Lappeenranta University of Technology

School of Energy Systems

Energy Technology

BH10A0202 Energiatekniikan kandidaatintyö

Chemical-looping combustion simulation model with Aspen PLUS

Hapenkantajapolton simulaatiomalli Aspen PLUS – ohjelmistoa käyttäen

Examiner: Dr. Petteri Peltola

Supervisor: Dr. Petteri Peltola

Lappeenranta 25.4.2018

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ABSTRACT

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Bachelor's thesis

2018

27 pages, 10 figures, 7 tables

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Keywords: Chemical-looping combustion, carbon dioxide, Aspen PLUS

Global warming is one of the greatest challenges the humanity will face in the coming decades. Greenhouse gases are a major source of global warming and one of them is carbon dioxide, which is the most significant long-living greenhouse gas. Increasingly larger amounts of CO_2 are being created in combustion reaction of fossil fuels. Carbon capture and sequestration (CCS) methods are being developed to try and counter the increasing amount of CO_2 in the atmosphere.

Chemical-looping combustion (CLC) is a rather new technology that has a built-in way to remove carbon dioxide from the flue gases and store it. CLC does not need expensive extra components that lower the efficiency of the power plants to remove carbon dioxide. How CLC differs from conventional power plant process, is the way oxygen is delivered to the combustion. Metallic oxide is circulated between the two reactors and it gives the combustion reaction the oxygen required for the combustion.

This thesis will introduce a simulation done with Aspen PLUS to model the process and the heat flows included. The simulation will be validated with values found from literature and tested by changing its parameters.

TIIVISTELMÄ

Lappeenranta University of Technology

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Energiatekniikan koulutusohjelma

Aatu-Ville Väänänen

Hapenkantajapolton simulaatiomalli Aspen PLUS –ohjelmistoa käyttäen

Kandidaatintyö

2018

27 sivua, 10 kuvaa, 7 taulukkoa

Tarkastaja: TkT Petteri Peltola

Ohjaaja: TkT Petteri Peltola

Hakusanat: Hapenkantajapoltto, hiilidioksidi, Aspen PLUS

Ilmastonmuutos ja on yksi isoimmista haasteista jonka ihmiskunta tulee kohtamaan tulevina vuosikymmeninä. Hiilidioksidi (CO_2) on merkittävin ihmistoiminnan tuottama kasvihuonekaasu, joka kiihdyttää ilmaston lämpenemistä. Ihmiskunnan teollistumisen jälkeen, CO_2-tuotanto on ollut jatkuvassa nousussa fossiilisten polttoaineiden polton takia. Hiilidioksidin talteenotto ja varastointiin (Carbon Capture and Sequestration CCS) liittyviä metodeita yritetään jatkuvasti kehittää, jotta hiilidioksidipäästöjä voitaisiin vähentää.

Hapenkantajapoltto (Chemical-Looping Combustion CLC) on kehityksessä oleva teknologia, joka mahdollistaa hiilidioksidin erotuksen savukaasuista ilman kalliita, kokonaishyötysuhdetta vähentäviä lisälaitteita. CLC poikkeaa perinteisestä voimalaitospoltosta niin, että polttoreaktion happi ei tule ilmasta vaan hapenkantajamolekyylistä. Hapenkantajamolekyylinä käytetään yleensä metallioksidia, jota kuljettaa happea CLC prosessin reaktorista toiseen.

Tässä työssä esitellään Aspen PLUS -simulointiohjelmalla simuloitu CLC prosessi, ja perehdytään simulaation energiavirtoihin. Energiavirrat laskemalla voidaan vahvistaa simulaation toimivuus. Lopuksi testataan simulaation toimivuutta vaihdellen sen parametreja.

CONTENTS

LIST OF SYMBOLS AND ABBREVIATIONS

Roman symbols

H	Enthalpy	kJ/mol
	Enthalpy flow	kJ/s

Subscripts

ar	Air reactor
c	Combustion
fr	Fuel reactor

Abbreviations

CCS	Carbon capture and sequestration
CLC	Chemical looping combustion
GHG	Greenhouse gas
GT	Gas turbine
HRSG	Heat recovery steam generator
IEA	International Energy Agency
IGCC-CLC	Integrated gasification combined cycle with chemical looping combustion
YSZ	Yttria-stabilized zirconium

1 INTRODUCTION

Some of the most potential greenhouse gases (GHGs) like carbon dioxide and nitrous oxides are being produced by the energy producing industry from burning carbon-based fossil fuels. Since those fuels are the main source of energy from combustion reactions, the energy industry is producing a considerable amount of manmade GHG's (Bhoje et al. 2013). This has led to corporations and researchers to search for methods for reducing CO_2 emissions through improving overall energy efficiency and changing fuels to something less polluting or finding methods to produce GHG free energy. Other methods to reduce CO_2 emissions from fossil fuel burning plants would be amine scrubbing, membranes to capture the carbon dioxide emissions, chilled ammonia technologies or using pure oxygen to burn the fuel, but all of these methods drastically reduce the efficiency of the power plant and increase the price of the electricity they would produce (Ishida & Jin 1997). The net power efficiency lost in the CO_2 separation processes is estimated to be around 5 to 15 percent (IEA 1993).

Power plants with chemical looping combustion (CLC) technology offer a different method of reducing CO_2 emissions and higher net power efficiencies than other separation technologies. Combustion of the fuel in CLC plant happens by oxidizing the fuel with an oxygen carrier. Oxygen carrier is a compound that contains oxygen and can donate it to the combustion reaction by reducing itself. The reduced oxygen carrier is then circulated in to a second reactor in which it oxidizes again by reacting with air. This completes the oxidizing-reduction cycle and the carrier can be used repeatedly in the combustion process. In CLC plants air never comes into a direct contact with fuel in this way, the only products from the combustion reaction are carbon dioxide and water vapour. Almost pure carbon dioxide can be obtained by condensing the water vapour into liquid and thus carbon dioxide can be stored and kept away from the atmosphere. (Anhenden & Svedberg 1998)

The aim of this work is to first introduce chemical-looping combustion as a process, and then to create a simple working simulation of it using gaseous fuel and a metal oxide as the oxygen carrier. Aspen PLUS will be used as the simulation engine. After that, the simulation will be tested by calculating the enthalpies formed in the process, and modified to use different oxygen carrier, smaller yields of carbon dioxide and higher mass flows.

2 CHEMICAL-LOOPING COMBUSTION

In this chapter, chemical-looping combustion will be introduced. Oxygen carrier usage, reactor design and the energy production with chemical-looping combustion process will also be discussed.

