text{FeO} \]

Coal devolatilization:
\[ \text{Coal} \rightarrow \text{C} + \text{CH}_4 \]
\[ \text{CO} + \text{FeO} \rightarrow \text{Fe} + \text{CO}_2 \]
\[ \text{C} + \text{CO}_2 \rightarrow 2 \text{CO} \]

Chargasification and particle reduction:
\[ \text{C} + \text{CO}_2 \rightarrow 2 \text{CO} \]
\[ \text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2 \]
\[ \text{CO} + \text{FeO} \rightarrow \text{Fe} + \text{CO}_2 \]
\[ \text{H}_2 + \text{FeO} \rightarrow \text{Fe} + \text{H}_2\text{O} \]
Figure 4.5 Simplified process flow diagram for a commercial-scale CDCL power plant
Figure 4.6 A schematic diagram for the CDCL-SOFC system
Table 4.1 Comparison of process simulation results for the CDCL Plant with results for the Base Plant and MEA Plant.

<table>
<thead>
<tr>
<th></th>
<th>Base Plant</th>
<th>MEA Plant</th>
<th>CDCL Plant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal Feed Rate (kg/h)</td>
<td>185,759</td>
<td>256,652</td>
<td>207,072</td>
</tr>
<tr>
<td>Heat Input (MW&lt;sub&gt;t&lt;/sub&gt;)</td>
<td>1,400</td>
<td>1,935</td>
<td>1,561</td>
</tr>
<tr>
<td>CO&lt;sub&gt;2&lt;/sub&gt; Emission Rate (kg/MWh&lt;sub&gt;net&lt;/sub&gt;)</td>
<td>802</td>
<td>111</td>
<td>28</td>
</tr>
<tr>
<td>CO&lt;sub&gt;2&lt;/sub&gt; Capture Efficiency&lt;sup&gt;a&lt;/sup&gt; (%)</td>
<td>0</td>
<td>90.2</td>
<td>97.0</td>
</tr>
<tr>
<td>Steam Cycle Gross Power (kW)</td>
<td>580,400</td>
<td>662,800</td>
<td>641,820</td>
</tr>
<tr>
<td>Gross Efficiency (HHV, %)</td>
<td>41.5</td>
<td>34.3</td>
<td>41.2</td>
</tr>
<tr>
<td>Auxiliary Power Requirements (kW)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coal Handling, Pulverizing, Feed</td>
<td>-3,220</td>
<td>-4,360</td>
<td>-4,590</td>
</tr>
<tr>
<td>Sorbent/Carrier Particle Handling</td>
<td>-890</td>
<td>-1,250</td>
<td>-1,360</td>
</tr>
<tr>
<td>Ash Handling</td>
<td>-530</td>
<td>-740</td>
<td>-690</td>
</tr>
<tr>
<td>Primary Air and Forced Draft Fans</td>
<td>-2,960</td>
<td>-4,100</td>
<td>-13,160</td>
</tr>
<tr>
<td>Induced Draft Fans</td>
<td>-7,050</td>
<td>-11,120</td>
<td>-9,850</td>
</tr>
<tr>
<td>Enhancer Gas Recycle Compressor</td>
<td>0</td>
<td>0</td>
<td>-1,560</td>
</tr>
<tr>
<td>SCR, Baghouse, FGD</td>
<td>-3,090</td>
<td>-4,280</td>
<td>-3,020</td>
</tr>
<tr>
<td>MEA System Auxiliaries</td>
<td>0</td>
<td>-20,600</td>
<td>0</td>
</tr>
<tr>
<td>CO&lt;sub&gt;2&lt;/sub&gt; Compressor</td>
<td>0</td>
<td>-44,890</td>
<td>-43,790</td>
</tr>
<tr>
<td>Miscellaneous Balance of Plant</td>
<td>-2,000</td>
<td>-2,000</td>
<td>-2,000</td>
</tr>
<tr>
<td>Steam Turbine Auxiliaries</td>
<td>-400</td>
<td>-400</td>
<td>-400</td>
</tr>
<tr>
<td>Condensate Pumps</td>
<td>-800</td>
<td>-560</td>
<td>-810</td>
</tr>
<tr>
<td>Ground Water Pumps</td>
<td>-480</td>
<td>-910</td>
<td>-590</td>
</tr>
<tr>
<td>Circulating Water Pump</td>
<td>-4,730</td>
<td>-10,100</td>
<td>-6,370</td>
</tr>
<tr>
<td>Cooling Tower Fans</td>
<td>-2,440</td>
<td>-5,230</td>
<td>-3,290</td>
</tr>
<tr>
<td>Transformer Losses</td>
<td>-1,820</td>
<td>-2,290</td>
<td>-2,010</td>
</tr>
<tr>
<td>Total Auxiliaries</td>
<td>-30,410</td>
<td>-112,830</td>
<td>-93,490</td>
</tr>
<tr>
<td>Net Power (kW)</td>
<td>549,990</td>
<td>549,970</td>
<td>548,330</td>
</tr>
<tr>
<td>Net Plant Efficiency (HHV, %)</td>
<td>39.3</td>
<td>28.5</td>
<td>35.2</td>
</tr>
<tr>
<td>Energy Penalty&lt;sup&gt;b&lt;/sup&gt;</td>
<td>-</td>
<td>27.6%</td>
<td>10.6%</td>
</tr>
</tbody>
</table>

<sup>a</sup>Calculated as (Carbon in CO<sub>2</sub> Product) ÷ (Carbon in Coal – Unburned Carbon in Ash + Carbon in FGD Reagent – Carbon in FGD Byproduct).

<sup>b</sup>Relative to Base Plant; includes energy for CO<sub>2</sub> compression.
Table 4.2 Unit price assumptions for variable O&M cost calculations.

<table>
<thead>
<tr>
<th>Material</th>
<th>Unit Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal (delivered)</td>
<td>$1.55 / GJ</td>
</tr>
<tr>
<td>Limestone (delivered)</td>
<td>$23.84 / tonne</td>
</tr>
<tr>
<td>Water</td>
<td>$0.29 / m³</td>
</tr>
<tr>
<td>Water Treatment Chemicals</td>
<td>$0.37 / kg</td>
</tr>
<tr>
<td>Solid Waste Disposal</td>
<td>$17.89 / tonne</td>
</tr>
<tr>
<td>Gypsum</td>
<td>$0 / ton</td>
</tr>
<tr>
<td>Activated Carbon</td>
<td>$2.31 / kg</td>
</tr>
<tr>
<td>Ammonia (19% NH₃)</td>
<td>$0.14 / kg</td>
</tr>
<tr>
<td>SCR Catalyst</td>
<td>$5,775.94 / m³</td>
</tr>
<tr>
<td>Caustic Soda</td>
<td>$0.48 / kg</td>
</tr>
<tr>
<td>Sulfuric Acid</td>
<td>$0.15 / kg</td>
</tr>
<tr>
<td>MEA Solvent</td>
<td>$2.48 / kg</td>
</tr>
<tr>
<td>Oxygen Carrier Particles</td>
<td>$2.20 / kg</td>
</tr>
</tbody>
</table>
Table 4.3 Comparison of estimated capital costs ($000) for the Base Plant, MEA Plant, and CDCL Plant.

<table>
<thead>
<tr>
<th></th>
<th>Base Plant</th>
<th>MEA Plant</th>
<th>CDCL Plant</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>TOTAL PLANT COSTS</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coal &amp; Sorbent Handling</td>
<td>$38,365</td>
<td>$47,015</td>
<td>$40,749</td>
</tr>
<tr>
<td>Coal &amp; Sorbent Prep and Feed</td>
<td>$18,059</td>
<td>$22,442</td>
<td>$29,274</td>
</tr>
<tr>
<td>Feedwater &amp; Misc. BOP Systems</td>
<td>$79,149</td>
<td>$102,552</td>
<td>$84,667</td>
</tr>
<tr>
<td>PC Boiler &amp; Accessories&lt;sup&gt;a&lt;/sup&gt;</td>
<td>$296,317</td>
<td>$369,144</td>
<td>$0</td>
</tr>
<tr>
<td><strong>CDCL Equipment</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reducer, Combustor, and Accessories&lt;sup&gt;b&lt;/sup&gt;</td>
<td>$0</td>
<td>$0</td>
<td>$425,879</td>
</tr>
<tr>
<td>Makeup Carrier Particle Handling &amp; Storage</td>
<td>$0</td>
<td>$0</td>
<td>$1,154</td>
</tr>
<tr>
<td>CO&lt;sub&gt;2&lt;/sub&gt; Stream Baghouse &amp; Acid Gas Scrubber</td>
<td>$0</td>
<td>$0</td>
<td>$28,153</td>
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<tr>
<td>CO&lt;sub&gt;2&lt;/sub&gt; Stream Condenser</td>
<td>$0</td>
<td>$0</td>
<td>$9,728</td>
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<tr>
<td>MEA System</td>
<td>$0</td>
<td>$421,183</td>
<td>$0</td>
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<tr>
<td>CO&lt;sub&gt;2&lt;/sub&gt; Compression and Drying</td>
<td>$0</td>
<td>$47,599</td>
<td>$46,544</td>
</tr>
<tr>
<td>FGD &amp; Accessories</td>
<td>$95,155</td>
<td>$120,121</td>
<td>$100,687</td>
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<td>Baghouse &amp; Accessories</td>
<td>$33,438</td>
<td>$43,214</td>
<td>$35,527</td>
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<tr>
<td>Ductwork and Stack</td>
<td>$37,291</td>
<td>$37,526</td>
<td>$44,086</td>
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<tr>
<td>Steam Turbine Generator</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Steam TG &amp; Accessories</td>
<td>$70,507</td>
<td>$77,546</td>
<td>$75,651</td>
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<tr>
<td>Turbine Plant Auxiliaries and Steam Piping</td>
<td>$45,441</td>
<td>$54,565</td>
<td>$48,755</td>
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<tr>
<td>Cooling Water System</td>
<td>$37,371</td>
<td>$60,965</td>
<td>$43,675</td>
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<tr>
<td>Ash/Spent Sorbent Handling System</td>
<td>$12,626</td>
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<td>$15,009</td>
</tr>
<tr>
<td>Accessory Electric Plant</td>
<td>$51,068</td>
<td>$80,931</td>
<td>$54,793</td>
</tr>
<tr>
<td>Instrumentation and Control</td>
<td>$21,555</td>
<td>$25,838</td>
<td>$24,706</td>
</tr>
<tr>
<td>Improvements to Site</td>
<td>$14,054</td>
<td>$15,717</td>
<td>$17,599</td>
</tr>
<tr>
<td>Buildings and Structures</td>
<td>$55,506</td>
<td>$60,557</td>
<td>$17,433</td>
</tr>
<tr>
<td><strong>OWNER'S COSTS</strong></td>
<td>$207,613</td>
<td>$361,622</td>
<td>$310,659</td>
</tr>
<tr>
<td><strong>TOTAL OVERNIGHT COST</strong></td>
<td>$1,113,515</td>
<td>$1,963,645</td>
<td>$1,454,728</td>
</tr>
</tbody>
</table>

<sup>a</sup>Includes boiler, air preheater, SCR, and FD and ID fans. <sup>b</sup>Includes reducer, combustor, steam tubes, L-valves and zone seals, air preheater, FD and ID fans, cross heat exchanger, and enhancer gas boost compressor.
Table 4.4 Economic analysis results for the Base Plant, MEA Plant, and CDCL Plant.

