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Generation of hydrogen from biogas with inherent carbon dioxide sequestration via a hybrid chemical looping – steam iron process

Master of Science Thesis

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Department of Energy and Environment
Division of Energy Technology
CHALMERS UNIVERSITY OF TECHNOLOGY
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Notorious for its substantial contribution to anthropogenic climate change, the power industry has been implied to provide long and short term solutions for its emissions of the greenhouse gas CO_2 . Possible approaches include more effective energy conversion and consumption, utilization of less carbon intensive fuels or shifting to renewable energy sources. Still, most analysts agree that fossil fuels will be dominating the energy market in the near future, and as a consequence novel concepts for combustion of fossil fuels without emissions of CO_2 to the atmosphere such as Carbon Capture and Storage have attracted great interest. An innovative technology for CO_2 capture is Chemical Looping (CL) combustion, in which a solid oxygen carrier material performs the task of transporting oxygen between two reactors. Flexible in terms of fuel types (solid, gas) the chemical looping concept provides easily sequestrable CO_2 , potentially at low cost and without energy penalty. A wide range of designs are possible, depending on the targeted end-product. One much desired product considered as a potential alternative to fuels in transport industry is hydrogen, production of which is far from clean and simple.

In this study, hydrogen production via the steam-iron reaction in a process configured in similar fashion as chemical looping combustion is examined. The hybrid chemical-looping-steam-iron system proposed in the study consists of three fluidized bed reactors, a fuel reactor, a steam reactor and an air reactor. Selected on its ability to achieve multiple oxidation states and suitable thermodynamic properties, iron oxide is transported through the interconnected fluidized beds in a cyclic manner. In the fuel reactor, fuels such as methane, syngas and biogas from gasifier are oxidized with oxygen provided by Fe_2O_3 , producing CO_2 , H_2O and FeO . In the steam reactor, FeO is oxidized to Fe_3O_4 with steam, producing H_2 . Finally, in the air reactor Fe_3O_4 is oxidized to Fe_2O_3 with air producing heat to sustain the endothermic reactions in the other reactors.

The potential of the process was examined by thermodynamically modeling with Aspen Plus software, while an experimental approach was used to examine if the proposed approach would be practically feasible. Methane, syngas and gasifier output simulated biogas fuels were tested with the aim of examining the fuel composition effect on the overall efficiencies. Between analyzed fuels, syngas indicated the highest net hydrogen efficiencies, with values as high as 86.1% for a stoichiometric steam feed ratio, to 76.14% for an excess steam ratio. Meanwhile biogas system, due to its low heating values and steam presence in the fuel composition displayed the lowest net efficiencies with 68.1 and 42.5% for stoichiometric and excess steam feed ratios.

The experiments were conducted in a batch fluidized bed reactor at a temperature range between 700 to 950°C. Different fuels and oxygen carrier materials were examined. The results indicated that operation with synthetic iron oxide particles supported on MgAl_2O_4 and syngas as fuel was feasible,

while the use of waste materials and natural minerals as oxygen carrier and simulated biogas a fuel were much more challenging.

Keywords: iron-steam process, chemical looping, hydrogen production, biogas.

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List of Abbreviations and Symbols

Abbreviations

AR	Air Reactor
B	Biogas
CCS	Carbon Capture and Storage
CL	Chemical Looping
C_nH_{2m}	Generic representation for hydrocarbon fuels
FMA	Synthetic iron oxide with Magnesium Aluminate as support
FR	Fuel Reactor
GHG	Green House Gas
IL	Ilmenite
IOS	Iron Scale Oxides
(l)	Liquid state
Me/Me_xO_{y-1}	Metal Oxide in its reduced state
MeO/Me_xO_y	Metal Oxide in its oxidized state
OC	Oxygen Carrier
S	Syngas fuel
$S_{stoic.}$	Stoichiometric steam to fuel ratio
SR	Steam Reactor
Tr.Pt.	Triple Point
(v)	Vapor state
wt	Weight fraction
XRD	X-ray powder diffractometry

Symbols

ΔH°	[kJ/mol]	Standard Enthalpy of reaction
γ	[%]	Efficiency, yield
τ	[s]	Residence time
C_p	[J/kg/K]	constant pressure heat capacity
d	[μm]	Particle diameter
H_i	[kJ/mol]	Low heating value of component i
n_i	[mol, mol/s]	Mol number, rate of component i
Q_{hot}	[MW]	Minimum hot utility
Q_{HR}	[MW]	External Heat duty
p_i	[bar]	Partial pressure of component i
t	[s, min]	Time
T	[°C/K]	Temperature
U	[mL _n /min]	Volumetric flow rate
ω	-	Mass-based reduction degree
x_i	-	Mol fraction of component i
dt	-	Time derivativ

1. INTRODUCTION

1.1 Background

In the two centuries following the beginning of the industrial revolution, generation of heat and power via combustion of fossil fuels has become a central part of our societies. Over the decades, the power industry has experienced continuous progress in its technologies, giving rise to more efficient and economic processes. Still, concerns over the buildup of high concentrations of greenhouse gases' (GHGs) such as CO₂ in the atmosphere has pushed society to a green awareness. It is now widely accepted that the power industry will need to put limitations on the emissions of greenhouse gases such as carbon dioxide.

Notorious for its substantial role in the GHG effect[1], the power industry has been implied to provide long and short term solutions such as more effective energy conversion and consumption, utilization of less carbon intensive fuels or shifting to renewable energy sources solar, wind power)[2]. Concerning the less carbon intensive fuels, biomass utilization has acquired a great deal of attention lately. Biomass in itself is defined as any organic material recently living organisms, based on carbon, oxygen and hydrogen as main elements. It can be either directly used to provide heat or converted to biofuels, such as bioethanol, biogas or syngas. Conversion to gaseous biofuels is realized by gasification or partial oxidation of the biomass to simple gas mixtures of carbon monoxide (CO), hydrogen (H₂), water (H₂O), carbon dioxide (CO₂), methane (CH₄), volatile hydrocarbons and nitrogen (N₂). Depending on the gas compositions these gaseous biomass products can either be called synthesis gas (Syngas) with carbon monoxide and hydrogen as dominative part or biogas with various gas compounds, including water as well.

Agreeing that fossil fuels will still be in circulation and dominating the energy market, novel concepts such as Carbon Capture and Storage have attracted great interest in the last decades. The notion includes three steps: capturing and high pressure compression of CO₂ produced by industries as a side-product, its transport to storage sites and long term storage [2].

Addressing to the first step, CO₂ capture technologies have evolved in three main categories; as pre-combustion, oxy-fuel combustion and post-combustion technologies. Nevertheless, these systems require a significant amount of energy, which in turn has a negative effect in the energy prices. Taking in consideration this drawback, other alternatives have been proposed, providing shortcuts to easier CO₂ capture. One such potential technology is Chemical Looping (CL) combustion, an emerging concept with potentially lower incremental in electricity prices than other CCS technologies for CO₂ sequestration [3-5].

1.2 Chemical Looping Combustion

The chemical-looping (CL) concept includes different processes depending on fuel type used and the desired products, be it heat, power, syngas/biogas or hydrogen [4-7]. In general, as a concept it refers to oxidation of fuels with oxygen carrier solid material (MeO) in a circulating fluidized reactors system (see fig.1), while the resulting oxygen depleted solid (Me) is circulated back to fluidized air reactor to be oxidized with air to its most oxidized state.

The most commonly proposed chemical-looping process is chemical-looping combustion, in which the sum of reactions (eqn.1 and eqn.2) and net energy released are the same as in ordinary combustion. Here the flue gas from the fuel reactor consists essentially of CO₂ and H₂O. Hence cooling in a condenser is all that is needed to obtain almost pure CO₂, suitable for sequestration. This concept allows oxidation of various fuels with inherent capture of carbon dioxide, which could then be sequestered and prevented from being emitted into the atmosphere [4, 8].

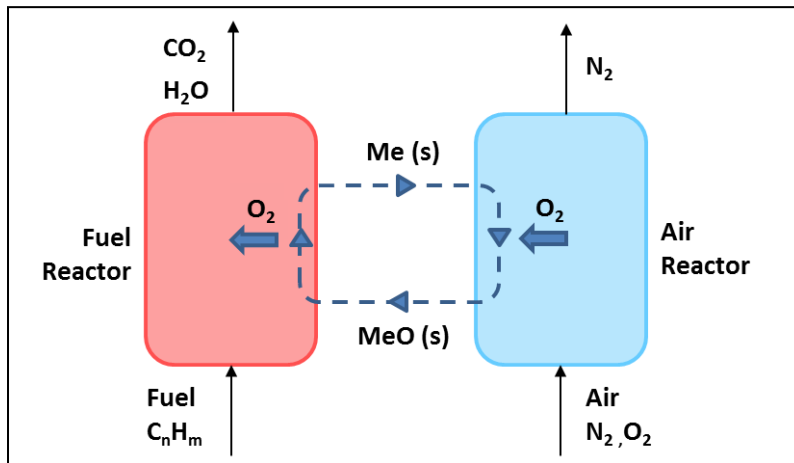
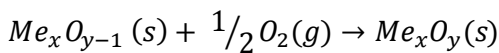
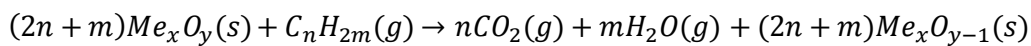


Figure 1.1. Chemical looping combustion concept.

Equation 1 – Metal oxide oxidation with air



Equation 2 – Fuel oxidation with metal oxide

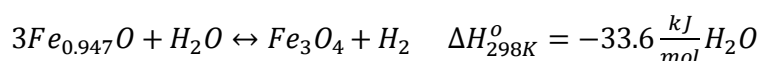


The chemical-looping concept has also found application in liquid fuel combustion and in biomass gasification, in which it could be used for tar cleaning ([9-15]. Basically, small amounts of oxygen is supplied from a solid oxygen carrier to gasified biomass, in order to oxidize tar components and produce a tar free gas mixture of carbon monoxide, hydrogen, methane, carbon dioxide and steam. This tar free biogas would then require further processing in order to conform to industrial standards.

1.3 Hydrogen as alternative energy carrier

Once considered as a futurist fuel, hydrogen, are nowadays considered as an intriguing energy carrier and an alternative to oil and fuels used in transport industry. With its large energy carrying capacity and with water as its only clean, green end-product, the use of hydrogen as energy carrier have attracted a significant research attention. Still, hydrogen production is presently far from green and simple. Currently used as an intermediate reactant in chemical industry, hydrogen production can be realized by processes such as steam reforming of natural gas, autothermal reforming, catalytic partial oxidation, electrolysis processes and lately suggested sorption enhanced chemical-looping reforming [16-18]. Another alternative revived together with chemical looping concept is the old steam-iron process [5, 19-22]. The process was first introduced by Messerschmitt and Lane [23, 24], and provides hydrogen from a slightly exothermic water splitting reaction (eqn.3) via iron oxides redox pairs of $\text{Fe}_3\text{O}_4/\text{Fe}_{0.947}\text{O}$.

Equation 3 – Steam reduction with magnetite



1.4 Iron oxide as an oxygen carrier

Extensively studied as oxygen carrier material for chemical looping applications, it is well established that iron oxide would be a feasible oxygen carrier for chemical-looping combustion. It has a moderate oxygen transport capacity, possessing decent reactivity with air and fuels can provide complete conversion of fuel to CO_2 and H_2O , has good resistance to carbon deposition, high chemical and mechanical stability, etc.[7, 12, 21, 25]. It also fulfills requirements such as being non-toxic and available at low costs. Generally oxygen carrier particles are utilized with an inert porous support such as MgAl_2O_4 , Al_2O_3 , TiO_2 , yttria-stabilized zirconia [7, 26-28], which enables higher surface area during reaction, enhanced mechanical stability and attrition resistance. MgAl_2O_4 as a support possesses a higher melting point and chemical resistance [27, 29, 30]. Johansson and his coworkers concluded that a weight ratio of 60% of Fe_2O_3 on 40% MgAl_2O_4 sintered at 1100°C showed the highest reactivity and resistance to agglomeration.

Many oxygen carrier materials possess multiple oxidation states [21]. Iron oxide is known for having of four oxidation states: hematite (Fe_2O_3), Magnetite (Fe_3O_4), wüstite ($\text{Fe}_{0.947}\text{O}$) and metallic iron (Fe). This characteristic has been elaborated into a hybrid three-reactor chemical looping process by different authors such as Chiesa et al.[19], Ryden and Arjmand[5] and Chen et al.[31]. The process shown in figure 2 and summarized reaction-wise in equation 4-7, involves the reduction of Fe_2O_3 to $\text{Fe}_{0.947}\text{O}$ by gaseous fuels such as methane or syngas and oxidized with to a second oxidation state, known as Fe_3O_4 and finally oxidized with air to initial state of Fe_2O_3 . During this process, beside heat being provided by the air oxidation step and transferred to each reaction step by the iron oxide

particles, easily sequestrable CO_2 in fuel oxidation phase and hydrogen is being produced in the steam reduction phase.

For the chemical looping concept, fluidized bed reactors have been adopted, fitting best the working principles in CL. The fluidization characteristic of these reactors provides the oxygen transfer from air to fuel reactor, at the same time keeping a uniform mixing and eliminating any radial/axial concentration and temperature gradients in the reactor volume.

