THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Hydrogen production from fossil fuels with carbon dioxide capture, using chemical-looping technologies

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Göteborg, Sweden, 2008

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ABSTRACT

Carbon capture and storage have been receiving increasing interest lately, mainly as an option to reduce CO_2 emissions from the power sector. The concept could be adapted for production of H_2 as well, which would provide a carbon free energy carrier that could be used for example as transportation fuel. In this doctoral thesis, the option to use chemical-looping technologies to produce H_2 from fossil fuels with CO_2 capture is explored.

In chemical-looping combustion, direct contact between fuel and combustion air is avoided. Instead, a solid oxygen carrier performs the task of bringing oxygen from the air to the fuel. Thus, the resulting CO_2 and H_2O are not diluted with N_2, and pure CO_2 can easily be recovered by cooling and condensation. The heat of reaction is the same as for ordinary combustion. Chemical-looping reforming uses the same basic principles as chemical-looping combustion, but operates at understoichiometric conditions. Therefore chemical-looping reforming can be said to be a process for partial oxidation of hydrocarbon fuel into H_2 and CO, where chemical looping is used as a source of undiluted oxygen.

In the theoretical part of this work, the technical feasibility to use chemical-looping technologies for production of H_2 with CO_2 capture has been examined. Two main ideas have been explored. Steam reforming integrated with chemical-looping combustion means that chemical-looping combustion is used for CO_2 capture and as heat source for generation of H_2 via the endothermic steam reforming reaction. Chemical-looping autothermal reforming utilizes understoichiometric conditions and the possibility to add some H_2O to the fuel, in order to have both partial oxidation and steam reforming reactions occurring in the same reactor vessel. This way, a thermo neutral process is obtained. It is found that both options have potential to provide substantial advantages compared to conventional technologies. Thermodynamic modelling shows that reformer efficiencies of 80% or higher, including CO_2 capture and CO_2 compression, seem to be obtainable with both processes.

In the experimental part, chemical-looping reforming and chemical-looping combustion has been demonstrated in two different circulating-fluidized bed reactors. In total, over 200 hours of experiments have been recorded. Natural gas was used as fuel, and four different NiO-based materials have been used as oxygen carrier. Process conditions have varied from almost complete combustion into CO_2 and H_2O, to almost stoichiometric partial oxidation into CO and H_2. The reactor temperature has been between 800 and 950ºC. The experiments worked very well, but occasionally limited formation of solid carbon could occur in the reactor. Adding 25-30% H_2O or CO_2 to the natural gas reduced this tendency significantly.

In addition to this, a few unconventional materials that could be used as oxygen carrier in chemical-looping applications have been examined by reduction with CH_4 in a fixed-bed reactor at 900ºC. Some potentially useful materials were identified, such as $La_x Sr_{1-x}FeO_{3-\delta}$ perovskites and mixtures of Fe_2O_3 and NiO supported on $MgAl_2O_4$.

Keywords: Chemical-looping reforming, chemical-looping combustion, steam reforming, partial oxidation, hydrogen, synthesis gas, carbon capture and storage

LIST OF PUBLICATIONS

This thesis is based on the work contained in following papers, referred to by roman numbers in the text:

I. Rydén M, Lyngfelt A. Hydrogen and power production with integrated carbon dioxide capture by chemical-looping reforming. Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies, Vancouver, Canada, 2004.

II. Rydén M, Lyngfelt A. Using steam reforming to produce hydrogen with carbon dioxide capture by chemical-looping combustion. International Journal of Hydrogen Energy, v 31, p 1271-1283, 2006.

III. Rydén M, Lyngfelt A, Mattisson T. Synthesis gas generation by chemical-looping reforming in a continuously operating laboratory reactor. Fuel, v 85, p 1631-1641, 2006.

IV. Rydén M, Lyngfelt A, Mattisson T. Chemical-looping combustion and chemical-looping reforming in a circulating fluidized-bed reactor using Ni-based oxygen carriers. Submitted for publication 2008.

V. Rydén M, Lyngfelt A, Mattisson T, Chen D, Holmen A, Bjørgum E. Novel oxygen-carrier materials for chemical-looping combustion and chemical-looping reforming; $La_xSr_{1-x}Fe_yCo_{1-y}O_{3-\delta}$ perovskites and mixed-metal oxides of NiO, Fe_2O_3 and Mn_3O_4. International Journal of Greenhouse Gas Control, v 2, p 21-36, 2008.