<table>
<thead>
<tr>
<th></th>
<th>Base Plant</th>
<th>MEA Plant</th>
<th>CDCL Plant</th>
</tr>
</thead>
<tbody>
<tr>
<td>First-Year Capital Cost ($/MWh)</td>
<td>31.7</td>
<td>59.6</td>
<td>44.2</td>
</tr>
<tr>
<td>First-Year Fixed O&amp;M Cost ($/MWh)</td>
<td>8.0</td>
<td>13.0</td>
<td>9.6</td>
</tr>
<tr>
<td>First-Year Fuel Cost ($/MWh)</td>
<td>14.2</td>
<td>19.6</td>
<td>15.9</td>
</tr>
<tr>
<td>First-Year Variable O&amp;M Cost ($/MWh)</td>
<td>5.0</td>
<td>8.7</td>
<td>8.7</td>
</tr>
<tr>
<td>First-Year Cost of Electricity ($/MWh)</td>
<td>58.9</td>
<td>100.9</td>
<td>78.4</td>
</tr>
<tr>
<td>% Increase Over Base Plant</td>
<td>-</td>
<td>71.3</td>
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Chapter 5

Chemical Looping Processes for Hydrogen and Power Co-Production

5.1 Introduction

As the most abundantly reserved fossil fuel, coal accounts for 40% of the electricity generated worldwide and is projected to remain as an important fossil energy source within the foreseeable future.\textsuperscript{1} Compared to other fossil fuels such as crude oil and natural gas, coal is more carbon intensive and difficult to convert. The conventional pulverized coal combustion (PCC) plants convert approximately a third of the energy in coal into electricity. An additional 40% energy penalty may occur when a mono-ethanol amine (MEA) based carbon capture system is retrofitted to the plant for CO\textsubscript{2} capture.\textsuperscript{25} With the CO\textsubscript{2} regulation looming over the horizon, efficient coal conversion and CO\textsubscript{2} control strategies are highly desired.

Hydrogen and electricity are commercially produced from coal through gasification processes. Compared to PCC, coal gasification can potentially be more efficient especially when CO\textsubscript{2} capture is mandatory. However, CO\textsubscript{2} capture will nevertheless reduce the efficiency of a conventional coal gasification plant by up to 24%.\textsuperscript{25} More advanced approaches such as membrane enhanced water gas shift (WGS) processes and syngas chemical looping (SCL) process are being developed to improve the performance of coal gasification under a carbon constrained scenario.\textsuperscript{25, 112} The
membrane enhanced WGS process integrates hydrogen or CO₂ selective membrane to the WGS reactor to simultaneously remove the WGS reaction product, thereby increasing the product yield. The chemical looping approach, on the other hand, indirectly converts coal derived syngas into separate streams of concentrated CO₂ and H₂ through the assistance of a reactive reaction medium, avoiding the CO₂ separation step. Previous studies investigate one or more novel technologies mentioned above for either power production or hydrogen generation.²⁵,¹¹² A comprehensive study that includes all four baseline and novel technologies for hydrogen and power co-production, however, has not been performed.

The present study is intended to assess the relative performances of the various options of coal conversion processes aforementioned under a carbon constrained scenario. Specifically, the efficiencies of hydrogen production and power generation and the economic performance for these processes are presented. The analysis conducted uses the cost and performance baseline for fossil energy plants (baseline studies) published by USDOE.⁶ Factors that may involve uncertainty in this study are analyzed and discussed.

5.2 Hydrogen and Electricity Co-Production Process Overview

In this section, the four baseline and novel coal gasification processes, i.e. the baseline coal gasification process, H₂ selective membrane enhanced WGS process, CO₂ selective membrane enhanced WGS process, and syngas chemical looping (SCL) process, are introduced.
5.2.1 Coal Gasification – WGS Process

The flow diagram of the baseline coal gasification process configured for hydrogen and electricity co-production is given in Figure 5.1. The coal gasification process is used as the base case process in this article. As can be seen from Figure 5.1, a Shell SCGP dry-feed, entrained flow gasifier with gas quench configuration is utilized. In this process, coal is first pulverized and dried. The coal powder is then pressurized in the lock hopper and introduced to the gasifier (1,424 °C and 4.2 MPa) to be partially oxidized with concentrated oxygen from the cryogenic air separation unit. The high temperature raw syngas from the gasifier is then quenched to ~910 °C with low temperature syngas recycled from a particulate removal unit downstream. The quenched syngas is then introduced to a syngas cooler which cools the syngas down to ~400 °C. The cooled syngas is then introduced to the particulate removal unit where the entrained fly ash is removed from the syngas. A portion (~1/2) of the particulate free syngas is recycled to the gasifier for quenching purpose. The remaining syngas is introduced to the hot/warm gas cleanup unit (HGCU) which removes gaseous pollutants such as hydrogen chloride, sulphides, ammonia, etc. The clean syngas from HGCU is then saturated with steam (H₂O:CO=2:1) before entering a two-stage WGS reactor. In the WGS reactor, which operates at 3.7 MPa and 230 °C, nearly 95% of the CO is converted to H₂. The hydrogen rich gas stream then flows to a heat recovery and steam generator (HRSG) for cooling and heat recovery. Subsequently, the bulk quantity of CO₂ in the hydrogen rich gas stream is removed using such solvent as dimethyl ethers of polyethylene glycol.
(DEPG) in a SELEXOL process. The resulting hydrogen stream is further purified using pressure swing adsorption (PSA) units. The tail gas from the PSA is combusted for electricity generation. This process can also be configured to co-produce power and hydrogen. In the case when electricity is not the primary product, electricity generation capacity is controlled by the hydrogen recovery ratio in the PSA units, i.e. the ratio between the hydrogen in the PSA product gas and that in the feed gas. A low hydrogen recovery ratio leads to more power and less hydrogen and vice versa. Under such a configuration, electricity is generated in a boiler which uses the PSA tail gas as the fuel.

In the case when electricity is the primary product, a hydrogen fueled combined cycle system is used to combust the PSA tail gas and a portion of the hydrogen product. When electricity is the only product, the gaseous product from the SELEXOL is directly combusted in the combined cycle system. Under such a configuration, the process becomes an advanced IGCC process with CO₂ capture. Compared to existing coal gasification plants, the coal gasification process in this study uses an HGCU as opposed to a solvent based pollutant removal system for syngas cleaning. This ensures that the performances of all four processes are based on identical syngas generation and cleanup systems.

Since a significant amount of heat is required in the solvent based acid gas removal system such as MDEA or SELEXOL, separation of CO₂ from H₂ in the baseline coal gasification processes can be energy intensive. Various studies have indicated that the energy penalty for CO₂ capture can be reduced through either the membrane based
separation techniques or the chemical looping strategy. The three novel processes presented in this article include both membrane and chemical looping enhanced coal gasification processes.

5.2.2 H₂ or CO₂ Selective Membrane Enhanced WGS Processes

A membrane is a selective barrier between two phases. The molecules or small particles can transport from one phase to the other through the membrane. A H₂ or CO₂ selective membrane can be utilized in gasification processes to reduce the energy penalty for CO₂ capture and to enhance the yields of hydrogen and/or electricity. The membrane based systems studied in this article integrate the functions of WGS and CO₂ separation in a single unit using either H₂- or CO₂-selective membrane. Such configurations are shown in Figures 5.2a and 5.2b.

Figure 5.2a illustrates a configuration when a H₂-selective membrane is used to co-produce hydrogen and electricity. In order to make the process directly comparable to the baseline process, an identical syngas generation, quenching, and cleanup system is used. The clean syngas is sent to the membrane-WGS reactor which is operated at 400 °C. The membrane-WGS reactor has two compartments, i.e. reaction side which operates at 3.7 MPa and product side which operates at ~2 MPa. The two compartments are segregated by a semi-permeable membrane that is selective to hydrogen. In the reaction side, the CO in the syngas is converted to H₂ and CO₂ via the WGS reaction. The H₂ produced in the reaction side continuously permeates through the membrane to the
product side. In order to maintain a low hydrogen partial pressure at the product side, steam is used as the sweeping gas. As a result, the gaseous mixture from the product side is a mixture of steam and hydrogen. High purity H₂ product can be obtained after condensing the gaseous mixture. The hydrogen can either be a product or combusted with air for power generation. Removal of hydrogen from the reaction side enhances the WGS reaction, which is limited by thermodynamic equilibrium. It is reported that the molar ratio between H₂O and CO in the reaction side can be as low as 1.6 for a 95% CO conversion at ~400 °C. The exhaust gas from the reaction side, which is a concentrated CO₂ stream mixed with CO, hydrogen, N₂, etc, is cooled and liquefied. Non-condensable gases are separated and then combusted for heat/power generation. The condensed CO₂ is further compressed and sequestered. When electricity is the only desired product, N₂ from ASU can be used as the sweeping gas after minor recompression.

The underlying principle for the CO₂ selective membrane WGS process shown in Figure 5.2b is similar to the system shown in Figure 5.2a. The only difference lies in the type of membrane used for separating the shifted syngas. In this configuration, a CO₂-selective membrane is used to divide the reaction side and the product side in the membrane reactor. As a result, CO₂ rather than H₂ will be transferred from the reaction side to the product side. The simultaneous removal of CO₂, which is another product of the WGS reaction, can also enhance the reaction. The CO₂ stream in the product side, swept by steam, can be directly sequestered while the H₂-rich stream in the reaction side
can either be purified with PSA units to obtain a hydrogen product or combusted with air for power generation.

5.2.3 Syngas Chemical Looping Process

The process configuration of the Syngas Chemical Looping (SCL) Process for hydrogen production is illustrated in Figure 5.3. Again, the syngas generation, quenching, and cleanup systems in this process are identical to those in the baseline process. The clean syngas is cooled to 500 °C before it is introduced to a hot gas cleanup unit to strip the sulfur level down to 5 ppm. The low sulfur syngas is then introduced to the SCL block for hydrogen and power co-generation. The SCL block consists of three main reactors: the reducer, the oxidizer, and the combustor. In the reducer, the conditioned syngas from the hot gas cleanup unit is used to reduce iron oxide (Fe$_2$O$_3$) composite particles. The syngas is completely converted into carbon dioxide and water while the iron oxide composite particles are reduced to a mixture of Fe and FeO. The Fe/FeO particles leaving the reducer are then introduced into the oxidizer. In the oxidizer, the reduced particles react with steam to produce hydrogen. Meanwhile, the Fe and FeO particles are oxidizer to Fe$_3$O$_4$. The Fe$_3$O$_4$ formed in the oxidizer is further regenerated to Fe$_2$O$_3$ in an entrained flow combustor which also transports solid particles discharged from the oxidizer to the reducer inlet, completing the chemical loop. Additional electricity can be produced through combustion of a portion or all of the hydrogen product from the oxidizer. In an alternative configuration, a sub-stoichiometric amount of steam is introduced to the oxidizer. As a result, the heat generated in the combustor is
increased. Therefore, the SCL process is capable of producing hydrogen and electricity at various ratios through the utilization of both chemical-looping gasification and chemical-looping combustion concepts.