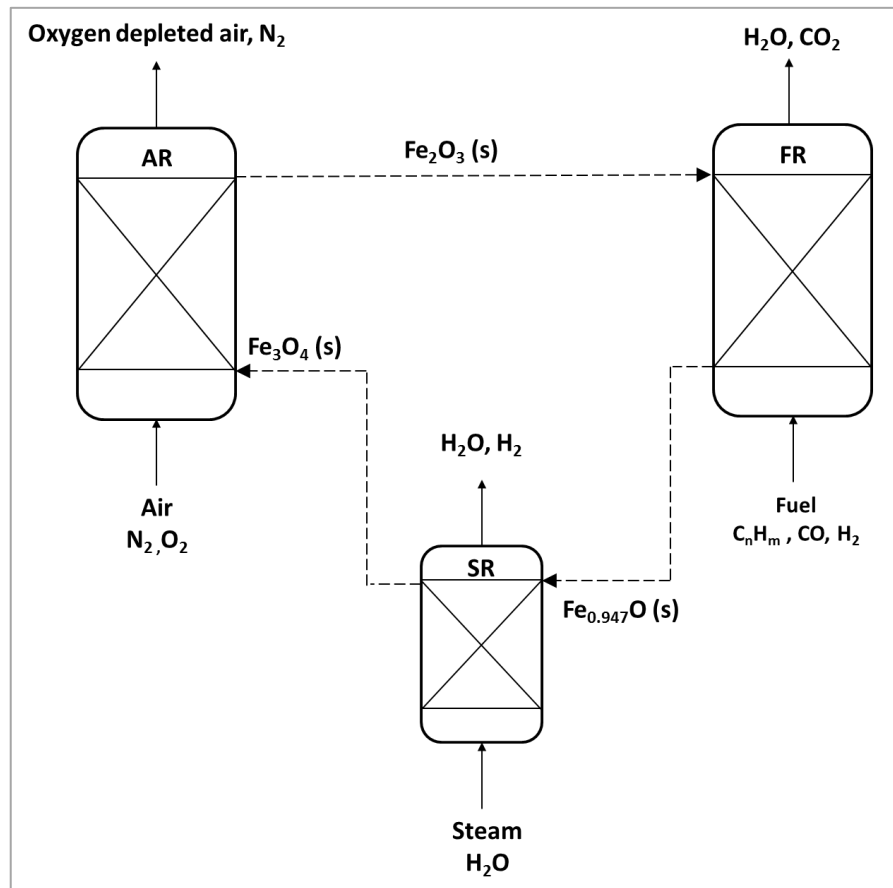


Figure 1.2. Three reactor-chemical looping combustion with iron- step process.

1.5 Aim and Scope

The objective of this work is to examine how an industrial process for converting biogas to hydrogen via the steam-iron reactions could be designed and optimized. The hybrid chemical-looping-steam-iron system proposed in the study consists of three fluidized bed reactors, a fuel reactor, a steam reactor and an air reactor. Selected on its ability to achieve multiple oxidation states, iron oxide will be transported through the interconnected fluidized beds in a cyclic manner. In the fuel reactor, fuel in the form of biogas will be oxidized to CO_2 and H_2O , while Fe_2O_3 will be reduced to $\text{Fe}_{0.947}\text{O}$. In the steam reactor, steam will be reduced to H_2 while $\text{Fe}_{0.947}\text{O}$ will be oxidized to Fe_3O_4 . Finally, in the air reactor Fe_3O_4 will be oxidized to Fe_2O_3 with air producing heat. The potential of the process will be examined by thermodynamically modeling, while an experimental approach will be used to examine if the proposed approach is feasible or not.

1.6 Thesis outline

The report starts with an introduction to Carbon Capture and Storage (CCS) technologies, chemical looping concept and how it can be featured in iron-steam process aiming at multiple targets such as hydrogen/heat/power production and easily sequestrable carbon dioxide.

In the second chapter a theoretical analysis of the system is performed, where the system definition, assumptions and methodology with Aspen Plus software are explained.

The report continues with the experimental section, describing the experiment procedure, what type of reactors, parameters, fuels and oxygen carriers utilized and why were they utilized.

In the following chapter, results of both theoretical and experimental analysis are presented, compared and discussed. In different case scenarios, systems parameters are optimized accordingly to reach the optimum fuel conversion, net efficiencies, and hydrogen yields.

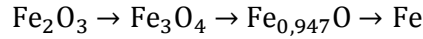
Based on the results, the report ends with conclusions and references of scientific papers referred to.

2. METHODOLOGY

2.1 Thermodynamic analysis of the system

Fuel reactor

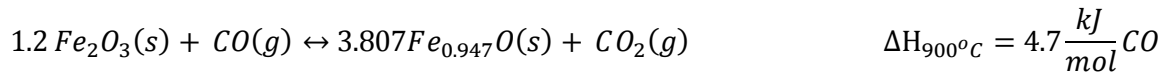
In the fuel reactor as mentioned above, gaseous fuels such as syngas or gasifier gas will reduce hematite to magnetite, wustite (preferably) or metallic iron according to the following reactions:



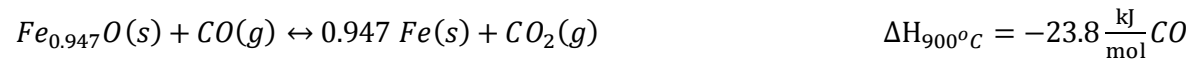
Equation 4 – Hematite reduction to magnetite with carbon monoxide



Equation 5 – Hematite reduction to wustite with carbon monoxide



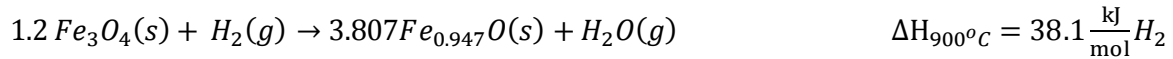
Equation 6 – Wustite reduction to metal iron with carbon monoxide



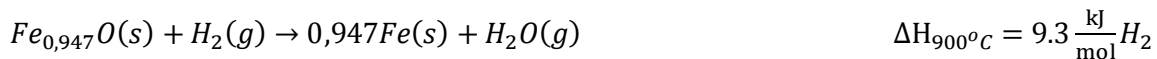
Equation 7 – Hematite reduction to magnetite with hydrogen



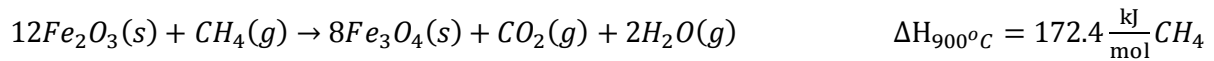
Equation 8 – Magnetite reduction to wustite with hydrogen



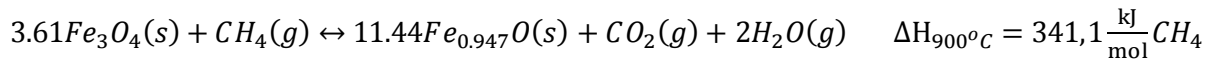
Equation 9 – Wustite reduction to metal iron with hydrogen



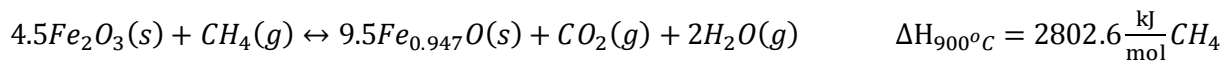
Equation 10 – Hematite reduction to magnetite with methane



Equation 11 – Magnetite reduction to wustite with methane



Equation 12 – Hematite reduction to wustite with methane



Referring to reactions 4-12, hematite reduction takes place in two step reactions for any gaseous fuel, first exothermic magnetite reduction, followed by endothermic wustite reduction. It is the second reduction transition that controls the overall process kinetics, as diffusion to inner surfaces becomes more difficult with the ongoing surface reactions. In order to reduce this effect inert support materials have been used, which with their porous structure, increase the reactive surface area at a great extent.

Maximizing wustite production may lead to several complexities, with the possibility of reduction to metallic iron particles. This, on the other hand implies a high risk of agglomeration, sintering and carbon formation by the Boudouard reaction or by thermal decomposition of hydrocarbons catalyzed by metallic iron, as shown in reaction 13 and 14[32, 33] respectively. Though highly unfavorable energetically especially reaction 13 at temperatures above 600°C, these reactions represent serious consequences as the surface defects/vacancies in these oxides increase with reduction. Once metal dusting starts to take place, these vacancies activate CO chemisorption to the solid particles, leading to carbon deposition and oxygen carrier contamination[34].

Equation 13 – Boudouard reaction



Equation 14 – Hydrocarbons cracking



Temperature, pressure and fuel composition are the main factors affecting these phenomena. In syngas fuel cases, high CO concentration would trigger carbon deposition. Based on the Ellingham equilibrium phase diagram in figure 2.1, at higher temperatures, the critical CO and H₂ concentrations for metallic iron formation increase. This requires for instance at 800°C, concentrations of H₂ and CO higher than 66.4% H₂ and 65.1% CO volumetric concentrations. In both syngas and gasifier gases of this study this condition is hardly reached. As for the gasifier gas case, steam presence is supposed to prevent carbon deposition, as it has been reported by Cho and Ishida [7, 33].

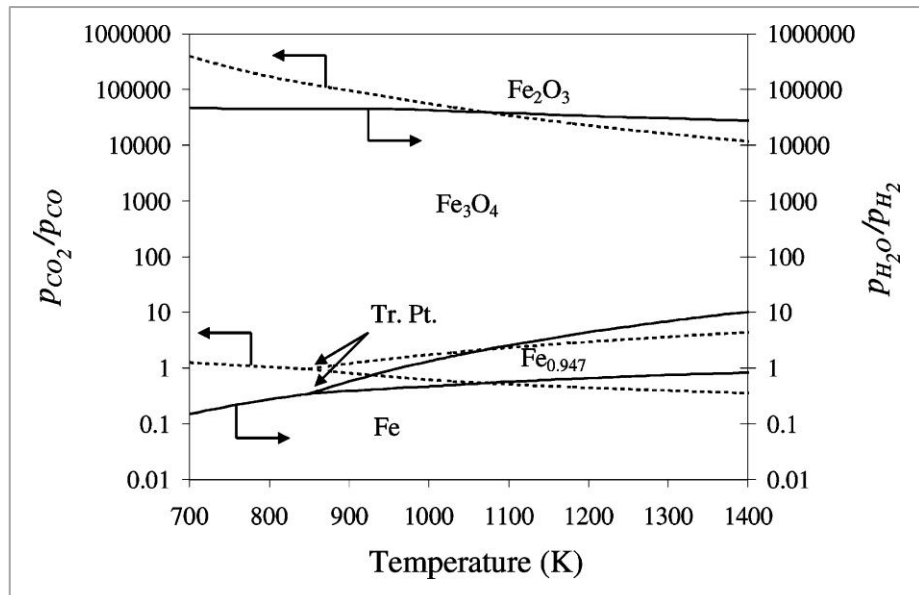
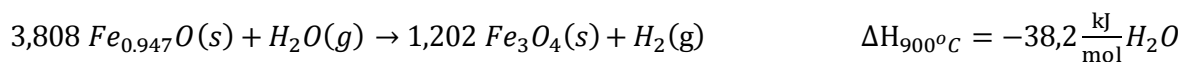


Figure 2.1. Ellingham Equilibrium phase diagram for iron oxides. [35]

Steam reactor

In steam reactor, provided that the reduced oxygen carriers are not contaminated with char or sulfur during the fuel reduction phase, the only gaseous products will be hydrogen and steam. Based on this assumption, the only reaction observed in the steam reactor is the exothermic oxidation of wustite to magnetite with steam. The degree of reaction is highly depend on temperature, with an optimum range between 600-800°C [32] where the highest hydrogen production is seen at temperatures lower than 600°C.

Equation 15 – Steam reduction with wustite



Air reactor

The main target of air reactor is to oxidize magnetite back to hematite, meanwhile providing heat for the system. Another alternative would have been to eliminate this step and oxidizing wustite ($\text{Fe}_{0.947}\text{O}$) straight to hematite in steam reactor. But due to thermodynamic constraints as shown in equilibrium diagram for iron oxide, very high temperatures and very low hydrogen concentration are required. Such requirements oppose the main aim of this study. As a result a third oxidization has been considered, in which magnetite is oxidized to hematite according to equation 16.

Equation 16 – magnetite oxidation to hematite



2.2 Aspen Plus Simulation

The three reactor system was modeled in with computer aided design program Aspen Plus. Simulation of the process provided the output gas and solid concentrations after each reactor, the reduction/oxidation degrees of iron oxides and assessment of energy duties for each reactor. The fluidized bed reactors were simulated with equilibrium RGibbs reactors, shown in figure 1.2, which provided simultaneous phase and chemical equilibrium for both gas and solid phases. The equilibrium conditions were assumed based on the high temperatures and long enough residence times in the reactors. The reactors were analyzed at steady state in isobaric, isothermal conditions. Assuming that heat transfer rate through circulation of oxygen carriers was large and fast enough, an adiabatic process could be assumed. Fuel reactor was composed of three reactors, simulating a multistage counter-current reactor, a tactic which allows control over partial pressure ratio of CO₂/CO. The counter-current mode enables a better fuel conversion at the top (high p_{CO₂}/p_{CO}) and at the bottom, low p_{CO₂}/p_{CO} for higher Fe₂O₃ conversion to Fe_{0.947}O[36].

Temperature, feed rate and oxygen carriers feed rate were tested to assess the conditions which gave the optimum hydrogen production rate at adiabatic conditions, where heat for the endothermic reactions in fuel reactor was provided by the heat transfer of oxygen carriers.

Due to different stoichiometric that each fuel (methane, syngas, and biogas) had in combustion with iron oxides, setting a general parameters set-up that could fit to every system did not give the wanted result of adiabatic reactors. Instead different steam/air flow rates and temperatures had to be utilized. In order to obtain zero-heat-duty reactors for each phase, the steam and air temperatures were adjusted so that the endothermic and exothermic effects imposed by reactions could be eliminated inside the reactors. On the other hand, this required heating supply for the preheating of inlet streams, which by looking at the overall heat balance it implied that the overall system is not an adiabatic one.

In order to assess the external heating and cooling supply composite curve analysis was performed. The hot stream were considered the outlet streams such as flue gases from fuel reactor, steam and hydrogen mixture from steam reactor and oxygen depleted air outlet stream from air reactor. The constant pressure heat capacities used for each component are tabulated in Appendix I. With such an analysis, it was aimed to assess the system capacity for internal heat exchange to avoid extra energy consumption and also the external heating and cooling demand.