2.1 Oxygen carriers

Chemical-looping combustion process has emerged as a good alternative for a regular combustion process due to its inherit possibility of reducing carbon dioxide emissions to the atmosphere. CLC does not require the use of an expensive and power consuming CO_2 recovery option because it is based on only producing CO_2 and water vapour in the outlet stream of the fuel reactor.

The idea behind CLC was first introduced in 1954 as a process of producing pure CO_2 from fossil fuels using two connected fluidized beds (Lewis & Gilliland, 1954). The first more accurate version of a CLC process was introduced in 1983 by Richter and Knoche. After that it has been presented as a way to increase thermal efficiency of power plants and a possibility of capturing CO_2 from burning fossil fuels to reduce the impact of the combustion reaction to the climate. The main contributors to researching CLC process have been Chalmers University of Technology in Sweden, CSIC-ECB in Spain and Korea Institute of Energy Research in Seoul South Korea. The first CLC process with gaseous fuels was introduced in 2003 and with solid fuels in 2006 (Lyngfelt 2004 & 2007). (Lyngfelt et al. 2008)

Chemical looping combustion is based on having two different reactors or fluidized beds, one for air and one for fuel as shown in Fig 2.1. Combustion take place in the fuel reactor. Oxygen for the combustion reaction comes from the oxygen carrier compound, which is a metal oxide. The reaction of the combustion is the following:

$$(2n+m)Me_xO_y + C_nH_{2m} \rightarrow (2n+m)\ Me_xO_{y-1} + mH_2O + nCO_2 \qquad (1)$$

The products of the combustion, only contain water vapour and carbon dioxide, so pure carbon dioxide can be obtained after condensing the water to liquid. The reduced oxygen carrier is then transported into the air reactor, where it oxidizes according to the following reaction:

$$Me_xO_{y-1} + ½O_2 \rightarrow Me_xO_y \quad (2)$$

From the air reactor, the only product is the oxidized oxygen carrier with the flue gas also containing N_2 and O_2. The oxygen carrier can then be fed back into the fuel reactor to give an oxidizing agent to the combustion reaction. The only flue gases from the reaction are H_2O and CO_2 from the fuel reactor, and N_2 and O_2 from the air reactor. In a real life situation, some carbon monoxide can also be formed, but since the amount of it is so little, it is mostly ignored in this work. Since nitrogen is present in a different flue gas than the carbon dioxide, pure CO_2 stream can be obtained without the need for separating the two gases. In addition, CLC process also minimizes the NO_x formation, since the combustion happens in an air free environment without any nitrogen present. Oxygen carrier particles keep circulating in the process and the same molecules can theoretically react endlessly without the need for being replaced. Again, in a real life situation some decomposition of the oxygen carrier particles happen, but for the sake of this research it is also ignored. (Lyngfelt et al. 2008)

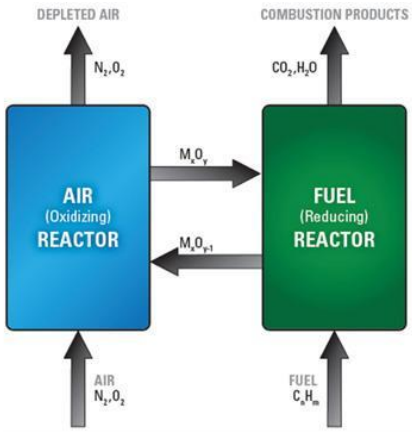

Fig 2.1. Chemical looping combustion. Two different reactors for air and fuel, and metal oxide circulating between them. (National Energy Technology Laboratory)

As stated above, oxygen carrier in the CLC process is a metal oxide. It has been researched that for a CLC system with methane as fuel, Mn_3O_4/MnO, Fe_3O_4, NiO/Ni, Cu_2O/Cu and CoO/Co are feasible to use as the oxygen carrier (Mattisson & Lyngfelt, 2001). A feasible oxygen carrier means that the carrier must have an affinity to react with the fuel gas, namely

methane in this work, and it also must readily react with oxygen in the air reactor with a sufficient rate of reaction. It also has to have enough strength to limit particle breakage and attrition, to be able to sustain multiple redox reactions and to reduce the maintenance required to keep the equipment running respectively (Lyngfelt et al. 2001). Usually, in order to increase the rate of reaction and the physical strength of the oxygen carrier particles, an inert substance is used with the oxygen carrier. This inert substance does not react chemically in the process, but improves the physical strength of the oxygen carrier and enhances the ion permeability of the solid molecule, increasing the rate of reaction with oxygen (Jin et al. 1998). Common inert substances include Al_2O_3, TiO_2, MgO and yttria-stabilized zirconium (YSZ). Usually the particles are quite large in diameter, up to 2 mm (Lyngfelt et al. 2001). This leads to the particles not damaging the process equipment as much as smaller particles could, and still being able to be transported from fluidized bed to another and having big enough surface area for the rate of reaction with the fuel gas to be adequate.

In Fig 2.2, the effect of temperature to the reaction in the fuel reactor can be seen. The rate of reaction is close to same initially but after approximately ten seconds, it drops significantly when the temperature comes down from 1000 °C. This leads to having to keep the fuel reactor in higher temperatures to increase the rate of reaction.

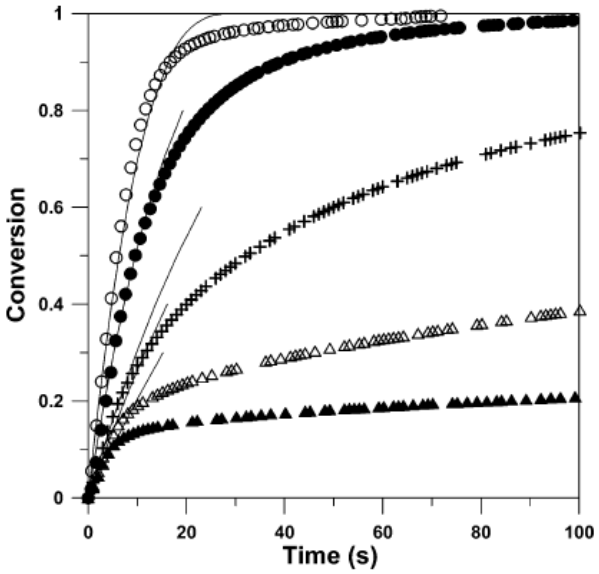

Fig 2.2. Effect of temperature on the reduction reaction of $NiO/MgAl_2O_4$ with CH_4 (10%) at 800°C (▲), 850°C (Δ), 900°C (+), 950°C (●) and 1000°C (○)(Zafar et al. 2007).