Contribution by the author:

I. Principal author, responsible for modelling, data evaluation and writing.
II. Principal author, responsible for modelling, data evaluation and writing.
III. Principal author, responsible for experimental work, data evaluation and writing.
IV. Principal author, responsible for experimental work, data evaluation and writing.
V. Principal author, responsible for experimental work, data evaluation and writing.

Related publications not included in the thesis:

- Rydén M. Hydrogen production by reforming of natural gas with carbon dioxide capture by chemical-looping combustion. Proceedings of the 4th Nordic Minisymposium on Carbon Dioxide Capture, Espoo, Finland, 2005.

- Abad A, Mattisson T, Lyngfelt A, Rydén M. Chemical-looping combustion in a 300 W continuously operating reactor system using a manganese-based oxygen carrier. Fuel, v 85, p 1174-1185, 2006.

- Rydén M, Lyngfelt A, Mattisson T. Two novel approaches for hydrogen production; chemical-looping reforming and steam reforming with carbon dioxide capture by chemical-looping combustion. Proceedings of the 16th World Hydrogen Energy Conference, Lyon, France, 2006.

- Rydén M, Lyngfelt A, Mattisson T. Production of H_2 and synthesis gas by chemical-looping reforming. Proceedings of the 8th International Conference on Greenhouse Gas Control Technologies, Trondheim, Norway, 2006.

- Johansson M, Mattisson T, Rydén M, Lyngfelt A. Carbon Capture via Chemical-Looping Combustion and Reforming. Proceedings of the International Seminar on Carbon Sequestration and Climate Change, Rio de Janeiro, Brazil, 2006.

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INTRODUCTION

1.1 The greenhouse effect and global warming

In 1827 the French mathematician Joseph Fourier wrote an essay concerning the temperature of the earth [1]. In this essay he introduced the idea that certain gases in the atmosphere exerts a thermal blanketing that keeps the planets surface warmer than it otherwise would be. The heating effect that these gases have on our planet has become known as the greenhouse effect and the gases as greenhouse gases. The greenhouse effect can be visualized by a simplified energy balance of the earth's surface, see Figure 1.

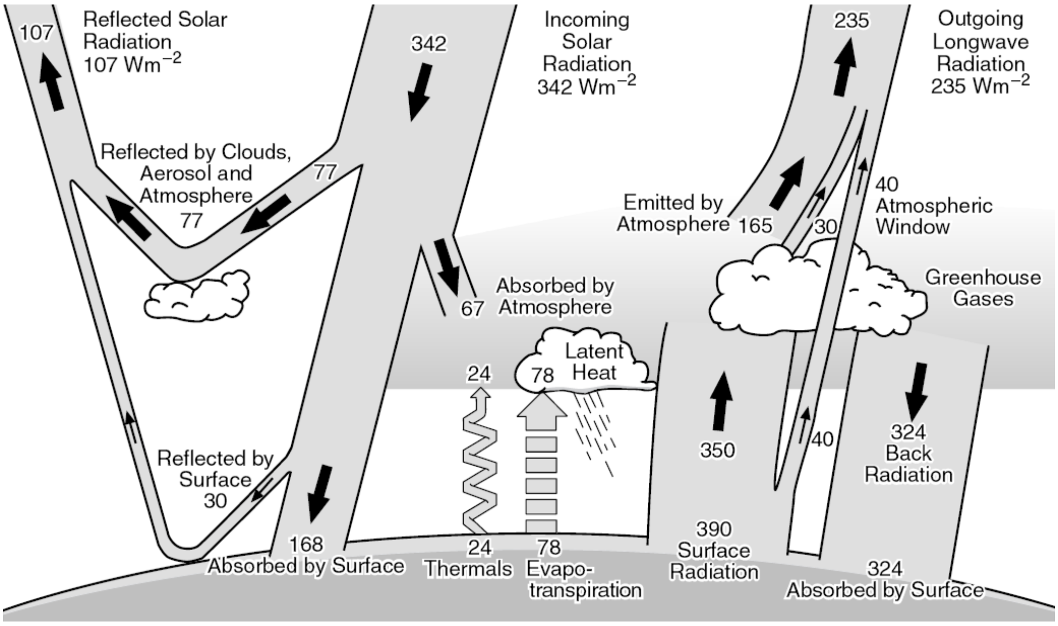

Figure 1. The energy balance of the earth. About half of the incoming solar radiation passes through the clouds and the atmosphere and is absorbed by the surface. Parts of the resulting heat is reemitted back as thermal infrared radiation, which in turn is absorbed and reradiated by greenhouse gases in the atmosphere and causes the greenhouse effect. IPCC [2, 3].