2.3 Process performance

The process performance was assessed through equations 17, 18, 19 with γ_{H_2-eff} , γ_{H_2-pure} , γ_{CO_2} representing respectively the efficiencies for overall fuel combustion, hydrogen production and fuel conversion.

Equation 17 – Net hydrogen production efficiency

$$\gamma_{H_2-eff} = \frac{(H_{H_2} \cdot n_{H_2,out}) + Q_{HR}}{(H_{i,fuel} \cdot n_{fuel,in})}$$

Equation 18 – Hydrogen yield

$$\gamma_{H_2-pure} = \frac{n_{H_2,out}}{n_{steam,in}}$$

Equation 19 – Carbon dioxide yield

$$\gamma_{CO_2} = \frac{n_{CO_2,out}}{n_{fuel,in}}$$

3. EXPERIMENTAL

The main goal of conducting experiments was to demonstrate the feasibility of the proposed concept and analyze the effects that different oxygen carriers have on the system.

The experiments were carried out in a batch reactor at the division of Environmental Inorganic Chemistry at Chalmers University of Technology. Three iron based oxygen carriers, one synthetic, a waste product from steel industry, namely iron oxide scales and one natural mineral known as ilmenite, was examined by reduction with syngas/biogas, followed by oxidization with steam and air, consecutively.

3.1 Experimental setup

The experiments will be performed in a batch fluidized bed reactor at the department of inorganic environmental chemistry.

The experimental set up shown in figure 3.1 [6] consists of a quartz reactor with a length of 870 mm, an inner diameter of 22 mm and a porous quartz plate placed 370 mm above the bottom, onto which the oxygen carrier particles were placed. Other elements are the gas analyzer, sample gas cooler, steam generator, electrically heated furnace, etc.

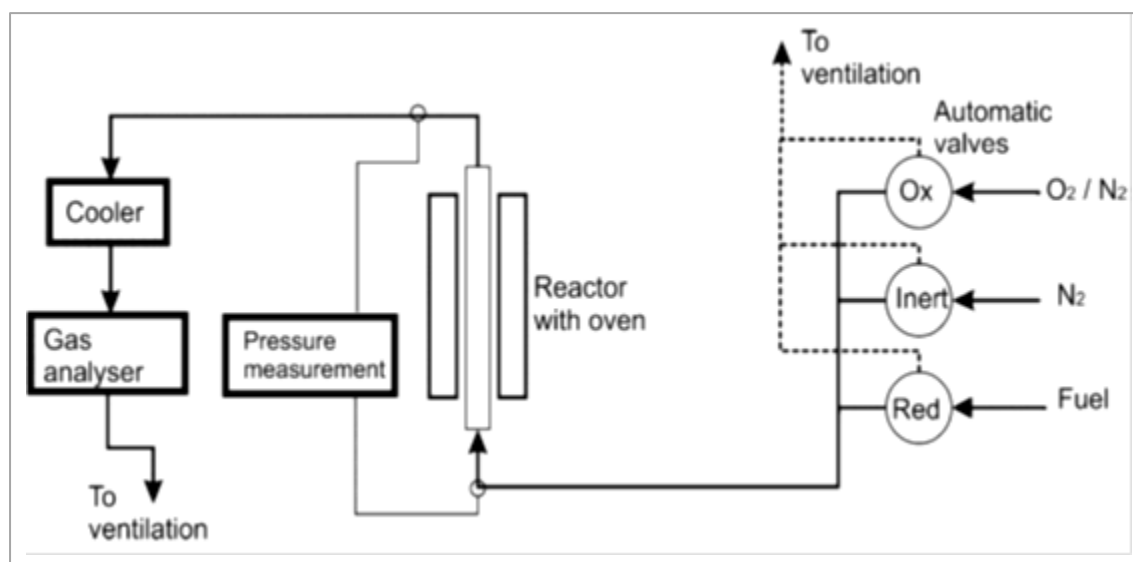


Figure 3.1. Schematic representation of the experimental set-up.

The amount of oxygen carrier used was 15 g of particles in the size range 125 – 180 μm . This resulted in a bed height varying from 15 to 38 mm, depending on differences in bulk density.

Prior to experiments the system and gas analyzers was carefully calibrated with respect to gas flows and steam generation rate

Second step was heating up the reactor at atmospheric pressure to the specified temperature for the oxidation step. During heat up, the reactor was fluidized with a flow of 5% oxygen in nitrogen.

The aim of the experiments was to simulate a chemical looping process with three reactors. Therefore each experimental cycle included three distinct phases; reduction of oxygen carrier particles to FeO with simulated biogas/syngas, H_2 generation by oxidation of FeO to Fe_3O_4 with steam/nitrogen mixture, and oxidation of Fe_3O_4 to Fe_2O_3 with air. In between each phase the reactor was flushed for 60 s with nitrogen, in order to avoid mixing of reactive gases.

The fuel flow rate was 450 ml/min, which was applied for 150 to 250 s depending on the oxygen carrier type. For the other phases the gas flows were 900 ml/min. The dry gas products concentrations from the reactor were measured in a gas analyzer (Rosemount NGA-2000). The procedure was run at a temperature interval between 800 - 950°C. For each temperature set two cycles were carried out in order to ensure repeatability of the results.

3.2 Oxygen Carriers

The hydrogen production concept was tried with three iron oxide based oxygen carriers. The particle size range of these particles is between 125 – 180 μm . The first one is synthetic oxygen carrier of 60 wt. % Fe_2O_3 supported on 40 wt. % $MgAl_2O_4$ which is produced via freeze granulation process. The same oxygen carriers have been used by Rydén and Arjmand study for the production of hydrogen via steam-iron process[5]. This material was selected for its high reactivity, stability to agglomeration and stability with the inert material serving as a support.[30]

The other two oxygen carriers, iron oxide scales (IOS) and ilmenite, were chosen because of their high availability and low costs. Iron oxide scales (IOS) is a waste product generated during rolling of steel sheets and ilmenite is an iron-titania mineral which is mined and used for production of rutile (TiO_2).

Iron oxide scales are characterized by consisting of more than 99 wt% Fe_2O_3 , with the balance being Si, Al, Mn Ca, P and their oxides. Ilmenite consists of iron and titania oxides such as $FeTiO_3$ and Fe_2O_3 , in fresh particles' morphology [25, 37]. In the present study the ilmenite mineral utilized are freshly activated particles, i.e. undergone an oxidation/reduction cycle, a treatment which increases their porosity and consequently increased reactivity [6, 9, 28] and decelerates defluidization [38]. During this first cycle, X-ray powder diffractometry (XRD) indicated that the morphology of the ilmenite had changed to Fe_2TiO_5 (pseudobrookite), TiO_2 (rutile) and Fe_2O_3 (hematite) [37].

Two types of fuel were examined, syngas and simulated product gas from biomass gasification. Apart from known as less carbon intensive fuels, these gases are already produced from indirect gasification of biomass in the laboratories of Energy Technology division in Chalmers University of Technology.

Due to the tendency of metallic iron formation during CH₄ combustion step [39] only synthetic iron oxide particles were considered for the gasifier fuel experiments.

3.3 Fuel gases

The experimental procedure follows in two different fuel classes, syngas with a composition is 50 vol% H₂ and 50 vol% CO and simulated biogas with a dry composition of 43 vol% CO, 23 vol% H₂, 15 vol% CO₂, 14 vol% CH₄ and 5vol% C₂H₄. Further, the simulated biogas was diluted with 50 vol% steam, in order to provide a fuel composition similar to the one produced in the Chalmers gasifier. In fuel reactor, the fuel gases reduce oxygen carriers to Fe₃O₄ and Fe_{0.947}O. Then, in steam reactor, the reduced particles are exposed to excess steam flows until hydrogen concentration reached a constant value of 0.2 vol%. Finally in air reactor, Fe₃O₄ is fully oxidized to Fe₂O₃ with 5% O₂ in N₂.

The residence time in fuel reactors is determined by the mass-based reduction degree (ω) of the oxygen carriers at the exit of reactor. This parameter (eqn.20) defines the mass reduction percentage of oxygen carriers due to oxygen loss during reduction from most oxidated state (Fe₂O₃) to Fe₃O₄ and Fe_{0.947}O.

Equation 20 – Mass-based degree of reduction

$$\omega = \frac{m}{m_{ox}}$$

Where m is the instantaneous mass of oxygen carriers and m_{ox}, the mass at the most oxidated state. In this experiment, a composition of Fe₃O₄ and Fe_{0.947}O is the final desired oxidation state. An average ω for such composition is 1.3 – 4.0 wt% for pure Fe₂O₃ and 3.3 – 10.0 wt% for synthetic Fe₂O₃.MgAl₂O₄. To achieve this ω , the optimum residence time in the fuel reactor is calculated by a species mass balance within the reactor and represented as [5]:

Equation 21 – Instantaneous mass-based degree of reduction

$$w_i = w_{i-1} - \int_{t_0}^{t_{final}} \frac{\dot{n}_{out} M_o}{m_{ox}} (4x_{CO_2} + 3x_{CO} - x_{H_2}) dt$$

with w_i and w_{i-1} representing two consecutive mass conversions at a differential time t, while $\dot{n}_{out}$, stands for the molar flow rates of dry gases at the exit of fuel reactor, M_o for the molecular weight of oxygen and x_i for the instantaneous molar composition of each gas.

In table 3.1 and 3.2 are shown the experimental sets with specific parameters.

Table 3.1. Experimental parameters for syngas case.

Sample ID	OC	T(°C)	τ (s)	U_{FR} (mL _n /min)	U_{SR} (mL _n /min)	U_{AR} (mL _n /min)
S-FMA-950	Fe ₂ O ₃ .MgAl ₂ O ₄	950	150	450	900	900
S-IO5-950	IOS	950	245	450	900	900
S-IL-950	ilmenite	950	150	450	900	900
S-FMA-900	Fe ₂ O ₃ .MgAl ₂ O ₄	900	150	450	900	900
S-IL-900	ilmenite	900	150	450	900	900
S-FMA-850	Fe ₂ O ₃ .MgAl ₂ O ₄	850	150	450	900	900
S-FMA-800	Fe ₂ O ₃ .MgAl ₂ O ₄	800	150	450	900	900

Table 3.2. Experimental parameters for simulated biogas simulation case.

Sample ID	OC	T(°C)	τ (s)	U_{FR} (mL _n /min)	U_{SR} (mL _n /min)	U_{AR} (mL _n /min)
B-T50-950	Fe ₂ O ₃ .MgAl ₂ O ₄	950	50	450	900	900
B-T100-950	Fe ₂ O ₃ .MgAl ₂ O ₄	950	100	450	900	900
B-T120-950	Fe ₂ O ₃ .MgAl ₂ O ₄	950	120	450	900	900
B-T130-950	Fe ₂ O ₃ .MgAl ₂ O ₄	950	130	450	900	900
B-T150-950	Fe ₂ O ₃ .MgAl ₂ O ₄	950	150	450	900	900
B-T200-950	Fe ₂ O ₃ .MgAl ₂ O ₄	950	200	450	900	900
B-T100-900	Fe ₂ O ₃ .MgAl ₂ O ₄	900	100	450	900	900
B-T100-850	Fe ₂ O ₃ .MgAl ₂ O ₄	850	100	450	900	900
B-T100-800	Fe ₂ O ₃ .MgAl ₂ O ₄	800	100	450	900	900

4. RESULTS AND DISCUSSION

ASPEN Plus analysis

4.1 Phase equilibrium - Temperature dependence

As a first of the simulations in Aspen Plus, gas and solid equilibrium phases were assessed and tabled as functions of temperature in tables 4.1, 4.2, 4.3, 4.4. In all the temperatures tested, no complete fuel conversion is observed. Reduction degree to wustite ($\text{Fe}_{0.947}\text{O}$) increases with temperature, with a straight conversion to CO_2 and H_2O . Meanwhile, at lower degree significant presence of CO and H_2 as intermediate products is observed. Beside temperature effect, fuel composition plays an important role to reduction degree. Three types of fuel were analyzed: methane, syngas and gasifier gas simulated composition gas according to Seemann and Thunman reported case of wood pellets gasification[40]. In the cases when methane is present in the fuel composition, methane-steam reforming (Eqn. 18) influences the system kinetics greatly at low temperatures. Whereas steam presence in gasifier gas fuel, affects negatively hematite-wustite reduction. In none of the fuel reactor's cases, metallic iron formation is observed.

Table 4.1. Solid and gaseous equilibrium compositions for 200 CH_4 /895,5 OCs (mol/s) case.

T (°C)	Solid phase				Gaseous phase				
	Fe_2O_3	Fe_3O_4	$\text{Fe}_{0.947}\text{O}$	Fe	CH_4	CO	CO_2	H_2	H_2O
600	0	0.216	0.784	0	0.009	0.074	0.256	0.289	0.371
700	0	0.004	0.996	0	0	0.004	0.329	0.014	0.653
800	0	0	1.000	0	0	0.003	0.331	0.005	0.661
900	0	0	1.000	0	0	0.003	0.330	0.005	0.662
1000	0	0	1.000	0	0	0.004	0.330	0.004	0.662
1100	0	0	1.000	0	0	0.004	0.329	0.004	0.663

No carbon deposition was observed during simulations

Table 4.2. Solid and gaseous equilibrium compositions for 200 syngas/393 OCs (mol/s).

T (°C)	Solid phase				Gaseous phase				
	Fe_2O_3	Fe_3O_4	$\text{Fe}_{0.947}\text{O}$	Fe	CH_4	CO	CO_2	H_2	H_2O
600	0	0.431	0.569	0	0	0.143	0.366	0.251	0.240
700	0	0.069	0.931	0	0	0.047	0.453	0.072	0.428
800	0	0	1.000	0	0	0.001	0.499	0.001	0.499
900	0	0	1.000	0	0	0.001	0.499	0.001	0.499
1000	0	0	1.000	0	0	0.001	0.499	0.001	0.499
1100	0	0	1.000	0	0	0.001	0.499	0.001	0.499

No carbon deposition was observed during simulations

Table 4.3. Solid and gaseous equilibrium compositions for 200 biogas/148 OCs (mol/s) case.