5.3 Process and Economic Analysis Models and Methods

Aspen Plus® simulation is performed to compare the energy conversion efficiencies of the four processes described in the previous section. Aspen Plus® has a comprehensive physical property database. Therefore, most of the chemical species involved in the process can be selected directly from this database. The nonconventional components such as coal and ash are specified using a general coal enthalpy modulus embedded in the Aspen software. After the chemical species in the process are defined, the related physical property methods are selected among the various choices for the simulator. In this simulation, the global property method used is PR-BM, and the local property methods are specified whenever required. In order to ensure the comparability of the process and economic analysis results, a common set of assumptions for coal type, coal processing rate, carbon conversion of the gasifier, reactor heat loss, CO₂ capture rate, etc are used. The assumptions are consistent with those in the process analyses performed by USDOE. This is followed by cost analysis based on the USDOE baseline studies. ¹⁰⁴

5.3.1 Common Assumptions and Model Setup for Process Analysis
In order to impartially evaluate the performance of the four processes, a common set of assumptions and modeling parameters are defined:

1. The CO$_2$ capture rate is 90% for all four processes.
2. The ambient temperature is 25 °C and the ambient pressure is 0.1 MPa.
3. Illinois #6 coal is used. The properties of the Illinois #6 coal are shown in Table 5.1.
4. The coal processing capacity of the gasifier is 132.9 tonnes/hour (1000 MW$_{th}$, HHV).
5. The Shell SCGP gasifier with gas quench configuration is used for all the processes.
6. The carbon conversion in the gasifier is 99.5% and the heat loss in the gasifier is 1% of the HHV of coal.
7. Air consists of 21% O$_2$ and 79% N$_2$ by volume.
8. The oxygen purity from ASU is 95% by volume. A small amount of N$_2$ from ASU is used for coal injection to the gasifier.
9. The ratio of O$_2$, dry coal, and steam in the gasifier is 0.83:1:0.09 by weight.
10. The solids circulating in the SCL consist of 70 wt.% Fe$_2$O$_3$ and 30 wt.% inert support.
11. The H$_2$ product is compressed to 6 MPa for subsequent transportation.
12. CO$_2$ is compressed to 15.3 MPa for sequestration.
13. The pressures in the steam cycle are 12.4/3/0.4 MPa, and the high pressure (HP) and intermediate pressure (IP) steam is superheated to 566 °C in a regular Rankine cycle or 538 °C in a combined cycle. The temperature of the flue gas in the stack is 132 °C.
14. Most of the compressors are designed with four stages and the outlet temperature of the compressor intercooler is 40 °C.
15. The mechanical efficiency of pressure changers such as compressors and expanders is 1 while their isentropic efficiency is 0.8–0.85.

16. In the membrane reactor, sweep gas and feed gas flow countercurrently.

17. In the membrane enhanced WGS reactor, the pressure at the reaction side is 3.7 MPa, while the pressure at the product side varies from 1 MPa to 2 MPa.

18. The gas and solids conversions in the SCL system are based on experimental results.\textsuperscript{55}

19. The energy consumption for CO\textsubscript{2} separation is 100 kWh per ton of CO\textsubscript{2} for SELEXOL system.\textsuperscript{123}

20. The turbine system can be flexibility operated at various loads, the inlet firing temperature of the gas turbine is \textasciitilde1,320 °C.

21. Required hydrogen purity is 99.9+\%.

22. The auxiliary power for the plant, which accounts for the power required for equipments other than the pressure changers, is 5–10 MW\textsubscript{e}.

To accurately simulate the individual unit in the flow sheet, an appropriate Aspen Plus\textsuperscript{\textregistered} model (or models) for each unit are determined. These models are listed in Table 5.2.

\textbf{5.3.2 Coal Processing and Gasification System}

Shell Coal Gasification Process (SCGP) is used for all the four cases. Illinois #6 coal is first crushed and pulverized to fine powder at a rate of 132.9 tonnes/hour. The
pulverized coal is then dried to 5% moisture content by warm flue gas. The dried coal powder is then pressurized and pneumatically fed into the gasifier with 15.85 tonnes/hour of N\textsubscript{2} through a lock hopper assembly. The operating pressure of the gasifier is 4.2 MPa and the temperature is 1,424 °C. The temperature of the gasifier is moderated by a water cooled membrane wall through which high pressure steam is generated. The temperature of the gasifier is notably above the slagging temperature of ash. As a result, ash is removed in liquid form from the bottom of the gasifier. The heat loss in the gasifier is assumed to be 1% of the total heating value of the coal feedstock.

An Air Separation Unit (ASU) is used to produce oxygen for the gasifier. The oxygen used for gasification contains 95% O\textsubscript{2} by volume balanced with 5% N\textsubscript{2}. The oxygen and steam consumption are determined based on the feedstock compositions and the gasifier operating conditions. For the case of the SCGP gasifier in the present study, the oxygen consumption in terms of the mass flow rate ratio of oxygen to dry coal is 0.83. The corresponding mass flow rate ratio of steam to dry coal is ~0.09. In the ASU, ambient air is first filtered and desiccated. It is then compressed to 1.3 MPa via a four-stage intercooled air compressor. The compressed air is subsequently introduced to a cryogenic column which separates the compressed air into oxygen and nitrogen. The separated oxygen leaves the column and its heat exchanger network at ~32 °C and 0.86 MPa before it is further compressed to 5.1 MPa for gasification purpose. The nitrogen exits the ASU at ~32 °C and 0.39 MPa. A small amount of the nitrogen is compressed to 5.62 MPa for coal feeding, while the remaining nitrogen is used as a gas turbine coolant.
after being pressurized to 3.17 MPa. The energy consumptions for all the compressors related to ASU are considered in the analysis.

The gas quench option is used to rapidly cool the raw syngas to a temperature lower than the ash softening temperature. In this step, a stream of the low temperature syngas is recycled to mix with the high temperature raw syngas exiting from the gasifier. The mixing step reduces the syngas temperature to ~910 °C. The raw syngas is then sent to heat exchangers for cooling and particulate removal. 45~52% of the cooled syngas is split and repressurized to 4.2 MPa for recycling, and the remainder is sent downstream for hot gas cleanup. The HGCU removes HCl using Na$_2$CO$_3$, H$_2$S/COS using ZnO, and Hg and NH$_3$ using a novel intermediate temperate technology. A direct sulfur reduction process (DSRP) is used to recover sulfur and regenerates ZnO simultaneously.

### 5.3.3 Heat Recovery and Power Generation System

In order to ensure the comparability among all the processes, a set of common heat recovery strategies and power generation equipments are used for all four cases:

- When more than 35% (HHV basis) of the product is hydrogen, only Rankine cycle, i.e. HRSG and steam turbines, is used for power generation. The corresponding steam conditions in the HRSG are 12.4 MPa/ 566°C/ 566 °C. In order to superheat pressurized steam, an additional firing section is installed in the HRSG to combust tail gas and hydrogen fuel at ambient pressure. A gas turbine is not used in order to reduce the cost of the plant.
• When less than 35% (HHV basis) of the product is hydrogen, i.e. electricity is the primary product, a Brayton and Rankine combined cycle system is used for more efficient power generation. In most cases, the hydrogen fuel is diluted with nitrogen and combusted at 1315-1325°C, 3.1 MPa in the gas turbine. The steam conditions in HRSG are 12.4 MPa/ 538°C/ 538 °C under this configuration. The lower steam superheating temperatures result from the low firing temperature of the hydrogen fueled turbine.

5.3.4 Baseline Gasification Process

The ASPEN simulation flow sheet for the baseline coal gasification process is shown in Figure 5.4. In this process, the carbon monoxide in the cleaned syngas is converted in the WGS reactor with steam. The molar flow rate ratio of steam and CO is 2:1. The WGS reactor is operated at 230 °C, 3.7 MPa. The CO conversion is 95%. The subsequent SELEXOL unit captures 90% of the carbon in the shifted syngas, producing a hydrogen rich stream (~ 3 MPa) and a CO₂ stream (~0.5 MPa). The hydrogen rich stream from the SELEXOL unit is purified in the pressure swing absorption (PSA) units at ~3 MPa. A hydrogen recovery ratio of ~77% is used when hydrogen is the only product. By doing so, combustion of the tail gas from PSA can generate sufficient power to compensate the parasitic energy requirement. The tail gas discharged from PSA is assumed to be 0.2 MPa. When a gas turbine is used, the tail gas is recompressed to 3.2 MPa for power generation. The pressure of the CO₂ and H₂ leaving the plant are at 15.3
MPa and 6 MPa, respectively. Compressors are used as necessary to compress or recompress the intermediate and final products of the process.

Sensitivity analyses were performed to evaluate the effects of various operating parameters on the performance of the baseline gasification process. First, the hydrogen production scenario was determined by balancing the net electricity output to zero. The hydrogen produced under such a scenario is defined as the full hydrogen production capacity. Next, process analyses were performed under the conditions when hydrogen was produced at 80% and 60% of the full capacity. Within this operation range, the variation of the hydrogen production rate was controlled by the hydrogen recovery ratio of the PSA. No gas turbine was used in this operation range. When hydrogen was produced at 40% and 20% of the full capacity, a gas turbine is added to the process. The product distribution was controlled by splitting part of the hydrogen stream from SELEXOL to the gas turbine. When electricity was the only product from the process, the hydrogen rich gas from the SELEXOL unit was directly sent to the gas turbine. Therefore, the PSA units were bypassed. A separate sensitivity analysis is performed to study the effects of steam to carbon monoxide ratio in the WGS reactor for both hydrogen production and electricity generation scenarios. The steam to CO molar ratios examined ranging from 1.7 to 2.3.

5.3.5 Membrane Based Coal to Hydrogen Processes
Since the membrane enhanced the WGS reaction by removing the reaction product, the membrane enhanced WGS reaction could be operated at a lower steam to carbon monoxide ratio and a higher temperature. In the present study, the membrane enhanced WGS reactor was operated at 400 °C with a steam to carbon monoxide molar ratio of 1.6:1. The operating pressure of the reaction side was 3.7 MPa. The product side was typically operated at 1~2 MPa. The typical molar flow rate ratio between the sweep gas and the feed gas, including steam and syngas was 0.4:1. It is noted that the driving force for mass transfer through the membrane was the partial pressure difference of the permeable gas between the reaction side and product side.

In the H₂-selective membrane enhanced process, 95% of the carbon monoxide was shifted to hydrogen with 90% of the hydrogen recovered at the product side. At a sweep to feed gas flow rate ratio of 0.4 and product side operating pressure of 2 MPa, various hydrogen production rates were simulated and analyzed. Sensitivity analyses as shown in Table 5.3 were also performed to evaluate the effect of sweep and to feed gas flow rate ratios (0.3, 0.4 and 0.5) and product side operating pressures (1.8, 2 and 2.2 MPa) for both hydrogen production and power generation cases.

The operating conditions of the CO₂ selective membrane enhanced WGS reactor were similar to those of the H₂ selective membrane WGS reactor. Since CO₂ is the permeable substance, steam needs to be used as the sweeping gas. The typical operating pressure at the product side is 1.2 MPa, which is lower than the H₂ membrane case. The
CO conversion is 95% at the reaction side with CO$_2$ recovery ratio of 90% at the product side. To eliminate the impurities in raw hydrogen product from the reaction side, PSA is used for H$_2$ purification. As illustrated in Table 5.4, sensitivity analyses similar to the H$_2$ membrane case are performed.

5.3.6 Syngas Chemical Looping Process

The SCL process coproduces hydrogen and electricity with in-situ CO$_2$ separation. To evaluate the performance of the SCL process, the results from bench scale test are used. The results indicate ~50% iron oxide conversion with near complete syngas conversion at 900 °C.$^{55}$ The steam to hydrogen conversion was found to exceed 60% (60% is used in the analysis). The air in the combustor is 10% above the stoichiometric amount. The oxygen carrier contains 70% Fe$_2$O$_3$ by weight balanced with inert support. The corresponding solids circulation rate in the commercial plant is 1,551 tonnes/hour. In the current simulation, the reducer is operated at 900 °C and 3.1 MPa. The oxidizer operates at 790 °C and 3.1 MPa. The combustor is operated at same pressure with operating temperature of 1050 °C. All three reactors are operated at near adiabatic conditions.

