SIMULATION OF CHEMICAL LOOPING COMBUSTION USING COAL AND BIOMASS MIXTURES

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by

Mayur D Kevat

Department of Mechanical Engineering

Indian Institute of Technology Guwahati, Guwahati, India

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CERTIFICATE

It is certified that the work contained in this thesis entitled **“SIMULATION OF CHEMICAL LOOPING COMBUSTION USING COAL AND BIOMASS MIXTURES”**, by **Mayur D Kevat**, has been carried out under our supervision and that this work has not been submitted elsewhere for a degree.

January 2018
IIT Guwahati

Dr. Tamal Banerjee
Professor
Department of Chemical Engineering
Indian Institute of Technology Guwahati

Dr. Vinayak Kulkarni
Associate Professor
Department of Mechanical Engineering
Indian Institute of Technology Guwahati

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SYNOPSIS

The combustion of fossil fuel produces a massive amount of carbon dioxide (CO_2), leading to increased global warming. Efforts are required to work on technologies that reduce CO_2 emission. Different technologies are suggested to capture the CO_2 such as pre-combustion, post-combustion and oxy-fuel combustion. These processes are highly energy intensive and result in increasing the cost of carbon capture. Chemical Looping Combustion (CLC) is a viable solution for the efficient fuel combustion with inherent CO_2 separation. The CLC process is based on the strategy of supplying oxygen from combustion air through carrier materials. The carrier material passes through the air and fuel reactor and executes the fuel combustion without direct contact between air and fuel by means of recycle type redox reaction. After the oxidation of fuel gases, N_2-free flue gas is obtained from the fuel reactor. The oxygen carrier here first gets reduced in the fuel reactor and then gets oxidized in the air reactor as per the following reactions.

$$2Me_xO_y \leftrightarrows O_2 + 2Me_xO_{y-1} \tag{1}$$

Since there is no direct contact between combustion air and fuel, a higher concentration of CO_2 and H_2O are generated in the fuel reactor. H_2O can easily condense which makes pure CO_2 ready for the capture. Hence, no extra energy needed like in other technologies for the CO_2 separation.

Chemical Looping with Oxygen Uncoupling (CLOU) is a variant of CLC process with absence of the rate-limiting char gasification step in CLC. CLOU uses the carrier particles which have special characteristics so as to produce gaseous oxygen at a suitable partial pressure and desired temperature. CLOU has proven to be a novel method to burn solid fuels in gas-phase oxygen without the need for an additional energy intensive such as the air separation unit. Many researchers have suggested that the CLC and CLOU concept with interconnected fluidized bed is more feasible for the solid fuels like coal, petcoke and biomass.

A significant amount of work has been investigated on CLC and CLOU of coal and petroleum coke but limited studies are available with biomass as fuel. Biomass is an interesting fuel to be tested in both CLC and CLOU owing to its abundant availability in a country such as India. Combustion of biomass has received extensive investigation in the field of economy and energy utilisation. The advantage of using biomass as CLC fuel can lead to the capture of CO_2 through its combustion. This will inherently lead to negative CO_2 emission, as the CO_2 released in combustion is being continuously removed from the atmosphere during biomass growth. Thus use of pure biomass in CLC and CLOU needs to be explored for the reduction of carbon imprint. Keeping the advantages in mind, the current thesis employs ASPEN Plus to simulate and analyse solid fuel conversion process in the interconnected fluidized bed reactor system using biomass and coal mixture as fuel. The aim of the present work is also to develop a model mimicking the experimental study of CLC and CLOU of pure biomass and mixture of coal and biomass using Fe_2O_3 and CuO oxygen carriers respectively, in interconnected fluidized bed combustion.

The following subsections summarizes the key findings of the thesis:

Chapter 3 presents the procedure to carry out CLC and CLOU simulation of solid fuel through ASPEN Plus simulator. Different inbuilt reactor components are used to simulate the actual interconnected fluidized bed experimental set-up. In the subsequent sections, step by step procedure is described to evaluate the simulation process for CLC and CLOU of solid fuel.

In **Chapter 4**, combustion of biomass using chemical looping is reported. Here iron-based metal oxide (Hematite Fe_2O_3) is considered for the combustion of biomass. Oxidation and reduction reactions of oxide particles are analyzed in the air and the fuel reactors, respectively. A simulation study was carried out using the published experimental data for the biomass in chemical looping combustion. The deviation between the experimental values and the simulation results was found primarily due to the assumption of neglecting the effects of miscellaneous energy losses in fluidization process. The effect of fuel reactor temperature on gas concentration, conversion efficiency and carbon capture efficiency is presented. It was established that due to the poor oxygen transport capacity of iron-based oxygen carrier particles, the conversion efficiency was found to decrease with increase in the fuel reactor temperature. On one end higher fuel reactor temperature causes an increase in the concentration of CO, while on the other end it tends to decrease the CO_2 concentration in the fuel reactor. In the air reactor, the concentration of O_2 remained constant, while for CO_2 it was found to decrease with increase in fuel reactor temperature. Carbon capture efficiency was found to increase with an increase in fuel reactor temperatures, i.e., 96.73% at 720 °C to 98.95% at 930 °C. Effect of gasification agent and solid circulation rate on char conversion and carbon capture efficiency are also deduced. Significant benefits are however not obtained using either CO_2 or steam as a gasifying agent. The difference in carbon capture efficiency was found to be 2.7%, for CO_2 as compared to steam as gasification agent at temperature of 930 °C. It was concluded that CO_2 can easily replace steam as gasification agent, since significant changes were not seen in terms of char conversion and carbon capture efficiency. For some representative cases, numerical results are compared with experimental results available in the literature. The results are found to compare fairly well.

Chemical Looping Combustion (CLC) and Chemical Looping with Oxygen Uncoupling (CLOU) of biomass are known to play a significant role in the carbon capture process. The integral part of CLC and CLOU for solid fuels such as biomass consists of interconnected fluidized air and fuel reactor. The heat recovery/loss in both of the reactors and other components were also analysed so as to commercialize these biomass fuel based on CLC and CLOU configuration. An oxygen carrier composition similar to published literature for coal as fuel for CLC and CLOU is then used to study biomass as CLC and CLOU fuel. This led us to adopt a catalyst combination of 60% Fe_2O_3/Al_2O_3 and 40% CuO/ZrO_2 for CLC and CLOU, respectively. When compared with conventional fossil fuel such as coal, the results gave the ratio, namely kg oxygen carrier/kg fuel as 66.4 and 75 for CLC and CLOU, respectively in the fuel reactor. For coal, it was found to be higher as 98 and 129 for CLC and CLOU, respectively having similar catalyst composition.

For biomass CLOU, a 51% conversion is realized in the fuel reactor and 48% in air reactor. The energy analysis gave a difference in energy output between CLC and CLOU to be 43 W_{th} i.e., 201 W_{th} in CLOU and 158 W_{th} in CLC. Overall the results are in line with respect to oxygen carrier composition as used in experimental study for bituminous coal. It was observed that a less costly and high melting point Fe based oxide particles can be recommended for CLC when compared to the high cost and less melting point of Cu based particles in CLOU for economic energy analysis. Moreover, the low melting temperature of Cu based oxygen carrier needs proper attention since working with biomass may create agglomeration and defluidization within the system. On the other hand, to take advantage of a faster rate of oxygen generation with a highly reactive fuel, an optimized fuel reactor temperature should be chosen. Thus in short a lesser requirement of Cu based oxygen carrier for the combustion of similar mass of fuel in the fuel reactor reduces the reactor volume in the plant design. Reactor design with minimum residence time of the particles in the fuel reactor could eventually improve the combustion efficiency in CLC.

Chapter 5 conveys the simulation of chemical looping combustion (CLC) of biomass and coal mixture. Hematite is used as an oxygen carrier for the combustion of the solid fuels. The simulation results were validated with the published experimental data such as the concentration of different gases in the reactors, the conversion efficiency, oxide oxygen fraction and carbon capture efficiency. The concentration of CO and CO_2 in the fuel reactor was found to increase while the CO_2 concentration in the air reactor decreases with increase in the fuel reactor temperature. However, due to poor oxygen transport capacity of iron-based oxygen carrier particles, the conversion efficiency decrease with increase in fuel reactor temperature. Variations in carbon capture efficiency and oxide oxygen fraction as a function of different mass fractions of coal and biomass in the mixture, gasification agents and solid circulation rate were also performed. The carbon capture efficiency and oxide oxygen fraction are found to increase with the fuel reactor temperature. The difference between carbon capture efficiency (η_{cc}) and oxide oxygen fraction (η_{oo}) confirms the presence of unconverted carbonaceous gases in the fuel reactor. The values of ($\eta_{cc} - \eta_{oo}$) were less at higher fuel reactor temperature as compared to lower fuel reactor temperature for various coal-biomass mixture configurations. The difference ($\eta_{cc} - \eta_{oo}$) is less for the coal and biomass mixture with a higher concentration of biomass (0.49%) as compared to the higher concentration of coal in the mixture (1.31%) for respective fuel reactor temperature of 980 °C. Experimental evidence suggests that presence of alkali and alkaline earth metals in biomass reduces the gasification temperature and activation energy of coal. Therefore, co-combustion of biomass and coal is found to increase the coal char gasification. This has further improved the char conversion in the fuel reactor which resulted in a lower CO_2 concentration in the air reactor. Higher mass fractions of biomass in the coal and biomass mixture has also resulted in higher conversion of coal char particles thereby increasing carbon capture efficiency from 95.78% to 98.86% within the desired temperature range. The results shows that the higher mass fractions of coal in the biomass and coal mixture acts in a similar manner as CLC of pure coal. Simulation results agreed well with experimental results of CLC of pure coal. A higher mass fraction of steam improves the gasification of solid fuels, thus increasing the carbon capture efficiency. No significant change in carbon capture efficiency were found using CO_2 and steam together as gasification agent in CLC of coal and biomass mixture. CO_2 as gasification agent may reduce the cost of carbon capture due to reduction in cost involved in steam generation. No significant changes in carbon capture efficiency were also observed with higher oxygen carrier to fuel ratio with coal and biomass mixture as CLC fuel.

Chapter 6 includes a detailed simulation process considering equal fraction of coal and biomass mixture with copper based (CuO) oxygen carrier. In this chapter, first the simulation results are validated with experimental results of CLOU of pure coal based on experimental study. Then predicted numerical results for CLOU of coal and biomass mixture are compared with CLOU of pure coal to observe the variation in performance parameters by replacing coal with biomass. The performance parameters such as, concentration of different gases in air and fuel reactors, carbon capture efficiency, oxygen carrier conversion in fuel reactor and the energy analysis is also predicted.

Chapter 7 includes the concluding remarks based on the simulation study and future scope.

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Nomenclature

Abbreviations

AR	Air Reactor
CC	Carbon Capture
Char	Carbon in char particles
FR	Fuel Reactor
g	Gas
OC	Oxygen Carrier
Out	Outlet stream of reactor
ox	Oxidised
red	Reduced
s	Solid

SF	Solid Fuel
Vol	Volatile matter

Greek/Roman Symbols

η_{cc}	carbon capture efficiency (%)
$\eta_{conversion}$	conversion efficiency (%)
η_{oo}	oxide oxygen fraction (%)
λ	stoichiometric air ratio
Ω_{SF}	stoichiometric moles of O_2 to convert 1 kg of solid fuel (mol/kg)
Φ	oxygen carrier to fuel ratio

Others

$\dot{m}_{fuel}$	mass flow rate of pure solid (or mixture of solid) fuel (kg/h)
$F_{C,vol}$	molar flow rate of carbon in volatile matter (mol/s)
$F_{i,AR}$	molar flow of species i in the air reactor inlet/outlet stream (mol/s)
$F_{i,FR}$	molar flow of species i in the fuel reactor inlet/outlet stream (mol/s)
f_i	mass fraction in solid fuel of element or compound i
F_{OC}	oxygen carrier circulation rate (kg/h)
M_i	atomic or molecular weight of i^{th} element or compound (kg/mol)

Me	metal oxide
$W_{i,AR}$	i^{th} species volume percentage in the air reactor outlet stream (%)
$W_{i,FR}$	i^{th} species volume percentage in the fuel reactor outlet stream (%)
X_{char}	char conversion

CHAPTER 1

Introduction

1.1 Introduction

Anthropogenic carbon dioxide (CO_2) emissions produced from fossil fuel combustion during energy generation is responsible for global warming. It has got great attention and according to Inter-governmental Panel on Climate Change (IPCC), attention must be focussed on to mitigate the harmful greenhouse gases. The effect of this emission has currently evoking great concern with respect to health and environment. In order to maintain the earth temperature that would be feasible for humans, the suggested concentration of CO_2 in atmosphere is 450 ppm [IPC, 2007]. Therefore, necessary action is required to control the emission of greenhouse gases in order to stabilize its concentration in the atmosphere. Carbon Capture and Storage (CCS) has been proposed as an option to reduce the emissions of CO_2 in fossil fuel powered power plants. CCS includes the capture of CO_2 gas from the reactor effluent that is produced from the combustion of the fossil fuel. Recent technologies such as post-combustion, pre-combustion and oxy-fuel combustion for CCS have inherent disadvantage of higher energy penalties [Figueroa et al., 2008, Hossain and de Lasa, 2008]. On other side, as an alternative, technologies based on renewable energy sources are not stable and sufficient to meet the current clean energy demand. Hence alternative capture strategies need to be explored. Out of them the promising one is Chemical Looping Combustion (CLC) which has been devised and adopted in this thesis.

1.2 Chemical Looping Combustion (CLC)

Chemical looping combustion (CLC) is seen as one of the major options for clean combustion technology with inherent CO_2 separation. This is realized by the complete combustion of solid fuels like coal and petcoke in CO_2 and H_2O, with almost nil or less energy penalty compared to other technologies for carbon capture. The CLC process is known to be carried out in batch reactor or with the much popular interconnected fluidized bed reactors [Berguerand and Lyngfelt, 2008, Shen et al., 2009a]. Experimental studies by [Gayan et al., 2013] listed some selected data for CLC of solid fuels with different experimental facilities. The studies suggested some design options to reduce the unburned compounds of solid fuel in the fuel reactor which shall result in the increase in the carbon capture efficiency. As shown in Figure 1.1 in CLC, the required oxygen for fuel combustion is usually supplied by metal oxides such as Fe_2O_3, NiO, CuO, and Mn_2O_3. Technical issues and the basic concept regarding the CLC of solid fuels using metal oxides are already discussed Comprehensively by [Cao and Pan, 2006]. Their study emphasize on the physical properties of various metal oxides and thermodynamic aspects of reduction reaction of metal oxides with volatiles and gasification products of solid fuels.

In CLC, the metal oxide passes through recycle redox reaction in two different reactors (fuel and air reactor) so that the fuel combustion occurs without direct contact between air and fuel. It should be noted that the gasification of solid fuel in CLC is a slow process and hence is considered as a rate limiting process. Moreover in interconnected fluidized CLC arrangement, the amount of heat produced is same as in conventional combustion. A thermal analysis of the CLC process using a number of possible oxygen carriers was simulation study carried out by [Jerndal et al., 2006]. The oxygen carrier gets reduced by volatiles and gasification products in a fuel reactor (Eq. 1.1) and then gets oxidized in the air reactor (Eq. 1.2) [Lyngfelt et al., 2001].

$$(2n+m)MeO + C_nH_{2m} \rightarrow (2n+m)Me + mH_2O + nCO_2 \tag{1.1}$$

$$Me + \frac{1}{2}O_2 \rightarrow MeO \tag{1.2}$$

Other than CLC, the other variant namely the Chemical Looping with Oxygen Uncoupling (CLOU) is being extensively studied. It involves generation of oxygen or uncoupling within the fuel reactor. This has been discussed in the next section.

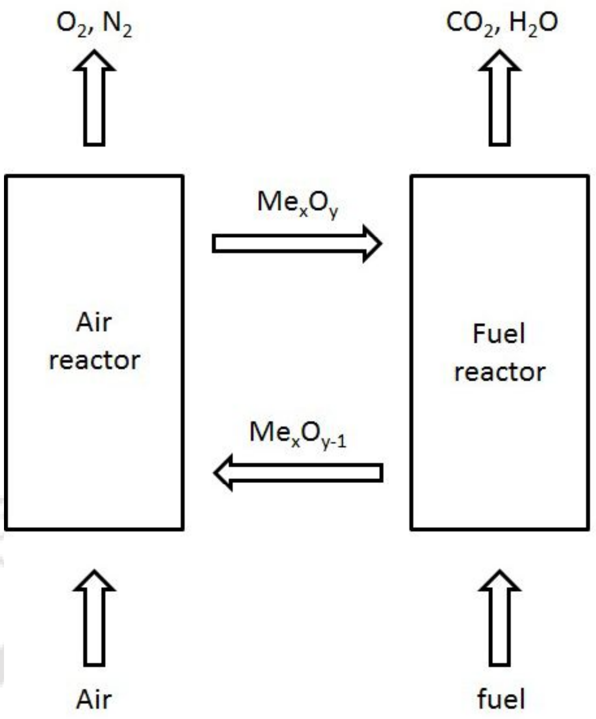

Figure 1.1: Schematic of chemical looping combustion (CLC) system. [Lyngfelt et al., 2001]

1.3 Chemical Looping with Oxygen Uncoupling (CLOU)

Chemical looping with oxygen uncoupling (CLOU) is more or less equivalent to CLC for the combustion of solid fuels together with CCS. The concept of CLOU was proposed in 2005 by Lyngfelt and Mattisson in a patent application [Lyngfelt and Mattisson, 2005]. It involves solid fuel combustion in gas-phase oxygen without the need for an energy intensive air separation unit. Therefore, gasification of solid fuel is no more needed and hence reaction rate is high as compared to CLC. It uses the oxygen carrier which has special ability to react with the oxygen in the atmospheric air and decomposes to gaseous oxygen. The reactions occurring are given below:

$$2Me_xO_y \rightarrow O_2 + 2Me_xO_{y-1} \tag{1.3}$$

$$Coal(s) \rightarrow Volatiles(g) + Char(C)(s) \tag{1.4}$$

$$Volatiles(g) + Char(C)(s) + (n + \frac{m}{2})O_2(g) \rightarrow mH_2O(g) + nCO_2(g) \tag{1.5}$$

Based on experimental outcome, Mattisson et al. [Mattisson et al., 2009] identified three metal oxide systems such as Mn_2O_3/Mn_3O_4, CuO/Cu_2O and Co_3O_4/CoO, which has desirable thermodynamic properties to decompose in gaseous oxygen. In CLOU, three processes were identified to carry out solid fuel combustion (Eq. 1.3-1.5). Here, in the air reactor the metal oxide captures oxygen from the atmospheric air, while in the fuel reactor the decomposition of the metal oxide generates gaseous oxygen. The gaseous oxygen reacts with a solid fuel and converts it to CO_2 and H_2O [Leion et al., 2009, Abad et al., 2012]. Figure 1.2 shows the differences in main processes to be carried out in the fuel reactor for the solid fuels combustion in CLC and CLOU [Leion, H. et al., 2011, Adanez et al., 2013].

Most of the reported data for CLC and CLOU uses fossil fuel such as coal explicitly, while few report the use of biomass as fuel component [Shen et al., 2009b, Adanez-Rubio et al., 2014, Gu et al., 2011, Mendiara et al., 2013]. Nowadays the combustion of pure biomass has aroused increasing attention for power generation. Use of biomass as fuel can generate negative CO_2 emission, because the CO_2 released in combustion is being continuously removed from the atmosphere during biomass growth. Moreover, co-combustion of different shares of biomass with coal is another favourable option to use large amount of biomass as fuel to meet energy demand with reduced greenhouse gas emission [Hein and Bemtgen, 1998, Nussbaumer, 2003, Basu et al., 2011, Khorshidi et al., 2014]. This is in view of that abundant amount of biomass available in country like India. Eventually, the main purpose is to move from a fossil fuel based energy production to a renewable i.e., co-combustion of biomass with coal. This will reduces the emission of CO_2 in the atmosphere which is our prime objective. We intend to design a CO_2 capture system which can be implemented with biomass as a CLC fuel for the carbon capture in the atmosphere.

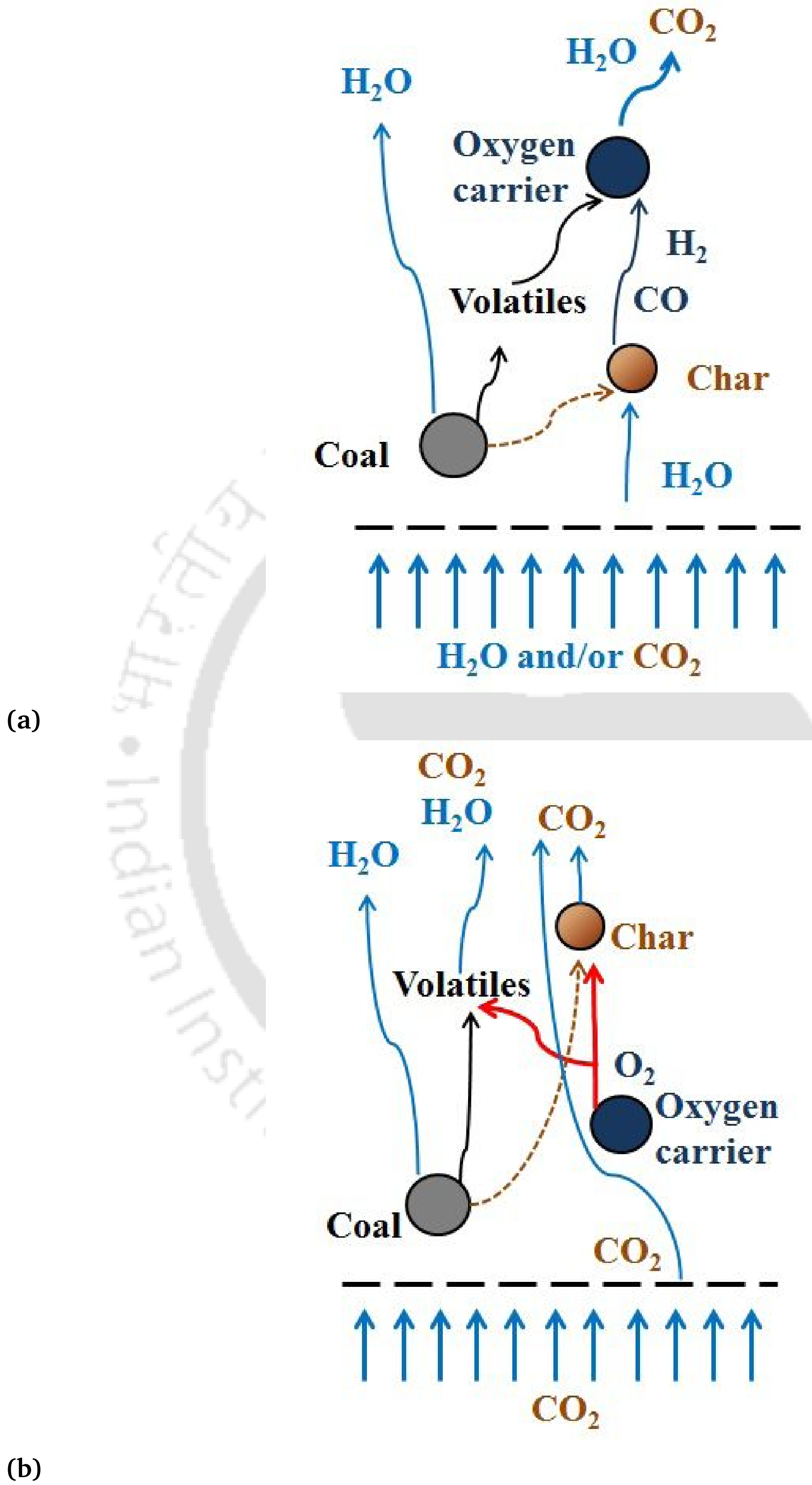

Figure 1.2: Solid fuel combustion phenomena in fuel reactor for (a) CLC and (b) CLOU configuration. [Adanez et al., 2013]

1.4 Objectives

The current research interest focusses to adopt biomass as a renewable fuel with carbon capture and storage. The objectives of the present work are stated below:

(1) *To carry out simulation study using the published experimental data for CLC of pure biomass and biomass/coal mixture* using ASPEN Plus solver. Published literature [Nikoo and Mahinpey, 2008, Meng et al., 2015, Jang et al., 2013] suggested that ASPEN Plus is able to successfully simulate gasification of solid fuel, CLC and CLOU of solid fuels based on steady state process using sensitivity analysis and design optimization. Hence ASPEN Plus has been adopted for this work.

(2) *Comparison of CLC and CLOU* with respect to different performance parameters such as fuel reactor temperature, solids circulation rate, and fuel inventory. The effect of these parameters will be evaluated based on the gas concentration, conversion efficiency, oxide oxygen fraction and carbon capture efficiency. We shall adopt both pure biomass and co-combustion of coal with biomass as fuel.
(3) *Energy analysis for a complete process* level and scale up studies to model the CLC and CLOU process for sawdust biomass based on published literature.

1.5 Organization of Thesis

The entire thesis is organized in seven chapters. While the first chapter introduces the basic concepts such as CLC and CLOU, the second chapter summarizes a comprehensive literature survey that has been carried out for solid fuel in CLC and CLOU configuration. The published literature also covers a wide range of experimental and numerical studies based on various features and performance parameters in CLC and CLOU.

Chapter 3 includes the procedure to carry out chemical looping combustion (CLC) and chemical looping with oxygen uncoupling (CLOU) simulation of solid fuel through ASPEN Plus simulator. Review of the literature has suggested interconnected fluidized bed system to execute either CLC or CLOU of pure solid fuels or mixture of solid fuels. Different inbuilt reactor components are used to simulate the actual experimental set-up. In the subsequent sections, step by step procedure is described to evaluate the simulation process for CLC and CLOU of solid fuel as per the experimental studies of Gu et al. [Gu et al., 2011] and Abad et al. [Abad et al., 2012].

Chapter 4 discusses the ASPEN Plus simulation of the pure biomass as CLC fuel using iron based (hematite Fe_2O_3) oxygen carrier as per published experimental data of Gu et al. [Gu et al., 2011]. In this chapter, a benchmarking study of CLC was performed to validate the gas concentration in fuel and air reactors, conversion efficiency and carbon capture efficiency. The effect of gasification agent and solid circulation rate on char conversion and carbon capture efficiency is also simulated. Thereafter energy analysis is carried out with sawdust biomass using the catalyst combination of 60% Fe_2O_3/Al_2O_3 and 40% CuO/ZrO_2 for CLC and CLOU, respectively as per published experimental data of Sahir et al. [Sahir et al., 2014].

Chapter 5 presents the simulation of the coal and biomass mixture as CLC fuel. Published experimental data of Gu et al. [Gu et al., 2011] is again used to simulate the flow process of CLC of coal and biomass mixture using hematite (Fe_2O_3) as an oxygen carrier. It shows the effect of different mass fractions of coal and biomass in mixture on conversion efficiency, carbon capture efficiency and oxide oxygen fraction. All the properties are reported as a function of the fuel reactor temperature. It then presents the simulation study so as to present the variation in carbon capture efficiency as a function of gasification agent and solid circulation rate.

Chapter 6 includes a detailed simulation process considering equal fraction of coal and biomass mixture with copper based (CuO) oxygen carrier. In this chapter, first the simulation results are validated with experimental results of CLOU of pure coal based on experimental study by Abad et al. [Abad et al., 2012]. Then predicted numerical results for CLOU of coal and biomass mixture are compared with CLOU of pure coal to observe the variation in performance parameters by replacing coal with biomass. The performance parameters such as, concentration of different gases in air and fuel reactors, carbon capture efficiency, oxygen carrier conversion in fuel reactor and the energy analysis is also predicted.

Chapter 7 includes the concluding remarks based on the simulation study and future scope.

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CHAPTER 2

Literature Review

2.1 Chemical Looping Combustion

Chemical-Looping Combustion (CLC) is a technology that prevents the CO_2 produced by fuel combustion from being mixed with the other gases in the exhaust. This is done by preventing the presence of air-nitrogen in the part of the reactor system where the fuel oxidation occurs. The principle is based on an oxygen carrier which circulates between two interconnected fluidized beds and is submitted to numerous cycles where it is alternatively oxidized in an air reactor and reduced in a fuel reactor, while providing the oxygen required for the fuel combustion.

Chemical looping combustion (CLC) and chemical looping with oxygen uncoupling (CLOU) have been investigated with different aspects to improve the carbon capture and storage (CCS). CCS involves the capture of CO_2 from the generation source, thereafter its cleaning, transporting and finally its storage. Different technologies are suggested to capture the CO_2 such as pre-combustion, post-combustion and oxy-fuel combustion [Figueroa et al., 2008]. All of these processes are highly energy intensive and result in increasing the cost of carbon capture. In that aspect, CLC is a viable solution for the efficient fuel combustion with inherent CO_2 separation from other gases in the fuel reactor. Chemical-looping combustion was first proposed in 1954 to produce concentrated CO_2 from combustion of fossil fuels as per the pioneering work of Lewis et al. [Lewis et al., 1951]. With growing interest towards environmental issues and impact of greenhouse gases emissions on climate change, the inherent CO_2 separation that CLC offers became an important focus for research.