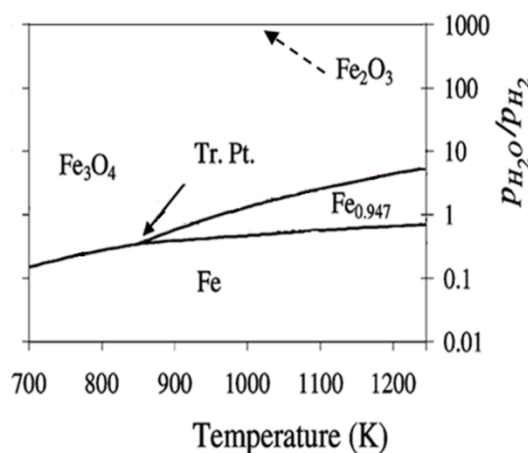
T (°C)	Solid phase				Gaseous phase				
	Fe ₂ O ₃	Fe ₃ O ₄	Fe _{0.947} O	Fe	CH ₄	CO	CO ₂	H ₂	H ₂ O
600	0	1.000	0.000	0	0.002	0.042	0.234	0.222	0.459
700	0	0.782	0.218	0	0	0.051	0.226	0.184	0.498
800	0	0.336	0.664	0	0	0.028	0.249	0.074	0.608
900	0	0.175	0.825	0	0	0.003	0.275	0.005	0.676
1000	0	0.163	0.837	0	0	0	0.278	0	0.682
1100	0	0.163	0.837	0	0	0	0.278	0	0.682

No carbon deposition was observed during simulations

In steam reactor simulations, the effect of changing temperature (shown in red dots) obeys the equilibrium phase diagram shown adjacent to table 4.4.

Table 4.4. Solid and gaseous equilibrium compositions for steam reactor.

T (°C)	Solid phase			Gaseous phase	
	Fe ₃ O ₄	Fe _{0.947} O	Fe	H ₂	H ₂ O
400	0.953	0.047	0	0.982	0.018
500	0.755	0.245	0	0.905	0.095
600	0.478	0.522	0	0.742	0.258
700	0.280	0.720	0	0.551	0.449
800	0.167	0.833	0	0.386	0.614
900	0.105	0.895	0	0.270	0.730



The highest hydrogen yields are observed at temperatures lower than 500°C. Operating at such temperatures brings disadvantages as the steam – iron oxide reactions are controlled by kinetics. Low temperatures would slow down the kinetics and hydrogen production rate, requiring catalyst particles[41]. Meanwhile in a real perspective, having such a temperature change from fuel reactor (900°C) to steam reactor (500°C) would create a heat surplus, demanding external cooling and creating more complexities.

4.2 Adiabatic system simulation results

In all the fuel cases, the temperatures of inlet air stream and of the reactors are chosen accordingly to reduce the heat duty in the reactors as much as possible, with as less as possible effect on the kinetics in the reactors. Meanwhile the fuel stream's temperature is chosen between 750-900°C, similar to gasifier outlet products' temperature. The steam inlet stream temperature is chosen to be 130°C. The oxygen carriers flow rate is a stoichiometric rate with the fuel cases in the fuel reactor. The reactors are modeled as fluidized bed reactors, where diffusion limitations are minimized, improving heat and mass transfer within the reactor. In the fuel reactor in order to maximize the Fe_2O_3 conversion to $Fe_{0.947}O$ the CO_2/CO partial pressure ratio in Ellingham phase diagram in figure 2.1, should be kept as low as possible. This is realized by utilizing a multi stage counter-current mode, i.e. a three reactor system.

In table 4.5 are presented the results for all systems regarding to fuel compositions. Due to thermodynamic constraints resulting from p_{H_2O}/p_{H_2} ratio at a specific temperature in the steam reactor, the hydrogen yield is limited to $\approx 51.4\%$ maximum yield for all fuel compositions. In all systems, an excess steam inlet rate inversely proportional to steam conversion efficiency is required to reach a complete Fe_3O_4 conversion. Because of this aspect, two different cases were analyzed for each fuel, one with stoichiometric steam/fuel feed ratio, where a hydrogen yield is 100% according to equation 18, and the other case with an excess steam inlet stream, in which hydrogen production is prioritized. At the same time, the second case is limited by the elimination of hot utility demand which results from preheating of the inlet streams. In the first case, a heat recovery potential from streams at temperatures higher than water-steam evaporation temperatures at 1 bar is possible, and it consists of more than 50% of total heat transfer in the system. This high quality heat is a result of insufficient steam amount added in steam reactor in order to completely convert wustite to magnetite. Instead only $\sim 27\%$ of wustite is converted. In such case, considering that the wustite conversion to hematite takes place in two exothermic steps sequentially as shown in equations 22 and 23, the heat produced in stoichiometric cases is greater than in excess steam cases giving rise heat recovery potential as demonstrated in pinch analysis results in figures 4.1,4,3 and 4.5.

Equation 22 – Partial oxidation of wustite to magnetite



Equation 23 – Magnetite oxidation to hematite



As a result, the net hydrogen efficiency decreased from the stoichiometric steam/fuel feed ratio to the excess steam ratio. This trend is observed in all fuel cases, with biogas system having the lowest yields. The reason for this case is the amount of steam in the fuel composition which consists of 50% of it. Due to this, the heat recovery potential is reduced to 42% compared to syngas case and to 21.8% compared to methane case.

Table 4.5. Aspen Plus simulation results for all fuel cases.

	Methane case		Syngas case		Biogas case	
	S_{stoic}	$S: 1.87 \times S_{\text{stoic}}$	S_{stoic}	$S: 1.95 \times S_{\text{stoic}}$	S_{stoic}	$S: 2.9 \times S_{\text{stoic}}$
n_{fuel} (mol/s)	200	200	200	200	200	200
n_{OC} (mol/s)	895.5	895.5	225	225	160.2	183.1
$n_{\text{steam-in}}$ (mol/s)	497	930	124.78	243	57	99
n_{air} (mol/s)	1290	780	325	180	200	150
T_{FR} (°C)	780	780	900	880	880	850
T_{SR} (°C)	720	720	720	720	720	720
T_{AR} (°C)	960	960	926	908	967	919
Outlet n_{H_2} (mol/s)	255.7	476.3	64.1	124.7	29.4	50.84
Useful- Q_{external} (MW)	70.89	0	29.99	10.20	15.49	1.88
Internal Heat exchange (MW)	55.23	78.52	10.42	16.52	13.11	17.07
Waste Heat (MW)	33	40	8.54	11.09	8.89	9.78
Hot utility demand Q_{hot} (MW)	0	2.25	0	0	0	0
y_{H_2} (%)	51.4	51.4	51.4	51.4	51.4	51.4
y_{CO_2} (%)	100	100	100	100	86.7	91
$y_{\text{H}_2\text{-eff}}$ (%)	83.7	72.3	86.1	76.14	68.1	42.5

Notes:

S_{stoic} : Steam to fuel rate ratio in no efficiency limitation case in eqn.15.

Useful- Q_{external} : is the useful heat recovery potential from the system at $T > 100^\circ\text{C}$.

Waste Heat: is the heat generated from streams' cooling/condensation at $T \leq 100^\circ\text{C}$.

Hot utility demand Q_{hot} : minimum heat demand by the system.

4.3 Composite curve analysis

As stated in the objective part, beside the hydrogen and sequestrable CO₂ production, an optimized system is most desired in thermal heat terms. With Aspen Plus program adiabatic systems were designed, i.e. no heat demand is required for the reactors. However, a great cold utility demand is observed together with the inlet streams (steam, inlet air streams) and outlet streams (flue gases, excess steam and hydrogen mixture and oxygen depleted air streams). The heat demand varies in every fuel system due to the different stoichiometric with oxygen carriers.

With composite curve analysis, one can realize a preliminary estimation of potential energy savings by internal heat recovery between inlet and outlet streams. Composite curve diagrams in figures 4.1-4.6 show the temperature versus heat duty relation between the hot and cold streams. In the stoichiometric steam/fuel ratio cases, three zones of heat transfer are identified: the external heat recovery potential, the internal heat recovery potential and the low quality cooling demand arising from steam condensation and cooling down to ambient temperatures. The methane case in figure 4.1 represents the highest external heat recovery while the biogas case (figure 4.5) exhibits the lowest capacity for heat recovery. As suggested in Chiesa et al. [19] research, there are different ways to integrate this heat recovery potential, such as high/intermediate pressure steam production, preheating of inlet streams, etc. Integration of such system represents also a complicated task, as 40-50% of heat transfer between hot and cold streams stands for the heat demand in water evaporation/steam condensation process at low temperature. The heat at such low temperature intervals cannot be used in heat recovery systems, being qualified as waste heat. In the non-stoichiometric cases, where hydrogen production is prioritized, the heat recovery is reduced due to high amount of heat required for steam production in steam reactor as shown in figure 4.2, 4.4 and 4.6.

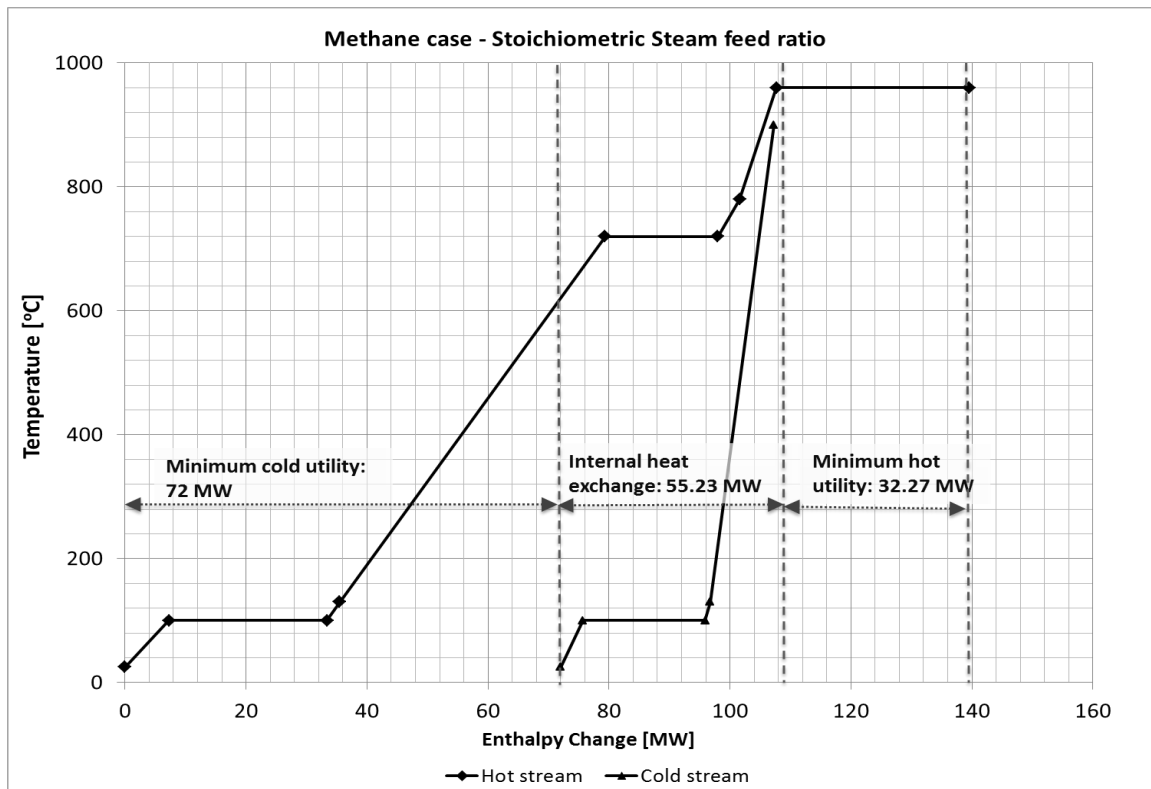


Figure 4.1. Composite curves for stoichiometric steam case in methane fuel system.

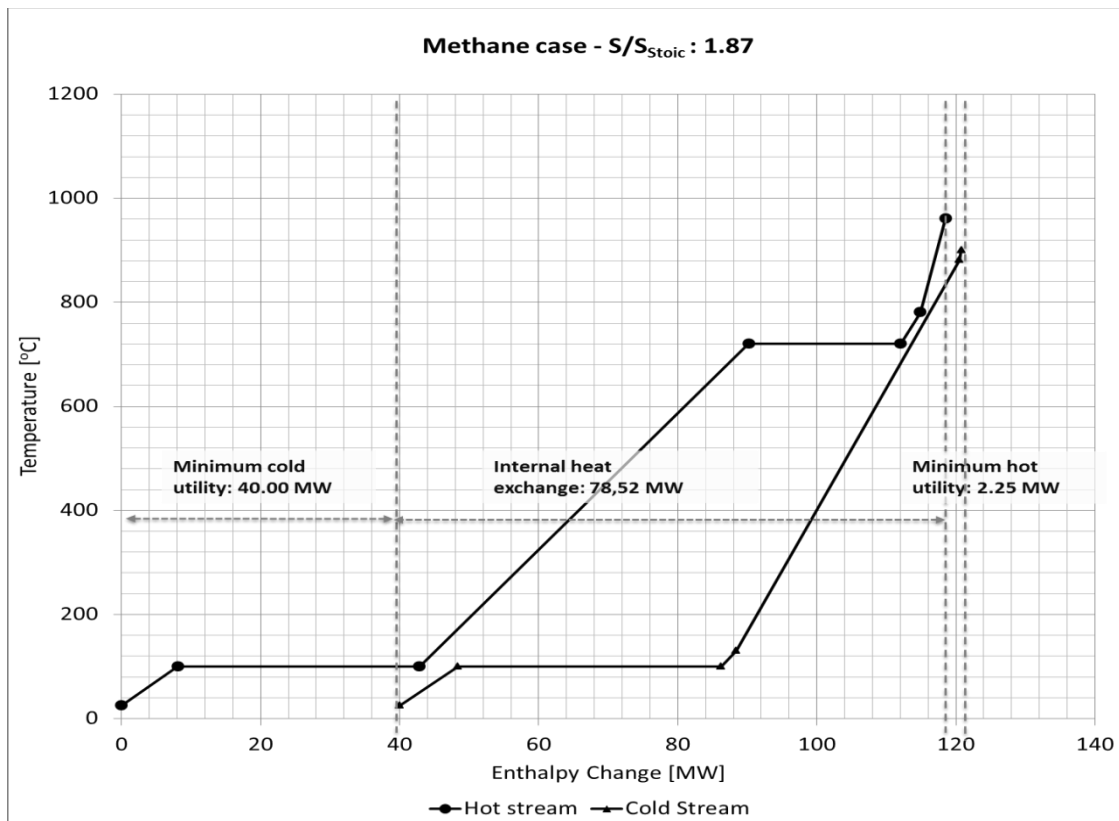


Figure 4.2. Composite curves for excess steam case in methane fuel system.