Science has come far the past 180 years. Today we know that the greenhouse effect is vital to the earth's climate system. At present, it boosts the temperature of our planet about 33ºC.

Without it our world would have been much colder, perhaps even incapable to harbour advanced life forms such as ourselves. It is easily realized that if the concentration of greenhouse gases in the atmosphere is altered, so is the greenhouse effect. If the changes are large enough, this should eventually have impact on the climate of our planet as well.

There are several greenhouse gases present in the atmosphere. The two most important are water vapour and CO_2. This has been known since 1861, when the British philosopher James Tyndall presented experiments that demonstrated the absorbing properties of these gases [4].

Human activities are not believed to influence the concentration of water vapour in the atmosphere directly, but that is not the case for CO_2. It is well established that our way of living is increasing the concentration of CO_2 in the atmosphere rapidly. Since 1958, direct measurements of CO_2 in the atmosphere are done on regular basis. In addition to this, the historic CO_2 concentrations for the past 700 000 years or so have been reconstructed with high accuracy by measuring the CO_2 concentration in air trapped in glacier ice cores. Thanks to these efforts, we know for certain that the CO_2 concentration in the atmosphere has increased more than 30% since the beginning of the industrial revolution, see Figure 2.

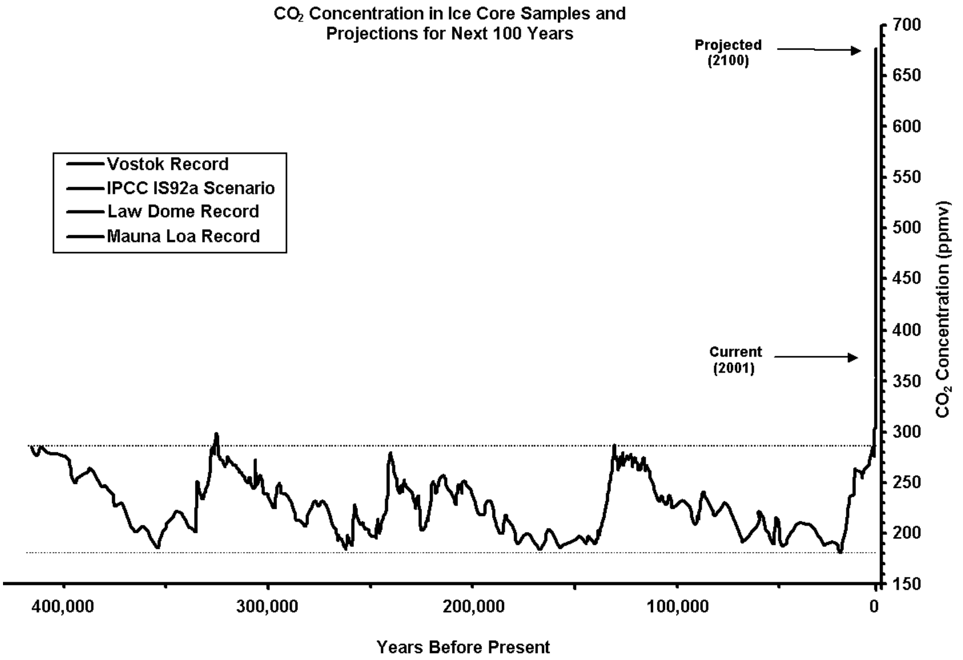

Figure 2. Atmospheric CO_2 concentration for the past 420 000 years estimated by measurements in ice core samples from the Vostok research station in Antarctica, combined with current measurements and a projection for year 2100. Adapted from IPCC [2].

In order to understand why this is happening, and where we eventually may end up, it can be useful to look back even farther than the mentioned 700 000 years. It is possible to make rough estimations of atmospheric CO_2 concentrations that go back hundreds of millions of years, for example by measuring boron to carbon ratio in ancient sediments. Such estimations show that there are several occasions in prehistoric times when the CO_2 concentration in the atmosphere have been much higher than today. The latest such occasion was the Jurassic period 145-200 million years ago, the pinnacle of the era of the dinosaurs. By then, the atmospheric CO_2 concentration was several times as high as today, and there is plenty of fossil evidence that even the arctic areas of our planet were covered with lush jungles. Since those sweaty days, vast amounts of CO_2 have been removed from the atmosphere. The carbon has not just disappeared though. Instead, it can be found solved in the oceans, bound in minerals and in other so called carbon reservoirs. Transportation of CO_2 from the atmosphere to other carbon reservoirs is naturally occurring, but very slow.