Previously, most of the work have focused on CLC of gaseous fuels [Adanez et al., 2006, Johansson et al., 2006, Abad et al., 2006, Leion et al., 2008a]. However recently, the direct application to solid fuels is also being explored due to its abundant availability and effective cost compared to gaseous fuel. The CO_2 capture from combustion of fossil fuels during power production needs to be vented into the atmosphere. Ishida and Jin [Ishida and Jin, 1997] presented the features of CO_2 recovery in a power plant in CLC of gaseous fuel. For enhanced oxygen transfer, selection of suitable metal oxide in CLC is a key factor for the optimum performance of the system. Their experimental studies investigated the performance of the supported metal oxides regarding its kinetics and stability using thermogravimetric analysis (TGA). It suggested that CLC could be a good candidate to assist CO_2 recovery from power plant. Lyngfelt et al. [Lyngfelt et al., 2001] suggested a tentative design of the CLC process for the solid fuel and discussed important aspects for judging its practical application.

Overall the CLC process requires good contact between volatile matter and gasification products of solid fuel with metal oxide particles. At the same time, it is expected that oxygen carriers should be active and stable under long hour fluidizing condition. As a result of thorough investigation, oxides based on Fe, Ni, Cu, Mn and Co have been identified as most potential oxygen carrier materials. Mattisson et al. [Mattisson et al., 2001] investigated the oxidation and reduction of Fe_2O_3 with air and methane respectively, using it in cyclic manner within a fixed bed reactor temperature of 950 °C. They concluded that rate of oxidation, reduction and conversion range of Fe_2O_3 is found to be suitable for the design of CLC based on interconnected fluidized bed system. Jerndal et al. [Jerndal et al., 2006] provided a comprehensive thermal investigation of oxygen carriers for CLC and CLOU. It featured out the advantages of nickel-based oxygen carriers as they can apparently withstand a higher operating temperature and are more efficient in transporting oxygen. It was also suggested that Fe_2O_3 has the advantages as an oxygen carrier of being easily available. Furthermore, different iron based oxides (Fe_3O_4 and FeO) are also environmental compatible and cheaper as compared to nickel based oxides [Wolf et al., 2005, Jerndal, E. et al., 2011, Abad et al., 2011, Wang et al., 2017]. Recently Lyngfelt [Lyngfelt, 2014] reviewed possible metal oxides and found that oxygen carrier materials other than ilmenite $FeTiO_3$ could provide significant improvement in solid fuel CLC performance.

The performance of iron based residue from alumina production was tested by Mendiara et al. [Mendiara et al., 2013b] using bituminous coal as solid fuel in CLC. It was concluded that such type of low cost material seems to be advantageous as an alternative to costlier oxygen carrier.

2.2 Oxygen Carrier

The vital properties from oxygen carrier particles such as high redox reaction rate, high resistance to attrition and thermal sintering in fluidizing condition is a necessity. To increase their reactivity, durability and fluidizability, oxygen carrier particles are deposited by the active metal oxides phase on an inert support such a SiO_2, TiO_2, ZrO_2, Al_2O_3 and *Yttria-stabilized zirconia* (YSZ). Cho et al. [Cho et al., 2004] also tested several oxygen carriers based on iron, nickel, copper and manganese oxides with aluminium and kaoline as supporting material. They developed simple procedure for testing and comparing the reactivity of supported metal oxide particles. Their study concluded that the aluminium oxide supported nickel and copper shows good reactivity. Furthermore, nickel based oxides seems to be most promising one with high strength while copper based oxides showed sign of agglomeration. In another study, reaction tests for $FeTiO_3$, Mn_3O_4 and NiO based oxides with different appropriate inert materials were carried out by Marcus et al. [Marcus et al., 2006] under alternate oxidising and reducing conditions. Reduction and oxidation were performed in gas mixture (50 %CH_4 /50% H_2O) and 5% O_2 in nitrogen, respectively. It was found that Ni based oxides were more reactive, followed by Mn and Fe based oxides.

In general, oxygen carriers with high reactivity, desired fluidization characteristic and strength were investigated for solid fuel CLC. de Diego et al. [de Diego et al., 2004] studied behaviour of some potential Cu based oxygen carrier particles for solid fuel CLC. Series of TGA testing were carried out to investigate the effect of carrier composition and preparation method on reactivity and combustion in CLC. Chuang et al. [Chuang et al., 2008] also focussed on preparation of Al_2O_3 supported CuO to enhance the ability of the resulting oxygen carrier. Different methods such as mechanical mixing, wet-impregnation and co-precipitation were used for the preparation and also to check the oxidation and reduction potential. They found that the carrier prepared by co-precipitation offered high fluidizing capability and resistance to agglomeration as compared to oxygen carrier prepared by other methods.

For optimized CLC performance, the oxygen carrier recirculation rate should be sufficient in the system so as to prevent the large temperature drop in the fuel reactor. It is hence important to maintain sufficient reaction temperature in the fuel reactor for solid fuel combustion to CO_2 and H_2O. Abad et al. [Abad et al., 2007] also tested Fe, Ni and Cu based oxide material in syngas (CO+H_2) at atmospheric and pressurised conditions. It was observed that all the oxygen carriers exhibited high reactivity during the reduction reaction. Additionally, general observation was found that the reactivity with H_2 was higher when compared to CO for all the considered metal oxide particles.

For complete combustion of fuel to CO_2 and H_2O, a high oxygen transport capacity is required from the oxygen carrier particles. Table 2.1 presents the oxygen transport capacity (R_{OC}) of some of the investigated oxygen carriers. It can be defined as:

$$R_{OC} = \frac{m_{ox} - m_{red}}{m_{ox}} \tag{2.1}$$

where, m_{ox} and m_{red} indicates the mass of oxidised and reduced metal oxide particles, respectively.

Table 2.1: Oxygen ratio R_{OC}, for the different pairs of metal/metal oxides. [Jerndal et al., 2006]

Metal Oxide Pair	R_{OC}
NiO/Ni	0.214
CuO/Cu	0.201
Cu_2O/Cu	0.112
Fe_2O_3/Fe_3O_4	0.033
Mn_2O_3/MnO	0.101
Mn_3O_4/MnO	0.070
Co_3O_4/Co	0.266
CoO/Co	0.214
$WO_3/WO_{2.722}$	0.019
$BaSO_4$/BaS	0.274
$SrSO_4$/SrS	0.348

Leion et al. [Leion et al., 2007] investigated experimentally the reaction between supported iron based oxygen carrier ($Fe_2O_3/MgAl_2O_4$) and petcoke in a laboratory fluidized bed reactor. It was found that conversion rate of petcoke increased with increase in the fuel reactor temperature and concentration of steam in fluidization gas. Berguerand and Lyngfelt [Berguerand and Lyngfelt, 2008] obtained experimental results for the South African coal in 10 kW_{th} capacity CLC unit using ilmenite as an oxygen carrier. They verified their experimental design with respect to proper fluidization and circulation of oxygen carrier particles in the system and concluded that ilmenite appeared to be a suitable material for solid fuel CLC.

2.3 Gasification Processes in CLC

Shen et al. [Shen et al., 2009a] provided fundamental aspects of the CLC of solid fuels. It was found that coal gasification was the main factor which controlled the CO and

CH_4 concentrations in the flue gas of the fuel reactor and carbon conversion efficiency during CLC of coal using NiO-based oxygen carrier. H_2 was not detected in the fuel reactor and carbon conversion efficiency was found to reach only 92.8%, even though the fuel reactor temperature was kept at 970 °C. Cuadrat et al. [Cuadrat et al., 2011] investigated the CLC of bituminous coal with ilmenite as an oxygen carrier in 500 W_{th} set-up. They assessed the effect of fuel reactor temperature and coal particle size on coal conversion and carbon capture efficiency. It was confirmed that the combustion efficiency increased from 70% to 95% at corresponding fuel reactor temperature of 870 °C to 950 °C, respectively. In line of the previous experimental study, Cuadrat et al. [Cuadrat et al., 2012a] also investigated the effect of solid circulation rate, oxygen carrier residence time, coal feed rate and gasification agent on CLC performance. The char conversion was found to increase with higher fraction of steam as compared to CO_2 as gasification agent.

Improved CLC performance was also found using CO_2 as gasification agent with the inclusion of carbon stripper for the solid fuel. Roberts and Harris [Roberts and Harris, 2007] reported the data of coal char conversion with a mixture of CO_2 and H_2O as gasification agent at reactant partial pressure of 0.1 to 1.0 MPa. Their study concluded that the presence of CO_2 reduces the rate of the gasification reaction (Char-H_2O) reaction. However, the main motivation to use CO_2 or mixture of CO_2-H_2O as gasification agent is to reduce the cost involved in the steam generation as pure CO_2 is readily available in the fuel reactor for the recirculation. Thus, it can further reduce the cost of carbon capture in CLC.

A simplified model was developed by Cuadrat et al. [Cuadrat et al., 2012c] on the basis of mass balance and chemical reactions taking place in the fuel reactor in solid fuel CLC. Developed model were compared with the experimental results of Cuadrat et al. [Cuadrat et al., 2012a] where bituminous Colombian coal and Ilmenite were considered as solid fuel and oxygen carrier, respectively. It predicted the effect of main operating variables such as solid inventory, fuel reactor temperature, oxygen carrier to fuel ratio and gasification agent on combustion and carbon capture efficiency. Leion et al. [Leion et al., 2008b] investigated the feasibility of synthetic iron ($Fe_2O_3/MgAl_2O_4$) and natural ilmenite mineral (Fe_2TiO_5) based oxide particles with six different coals and syngas (50% H_2/50% CO) in a fluidized bed reactor. It was found that both of the oxygen carrier particles reacted faster with intermediate gasification products (H_2 and CO). The conversion rate of coal with metal oxides were found to strongly depend on the volatile content of the coal. It was concluded that the conversion rate of high volatile content coal was found to be faster as compared to low volatile content coal.

In a similar manner, the feasibility study was also carried out by Cuadrat et al. [Cuadrat et al., 2012b] to assess the performance of CLC using different ranks of coal such as lignite, medium and low volatile bituminous and anthracite coal. It was found that increase in fuel reactor temperature has a beneficial effect with increase in carbon capture efficiency for all types of coal. It was also concluded that coal with high volatile content (lignite) has higher carbon capture efficiency as compared to low volatile content coal (anthracite). No change was observed in the performance parameters for lignite by replacing steam by CO_2 as gasification agent. Adanez et al. [Adanez et al., 2012] further reviewed the advancement in CLC prototype, chemical looping reforming (CLR), application of chemical looping for hydrogen production, development of mathematical models and kinetic studies in CLC.

Song et al. [Song et al., 2012] studied the effect of the fuel reactor temperature, coal type and operation conditions on release of nitrogen gaseous products in both the reactors. It was found that the formation of NO is less with more volatile content fuel as compared to less volatile content fuel. Furthermore, concentration of N_2 in the fuel reactor was found to increase with fuel reactor temperature. In another study, different CLC tests were performed by Song et al. [Song et al., 2013] using natural iron based oxides with two different coals within a defined fuel reactor temperature of 880-970 °C. Recently, Nandy et al. [Nandy et al., 2016] also summarised a review of CLC technology with its all-round technological advancement in the last decade. The review presented the advancement of using different kinds of fuels, evolution of oxygen carrier particles and the reactor system being used.

2.4 Biomass as a Feed in CLC

Biomass is an interesting solid fuel to be tested in CLC to assist CO_2 capture. Therefore, use of pure biomass and co-firing biomass with coal in CLC and CLOU needs to be explored. Limited experimental and numerical studies are available in literature where the biomass is deployed as CLC and CLOU fuel.

Lv et al. [Lv et al., 2004] developed small scale fluidized bed set-up to perform biomass gasification using air and steam as gasification agent. Experimental study investigated the effect of reactor temperature, steam to biomass ratio and biomass particle size on gas yield and carbon capture efficiency. The study assessed that a higher temperature favoured more H_2 production and gas yield. It was concluded that an optimum steam supply would improve the syngas quality compared to air gasification. Shen et al. [Shen et al., 2009b] used a 10 kW_{th} interconnected fluidized bed unit to perform the experiments using pine sawdust with iron oxide powder as oxygen carrier. Experimental study was carried out to demonstrate the effect of fuel reactor temperature on gas composition in both fuel and air reactors and conversion of carbonaceous gases to CO_2. A spouted bed configuration was adopted as fuel reactor in order to avoid biomass segregation in the bed and elutriation of fine biomass char particles. The fuel reactor temperature was varied from 740 to 920 °C and recycled CO_2 was used as the gasifying agent. They observed the presence of CO and CH_4 as unburnt gases at the fuel reactor outlet, while H_2 was not detected. It was also found that CH_4 concentration was not significantly affected by temperature. However, concentration of CO_2 was found to decrease and that for the CO increased with the increase in fuel reactor temperature. On other side, the CO_2 concentration at the air reactor outlet decreased with increase in fuel reactor temperature, indicating that more biomass char was consumed in the fuel reactor at higher temperatures.

Gu et al. [Gu et al., 2011] carried out a similar kind of experimental study in a 1 kW_{th} CLC system. The configuration of the CLC unit was same as spouted bed fuel reactor used by Shen et al. [Shen et al., 2009b]. They used sawdust as pure biomass and equal shares of sawdust/bituminous coal mixtures as CLC fuels. Here steam was the gasifying agent and an Australian iron ore was used as the oxygen carrier. They also studied the influence of fuel reactor temperature on effluent of both the air and fuel reactors, carbon capture efficiency and conversion efficiency. One of the important findings of their research was the difference between the experiments with pure biomass and biomass/coal mixtures, which were attributed mainly to fuel reactivity.

Biomass contained a higher amount of volatiles as compared to the used bituminous coal. This implied that temperature would not greatly affect the degree of gasification in the temperature range tested (720–930 °C) for pure biomass. In the case of biomass/coal mixture, fuel conversion would become more limited by the gasification of coal, reaction between gasification products (of biomass) and the oxygen carrier particles. Nevertheless, the carbon capture efficiency was found to increase with the fuel reactor temperature, reaching 99% at 980 °C. This is because the concentrations of CO_2 and CO were found to be increase with increase in the fuel reactor temperature. Gayan et al. [Gayan et al., 2004] performed co-combustion of sub-bituminous and lignite coal with Pine bark as biomass in circulating fluidized bed (CFB). They also analysed the effect of combustion temperature, percentage share of coal and biomass in mixture, excess air, and particle size distribution on carbon combustion efficiency. They prepared a mathematical model to compare the experimental results for carbon combustion efficiency at different operating conditions. Luo et al. [Luo et al., 2013] investigated direct CLC of Yimin coal and two different types of biomass (candlenut wood and Rice hull). A series of TGA tests were conducted for combustion of (a) pure biomass and coal, and (b) co-combustion of coal and biomass in CO_2 atmosphere using CuO as an oxygen carrier. It was found that the addition of K_2CO_3 and candlenut wood biomass ash decreased the gasification temperature and improved coal conversion. This is due to the fact that K_2CO_3 and biomass ash displayed catalytic activity. Further, it was concluded that biomass with high content of alkaline earth metal would be a potential inexpensive catalyst in co-combustion process. Catalytic effect of biomass alkaline metal on improvement of coal combustion was also presented by Gu et al. [Gu et al., 2011] in their experimental study.

Recently, Haykiri-Acma et al. [Haykiri-Acma et al., 2015] investigated the effect of carbonised biomass to improve the burning characteristic of coal and biomass co-combustion. Carbonisation of woody biomass was carried out at 600 °C which lowered the volatile content. The oxidation of produced biomass char was shifted to a higher temperature when compared to un-carbonised state i.e. co-combustion of biomass with coal. It was concluded that the carbonised biomass eliminates the segregation effect in co-combustion and allows the use of higher percentage of biomass in coal/biomass mixture. Hence, it was proved that such kind of co-combustion has great interest to lower environmental impact with improved burning characteristic. In other study, biomass torrefaction was performed by Sarvaramini and Larachi [Sarvaramini and Larachi, 2014] at temperatures below 300 °C which initiates partial decomposition of hemicellulose, cellulose and lignin biomass constituents. Resulting volatile matter were then burned over iron oxide oxygen carrier particles which converts most of volatile carbon to CO_2. Sahu et al. [Sahu et al., 2010] also carried out lab scale experiments for the co-combustion of coal and biomass. They considered different blends of biomass char and coal as a part of their experimental study to identify the optimum blending ratio. Their experimental results provided the TGA parameters, activation energy and ignition index of different blends. Better combustion performance was found with blends containing less than 50 % biomass char as compared to those with higher biomass char content. In line with the experimental investigations of Shen et al. [Shen et al., 2009b] and Gu et al. [Gu et al., 2011], the performance of Pine wood using iron ore as oxygen carrier were investigated by Mendiara et al. [Mendiara et al., 2013a]. A series of experiments investigated the effect of fuel reactor temperature, solid circulation rate and gasifying agent on the fuel and air reactor extent, carbon capture efficiency and the oxygen demand for the necessary combustion. They obtained high carbon capture efficiency in the fuel reactor which had a temperature range of 880-915 °C. They also proposed to recirculate the obtained CO_2 as gasifying agent in place of steam without compromising the carbon capture efficiency. The presence of tar from biomass pyrolysis in the fuel reactor outlet was studied for the first time. Huijun et al. [Huijun et al., 2015] carried out Biomass Gasification Chemical Looping (BGCL) with Ni based oxygen carrier. This particular concept was applied to utilize lattice oxygen from oxygen carrier instead of molecular oxygen of air. They investigated the effect of steam to biomass ratio and NiO content in supported oxide particle (NiO/Al_2O_3) on the carbon conversion and syngas yield. It was suggested that 30% NiO content would give optimum performance for BGCL. Further, it was found that CaO supported NiO/Al_2O_3 oxygen carrier helps to decrease the CO_2 concentration, while increase the CO and H_2 concentration. Recently, Huang et al. [Huang et al., 2015] also investigated the reactivity of biomass char with hematite (Fe_2O_3) under different atmospheric conditions in TGA. Limited carbon conversion was found at 1000 °C under inert atmosphere, but was found to increase under oxidising atmosphere. A similar effect was found with H_2O or CO_2 as gasification agent. An important conclusion was made regarding the combustion products of syngas (i.e, H_2O and CO_2). It recommended its use as gasification agent so as to obtain higher conversion efficiency and at the same time reduce the overall cost. In view of the composition differences between the biomass ash and the coal ash, the interaction between biomass ash and oxygen carrier would also be different from that between coal ash and oxygen carrier. Gu et al. [Gu et al., 2015] investigated the interaction between three typical biomass ashes and iron ore oxygen carrier during CLC. The SEM, XRD and XRF were used to characterize the oxygen carrier. The results are an important prelude for the development of biomass as CLC fuel.

2.5 CLOU Process

As explained in previous chapter, chemical looping with oxygen uncoupling (CLOU) is a variant to CLC for combustion of the solid fuels. The CLOU process requires special kind of oxygen carriers that have capability to decompose in gas-phase oxygen and oxidise with oxygen in atmospheric air. Exhaustive review has been carried out by Mattisson [Mattisson, 2013] for the oxygen carrier particles in CLOU process. It also provided a broad overview of the CLOU process, thermal analysis and experimental investigations of various oxygen carrier particles for the solid, liquid and gaseous fuels. The Cu, Mn and Co based oxides were the only one able to decompose these carriers to gaseous oxygen at a suitable pressure and a certain temperature range for CLOU process [Adanez-Rubio et al., 2018]. [Mattisson et al., 2009] presented the thermodynamic aspects of CLOU process using ZrO_2 supported CuO oxygen carrier. Their experimental study considered petroleum coke as solid fuel in batch reactor configuration. Results revealed that the average reaction rate of petroleum coke was a function of temperature and varied between 0.5%/s to 5%/s at corresponding reactor temperatures of 895 °C and 985 °C, respectively. In addition, these conversion rates of petroleum coke are found considerably higher than rates as obtained in CLC using iron based oxygen carrier. Eyring et al. [Eyring, E.M. et al., 2011] provided the preliminary analysis of CLOU using unsupported CuO and carbon as the solid fuel. The study also simulated the CLOU system to investigate the energy balance, solid circulation rate, oxygen carrier mass loading and carbon burnout in the fuel reactor and verified the same with published experimental results. Sahir et al. [Sahir et al., 2012] developed the methodology to conduct the decomposition and oxidation rates of Cu based oxygen carrier particles. Excellent agreement was found between independently developed rate analysis with experimental data of Mattisson et al. [Mattisson et al., 2009]. It was proposed that the results of the study could facilitate the design of CLOU based pilot plant. Arjmand et al. [Arjmand et al., 2012] also studied decomposition and oxidation kinetics of $MgAl_2O_4$ supported CuO based oxygen carrier particles. The oxygen carrier was produced using freeze-granulation and same was calcined at 950 °C. The oxidation and reduction rates were obtained in laboratory fluidized bed reactor in the temperature range of 850-900 °C. A detailed investigation of supported CuO oxygen carrier was carried also out by Gayan et al. [Gayan et al., 2012]. The investigation included the preparation of oxygen carriers using different methods such as wet-impregnation and mechanical mixing followed by palletization. They also checked the oxidation and decomposition capability of prepared oxygen carriers in TGA system using successive cycles.

Abad et al. [Abad et al., 2012] investigated the effect of fuel reactor temperature, coal feeding rate and solid circulation rate in a continuously operated CLOU plant using bituminous coal as fuel. They used $MgAl_2O_4$ supported CuO as an oxygen carrier particle. At higher fuel reactor temperature, the rate of decomposition was found to accelerate the char conversion in the fuel reactor. On the other side, increase in solid circulation rate results in decrease of residence time of oxygen carrier in the fuel reactor. This results in a slight decrease in char conversion and carbon capture efficiency. Adanez-Rubio et al. [Adanez-Rubio et al., 2013] investigated the performance characteristics of CLOU using different rank of coal. They performed series of experiments to investigate the effect of fuel reactor temperature and coal type on combustion and carbon capture efficiency. The obtained results were analysed and discussed in order to scale-up the CLOU system with different types of coal. Peterson et al. [Peterson et al., 2013] developed sustainable reactive and higher mechanical strength SiC supported CuO oxygen carrier particle to minimise the risk of agglomeration in CLOU. It proposed that a high porosity and a more internal surface of silicon carbide promoted the gas-solid reaction during combustion process. The reactivity was tested in TGA as well as in fluidized bed condition at higher temperature of 1000 °C. Zhao et al. [Zhao et al., 2014] explored the use of natural copper ore as oxygen carrier due to its low cost and high oxygen transport capacity. Performance investigation was carried out in CLOU process using Chinese anthracite coal. General trend was found that the oxygen release and uptake rate of oxygen carrier increases with fuel reactor temperature. The study also concluded that higher fuel reactor temperature, smaller coal particle size, lower superficial velocity and larger oxygen carrier to fuel ratio promotes high combustion efficiency and CO_2 concentration in the fuel reactor.

Adanez-Rubio et al. [Adanez-Rubio et al., 2014b] studied the behaviour of sulphur content in the solid fuel during continuous CLOU process using $MgAl_2O_4$ supported CuO as an oxygen carrier. They analysed combustion efficiency, carbon capture efficiency and split of sulphur between air and fuel reactor as a function of fuel reactor temperature. It was found that the concentration of SO_2 increased in the fuel reactor and decreased in the air reactor with increase in fuel reactor temperature. Additionally, it was concluded that high sulphur content solid fuel can be burnt in the CLOU using Cu based oxygen carrier to obtain high carbon capture efficiency. Adanez-Rubio et al. [Adanez-Rubio et al., 2014a] performed experimental study on Milled pine wood chips using Cu based oxygen carrier in 1.5 kW_{th} continuous operated CLOU unit. The experimental work focussed on the effect of the fuel reactor temperature on carbon capture efficiency, which was found to be high as 95% at 900 °C by adopting a low solid circulation rate. The char conversion rate was 3 to 4 times higher as compared to integrated gasification CLC (*i*G-CLC).

From literature survey, it was found that the most of the studies have been investigated based on CLC and CLOU of coal and petcock but limited with biomass as fuel. Peltola et al. [Peltola et al., 2014] presented the calculation procedure and design criteria for SiO_2 supported CuO oxygen carrier using medium volatile bituminous coal as fuel. Their study investigated the various design and operational parameters, thermal considerations, exergy analysis that needs to be explored for the CLOU process development. Their suggested calculation procedure for the said oxygen carrier was then applied successfully for any oxygen carrier in the combustion of the solid fuel in interconnected fluidized based system.

Leion et al. [Leion et al., 2009] carried out experiments in laboratory fluidized bed reactor to investigate the conversion rate of different solid fuels in CLOU. A 40% CuO supported on 60% ZrO_2 as an oxygen carrier and six different solid fuels including coal and biomass char were considered for the investigation. They concluded that the conversion of solid fuels in the CLOU is found to be faster (three to fifteen fold increase) as compared to CLC. Leion et al. [Leion, H. et al., 2011] also presented an overview of parameters that affects the solid fuel conversion in CLC and CLOU. It was suggested that a higher volatile content fuel generally converts rapidly as compared to a low volatile content in either CLC and CLOU. Furthermore, fuel conversion is governed by char gasification in CLC, while in CLOU it is limited by release of oxygen from the oxygen carrier. In CLC, char gasification in presence of steam is found to be faster as compared to CO_2 as gasification agent. Their study also concluded that H_2 can inhibit solid fuel char gasification in CLC whereas CO did not seem to have any effect. In another study, Keller et al. [Keller et al., 2011] also conducted experiments in a laboratory fluidized bed reactor to investigate the inhibition effect of gasification products (CO and H_2). A cyclically redox experiments were carried out using two different oxygen carrier. Different concentrations of CO and H_2 together with steam as gasification agent and 10% O_2 in N_2 were used as reduction and oxidation agents, respectively. Experimental results revealed that CO did not show any inhibition for the gasification of char particles. However the partial pressure of H_2 had significant effect on the char conversion. It was also found that a better reactivity of oxygen carrier may help to reduce the gasification inhibition effect.

Adanez et al. [Adanez et al., 2013] compared the *i*G-CLC and CLOU process using different rank of coal. In *i*G-CLC, ilmenite as well as Fe-enriched sand fraction (71% Fe_2O_3) and 60% CuO supported on $MgAl_2O_4$ for CLOU were used as an oxygen carrier. Three different types of coal such as lignite, bituminous and anthracite were used to compare the combustion and carbon capture efficiency as a function of fuel reactor temperature. Experimental investigation found that the combustion was seen towards completion in CLOU whereas incomplete for *i*G-CLC. This is due to the fact that the later requires some additional arrangements such as oxygen polishing step for the complete conversion of fuel. Use of Carbon Separation System (CSS) was also suggested for both in *i*G-CLC and CLOU process for complete combustion of solid fuels.

2.6 Modelling of CLC and CLOU

ASPEN Plus is a widely used process flow simulation software which is able to simulate a combustion processes involving solid, liquid and gaseous fuels based on steady state process, sensitivity analysis and design optimization. Nikoo and Mahinpey [Nikoo and Mahinpey, 2008] developed a comprehensive process model in ASPEN Plus for biomass gasification in an atmospheric fluidized bed gasifier. Their proposed model for the gasification includes both reaction kinetic modelling and hydrodynamic parameters. Simulation study concluded that production of hydrogen and carbon monoxide increases with steam to biomass ratio. Meng et al. [Meng et al., 2015] deployed ASPEN Plus to simulate and analyse the single stage and multi-stage solid fuel CLC system. The main aim was to propose a multi-stage CLC of coal in order to reduce the unburnt carbon in the fuel reactor. This will then lead towards extracting a maximum energy from the fuel. The dependency of net energy output on the reactor volume was also investigated using ASPEN Plus. Li et al. [Li et al., 2014] presented the overall process simulation of the co-firing torrefied biomass in a 220 MW_{th} coal-fired power plant in ASPEN Plus. Processes such as biomass drying, biomass torrefaction, devolatilization, char combustion and heat exchanger were simulated using inbuilt ASPEN Plus blocks. The simulated results were found to agree well with experimental results and same were used for the scale up of the existing set-up. Zhou et al. [Zhou et al., 2013] demonstrated the ability of ASPEN Plus by proposing a detailed process simulation of the CLOU experimental study of Abad et al. [Abad et al., 2012]. They compared the simulation results with experimental results of the reactor gas extent, carbon capture efficiency, decomposition of gaseous oxygen and energy released from both air and fuel reactors. Additionally, three different types of coal were considered to investigate their effects on CO_2 concentration in fuel reactor and the overall energy output in CLOU of coal.