Fig. 2.3 shows the experimental results of reactivity of three particles, NiO, CoO and Fe_2O_3 with the addition of 40% YSZ, by comparing time to fractional oxidation of the oxygen carrier. The left-hand side shows the reduction of the oxygen carrier by H_2 at 873K compared to time and the right-hand side of the Fig shows the oxidation of the oxygen carrier by air at 1273K. Note that the reduction is done by H_2 and not by CH_4 with which this paper is concerned, but similar results can be expected from the reduction of the oxygen carrier by CH_4. From Fig. 2.3, it can be seen that the combustion reaction in which the oxygen carrier reduces, is much faster than the reaction in the air reactor, so the rate of reaction of the whole process is controlled by the reaction in the air reactor. (Jin et al. 1998)

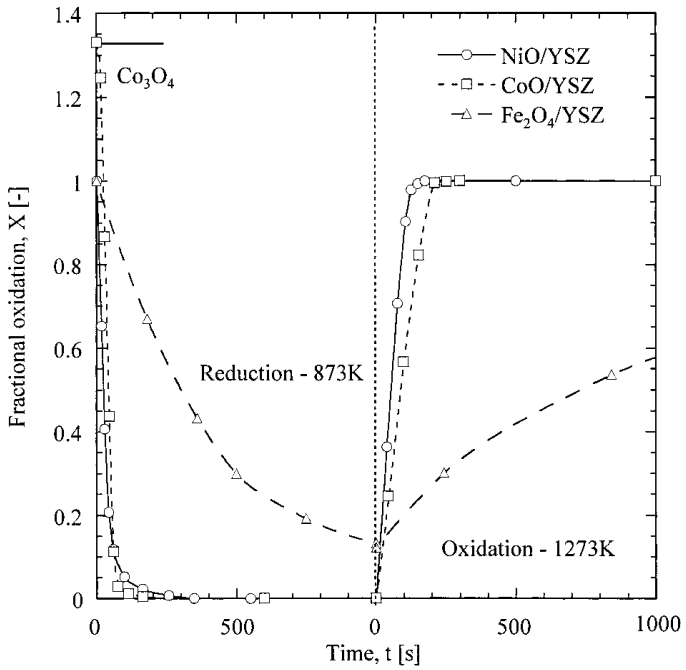

Fig 2.3. Comparison of reactivity of three YSZ-based reactants (Jin et al. 1998).

Fig. 2.4 shows the conversion of CH_4 to CO_2 when using NiO as the oxygen carrier. As seen from it, the conversion of CH_4 to CO_2 is close to 100% at around 700 °C but decreases, when the temperature gets higher, with the conversion being around 97.7% at 1200 °C. As stated above, the rate of reaction of conversion of CH_4 to CO_2 tends to go down drastically if the temperature is below 950 °C. This requires some compromise to be made between having purer end product in CO_2 or having faster rate of reaction in the fuel reactor. (Mattisson et al. 2006)2

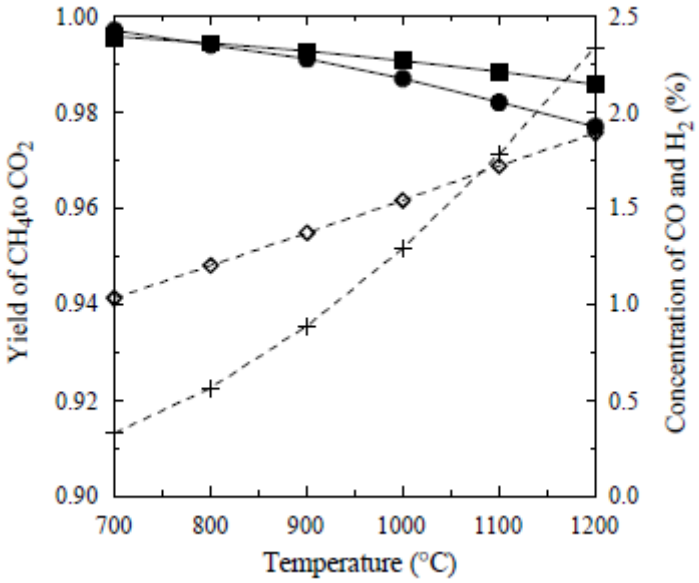

Fig 2.4. The gas yield, γ_{red}(●), γ_{heat}(■) and the concentrations of H_2(◊) and CO(+) as a function of temperature after condensation of H_2O (Mattisson et al. 2006).

This work will use nickel (II) oxide NiO, as the oxygen carrier because of its simple oxidation and reduction reactions and since it is widely recognized as one of the best oxygen carriers for a CLC process. For the sake of simplicity, the first simulation model is completed without an inert solution mixed with the oxygen carrier to validate the functionality of Aspen PLUS as the simulation engine for the process but it will be added later to see if the results differ from only using pure NiO/Ni as the oxygen carrier. With nickel (II) oxide and methane as the reactants in the process, the reactions (1) and (2) happening in fuel and air reactors respectively will go as follows (Anheden & Svedberg 1998):

$$4\ NiO + CH_4 \rightarrow 4\ Ni + 2\ H_2O + CO_2 \qquad \Delta H = 156\ MJ/kmol \qquad (3)$$

$$4\ Ni + 2\ O_2 \rightarrow 4\ NiO \qquad \Delta H = -959\ MJ/kmol \qquad (4)$$

So for every mole of methane, four moles of NiO is required for a stoichiometric reaction in the fuel reactor. And for every mole of oxygen in the air reactor, two moles of nickel is required for a stoichiometric reaction. Reaction 3 is endothermic at 950 °C with a ΔH = 134,4 kJ/mol CH_4 and reaction 4 is exothermic at the same temperature with a ΔH = -468,9 kJ/mol O_2. The

combination of these yield the combustion reaction of methane with air, with a ΔH = -802,4 kJ/mol CH_4. The heat released in the air reactor is about 17% greater than in a conventional combustion reaction of methane, and the corresponding amount of energy is absorbed in the fuel reactor of the endothermic reaction. Thus CLC process is theoretically equal to a conventional combustion process in regards to energy yield. (Mattisson et al. 2006)

2.2 Reactor design

Since the process requires a good contact between the solid oxygen carrier and the gaseous fuel, interconnected fluidized beds seem to have an advantage of other, alternative designs. Lyngfelt et al. suggest a system composed of two interconnected fluidized beds, a high-velocity riser and a low-velocity bubbling fluidized bed in their paper published in 2001. (Lyngfelt et al. 2001)