The most intriguing carbon reservoir that was built up during these prehistoric times is the so called fossil fuels, which include oil, coal and natural gas. It is generally believed that fossil fuels are dead organisms that have been transformed into various carbon compounds by the combined forces of age, heat and pressure. When fossil fuels are burnt, these ancient carbon resources that has been build up during millions of years is released to the atmosphere as CO_2.

From a geological point of view, large-scale extraction and combustion of fossil fuels is an incredibly rapid process. It has only been going on for a little more than hundred years and if nothing is done this once gargantuan stockpile of prehistoric carbon could be depleted in a not so distant future. Oil and natural gas resources are already strained in many parts of the world. By contrast, the time scale for transportation of CO_2 from the atmosphere into other carbon reservoirs is at least several thousand, or in the case of fossil fuels even millions of years. Therefore, combustion of fossil fuels inevitably results in increased concentration of CO_2 in the atmosphere.

It took until 1896 before combustion of fossil fuels was linked to Fourier's idea about the greenhouse effect, via Tyndall observations of the absorptive properties of CO_2. This year the Swedish chemist Svante Arrhenius published his famous article *On the influence of carbonic acid in the air upon the temperature of the ground* [5], in which he argues that the concentration of CO_2 in the atmosphere has a strong influence on the climate of the earth. His theory was immediately questioned, but Arrhenius defended his work and eventually his ideas were accepted by the scientific community.

It is interesting to notice that Arrhenius was by no means an alarmist. On the contrary, he was an optimist. He even argued in favour of increased CO_2 emissions. In his book *Worlds in the making* from 1908 he suggested that human emission of CO_2 could prevent the world from entering a new ice age, and that a warmer planet would be necessary to feed the rapidly increasing world population. Arrhenius was not the only one who pondered about this topic. It is said that highly respected scientists such as Walther Nernst, the Nobel Prize receiver, the developer of the Nernst equation and the third law of themodynamics, the inventor of the electronic piano etc, even fantasized about setting fire to whole coal seams in order to release CO_2 for a rapid warming of the earth. Such ideas may seem completely out of place today, but Arrhenius and Nernst were working in a very different scientific and intellectual setting. They also failed to predict the immense growth of industrial activities that occurred in the 20th century. Arrhenius thought that a doubling of the atmospheric CO_2 should take 3000 years. At present, it seems like it could happen within this century.

While some of the early predictions about the influence of human activities on the climate of the earth were somewhat off the mark, others were not. Today we know not only that the atmospheric concentration of CO_2 is increasing, but that the temperature of the earth is rising as well. Temperatures and precipitation have been carefully monitored for centuries. The first meteorological network was formed in Italy as early as in 1653, while the international meteorological organization was formed in 1873 [3]. Therefore we know for sure that the average global surface temperature of our planet has increased at least a half degree centigrade since the beginning of the industrial era, see Figure 3 below. A half degree may not sound like a big deal but the temperature of the earth is actually believed to be warmer today than it has been for several thousands of years.

Temperature can be estimated by measuring the occurrence of various temperature dependent isotopes naturally present in the air. Hence ice core samples that contain trapped air provide information not only about past atmospheric CO_2 concentrations, but some information about the climate history of the earth as well. Therefore it is known that there is indeed a strong correlation between the CO_2 concentrations in the atmosphere and the climate, see Figure 4 below.

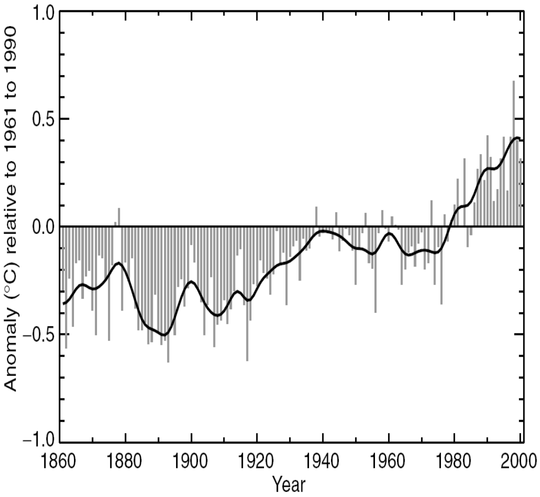

Figure 3. Annual anomalies of global land-surface air temperature, average for the northern and southern hemispheres with the period between 1961 and 1990 used as reference. IPCC [2].