When hydrogen is the only product, 249.4 tonnes/hour of medium pressure steam is injected to the oxidizer at about 300 °C. The flow rate of the compressed air to the oxidizer is 173.1 tonnes/hour. Three hot gas streams, i.e. concentrated H$_2$O/CO$_2$ stream from the reducer, H$_2$O/H$_2$ stream from the oxidizer, and the exhaust gas stream from the
combustor, are produced from the SCL reactors. Heat is extracted from both the reducer and oxidizer product gas streams for steam generation. Meanwhile, the steam in the product gas streams condenses out, resulting in high purity CO₂ and H₂ streams. 90% of the CO₂ rich stream from the reducer is sequestered after condensation. The exhaust gas from the combustor enters the HRSG section where it is cooled to 500 °C. It is then filtered and expanded to ambient pressure.

When electricity is produced from the process, a portion or all of the hydrogen product is used for power generation via combustion. To enhance the power generation, 10% of the clean syngas is directly sent to the gas turbine without entering the SCL reactor system. The exhaust gas from the combustor is also sent to the gas turbine after particulate removal. Sensitivity analyzes are carried out to evaluate the effects of iron oxide conversion in the reducer and steam conversion in the oxidizer.

5.3.7 Economic Analysis

Economic analyses are performed using assumptions consistent with the USDOE baseline studies. 2007 dollars are used. The cost of coal is assumed to be $45.32/tonne delivered. The cost of the baseline coal gasification plant is scaled down from the standard gasification plant in the baseline studies using an exponential factor of 0.85. The labor cost is also scaled down using the same factor. The variable costs such as those for catalysts, water, solvents, etc are scaled down linearly. The costs of the membrane and SCL based gasification processes are estimated by adding the cost of common
equipments such as gasifier, ASU, HGCU, etc and specialty equipments such as the membrane enhanced WGS reactor or the SCL reactors. The size and cost of the membrane is estimated based on cost performance target set forth by USDOE whereas the cost of the SCL reactor is based on reactor size estimation coupled with published cost of a biomass gasifier operated at conditions comparable to the SCL reactors.\(^{124}\) The results are consistent with the cost estimation by Noblis systems.\(^{114}\) In order to account for the technological uncertainties of the novel processes, an additional process contingency of 10% is applied to both the membrane and SCL based processes.

Both the electricity generation case and the hydrogen production case are analyzed. When electricity is the only product, levelized cost of electricity (LCOE) is estimated using the methodology suggested by USDOE baseline studies.\(^{104}\) A cost of 0.4 cents/kWh is added to LCOE to account for the cost of transportation, sequestration, and monitoring of CO\(_2\). With the absence of standard analysis method for coproduction cases, an equivalent LCOE is estimated by converting hydrogen to electricity equivalent by multiply the hydrogen production rate (in MW\(_{th}\), HHV basis) with a factor of 0.6. Such a factor corresponds to the energy conversion efficiency of an advanced combined cycle system for gaseous fuel combustion. This is followed by calculation of equivalent LCOE. Since the USDOE cost and performance target rather than the actual performances is used to estimate the cost of membrane systems, one should expect notable degree of uncertainty associated with membrane systems. In addition, since the size of the SCL system is estimated based on testing results obtained from bench and sub-pilot scale
reactor systems, a moderate degree of uncertainty can also exist for the estimated SCL reactor cost. To account for such uncertainties, sensitivity analyses are performed on costs of the membrane reactors and the SCL system for the electricity generation case. The range of the sensitivity analysis is ±50% of the standard estimated cost of the novel system.

5.4 Results and Discussion

Based on the parameters and process configurations described in the previous section, Aspen simulations and economic analyses are conducted. The syngas composition at the outlet of the gasifier, which is used in all four processes, is given in Table 5.5.

The key techno-economic analysis results for all four processes operated under standard conditions are summarized in Table 5.6. From the process efficiency standpoint, the SCL process and the H₂ selective membrane enhanced WGS process have the highest thermal efficiency for hydrogen production and electricity generation. Although lower than the two aforementioned processes, the efficiencies of the CO₂ selective membrane enhanced WGS process are around 2% higher than the baseline process for both hydrogen and power generation. The baseline gasification process, although less efficient than the three novel processes, performs better than existing gasification plants due to the incorporation of HGCU. Economic performances of the four gasification processes are discussed in Section 5.4.3.
5.4.1 Sensitivity Analyses of hydrogen production capacity

Figure 5.5 illustrates the effect of product distributions on energy conversion efficiencies of the four gasification processes. As can be seen from Figure 5.5, all the four processes show a similar overall trend, i.e. higher H₂ capacity corresponds to higher energy conversion efficiency. Since the hydrogen production capacity is directly proportional to the hydrogen production efficiency, the hydrogen production efficiency (HHV to hydrogen produced/HHV of coal feedstock) curve shows a linear trend. In contrast, the electricity generation efficiency (HHV of electricity generated/HHV of coal feedstock) does not have a linear relationship with respect to the hydrogen production efficiency. A sharp increase in electricity generation efficiency from 60% hydrogen production capacity to 40% hydrogen production capacity was observed due to the addition of the gas turbine which is more efficient but more costly. It is noted that the power generation efficiency of the baseline process is roughly 0.8% more efficient than a comparable case in the DOE baseline studies. The improvement lies in the utilization of the HGCU as opposed to a solvent based pollutant removal system.

When operated at 100% H₂ capacity, baseline process can achieve at most 60.2% efficiency (HHV). When membrane is used to enhance hydrogen product, the efficiency can be improved to 64.8% for H₂ selective membrane and 61.8% for CO₂ selective membrane. The efficiency of the SCL process is estimated to be 65.7% (include 2.5% net electricity). As shown in the next section, the efficiency can be even higher when the iron
oxide conversion in the reducer is higher than 50%. When hydrogen and electricity are co-produced, taking 40% hydrogen capacity as the example, the baseline process yields an overall efficiency of 45.1% (21% in electricity output and 24.1% hydrogen output). The efficiency is 47.8% (21.9% in electricity and 25.9% in hydrogen) for the H₂ selective membrane enhanced WGS process, 44.9% (20.2% in electricity and 24.7% in hydrogen) for the CO₂ selective membrane enhanced WGS process, and 48.1% (22.8% in electricity and 25.3% in hydrogen) for the SCL process.

When the only product from the process is electric power (0% H₂ capacity), baseline process is 32.8% (HHV) efficient. To compare, the H₂ selective membrane enhanced WGS process is 36.7% efficient, the CO₂ selective membrane enhanced WGS process is 34.4% efficient, and the efficiency for the SCL process is 34.7%. The high efficiency of the H₂ selective membrane process results from the reduction in steam consumption through the utilization of nitrogen, as opposed to steam, as the sweeping gas for power generation. Such a strategy, however, does not apply to the CO₂ membrane process. The SCL process can yield higher electricity generation efficiency provided that the particulates in the combustor exhaust gas can be reduced to a level acceptable to gas turbine or expanders at high temperature (~ 1,000°C). Under such a configuration, the SCL process can be 36.6% efficient for power generation, which is similar to the H₂ membrane process.

5.4.2 Sensitivity Analyses of process operating parameters
a. Baseline Process

The steam to carbon monoxide ratio is an important operating parameter for the WGS step. A higher steam to carbon monoxide ratio can result in a higher reaction rate and carbon monoxide conversion. High steam consumption, however, can negatively affect the process efficiency. Figure 5.6 illustrates the performances of the baseline process at different steam to carbon monoxide ratios. When hydrogen is produced at 100% capacity, the process efficiency is reduced from 61.0% to 59.5% when the ratio is increased from 1.7 to 2.3. When the process is configured to only produce power, the process efficiency is reduced from 33.0% to 32.7% when the ratio is increased from 1.7 to 2.3. To generalize, a low steam to carbon monoxide ratio is preferred in the baseline process from energy conversion efficiency standpoint.

b. Membrane Based Processes

The performance of the membrane is of key performance to the overall process performance. In the present study, the selectivity of the membrane is assumed to be 100%. Results from sensitivity analyses of product side operating pressure and sweep to feed flow rate ratio are shown in Figure 5.7. As can be seen from Figures 5.7.a and 5.7.c, a higher product side operating pressure leads to a higher efficiency for the both membrane based processes by reducing the work required for product compression. However, a high operating pressure at the product side decreases the flux of the permeable material and hence leads to a larger and more costly membrane reactor. Figures 5.7.b and 5.7.d illustrate the effects of sweep to feed ratio in the membrane based
processes. When steam is used as the sweeping gas, a high sweep to feed ratio leads to higher steam consumption and hence a lower process efficiency. In contrast, when nitrogen is used as the sweeping gas, as illustrated in the power production scenario for the H₂ selective membrane based process, a higher sweep to feed ratio slightly increases the power generation efficiency by providing higher flux to the gas turbine system.

c. SCL Process

Higher iron oxide conversion in the reducer leads to lower solids circulation rate and more effective conversion of fuel to hydrogen. The effect of the iron oxide conversion on the overall process efficiency is illustrated in Figure 5.8.a. When the hydrogen capacity is 100%, increase in iron oxide conversion from 40% to 60% leads to a process efficiency increase from 62.7% (4.1% in electricity and 58.6% in hydrogen) to 67.6% (1.5% in electricity and 66.1% in hydrogen). When electricity is the only product, the same increase in iron oxide conversion leads to a process efficiency increase from 34.0% to 34.9%. A higher steam conversion in the oxidizer reduces the steam usage. Therefore, a higher steam conversion leads to higher process efficiency. As illustrated in Figure 5.8.b, when the steam conversion is increased from 50% to 70%, the efficiency of the SCL process at 100% hydrogen capacity is increased by 0.6%. A 1% increase in electricity generation efficiency is projected when the SCL process is configured for power generation.

5.4.3 Process Economics
Following the method described in Section 5.3.7, the economic performances of all four processes are analyzed for: Case I. hydrogen production (100% hydrogen capacity); Case II. Electricity generation (0% hydrogen capacity). The resultant LOCEs are given in Figure 5.9. Table 5.7 further accounts for the uncertainties associated with the cost of the novel systems and their effects on LCOE. As can be seen from Figure 5.9, the SCL process is the most favorable process for hydrogen generation. The equivalent LCOE for the SCL process is nearly 11% lower than that for the baseline gasification process. The equivalent LCOE for the SCL process is 5% lower even when compared with the hydrogen membrane enhanced WGS process. The CO₂ membrane process is the least cost effective among the three novel technologies. Nevertheless, the equivalent LCOE for the CO₂ membrane enhanced WGS process is 2% lower than the baseline gasification process. In terms of power generation, the hydrogen membrane enhanced WGS process is likely to be the more favorable option. The LCOE for the hydrogen membrane enhanced WGS is 10% lower than the baseline IGCC process. The cost reductions for the CO₂ membrane enhanced WGS process and the SCL process are 8.5% and 7.2% respectively. Even when the uncertainties associated with the cost and performances of the novel systems are taken into account, the SCL process can still produce electricity at least 6.5% cheaper than the baseline process or 14.2% cheaper than the conventional IGCC process without HGCU. For the H₂ membrane and CO₂ membrane enhanced WGS processes, the minimum LOCE reductions are 7.9% and 6.1% respectively for electricity generation. It is noted that the choice of the ranges for the sensitivity analyses is somewhat arbitrary. The analysis, however, does show that the
novel SCL process and H₂-Membrane enhanced WGS process possess considerable margin of safety to be more cost competitive than the baseline gasification process. Throughout the analysis, the durability of the H₂ membrane is assumed to be 5 years, which is consistent with DOE’s H₂ membrane cost performance target for 2015. Under such an assumption, the H₂ membrane enhanced WGS system is the more favorable choice for power generation; however, the cost and performance uncertainty of this novel process could be high. The SCL process is the more cost effective choice for hydrogen production and could also be an ideal choice for electricity generation. The CO₂ membrane enhanced WGS process, although projected to perform better than baseline gasification, is the least favored among the three novel processes. The reasons, as discussed earlier, include the need for an additional step to purify H₂ and the high steam consumption in the purging step. In addition, the current study assumes perfect membrane with 100% selectivity. Since the actual selectivity of CO₂-selective membrane is often much lower, the performance of the CO₂-selective membrane system can be further penalized by the potential requirement for additional CO₂ purification steps. Economic analysis also indicates that process efficiency and cost and durability of the novel system are the key factors that affect the overall process economics.