Fig. 2.5 shows the layout of the two fluidized beds interconnected in the process of chemical looping combustion. Number one in the Fig. 2.5 depicts the air reactor, in which the air is pumped from the bottom of the bed with high-velocity to oxidize the oxygen carrier. In number 3, or the low-velocity bed, oxygen is then transferred from the oxygen carrier to the fuel, and the reduced oxygen carriers are returned to the air reactor by gravity. The bed material used in the fluidized beds is the metal oxide used as the oxygen carrier in the process. Flue gas leaves from the top of the low-velocity bed, as the oxidized oxygen carrier is flowing to the fuel reactor. The circulation in the beds is created by the high velocity of the gas in the air reactor. Some oxygen carrier particles are carried away from the air reactor to the flue gas channel, but they are recovered with the use of a cyclone and led back to the fuel reactor. Water and carbon dioxide are led to the condenser from the fuel reactor, and after condensing the water, remaining carbon dioxide is being compressed and cooled to yield liquid CO_2. (Lyngfelt et al. 2001)

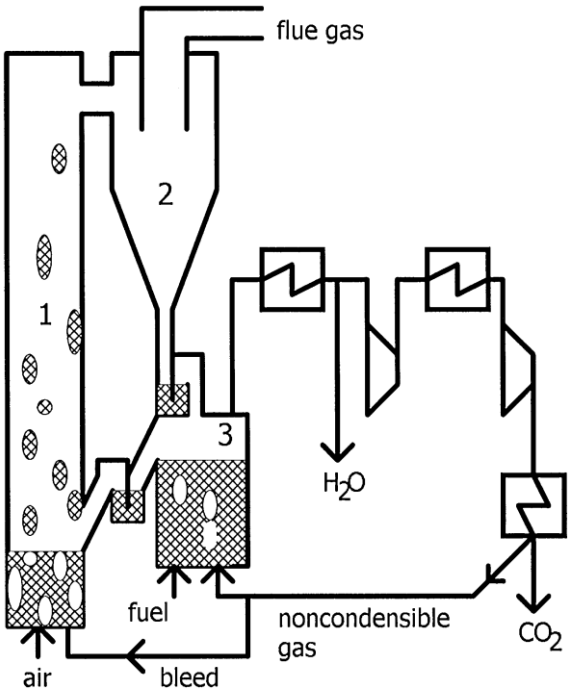

Fig 2.5. Layout of two interconnected fluidized beds in chemical-looping combustion process. (Lyngfelt et al. 2001).

2.4 Energy production with chemical-looping combustion

In a CLC process, the thermal energy is converted to mechanical energy via gas or steam turbines. In this section, flowchart containing some most basic processes needed in a CLC process is introduced and explained.

Fig. 2.6 shows a diagram for integrated gasification combined cycle with chemical-looping combustion. Since it is a gasification process, it uses solid fuel, from which the combustible substances are turned into gas different from the focus of this work. Nevertheless, the process is the same to the process used in this work after the gasification part. The process in Fig. 2.6 uses Fe_2O_3/FeO as the oxygen carrier. The gas reacts with the oxygen carrier in the fuel reactor from which the exhaustion gas continues to heat recovery steam generator (HRSG). Steam from HRSG is then fed into the steam turbine for power generation. The oxygen carrier oxidizes in the air reactor, from which the O_2 depleted air is fed into the gas turbine (GT) from which power is generated. CO_2 is separated from water after HRSG and fed into compressor from which it goes to CO_2 storage. (Fennell et al. 2015)

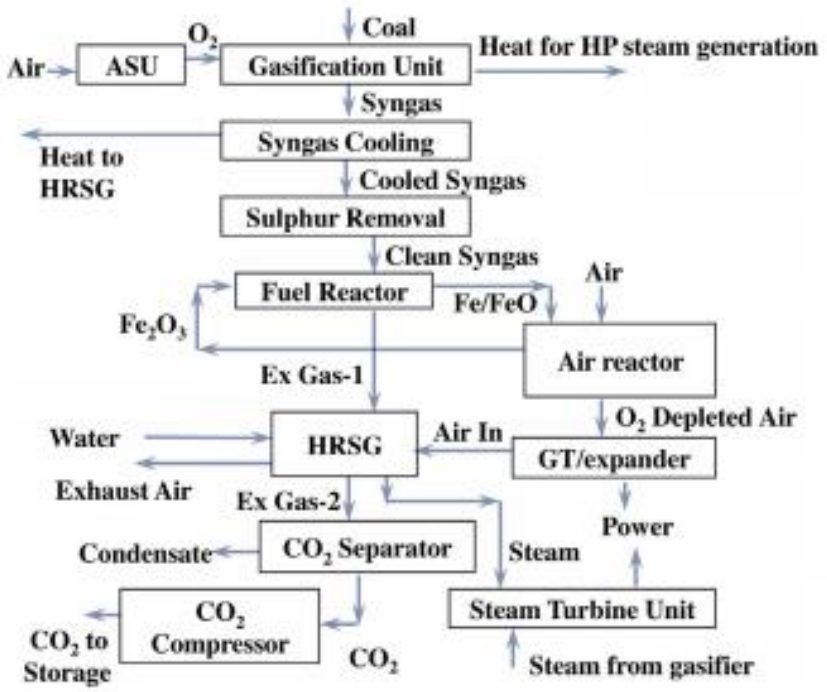

Fig 2.6. Simplified block diagram for IGCC-CLC (integrated gasification combined cycle with chemical-looping combustion). (Fennell et al. 2015)

3 ASPEN PLUS SIMULATION MODEL OF CLC PROCESS

In this section of the paper, the first simulation model is introduced. The components and flows in it will be discussed and some choices taken will be explained to get an insight into how the simulation is constructed. Enthalpy calculations and a summary of the most important enthalpy flows within the simulation will also be presented here.

3.1 Introducing Aspen PLUS simulation model for simplified CLC process

Fig. 3.1 shows the simple but working layout of the CLC process used in this research, containing all the necessary components and flows. The layout contains two reactors, FUELREAC and AIRREAC, for fuel reactor and air reactor respectively. SEP1 and SEP2 are the separators used to separate Ni from CO_2 and H_2O, and NiO from N_2 and possible excess oxygen respectively. Both of the reactors are working at an atmospheric pressure of 1 bar and they are set to be isothermal, so the temperature in the reactors does not change but stays the same during the entire reaction. It is required to add heat into the fuel reactor during the process, since it is an endothermic reaction, and air reactor gives out heat during the reaction being an exothermic reaction.