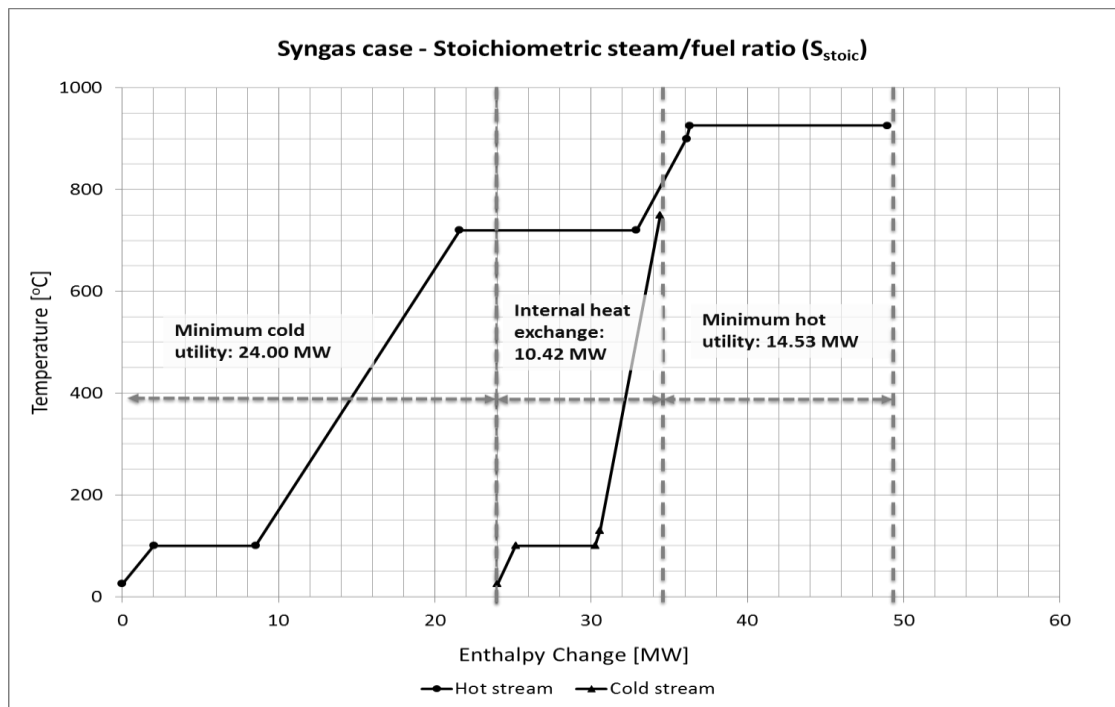


Figure 4.3. Composite curves for stoichiometric steam case in syngas fuel system.

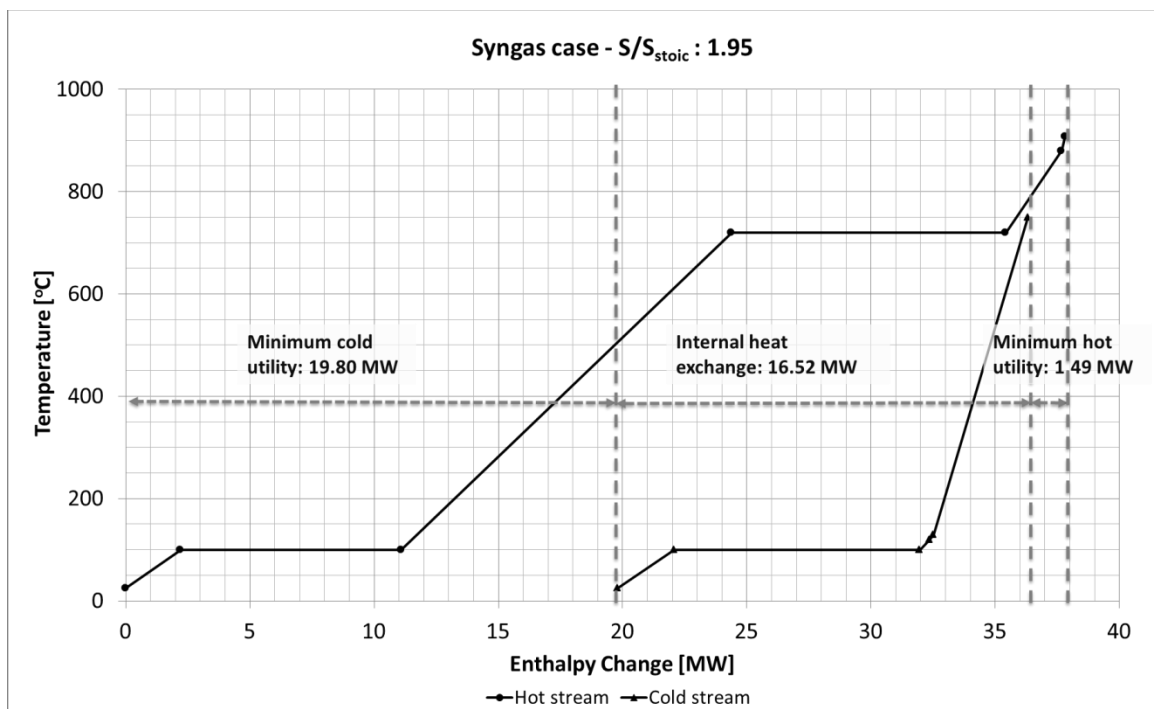


Figure 4.4. Composite curves for excess steam case in syngas fuel system.

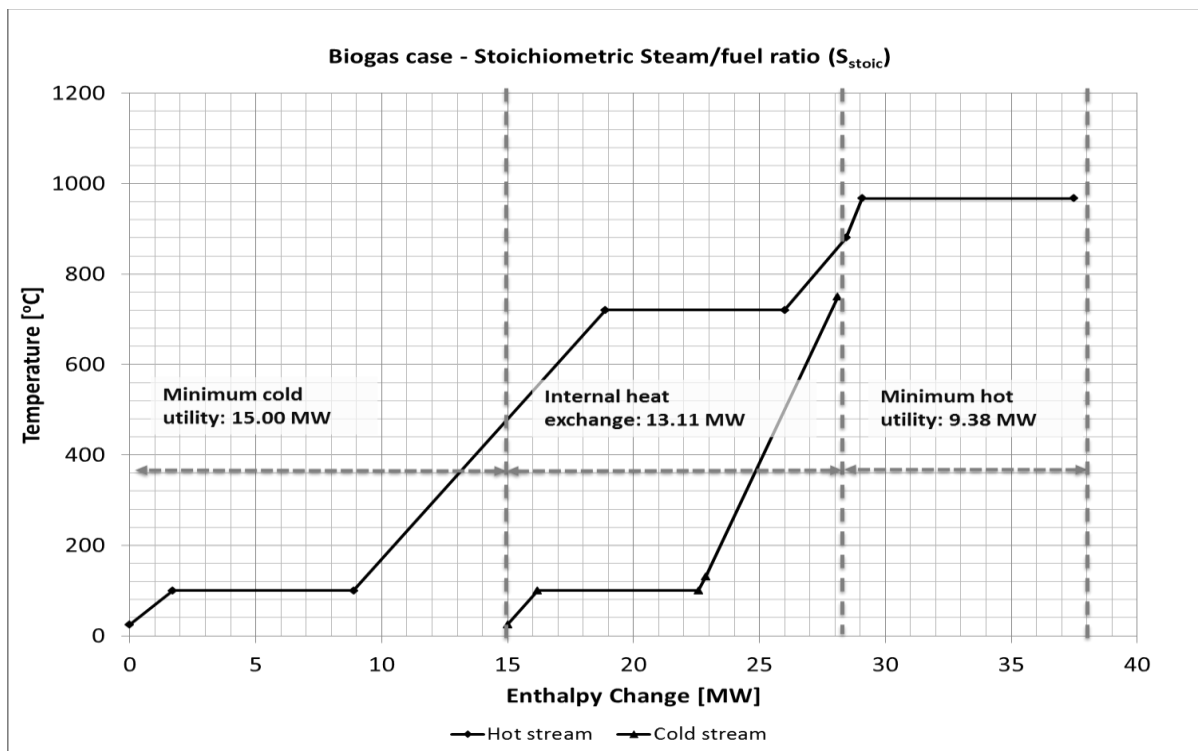


Figure 4.5. Composite curves for stoichiometric steam case in biogas fuel system.

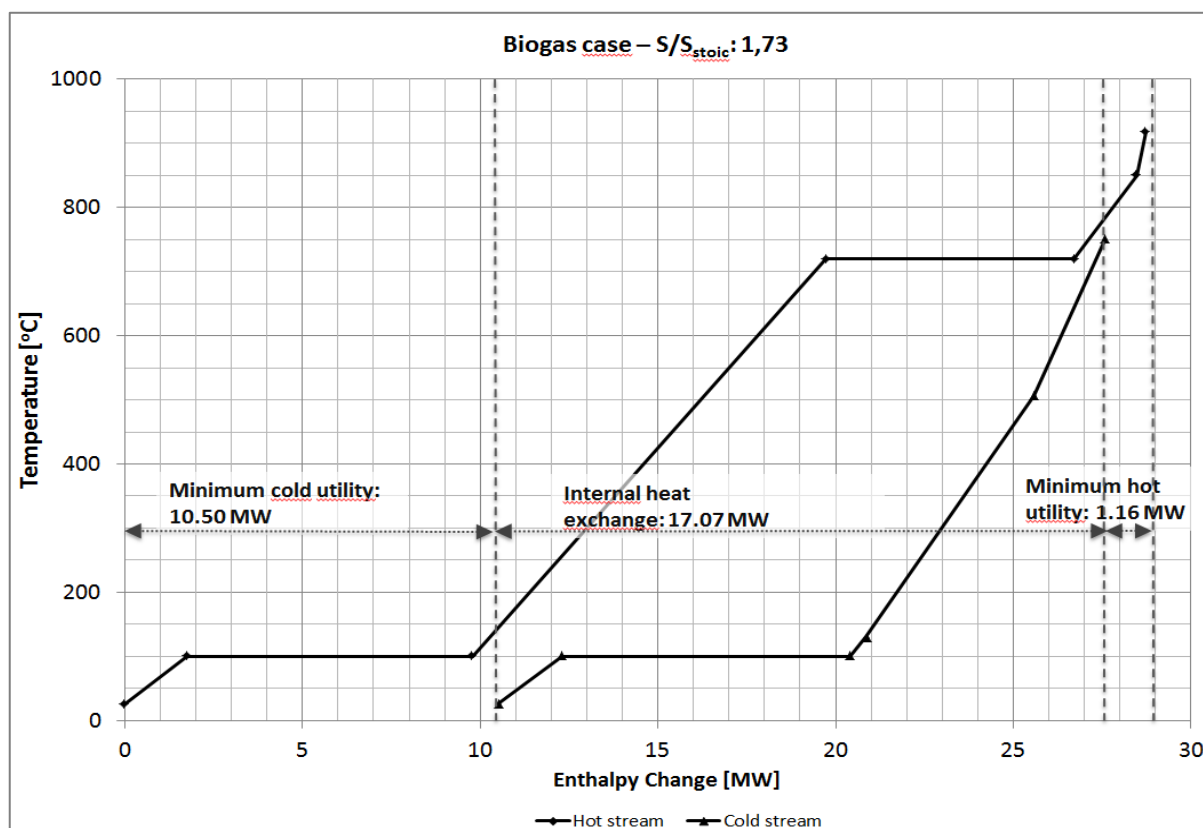


Figure 4.6. Composite curves for excess steam case in biogas fuel system.

4.4 Experimental results

As mentioned in experimental description, two types of fuel (syngas and biogas from gasifier outlet), four temperatures (950, 900, 850, 800°C) and three types of oxygen carriers (synthetic hematite, iron scale oxides and ilmenite) were tested. In figure 4.7, a typical cycle of fuel reduction, steam oxidation and air oxidation of synthetic oxygen carrier particles at 950°C is shown as an example. Graphs for similar cycles with different fuels and oxygen carriers can be found in Appendix II and III.

For each oxygen carrier type, two full cycles were conducted at each temperature. Using synthetic oxygen carrier particles, it was possible to examine all temperatures with syngas as fuel, while with gasifier gas the system was stable at 950°C. At lower temperatures it was not possible to perform experiment without risking defluidization of the system. In the other oxygen carriers' cases (ilmenite and iron oxide scales), the experiments were limited to experiments with syngas as fuel and temperature at 950°C, due to high agglomeration observed after the first two cycles.