Sahir et al. [Sahir et al., 2014] developed a process simulation for PRB bituminous coal in CLC and CLOU using Fe_2O_3/Al_2O_3 and CuO/ZrO_2 based oxygen carriers, respectively. Their developed process models evaluated the material and energy requirements for a pilot-scale unit by incorporating results from previously reported kinetic studies on lab-scale units. Their study performed an economic analysis which can address the key technical challenges required to develop CLC and CLOU for solid fuel. Li et al. [Li et al., 2010] simulated the Biomass Direct Chemical Looping (BDCL) process using ASPEN Plus. A multistage model was developed to investigate system performance and mass and energy management scheme for BDCL process. The developed model also predicted the optimum operating conditions for the reactors used. The results also showed that the BDCL process was significantly more efficient than conventional biomass conversion processes. The process had the potential in thermo-chemically converting biomass to hydrogen and/or electricity with high efficiency. Simulation study by Gopaul et al. [Gopaul et al., 2014] compares the two Chemical Looping Gasification (CLG) processes using poultry litter as biomass for H_2 production using the ASPEN Plus simulator.

Overall the literature survey revealed that credible platform could be provided by ASPEN Plus for successful simulation of solid fuel CLC especially when a wide range of experimental data with CLC and CLOU is available. ASPEN Plus can be used for developing and simulating a flowsheet in scaling up a CLC or CLOU process using published experimental data. However, limited work has been published regarding the combustion of biomass and co-combustion of coal and biomass using CLC and CLOU configuration. Also, using biomass in the co-combustion with coal may propose as the short term solution for mitigation of CO_2 concentration in the atmosphere. It also offers lower cost of carbon capture than any other CO_2 capture technologies [Khorshidi et al., 2013]. We shall hence focus on the use of this platform to simulate the CLC and CLOU of Biomass and/or Coal mixture and also evaluate its material and energy balances. The next chapter discusses the ASPEN Plus model of CLC and CLOU in general and procedure to carry out the process simulation. Thereafter chapter 4, 5 and 6 discusses the results for biomass and coal/biomass mixtures in term of performance parameters such as carbon capture efficiency, char conversion, the overall conversion to carbonaceous gases and energy analysis in CLC and CLOU.

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CHAPTER 3

Computational Details

3.1 Introduction

Large process industries and power plants needs to employ many components or operation to perform its assigned task. Many components together form a process flow sheet with definite direction. Process flowsheet can simply be defined as a blue print of a plant or part of it. It identifies all feed streams, unit operations, streams that inter-connect the unit operations and finally the product streams. Solution of chemical processes through process flow sheet is a fundamental aspect for any chemical engineer. Operating conditions and other technical details are included depending on the detail level of the flowsheet. The level can vary from a rough sketch to a very detailed design specification of a complex plant. For steady-state operation, any process flowsheet leads to a finite set of algebraic equations. For a case where we have only one reactor with appropriate feed and product streams the number of equations may be manageable by manual hand calculations or simple computer applications.

The complexity of a flowsheet increases with inclusion of number of components and recycle streams. At this point, the number of equations needs to be solved simultaneously. In these cases, solving the set of algebraic equations becomes a challenge in itself. In this scenario computer applications or process flowsheet simulators specialized in solving these kinds of large equation sets is necessary. Some well-known process flowsheet simulators known till date are ASPEN Plus and CHEMCAD [Nikoo and Mahinpey, 2008, Sahir et al., 2014, Meng et al., 2015, Lu et al., 2005]. These products have highly refined user interfaces and on-line component databases. They are used in real world applications from interpreting laboratory scale data to monitoring a full scale plant. In the current thesis we have adopted ASPEN due to its extensive reactor modules which is core application of this thesis.

3.2 ASPEN based Simulation

ASPEN Plus is a sequential modular simulator to obtain solution of flowsheet based on chemical processes employed by chemical engineers. ASPEN stand for the Advanced System for Process Engineering and it was developed by researchers at MIT. The sophisticated software package can be used in almost every aspect of process engineering from design stage to cost and profitability analysis. It has a built-in model library for reactors, separators, heat exchangers and distillation columns to name a few. Customized or property models can extend its model library. The user models are created with FORTRAN subroutines or Excel worksheets and can then be added to its model library. During the calculation of the flow sheet any missing parameter can be estimated by inbuilt library for group contribution methods such as UNIFAC.

The ASPEN Plus document format can retain the results and run information. In backup mode the work get saved as a standard ASCII text file and changes made in this file can be used as an input to the simulation engine from the command line. It is easy to transfer this file from one machine to another. However, it does not retain the results or run information in it. Moreover, a project can be saved as a 'Template' and can used as a starting point for another simulation. While working on a project it is a good idea to save the simulation in ASPEN Plus document format. A file in backup format will be hence created automatically.

3.3 Application to CLC and CLOU

In the present thesis, chemical looping combustion (CLC) and chemical looping with oxygen uncoupling (CLOU) of solid fuel is simulated and analysed using ASPEN Plus simulator. Most of the literature as seen in chapter 2 has suggested interconnected fluidized bed system to execute either CLC or CLOU of solid fuels. In this regard, different inbuilt models for reactors are used to simulate the actual experimental setup. In the subsequent sections, step by step procedure is described to evaluate the

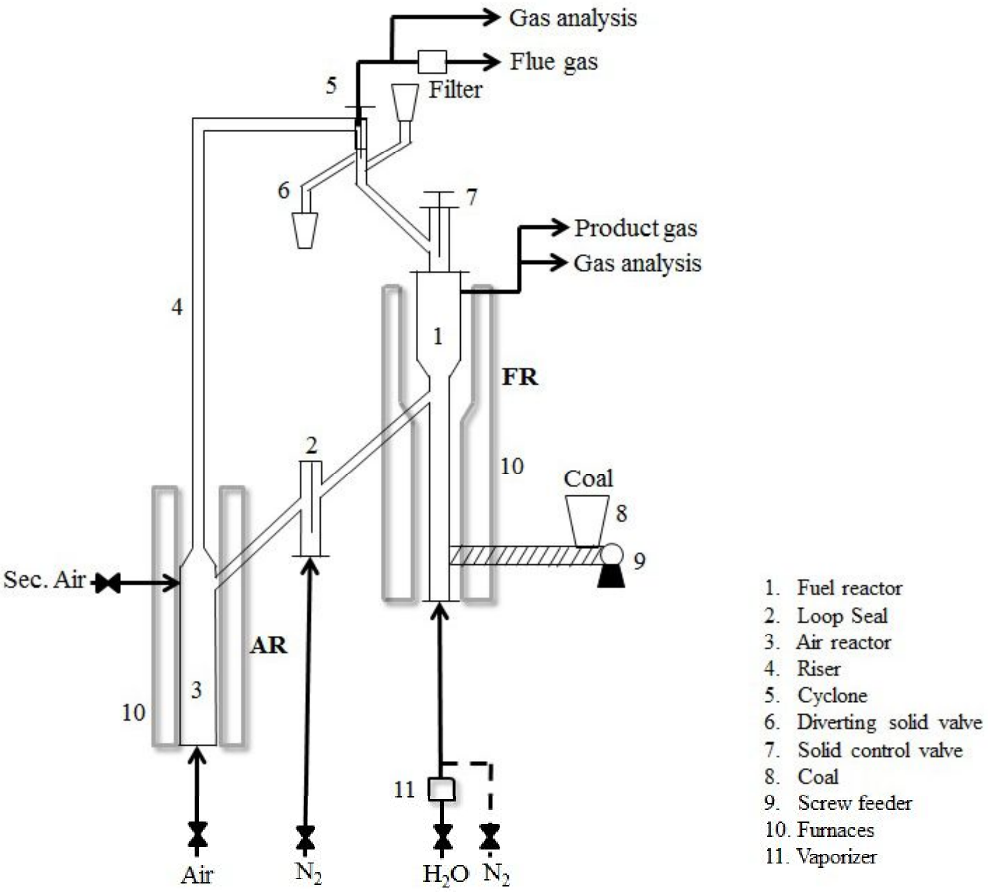

Figure 3.1: Schematic view of the CLC or CLOU experimental set-up. [Abad et al., 2012]

simulation process for CLC and CLOU of solid fuel as per the setup given in Figure 3.1.

The heart of CLC and CLOU processes is focussed on the use of strategies to supply required oxygen for fuel combustion indirectly by oxygen carrier particles. Therefore, selection of oxygen carrier particles for CLC and CLOU of solid fuels play a key role. For full conversion of solid fuel in the fuel reactor, the oxygen carrier flow rate needs to be decided in advance based on solid fuel flow rate. The circulation rate of oxygen carrier particles in the system is calculated by Eq. (3.1) [Mendiara et al., 2013]:

$$\Phi = \frac{F_{OC} R_{OC}}{\dot{m}_{SF} \Omega_{SF}} \tag{3.1}$$

Where, F_{OC} and R_{OC} indicates the mass flow rate (kg/h) and oxygen transport capacity of oxygen carrier particle, respectively. $\dot{m}_{SF}$ is the solid fuel feed rate in kg/h to the fuel reactor. The value of Ω_{SF}, kg of $\mathrm{O_2}$ required to convert the one kilogram of solid fuel into $\mathrm{CO_2}$ and $\mathrm{H_2O}$, can be calculated from the ultimate and proximate analysis of coal (or biomass) and is given by [Abad et al., 2012]:

$$\Omega_{SF} = \frac{f_C}{M_C} + 0.25\frac{f_H}{M_H} + 0.5\frac{f_N}{M_N} + \frac{f_S}{M_S} - 0.5\frac{f_O}{M_O} \tag{3.2}$$

where, f_i and M_i is the fraction and molecular weight of i^{th} component, respectively in ultimate analysis of solid fuel. A value of Φ=1 corresponds to the stoichiometric flow of oxygen carrier in CLC or CLOU so as to fully convert the considered solid fuel into $\mathrm{CO_2}$ and $\mathrm{H_2O}$.

3.3.1 CLC Process Simulation in ASPEN Plus

The simulation of CLC process with interconnected fluidized bed reactors is developed using ASPEN Plus process simulator as given in Figure 3.2 which resembles the actual experimental setup (Figure 3.1). In the present simulation study, the solid fuels such as pure biomass and mixture of coal and biomass is considered using iron based oxygen carrier [Gu et al., 2011]. The following reactions are said to take place inside the fuel and air reactor. The details of the reaction within each ASPEN component is explicitly specified in Table 3.1.

$$Biomass(s) \rightarrow Volatiles(g) + Char(C)(s) \tag{3.3}$$

$$Char(C)(s) + H_2O \rightarrow CO(g) + H_2(g) \tag{3.4}$$

$$CO(g) + 3Fe_2O_3(s) \rightarrow CO_2(g) + 2Fe_3O_4(s) \tag{3.5}$$

$$H_2(g) + 3Fe_2O_3(s) \rightarrow H_2O(g) + 2Fe_3O_4(s) \tag{3.6}$$

$$CH_4(g) + 12Fe_2O_3(s) \rightarrow 2H_2O(g) + CO_2(g) + 8Fe_3O_4(s) \tag{3.7}$$

$$\frac{1}{2}O_2(g) + 2Fe_3O_4(s) \rightarrow 3Fe_2O_3(s) \tag{3.8}$$

$$UnconvertedChar(C)(s) + O_2(g) \rightarrow CO_2(g) \tag{3.9}$$

The ASPEN Plus model of CLC of solid fuel (Figure 3.2), presents the connection of various components to represent the system level processes. Combustion of solid fuel includes processes like devolatilization of solid fuel, reduction of oxygen carrier particles and combustion of volatiles and char particles. It is not possible to simulate all these processes in a single ASPEN Plus component. Therefore, it is divided in various ASPEN Plus blocks. RYIELD is a specific yield based reactor which is used when product distribution is known without reaction stoichiometry. The yield of each component can be specified either in moles or mass per unit mass of fuel feed.

As shown in Table 3.1, pyrolysis of the solid fuel (e.g., biomass) is carried out in the RYIELD reactor. In present simulation, the yield of each component is specified in mass per unit feed of biomass fuel [Zhou et al., 2013]. The product of RYIELD reactor is transferred to RGIBBS reactor for residual char gasification using either steam (H_2O) or carbon dioxide (CO_2). RGIBBS establishes the chemical equilibrium composition between reactant and product. This reactor helps us in dealing with single phase or multi-phase reaction. RSTOIC is a stoichiometry based reactor which permits the use of a number of reactions.

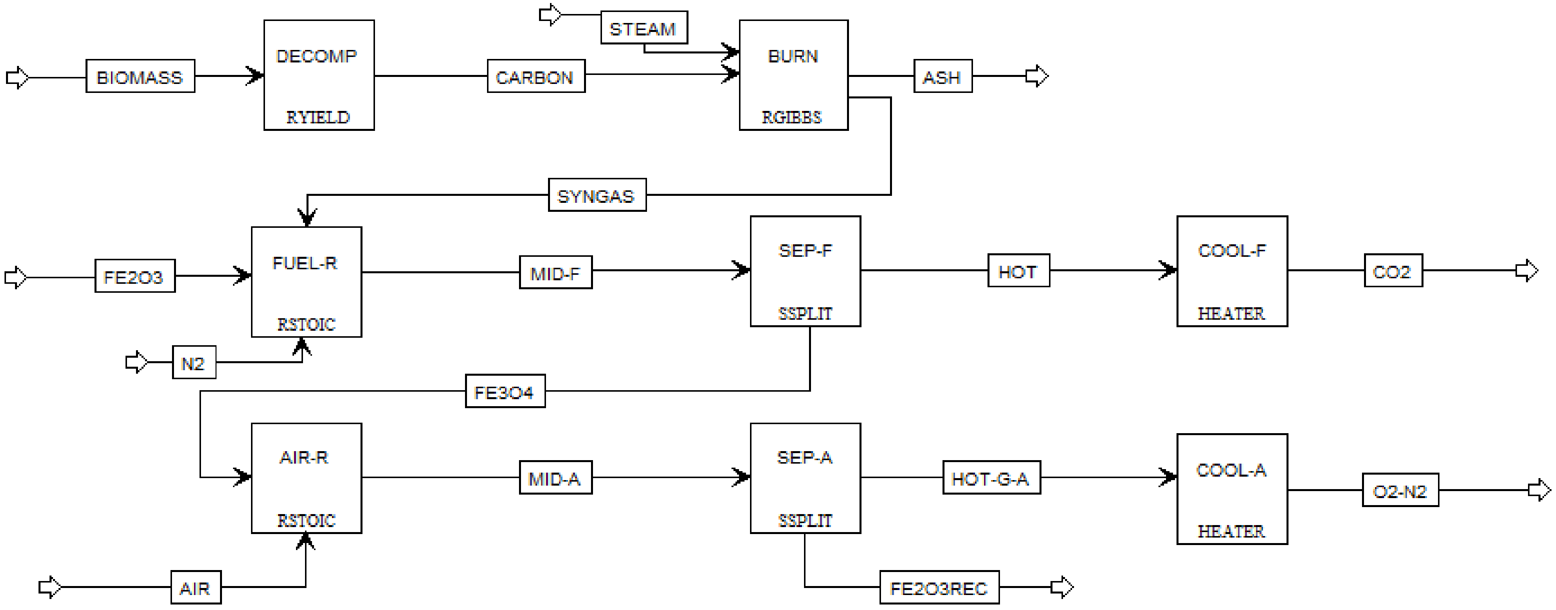

Figure 3.2: Overall Flow Sheet of CLC Process in ASPEN

Here one needs to provide a suitable molar extent of conversion or fractional conversion of a reactant. RSTOIC (fuel reactor) represents the combustion of generated flue gases in presence of oxygen carrier (e.g., Fe_2O_3) to produce CO_2, H_2O and Fe_3O_4 (Eq. 3.5-3.7) in fuel reactor. The above mentioned three reactors together present the fuel reactor of experimental set-up. This was necessitated as a single reactor was not able to model simultaneously pyrolysis of solid fuel, gasification of char particles and combustion of volatiles and gasified extents. The reduced oxygen carrier particles and a fraction of unconverted char particles moves to the air reactor via loop-seal. Loop-seal here prevents the gas flow between the two reactors. The air reactor is also modelled as RSTOIC reactor, where reduced metal oxide particles get oxidised by O_2 in atmospheric air (Eq. 3.8). Unconverted char particles also tend to react with the oxygen in air (Eq. 3.9). Thus the exit flue gas stream of air reactor contains unreacted O_2, N_2 and a small part of CO_2. Oxidized metal oxide particles then get transferred to fuel reactor via riser and cyclone separator. Cyclone separator then collects the oxidized particles, before sending it into fuel reactor to start a new cycle. To simulate the same, the mass flow rate of inlet metal oxides to fuel reactor (FE2O3) and outlet metal oxide from air reactor (FE2O3REC) are assumed to be same. This helps to accomplish the recirculation of metal oxide (Figure 3.2).

3.3.2 CLOU Process Simulation in ASPEN Plus

The CLOU process simulation with interconnected fluidized bed reactors is developed using ASPEN Plus process simulator as given in Figure 3.3. It presents the material streams that connect various ASPEN components to represent the system level processes. As discussed earlier, devolatilization of the solid fuel is carried out in the RYIELD reactor. The products of RYIELD reactor is transferred to RGIBBS reactor. As shown in Table 3.2, RSTOIC (fuel reactor) represents the reduction of oxygen carrier (e.g., CuO) to gaseous oxygen and its reduced form (Cu_2O). As shown in Figure 3.3, the gaseous oxygen is transferred to RGIBBS reactor and oxidation of volatiles and syngas is carried out in presence of gaseous oxygen to produce major concentration of CO_2 and H_2O

Table 3.1: ASPEN Plus Process model components to represent CLC system

Name	Model in ASPEN Plus	Function	Reactions
DECOMP	RYIELD	devolatilization of biomass	Eq. (3.3)
RGIBBS	RGIBBS	biomass char gasification	Eq. (3.4)
FUEL-R	RSTOIC	oxygen carrier reduction by volatilization and gasification products	Eq. (3.5-3.7)
AIR-R	RSTOIC	oxidation of reduced metal oxides and char conversion	Eq. (3.8-3.9)
SEP-F	SSPLIT	separation of reduced oxygen carrier particles and flue gas	
SEP-A	SSPLIT	separation of oxidized carrier particles and flue gases	
COOL-F	HEATER	fuel reactor exit gas stream cooler	
COOL-A	HEATER	air reactor exit gas stream cooler	

(Eqs. 3.10-3.12). The above mentioned three reactors together present the fuel reactor of experimental set-up. The details of the reaction within each ASPEN component are explicitly specified in Table 3.2.

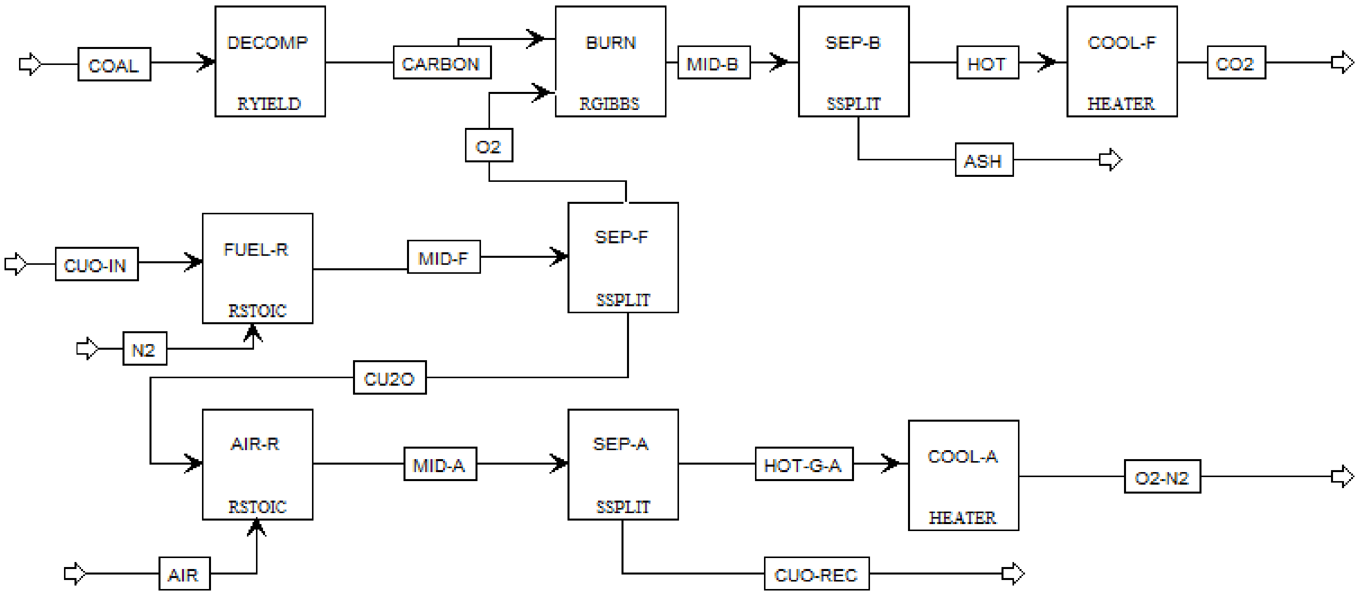

Figure 3.3: Overall Flow Sheet of CLOU Process in ASPEN

Table 3.2: ASPEN Plus Process model components to represent CLOU system

Name	Model in ASPEN Plus	Function	Reactions
DECOMP	RYIELD	devolatilization of coal	Eq. (3.10)
RGIBBS	RGIBBS	combustion of volatiles and char with gaseous oxygen	Eq. (3.12)
FUEL-R	RSTOIC	oxygen carrier conversion	Eq. (3.11)
AIR-R	RSTOIC	oxidation of reduced metal oxides	Eq. (3.13)
SEP-B	SSPLIT	ash and flue gas separation	
SEP-F	SSPLIT	O_2 and Cu_2O separation	
SEP-A	SSPLIT	CuO and gas separation	
COOL-F	HEATER	fuel reactor exit gas stream cooler	
COOL-A	HEATER	air reactor exit gas stream cooler	

After combustion of solid fuel in the fuel reactor, reduced oxygen carrier particles (Cu_2O) are moved to RSTOIC (air reactor) to carry out oxidation using oxygen in atmospheric air as presented in Eq. (3.13). Oxidized particles from the air reactor are transferred to the fuel reactor to start a new cycle. To simulate the same in ASPEN Plus, as shown in Figure 3.3, the mass flow rate of stream in the fuel reactor (CUO-IN) and exit stream from the air reactor (CUO-REC) are assumed to be same so as to accomplish the re-circulation of oxygen carrier particles. Such type of recirculation cannot be simulated explicitly in ASPEN Plus.

$$Coal(s) \rightarrow Volatiles(g) + Char(C)(s) \tag{3.10}$$

$$4CuO(s) \rightarrow O_2(g) + 2Cu_2O(s) \tag{3.11}$$

$$Char(C)(s) + Volatiles(g) + O_2(g) \rightarrow H_2O(g) + CO_2(g) \tag{3.12}$$

$$O_2(g) + 2Cu_2O(s) \rightarrow 4CuO(s) \tag{3.13}$$

The next chapter will discuss experimental validation of CLC using sawdust biomass in terms of gas concentration in reactors, conversion efficiency and carbon capture efficiency. It also focuses on energy analysis in CLC and CLOU configuration for sawdust biomass based on experimental results of coal.

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CHAPTER 4

Chemical Looping Combustion of Biomass

4.1 Introduction

Chemical Looping Combustion (CLC) has shown to be an effective way for the mitigation of greenhouse gases in atmosphere and has emerged as one of the most promising technologies for CO_2 capture. Both CLC and Chemical Looping with Oxygen Uncoupling (CLOU) have been investigated on the basis of fuel feeding rate and solid circulation rate in various studies. Further the effect of fuel reactor temperature on carbon capture efficiency and combustion efficiency has also been studied extensively. A significant amount of work has been investigated on CLC and CLOU of coal and petroleum coke but limited studies are available with biomass as fuel [Berguerand and Lyngfelt, 2008, Leion et al., 2008, Mattisson et al., 2009, Abad et al., 2012]. In this chapter, initially we will perform the CLC of biomass with the available experimental data of Shen et al. [Shen et al., 2009] and Gu et al. [Gu et al., 2011]. Thereafter both CLC and CLOU operation will be targeted on the same biomass using a oxygen carrier that was used by Sahir et al. [Sahir et al., 2014] for coal. This was required so as to compare the energy efficiencies of a both coal and biomass using similar kind of oxygen carrier.

4.2 Process Simulation of CLC in ASPEN Plus

The flowsheet for CLC with biomass is shown in Figure 4.1. In our study, the oxygen carrier used is 81.1% of Fe_2O_3 which is the reactive component and 15% SiO_2 and 2.9% Al_2O_3 as inert components (Table 4.1).

Table 4.1: Chemical Composition of Iron Ore (wt%) [Gu et al., 2011]

Fe_2O_3	SiO_2	Al_2O_3	P_2O_3	MnO	MgO	TiO_2	CaO	SO_3	Cr_2O_3	K_2O	NiO	V_2O_5
81.1	15	2.9	0.1	0.29	0.36	0.06	0.07	0.01	0.01	0.02	0.02	0.01

The sizes of fuel and oxygen carrier particles are used as 200-450 μm and 100-300 μm respectively. Table 4.2 shows the ultimate and proximate analysis of sawdust. The fuel reactor temperature is varied from 720 °C to 930 °C. It has been observed that at this temperature range, gasification of biomass is more efficient. Further at this temperature, it was also observed that less char particles move to the air reactor along with the reduced oxygen carrier particles. This eventually increases the carbon capture efficiency. The procedure to carry out the process simulation in ASPEN Plus along with function and significance of each ASPEN component is already discussed in chapter 3, hence this is not taken up here.

Table 4.2: Proximate and Ultimate analysis of Sawdust. [Gu et al., 2011]

Proximate analysis (wt%)		**Ultimate analysis (wt%)**		**LHV (MJ/kg)**
Moisture	14.28	Carbon	37.43	14.5
Volatile matter	74.61	Hydrogen	5.61	
Fixed carbon	10.1	Oxygen	40.55	
Ash	1.01	Nitrogen	1.02	
		Sulphur	0.1	

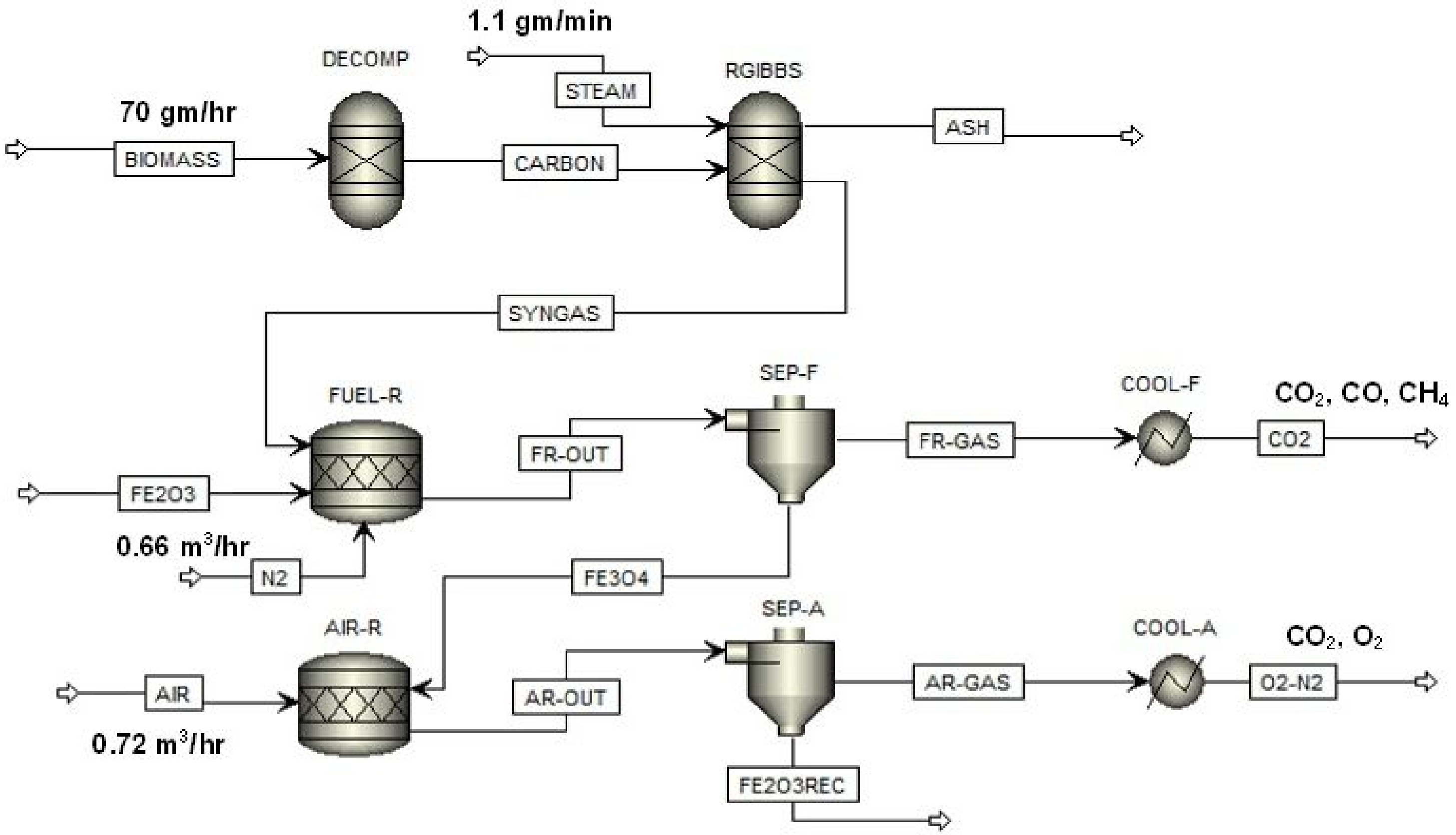


Figure 4.1: Overall flow sheet of CLC process in ASPEN Plus.