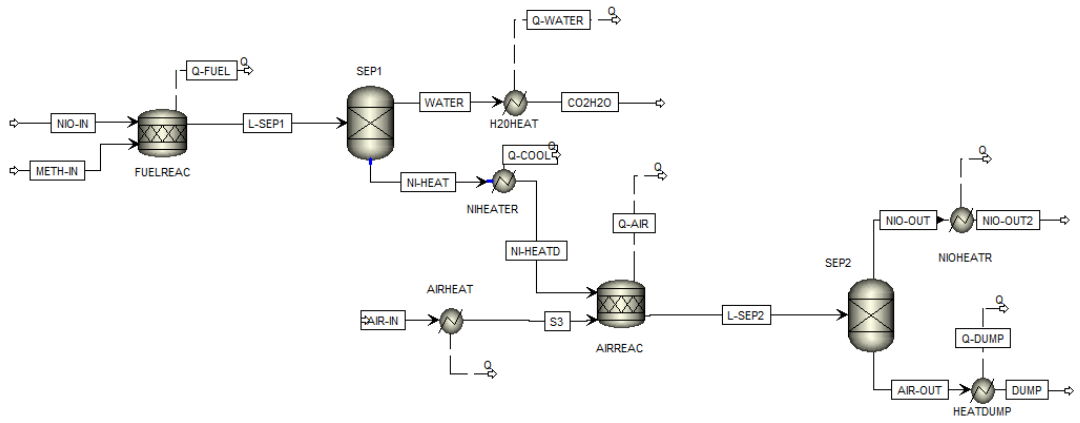

Fig 3.1. Layout of Aspen PLUS simulation of simplified CLC process.

As seen from Table 3.1, the reactions in both fuel and air reactors are in stoichiometric balance. This obviously is not true in a real situation, but it is used here for the sake of simplicity and to try to validate using Aspen PLUS as the simulation program. Also apparent from Table 3.1 is that the oxygen carrier used here is in a pure form, no inert substance is included in the

simplified version of the process.

Table 3.1. Composition of inlet streams to the process and their pressures and temperatures.

	Composition [kmol/hr]	Temperature [K]	Pressure [Bar]
NIO-IN	NiO: 80	298,15	1
METH-IN	CH_4: 20	298,15	1
AIR-IN	N_2: 150,79 O_2: 40	298,15	1

Both reactors used in the simulation are so-called stoichiometric reactors, meaning they require reaction formulas and conversion rates stated for them. The temperature in the fuel reactor is 950 °C because, as seen from Table 3.2, the rate of reaction tends to get a lot smaller if the temperature goes below it.

Table 3.2. Type of the reactors used with the working temperatures and pressures.

	Type	Temperature [K]	Pressure [Bar]
FUELREAC	RStoic	1223,15	1
AIRREAC	RStoic	1273,15	1

All the heaters, except AIRHEAT and NIHEATER, are set to cool the outlet to 25 °C and acquire the heat from it. AIRHEAT and NIHEATER are used to warm up input air to air reactor and the nickel from fuel reactor to the temperature of the air reactor. NIO-OUT2 pumps out the oxygen carrier NiO at 25 °C from the process, but in a real life situation it would of course circulate back to the fuel reactor, it's been left out here for the sake of simplicity and to make the enthalpy calculations easier.

Table 3.3 confirms, that all the reactions are stoichiometric, the moles are in balance, and only thing that does not react is the nitrogen, which is only there because it is present in the intake air. NiO amount from the outlet is the same as the inlet to the fuel reactor, as it should be, for the process to be continuous.

Table 3.3. Outlet streams from the process, their compositions, temperatures, and pressures.

	Composition [kmol/hr]	Temperature [K]	Pressure [Bar]
CO2H2O	H_2O: 40 CO_2: 20	298,15	1
NIO-OUT2	NiO: 80	298,15	1
DUMP	N_2: 150,79	298,15	1

3.2 Validation of Aspen PLUS as a simulation engine

Now to get a grasp on the energy produced in the process, and to validate the simulation to work and Aspen PLUS to be used as a simulation engine for this type of a process, enthalpy calculations must take place. First, it is necessary to calculate the energy contained in methane gas and that can be done by multiplying the heat of combustion of methane gas by the mole flow or mass flow of methane. Heat of combustion is the heat released when a substance undergoes a combustion with oxygen under standard conditions, meaning temperature of 273,15 K and pressure of $1*10^5$ Pa. For methane, the heat of combustion is ΔH_C = -890,7 ± 0,4 kJ/mol (Pittam & Pilcher 1972). And as seen from Table 3.3, 20 kmol/hr of CH_4 is being fed to the process so:

$$\Delta H = -890{,}7\,\frac{\text{kJ}}{\text{mol}} * 20\,\frac{\text{kmol}}{\text{hr}} * \ 1000\,\frac{\text{mol}}{\text{kmol}} * \frac{1}{3600}\,\frac{\text{hr}}{\text{s}} \approx \ 4950\,\frac{\text{kJ}}{\text{s}} \ \approx \ 5\ \text{MW} \qquad (5)$$

Heat released from burning the methane fed into the process is about 5 MW.

To validate Aspen PLUS as a reliable tool to simulate and calculate enthalpy calculations and energy balance, a simple reaction setup is shown in Fig. 3.2. Methane and air containing oxygen and nitrogen are fed into the boiler where they react to form carbon dioxide and water. Nitrogen exits the boiler without reacting.

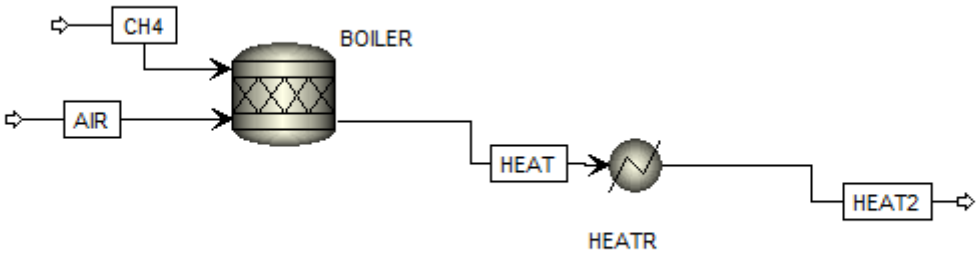

Fig 3.2. Reaction of air with methane gas, simulated with Aspen PLUS.

The reactants are fed in to the boiler at 298,15 K or 25 °C and the reaction takes place in an isothermal environment at 1173,15 K or 900 °C. The heater (HEATR) then cools the products back down to 298,15 K or 25 °C. The pressure of the boiler is 1 bar.