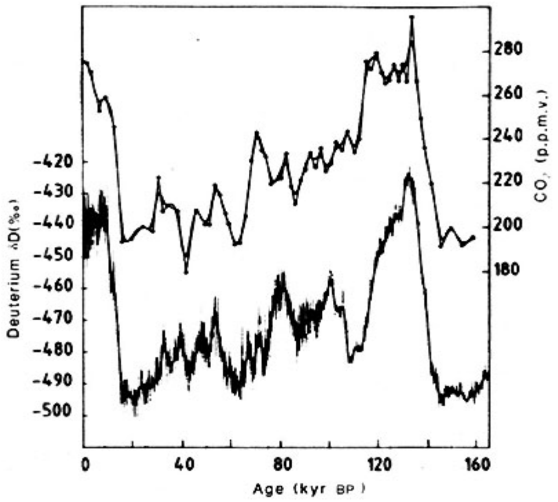

Figure 4. Atmospheric concentrations of CO_2 (upper curve) and the temperature dependent isotope deuterium (lower curve) plotted against age, expressed as thousands of years before present. From Barnola et al [6].

At the first glance, Figures 2-4 may appear to be rather solid proof that CO_2 emitted into the atmosphere by humans increase the CO_2 concentration in the atmosphere and that this results in a warmer climate. In truth, the correlations are much more complicated. There are other factors than combustion of fossil fuels that contributes to the amount of greenhouse gases present in the atmosphere, and there are also other factors than the atmospheric concentration of greenhouse gases that affects the climate of the earth. In fact, the complexity of the earth's climate system is a considerable scientific challenge. It is also practically impossible to perform controlled experiments on the planet as a whole, and then observe the results. This is an important consideration, since only such planet-scale experiments, incorporating all interacting processes and feedbacks could truly verify or falsify hypotheses about global warming.

Because of this, any theory that involves the earth's climate will be vulnerable to critique, unless it is based on very robust science. Typically, modern climate science relies on clearly verifiable hypotheses, which can be incorporated into increasingly sophisticated computer models. During later years, countless empirical tests and immense modelling has built up a massive body of knowledge about the climate system of the earth. These activities have refined the understanding of many aspects of the climate system, and while there still are areas that are not fully explored or understood, the general consensus among climatologists is that increased CO_2 concentration in the atmosphere has an actual and considerable heating effect on our planet.

In later years, concerns about this so called global warming have been growing steadily. This is hardly surprising. If we define risk as the probability of an event multiplied with consequence if the event occurs, we realize that global warming is an immense risk to both people and the environment in many countries. According to the Intergovernmental Panel on Climate Change "*evidence is now unequivocal that humans are causing global warming"* [3]. The consequences of a sudden increase in the global average temperature with a few degrees would likely include sea level rise due to polar melting and thermal expansion of the sea, as well as considerable changes in precipitation patterns. This in turn would have huge impact on land, food and water resources, and could also result in collapse of whole ecosystems and catastrophic losses in biodiversity. In summary, the probability that human activities are causing global warming is very high and the expected economical and environmental consequences are extremely grave. Hence there can be no doubts that anthropogenic climate change is one of the greatest risks threatening our society today.

To mitigate the impact of this unsettling development, global CO_2 emissions would need to be reduced greatly in the near future. This is a challenging task, to say the least. Almost all activities associated with our modern societies are dependent on fossil fuels. They are used for production of vehicle fuels, for generation of electricity, as raw material in industrial processes, for household heating, for production of fertilizers to the agriculture sector and for many other applications. At present, well over 80% of the primary energy consumption of the world comes from combustion of oil, coal and natural gas.

1.2 Ways to reduce anthropogenic CO_2 emissions

There are several options available to decrease global CO_2 emissions. In order to identify these options, it can be helpful to consider the major factors influencing CO_2 emissions and relate them to energy consumption. This can be done with the simple but useful Kaya identity [7], see expression (1).

$$F = P \times (G/P) \times (E/G) \times (F/E) \qquad (1)$$

In the Kaya identity, F represents global CO_2 emissions from human sources, P is global population, G is world gross domestic product, E is global primary energy consumption, *(G/P)* is global per-capita gross domestic product, *(E/G)* is the global energy intensity, and *(F/E)* is the global carbon intensity of energy.