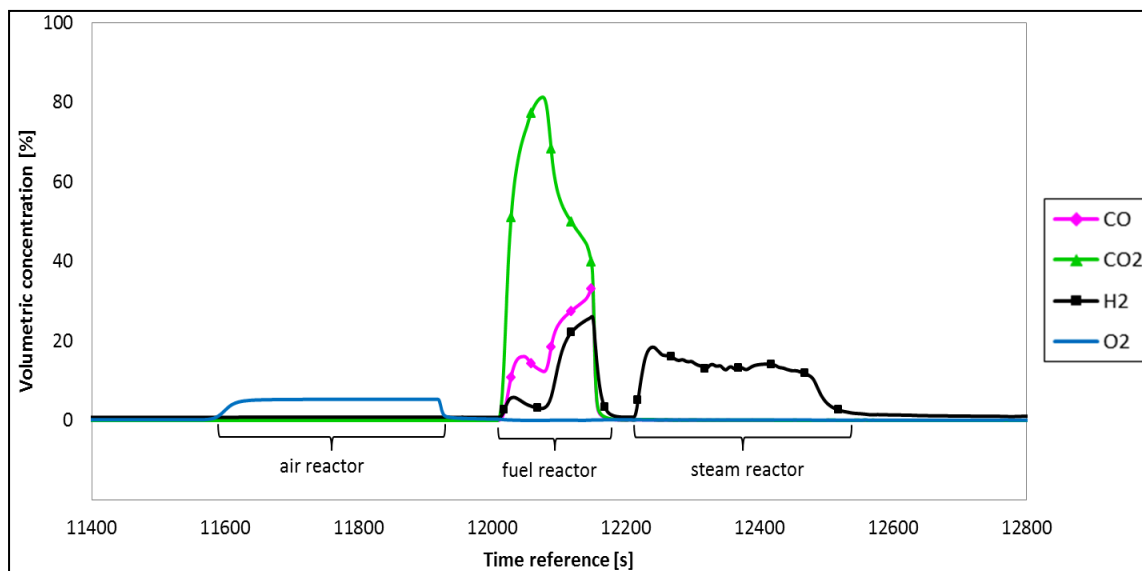


Figure 4.7. Volumetric profiles of dry gases during one cycle of syngas fuel combustion with 15 g of synthetic hematite at 950°C.

Referring to figure 4.7, three main phases are observed. The first one belongs to the oxidation of magnetite to hematite with 5% O₂ in nitrogen. The duration of this phase depended on the stability of final O₂ concentration to 5% vol., implying a complete oxidation to hematite. The second phase, or the middle peaks in figure 4.7, refers to reduction of hematite to wustite with fuel gas. The residence time was set as 150 seconds for synthetic oxygen carrier particles and ilmenite in the syngas case and varied in gasifier gas case, while for iron oxide scales it was set at 245 seconds. The reason for the longer reduction time for iron oxide scales is that those consists of 99% Fe₂O₃, while the synthetic particles and ilmenite consisted of 40-50% Fe₂O₃. Because of this iron oxide scales has higher oxygen transfer capacity and require longer reduction time in order to become reduced to FeO.

Carbon dioxide profile displays the opposite pattern of carbon monoxide and hydrogen profiles, reflecting perfectly the product and reactant concepts. Two peaks of CO_2 are observed during the fuel reduction. This can be explained with the assumption that the hematite reduction occurs in sequential order: first hematite phase exhaustion to magnetite then magnetite exhaustion to wustite. This assumption is justified with oxidation state change with the variation of $p_{\text{CO}_2}/p_{\text{CO}}$ in Ellingham equilibrium phase diagram in figure 2.1.

Another interesting point is the slope characterizing the modest rise of the second peak in the fuel reactor. The difference between the two peaks slope points that in the second phase transition apart from partial pressure ratio of products to reactants factor, there are multiple actors such as mass transfer, reaction kinetics that affect magnetite conversion to wustite.

The fuel conversion to CO_2 is not complete as the all gases are present at any time. Assuming an ideal gas behavior, $p_{\text{CO}_2}/p_{\text{CO}}$ at the second peak is around ~ 1.3 , suggests according to Ellingham diagram (Fig.2.1) that after 150 s the oxygen carriers' oxidation phase is wustite. In the results interpretation part, due to measurements limitations on hydrogen and steam data, only the carbon conversions of carbon monoxide(CO) and methane (CH_4) have been considered.

In the third phase, the oxygen carriers represented by magnetite and wustite are steam-oxidized to magnetite as suggested by reaction 15. The area under this curve indicates the total amount of hydrogen produced in this oxidation phase.

Syngas fuel case

As mentioned above, the results are based only on carbon conversions at highest carbon dioxide production instant. Figure 4.8 shows the gas yields in a two transition phases, hematite-to-magnetite and magnetite-to-wustite. Based on unreacted-core shrinking model for gas-solid particles reactions, the first transition is greatly affected by diffusion phenomenon, displaying much higher carbon yields than the second phase where the diffusion resistance through the pores to reach for the bulk oxygen increases significantly.

During hematite to magnetite transition period an inverse effect is observed with temperature in the carbon yields. Such trend is actually supported by the equilibrium phase diagram in figure 2.1, meaning that at higher temperatures the equilibrium transition of hematite to magnetite takes place at lower partial pressures of CO_2 , concluding that less CO conversion is carried out.

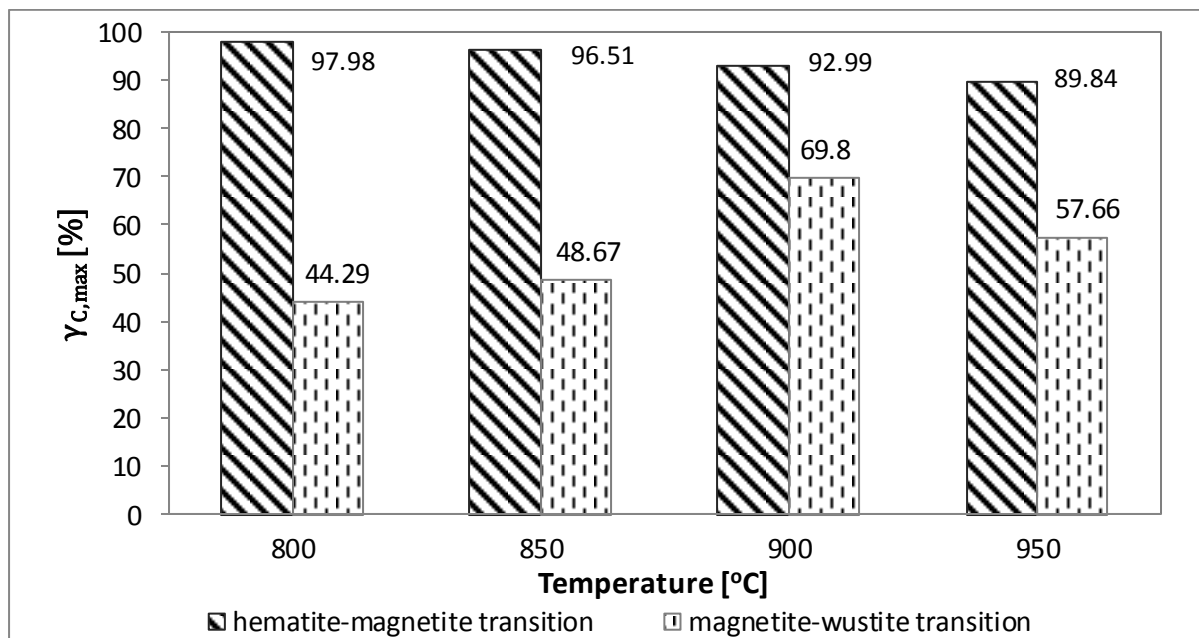


Figure 4.8. Carbon monoxide and hydrogen conversion degrees as functions of temperature in fuel reactor with synthetic oxygen carrier particles.

In the second transition, when it comes to temperature effect an increase is observed in this transition's yields, just as expected from the equilibrium phase diagrams in figure 2.1, where higher partial pressures CO_2 are required with increasing temperatures for the magnetite-to-wustite transition to take place.

In figure 4.9 are presented the hydrogen yields in the steam reactors at different temperatures for synthetic oxygen carriers. In order to avoid experimental measuring inaccuracies, the evaluation of hydrogen yields is limited to the highest peak of hydrogen production instants. The experimental

hydrogen yields shown in figure 4.9, are comparatively same with a value of 40% at 800°C case for the experimental and 38.9 % for the Aspen syngas case (table 4.4), for an equivalent temperature.

As expected from equilibrium phase concentrations, a decreasing tendency of hydrogen yields is observed with increasing temperatures.

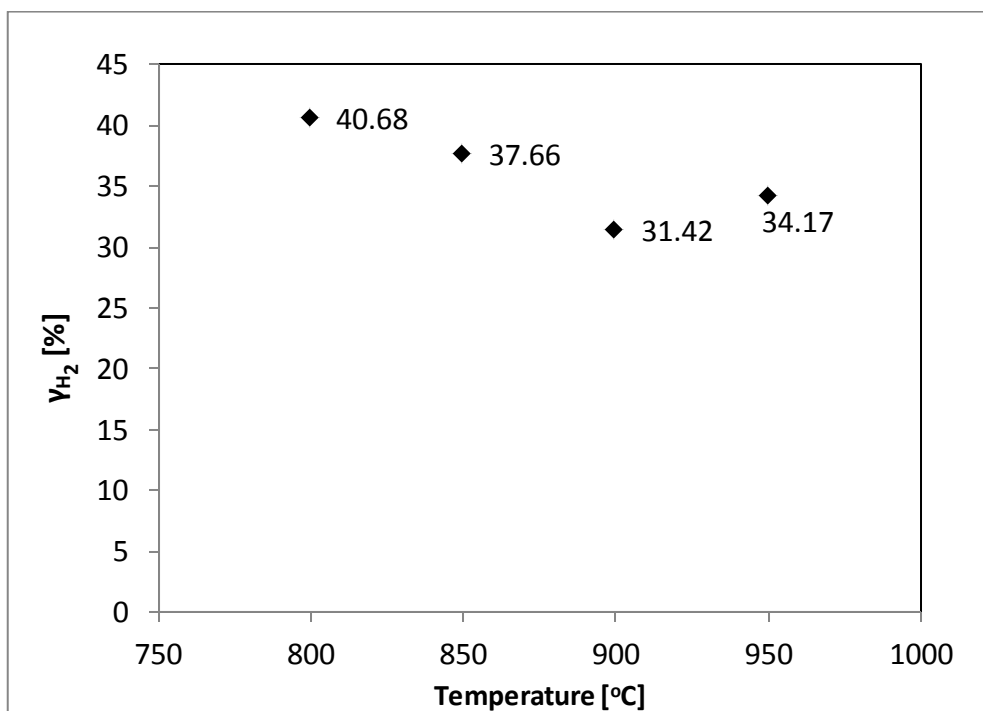


Figure 4.9. Variation of hydrogen yield with temperature in syngas as fuel and iron oxides steam reactor.

Oxygen carrier type effect on hydrogen production capacity

Figure 4.10 shows the fuel conversion yield for syngas fuel at 950°C and the hydrogen yields in steam reactor stage for all the oxygen carriers used. The results are deduced from the first two cycles afterwards the system started to defluidize in iron scale oxides and ilmenites. The fuel conversion is very satisfactory with highest value belonging to active ilmenite system. But no phase-wise reaction in fuel reactor was observed in ilmenite experiments. This implies that very little or no wustite formation has taken place.

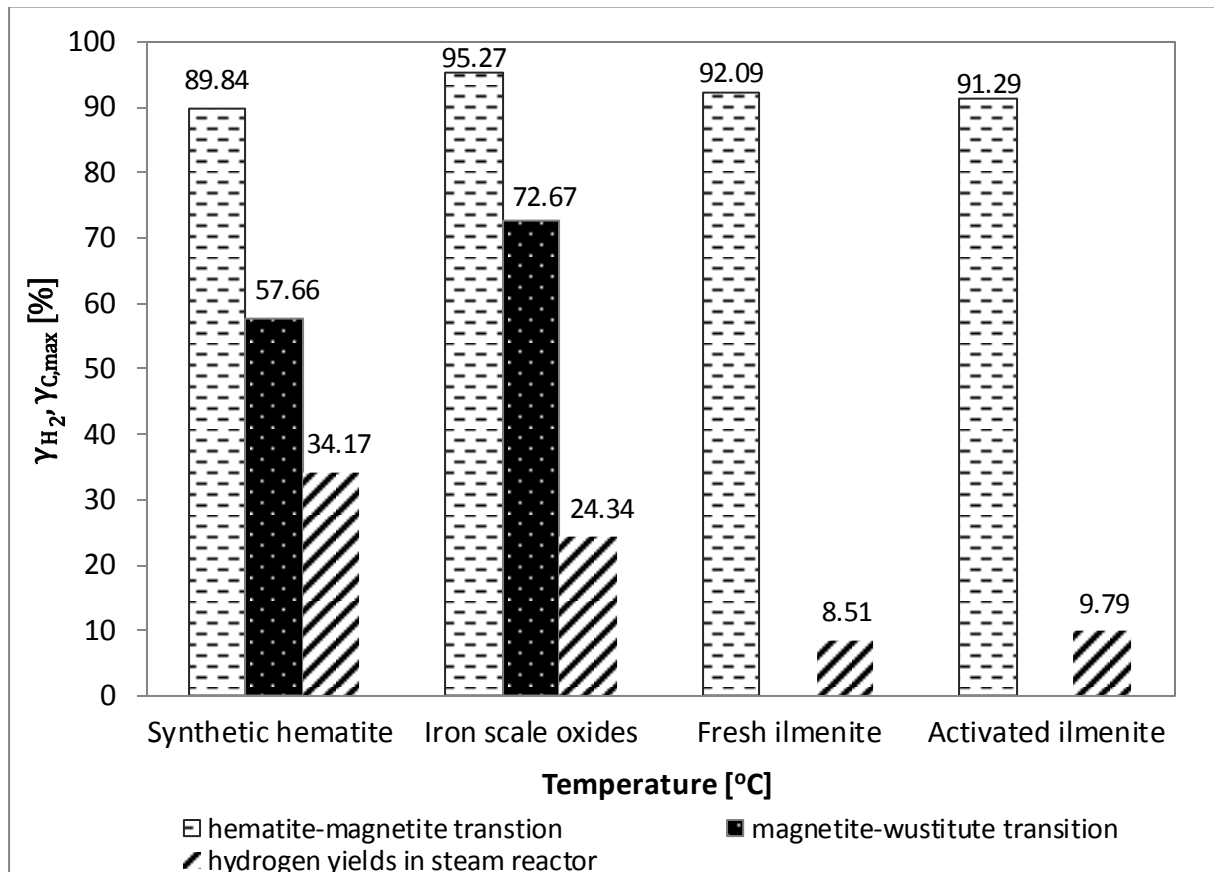


Figure 4.10. Syngas fuel conversion at 950°C in the fuel reactor Hydrogen production yield in steam reactor for each of the oxygen carriers used in syngas fuel case at 950°C.