Table 3.4. Composition, temperature and enthalpy flow of the streams CH_4, AIR and HEAT2.

	Composition [kmol/hr]	Temperature [K]	Enthalpy flow [kJ/s]
CH_4	CH_4: 20	298,15	-414,1
AIR	O_2: 40 N_2: 150,8	298,15	-0,4
HEAT2	H_2O: 40 CO_2: 20 N_2: 150,8	298,15	-5321,81

The enthalpy difference that the reaction creates is calculated as follows:

$$\Delta H = -5321{,}81\,\frac{\text{kj}}{\text{s}} - \left(-0{,}4\,\frac{\text{kJ}}{\text{s}} + \left(-414{,}4\,\frac{\text{kj}}{\text{s}}\right)\right) = -4907\,\frac{\text{kJ}}{\text{s}} \quad (6)$$

So the Aspen PLUS simulation yields a result that is almost equal to the ideal combustion of methane gas. The thermal power generated is again, as it should be, approximately 5 MW. Aspen PLUS seems to be a reliable tool to perform at least simple enthalpy calculations through its simulation engine.

3.3 Enthalpy flows of the simulation

In this section, the enthalpy flows of the simulated reaction will be looked into. As seen above in Section 3.2, the reaction should produce approximately five megawatts of thermal energy. Table 3.5 summarizes the most important streams of the simulations and gives their enthalpy flow, from which the theoretical thermal energy yield of this simulation can be calculated. The total yield is calculated by subtracting the enthalpy of inlet streams from the enthalpy of the outlet streams. Inlet streams in this simulation are NiO-IN, METH-IN and AIR-IN. Outlet streams are CO_2H_2O, NiO-OUT2 and DUMP. Since NiO-IN and NiO-OUT2 cancel each other out and DUMP and AIR-IN are zero enthalpy streams the thermal energy from the reaction will be:

Table 3.5. Compositions and enthalpy flows of the relevant streams in the simulation.

	Composition [kmol/hr]	Enthalpy flow [kJ/s]
NiO-IN	NiO: 80	-5327
METH-IN	CH_4: 20	-414
L-SEP1	H_2O: 40 CO_2: 20	-3292
CO_2H_2O	H_2O: 40 CO_2: 20	-5323
NI-HEATD	Ni: 80	855
AIR-IN	N_2: 150,8 O_2: 40	0
S3	N_2: 150,8 O_2: 40	1720
L-SEP2	NiO: 80 N_2: 150,8	-2825
NiO-OUT2	NiO: 80	-5327
DUMP	N_2: 150,8	0

$$\Delta H = -5323\,\frac{kJ}{s} - \left(-414\,\frac{kJ}{s}\right) = \mathbf{-4909\,\frac{kJ}{s}} \quad (7)$$

It is basically identical to the enthalpy from the Section 3.2, which it should be since the reaction is the same, just performed in more steps to eliminate the formation of nitrogen oxides and help the recovery of carbon dioxide.

It is also worth taking a look into the enthalpy changes happening during the chemical reactions in air and fuel reactors. Inlet streams to air reactor are NI-HEATD and S3 and the only outlet stream is L-SEP2. The enthalpy change in the air reactor is:

$$\Delta H_{ar} - 2825\,\frac{kJ}{s} - \left(1720\,\frac{kJ}{s} + 855\,\frac{kJ}{s}\right) = \ -5400\,\frac{kJ}{s} \quad (8)$$

Since the reaction in the air reactor is exothermic, it means that the reactor must be cooled down during the reaction to keep it isothermal at 1273,15 K.

Inlet streams to the fuel reactor are NiO-IN and METH-IN, and the only outlet stream is L-SEP1. Thus, the same equation as above can be used to calculate the change in enthalpy within the fuel reactor:

$$\Delta H_{fr} - 3292\,\frac{kJ}{s} - \left(-5327\,\frac{kJ}{s} + \left(-414\,\frac{kJ}{s}\right)\right) = 2449\,\frac{kJ}{s} \quad (9)$$

The reaction in the fuel reactor seems to be highly endothermic, so the reactor requires a lot of heating to keep it at the isothermal temperature of 1223,15 K. Theoretically endothermal reactors are better, since they do not have the same risk of the reaction accidentally accelerating for example in the case of a failure in the cooling system of the reaction as in exothermic reactors. In the end, the air reactor is so little exothermic here so it should not be a problem in an actual power plant.

4 CHANGING THE PARAMETERS OF THE SIMULATION

In this chapter, the established simulation is taken further to compare results with change in the yield of CO_2 from CH_4 and also to take into account another possible oxygen carrier and compare differences between them. The mass flow of methane will also be increased and the results of the increase studied.

4.1 Conversion of CH_4 to CO_2

The conversion of CH_4 to CO_2 in the fuel reactor is not 100% in a real process. Thermodynamic analysis of CH_4 as a fuel confirms the yield of CO_2 and H_2O from CH_4 to be between 97.7% and 99.8% within the temperature range of 700-1200 °C (Mattisson et al. 2006). Since the fuel reactor in this paper is set to 950 °C, it can be approximated that the actual yield would be around 98.5%.

Using Aspen PLUS, the conversion coefficient of CH_4 to CO_2 and water can be easily changed. Table 6 shows the energy recovered from the process and the percentage of the energy recovered compared to the 100% conversion case. It can be seen that the energy recovered does not go down exactly as much as the conversion changes but a little bit more. This is due to the excess methane going to waste in the simulation and not being used in the process since the conversion is not 100% and the reaction is not in stoichiometric balance anymore. Nonetheless, the molar enthalpy of the reaction stays the same, the energy is just not produced as fast when the conversion is not 100%.

Table 4.1. The energy yield of the process compared to the change in conversion of CH4 to CO2 and water.

Conversion	100%	99,5%	99%	98,5%	98%
Energy recovered [kW]	4910	4882	4856	4829	4803
Percentage compared to the 100% case	100%	99,43%	98,90%	98,35%	97,82%

Fig. 4.1 shows the conversion of CH_4 to CO_2 and water again, and as already stated above, the change in energy released in the process is practically linear compared to the change in the fractional conversion.