4.3 Results and Discussion

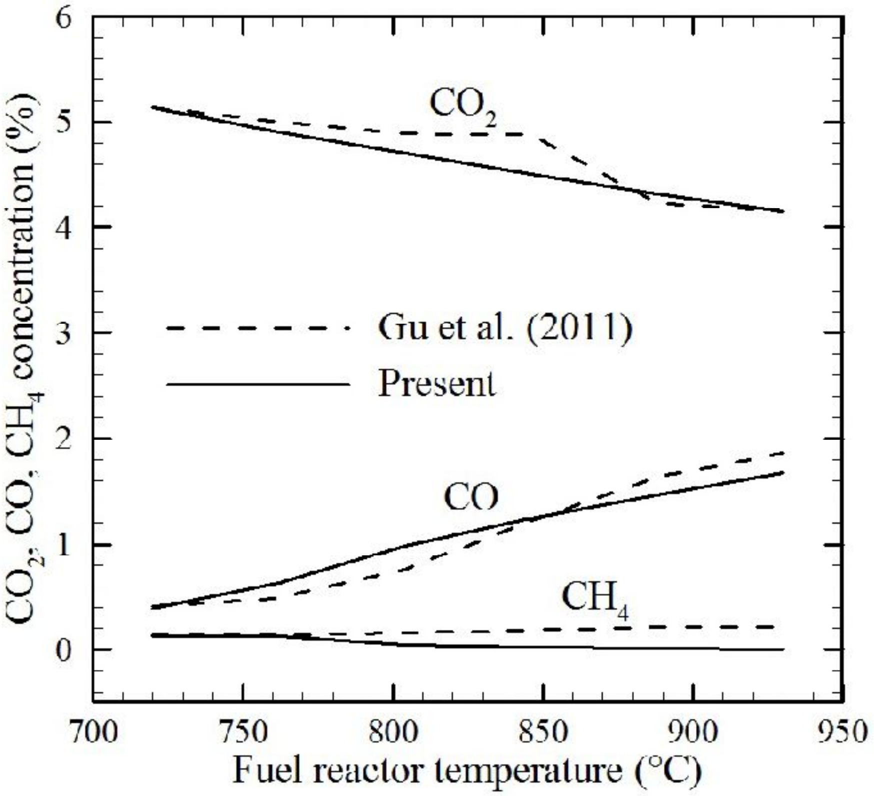
In this section, validation of experimental results is carried out. Simulation results are also presented to illustrate the effect of solid circulation rate and gasification agent on char conversion and carbon capture efficiency.

4.3.1 Gas Concentration in Reactors

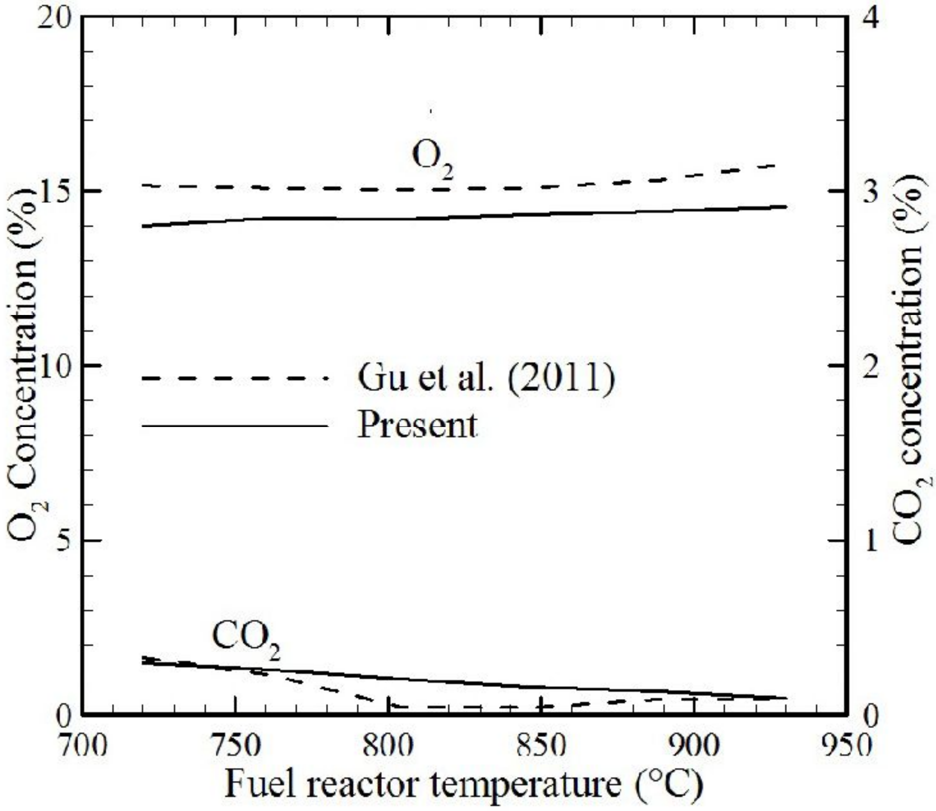
The effect of fuel reactor temperature is crucial for CLC of biomass in interconnected fluidized bed reactors. The results are presented to demonstrate the effect of fuel reactor temperature on gas concentration (Figure 4.2). As shown in Figure 4.1, the concentration of gases in the fuel reactor namely CO_2, CO and CH_4 were measured in the CO2 stream (Figure 4.1). In a similar manner O_2 and CO_2 from air reactor were measured in the O2-N2 streams. Figure 4.2a compares the simulated and experimental results of CO_2, CO, and CH_4 concentration in flue gases of fuel reactor as a function of fuel reactor temperature. It is observed that the presence of high temperature improves the biomass gasification and generates a higher fraction of CO and H_2. Owing to the poor oxygen transport capacity of Fe_2O_3, there is invariably an insufficient amount of oxygen for the complete combustion to CO_2. H_2 is not detected in the fuel reactor effluent which agrees with the experimental analysis as reported earlier [Shen et al., 2009, Gu et al., 2011]. Thus, concentrations of CO in flue gas of fuel reactor will increase rapidly, while concentration of CO_2 is seen to decrease. However, CH_4 concentration of the flue gas in fuel reactor is seen to remain constant.

The effect of fuel reactor temperature on the flue gas concentration of the air reactor was also investigated as shown in Figure 4.2b. In air reactor, the concentration of O_2 nearly remains same throughout the experiment, while concentration of CO_2 tends to decreases in flue gas with temperature.

The concentration of CO_2 in air reactor is made up of gas leakage from fuel reactor to air reactor and the product of residual char burnt in the fluidized bed air reactor.



(a)



(b)

Figure 4.2: Variation of (a) CO_2, CO, and CH_4 concentration in fuel reactor (b) O_2 and CO_2 concentration in air reactor with fuel reactor temperature.

Biomass char gasification gets enhanced at higher fuel reactor temperatures, thereby reducing char particles significantly in the fuel reactor. Subsequently, less char moves from fuel reactor to the air reactor. Thus, concentration of the CO_2 in air reactor flue gas was also found to decrease. Overall the predicted concentrations of CO_2, CO, CH_4 gases in fuel reactor and concentrations of O_2, CO_2 in air reactor agree fairly well with experimental results.

4.3.2 Conversion and Carbon Capture Efficiency

The performance of CLC in interconnected fluidized bed reactor system can be evaluated by the amount of carbon in biomass that is converted to CO_2 in the fuel reactor. Figure 4.3a shows the conversion efficiency ($\eta_{conversion}$) as a function of fuel reactor temperature. CO_2 conversion efficiency can be calculated as [Gu et al., 2011]:

$$\eta_{conversion} = \frac{W_{CO_2,FR}}{W_{CO_2,FR} + W_{CO,FR} + W_{CH_4,FR}} \tag{4.1}$$

where, $W_{CO_2,FR}$, $W_{CO,FR}$ and $W_{CH_4,FR}$ denote the volume percentage of CO_2, CO and CH_4 at the exit of the fuel reactor, respectively. The definition assumes that carbonaceous gases only contain CO_2, CO and CH_4 in flue gases of fuel reactor.

Conversion efficiency is an indicator of the carbonaceous gases in flue gas of fuel reactor that get converted to CO_2. Higher fuel reactor temperature generally tends to accelerate the gasification. However, due to poor oxygen transport capacity of Fe_2O_3, sufficient oxygen is not available for complete combustion to CO_2. Thus, an increase in fuel reactor temperature leads to the formation of more combustible carbonaceous gases while decrease leads to the conversion of the same to CO_2.

Predicted results using ASPEN Plus simulation and experimental results of Gu et al. [Gu et al., 2011] agree fairly well (Figure 4.3a). The carbon captured in the system comprises of the carbon contained in the volatile matter and the carbon in the char. Carbon capture efficiency depends on the conversion of char in the fuel reactor, X_{char}.

Char conversion is calculated by considering that the carbon in gases from the fuel reactor comes from the carbon content of both volatiles and converted char. Thus, the carbon from reacting char is simply the inlet carbon minus the flow of carbon in volatiles, $F_{C,vol}$. This char conversion can be calculated as [Mendiara et al., 2013]:

$$X_{char} = \frac{[F_{CO_2,FR} + F_{CO,FR} + F_{CH_4,FR} - F_{C,vol}]_{out}}{[F_{CO_2,FR} + F_{CO,FR} + F_{CH_4,FR} + F_{CO_2,AR} - F_{C,vol}]_{out}} \tag{4.2}$$

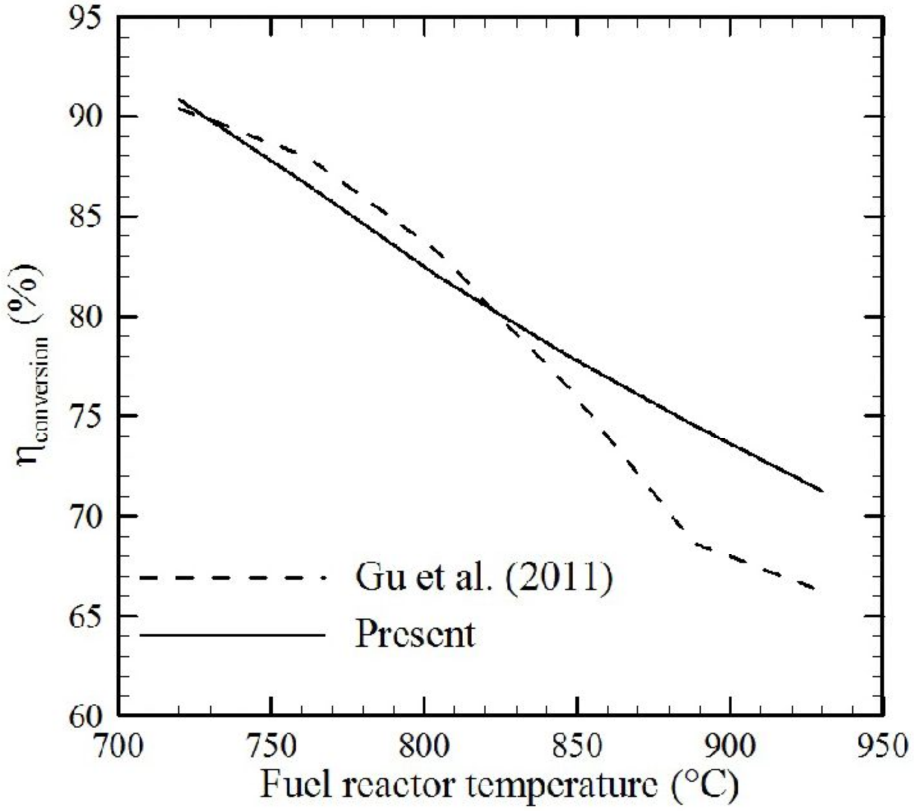
where, $F_{CO_2,FR}$, $F_{CO,FR}$ and $F_{CH_4,FR}$ are molar flow of CO_2, CO and CH_4 gas respectively, at exit of the fuel reactor. $F_{CO_2,AR}$ is molar flow of CO_2 at the exit of the air reactor while $F_{C,vol}$ is the carbon content in volatile matter. This definition also assumes that CO_2, CO and CH_4 are the only carbonaceous gases in flue gas originating from the fuel reactor. The carbon content in volatile matter can also be calculated using ultimate and proximate analysis of the sawdust as shown in Table 4.2 [Abad et al., 2012].

Figure 4.4 shows the variation of char conversion (X_{char}) and carbon capture efficiency (η_{cc}) with fuel reactor temperature. Carbon capture efficiency can be calculated as [Mendiara et al., 2013]:

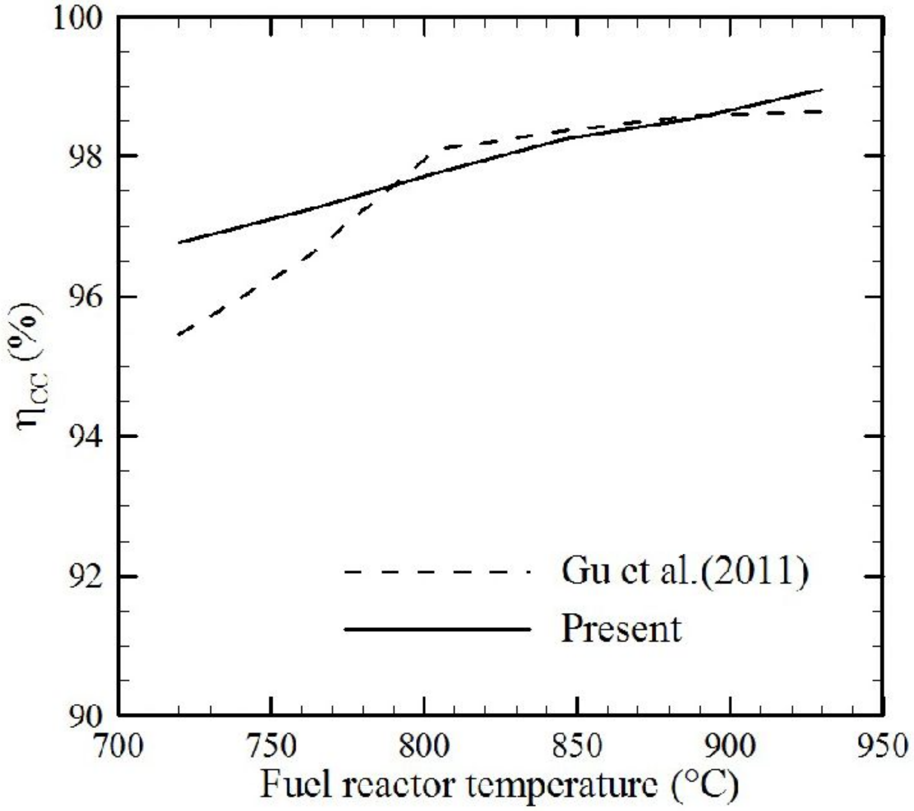
$$\eta_{cc} = \frac{[F_{CO_2,FR} + F_{CO,FR} + F_{CH_4,FR}]_{out}}{[F_{CO_2,FR} + F_{CO,FR} + F_{CH_4,FR} + F_{CO_2,AR}]_{out}} \tag{4.3}$$

The result for char conversion as a function of fuel reactor temperature is found to be similar to the results of Shen et al. [Shen et al., 2009].

It was found that a higher char conversion in the fuel reactor leads to a higher carbon capture efficiency. Figure 4.3b compares the predicted and experimental results of Gu et al. [Gu et al., 2011]. In an interconnected fluidized reactor system, the unconverted char particles in fuel reactor along with reduced oxygen carrier particles enter the air reactor. It results in a decrease in the carbonaceous gases. Thus a higher fuel reactor temperature also leads to a more efficient char conversion in the fuel reactor. Therefore,



(a)



(b)

Figure 4.3: Variation of (a) Conversion efficiency and (b) Carbon capture efficiency with fuel reactor temperature.

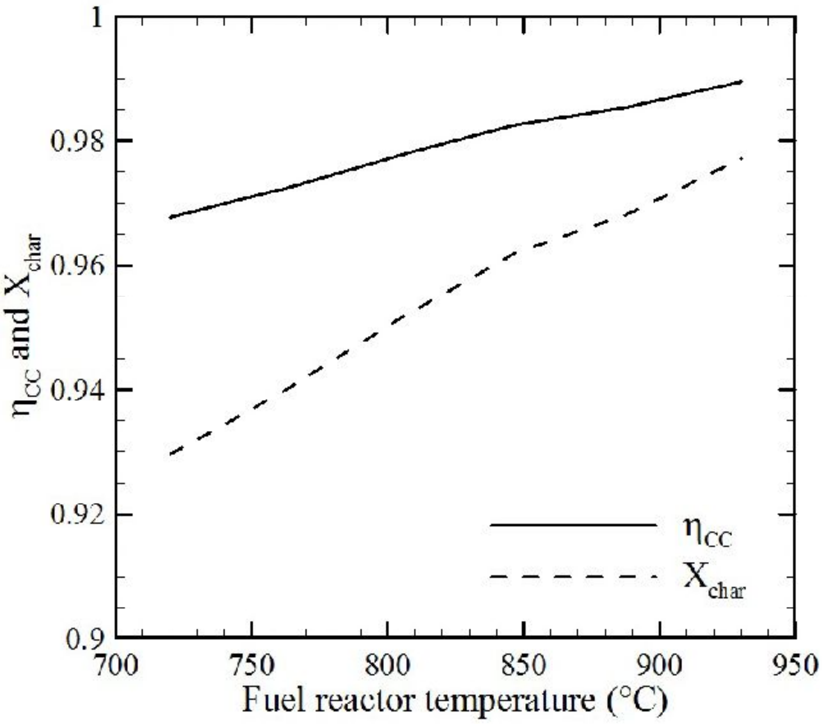


Figure 4.4: Variation of char conversion and carbon capture efficiency with fuel reactor temperature.

very little char would be transferred to the air reactor at higher temperatures. In a similar manner higher temperature leads to reduced CO_2 concentration in flue gases in air reactor, which ultimately leads to better carbon capture efficiency.

4.3.3 Effect of Solid Circulation Rate

Solid circulation rate is defined as the amount of oxygen carrier particles transferred in the system per unit time. The increase in solid circulation rate increases the oxygen available for the combustion of the gases generated during devolatilization/gasification of biomass fuel in the fuel reactor. From the previous work by Mendiara et al. [Mendiara et al., 2013] with pine wood as biomass fuel, it was known that the higher value of oxygen carrier to fuel ratio (Φ) would not affect char conversion and carbon capture efficiency significantly.

Figure 4.5 shows the effect of solid circulation rate on char conversion and carbon capture efficiency of biomass CLC. The solid circulation rate was varied from 2.24 to 10.08

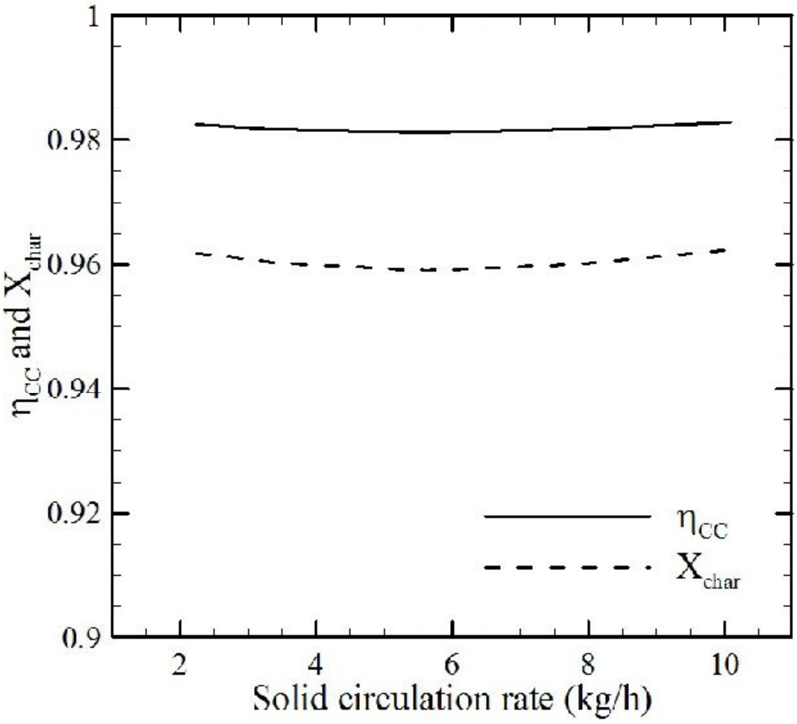


Figure 4.5: Variation of char conversion and carbon capture efficiency with solid circulation rate.

kg/h, corresponding to Φ values from 1 to 4.5 (Eq. 3.1). The fuel reactor temperature was maintained at 846 °C. It is seen that no significant changes were observed in char conversion and carbon capture efficiency. At high solid circulation rate, the results are found to be similar regarding the char conversion and carbon capture efficiency as observed experimentally by Mendiara et al. [Mendiara et al., 2013]. Results have revealed that higher oxygen carrier to fuel ratio (Φ) leads to sufficient oxygen for the combustion of flue gases. However, significant benefits with respect to char conversion and carbon capture efficiency were not observed. Hence, other options should be explored to improve the performance of CLC of biomass.

4.3.4 Effect of Gasifying Agent

In most of the experimental CLC work, steam was used as gasifying agent. Results from previous Cuadrat et al. [Cuadrat et al., 2012] work with coal, have shown that the use of CO_2 as gasification agent had limited effect on carbon capture efficiency. Char

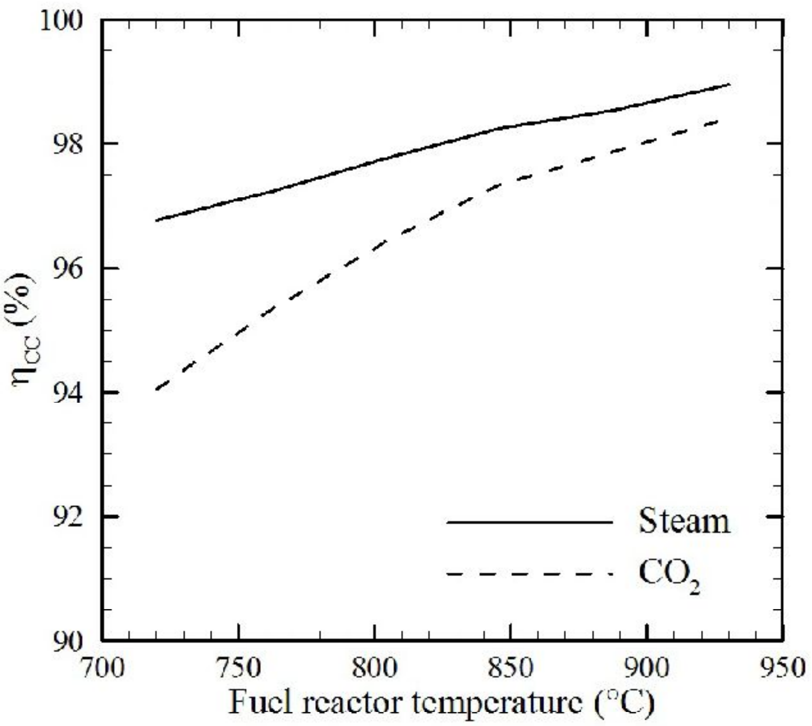


Figure 4.6: Variation of carbon capture efficiency with steam and CO_2 as gasification agent.

gasification was found to be lower while using CO_2 as gasifying agent when compared to steam. In the flowsheet, CO_2 is considered as the gasifying agent for the following two reasons: first, CO_2 is readily available as a flue gas and secondly the cost associated with steam generation is generally avoided. This is the reason we tried to explore this fact in the flow sheet (Figure 4.1).

Figure 4.6 shows the effect of CO_2 and steam as gasifying agent on carbon capture efficiency. At fuel reactor temperatures of 720 °C to 930 °C, the difference in carbon capture efficiency is 2.7% and 0.53%, respectively, using CO_2 as compared to steam as gasification agent. Significant benefits are not obtained using either CO_2 or steam as gasifying agent. Thus, it can be concluded that dry CO_2 from the gas leaving the fuel reactor can be used instead of steam as gasification agent in biomass CLC. This was also concluded by Mendiara et al. [Mendiara et al., 2013] in their experimental study.

4.4 Energy Analysis

Comparison of material and energy analysis has been carried out for sawdust biomass combustion in CLC and CLOU using ASPEN Plus flow sheeting. Oxygen carrier composition is considered based on published work of Sahir et al. [Sahir et al., 2014] for comparison of energy analysis using sawdust biomass as CLC and CLOU fuel. CLC is carried out with 60% Fe_2O_3 on Al_2O_3 along with a circulation rate of 66.4 kg oxygen carrier/kg biomass fuel. In a similar manner simulation were carried out with CLOU having 40% CuO on ZrO_2 based oxygen carrier with a circulation rate of 75 kg oxygen carrier/kg biomass fuel.

4.4.1 CLC of Biomass

We shall now initiate a flowsheet as per the reported OC or oxygen carrier of Sahir et al. [Sahir et al., 2014] which is 60% Fe_2O_3/Al_2O_3. This was necessitated for a comparable prediction of energy analysis for both CLC and CLOU. In a similar work, Meng et al. [Meng et al., 2015] used RPLUG reactor for the gasification step of coal. It incorporated small reactors to carry out complete combustion of coal. In the present work, RYIELD reactor has been used so as to consider a complete conversion of biomass as it is considered a highly reactive fuel when compared to coal. This ensures that multi-staging is not required for biomass fuel to carry out complete conversion. Moreover, the working pressure of fuel reactor and air reactor as used in Meng et al. [Meng et al., 2015] was kept at 10 atm since gasification process gets improved at higher pressure. The current work was carried out at atmospheric pressure on similar lines as Gu et al. [Gu et al., 2011].

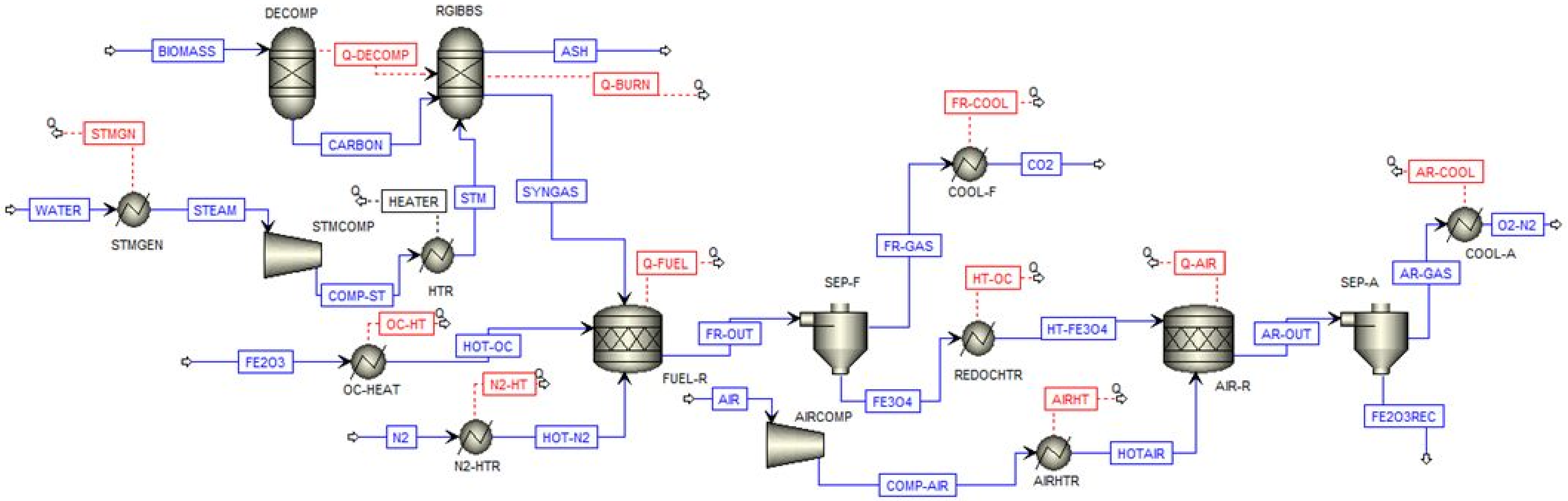


Figure 4.7: Process flow sheet for CLC of Sawdust with 60% Fe_2O_3/Al_2O_3.