Synthetic iron oxide particles and iron oxide scales exhibit a significant hydrogen production capability while the ilmenite shows little hydrogen production ability, even in its activated state. This is most likely due to the absence of an intermediate oxidation state in ilmenite as stated in Leion et al.[6].

Gasifier gas fuel case

The gasifier gas case experiments were limited only to synthetic hematite and two temperatures (950 and 900 °C). As observed in figures 4.11, in fuel reactor stage, the hematite reduction occurs sequentially to magnetite (first peak in CO₂ curve) and lastly to wustite (second peak in CO₂ curve).

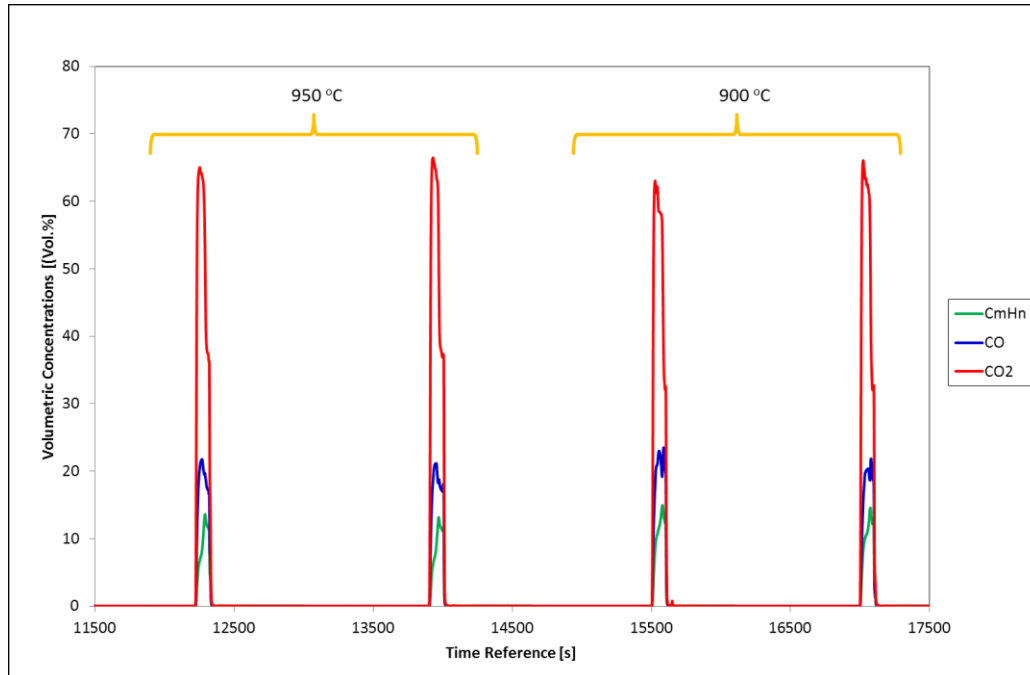


Figure 4.11. Dry gas (CO, CO₂ and C_mH_n) profiles for gasifier gas case at 950 and 900°C.

The fuel conversion degrees at 950/900°C have been calculated and graphically shown in figure 4.12 as 70.85/70.50 % for the hematite-to-magnetite transition phase and 56.53 /51.40 % for magnetite-to-wustite transition. Due to high partial pressure ratio of CO₂/CO resulting from the presence of methane, a lower magnetite transition results based on equilibrium data, which in turn has affected the wustite transition and produced less hydrogen in wustite oxidation process. On the second transition phase no difference is observed between syngas and gasifier gas simulation cases, as the process regardless of fuel composition is controlled by same mechanism of oxidation product layer diffusion control.

A decreasing tendency of carbon yields is observed with decreasing temperatures, which might have been caused by the steam presence in the fuel, triggering complex multiple equilibrium reactions and hindering fuel combustion to carbon dioxide. In the 950°C case, the carbon yield for the second transition is greater than the 900°C case, showing that this step, beside diffusion control is significantly affected by reaction kinetics as suggested in Ishida et al. study[7]. The higher the temperature the more wustite is converted and in turn the higher the hydrogen yield is in steam reactor.

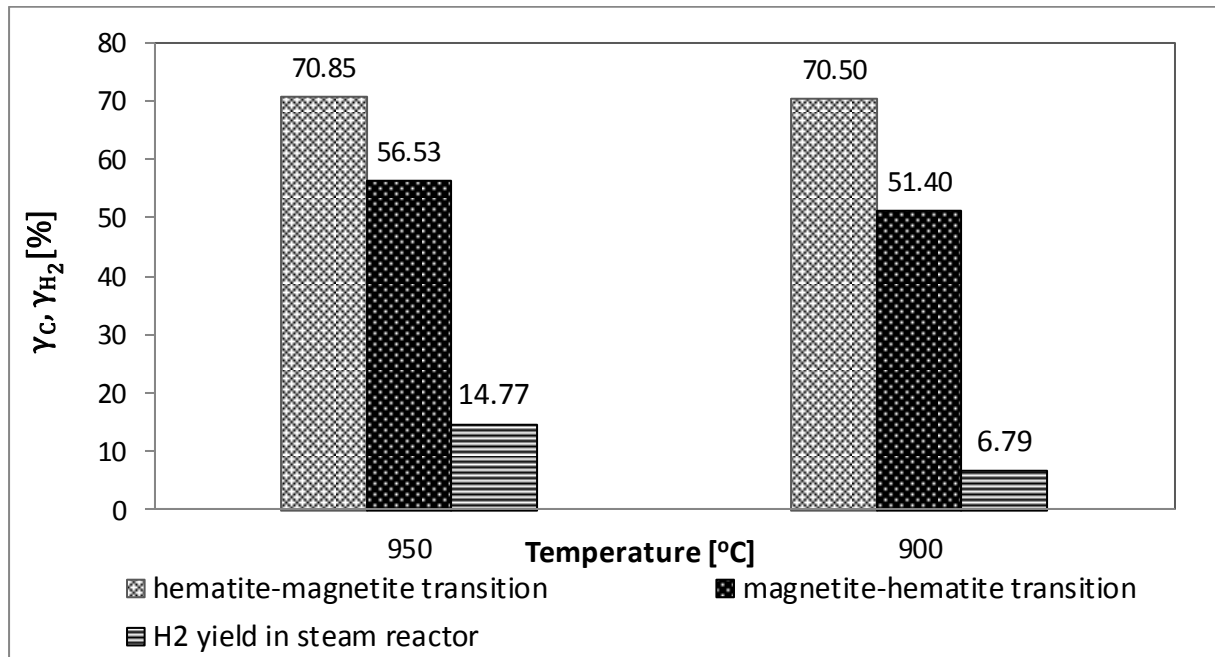


Figure 4.12. Summary of fuel combustion yields in fuel reactor and hydrogen production yield in steam reactor, with gasifier gas as fuel at 950 and 900 °C.

5. CONCLUSIONS

In this study, hydrogen production from a hybrid chemical-looping-steam-iron system consisting of three interconnected reactors was designed and optimized. The proposed system was examined thermodynamically with Aspen Plus software and experimentally studied to demonstrate the viability of this process. In the thermodynamic modeling the oxygen carriers utilized were composed of iron oxide supported on magnesium aluminate meanwhile in the experimental approach three different oxygen carriers, namely synthetic iron oxide, iron scale oxides and ilmenite, all composed of iron oxide but with different morphologies, were tested. Three different fuels, methane, syngas and biogas from gasifier, were analyzed in Aspen Plus model, while in experimental part syngas and biogas were tested. Hydrogen production in steam reactor was achieved in both approaches, showing a 51.4% hydrogen yield at 720°C in Aspen Plus model and ~40% at 800°C in experimental. The difference between these two approaches was explained with the different controlling mechanisms proposed in Aspen Plus from the real case. Based on an equilibrium approach in Aspen Plus, the gas-particle redox reactions were strongly dependent on temperature, regardless of fuel type used. In experimental on the contrary, the yields varied greatly from syngas to biogas fuel cases, with steam presence increasing the complexity of redox mechanism.

In Aspen Plus modeling at a constant steam reactor temperature of 720°C, two different approaches were analyzed. The first approach, in which a stoichiometric steam to fuel ratio was selected, an external heat recovery is prioritized where high quality heat is produced and successfully manageable in integrated power production and heating systems. On the other case, an excess steam to fuel ratio was chosen in order to prioritize pure hydrogen production. By following such approach, the chances for an external heat recovery are minimized to insignificant values. Nonetheless, the parameters were selected so that the system was thermally self-sustaining, providing internal heat exchange between cold and hot streams by internal heat exchange systems for preheating of inlet streams and eliminating thus external heating and cooling demands.

Between analyzed fuels, syngas indicated the highest net hydrogen efficiencies, with values as high as 86.1% for a stoichiometric steam feed ratio, to 76.14% for an excess steam ratio. Meanwhile biogas system, due to its low heating values and steam presence in the fuel composition displayed the lowest net efficiencies with 68.1 and 42.5% for stoichiometric and excess steam feed ratios. In the syngas and methane cases, a complete fuel conversion was observed meanwhile in biogas case, the fuel converted to 90%.

In experimental part, differently from Aspen Plus model, fuel conversion was almost complete with a carbon yields varying from 97.98% for syngas – synthetic iron oxide system at 800°C to 70.85% for biogas–synthetic iron oxide system at 950°C. High fuel conversions were recorded for the iron scale oxides and ilmenite particles.

Among oxygen carrier particles utilized, synthetic iron oxides showed the highest hydrogen yields in steam oxidation phase but also in terms of stability and defluidization resistance, allowing from several cycles of analysis. The other oxygen carriers on the other side were much less stable and showed a great tendency to defluidization. A factor this which limited experiments at lower temperatures and with biogas fuel. In terms of hydrogen production capacity, both synthetic and iron scale oxides showed good hydrogen yields. However, the contrary was observed for ilmenite, which due to its lack of wustite oxidation phase, both fresh and active ilmenite trials were unsuccessful in hydrogen production.

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Appendices

Appendix I – Pinch analysis parameters

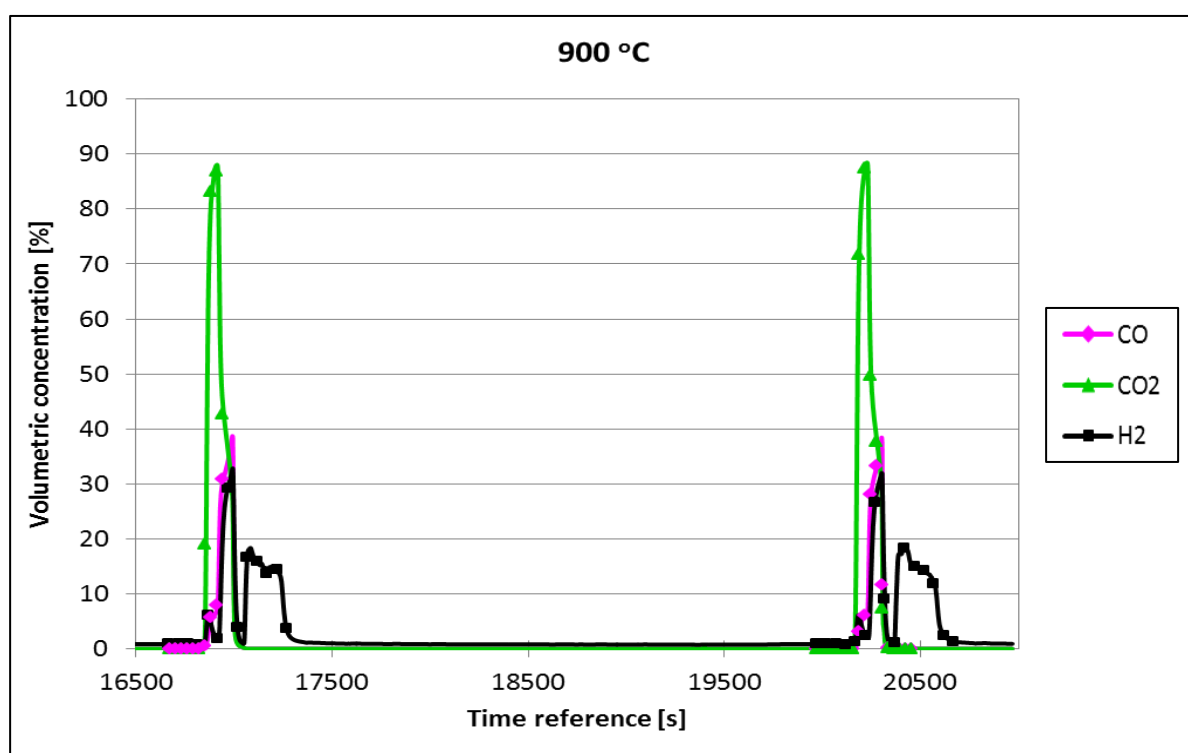
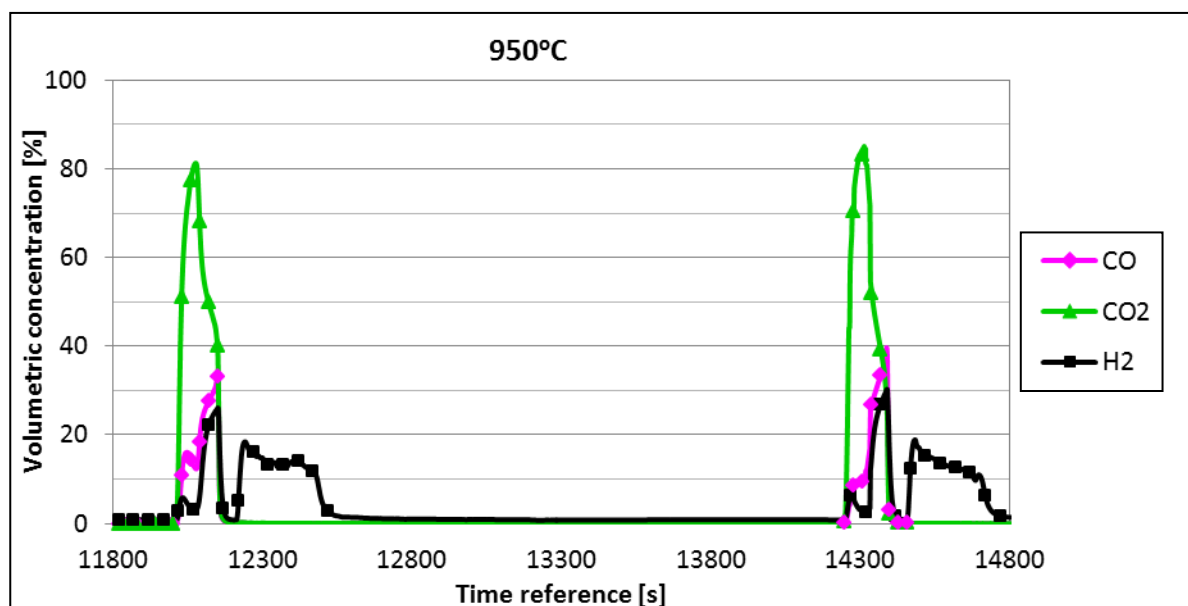
Based on a simplified heat capacity calculation:

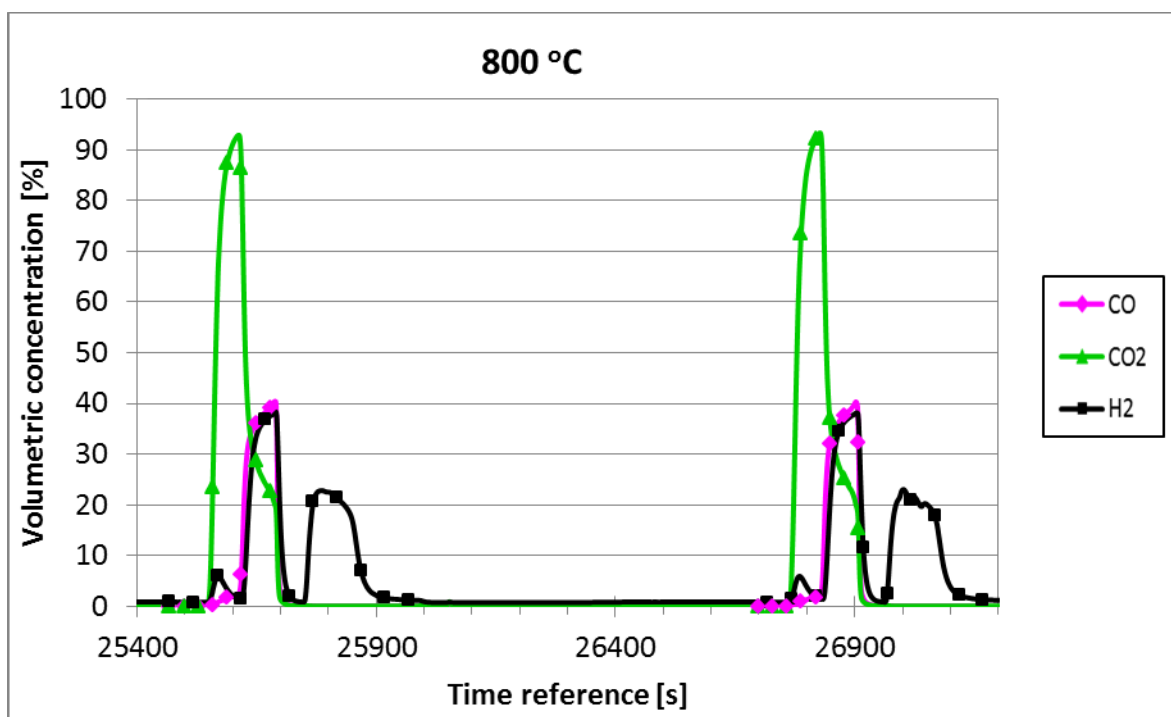
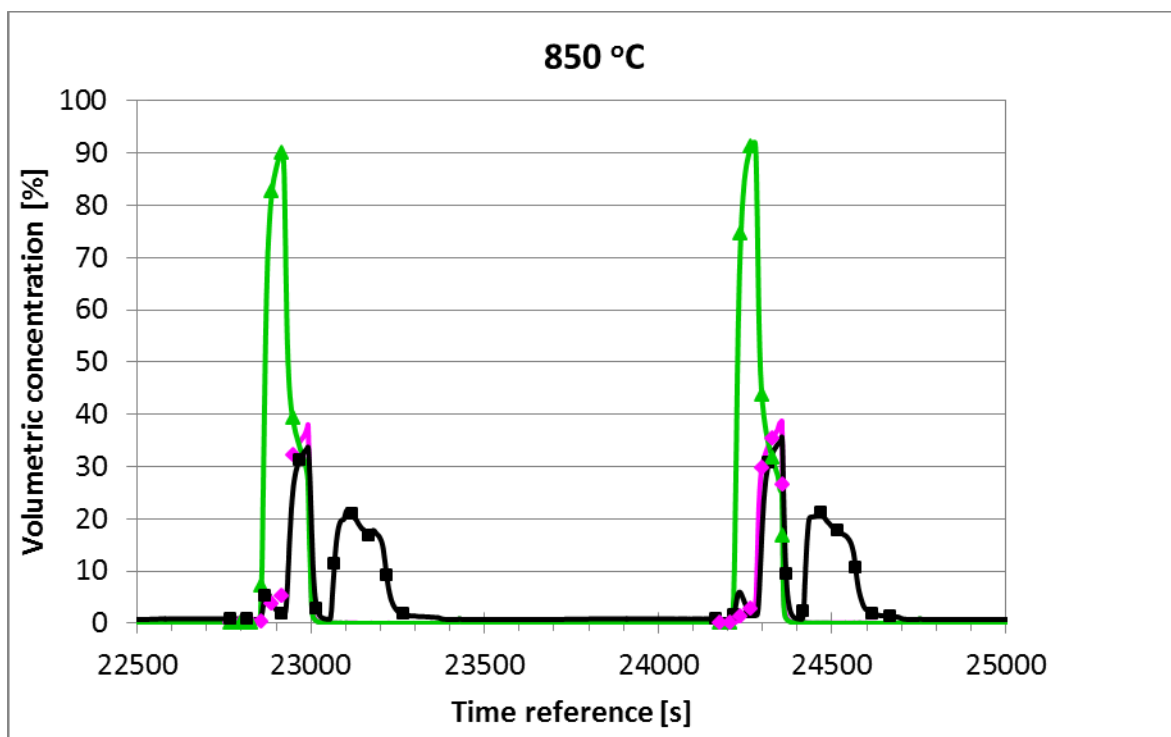
$$C_p = a + bT$$

	a	b	Cp _{avg} (J/kg/K)				
T(oC)	–	–	75	115	415	750	800
T (K)	–	–	348	388	688	1023	1173
CO	29.6127	0.0030	1095.01	1099.306429	1131.56	1167.57	1183.69
CO2	44.3191	0.0073	1064.99	1071.625	1121.4	1176.98	1201.86
H2	27.3198	0.0034	14242.8	14309.8	14812.3	15373.4	15624.7
H2O (l)	75.2880	0.0066	4309.88	–	–	–	–
H2O(v)	32.4766	0.0086	1970.91	1990.064444	2133.73	2294.16	2365.99
N2	29.2313	0.00307	1082.13	1086.516429	1119.41	1156.14	1172.59
CH4	44.2539	0.02273	3260.25	3317.0713	3743.26	4219.17	4432.26

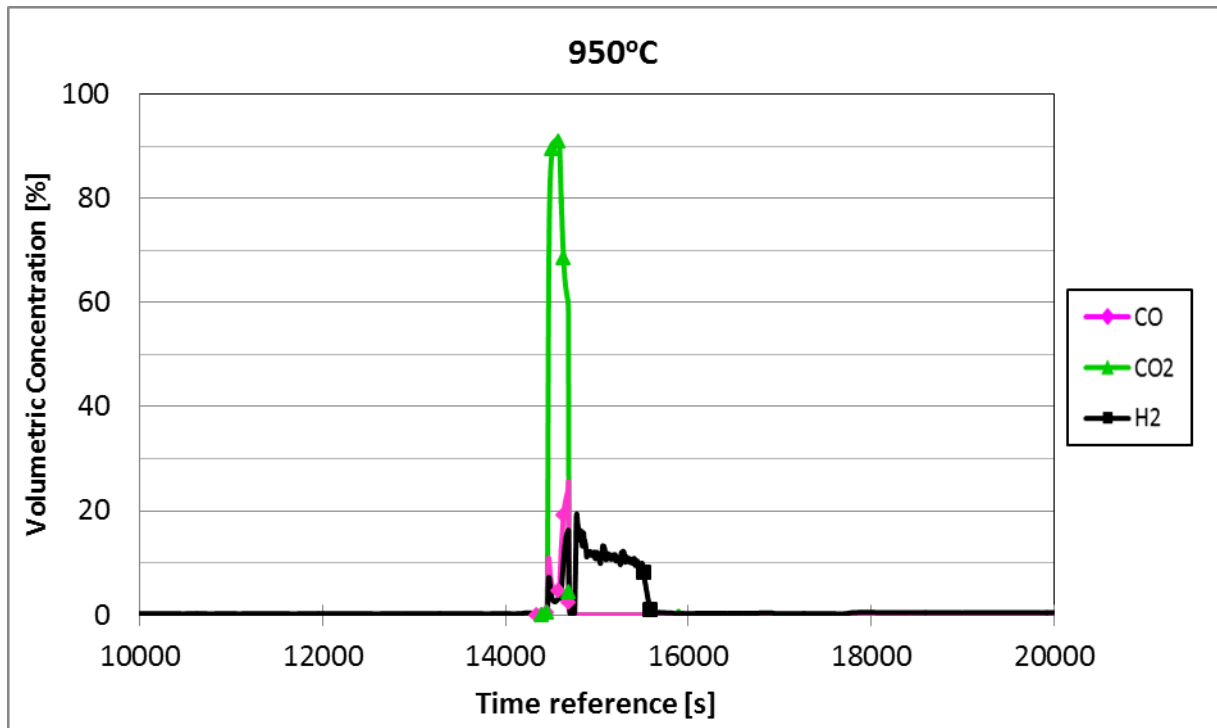
Appendix II - Syngas Experimental results

Synthetic $\text{Fe}_2\text{O}_3 \cdot \text{MgAl}_2\text{O}_4$

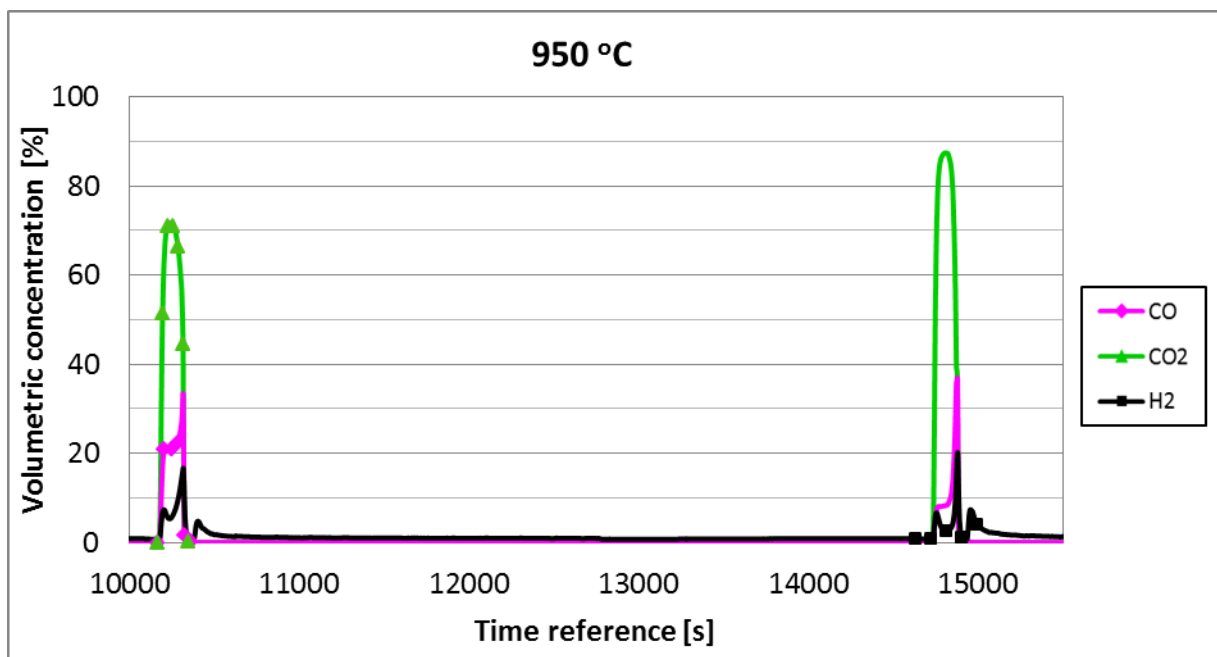




Iron Scale Oxides



Active ilmenite



Appendix III– Gasifier gas experimental results

Synthetic hematite