Most scenarios predicting the future development of the world suggests that the world population *(P)* and the global per-capita gross domestic product *(G/P)* will continue to increase in the near future. It can be argued, with some merit, that changing these trends is undesirable or even impossible. Global population will likely continue to rise for some decades to come, and economic growth can help to improve the life situation for people in impoverished and underdeveloped parts of the world. Therefore, it can be said that the Kaya identity implies that achieving deep reductions in CO_2 emissions will require either major reductions of global energy intensity *(E/G)*, or a steep reduction of carbon emissions from energy technology *(F/E)*.

There are several options available to achieve these goals. A comprehensive review can be found in the IPPC report, especially the part about mitigation [2, 3]. The most frequently discussed options to reduce greenhouse gas emissions are summarized below:

- ***Reduce global energy intensity***
  If the energy sector's share of the world economy is reduced, so is *(E/G)* in expression (1). This could be achieved either by more efficient energy use in production and consumption of goods and services, or by a change in consumption patterns away from particularly energy-demanding products. Reducing global energy intensity should be a technically sound and economically rational way to start limiting global CO_2 emissions, but it is not likely that it would be enough to mitigate global warming.

- ***Increase the use of renewable energy sources***
  Renewable energy sources produce no direct CO_2 emissions, so increased use would reduce the *(F/E)* factor in expression (1). Unfortunately, replacing fossil fuels with renewable energy is a gigantic task. Most rivers suitable for hydro power are already developed. Wind power and solar power are promising and have large potential, but still have some way to go until they become major players on the global energy market. Production of various kinds of biofuels is technically possible, but limited by lack of fertile land and fresh water resources. There are also concerns that large-scale use of biofuels would compete with food production, which could increase the problems with food scarcity in poor countries.

- ***Increase the use of nuclear power***

  Nuclear power produces no direct CO_2 emissions, so increased use would reduce the *(F/E)* factor in expression (1). Very few nuclear power plants have been constructed the last 25 years though. The private sector, which dominates the power sector in most developed countries nowadays, has shown only modest interest in nuclear power. This can likely be contributed to high investment costs and complex juridical setting. In addition to this, nuclear power also involves political considerations such as the risk for weapon proliferation, the problematic waste disposal and a lack of public acceptance in many countries. It shall also be noted that nuclear power is not a renewable energy source, and that deposits of uranium suitable for extraction with present technology are limited. However, uranium is fairly abundant and exists in very low concentrations both in the oceans and in the earth's crust. Therefore it seems reasonable to believe that improved extraction methods and higher price would increase the commercially viable deposits considerably. It is also possible to improve fuel utilization by nuclear breeding, or by improved processing of depleted fuel. Both these options are highly controversial though. It could also be possible to construct nuclear reactors that use thorium as fuel, which would broaden the resource base further.

- ***Switch to less carbon intensive fuels***

  If coal is replaced by oil or natural gas, the emission of CO_2 per unit energy produced decreases. This is because coal contains more carbon per unit of energy than oil and natural gas. Hence fuel switch away from coal to other fuels could be used to reduce CO_2 emissions by reducing the *(F/E)* factor in expression (1). This concept has two obvious shortcomings. Firstly, oil and natural gas are fossil fuels that emit CO_2 to the atmosphere when utilized. Secondly, the known deposits of oil and natural gas are limited and strained, while there are immense amounts of coal available at relatively low cost. So in medium or long term, fuel switch from coal to fossil fuels with less carbon intensity does not seem like a viable strategy.

- ***Enhance CO_2 uptake in biomass***

  Growing plants consume atmospheric CO_2 through photosynthesis. The CO_2 is converted to various carbon containing compounds building up biomass. So if the total amount of biomass on the earth were increased, considerable amounts of CO_2 could be drained from the atmosphere. This could be achieved for example by growing forests in deserts and arid lands. At present, the opposite is happening. In many parts of the world old forests are cut down for wood and farmland. Such large-scale deforestation contributes to increased CO_2 concentration in the atmosphere instead.

- ***Decrease non-CO_2 greenhouse-gas emissions***
  Although CO_2 is considered as the most important contributor to anthropogenic climate change, there are other contributors as well. Greenhouse gases released by human activities include CH_4, as well as various nitrogen oxides and halocarbons. Naturally, reducing emissions of such gases would not reduce global CO_2 emissions, but it could reduce the impact of anthropogenic climate change somewhat.

- ***CO_2 capture and storage***
  This thesis deals with technologies that can be used for CO_2 capture and storage, a way to reduce the *(F/E)* factor in expression (1) that is presented in section 1.3 below.