Figure 4.7 shows the biomass CLC process flow sheet in ASPEN Plus simulator for material and energy analysis. A fuel flow rate of 70 gm/h is considered for both the CLC and CLOU arrangements. Devolatilization and char gasification in presence of steam is presented by RYIELD and RGIBBS reactors respectively. The actual combustion takes place in RSTOIC reactor by the reduction of oxygen carrier to the previously generated volatile matter and syngas. The reduced oxygen carrier particle along with unconverted char particles then moves to the air reactor. The air reactor here is modelled as RSTOIC reactor, where reduced metal oxide particles get oxidised by O_2 in atmospheric air (Eq. 3.8). In the air reactor, unconverted char particles also react with the oxygen in air (Eq. 3.9). The exit flue gas stream of air reactor contains unreacted O_2, N_2 and some CO_2. Thereafter the oxidized metal oxide particles get transferred to fuel reactor to commence a new cycle. To simulate the same, inlet metal oxide stream to fuel reactor (FE2O3) and outlet metal oxide from air reactor (FE2O3REC) are assumed to accomplish the recirculation of metal oxide (Figure 4.1). The process of solid fuel combustion in the CLC fuel reactor is shown in Figure 1.2a. Char gasification proceeds with either steam or CO_2.

As discussed earlier, gasification process is the rate limiting process in CLC. However, due to the high reactivity of the biomass fuel, the generation of volatile matter and syngas is quite high. Further the solid-gas reaction between oxygen carrier particles and generated products is a slow reaction. Therefore the exhaust gas of the fuel reactor contains unburned products like CO, H_2 and CH_4 along with CO_2 [Shen et al., 2009, Gu et al., 2011, Mendiara et al., 2013]. The required energy for the fuel reactor is generally supplied from the air reactor by oxygen carrier particles. Thus the air reactor temperature must be higher than fuel reactor temperature so as to achieve enhanced energy recovery from both the reactors.

To increase the oxidation of unburned products, the contact period of volatile matter and syngas with metal oxide should be high. This requires a larger residence time for the oxygen carrier particles in the fuel reactor. The analysis carried out in this study takes into account a residence time of 8 minutes in the fuel reactor for oxygen carrier based on previous experimental study [Mendiara et al., 2013]. On the other hand, higher value of oxygen carrier to fuel ratio (Φ) decreases the residence time in the fuel reactor. This will result in higher pressure drop and higher energy penalty for the fluidization of the particles. Moreover, increase in solid circulation rate of oxygen carrier also does not improve the carbon capture efficiency [Mendiara et al., 2013]. Thus a compromise needs to be arrived between oxygen carrier to fuel ratio and the residence time in the fuel reactor.

The air flow rate is kept at 351 gm/h for the CLC analysis. This analysis assumes an oxygen carrier residence time of 2 minutes in the air reactor, slightly higher than the measured combustion of pine sawdust using hematite as an oxygen carrier [Mendiara et al., 2013].

Table 4.3: Energy recoveries/utilization (W_{th}) in system components with CLC (Notations are as per Figure 4.7)

Energy Produced/Required	**Fuel reactor at 930 °C, Air reactor at 900 °C**	**Fuel reactor at 804 °C, Air reactor at 850 °C**
Fuel Reactor(Q-BURN+Q-FUEL)	-35	-55
Energy required/provided by oxygen carrier for fuel reactor (OC-HT)	-64	92
Total Fuel reactor	**-99**	**37**
Air reactor (Q-AIR)	251	263
Energy required/provided by oxygen carrier for air reactor operation (HT-OC)	56	-83
Heat air from 25°C to air reactor temperature (AIRHT)	-91	-85
Total Air Reactor	**216**	**95**
Heat steam from 150 °C to fuel reactor temperature (STMGN+HEATER)	-81	-76
Cool air reactor exhaust to 25 °C (AR-COOL)	76	71
Cool fuel reactor exhaust to 150 °C (FR-COOL)	171	141
Heating fluidizing gas from 25 °C to fuel reactor temperature (N2-HT)	-115	-98
Fluidization, Pumping and compression	-12	-12
TOTAL	**156**	**158**

Table 4.3 shows the two scenarios for the energy recoveries in the CLC simulation blocks and streams (Figure 4.7). The first scenario presents the fuel reactor at 930 °C, and air reactor at 900 °C. It shows that 99 W_{th} of energy needs to be supplied to the fuel reactor. The second scenario shows the analysis with the consideration of fuel reactor at 804°C, and air reactor at 850 °C. In this scenario, it is possible to gain 37 W_{th}

of energy from the fuel reactor along with energy recovered from the air reactor. This condition is not significant as the experimental set-up used by Gu et al. [Gu et al., 2011] was kept in the oven to compensate for the heat loss during the operation. This was possible due to the smaller capacity of an experimental set-up of 1 kW_{th}. Following a similar trend, Mendiara et al. [Mendiara et al., 2013] used separate electrical furnaces to supply necessary heat for the operation in a 500 W_{th} experimental set-up.

It should be noted that the selection of temperature in the respective reactors for the energy analysis is based on the conditions used in an earlier published experimental work of Shen et al. [Shen et al., 2009] and Mendiara et al. [Mendiara et al., 2013]. The results shown in the Table 4.3 for two different scenarios for CLC of biomass is in line with the results presented by Sahir et al. [Sahir et al., 2014] for the sub-bituminous coal. Approximately 158 W_{th} of energy could be recovered for the CLC of sawdust biomass with iron based oxygen carrier particle. As limited experimental studies were available for the CLC and CLOU of the biomass, the analysis is carried out based on the information available in the [Shen et al., 2009, Gu et al., 2011, Mendiara et al., 2013, Adanez-Rubio et al., 2014] literatures.

4.4.2 CLOU of Biomass

As presented in published literature [Abad et al., 2012, Adanez-Rubio et al., 2014], CLOU affords the combustion of the fuel in presence of gaseous oxygen. Production of gaseous oxygen is carried out by decomposition of oxygen carrier (CuO) in the fuel reactor (Eq. 3.11). A 40% CuO supported on ZrO_2 is considered as oxygen carrier in this simulation study. ZrO_2 acts as a supporting material to CuO and provide better strength to withstand higher fuel reactor temperature [Mattisson et al., 2009]. CLOU does not involve the gasification of the fuel char; hence the rate of combustion in the fuel reactor is high as compared to CLC [Mendiara et al., 2016]. It shows that compared to CLC, the residence time of oxygen carrier particles in the fuel reactor is also less. As a result, the fluidization energy cost is lower in CLOU as compare to CLC. It had been reported that the fluidization agent does not have any influence on the decomposition of oxygen carrier particles in the fuel reactor [Leion, H. et al., 2011]. Hence in present simulation, N_2 is used as a fluidization agent as per experimental work of Gu et al. [Gu et al., 2011] for comparison purpose of CLC and CLOU of sawdust biomass.

The process flow diagram of chemical looping with oxygen uncoupling (CLOU) for the sawdust is shown in Figure 4.8. As discussed in previous chapter, for accounting the combustion of fuel and decomposition of oxygen carrier particles in the fuel reactor, all the three variants are used (RYIELD, RGIBBS and RSTOIC). An air flow rate of 421 gm/h is used for the analysis for CLOU so as to fulfil the accomplished combustion with excess oxygen in the fuel reactor. CuO decomposition and Cu_2O oxidation with air in the fuel and the air reactor, respectively, is represented by Eq. (3.11) and Eq. (3.13).

The oxygen generation capacity of CuO was found to increase with the temperature of fuel reactor temperature. Adanez-Rubio et al. [Adanez-Rubio et al., 2014] concluded experimentally that more reactive fuel supports oxygen generation rate in the fuel reactor. In this study, the ratio of kg oxygen carrier/kg biomass is kept at 75 and sahir et al. [Sahir et al., 2014] has calculated corresponding ratio for coal as 129. However, a high volatile content and a more reactive char of the sawdust biomass do not present a significant difference in reaction rate in the CLC and CLOU.

Calculation of residence time is based on reduction and oxidation of OC which takes place in fuel and air reactor respectively. It helps to maintain the mass flow rate of OC at air reactor outlet and fuel reactor inlet. The equations used are [Eyring, E.M. et al., 2011]:

$$\tau_{FR} = \frac{1}{k_{r,CuO}} \ln \left(\frac{1}{1 - \left(\frac{\Delta X_s}{X_{CuO,AR}} \right)} \right) \tag{4.4}$$

$$\tau_{AR} = \frac{1}{k_{r,Cu_2O}} \ln \left(\frac{1}{1 - \left(\frac{\Delta X_s}{1 - X_{CuO,FR}} \right)} \right) \tag{4.5}$$

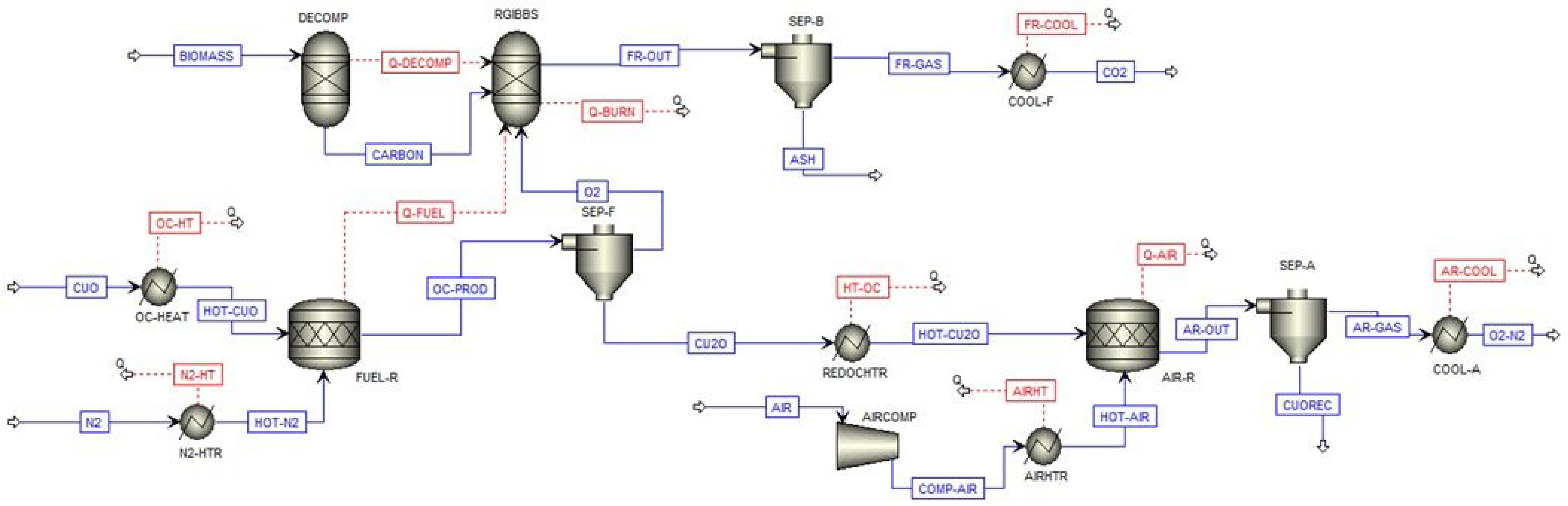


Figure 4.8: Process flow sheet for CLOU of Sawdust with 40% CuO/ZrO_2.

Here, $k_{r,CuO}$ and k_{r,Cu_2O} are the kinetic rate constants. Based on the above two equations, the residence time was calculated. The minimum loading quantity of Cu/MW_{th} of fuel is a function of mole ratio of CuO at exit of fuel reactor $X_{CuO,FR}$ and difference in mole ratio (ΔX_s). In the present simulation study, the values for $X_{CuO,FR}$ and (ΔX_s) have been kept as 0.32 and as 0.33, respectively. The approximate value of copper based oxygen carrier loading as obtained from Eyring et al. [Eyring, E.M. et al., 2011] is 128 kg Cu/MW_{th}. This gives a corresponding value of 160 kg CuO/MW_{th}. The conversion factor used in air and fuel reactor are chosen according to the temperature of air and fuel reactor [Eyring, E.M. et al., 2011]. The mole ratio of CuO at exit of fuel reactor $X_{CuO,FR}$ and difference in mole ratio (ΔX_s) realises a 51% conversion in the fuel reactor and 48% conversion in air reactor, respectively. Based on these data, the corresponding residence time were 32 and 44 seconds in the fuel reactor and air reactor, respectively.

For the energy analysis, the fuel reactor temperature is kept as 930 °C, while the air reactor temperature is at 900 °C. This is required so as to compare the energy recovery with CLC as discussed in the previous section. Table 4.4 presents the energy contributions and energy requirement associated with the various components and streams in ASPEN Plus simulator (Figure 4.8). The second scenario (Table 4.3) could not be worked out in CLOU as the decoupling process get strengthened due the higher temperature of 900 °C in the fuel reactor [Adanez-Rubio et al., 2014]. Results in Table 4.4 shows that the energy recovery is possible from both the reactors. Previously (in CLC) the recovery of fuel reactor was not possible. Moreover, the energy has to be supplied from the air reactor using the same corresponding temperatures for respective reactors. For comparison, 201 W_{th} is recovered from the CLOU process and the energy recovery from both the reactors in CLOU provides pathway for the complete solid fuel combustion to CO_2 and H_2O.

Overall the results are in line with respect to OC composition as used by Sahir et al. [Sahir et al., 2014]. For coal, the difference in energy output between CLC and CLOU

Table 4.4: Energy recoveries/utilization (W_{th}) in system components with CLOU (Notations are as per Figure 4.8)

Energy Produced/Required	**Fuel reactor at 930 °C, Air reactor at 900 °C**
Fuel Reactor(Q-BURN)	38
Energy required/provided by oxygen carrier for fuel reactor (OC-HT)	-28
Total Fuel reactor	**10**
Air reactor (Q-AIR)	150
Energy required/provided by oxygen carrier for air reactor operation (HT-OC)	27
Heat air from 25°C to air reactor temperature (AIRHT)	-104
Total Air Reactor	**73**
Cool air reactor exhaust to 25 °C (AR-COOL)	94
Cool fuel reactor exhaust to 150 °C (FR-COOL)	142
Heating fluidizing gas from 25 °C to fuel reactor temperature (N2-HT)	-115
Fluidization, Pumping and compression	-3
TOTAL	**201**

was found to be 84 kW_{th} (513 kW_{th} in CLOU - 429 kW_{th} in CLC); whereas in our work, for biomass it was 43 W_{th} (201 W_{th} in CLOU - 158 W_{th} in CLC). However, if we proceed for scale-up simulation with higher biomass feeding rate as shown by Zhou et al. [Zhou et al., 2013], we can expect a small difference in energy output for biomass fuel as compared to coal. This is primarily due to the constraint of complete combustion as gasification of char is a rate limiting process in CLC. In case of biomass, complete combustion is achieved due to faster reaction because of a higher volatile content as compared to coal. Hence in summary a complete combustion of fuel is proportional to energy output. Further for the CLC and CLOU of biomass; the difference in complete combustion is less as compared to coal [Mendiara et al., 2016, Leion, H. et al., 2011]. Hence a less costly and high melting point Fe based oxide particles can be recommended for CLC when compared to the high cost and less melting point of Cu based particles in CLOU to get a similar energy output for biomass.

With Biomass being studied exclusively in this chapter, we should now focus our attention on coal and biomass mixture as an alternate fuel for combustion in the next chapter. The co-combustion of biomass and coal as CLC fuel using iron based oxygen carrier particles will be attempted in the next chapter. Different performance parameters such as carbon capture efficiency, conversion efficiency and oxide oxygen fraction is again validated in ASPEN Plus. It shall also present the effect of different mass fraction of coal and biomass in mixture on the performance parameters.

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CHAPTER 5

Chemical Looping Combustion of Coal and Biomass

5.1 Introduction

As seen from previous chapter, the use of biomass as solid fuel in CLC can result in negative carbon emission as the $\mathrm{CO_2}$ produced with the combustion of biomass is previously removed from atmosphere during its growth [Li et al., 2014]. Biomass as fuel has been comprehensively studied in chapter 4 of the thesis. However, limited work has been published regarding the co-combustion of coal and biomass as CLC fuel. Hence the co-combustion of biomass and coal is proposed as the short term solution for mitigation of $\mathrm{CO_2}$ concentration in the atmosphere. It also offers lower cost of carbon capture than any other $\mathrm{CO_2}$ capture technologies [Khorshidi et al., 2013]. In the current context, the mixture of coal and biomass as fuel source also needs to be investigated both in terms of performance factors as well as energy consumption. The choice of oxygen carrier needs to be initially decided based on CLC results of previous work. Iron based oxide particles exhibit high reactivity during long continuous run with complete conversion of solid fuels [Mendiara et al., 2013, Nandy et al., 2016, Cuadrat et al., 2011, Basu et al., 2011]. Co-firing of different mass fractions of biomass with coal is also found to improve the plant performance and provide additional carbon credits [Basu et al., 2011, Khorshidi et al., 2013, Gayan et al., 2004, Li et al., 2015, Gu et al., 2011, Luo et al., 2013]. This will reduce the overall cost of carbon capture.

Shen et al. [Shen et al., 2009] investigated the CLC of sawdust with hematite as an oxygen carrier in 10 kW_{th} unit. Roberts and Harris(2007) [Roberts and Harris, 2007] reported coal char reaction with the mixture of $\mathrm{CO_2}$ and $\mathrm{H_2O}$ as gasification agent. Within the different oxides of iron, the conversion of hematite ($\mathrm{Fe_2O_3}$) to magnetite ($\mathrm{Fe_3O_4}$) reports the favourable conversion from thermodynamic point of view in CLC for the complete conversion of solid fuels to $\mathrm{CO_2}$ and $\mathrm{H_2O}$ [Gu et al., 2011, Shen et al., 2009].

Keeping the advantages in mind, this chapter focuses on CLC simulation of biomass and coal mixture as fuel in ASPEN Plus. Published experimental data of Gu et al. [Gu

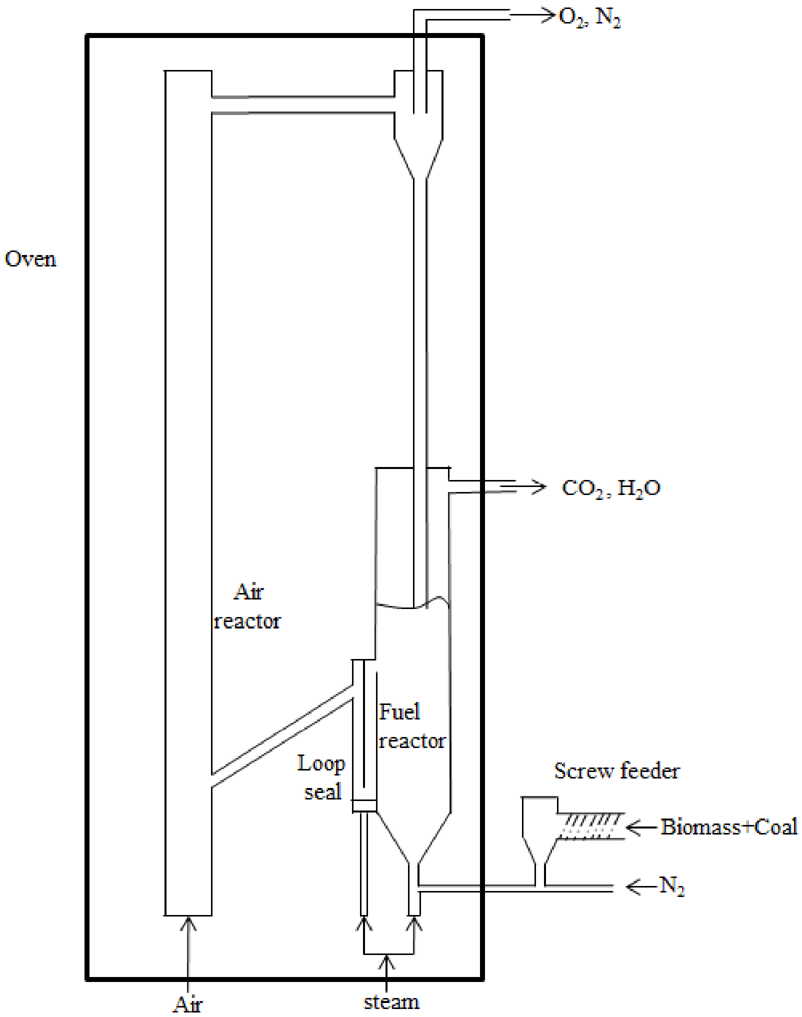


Figure 5.1: Schematic view of the experimental set-up. [Gu et al., 2011]

et al., 2011] will be used to simulate different processes of CLC using hematite (Fe_2O_3) as an oxygen carrier. The fuel reactor temperature range of 900-980 °C is used which is the same as per experimental condition. The effect of different mass fractions of coal and biomass in mixture on conversion efficiency, carbon capture efficiency and oxide oxygen fraction is also computed. Variation in carbon capture efficiency as a function of gasification agent and solids circulation rate is further discussed.

5.2 Process Simulation in ASPEN Plus

The experimental set-up as used by Gu et al. [Gu et al., 2011] will be used to model the co-combustion of biomass with coal using iron based oxygen carrier (Figure 5.1).

Table 5.1: Proximate and Ultimate analysis of Coal and Sawdust. [Gu et al., 2011]

	Sawdust	**Coal**
Proximate analysis (wt%)		
Moisture	14.28	6.01
Volatile matter	74.61	35.1
Fixed carbon	10.1	54.13
Ash	1.01	4.76
Ultimate analysis (wt%)		
Carbon	37.43	69.57
Hydrogen	5.61	4.3
Oxygen	40.55	13.81
Nitrogen	1.02	1.03
Sulphur	0.1	0.52
LHV (kJ/kg)	14.5	27.1

The set-up consists of two fluidized bed reactors connected by a loop-seal and cyclone separator. High velocity circulating fluidized bed as the air reactor and spout-fluidized bed as the fuel reactor were used. The spout-fluidized bed is connected to a fast fluidized bed with loop-seal at the bottom. The loop-seal is a rectangular fluidized bed. Loop-seal allows only reduced oxygen carrier particles and prevents the gas contamination between the two reactors. Sawdust as biomass and bituminous coal were used as fuels. Iron based oxygen carrier (Fe_2O_3) is used as the oxygen carrier.

Table 5.1 shows the ultimate and proximate analysis of the coal and biomass used to carry out simulation study. The size of fuel and oxygen carrier particles are 200-450 μm and 100-300 μm respectively, and is used in the ASPEN Plus simulation at atmospheric condition. The air flow rate and steam flow rate were used as 0.84 m^3/h and 2.5 gm/min respectively, while the N_2 flow rate was taken as 0.27 m^3/h. Fuel feeding rate in the fuel reactor was 120 gm/h using equal shares of mass fractions of biomass and coal using iron based oxygen carrier. The fuel reactor temperature is varied from 900 °C to 980 °C.

The CLC process simulation with interconnected fluidized bed reactors is developed using ASPEN Plus process simulator as given in Figure 5.2 and resembles the actual experimental setup of Figure 5.1. The ASPEN Plus model of CLC of coal and biomass mixture as shown in Figure 5.2, presents the connection of various components to represent the system level processes. Pyrolysis of the coal and biomass is carried out in the individual RYIELD reactors [Li et al., 2014]. The products of both RYIELD reactors are transferred to RGIBBS reactor for residual char gasification using steam. RSTOIC (fuel reactor) represents the combustion of generated flue gases in presence of oxygen carrier (Fe_2O_3) to produce CO_2, H_2O and Fe_3O_4 (Eq. 5.1-5.3) in fuel reactor. The above mentioned three reactors together present the fuel reactor of experimental set-up. This was necessitated as a single reactor was not able to model simultaneously pyrolysis of coal and biomass, gasification of char particles and combustion of volatiles and gasified extents. To carry out the process simulation in ASPEN Plus along with function and significance of each ASPEN component is discussed in chapter 3.

$$CO(g) + 3Fe_2O_3(s) \rightarrow CO_2(g) + 2Fe_3O_4(s) \tag{5.1}$$

$$H_2(g) + 3Fe_2O_3(s) \rightarrow H_2O(g) + 2Fe_3O_4(s) \tag{5.2}$$

$$CH_4(g) + 12Fe_2O_3(s) \rightarrow 2H_2O(g) + CO_2(g) + 8Fe_3O_4(s) \tag{5.3}$$

$$\frac{1}{2}O_2(g) + 2Fe_3O_4(s) \rightarrow 3Fe_2O_3(s) \tag{5.4}$$

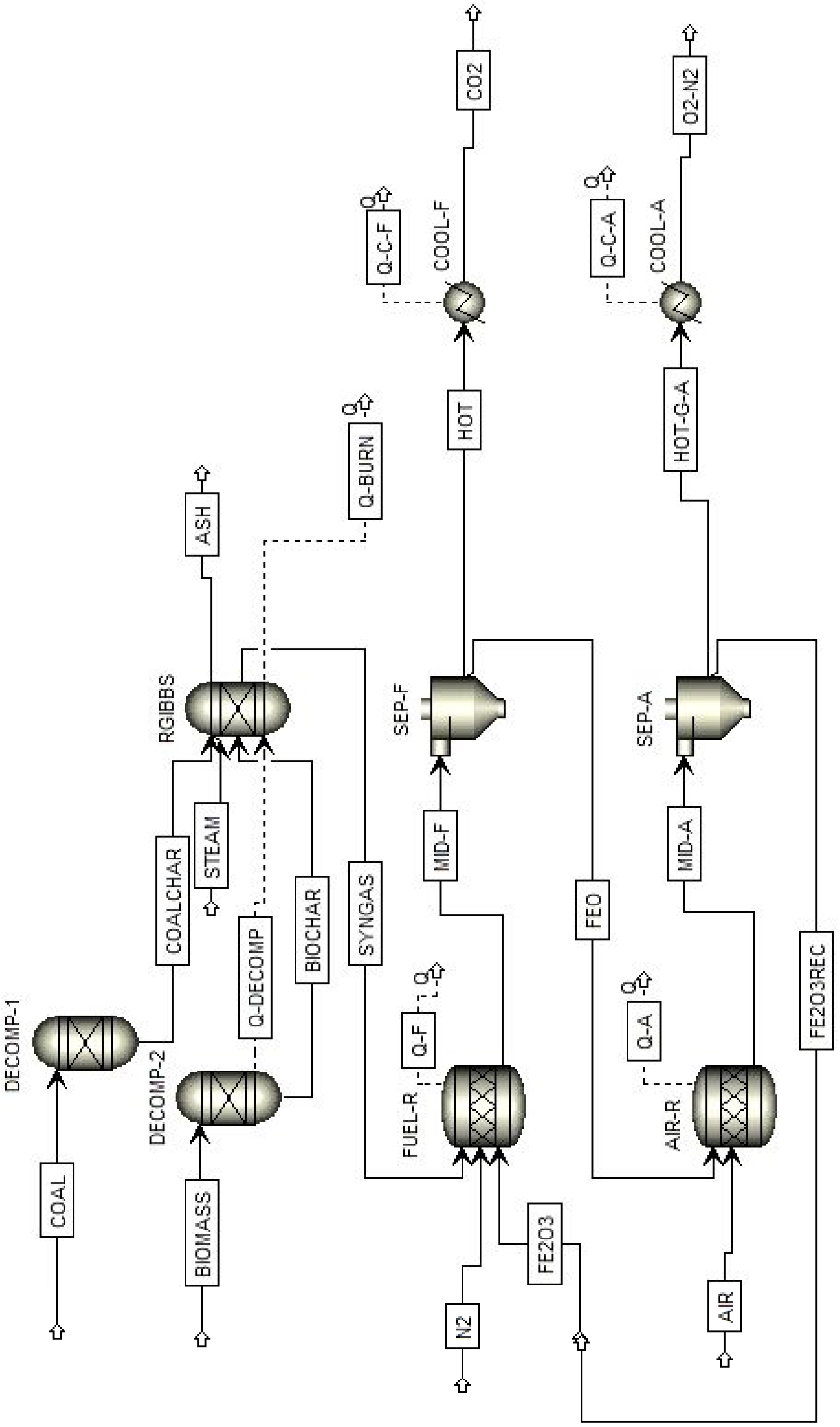


Figure 5.2: Overall process flow sheet of CLC in ASPEN Plus.