As discussed in the previous section, the chemical looping gasification process can also directly handle solid fuels such as coal and biomass. The fuel direct chemical looping process could further improve the efficiency and reduce the cost by removing the capital intensive gasifier and air separation unit. For example, biomass direct chemical
looping process could produce hydrogen at an efficiency of 70%,\textsuperscript{125} while the coal direct chemical looping process efficiency could reach as high as 80%\textsuperscript{25} The advantage of the chemical looping gasification process is its advanced energy management and integrated carbon dioxide separation feature.

5.5 Other Chemical Looping Processes for Hydrogen Production

Mode 1 looping system can be also adopted for hydrogen production. Two chemical looping reforming (CLR) schemes have been proposed for natural gas conversion to hydrogen. Ryden and Lyngfelt integrated the CLC system with the steam methane reforming (SMR) system, as shown in Figure 5.10\textsuperscript{126} In this process, CLC system provides heat to the SMR system via a shell and tube reactor design that integrates the reducer and reformer together. The integrated reducer/reformer reactor is composed of a low-velocity bubbling fluidized bed with reformer tubes that are placed inside the reactor. The tubes are filled with reforming catalysts that convert steam and methane into syngas. The syngas from the reformer tubes is then shifted to a hydrogen rich stream in a water gas shift reactor before it is purified in the pressure swing adsorption (PSA) unit downstream. The tail gas from the PSA is used as the fuel for the reducer. The methane reforming reaction scheme in the CLC-SMR process is practically identical to the traditional steam methane reforming (SMR) process with the exception of the heat integration scheme for the reformer. In the traditional SMR process, the heat required for steam methane reforming is provided by combustion of fuel exterior to the reformer tubes. In contrast, the CLC-SMR process uses high temperature oxygen carrier particles as a heat transfer medium. The advantages of the CLC-SMR scheme include its
in-situ CO₂ capture and tail gas utilization. Theoretical analysis indicates that the CLC-SMR process has the potential to achieve a higher H₂ yield than the conventional SMR process. Therefore, it could offer a promising alternative for a reforming operation. However, a number of challenges including the heat requirements for the reducer/reformer and potential erosion of the reformer tubes need to be addressed before the process can be considered viable. In addition, the CLC-SMR process still requires the investment of a water gas shift reactor to enrich hydrogen and a PSA unit to remove CO₂.

The autothermal chemical looping reforming (a-CLR) process is another approach for chemical looping reforming of methane. As shown in Figure 5.11, the a-CLR system is similar to a conventional CLC system, which consists of the reducer and the combustor. The difference between a-CLR and CLC process lies in the extent of oxidation in the reducer. In the a-CLR reducer, methane is not fully oxidized to CO₂ and H₂O. Instead, the oxygen carrier particles only provide oxygen for partial oxidation of methane to CO and H₂. Nickel-based oxygen carrier particles are usually used in the a-CLR process because of its high selectivity towards syngas. The syngas from the reducer is first mixed with steam and then routed to a water-gas shift reactor for hydrogen production. The resulting gas contains a significant amount of CO₂, and thus, requires further treatments such as acid gas removal and pressure swing adsorption. Compared with the traditional SMR process, the heat supply from external combustion is avoided in the a-CLR process. The looping particles carry both oxygen and heat to the reducer for natural gas reforming. Process analysis indicates that the a-CLR process could result in
higher hydrogen yield as compared to the natural gas reforming process. However, the a-CLR system does not take advantage of its inherent CO₂ separation capability, and it still requires conventional technologies for hydrogen purification and CO₂ capture.

RTI is also developing a dual fluidized bed chemical looping gasification process for biomass conversion to hydrogen. The schematic flow diagram is shown in Figure 5.12. The key difference between RTI’s process and the Biomass Direct Chemical Looping (BDCL) process is that in RTI's process, the oxygen carrier transitions between Fe₃O₄ and FeO at a moderate temperature range (400-600 °C). In the reducer, Fe₃O₄ partially oxidizes biomass with the help of enhancing agents such as CO₂ and steam. The resulting gas contains a significant amount of valuable heat and can also be used for external combustion to provide heat for the reducer operation. The oxygen carrier is reduced from Fe₃O₄ to FeO and then introduced to the oxidizer for hydrogen generation with steam. Since the process operates at moderate temperature conditions, the oxygen carrier life could be extended. However, the oxygen carrier conversion is only about 10% during the redox cycle, which limits the oxygen carrying capacity and increases the solid circulation rate. In addition, the low temperature operation could restrict the process heat integration and lower the overall process efficiency.

5.6 Conclusions

Four baseline and novel coal based hydrogen and electricity co-production processes are analyzed. The studies indicate that the novel processes, especially the SCL
process and the H₂ membrane enhanced WGS process, have the potential to be notably more efficient and cost effective than the conventional and baseline gasification processes under a carbon constrained scenario. For hydrogen production, the SCL process delivers the highest efficiency. This is followed by the H₂ membrane enhanced WGS process and the CO₂ membrane enhanced WGS process. In terms of power generation, the H₂ membrane enhanced WGS process is the most efficient followed by the SCL process and the CO₂ membrane enhanced WGS process. The economic performances of the processes show similar trends. The factors that may affect the energy conversion efficiencies of the membrane based gasification processes include the flow rate ratio between the sweep and feed gas and the product side operating pressure. The cost and durability of the membrane are likely to be the key factors that affect the economic performance of the membrane based gasification processes. The efficiency of the SCL process can be affected by the conversion of the chemical looping particles in the reducer as well as the steam conversion in the oxidizer. The cost uncertainty associated with the SCL reactor is considered to be moderate. Resulting from the improved energy conversion efficiency coupled with the simplified carbon conversion and capture scheme, the SCL process and the H₂ membrane enhanced WGS process can be notably cost advantageous compared to the conventional and baseline gasification processes under a carbon constrained scenario.
Figure 5.1 Schematic diagram of the baseline coal gasification for hydrogen and electricity co-generation using Shell dry-fed gasifier with gas quench option
Figure 5.2 Schematic diagram of (a) H2-selective membrane enhanced process for hydrogen and electricity co-production (b) CO2-selective membrane enhanced process for hydrogen and electricity co-production, using Shell dry-fed gasifier with gas quench option
Figure 5.3 The SCL process for hydrogen and electricity co-production using Shell dry-fed gasifier with gas quench option
Figure 5.4 ASPEN Plus® flow diagram for the baseline gasification process
Figure 5.5 Sensitivity analysis of product distributions for (a) the baseline gasification process; (b) the H2 membrane enhanced WGS process; (c) the CO2 membrane enhanced WGS process; and (d) the SCL process
Figure 5.6 Sensitivity analysis of the WGS steam to carbon monoxide molar ratio in the baseline process
Figure 5.7 Sensitivity analyses of (a) product side operating pressure in the H2 selective membrane enhanced WGS process; (b) sweep to feed gas molar flow rate ratio in the H2-selective membrane enhanced WGS process; (c) product side operating pressure in the CO\textsubscript{2} selective membrane enhanced WGS process; and (d) sweep to feed gas flow rate ratio in the CO\textsubscript{2} selective membrane enhanced WGS process.
Figure 5.8 Sensitivity analysis of (a) iron oxide conversion in the reducer; and (b) steam conversion in the oxidizer for the SCL process
Figure 5.9 Comparisons of LCOE and equivalent LCOE among the four indicated processes.
Figure 5.10 Schematic flow diagram of the Chemical Looping Combustion integrated with the Steam Methane Reforming Process (CLC-SMR).
Figure 5.11 Autothermal chemical looping reforming process
Figure 5.12 RTI chemical looping process
Table 5.1 Physical and chemical properties of Illinois #6 coal

<table>
<thead>
<tr>
<th></th>
<th>Constituents (wt.%, As-Received)</th>
<th>Constituents (wt.%, dry)</th>
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<tr>
<td><strong>Proximate Analysis</strong></td>
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<tr>
<td>Moisture</td>
<td>11.12</td>
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<td>Volatiles</td>
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<tr>
<td>Ash</td>
<td>9.7</td>
<td>10.91</td>
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<tr>
<td>HHV (MJ/kg)</td>
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<td>30.53107</td>
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<tr>
<td><strong>Ultimate Analysis</strong></td>
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<td></td>
</tr>
<tr>
<td>Moisture</td>
<td>11.12</td>
<td></td>
</tr>
<tr>
<td>Ash</td>
<td>9.7</td>
<td>10.91</td>
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<tr>
<td>Carbon</td>
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<td>71.72</td>
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<tr>
<td>Hydrogen</td>
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<td>5.06</td>
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<tr>
<td>Nitrogen</td>
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<td>1.41</td>
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<td>Chlorine</td>
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<td>0.33</td>
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<td>Sulfur</td>
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<td>2.82</td>
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<tr>
<td>Oxygen</td>
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<td>7.75</td>
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Table 5.2 Aspen models for the key units

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<th>Unit Operation</th>
<th>Aspen Plus® Model</th>
<th>Comments/Specifications</th>
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<tr>
<td>Air Separation Unit</td>
<td>SEP</td>
<td>Energy consumption of the ASU is based on specifications of commercial ASU/compressors load</td>
</tr>
<tr>
<td>Coal Decomposition</td>
<td>RYIELD</td>
<td>Virtually decompose coal to various components (prerequisite step for gasification modeling)</td>
</tr>
<tr>
<td>Coal Gasification</td>
<td>RGIBBS</td>
<td>Thermodynamic modeling of gasification</td>
</tr>
<tr>
<td>HGCU</td>
<td>SEP</td>
<td>HGCU Performance is based on literature report</td>
</tr>
<tr>
<td>WGS</td>
<td>RSTOIC or RGIBBS</td>
<td>Simulation of conversion of WGS reaction is based on either WGS design specifications or thermodynamics</td>
</tr>
<tr>
<td>SELEXOL</td>
<td>SEP or RADFRAC</td>
<td>Simulation of acid gas removal is based on design specifications</td>
</tr>
<tr>
<td>Burner</td>
<td>RGIBBS or RSTOIC</td>
<td>Modeling of H$_2$/syngas combustion step</td>
</tr>
<tr>
<td>HRSG</td>
<td>MHEATX</td>
<td>Modeling of heat exchanging among multiple streams</td>
</tr>
<tr>
<td>Gas Compressors</td>
<td>COMPR or MCOMPR</td>
<td>Evaluation of power consumption for gas compression</td>
</tr>
<tr>
<td>Heater and Cooler</td>
<td>HEATER</td>
<td>Simulation of heat exchange for syngas cooling and heating</td>
</tr>
<tr>
<td>Turbine</td>
<td>COMPR</td>
<td>Calculation of power generated from gas turbine and steam turbine</td>
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Table 5.3 Sensitivity analysis of parameters for the H₂ selective membrane enhanced WGS Process

<table>
<thead>
<tr>
<th></th>
<th>Sweep to Feed Ratio (kmol/hr)</th>
<th>Gas Flow Rate (kmol/hr)</th>
<th>H₂ Flow Rate (kmol/hr)</th>
<th>x_H₂</th>
<th>Pressure (MPa)</th>
<th>P_H₂ (MPa)</th>
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<tr>
<td><strong>Reaction Side</strong></td>
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<tr>
<td>0.40</td>
<td>22102.61</td>
<td>6798.50</td>
<td>0.31</td>
<td>3.70</td>
<td>1.14</td>
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<td>0.40</td>
<td>17707.79</td>
<td>8866.75</td>
<td>0.50</td>
<td>2.00</td>
<td>1.00*</td>
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<tr>
<td>0.40</td>
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<td>8866.75</td>
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<td>8866.75</td>
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<td>0.50</td>
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<td>0.45</td>
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<tr>
<td><strong>Product Side</strong></td>
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<td></td>
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</table>