1.3 An introduction to CO_2 capture and storage

If CO_2 is captured in flue gases from a combustion process and prevented from reaching the atmosphere it will not contribute to the greenhouse effect. In this way, fossil fuels can be used without impact on the climate of the earth. The idea is usually referred to as carbon capture and storage or carbon sequestration, and has received much interest in later years. Carbon capture and storage is not restricted to direct combustion of fossil fuel, but could also be used in other major CO_2-emitting industries such as steel, cement, synthetic fuel and ammonia plants, biomass combustion, refineries, natural gas processing facilities etc. The most inclusive source for information about carbon sequestration is IPCC:s special report on CO_2 capture and storage [8]. Many governments, international organisations and major corporations have also produced technical summaries and technological roadmaps about the topic, including the U.S. Department of Energy [9]. Reviews in academic press include for example those by Yamasaki [10], Anderson and Newell [11], and Benson and Surles [12].

One positive characteristic of carbon capture and storage is that it does not necessarily require new and unproven technologies. Most of the required process components are already known and commercially available. Hence carbon capture and storage has potential to have real impact on the global CO_2 emissions even in a relatively near future, see Figure 5.

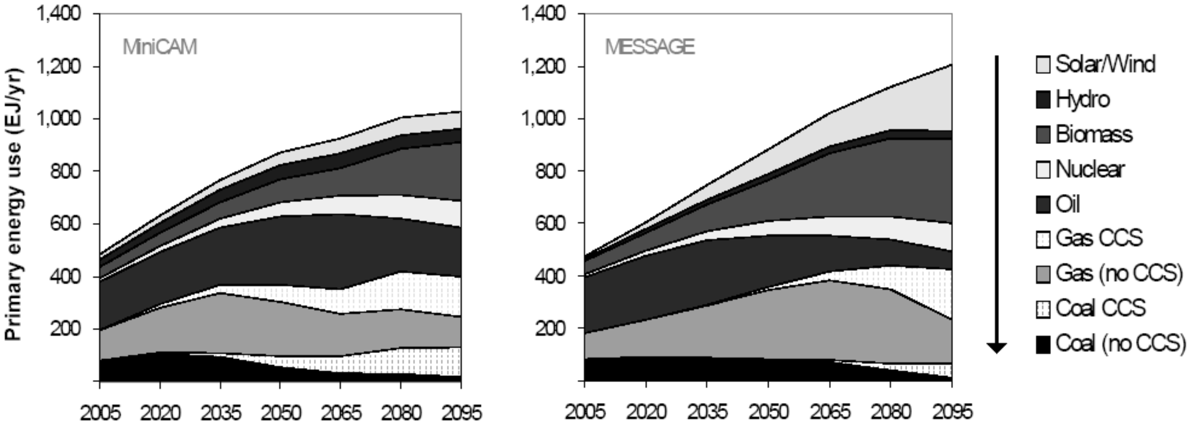

Figure 5. World primary energy production as function of time, for two different scenarios (B2-550-MiniCAM2, B2-550-MESSAGE2) suggested by IPCC [8]. In both cases carbon capture and storage ends up playing a major role in prohibiting emissions.

The relative maturity and simplicity of carbon capture and storage is also reflected in policy statements from various organisations. For example, in its sustainable power generation communication in 2007 [13], the European Commission stated that it intends to work to:

- *"Design a mechanism to stimulate the construction and operation by 2015 of up to 12 large-scale demonstrations of sustainable fossil fuels technologies in commercial power generation in the EU."*

- *"Provide a clear perspective when coal- and gas-fired plants will need to install* CO_2 *capture and storage. On the basis of existing information, the Commission believes that by 2020 all new coal-fired plants should to be fitted with* CO_2 *capture and storage and existing plants should then progressively follow the same approach..."*

So there are many factors that indicate that carbon capture and storage will have an important role to play in the efforts to reduce global CO_2 emissions. This will require technologies for CO_2 capture, CO_2 transportation and CO_2 storage. The current state of knowledge is briefly presented below.

1.3.1 CO_2 capture

The aim with CO_2 capture is to obtain sufficiently pure CO_2. High purity means that less energy and space is needed for compression, transportation and storage of the captured CO_2. Certain impurities, for example H_2O, may also make transport and storage technically more complicated due to corrosion. Other impurities, for example sulphur compounds, may add juridical complications because of existing international treaties.