After combustion of coal and biomass mixture in the fuel reactor, reduced oxygen carrier particles (Fe_3O_4) are moved to RSTOIC (air reactor) to carry out oxidation (Eq. 5.4) using oxygen in atmospheric air. Oxidized particles from the air reactor are transferred to the fuel reactor to start a new cycle. To simulate the same in ASPEN Plus as shown in Figure 5.2, the mass flow rate of stream in the fuel reactor (FE2O3) and exit stream from the air reactor (FE2O3REC) are assumed to be same so as to accomplish the re-circulation of oxygen carrier particles. In CLC system of interconnected fluidized bed reactors, some unconverted residual char particles would exit from the fuel reactor to the air reactor. This gets reacted with atmospheric air. Thus the exit flue gas stream of the air reactor contains unreacted O_2, N_2 and CO_2. At higher fuel reactor temperature most of the char is converted in the fuel reactor. Thus, less char would be present in the air reactor, which would lead to lower CO_2 concentration in the air reactor.

5.3 Results and Discussion

5.3.1 Gas Concentration in Reactors

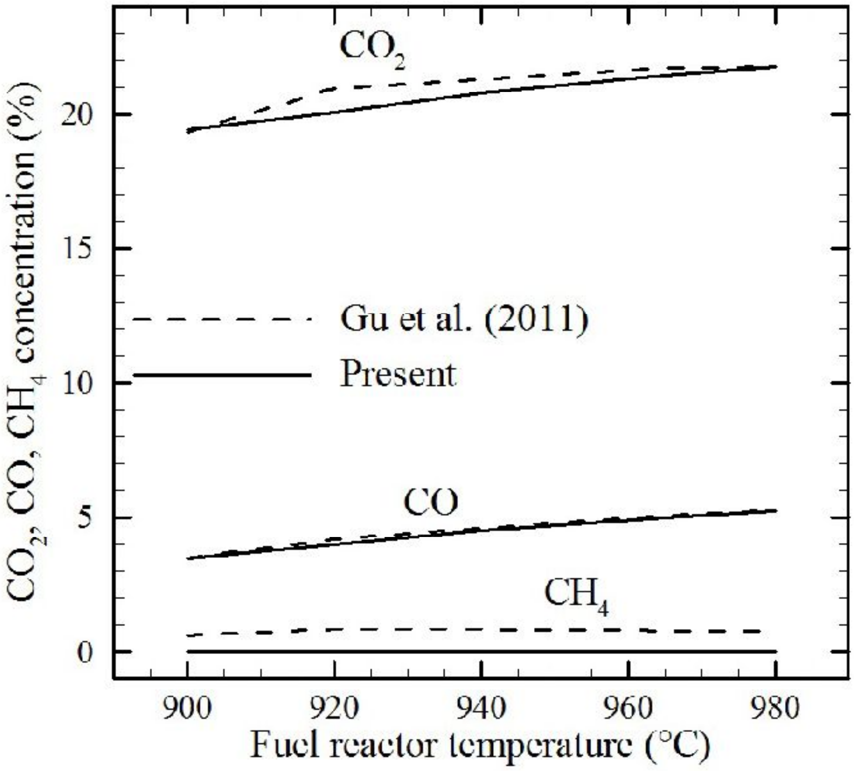
Figure 5.3a shows the comparison of experimental and numerically computed concentrations of different gases in the fuel reactor when a mixture (mass %) of biomass and coal (1:1) are used as fuel [Gu et al., 2011]. Fuel reactor temperature is varied from 900 to 980 °C. It is observed that the concentrations of CO and CO_2 in fuel reactor increases with the increase in the fuel reactor temperature, while the concentration of CH_4 was found to be independent of the fuel reactor temperature.

The mixture of biomass and coal get combusted in the fuel reactor [Luo et al., 2013]. Devolatilization of biomass and coal takes place at lower fuel reactor temperature. For biomass fuel, char particle conversion is faster due to the highly reactive fuel as compared to coal fuel. This may accelerate the syngas (CO and H_2) production, leading to reduction in time available for oxidation of the fuel because of the poor oxygen transport capacity of the iron based oxygen carrier particles. This leads to a increase in CO concentration. Char gasification using steam is rather a slow process in solid fuels CLC. However, the presence of alkaline earth metals in biomass can act as a catalyst in decreasing the activation energy for coal fuel. Therefore, we can expect that the products of coal and biomass gasification can interact more actively with oxygen carriers with the increase in the fuel reactor temperature. This process causes better oxidation and hence CO_2 concentration increases in the fuel reactor. Figure 5.3b presents the variation of gas concentration in the air reactor as a function of the fuel reactor temperature. With increase in the fuel reactor temperature, O_2 concentration remains constant while CO_2 concentration decreases. This is due to the fact that most of the char converted in the fuel reactor at higher fuel reactor temperature result in lesser or no char in the air reactor, leading to decrease in the CO_2 concentration.

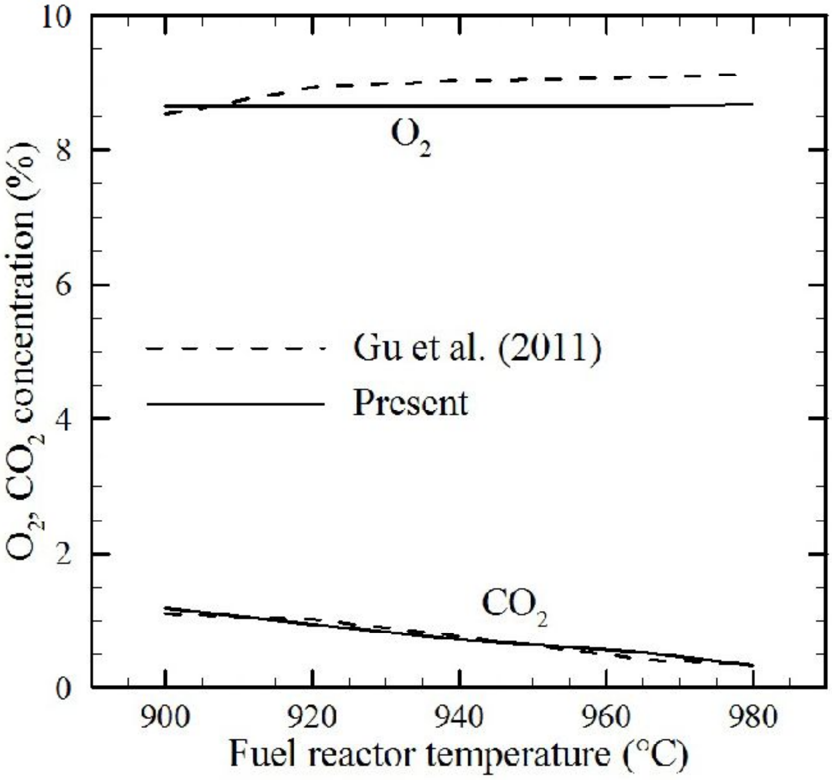
5.3.2 Conversion Efficiency

Figure 5.4 shows the variation of the conversion efficiency with the fuel reactor temperature. It represents the measure of the amount of carbonaceous gases converted to CO_2 in the fuel reactor and is defined as Eq. (4.1).

At higher fuel reactor temperatures, the production of the carbonaceous gases in the fuel reactor increases due to endothermic nature of char gasification reaction. Due to the poor oxygen transport capacity of the iron based oxygen carrier, carbonaceous gases do not completely convert to CO_2. This leads to decrease in the conversion efficiency. Thus the CLC of coal and biomass mixture with equal (1:1) and higher mass fraction of coal in the mixture resembles a CLC of pure coal. Figure 5.4 also shows the effect of different mass fractions of coal and biomass mixture on conversion efficiency. Ex-



(a)



(b)

Figure 5.3: Variation of (a) CO_2, CO, and CH_4 concentration in fuel reactor (b) O_2 and CO_2 concentration in air reactor with fuel reactor temperature.

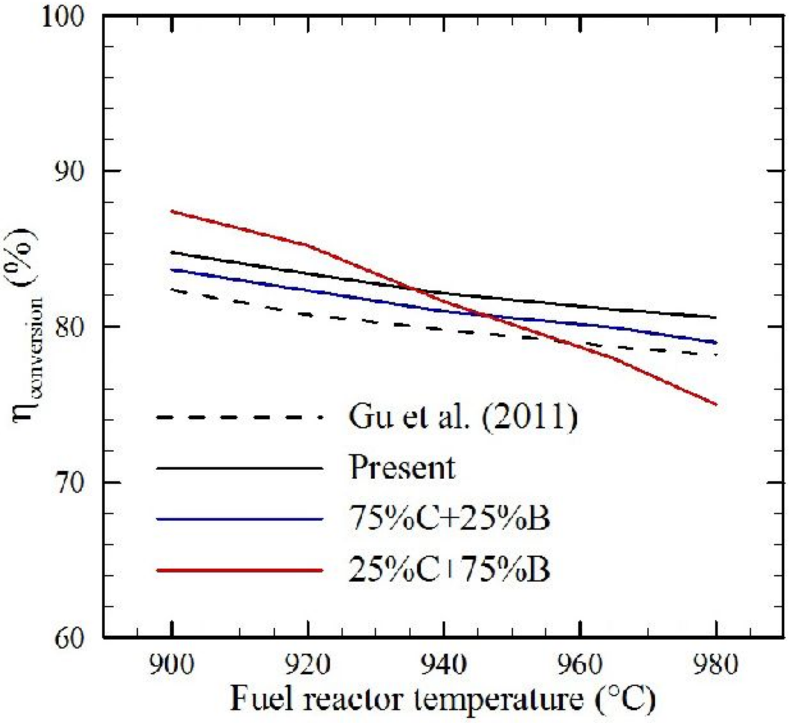
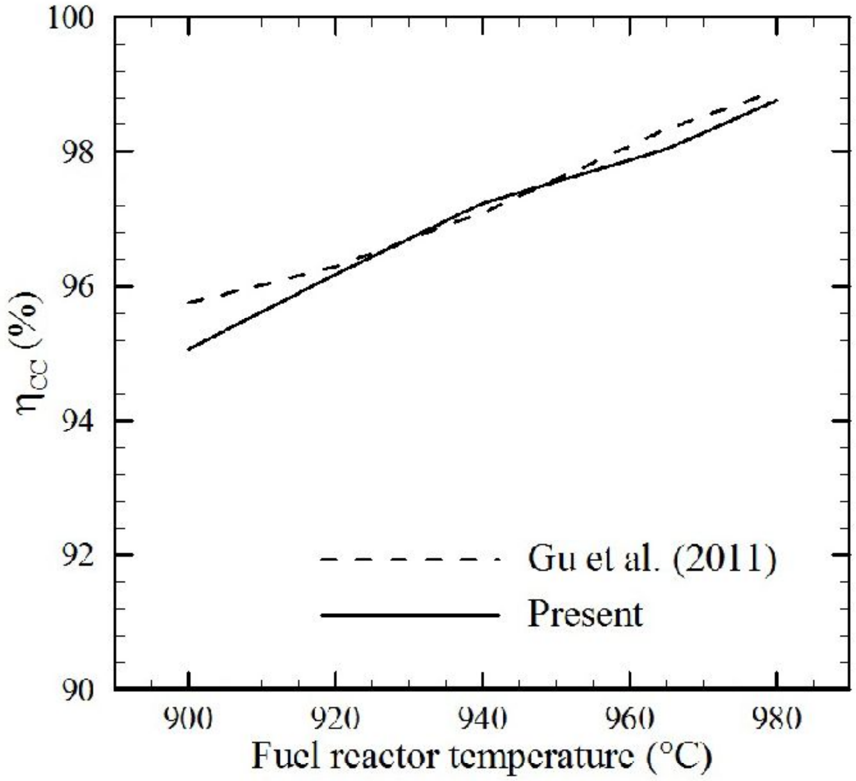
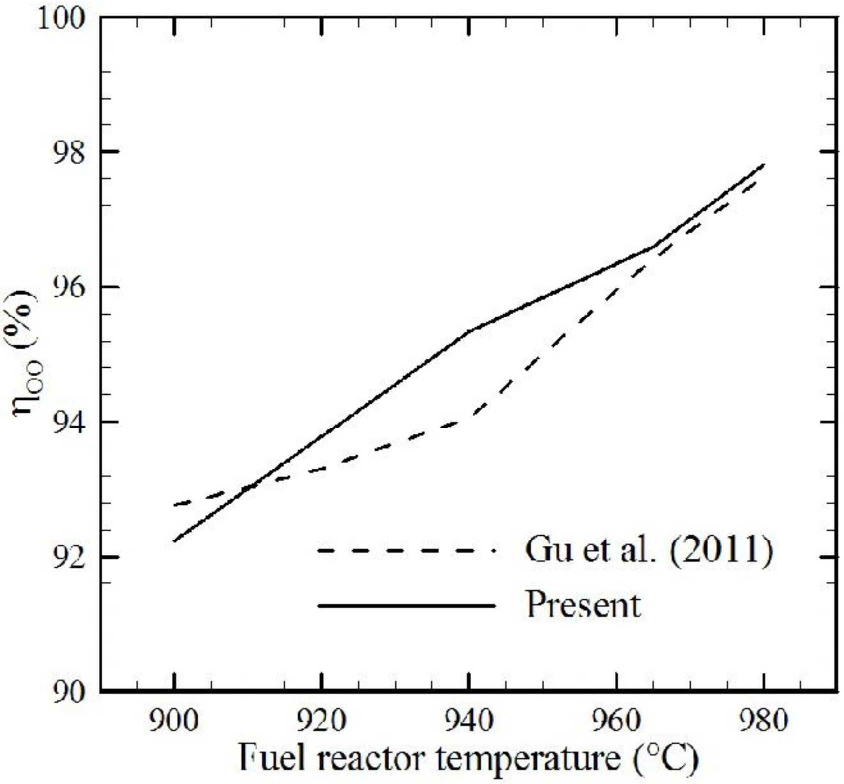


Figure 5.4: Variation of Conversion efficiency with fuel reactor temperature.

perimental results corresponding to pure coal as CLC fuel agrees well with numerical results corresponding to higher mass fraction of coal in the coal and biomass mixture as CLC fuel [Hai-ming et al., 2010]. Similarly, CLC of coal and biomass mixture with higher mass fraction of biomass behaves like CLC of pure biomass. Numerically computed conversion efficiency trend corresponds to higher mass fraction of biomass in the mixture. It can be seen in Figure 5.4 that higher fraction of biomass in the mixture increases the gasification rate primarily due to the large fraction of highly volatile fuel and thereby increases the syngas concentration. On the contrary the poor oxygen transport capacity of iron based oxygen carrier does not convert the higher concentration of syngas in the fuel reactor which results in fast decrease in the conversion efficiency. This agrees well, with the experimental results of Shen et al. [Shen et al., 2009] and Gu et al. [Gu et al., 2011] corresponding to the pure biomass as fuel.



(a)



(b)

Figure 5.5: Variation of (a) Carbon capture efficiency and (b) Oxide oxygen fraction with fuel reactor temperature.

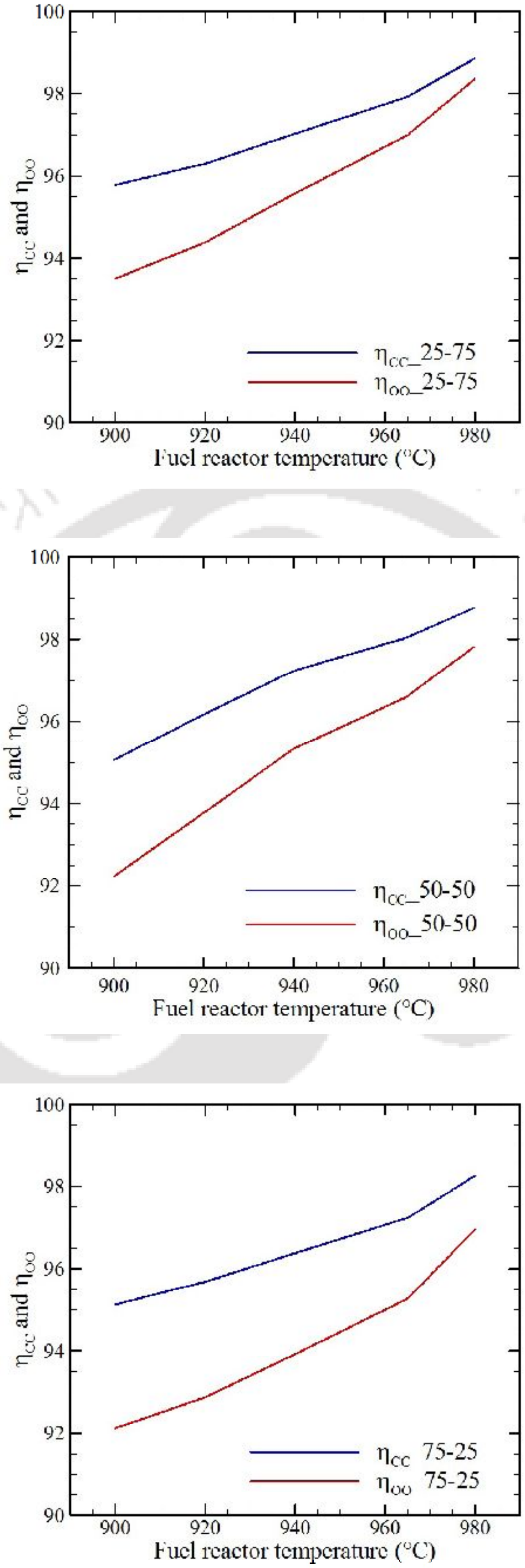
5.3.3 Carbon Capture Efficiency and Oxide Oxygen Fraction

Figure 5.5a presents the carbon capture efficiency as a function of fuel reactor temperature. Carbon capture efficiency depends on the amount of char converted in the fuel reactor at a specified fuel reactor temperature and is defined as Eq. (4.3).

As explained earlier, at higher fuel reactor temperature, the amount of char conversion in the fuel reactor increases due to the endothermic nature of gasification reaction. Therefore, less char would evolve with reduced oxygen carrier particles in the air reactor. Thus decrease in the concentration of $\mathrm{CO_2}$ in the air reactor would increase the carbon capture efficiency. From Eq. (4.2), it is clear that higher char conversion in the fuel reactor results in higher carbon capture efficiency. Figure 5.5b presents the oxide oxygen fraction as a function of fuel reactor temperature. This is defined as [Gu et al., 2011]:

$$\eta_{oo} = \frac{0.21 - W_{O_2,AR} - W_{CO_2,AR}}{0.21 - W_{O_2,AR} - (0.21 \times W_{CO_2,AR})} \tag{5.5}$$

where, $W_{CO_2,AR}$ and $W_{O_2,AR}$ denote the volume percentage of $\mathrm{CO_2}$ and $\mathrm{O_2}$ gases at the exit of the air reactor, respectively.



(a)

(b)

(c)

Figure 5.6: Variation of carbon capture efficiency and oxide oxygen fraction with fuel reactor temperature considering (%Coal/%Biomass) fraction (a) 25/75, (b) 50/50 and (c) 75/25.

Eq. (5.5) gives us the oxide oxygen fraction which in turn depends on the concentration of CO_2 in the air reactor. This is due to the fact that in the defined temperature range the O_2 concentration is almost independent of temperature while concentration of CO_2 decreases in the air reactor. As a higher fraction of char is converted in the fuel reactor, less char particles are present in the air reactor. Numerically computed values of η_{cc} and η_{oo} agrees well with the experimental results. Differences in respective values of η_{cc} and η_{oo} is due to the fact that ASPEN Plus does not consider the miscellaneous losses occurring due to the hydrodynamic condition in fluidized bed combustion [Zhou et al., 2013, Meng et al., 2015].

One of the important advantages of the biomass over coal as a fuel is the availability of higher concentrations of alkali and alkaline earth metal in reactive form within biomass. Luo et al. [Luo et al., 2013] investigated experimentally that the presence of alkali and alkaline earth metals in the fuel reactor reduces the gasification temperature and activation energy of coal. Thus, the presence of alkali and alkaline earth metals increases the coal conversion in the fuel reactor. Therefore, biomass with the high alkali and alkaline earth metals acts as an inexpensive catalyst for the co-combustion of coal and biomass. This understanding suggests that, biomass acts a fuel and a catalyst at the same time. Gu et al. [Gu et al., 2011] concluded in their experimental study that the co-combustion of biomass and coal may reduce the chances of agglomeration and sintering of the oxygen carrier particles. This is a critical issue in CLC of pure biomass. The CLC of different mass fractions of coal and biomass mixture in the fuel reactor may also affect the carbon capture efficiency.

Figure 5.6 shows the effect of different mass fractions of coal and biomass in the mixture on carbon capture efficiency and oxide oxygen fraction using the same temperature range as used by Gu et al. [Gu et al., 2011]. It shows that values of both η_{cc} and η_{oo} increases with increase in the fuel reactor temperature using different mass fractions of coal and biomass in the mixture. The experimental study of Gu et al. [Gu et al., 2011] suggested that the difference between η_{cc} and η_{oo} (i.e., η_{cc} - η_{oo}) shows the presence of

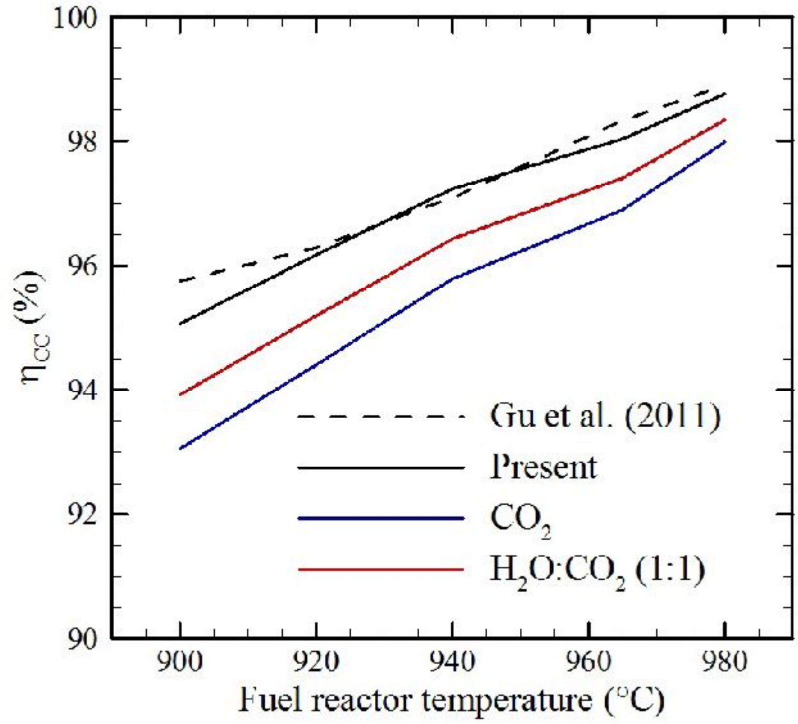


Figure 5.7: Variation of carbon capture efficiency with steam and CO_2 as gasification agent.

unconverted carbonaceous gases like CO and CH_4 in the fuel reactor. Equal values of η_{cc} and η_{oo} implies that the combustible gases are converted to CO_2 in the fuel reactor. Figure 5.6a,b shows that the higher deviation between η_{cc} and η_{oo} is found with equal and higher mass fractions of coal in the mixture as compared to higher fractions of biomass in the mixture. This result is in-line with the experimental results of Gu et al. [Gu et al., 2011] using pure biomass as CLC fuel. In their experimental study, Luo et al. [Luo et al., 2013] also found that higher mass fraction of biomass in the coal and biomass mixture increases the coal char conversion in the fuel reactor even at lower fuel reactor temperature. This would increase the both carbon capture efficiency and oxide oxygen fraction at a given fuel reactor temperature. Therefore, the deviation between η_{cc} and η_{oo} is less with higher fraction of biomass in the coal and biomass mixture.

5.3.4 Effect of Gasification Agent

Steam and CO_2 are the most commonly used gasification agents for the CLC of solid fuels in the interconnected fluidized bed reactors [Hai-ming et al., 2010, Gu et al., 2011, Luo et al., 2013, Roberts and Harris, 2007, Cuadrat et al., 2012]. Figure 5.7 shows the variation in carbon capture efficiency as a function of fuel reactor temperature using steam and CO_2 as gasification agent. The simulation study also carried out using equal fractions of steam and CO_2 (1:1) together as gasification agent to observe the effect on carbon capture efficiency. The char conversion while using CO_2 is less as compared to steam. Cuadrat et al. [Cuadrat et al., 2012] carried out gasification of coal using steam, CO_2 and; steam + CO_2 together in their experimental study. Their study concluded that the char conversion increases with higher fractions of steam in the gasification agent.

In the present simulation we have adopted a mixture of coal and biomass as CLC fuel and it is expected that mixture having higher concentration of biomass have no significant effect of gasification agent on carbon capture efficiency. Roberts and Harris [Roberts and Harris, 2007] presented a model that represents the coal char reaction at high pressure in mixtures of CO_2 and H_2O. It was observed that reaction of coal char is not sum of the reaction rates obtained by using individual CO_2 and H_2O as gasification agent. Mendiara et al. [Mendiara et al., 2013] observed no significant effect on the carbon capture efficiency using CO_2 or H_2O as gasification agent for pure biomass as CLC fuel. Further, Luo et al. [Luo et al., 2013] used CO_2 as gasification agent in their experimental study using mixture of coal and biomass as CLC fuel. It was found that pyrolysis of coal was initiated later as compared to pyrolysis of pure coal in the presence of biomass. This is due to combustion process occurring at lower temperature.

In the present simulation study, the difference in carbon capture efficiency is 1.12% and 0.42% at 900 °C and 980 °C fuel reactor temperatures, respectively, using pure steam and a mixture of equal fractions of steam and CO_2 as gasification agents. No significant differences were found in carbon capture efficiency at lower as well as at higher fuel reactor temperatures using steam and CO_2 together as compared to pure steam as gasification agent. Therefore, a fraction of CO_2 along with steam can be used as a gasification agent without compromising on carbon capture efficiency. Moreover, using CO_2 as gasification agent can reduce the cost of carbon capture as almost pure

CO_2 is readily available in the fuel reactor exit. On the other hand, a reduction in steam generation cost can further reduce the carbon capture cost.

5.3.5 Effect of Solid Circulation Rate

The amount of oxygen carrier particles circulated per unit time in the system is termed as solid circulation rate. In this simulation, the flow rate of oxygen carrier particles was varied from 5.67 to 19.85 kg/h. The corresponding values of the oxygen carrier to fuel ratio (Φ) was 1 to 3.5. Figure 5.8 shows the carbon capture efficiency, as a function of a solid circulation rate at a constant fuel reactor temperature of 940 °C using equal fraction of biomass and coal mixture as CLC fuel. The change in the carbon capture efficiency is insignificant with increase in the solid circulation rate. At a higher value of solid circulation rate, the availability of oxygen is high enough for the complete fuel combustion, but the residence time of the char particles tends to decrease in the fuel reactor. This is due to the fact that complete char combustion is not possible owing to lower residence time. This will in turn result in a slight decrease in the carbon capture efficiency. Therefore, availability of required oxygen is necessary along with minimum residence time for conversion of solid fuel char in the fuel reactor. Gu et al. [Gu et al., 2011] pointed out that a alternative fuel reactor configuration needs to be explored for higher residence time of solid fuel in CLC application.

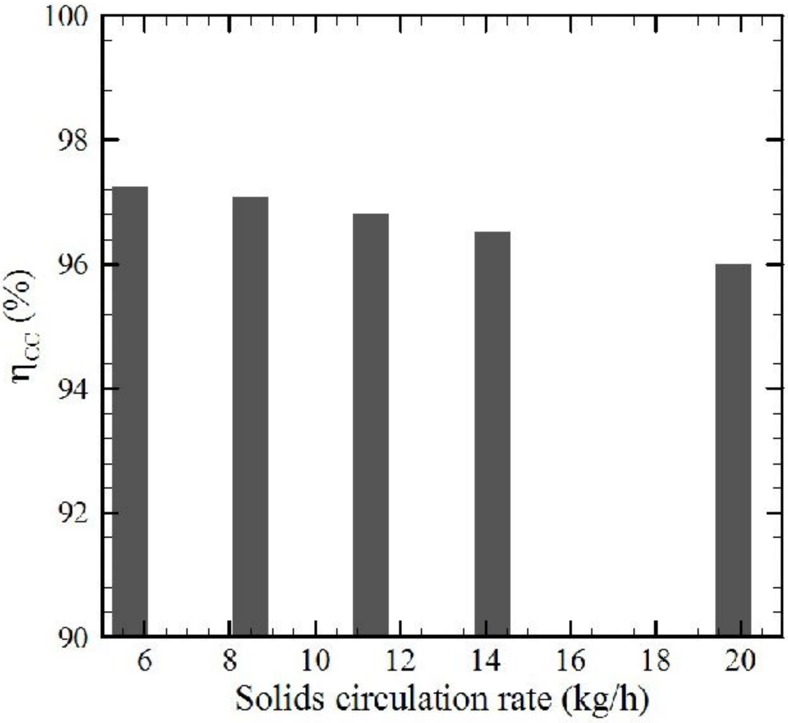


Figure 5.8: Variation of carbon capture efficiency with solid circulation rate.