*Standard parameters for other analyses.
Table 5.4 Sensitivity analysis parameters for the CO₂ selective membrane enhanced WGS Process

<table>
<thead>
<tr>
<th></th>
<th>Sweep to Feed Ratio</th>
<th>Overall Flowrate (kmol/hr)</th>
<th>CO₂ Flowrate (kmol/hr)</th>
<th>X_{CO₂}</th>
<th>Overall Pressure (MPa)</th>
<th>P_{CO₂}(MPa)</th>
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<tbody>
<tr>
<td><strong>Reaction Side</strong></td>
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<td></td>
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<tr>
<td></td>
<td>22102.61</td>
<td>3610.98</td>
<td>0.16</td>
<td>3.70</td>
<td>0.60</td>
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<tr>
<td><strong>Product Side</strong></td>
<td>0.40</td>
<td>15148.64</td>
<td>6307.59</td>
<td>0.42</td>
<td>1.40</td>
<td>0.58</td>
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<td>15148.64</td>
<td>6307.59</td>
<td>0.42</td>
<td>1.20</td>
<td>0.50*</td>
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<td>15148.64</td>
<td>6307.59</td>
<td>0.42</td>
<td>1.00</td>
<td>0.42</td>
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<td>12938.38</td>
<td>6307.59</td>
<td>0.49</td>
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<td></td>
<td>0.50</td>
<td>17358.90</td>
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<td>0.44</td>
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* Standard parameters for other analyses.
Table 5.5 The Shell gasifier syngas composition

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<tr>
<th>Syngas Composition</th>
<th>Mole%</th>
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<tbody>
<tr>
<td>H$_2$O</td>
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</tr>
<tr>
<td>N$_2$</td>
<td>6.71</td>
</tr>
<tr>
<td>H$_2$</td>
<td>29.10</td>
</tr>
<tr>
<td>HCl</td>
<td>0.0939</td>
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<tr>
<td>CO</td>
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</tr>
<tr>
<td>CO$_2$</td>
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</tr>
<tr>
<td>NH$_3$</td>
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</tr>
<tr>
<td>COS</td>
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</tr>
<tr>
<td>H$_2$S</td>
<td>0.8324</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>0.0405</td>
</tr>
<tr>
<td>Total Flow (kmol/hr)</td>
<td>11704.60</td>
</tr>
<tr>
<td>Total Flow (kg/hr)</td>
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</tr>
<tr>
<td>Total Flow (m$^3$/hr)</td>
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</tr>
<tr>
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<td>Pressure (MPa)</td>
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Table 5.6 Comparison of the process analysis results

<table>
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<th>H₂ Membrane</th>
<th>CO₂ Membrane</th>
<th>SCL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal Feed (tonnes/hour)</td>
<td>132.9</td>
<td>132.9</td>
<td>132.9</td>
<td>132.9</td>
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<tr>
<td>Carbon Capture (%)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Case I. Net Electricity (MW)</td>
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<td>0.1</td>
<td>0.1</td>
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<tr>
<td>Case I. Hydrogen Product (tonne/hr)</td>
<td>15.28</td>
<td>16.44</td>
<td>15.68</td>
<td>16.02</td>
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<td>Case I. Efficiency (%)</td>
<td>60.2</td>
<td>64.8</td>
<td>61.8</td>
<td>65.7</td>
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<tr>
<td>Case I. Total Plant Cost ($Million)</td>
<td>822.3</td>
<td>819.4</td>
<td>769.5</td>
<td>801.6</td>
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<tr>
<td>Case I. Equivalent LCOE (%)</td>
<td>92.0</td>
<td>86.5</td>
<td>90.0</td>
<td>82.3</td>
</tr>
<tr>
<td>Case II. Net Electricity (MW)</td>
<td>328.0</td>
<td>364.8</td>
<td>344.4</td>
<td>346.8</td>
</tr>
<tr>
<td>Case II. Efficiency (%)</td>
<td>32.8</td>
<td>36.5</td>
<td>34.4</td>
<td>34.7</td>
</tr>
<tr>
<td>Case II. Total Plant Cost ($Million)</td>
<td>920.2</td>
<td>898.6</td>
<td>861.8</td>
<td>881.7</td>
</tr>
<tr>
<td>Case II. LCOE (%)</td>
<td>110.0</td>
<td>98.9</td>
<td>102.1</td>
<td>100.7</td>
</tr>
</tbody>
</table>

Case I refers to a co-production case in which a significant amount of hydrogen is produced; Case II refers to an electricity only case.
Table 5.7 Sensitivity analyses of the cost uncertainties for the novel processes (100% power generation for all cases)

<table>
<thead>
<tr>
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<th>H₂ Membrane</th>
<th>CO₂ Membrane</th>
<th>SCL</th>
</tr>
</thead>
<tbody>
<tr>
<td>LCOE Base Case ($/MWh)</td>
<td>98.9</td>
<td>102.1</td>
<td>100.7</td>
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<tr>
<td>LCOE Low Case ($/MWh)¹</td>
<td>96.4</td>
<td>100.2</td>
<td>98.7</td>
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<tr>
<td>LCOE High Case ($/MWh)²</td>
<td>101.3</td>
<td>103.3</td>
<td>102.9</td>
</tr>
<tr>
<td>Baseline IGCC LCOE ($/MWh)</td>
<td>110.0</td>
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<td></td>
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<tr>
<td>Conventional IGCC LCOE ($/MWh)³</td>
<td>119.9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

¹Low case refers to the LCOE when the cost of the novel system is 50% of the standard cost estimate; high case refers to the LCOE when the cost of the novel system is 150% of the standard cost estimate.

³Conventional IGCC process uses a solvent based syngas cleanup system as opposed to a hot gas clean up system.
Chapter 6
Chemical Looping Process for Liquid Fuel Synthesis

6.1 Introduction

In commercial coal to liquids (CTL) processes, liquid fuels are synthesized from coal derived syngas through the well-known Fischer-Tropsch (F-T) reaction:

\[ \text{CO} + 2\text{H}_2 \rightarrow -(\text{CH}_2)_n + \text{H}_2\text{O} \]

Since a CO to H\(_2\) molar ratio of around 1:2 is preferred in the above reaction, significant amount of CO in the syngas often needs to be converted to H\(_2\) through the water gas shift (WGS) reaction prior to F-T synthesis:

\[ \text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 \]

Current CTL processes emit the CO\(_2\) produced from gasification, WGS, and combustion reactions to the atmosphere; therefore, these processes are carbon intensive. The life cycle analysis (LCA) indicates that liquid fuels derived from coal emit nearly 2.5 times as much CO\(_2\) compared to liquid fuels produced from crude oil.\(^{129}\) Replacing a portion or all of the coal feedstock with biomass can reduce the life cycle CO\(_2\) emission;
however, the low energy density nature of biomass reduces the efficiency of the process. In addition, the F-T reaction is carried out at relatively low temperatures (typically ~250 °C) and is highly exothermic.\textsuperscript{130} This leads to inevitable exergy loss and hence relatively low process efficiency. Agrawal et al. proposed a H\textsubscript{2}CAR process to improve the efficiency and carbon utilization of the conventional CTL processes.\textsuperscript{131} In H\textsubscript{2}CAR process, H\textsubscript{2} produced from renewable energy sources is used to convert the CO\textsubscript{2} into CO through the reverse WGS reaction. This is followed by F-T reaction for liquid fuel synthesis. The challenge to such a process configuration lies in the absence of effective CO\textsubscript{2} separation technique as well as the high cost for H\textsubscript{2} production from renewable energy. In addition, the exergy loss associated with the exothermic F-T reaction remains to be an issue. An alternative approach includes the CO\textsubscript{2} hydrogenation reaction which combines reverse WGS reaction and F-T reaction in one step:

\[
\text{CO}_2 + 3\text{H}_2 \rightarrow -(\text{CH}_2)- + 2\text{H}_2\text{O}
\]

CO\textsubscript{2} hydrogenation is attractive since it provides an option for effective CO\textsubscript{2} utilization and H\textsubscript{2} storage. Moreover, it reduces the exothermicity in liquid fuel synthesis, rendering a potentially more efficient energy conversion scheme. Previous studies indicate that iron based F-T catalyst exhibits good activity in catalyzing CO\textsubscript{2} hydrogenation reaction.\textsuperscript{132,133} However, the absence of efficient CO\textsubscript{2} and H\textsubscript{2} separation and/or production techniques poses a key challenge towards the utilization of CO\textsubscript{2} hydrogenation.
In an article published in *Science*, Hildebrandt et al. proposed a novel coal to liquids (CTL) scheme in which coal is gasified into a mixture of CO₂ and H₂ instead of a mixture of CO and H₂ prior to CO₂ hydrogenation.¹³⁴ Exergy analysis performed in the article indicates that the “CO₂ gasification” scheme can significantly reduce the “net work input” required by the CTL process. Direct gasification of coal into CO₂ and H₂, however, is limited by the equilibriums of gasification and WGS reactions. A novel chemical looping gasification (CLG) process, which is currently being developed, adopts a unique approach for coal/biomass conversion. Through the assistance of an iron based composite oxygen carrier particle, the CLG process indirectly converts coal and/or biomass into separate streams of sequestrable CO₂ and H₂.²⁵ Exergy and process analyses and experimental results indicate that the CLG Process has the potential to be both efficient and cost-effective.⁵⁵,¹²⁵ Since CO₂ and H₂ are readily produced from the process, the integration of CLG with CO₂ hydrogenation has the potential to be an exergetically efficient and environmentally friendly process for liquid fuel synthesis from biomass or coal. A simplified schematic of the novel CLG – CO₂ hydrogenation process is shown in Figure 6.1. In the following sections, key methods and results from simple exergy analysis, comprehensive process simulation, and life cycle analysis of the CLG – CO₂ Hydrogenation process are presented.

### 6.2 Exergy Analysis

A simplified mass and energy flow diagram for a generic (indirect) coal/biomass to liquids (C/BTL) process is given in Figure 6.2. As can be seen, the process can be
broken down into two blocks, i.e. the liquid fuel synthesis block and the solid fuel oxidation block. The liquid fuel synthesis block converts solid fuel (biomass/coal) and water into liquid fuels and CO₂ whereas the solid fuel oxidation block oxidizes solid fuel with air or oxygen while producing CO₂. The energy (heat/work) released from fuel oxidation is used to facilitate the liquid fuel production. Solid fuel oxidation blocks are similar in the various process configurations; the key difference among the processes lies in the liquid fuel generation block.

This study investigates three process schemes for liquid fuel synthesis from biomass and coal, i.e. the conventional C/BTL process through gasification – F-T (Scheme I), the CO₂ gasification process proposed by Hildebrandt et al. (Scheme II),¹³⁴ and the CLG process proposed in the current study (Scheme III). The key reactions in the liquid fuel synthesis block for the three schemes are generalized in Table 6.1. To compare these processes, simple exergy analysis similar to that adopted by Hildebrandt et al. is performed in this section to examine the exergetic performances of the three process schemes.¹³⁴ Comprehensive ASPEN Plus® process simulations, which quantify the practical performances of the processes, are presented in the next section.