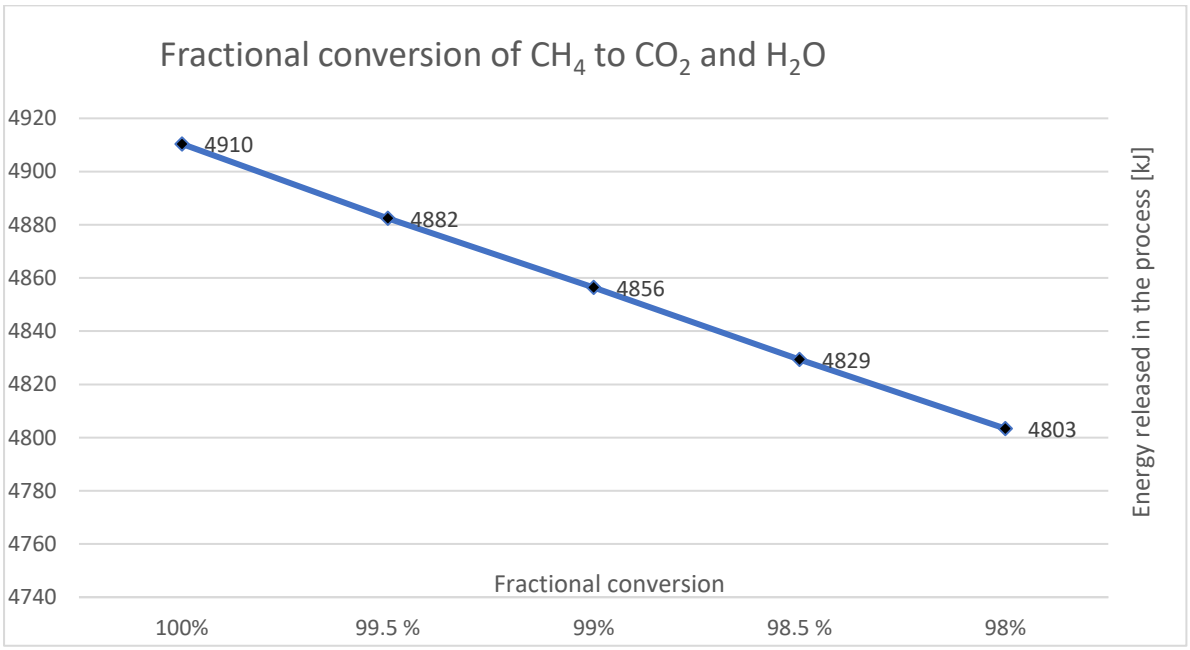

Fig 4.1. Fractional conversion of CH4 to CO2 and water and its effect on energy released in the process graphically represented.

4.2 Increasing the mass flow of fuel

Increasing the mass flow of the fuel leads to increase in the power available in the process. In this chapter, the mass flow of the fuel will be increased, and the effects of to the energy recoverable from the process studied.

The mass flow of methane in the control case was 20 kmol/hr, which is equal to 0,09 kg/s. This lead to 5 MW's of power being available from the process. The mass flow will first be quadrupled and then doubled three times. The mass flow of the oxygen carrier and the air fed into the air reactor will increase respective to the increase of methane. The results of this increase will be shown in Fig. 4.2 below.

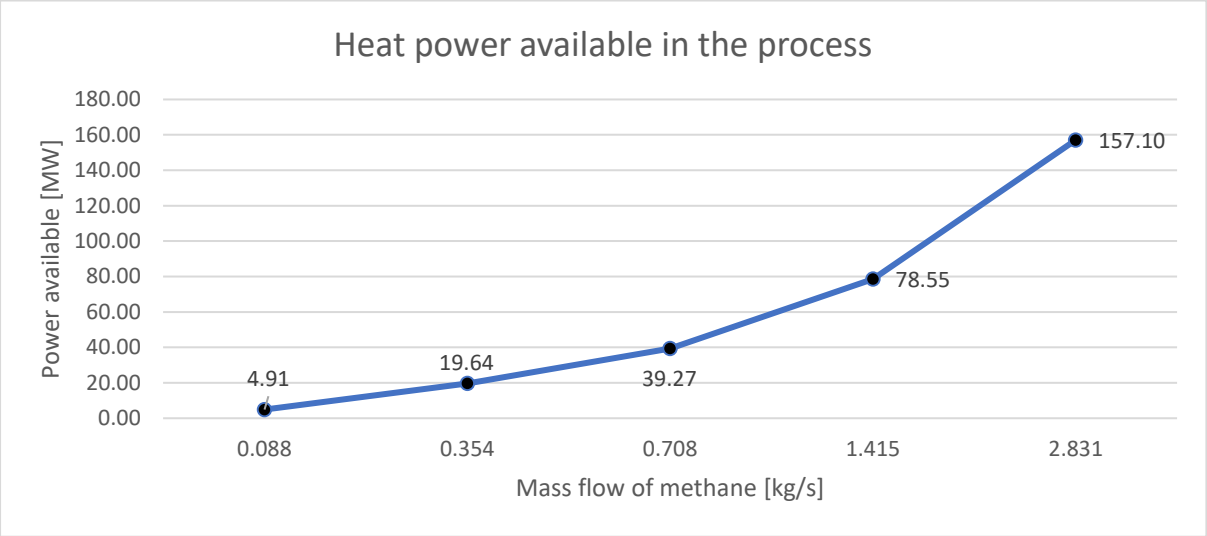

Fig 4.2. Effect of increasing the mass flow of methane to the power available in the process.

As seen from Fig 4.2, the power is increasing linear to the increase in the mass flow of methane.

4.3 Using CuO as an oxygen carrier

Multitude of other oxygen carriers than NiO/Ni can be used in chemical looping combustion. In this chapter, the control case using NiO/Ni as the oxygen carrier will be customized to be used with copper (II) oxide or cupric oxide. Copper (II) oxide has the formula of CuO and when reduced, it loses the oxygen atom and reduces to just copper. The reactions taking place with CuO/Cu oxygen carrier in fuel and air reactors are in Equations 5 and 6 respectively:

$$4\,CuO(s) + CH_4(g) = 4Cu(s) + 2H_2O(g) + CO_2(g) \quad (10)$$

$$Cu(s) + 0{,}5O_2(g) = CuO(s) \quad (11)$$

Since CuO/Cu's reaction with methane is much like the reaction between NiO/Ni and methane, the results from the simulation are expected to be rather similar, but it turns out that the main difference between these two oxygen carriers is that the reaction of CuO with CH_4 in the fuel reactor turns exothermic when the reaction of NiO with CH_4 was highly endothermic. This is considered to an advantage to CuO since it reduces the particle circulation needed to maintain constant fuel reactor temperature (Lyngfelt et al. 2008). Since copper has a melting point of 1085 °C, the reaction between CuO and CH_4 is usually done in lower temperatures. Since the reaction between CuO and CH_4 turns to exothermic when the temperature goes below 780 °C,

the fuel reactor temperature has been set to constant 750 °C in this paper. Air reactor remains at 900 °C due to the restrictions in the reaction rate.