Mendiara et al. [Mendiara et al., 2013] and Cuadrat et al. [Cuadrat et al., 2012] concluded experimentally that the high oxygen carrier to fuel ratio has insignificant effect on the carbon capture efficiency. Higher solid circulation rate results in insignificant benefit with respect to the char conversion and thus carbon capture efficiency. It is suggested to improve the design of the fuel reactor that should increase the residence time of the char particles in the fuel reactor. Published literature [Adanez et al., 2013, Lyngfelt, 2014, Berguerand and Lyngfelt, 2008, Cuadrat et al., 2011, Cuadrat et al., 2012] has proposed to supply an additional pure oxygen at the downstream of the fuel reactor (oxygen polishing) to fully convert the carbonaceous gases to CO_2, thus increasing the carbon capture efficiency. However, the production of pure oxygen represents an energy penalty and an extra cost of the process. This will necessitate high gas conversion in the fuel reactor with a optimum solid circulation rate. Hence, other options need to be explored to improve the conversion of carbonaceous gases in CLC of solid fuels. The next chapter investigates the other variant of CLC namely CLOU to understand the effect of using a mixture of coal and biomass as fuel.

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CHAPTER 6

Chemical Looping with Oxygen Uncoupling of Coal and Biomass

6.1 Introduction

As seen from the previous chapters 4 and 5, CLC is based on the strategy of supplying oxygen from atmospheric air through metal oxide particles. In this chapter we shall focus on the Chemical Looping with Oxygen Uncoupling (CLOU) behaviour of coal and biomass mixture. This is in continuation with the studies carried out in chapter 5 which discusses the CLC approach with the same fuel.

CLOU is the variant which avoids the rate limiting step of char gasification in CLC [Jerndal, E. et al., 2011, Adanez et al., 2013, Gu et al., 2011]. In CLOU, the metal oxides have the ability to generate gaseous oxygen with suitable partial pressure within the working temperature range (900-985 °C). In this case the fuel is combusted in the fuel reactor as compared to endothermic gasification in CLC. Only three materials have been identified as suitable oxygen carriers for CLOU, i.e., CuO/Cu_2O, Mn_2O_3/Mn_3O_4, and Co_3O_4/CoO [Mattisson et al., 2009]. Published literature have confirmed CLOU concept with interconnected fluidized bed for solid fuels such as coal, petcoke and biomass [Berguerand and Lyngfelt, 2008, Leion et al., 2009, Shen et al., 2009, Lyngfelt, 2014]. One such set-up as used for the CLOU of coal is depicted in Figure 6.1 [Abad et al., 2012].

As shown in Figure 6.1, the set-up consists of two fluidized bed reactors (air and fuel reactor) connected by a loop-seal and cyclone separator. The loop-seal is a rectangular fluidized bed and is fluidized with N_2 gas. Loop-seal allows only the reduced oxygen carrier particles and prevents the gas contamination between the two reactors. Since there is no direct contact between combustion air and fuel, higher concentration of CO_2 and H_2O are generated in the fuel reactor. At the product side, H_2O can easily condense which makes pure CO_2 ready for the capture. Hence, no extra energy is required for CO_2 separation.

Adanez-Rubio et al. [Adanez-Rubio et al., 2014] performed CLOU of milled pine wood

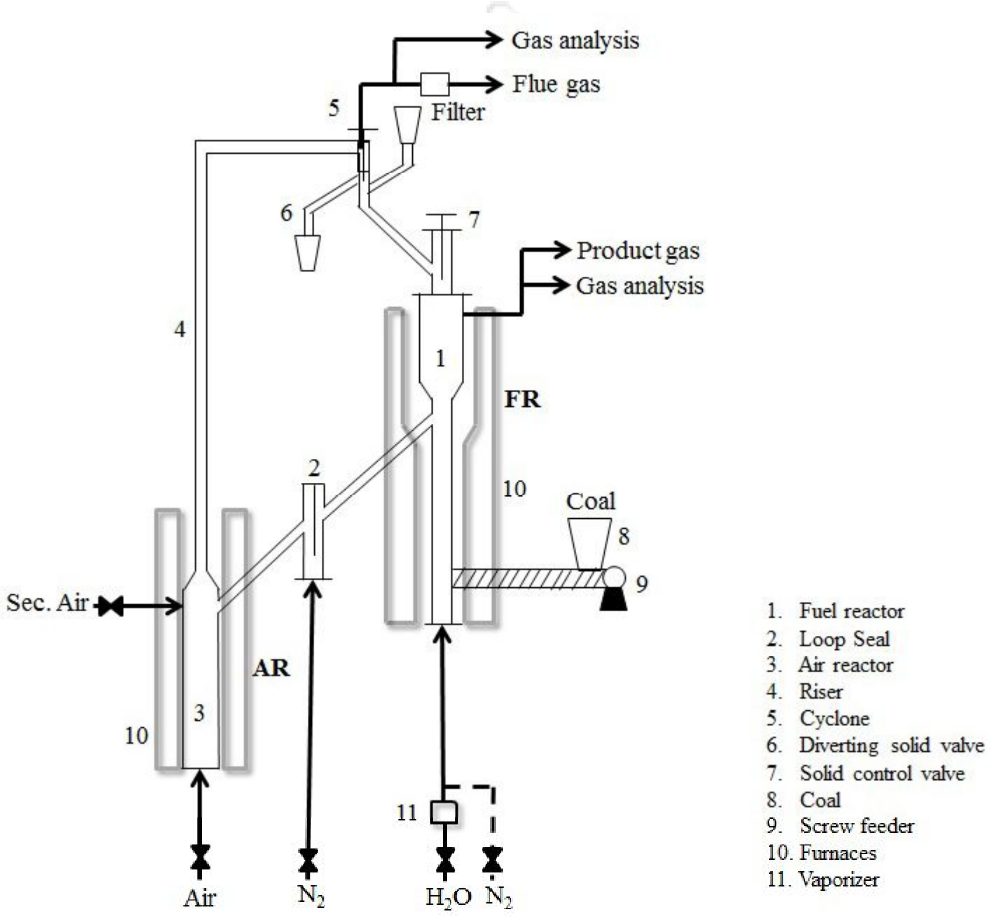


Figure 6.1: Schematic view of the experimental set-up. [Abad et al., 2012]

chips as fuel with CuO based oxygen carrier particles in a similar experimental set-up as shown in Figure 6.1. The char conversion rate was found to be 3 to 4 times higher than the corresponding CLC process at temperature higher than 900 °C. Further, Sarvaramini and Larachi [Sarvaramini and Larachi, 2014] studied the biomass torrefaction using the CLC concept. In this study, the combustion of torrefied volatiles was processed with iron based oxygen carrier where a 99% carbon release in the form of $\mathrm{CO_2}$ was found. Co-firing of different mass fractions of biomass with coal is also known to improve the plant performance and such arrangements may result in negative carbon emission and also provide additional carbon credits which will eventually reduce the overall cost of carbon capture [Basu et al., 2011, Khorshidi et al., 2013, Gayan et al., 2004, Li et al., 2015, Luo et al., 2013].

As discussed in chapter 3, ASPEN Plus based simulation has been able to successfully simulate the CLOU of solid fuels in interconnected fluidized bed reactors [Zhou et al., 2013, Sahir et al., 2014, Meng et al., 2015]. However, to our knowledge, no experimental work has been published for the co-combustion of coal with biomass using CLOU arrangement. The co-combustion of biomass and coal can hence be proposed as an economic and feasible solution for the mitigation of $\mathrm{CO_2}$ concentration in the atmosphere.

In this chapter, a detailed simulation is carried out considering equal fraction of coal and biomass mixture with copper based (CuO) oxygen carrier using ASPEN Plus simulator. Initially the simulation results are validated with experimental results of CLOU of pure coal. Then the predicted numerical results for CLOU of coal and biomass mixture are compared with CLOU of pure coal to observe the variation in performance parameters by replacing coal with biomass. The performance parameters such as, concentration of different gases in air and fuel reactors, carbon capture efficiency, oxygen carrier conversion in fuel reactor and the energy analysis is then validated.

6.2 Process Simulation in ASPEN Plus

The experimental set-up as used by Abad et al. [Abad et al., 2012] will be used to model the mixture of biomass with coal as CLOU fuel using copper based oxygen carrier (Figure 6.1). More details of experimental set-up and operating conditions are available elsewhere [Abad et al., 2012], hence is not discussed here. Sawdust and bituminous coal were used as fuels. Table 6.1 shows the ultimate and proximate analysis of the coal and biomass used for the present simulation study.

Table 6.1: Proximate and Ultimate analysis of Coal and Sawdust.

	Coal[a]	Sawdust[b]	Coal[b]
Proximate analysis (wt%)			
Moisture	2.3	14.28	6.01
Volatile matter	33	74.61	35.1
Fixed carbon	55.9	10.1	54.13
Ash	8.8	1.01	4.76
Ultimate analysis (wt%)			
Carbon	65.8	37.43	69.57
Hydrogen	3.3	5.61	4.3
Oxygen	17.6	40.55	13.81
Nitrogen	1.6	1.02	1.03
Sulphur	0.6	0.1	0.52
LHV (kJ/kg)	21.89	14.5	27.1

[a] Coal used for simulation, [Abad et al., 2012]

[b] Coal and Sawdust used for simulation, [Gu et al., 2011]

The size of fuel and oxygen carrier particles are 200-300 μm and 0.1-0.2 mm, respectively, and is used as an input to the ASPEN Plus simulation at atmospheric condition. The air flow rate used is 1.2 kg/h, while the N_2 flow rate was taken as 0.66 m^3/h. Fuel feeding rate in the fuel reactor was 120 gm/h using equal mass fraction of biomass and coal. These values are the same as used in the experimental schematic as shown in Figure 6.1. The fuel reactor temperature is then varied from 900 °C to 965 °C.

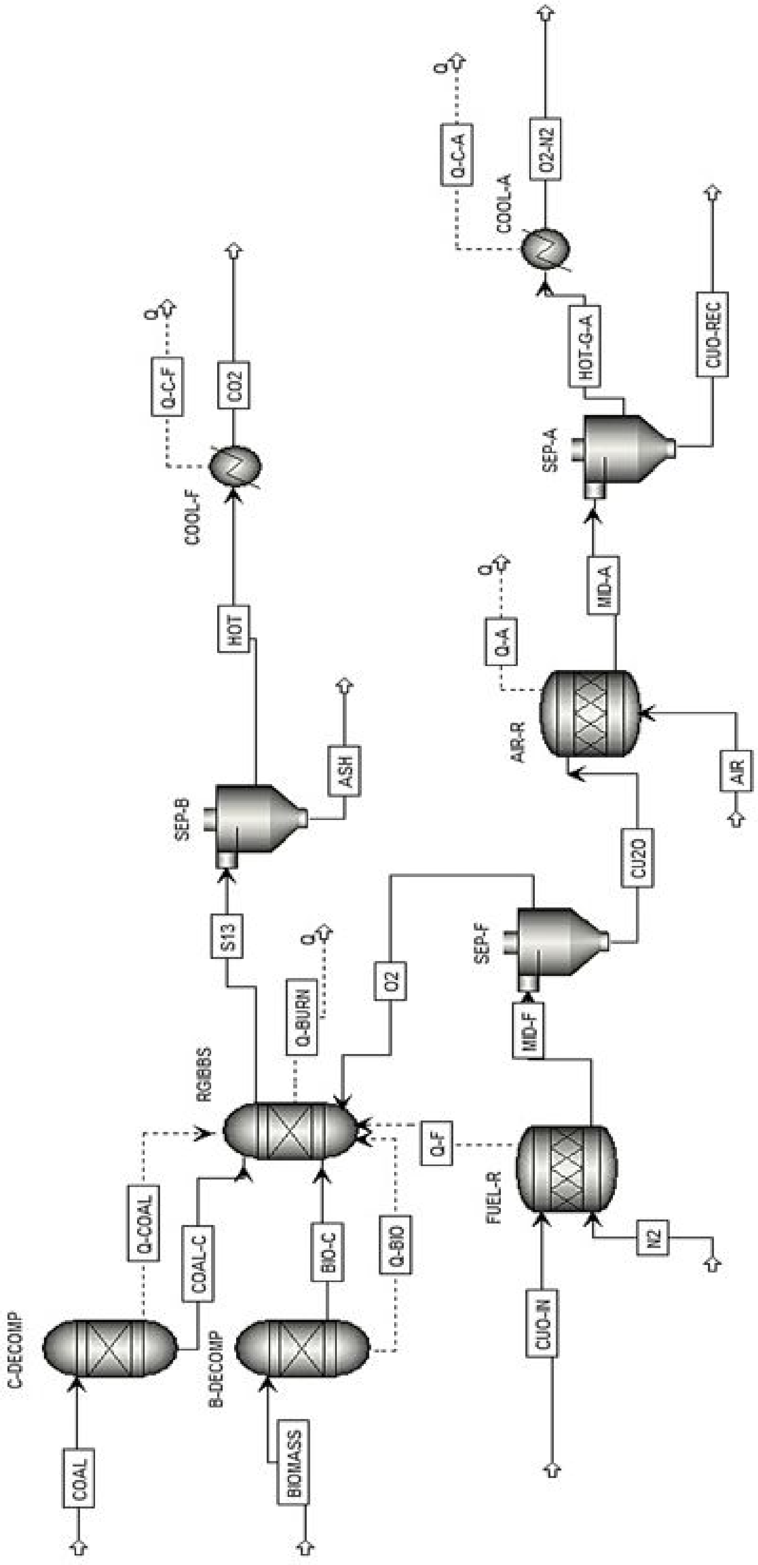


Figure 6.2: Overall flow sheet of CLOU process in ASPEN Plus.

The CLOU process simulation with interconnected fluidized bed reactors developed using ASPEN Plus process simulator as given in Figure 6.2. It presents the material and energy streams that connects various ASPEN components to represent the system level processes. As discussed in chapter 5, devolatilization of the coal and biomass is carried out in the individual RYIELD reactors [Li et al., 2014]. Here coal and biomass is decomposed to its constituent elements (Eq. 1.4 and 3.3). These elements are then combined in the RGIBBS reactor so as to obtain a predefined composition of syngas. As shown in Table 3.2, RSTOIC (fuel reactor) represents the reduction of copper based oxygen carrier to gaseous oxygen. In a similar manner the oxygen carrier namely CuO is uncoupled in the same RSTOIC reactor to provide oxygen and Cu_2O as per (Eq. 3.11). Further the oxidation of volatiles and syngas is carried out in RGIBBS reactor in presence of gaseous oxygen to produce major concentration of CO_2 and H_2O (Eq. 3.12). The Cu_2O produced in the fuel reactor is then transported to the air reactor to again get oxidized to CuO using the RSTOIC module using oxygen in atmospheric air (Eq. 3.13). Here the use of RSTOIC is made in both reactors since the extent of reaction i.e., of both reduction and oxidation of the metal oxide carrier is set to be equal. This is due to the fact that these rates need to be equal for its efficient transport. Hence to simulate the same in ASPEN Plus, as shown in Figure 6.2, the mass flow rate of stream in the fuel reactor (CUO-IN) and exit stream from the air reactor (CUO-REC) are assumed to be same so as to accomplish the re-circulation of oxygen carrier particles. Oxidized particles from the air reactor are then transferred to the fuel reactor to start a new cycle. The mass flow rate of oxygen carrier particles to RSTOIC (fuel reactor) can be calculated as shown in Eq. (3.1). It shows the amount of oxygen supplied by circulating oxygen carriers as compared to oxygen required for the complete combustion of fuel in the fuel reactor.

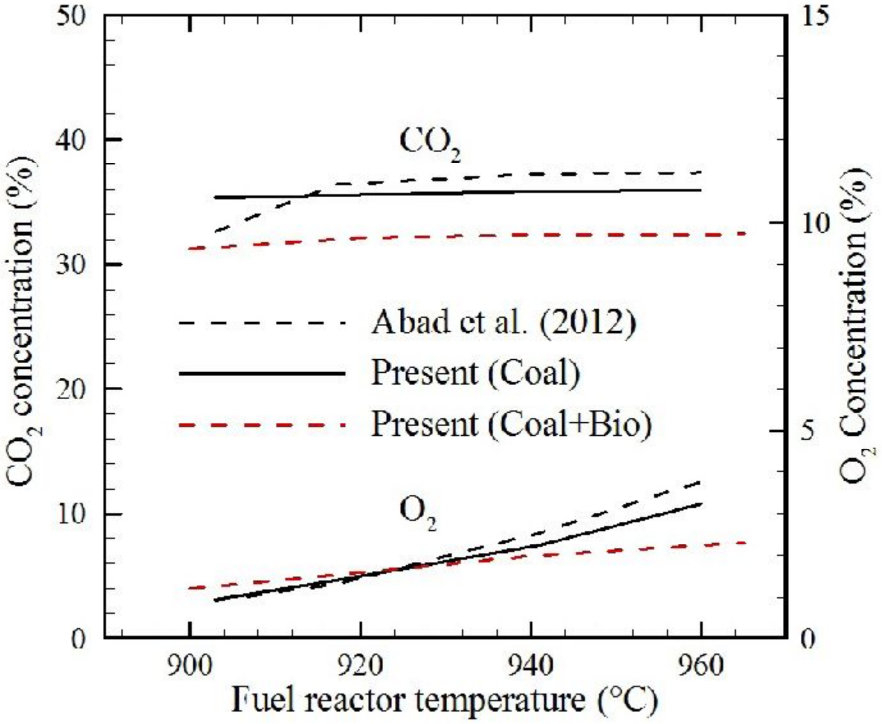
6.3 Results and Discussion

We shall now discuss the effect of the fuel reactor temperature and solid flow rate on various parameters. The parameters namely, the concentration of gases in reactors, oxygen carrier conversion in fuel reactor, carbon capture efficiency and molar flow rate of CO_2 in the fuel reactor are presented. In the ensuing sections, the predicted results are then compared with the experimental results using ASPEN Plus. In the present simulation study, the flow rate of pure coal and coal/biomass mixture is considered as 112 gm/h and 120 gm/h (equal fraction of coal and biomass), respectively, based on published literature [Abad et al., 2012, Gu et al., 2011].

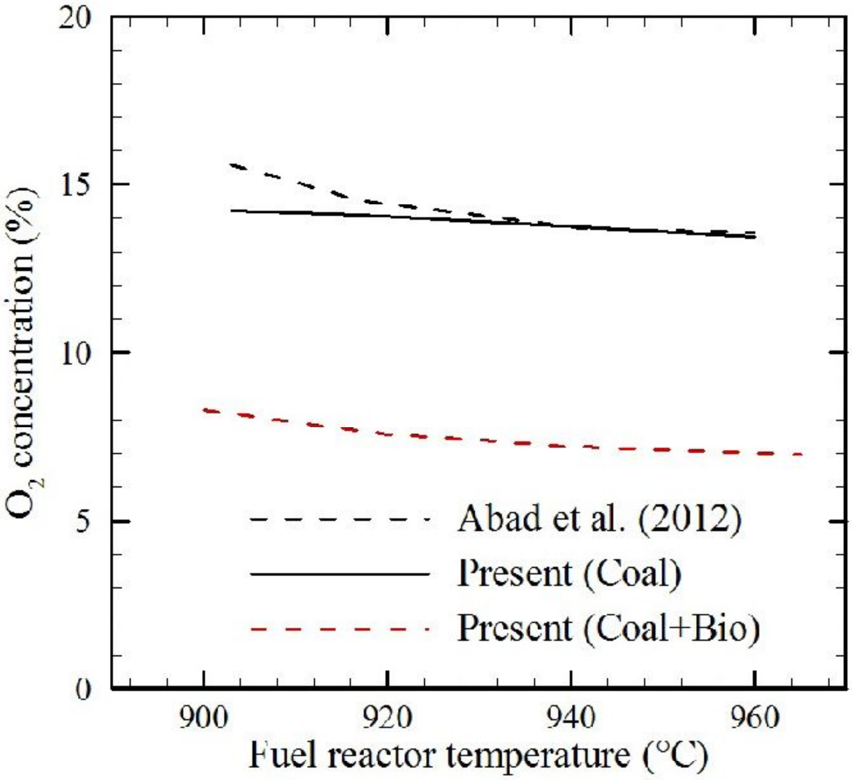
6.3.1 Gas Concentration in Reactors

Effect of the fuel reactor temperature is critical for the performance of solid fuel CLOU. Figure 6.3a shows the comparison of experimental and simulated results for concentration of different gases in the fuel reactor. The ultimate and proximate analysis of biomass and coal used for simulation is available in Table 6.1. For this simulation, the variation in fuel reactor temperature is considered from 900 to 965 °C as per published literature for CLC of coal and biomass mixture [Gu et al., 2011].

In the fuel reactor, the concentration of O_2 is found to increase with increase in fuel reactor temperature. It reveals that sufficient amount of gaseous oxygen is available for fuel conversion in the fuel reactor which implies that no unconverted flue gas is present in the fuel reactor. It is also observed that the concentrations of CO_2 in fuel reactor remains almost constant except at the initial stage which is at lower temperature. This may be due to limited availability of gaseous oxygen at lower temperature. This then increases with increase in fuel reactor temperature. The difference in CO_2 concentration for mixture of coal and biomass in fuel reactor is due to lower carbon content of the biomass fuel as compared to coal which is used for experiment studies. Concentration of O_2 is also found to increase with the demand of gaseous oxygen in the fuel reactor. Further the oxygen uncoupling effect gets strengthened at higher fuel reactor temperature. No significant changes is found in fuel reactor O_2 concentration which points out to the fact that the oxygen uncoupling effect is not affected by the replacement of coal and biomass mixture as fuel.



(a)



(b)

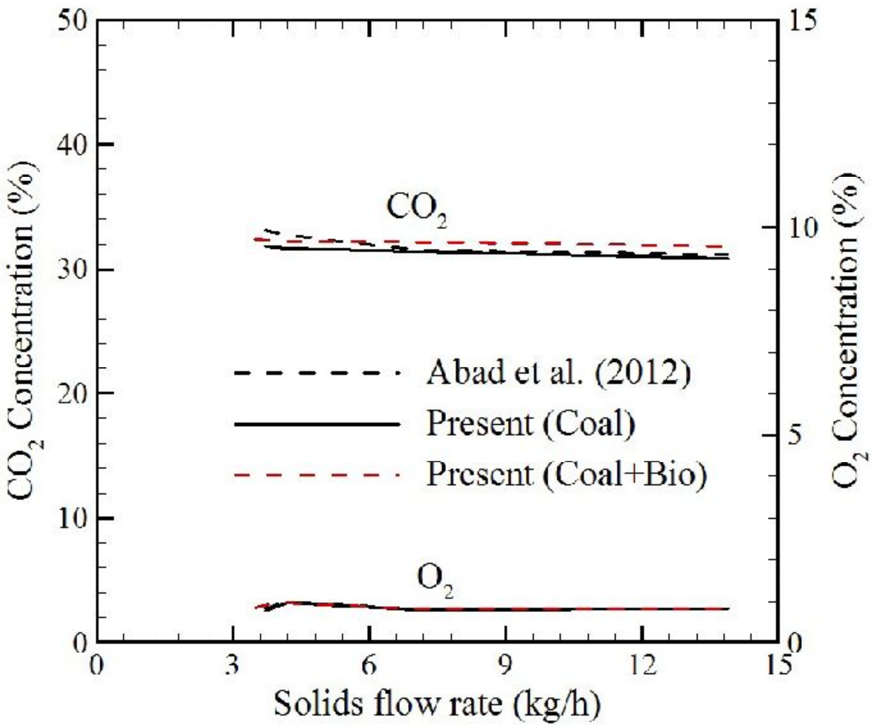
Figure 6.3: Variation of (a) CO_2 and O_2 concentration in fuel reactor (b) O_2 concentration in air reactor with fuel reactor temperature.

Figure 6.3b compares the experimental and predicted results for O_2 concentration in the air reactor with fuel reactor temperature. Here the O_2 concentration decreases with increase in fuel reactor temperature. This is primarily due to a higher conversion of oxygen carrier in the fuel reactor which invariably consumes a higher fraction of oxygen. This initiates the depletion of O_2 concentration in the air reactor. The difference in O_2 concentration is basically due to consideration of difference in stoichiometric air ratio, oxygen flow in air to oxygen demand (λ), for coal and biomass mixture which is 1.25 in the air reactor as compared 2.8 in the experiment studies for pure coal [Abad et al., 2012]. Overall, the predicted results for pure coal as well as mixture of coal and biomass are in good agreement with experimental results.

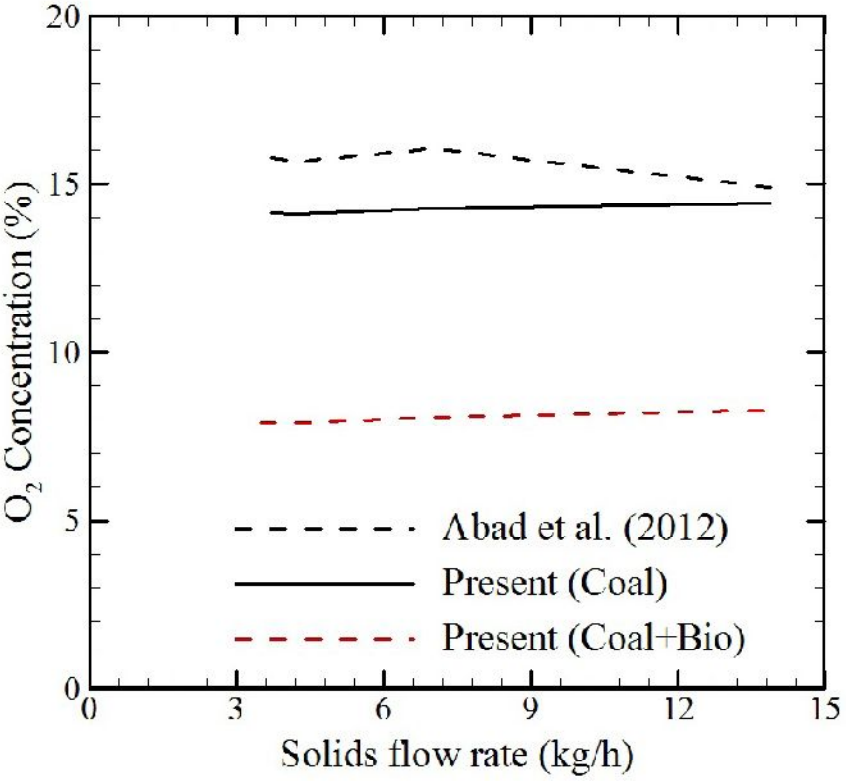
The amount of oxygen carrier particles circulated per unit time in the system is termed as the solid flow rate. In the simulation, the flow rate of oxygen carrier particles was varied from 3.48 to 13.9 kg/h. The corresponding values of the oxygen carrier to fuel ratio (Φ) was calculated to be ranging from 1 to 3.75. The fuel reactor temperature is considered constant at 900 °C for this simulation study. Figure 6.4a compares the experimental and predicted results for exhaust gases in the fuel reactor with different solid flow rate. Higher solid flow rate in the system gives higher oxygen for fuel conversion. It is observed that no significant change is found in concentration of either CO_2 or O_2 gas in the fuel rector at higher solid flow rate. It is also observed that no significant change in gas concentration is seen even by using mixture of coal and biomass as CLOU fuel. Figure 6.4b shows the O_2 concentration in the air reactor. The trend is similar for the experimental and simulated results for pure coal as well mixture of coal and biomass. The difference in O_2 concentration is due the difference in stoichiometric air ratio (λ) in simulation as compared to that used in experiments for pure coal.