The exergy analysis focuses on the liquid fuel synthesis block of the three process schemes using the following assumptions:

1. The feedstock, either biomass or coal, is considered as pure carbon;
2. The amount of carbon and steam used strictly follows the reaction stoichiometry given in Figure 6.2. The energy required to facilitate the conversion is provided by external work input;

3. The conversions for all chemical reactions are 100%, i.e., the reactions are not limited by the thermodynamic equilibriums;

4. Heat can be 100% recovered and can be converted to work reversibly using Carnot engines. Conversely, work can be used to generate heat via reversible heat pumps;

5. There is no pressure drop in the flow systems;

6. All reactions are carried out at 2.5 MPa;

7. Conventional and CO$_2$ gasification are carried out isothermally at 1500 K, The CDCL reactions are carried out at 1123 K, and the F-T reactions are carried out at 500 K;

8. All the reactants are preheated prior to gasification. Carbon is preheated to 850 K. All other reactants are preheated to the gasification temperature;

9. Physical properties of all the substances are obtained from physical property databanks in ASPEN Plus$^\text{®}$.

### 6.2.1 Conventional Approach

According to the paper presented by Hildebrandt, the net work input of coal-to-liquids schemes are determined using the heat requirement in the gasification step and the heat released in the F-T step. Thus, the work or exergy input for the gasification step is determined by:
\[ W_{in} = \Delta H_1 \times (1 - T_0 / T_1) \]  

(1)

Here, \( W_{in} \) is the work input for the gasification step; \( \Delta H_1 \) is the heat of the gasification reaction; \( T_0 \) is the ambient temperature; and \( T_1 \) is the gasification temperature. The ambient temperature and the gasification temperature are 298 K and 1500 K, respectively for both conventional and CO\(_2\) gasification schemes. The work output in the F-T step is calculated in a similar manner as:

\[ W_{out} = \Delta H_2 \times (1 - T_0 / T_2) \]  

(2)

Here, \( W_{out} \) is the work output in the F-T step; \( \Delta H_2 \) is the heat of the F-T reaction; and \( T_2 \) is the temperature of the F-T reaction, which is 500K for all the CTL schemes. The net work input is:

\[ W_{net} = W_{in} + W_{out} \]  

(3)

The aforementioned method identifies the process steps with the most significant work input and output; however, the work associated with heating and cooling of the various reactants and products is not taken into account. As will be illustrated in the following sections, the work/exergy for the heating and cooling steps, when it is taken into account, can notably affect the results of the net work input calculation.
6.2.2 CO\textsubscript{2} Gasification Scheme

A more accurate method to calculate the net work input adds up the heat inputs and outputs in all the process steps:

\[ W_{\text{net}} = W_{\text{in}} + W_{\text{out}} + W_{\text{cooling}} + W_{\text{heating}} \]  \hspace{1cm} (4)

Here, \( W_{\text{cooling}} \) is the total work output from all (reversible) cooling steps, and \( W_{\text{heating}} \) is the total work input of all (reversible) heating steps. To illustrate the differences between this approach and the approach adopted by Hildebrandt et al., the CO\textsubscript{2} gasification scheme is analyzed. The conventional gasification scheme and the CLG scheme can be analyzed in a similar manner.

The exergy analysis is carried out on the CO\textsubscript{2} gasification scheme, which is shown in Figure 6.3. In this scheme, coal and steam are irreversibly heated to temperatures indicated in the assumptions. Then, coal and steam are converted into H\textsubscript{2} and CO\textsubscript{2} isothermally at 1500K with external heat supplied. This is followed by reversibly cooling the H\textsubscript{2} and CO\textsubscript{2} to 500K, carrying out F-T reactions isothermally with simultaneous heat removal, and reversibly cooling the F-T products to ambient conditions. The heat and work input/output and exergy loss in each of the aforementioned steps are calculated using both ASPEN Plus® and spread sheet analysis. The results are shown in Figure 6.3. As can be seen, the work input of the gasification step and the work
output of the F-T step are very similar to those reported by Hildebrandt et al. (1239 vs. 1240 for gasification and 418 vs. 420 for F-T). However, when the work input/output in the cooling and heating steps is taken into account, the net work input of the process becomes 739 MW, which is approximately 80 MW lower than the 820 MW reported by Hildebrandt et al. This is due to the fact that the work output in the cooling steps is 82 MW higher than the work input in the heating steps. This work can be recuperated to the gasification step to reduce the net work input of the CTL process. Using the same method, the net work input for the conventional gasification scheme is calculated to be 856 MW as opposed to 1000 MW calculated by Hildebrandt et al.

### 6.2.3 Chemical Looping Gasification Scheme

The CLG scheme presented in the following section is a simplified version of the chemical looping gasification process. In the simplified CLG scheme, the steam-carbon reaction is carried out through the assistance of an iron oxide based reaction medium in two separate reactors, i.e. the reducer and the oxidizer. In the reducer, iron oxide converts carbon into CO₂. Meanwhile, the iron oxide is reduced. The reduced iron oxide then reacts with steam in the oxidizer to produce hydrogen. Meanwhile, the reduced iron oxide is regenerated into its original (oxidized) form. This is followed by recycling the regenerated iron oxide to the reducer to complete the chemical loop. It is assumed that no purging or make up of the iron oxide is necessary. Since the reaction equilibrium limitations are not considered in the current simulation for all CTL schemes, Fe₃O₄ is assumed to be able to convert 100% of the carbon into CO₂ and Fe/FeO is assumed to be
capable of converting 100% of the $\text{H}_2\text{O}$ into hydrogen. In the complete CLG process scheme which is analyzed in Section 2, a third reactor, i.e., a combustor, is used to combust a portion of the reduced particles into $\text{Fe}_2\text{O}_3$. The heat generated in the combustor and the oxidizer is used to compensate for the heat requirements in the reducer. The flow diagrams of the simplified and complete CLG schemes are given in Figure 6.4.

In the current simulation, the CLG reactors operate at 1123K. Such a temperature is proven to be feasible experimentally. All CLG reactors are operated at identical temperatures to ensure that the heat released from the exothermic reactors can be reversibly recuperated to the endothermic reactor. Since the assumptions used for the CLG analysis are identical to those used for conventional and CO$_2$ gasification schemes, the analysis for all three CTL schemes are directly comparable. Figure 6.5 presents analyses on the simplified CLG scheme. It is noted that a portion of the work input for the CLG gasification step is provided in the form of chemical exergy by introducing extra coal to the reducer. This is different from the conventional and CO$_2$ gasification cases where the work input is provided solely in the form of heat.

Although several aforementioned assumptions are idealized and do not represent the actual process conditions, they do provide a simple, preliminary evaluation of the various C/BTL schemes as shown by Hildebrandt et al.$^{134}$ The results of the exergy analysis are illustrated in Figure 6.6. The detailed analysis procedures are given in the
ESM. As can be seen, the CO$_2$ gasification scheme can potentially reduce the work input for conventional C/BTL process by 13.7%. CLG is even more attractive, requiring 27.9% less external work input than the conventional process. The reduced work input for CLG results from: i. effective exergy recuperation through chemical looping gasification reactions; ii. lower gasification temperature; iii. reduced exothermicity for liquid fuel synthesis.

6.3 Process Analysis

The preliminary exergy analysis indicates that both CLG and CO$_2$ gasification schemes have the potential to outperform the conventional process; however, the analysis is conducted using a set of idealized assumptions, which do not take into account the reaction equilibrium limitations (Assumption 3). Such an assumption, however, is unlikely to be accurate especially when CO$_2$ and H$_2$ are the desired gasification products. At typical coal/biomass gasification conditions, the gasification reactions favor the formation of CO and H$_2$ as opposed to CO$_2$ and H$_2$. Therefore, generation of a CO$_2$ and H$_2$ rich stream requires either simultaneous removal of CO$_2$ and/or H$_2$ from the gasifier or introduction of above stoichiometric amount of steam. Simple equilibrium calculations indicate that, at a gasification temperature of 1500 K, a steam to carbon ratio of 500:1 is required in order to achieve a CO$_2$: CO ratio of 100. Although steam/water could be recycled, significant exergy loss will inevitably occur during the cooling and reheating of steam and water. Therefore, CO$_2$ gasification through the addition of excessive steam will be less efficient than the conventional process. One potential approach to improve the
performance of CO$_2$ gasification process is to incorporate CO or H$_2$ membrane to the coal/biomass gasifier. However, ash and sulfur tolerant membranes that can operate at gasification temperatures have not been developed. In absence of an effective gasification scheme to directly convert biomass/coal into CO$_2$ and H$_2$, only conventional gasification process and CLG process are highlighted in this section. It is noted that reaction equilibrium limitations also apply to the conventional and CLG schemes. Their impact, however, is expected to be less significant for these two schemes since the reactions involved are thermodynamically favored under the proposed reaction conditions. In order to accurately quantify the performances of these processes for commercial liquid fuel synthesis, comprehensive process simulation models are developed using ASPEN Plus®. The ASPEN Plus® models use a common set of practical assumptions which take into account actual coal/biomass fuel compositions and practical limitations in reactant conversions and heat integrations. The process flow diagrams for the ASPEN Plus® simulations are given in Figure 6.7.

The key assumptions and modeling parameters are provided as given below:

- Ambient temperature is 25 °C, and barometric pressure is 1 atm;
- the thermal capacity of the systems is equivalent to 100 MW in HHV;
- The physical and chemical properties of switchgrass is listed in Table 6.2;
- Fluidized bed gasifier with water quench configuration is used for conventional and CO$_2$ gasification processes;
Air consists of 21% O\textsubscript{2} and 79% N\textsubscript{2} by volume;

The oxygen carrier particles consist of 55% Fe\textsubscript{2}O\textsubscript{3} and 45% SiC by weight;

The per-pass conversion and selectivity of the F-T or CO\textsubscript{2} hydrogenation reactor is identical to those given in Reference 1;

CO\textsubscript{2} is vented to atmosphere in the conventional and CO\textsubscript{2} gasification processes, while it is compressed to 150 atm for subsequent sequestration in the CLG process;

The gasifier and the reducer has a carbon conversion of 99%;

The pressure level in the steam cycle is 124/ 30/ 2 atm; the HP and IP steam is superheated up to 600 °C; and the stack temperature of flue gas is 120 °C;

All the compressors are designed using four stages, and the outlet temperature of each intercooler is 40 °C;

The mechanical efficiency for expanders and compressors is 1, whereas their isentropic efficiency is 0.8-0.9;

6.3.1 Process Configurations

The conventional indirect liquefaction process is illustrated in Figure 6.7.a. A bubbling fluidized bed gasifier is used to gasify biomass and produce CO rich syngas. The biomass feedstock is first dried to 5% moisture content by warm flue gas. The dried biomass feed rate is 20.2 metric ton/hr (or 19.2 metric ton/hr of 0% moisture dry biomass). Oxygen, steam, and biomass are fed to the gasifier at a ratio of 1: 1: 2 (by weight). The operating pressure of the gasifier is 31 atm, and the operating temperature is
1050 °C. The oxygen (95% O₂ and 5% N₂ by volume) is supplied from an air separation unit (ASU). The ambient air passes through filtration and desiccation, and is compressed to 7 atm via a four-stage air compressor. The cryogenic column divides the air stream into the oxygen stream and the nitrogen stream. The separated oxygen leaves the column and the heat exchanger network at ~30 °C and 1.5 atm, and is then compressed to 32 atm for downstream gasification.

Water quench is used for cooling the raw syngas to a target temperature and raising the steam to CO ratio for subsequent water gas shift (WGS) reaction. About 1.9 ton/hr of low temperature (200 °C, 31 atm) water is introduced to mix with the raw syngas exiting from the gasifier. The quench reduces the syngas temperature to 210 °C while removing the particles and ash. The steam content is raised up to 65% after quenching. After water quench, the syngas is divided into two streams. Part of the syngas flows to the WGS unit, which operates at 210 °C. The other part of the syngas goes to a COS hydrolysis reactor. The effluent gas products are then combined, resulting in syngas stream suitable for F-T synthesis. A two-stage SELEXOL unit is used to capture CO₂ and inorganic sulfur compound. The majority of the clean gas is then preheated and introduced to the F-T reactor. A small portion of the syngas goes to a pressure swing absorption (PSA) unit for pure H₂ production for the fuel upgrade sector.