Table 4.1 contains the necessary flows in the simulation, their compositions and enthalpy flows. Since the mass flow of the CH_4 is kept constant, same as in the control case with NiO, the enthalpy released in this case should also be the same, and the same method can be used to calculate the results.

Table 4.1. Composition and enthalpy flows of the streams when using CuO/Cu as the oxygen carrier.

	Composition [kmol/hr]	Enthalpy flow [kJ/s]
NiO-IN	CuO: 80	-3496
METH-IN	CH_4: 20	-414
L-SEP1	H_2O: 40 CO_2: 20	-3948
CO_2H_2O	H_2O: 40 CO_2: 20	-5323
NI-HEATD	Cu: 80	529
AIR-IN	N_2: 150,8 O_2: 40	0
S3	N_2: 150,8 O_2: 40	1720
L-SEP2	CuO: 80 N_2: 150,8	-1000
NiO-OUT2	CuO: 80	-3496
DUMP	N_2: 150,8	0

$$\Delta H = -5323\,\frac{kJ}{s} - \left(-414\,\frac{kJ}{s}\right) = -4909\,\frac{kJ}{s} \quad (12)$$

The enthalpy released in the overall reaction is exactly the same as in the control case, as it should be. The enthalpy flow of the reaction in the fuel reactor can also be calculated as before:

$$\Delta H_{fr} = -3948\,\frac{kJ}{s} - \left(-414\,\frac{kJ}{s} + \left(-3496\,\frac{kJ}{s}\right)\right) = -38\,\frac{kJ}{s} \quad (13)$$

As seen from here, the reaction in the fuel reactor is just slightly exothermic. In this case the

reactor needs to be cooled down to keep the temperature constant in opposed to the control case in which the reactor had to be warmed up to keep the temperature constant due to the reaction in it being endothermic.

5 DISCUSSION

The simulation model seems to be working as intended also when the parameters are changed in the chapter 4. In this chapter, key points concerning the results received, validity of them and the possible future development of this simulation are discussed.

5.1 Results

The results received from the simulation seem to be in line with data received by calculating the process by hand and with previous information about chemical-looping combustion processes. Since the same simulation has been tested with two different metal oxides as the oxygen carriers, different conversion coefficients of CH_4 to CO_2 and five different mass flows of methane, and the results are in line with previous known information, it can be said with certainty that the simulation is reliable in simple cases of chemical-looping combustion.

5.2 Future development of the simulation model

The simulation model introduced in this paper only scratches the surface of the capabilities of the simulation engine and could be taken a lot further. Possible and improvement to the simulation model would be using an inert solution with the oxygen carrier and seeing if it would affect the simulation in any way. Since inert solution is used to increase physical properties of the oxygen carrier and the rate of reaction of the chemical reactions taking place in the process, it should be also studied.

Since it cannot be guaranteed that the reactions, especially in the fuel reactor are completely pure, the next step to improve the model would be to consider the possible unwanted reduced species of the oxygen carriers. It is possible for the oxygen carrier to reduce to different species than to the purest form of the metal, for example it is possible for NiO to reduce to at least $Ni(OH)_2$ and $NiCO_3$ and CuO to CuOH, $Cu(OH)_2$, $CuCO_3$ and Cu_2O. These unwanted species of the oxygen carriers could create some unwanted situations within the process. It is possible to avoid these reduced species by making the circumstances within the fuel reactor to be as favorable as possible to the one reduced species that is wanted, but even then there is a possibility of having some unwanted species forming in the reactions.

The major component missing in the simple simulation done in this study, is the ability to see and study the rate of reactions. Since the rate of reaction is not considered here too much, the temperatures kept in the reactors are mainly just experimental data from studies done before, but it would be valuable to get to see the actual rate of reactions happening in both reactors here. The effects of temperature on the reaction rate of the chemical reactions has already been talked about in this study, and it would be vital to know, when major changes in the rate of reaction happen, to be able to test the possible parameters of temperature in the reactors. Aspen PLUS features rate of reaction calculations embedded in the simulation engine, but the amount of work and extra effort it would take to get sufficient results from it, is simply way beyond the scope of this study.

Aspen PLUS provides a possibility of calculating reactions in different blocks within the reactors. Since the reaction between the oxygen carrier and fuel is not instantaneous and does not happen in exactly same spot in the reactor, the simulation could be taken further by taking this into account and developing a method for calculating the rate of reaction and temperatures within different part of the fluidized beds. It could also be seen, how much of the metal oxide would react in which part of the reactor, since in a real-life application of this process, the reactions would not be stoichiometric and since the fluidized bed would use the metal oxide as the bed material, there would be a need to have a lot more of it than the stoichiometric amount required in the reaction. Since the amount of the oxygen carrier and the fuel would be different in each part of the fluidized bed, the rate of reaction would differ within the reactor. The largest part of the reactions would naturally occur in the densest part of the bed since there would be the most of solids present and it would create the most surface area for the reaction to occur (Ocone et al., 2014). This again is way beyond the scope of this study and thus ignored.

6 CONCLUSIONS

Chemical-looping combustion seems like a great technology to try and decrease the carbon dioxide emissions created by the energy industry. The technology to remove CO_2 from the flue gases without an expensive and inefficient extra equipment is a rather tempting possibility for future power plant processes while the energy sector is moving towards using renewable and less polluting energy sources. However, since the CLC process is still being studied and in its current form is too expensive to use in a major scale energy production, the technology currently cannot be trusted to be in the forefront of the change in the energy sector. But CLC has a chance to be a technology used in the change towards greener and less polluting forms of energy.

In this work, the simple simulation created using Aspen PLUS, gives a look into the process and the enthalpy flows within it. The simulation is validated by calculating the heat energy released by the reactions and the process and by comparing these results to previous information about the process and thermodynamics. The simulation works very well with the control case and is then tested with using CuO/Cu as the oxygen carrier, increasing the mass flow of the fuel and altering the conversion of CH_4 to H_2O, all separately. The simulation gives expected results in each of the cases.

Since the simulation is simple and passes by some parts of an actual CLC process, it would require some improvements to make it more reliable to be used in a base of a CLC plant. However, the enthalpy flow results acquired from the simulation seem to correspond with Figs and results from already established literature. It can be said, that with further research into the topic of CLC and improvements to the simulation, it could be developed into a reliable source of accurate information for study of CLC process.

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