6.3.2 Carbon Capture Efficiency

Carbon capture efficiency (η_{cc}) depends on the amount of char converted in the fuel reactor at a specified fuel reactor temperature and is defined as [Abad et al., 2012]:

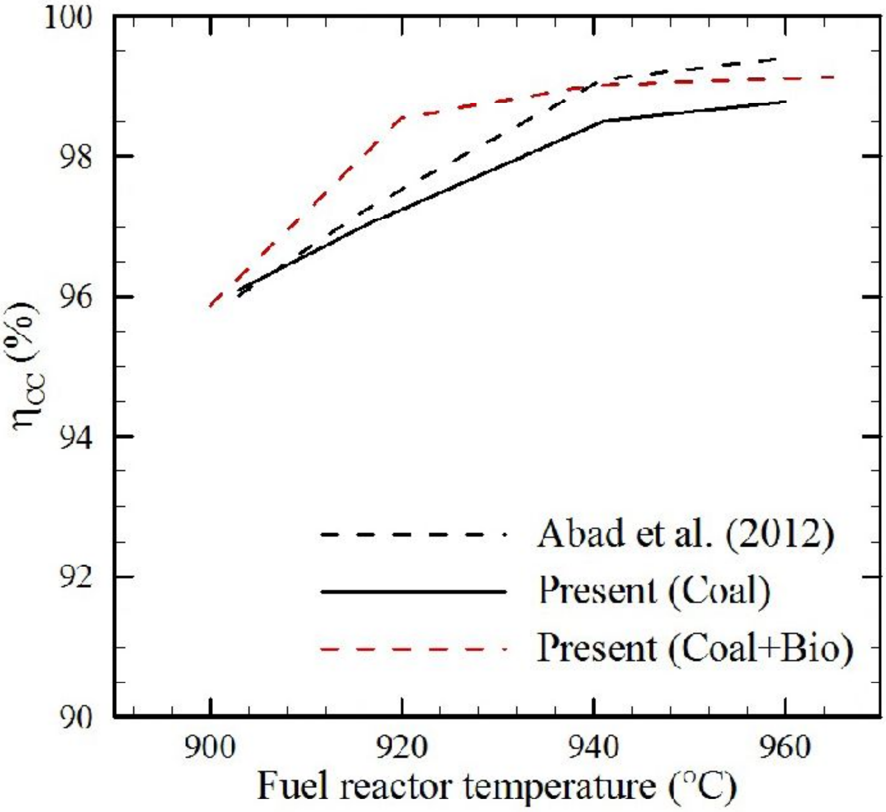


(a)

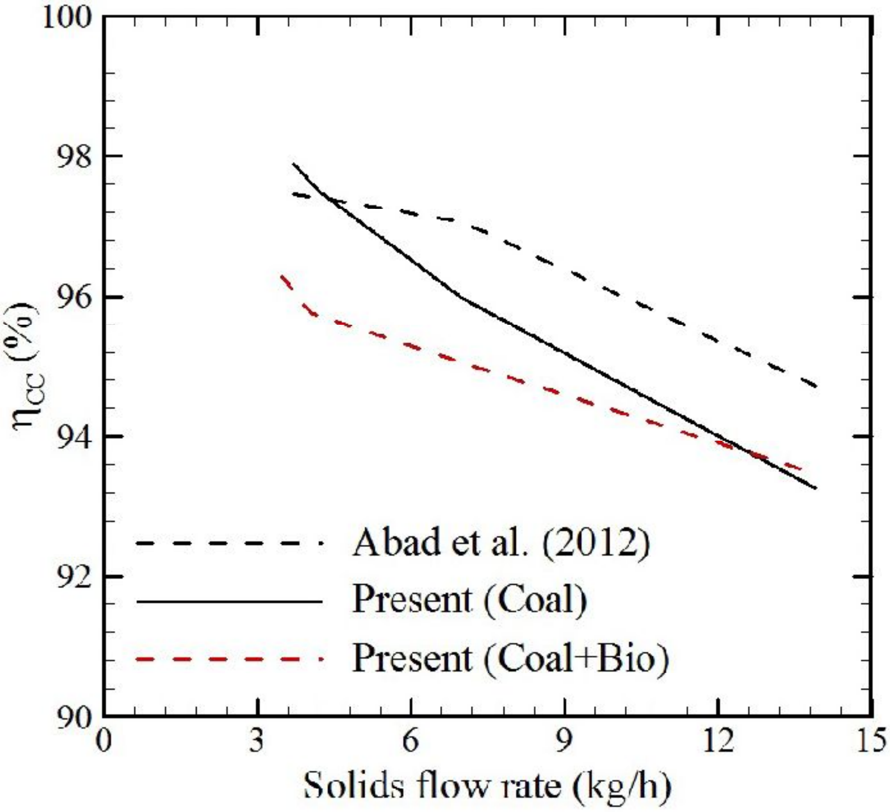


(b)

Figure 6.4: Variation of (a) CO_2 and O_2 concentration in fuel reactor (b) O_2 concentration in air reactor with solid circulation rate.



(a)



(b)

Figure 6.5: Variation of Carbon Capture efficiency with (a) fuel reactor temperature and (b) solid circulation rate.

$$\eta_{cc} = \frac{M_C F_{CO_2,out,FR}}{\dot{m}_{SF} f_C} \tag{6.1}$$

where, M_C and $F_{CO_2,out,FR}$ indicates the molecular weight of carbon and molar flow rate of $\mathrm{CO_2}$ at fuel reactor outlet, respectively. $\dot{m}_{SF}$ and f_C indicates the solid fuel (coal or mixture of coal and biomass) feed rate into the fuel reactor and mass fraction of carbon in fuel feed, respectively.

Figure 6.5a validates and compares the carbon capture efficiency as a function of fuel reactor temperature for pure coal and coal biomass mixture as CLOU fuel. It is a measure of the amount of carbon in fuel that enters the fuel reactor. This gets converted in the form of $\mathrm{CO_2}$ at the outlet of fuel reactor. The carbon capture efficiency is found to increase with increase in fuel reactor temperature. At higher fuel reactor temperature, devolatilization and char conversion of solid fuel get reinforced along with the oxygen carrier uncoupling, thereby increasing the gaseous oxygen in the fuel reactor. This results in higher fuel conversion and thereby higher carbon capture efficiency. Figure 6.5a also shows the carbon capture efficiency for coal and biomass mixture. The trend is found to be almost similar to pure coal and no significant change is found in carbon capture efficiency within the considered range of fuel reactor temperature. From these studies, it is clear that coal can easily be adopted and replaced with biomass without difference in carbon capture efficiency within the desired temperature range.

Figure 6.5b shows that at higher solid flow rate, carbon capture efficiency tends to decrease at constant fuel reactor temperature of 900 °C. For enhanced conversion of solid fuel either in CLC or in CLOU, the minimum residence time for the oxygen carrier particles is necessary in the fuel reactor. For this to happen, the solid flow rate between air and fuel reactor should be high enough to transfer necessary oxygen for fuel conversion along with the necessary heat balance. At higher solid flow rate, the residence time for the oxygen carrier particles tends to decrease resulting in lower char conversion of fuel particles and thereby lower carbon capture efficiency in the fuel reactor [Cuadrat et al., 2012].

6.3.3 Oxygen Carrier Conversion

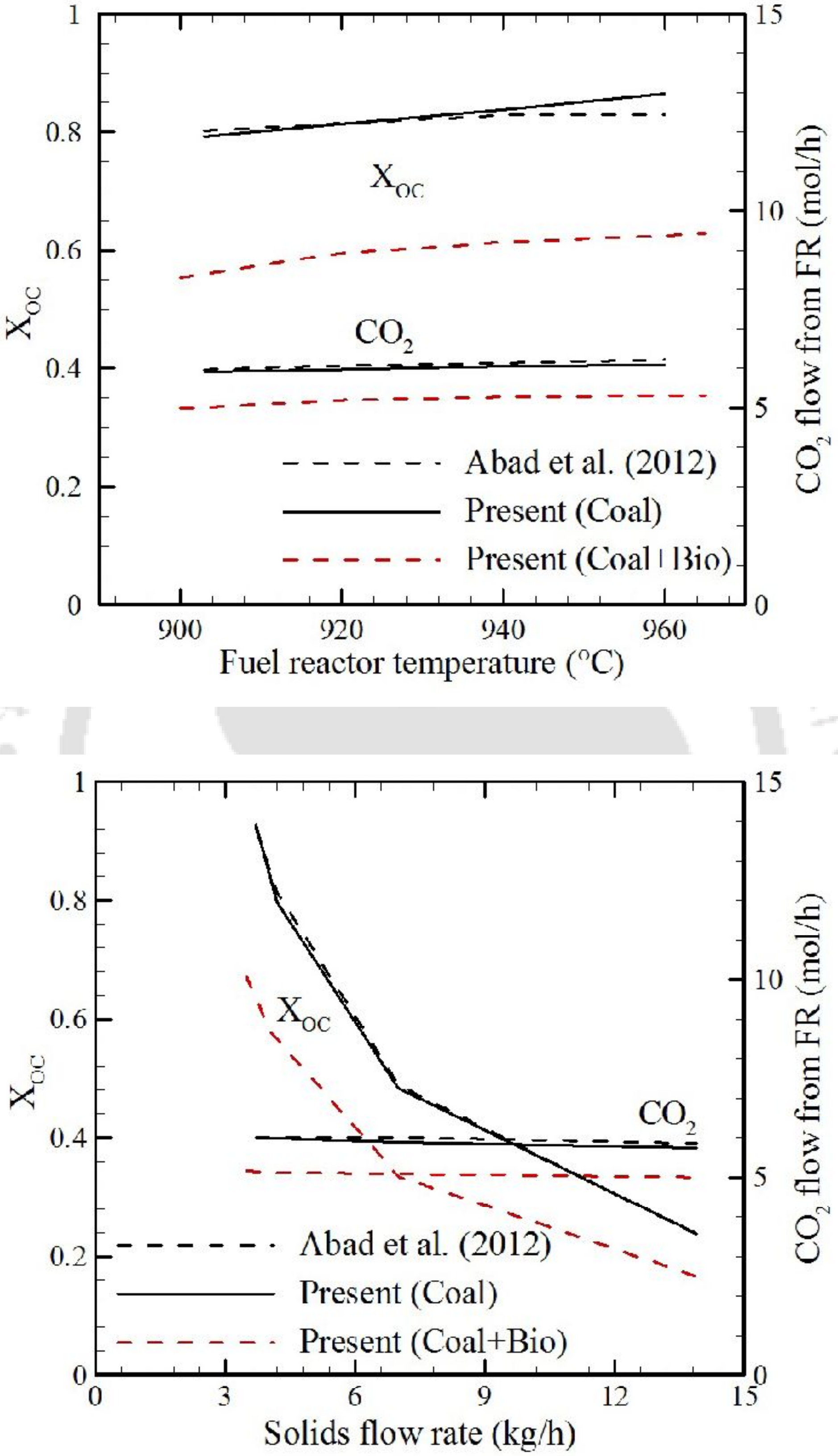
The oxygen carrier conversion defined as the fraction of oxygen carrier (CuO) that gets uncoupled to Cu_2O and O_2, and it is defined as [Abad et al., 2012]:

$$\Delta X_{OC} = \frac{\left(F_{CO_2,out,FR} + F_{O_2,out,FR} + 0.5(F_{CO,out,FR} + F_{H_2O,out,FR}) - 0.5\dot{m}_{SF}\left(\left(\frac{f_{H_2O}}{M_{H_2O}}\right) + \left(\frac{f_O}{M_O}\right)\right)\right) M_{O_2}}{0.25F_{CuO}} \tag{6.2}$$

Here, F_y is the concentration of dry gas 'y' in the fuel reactor exit, M_y is the molecular weight of compound 'y', $\dot{m}_{SF}$ is the solid fuel feeding rate, and f_i the mass fraction of coal in the compound 'i'. This is an essential parameter in CLOU as it relates the oxygen uncoupling from oxygen carrier particles in the fuel reactor. Experimental evidence suggests that oxygen carrier conversion increases with demand of flue gas and with increase in fuel reactor temperature [Adanez-Rubio et al., 2014].

Figure 6.6a shows the comparison between experimental and predicted results for oxygen carrier conversion (ΔX_{OC}) and molar flow rate of CO_2 in the fuel reactor. Overall the results are in good agreement for oxygen carrier conversion and molar flow rate for CO_2 in the fuel reactor. It is also observed that the nature of oxygen carrier conversion and carbon dioxide molar flow rate for coal and biomass mixture is more or less found to be similar to experimental results for pure coal.

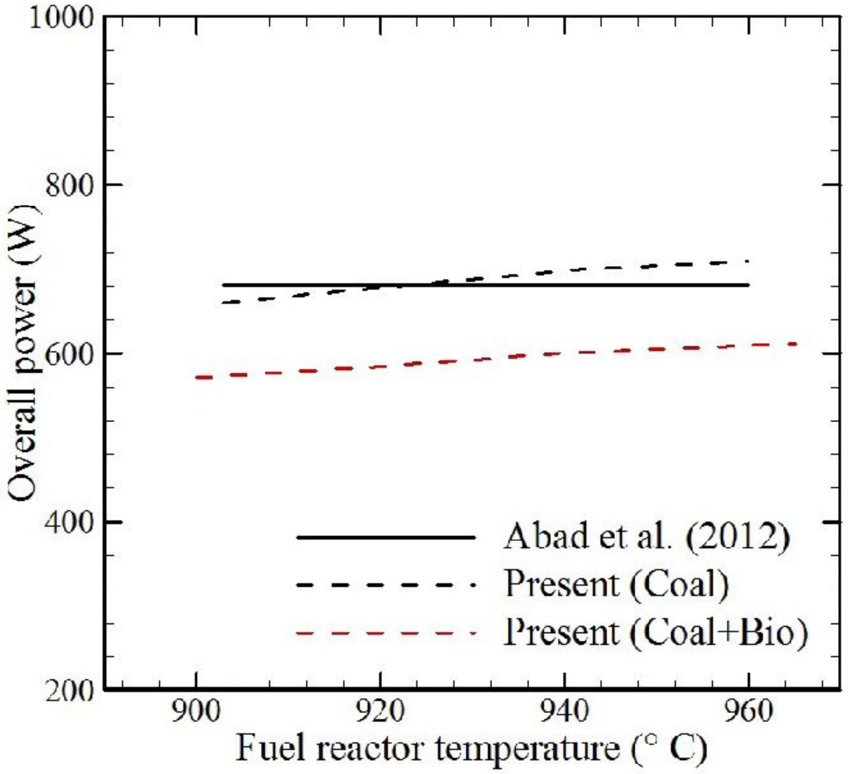
The oxygen carrier conversion is found to increase with fuel reactor temperature. This is due to the easy availability of higher concentrations of alkali and alkaline earth metal in reactive form within biomass moiety. Luo et al. [Luo et al., 2013] investigated experimentally that the presence of alkali and alkaline earth metals in the fuel reactor reduces the gasification temperature and activation energy of coal. Thus, the presence



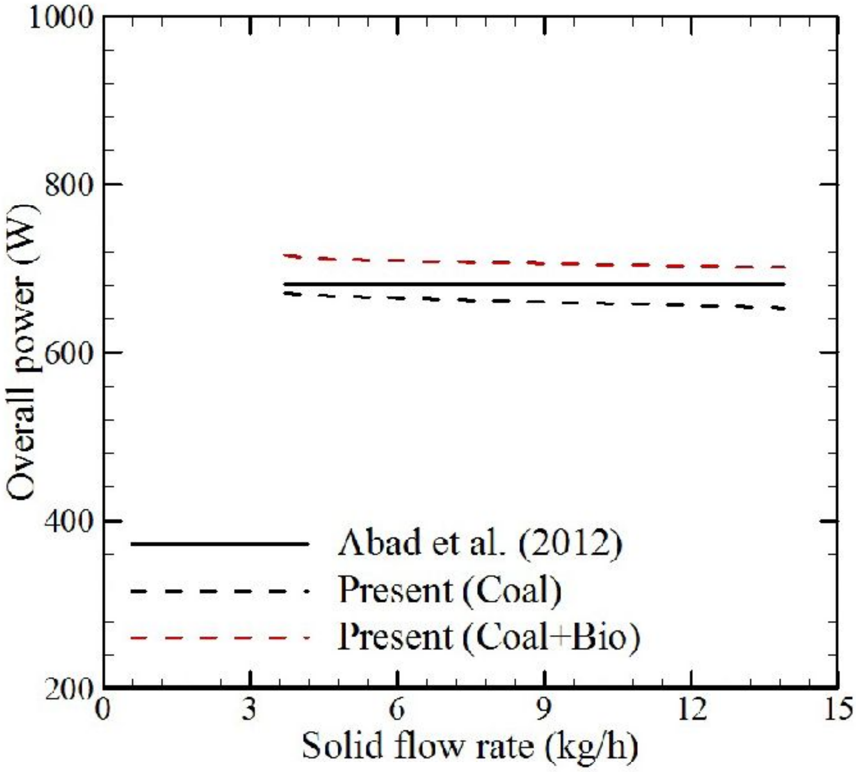
(a)

(b)

Figure 6.6: Variation of Oxygen carrier conversion and molar flow of CO_2 in fuel reactor with (a) fuel reactor temperature and (b) solid circulation rate.



(a)



(b)

Figure 6.7: Variation of thermal energy output with (a) fuel reactor temperature and (b) solid circulation rate.

of alkali and alkaline earth metals increases the coal conversion in the fuel reactor. Therefore, biomass with the high alkali and alkaline earth metals acts as an inexpensive catalyst for the co-combustion of coal and biomass. This suggests that, biomass can act as fuel and a catalyst simultaneously. Figure 6.6b shows the effect of oxygen carrier conversion and carbon dioxide molar flow rate with solid flow rate. It is found the oxygen carrier conversion decreases with increase in solid flow rate. As discussed earlier for better fuel conversion, the minimum residence time for oxygen carrier particles is necessary. Therefore, with increase in solid flow rate, no significant benefit is found for carbon capture efficiency. Experimental investigation for coal suggests a residence time of 300 to 470 s which is required for a char conversion of 97% to 99% at fuel reactor temperature range of 900-960 °C [Cuadrat et al., 2012].

6.3.4 Energy Analysis

Figure 6.7a,b compares the experimental and simulation results for the overall power output in coal and coal and biomass mixture when used as CLOU configuration. Figure 6.7a shows the thermal power output with different fuel reactor temperature while Figure 6.7b as based on different solid flow rates. The difference between simulation and experimental results could be due to neglecting the miscellaneous losses in ASPEN Plus due to hydrodynamic losses. It should be noted that ASPEN Plus does not consider the miscellaneous losses occurring in the fluidization process [Zhou et al., 2013].

Table 6.2: Thermal Power output (W_{th}) for ASPEN Plus components used in CLOU at different fuel reactor temperature (as per Figure 6.2)

Pure Coal

Temp. (°C)	Q-A	Q-BURN	Q-C-A	Q-C-F	Q-DECOMP	Q-F	Total
903	-249.38	151.62	566.27	191.86	-101.68	-505.28	660.37
917	-233.42	146.61	565.61	196.55	-103.34	-517.72	675.35
941	-205.39	135.53	564.39	204.89	-106.20	-540.56	699.42
960	-182.85	117.30	563.38	211.42	-108.06	-559.51	709.25

Coal and Biomass

Temp. (°C)	Q-A	Q-BIO	Q-BURN	Q-C-A	Q-C-F	Q-COAL	Q-F	Total
900	-249.38	-112.96	35.64	566.27	218.63	-54.25	-505.28	571.16
920	-233.42	-113.67	29.09	565.61	223.41	-55.23	-517.72	584.69
940	-205.39	-114.84	9.74	564.39	231.69	-56.65	-540.56	600.43
965	-182.86	-115.70	-7.16	563.38	238.47	-57.83	-559.51	611.83

Table 6.2 shows the power output for each ASPEN Plus component used in simulation for coal as well as for coal-biomass mixture at different fuel reactor temperature. Table 6.3 shows the power output for each ASPEN Plus component used in simulation for pure coal as well as for coal-biomass mixture at different solid flow rate.

Table 6.3: Thermal Power output (W_{th}) for ASPEN Plus components used in CLOU at different solid circulation rate (as per Figure 6.2)

Pure Coal								
Solid flow rate (kg/h)	**Q-A**	**Q-BURN**	**Q-C-A**	**Q-C-F**	**Q-DECOMP**	**Q-F**		**Total**
3.7	-234.44	69.55	664.20	171.19	-101.90	-393.05		670.50
4.2	-264.49	90.37	667.56	174.58	-101.87	-409.93		668.02
7	-244.31	70.84	665.30	171.24	-101.76	-393.90		663.07
13.9	-197.69	27.97	660.08	162.97	-100.87	-351.26		653.33
Coal and Biomass								
Solid flow rate (kg/h)	**Q-A**	**Q-BIO**	**Q-BURN**	**Q-C-A**	**Q-C-F**	**Q-COAL**	**Q-F**	**Total**
3.48	134.25	-112.79	71.43	286.33	223.15	-54.27	-472.34	715.16
4.03	134.80	-112.75	67.46	286.27	222.96	-54.10	-471.98	711.49
6.9	130.08	-112.66	68.59	286.80	222.34	-54.01	-467.47	707.80
13.64	123.98	-112.66	68.17	287.48	221.48	-53.71	-461.66	701.11

It should be noted that negative value indicates thermal power input rather than output. The thermal energy associated with the decomposition of coal in the RYIELD reactor and the oxygen carrier uncoupling in RSTOIC reactor stays within the system. So, it will not contribute in the thermal output; therefore, it is not considered for the calculation of thermal power output.

The predicted simulation results for CO_2 gas concentration is found to increase with the fuel reactor temperature. The value for the same is found as 35.34% to 35.91% for pure coal and 31.25% to 32.44% for coal and biomass mixture for the fuel reactor temperature range of 900 to 960 °C. The CO_2 gas concentration is found to slightly decrease with increase in solid circulation rate. This is primarily due to the lower residence of oxygen carrier particles in the fuel reactor at higher solid circulation rate [Cuadrat et al., 2012]. The value for the same is found as 31.83% to 30.84% for pure coal and 32.41% to 31.85% for coal and biomass mixture for the solid circulation rate of 3.7 to 13.9 kg/h at constant fuel reactor temperature of 940 °C.

Thermal energy output is also calculated for different fuel reactor temperature and solid circulation rate. Energy output is found to be increase with increase in the fuel reactor temperature, as higher temperature causes high fuel conversion in the fuel reactor. The trend of thermal energy output is found to be the same for pure coal and coal/biomass mixture as CLOU fuel (Figure 6.7). It is found to be 660 W_{th} to 709 W_{th} for pure coal and 571 W_{th} to 612 W_{th} for coal/biomass mixture within the fuel reactor temperature range of 900 to 960 °C. This closely resembles the experimental results of Abad et al. [Abad et al., 2012] which predicted the constant thermal energy output of 681 W_{th} at different fuel reactor temperature and solid circulation rate using pure coal as CLOU fuel. A difference is due to the fact that ASPEN Plus does not consider the miscellaneous losses that occurrs due to different hydrodynamic conditions in fluidized bed reactor. It should be noted that such kind of analysis plays an important role while carrying out carbon capture process along with thermal energy output. Overall in the present study by replacing coal with equal fraction biomass does not offer much in energy output. However it confirms the gaseous composition and carbon capture efficiency in the respective reactors. Therefore, it clearly shows that by using biomass we can save important energy sources such as coal without compromise in performance parameters for both the variants (CLC and CLOU).

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CHAPTER 7

Conclusions and Future Scope

7.1 Research Conclusions

Overall ASPEN Plus provides a very good platform to simulate the processes of CLC and CLOU of solid fuel in interconnected fluidized beds reactors. It is a promising alternative to evaluate the solid fuel CLC performance parameters. Effect of fuel reactor temperature on exit flue gas stream of air and fuel reactors, conversion and carbon capture efficiency were investigated. The predicted results on CLC of biomass agreed fairly well with experimental results. Deviation between the experimental values and the simulation results are mainly due to the assumption of neglecting the effects of miscellaneous energy losses in the model. Simulation results were also presented to show the effect of solid circulation rate and gasification agents (CO_2 and H_2O) on char conversion and carbon capture efficiency. It was concluded that CO_2 can easily replace steam (H_2O) as gasification agent, since significant changes were not seen in terms of char conversion and carbon capture efficiency.

Comparison of material and energy analysis has been carried out in chapter 4 for sawdust biomass combustion in CLC and CLOU using ASPEN Plus flow sheeting. CLC is carried out with 60% Fe_2O_3 on Al_2O_3 along with a circulation rate of 66.4 kg oxygen carrier/kg biomass fuel. In a similar manner, CLOU having 40% CuO on ZrO_2 based oxygen carrier with a circulation rate of 75 kg oxygen carrier/kg biomass fuel was also carried out. It was also observed that a less costly and high melting point Fe based oxide particles can be recommended for CLC when compared to the high cost and less melting point of Cu based particles in CLOU for economic operation. Moreover, the low melting temperature of Cu based oxygen carrier needs proper attention since working with biomass may create agglomeration and defluidization within the system. On the other hand, to take advantage of a faster rate of oxygen generation with a highly reactive fuel, an optimized fuel reactor temperature should be chosen. Thus in short a lesser requirement of Cu based oxygen carrier for the combustion of similar mass of fuel in the fuel reactor reduces the reactor volume in the plant design. Reactor design with minimum residence time of the particles in the fuel reactor could eventually improve the combustion efficiency in CLC. Scale-up of present scenario is also suggested. Predicted kinetic data can be recommended to design the pilot scale set-up of CLC.

Coal and biomass mixture as CLC fuel using Fe_2O_3 as an oxygen carrier was also simulated in chapter 5. The results shows that the higher and equal mass fractions of coal in the biomass and coal mixture acts in a similar manner as CLC of pure coal. The performance parameters such as gas concentrations in the fuel and air reactors, conversion efficiency and carbon capture efficiency as a function of fuel reactor temperature was computed. As compared to pure biomass as CLC fuel, the concentration of both CO and CO_2 in the fuel reactor was found to increase while CO_2 concentration in the air reactor remains same. The trend for conversion efficiency and carbon capture efficiency is found to be same in both the cases within the defined temperature range.

The oxide oxygen fraction (η_{oo}) is found to increase with the fuel reactor temperature in coal and biomass mixture as CLC fuel. The difference between carbon capture efficiency (η_{cc}) and oxide oxygen fraction (η_{oo}) confirms the presence of unconverted carbonaceous gases in the fuel reactor. The values of (η_{cc} - η_{oo}) were less at higher fuel reactor temperature as compared to lower fuel reactor temperature for various coal-biomass mixture configurations. Moreover the difference (η_{cc} - η_{oo}) is less for the coal and biomass mixture with higher concentration of biomass as compared to higher concentration of coal in the mixture for respective fuel reactor temperature. This may be due to the presence of alkali and alkaline earth metals in the biomass and enhancement in the char conversion at the higher fuel reactor temperature.

In CLC of solid fuel, a higher mass fraction of steam improves the gasification of solid fuels, thus increasing the carbon capture efficiency. No significant change in carbon capture efficiency were found using CO_2 and steam together as gasification agent in CLC of coal and biomass mixture. CO_2 as gasification agent may reduce the cost of carbon capture due to reduction in cost involved in steam generation. No significant changes in carbon capture efficiency were also observed with higher oxygen carrier to fuel ratio with coal and biomass mixture as CLC fuel.

In the concluding chapter, the simulation is also initiated using equal fraction of coal and biomass mixture in CLOU arrangement with CuO as an oxygen carrier. Parameters such as gas concentrations in the fuel and air reactors, carbon capture efficiency, oxygen carrier conversion and solid flow rate are validated against experimental data. No significant difference in terms of gaseous concentration in the reactors is found with the replacement of coal by biomass. The trend for O_2 concentration in the fuel reactor is found to be more or less same for coal and coal/biomass mixture. The oxygen carrier conversion in the fuel reactor with fuel reactor temperature and solid flow rate is found to be similar irrespective of the fuel. This indicates that the oxygen carrier uncoupling depends on the demand of flue gas in the fuel reactor. The predicted result also shows that the total thermal power output agrees well with varying fuel reactor temperature and solid flow rate.

7.2 Future Scope

Similar studies are required to be carried out for the carbon capture processes using other forms of biomass. One can use the simulation results to scale-up the present smaller capacity experimental set-up for CLC and CLOU. Considering biomass as CLC and CLOU fuel may eventually be beneficial to save coal. To overcome the limitation of not considering miscellaneous losses in fluidization process, it is suggested that commercial software like ANSYS or COMSOL may be used to carry out exact simulation process so as to predict the behaviour of the system in an economical manner.

Research Output

Refereed Journals

(1) Mayur D. Kevat, Tamal Banerjee. "Process Simulation and Energy Analysis for Chemical Looping Combustion and Chemical Looping with Oxygen Uncoupling with Sawdust Biomass." Energy Technology (2017) (DOI: 10.1002/ente.201700795)

(2) Mayur D. Kevat, Subhash C Mishra, P. Mahanta, C. Somayaji, Tamal Banerjee ."Simulation and Validation of Chemical Looping Combustion for mixtures of Coal and Biomass using Iron Based Oxygen Carrier." (2017) Chemical Engineering Research and Design (Submitted, CHERD-D-17-00518R1)

(3) Mayur D. Kevat, Tamal Banerjee. "Insights into the Co-Combustion of Coal and Biomass mixtures using a Copper based oxygen carrier in Chemical Looping Combustion." (2018) International Journal of Oil, Gas and Coal Technology (Submitted, IJOGCT-207365)

Conferences

(1) Mayur D. Kevat, Tamal Banerjee. "Comparison of Chemical Looping Combustion and Chemical Looping with Oxygen Uncoupling using Biomass." Recent Trends in Bioprocessing for Healthcare, Energy and Environment, Bioprocessing India 2017 (BPI-2017), IIT Guwahati, 9-11 December, 2017.

(2) Mayur D. Kevat, Tamal Banerjee. “ASPEN Plus based Chemical Looping Combustion of Sawdust Biomass.” Indian Chemical Engineering Congress, CHEMCON 2017, Haldia Institute of Technology, West Bengal, 27-30 December, 2017.