The F-T synthesis conversion is 80% per pass. The reaction heat is used for low pressure steam generation. 60% of the resulting gas is recycled to enhance liquid fuel
production, while the other part together with the light gas from fuel upgrade sector goes to boiler for combustion and steam generation. The HRSG produces steams at different temperature and pressure levels for hydrogen generation in the oxidizer (240 °C, 32 atm) and power generation (600 °C, 124 atm and 30 atm) in the steam turbines. In the steam turbine power generation cycle, the 124 atm high pressure steam is first expanded to 30 atm in the high pressure (HP) steam turbine and then reheated back to 600 °C before entering the intermediate pressure (IP) and low pressure (LP) steam turbines.

The CO₂ gasification process is similar to the conventional process. In the fluidized bed gasifier, the biomass feeding rate and the oxygen flow rate are the same as that in the conventional process. In order to obtain a CO₂ rich syngas from the biomass gasifier, the operating temperature is lowered to 800 °C. In addition, the steam flowrate is 115 times higher than the steam requirement in the conventional process, which is sufficient to drive the ratio between CO₂ and CO to 69.6. Due to the excess low temperature steam injection, the gasifier is in great heat deficiency. A significant amount of biomass is combusted outside of the gasifier to compensate the heat required for maintaining the gasifier temperature. After heat recovery, the syngas can directly goes to SELEXOL for partial CO₂ and H₂S removal. The CO₂ to H₂ ratio is tuned to 3:1 before F-T synthesis. Other process operating parameters are similar to the conventional process.
In the CLG process, as shown in Figure 6.7.b, the CO₂ and H₂ stream are produced from the reducer and oxidizer, respectively. The reducer operates at 910 °C and 31 atm, whereas the oxidizer operates at 800 °C and 31 atm. The oxygen carrier particle flows at 390 tons/hr to the reducer to fully convert biomass as well as recycled tail gas from fuel synthesis and upgrading block. The iron oxide conversion at the outlet of the moving bed reducer is about 48% under the given conditions. Steam is used in the oxidizer to partially oxidize the reduced iron oxide while generating hydrogen rich stream. The combustor then completely regenerates Fe₂O₃ at a temperature of 1250 °C with a hot air stream. From the CLG reactor system, 3 hot gas streams are produced, i.e. concentrated H₂O/CO₂ stream from the reducer, H₂O/H₂ stream from the oxidizer, and the flue gas stream from the combustor. All the hot gas streams are routed to the HRSG section. The warm flue gas from the HRSG section can be used to dry up the pulverized coal. After condensing out the steam, high purity CO₂ and H₂ streams can be obtained separately. All the sulfur in the biomass reacts with iron oxide to form SO₂, which can be removed with ease using existing technology. The sulfur free CO₂ stream is split into two streams, one stream mixes with hydrogen for CO₂ hydrogenation, while the other stream is compressed to 150 atm for sequestration. The light gas from the fuel synthesis and upgrading section is preheated and recycled to the reducer to enhance fuel production. No CO₂ is emitted from the CLG process.

6.3.2 Life Cycle Analysis
Life cycle analysis is performed using a method similar to that adopted in Reference 1:

Well to Wheel LCA CO₂ Emission = A + B + C + D – G

A – CO₂ emission associated with biomass production and transportation
B – CO₂ emission associated with liquid fuel synthesis
C – CO₂ emission associated with liquid fuel distribution
D – CO₂ emitted from liquid fuel combustion
E – CO₂ captured by biomass form the atmosphere (equivalent to the carbon content in biomass)

Reference 1 only analyzes the LCA CO₂ emission of diesel. The net carbon impact of the naphtha product is calculated by assuming petroleum derived naphtha is displaced by the synthesized naphtha. In this study, both naphtha and diesel are treated as liquid fuels. Therefore, the per barrel LCA CO₂ emission presented in this article represents an average LCA CO₂ emission split between synthesized naphtha and synthesized diesel with a volume ratio of roughly 1 : 2.

Several key assumptions used in the LCA include:
- GHG emission (in terms of CO₂ equivalent) associated with biomass production and transportation is 0.164 ton of CO₂ per dry ton of biomass
- CO₂ emission associated with synthetic diesel and naphtha distribution is identical to that associated with petroleum based diesel distribution in volumetric basis – 4.4 kg CO₂/bbl
- Liquid fuel is completely combusted during vehicle operation;
- Heating value of petroleum based diesel is 128,450 Btu/gal (LHV), heating values of synthetic diesel and naphtha are 123,670 Btu/gal (LHV) and 111,520 Btu/gal (LHV) respectively

The key results are generated in Table 6.3. Biomass (switchgrass) is used as the feedstock in this case. As can be seen from Table 6.3, CLG is nearly 32% more efficient compared to the conventional process. Moreover, the CO₂ produced from the CLG process is readily sequestrable. With CO₂ sequestration, the green liquid fuel produced from the CLG process is carbon negative from life cycle standpoint. Compared to petroleum based diesel fuel which emits more than 500 kg of CO₂ per barrel, combustion of each barrel of CLG green liquid fuel leads to a net CO₂ reduction from the atmosphere by 461.9 kg. Process and life cycle analyses also indicate that, even when coal is used as the feedstock, the liquid fuel produced from the CLG process (with carbon sequestration) emits less CO₂ than petroleum based liquid fuels. In the case when H₂ from renewable energy sources are affordable, H₂ can be added to the CLG scheme to achieve 100%...
carbon utilization. Under such a scenario, all the CO₂ produced form the process is hydrogenated for green liquid fuel production.

6.4 Integration with Fischer-Tropsch Synthesis

Given that conventional oil production is decreasing, liquid fuel synthesis from coal and/or biomass is becoming increasingly important to sustain the transportation sector. The chemical looping strategy becomes a viable method that can be conveniently integrated with liquid fuel synthesis systems to achieve improved energy conversion efficiency. For instance, the hydrogen generated in the chemical looping gasification system can be used in the Fischer-Tropsch (F-T) reactor to enhance the liquid fuel yield of an indirect coal to liquids (CTL) process. National Energy Technology Laboratory (NETL) of USDOE has conducted an independent study for the SCL–CTL process. Figure 6.8 shows the process flow diagram. In this study, the chemical looping system replaces the conventional water gas shift reactor and acid gas removal unit to adjust the CO to H₂ ratio in the feedstock for F-T synthesis. In addition, the light hydrocarbons from the F-T reactor exhaust is recycled to the reducer for CO₂ capture, while its chemical energy is transformed into the hydrogen product from the oxidizer. The analysis report states that “the (syngas) chemical looping systems such as that proposed by OSU have the potential to significantly (~10%) increase the yield of the conventional cobalt based F–T process and allow more efficient heat recovery and much lower (~19%) carbon emissions”.
6.5 Conclusions

A novel green liquid fuel synthesis process which integrates chemical looping gasification with CO₂ hydrogenation is proposed. The performance of the proposed CLG process is evaluated along with the conventional coal/biomass to liquids process and the CO₂ gasification process. A simple exergy analysis reveals that the CLG process is thermodynamically advantageous. Comprehensive process simulation further indicates that the proposed CLG process is 32% more efficient than the conventional process. Moreover, the green liquid fuel produced from the CLG process can be carbon negative. When switchgrass is used as the feedstock, for instance, 461.9 kg of CO₂ is captured from the atmosphere for every gallon of green liquid fuel burnt. Therefore, the proposed CLG scheme has the potential to be an efficient and environmentally friendly process for green liquid fuel production from biomass and/or coal.
Figure 6.1 Simplified schematic diagram of the CLG – CO$_2$ hydrogenation process
Figure 6.2 Simplified mass and energy flow diagram of a generic coal/biomass to liquids process
Figure 6.3 Heat and work input/output of the CO₂ gasification scheme
Figure 6.4 Schematic flow diagram of (A) simplified CLG process; and (B) complete CLG process
Figure 6.5 Heat and work input/output of the CLG scheme
Figure 6.6 Work flow diagrams for CO₂ gasification scheme and CLG scheme based on simple exergy analysis.
Figure 6.7 Flow diagrams of (a) conventional biomass to liquids process; and (b) chemical looping gasification integrated with CO$_2$ hydrogenation process
Figure 6.8 Syngas Chemical Looping enhanced Coal to Liquid (SCL-CTL) process
Table 6.1 Key reactions in the liquid fuel synthesis block for the three process schemes investigated in this study*

<table>
<thead>
<tr>
<th>Scheme</th>
<th>Syngas Generation and Conditioning</th>
<th>Liquid Fuel Synthesis</th>
<th>Overall Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scheme I</td>
<td>(high T) C + H₂O → CO + H₂</td>
<td>(low T) CO + 2H₂ → -(CH₂)⁻ + H₂O</td>
<td>3C + 2H₂O → 2-(CH₂)⁻ + CO₂</td>
</tr>
<tr>
<td></td>
<td>(low T) CO + H₂O → CO₂ + H₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Scheme II</td>
<td>(high T) C + 2H₂O → CO₂ + 2H₂</td>
<td>(low T) CO₂ + 3H₂ → -(CH₂)⁻ + 2H₂O</td>
<td></td>
</tr>
<tr>
<td>Scheme III</td>
<td>(high T) Fe₃O₄ + 2C → 3Fe + 2CO₂</td>
<td>(low T) CO₂ + 3H₂ → -(CH₂)⁻ + 2H₂O</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(high T) 3Fe + 4H₂O → Fe₃O₄ + 4H₂</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* The reactions given in the table are simplified.
Table 6.2  Physical and chemical properties of switchgrass

<table>
<thead>
<tr>
<th>Proximate Analysis</th>
<th>Wt% (As-Received)</th>
<th>Ultimate</th>
<th>Wt%, dry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>15</td>
<td>Moisture</td>
<td>0</td>
</tr>
<tr>
<td>Fixed Carbon</td>
<td>18.1</td>
<td>Ash</td>
<td>6.19</td>
</tr>
<tr>
<td>Volatiles</td>
<td>61.6</td>
<td>Carbon</td>
<td>46.96</td>
</tr>
<tr>
<td>Ash</td>
<td>5.3</td>
<td>Hydrogen</td>
<td>5.72</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>Nitrogen</td>
<td>0.86</td>
</tr>
<tr>
<td>HHV (MJ/kg, dry)</td>
<td>18.748</td>
<td>Chlorine</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sulfur</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Oxygen</td>
<td>40.18</td>
</tr>
</tbody>
</table>
Table 6.3 ASPEN simulation of conventional and CLG schemes for liquid fuel production from biomass

<table>
<thead>
<tr>
<th>Fuel Type</th>
<th>Conventional BTL</th>
<th>CLG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Processing Capacity (MW_{th})</td>
<td></td>
<td>100</td>
</tr>
<tr>
<td>Liquid Fuel Yield (bbl/day)</td>
<td>622</td>
<td>818</td>
</tr>
<tr>
<td>Energy Conversion Efficiency (HHV, %)</td>
<td>42.2</td>
<td>55.5</td>
</tr>
<tr>
<td>LCA CO$_2$ Emission (kg CO$_2$/bbl)</td>
<td>126.2</td>
<td>-461.9</td>
</tr>
<tr>
<td>LCA CO$_2$ Emission for Petroleum Based Diesel (kg CO$_2$/bbl)</td>
<td></td>
<td>512.5</td>
</tr>
</tbody>
</table>

1. Combined production rate for naphtha and diesel fuels


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