Industrial scale CO_2 capture has been practiced for more than 80 years. The aim has usually been purification of natural gas or synthesis gas. The most used method has been physical or chemical absorption, which involves scrubbing of the CO_2 containing gas with a liquid solvent. Physical absorption means that CO_2 is solved in the absorbing liquid at high pressure. Chemical absorption means that CO_2 reacts actively with the solvent and forms a weak chemical bond. In both cases, the resulting CO_2 rich solvent can be regenerated either by reduced pressure or by increased temperature, and high purity CO_2 is released. This type of technology could very well be used to capture CO_2 in flue gases from combustion. The concept is usually referred to as *post combustion* CO_2 *capture*.

Another option is to produce H_2 by reforming of fossil fuels and capture CO_2 within the process. Combustion of H_2 produces only H_2O, so H_2 from such a process could be used for energy production without CO_2 emissions, see section 1.4 below. This concept is usually called *pre-combustion* CO_2 *capture*. Chemical-looping autothermal reforming CLR(a) and steam reforming integrated with chemical-looping combustion, which are described in section 3 below, are process concepts that could be used for pre-combustion CO_2 capture.

A third option is to replace the combustion air in a power generating process with pure O_2 mixed with recirculated flue gases. In this way, the resulting flue gases will not be diluted with N_2 from the air. Instead, a flue gas consisting of only CO_2 and H_2O is obtained, and cooling and condensation is sufficient to obtain almost pure CO_2. This concept is usually referred to as *oxyfuel combustion*. Chemical-looping combustion, which is described in section 2.4 below, resembles oxyfuel combustion in the aspect that it produces a flue gas consisting of only CO_2 and H_2O. Chemical-looping combustion does not need pure O_2 to operate though, but utilizes a solid oxygen carrier instead.

It is also possible to capture CO_2 within various industrial processes. A reason to do so could be that CO_2 is present at high partial pressure, which simplifies CO_2 capture by absorption. This is the case for some widely used industrial processes, for example ammonia production. A summary of available concepts for large scale CO_2 capture can be found in Figure 6.

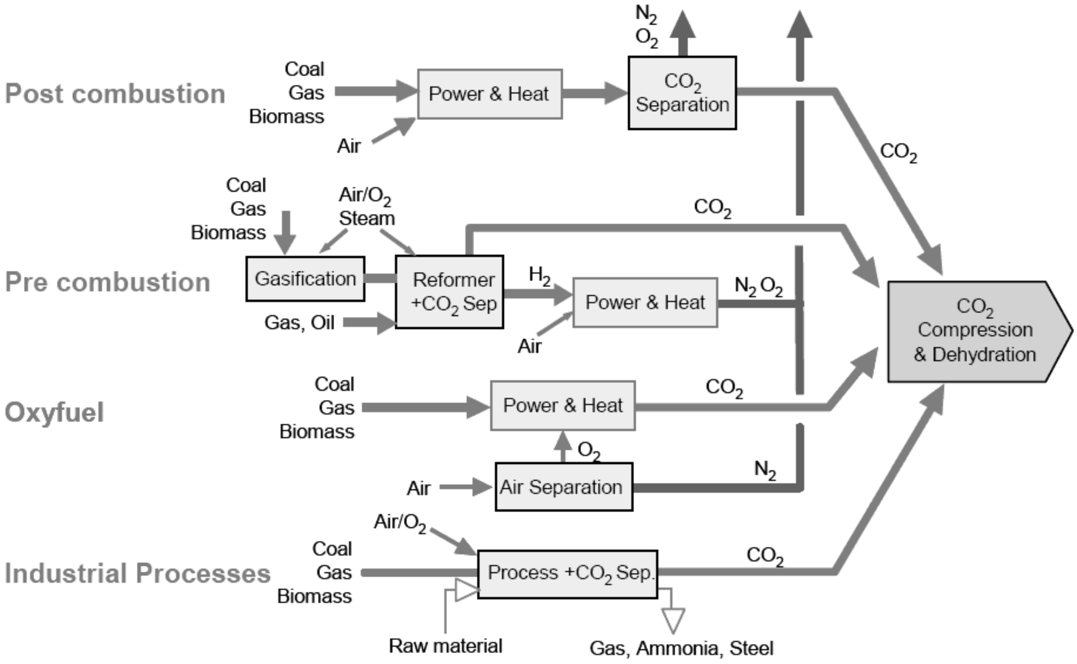

Figure 6: Possible routes for large scale CO_2 capture. IPCC [8].

1.3.2 CO_2 transportation

Large-scale transportation of CO_2 is nothing new. In western United States there is over 2500 km pipeline that transports over 40 million tons of CO_2 annually. This is done to provide CO_2 for enhanced oil recovery (EOR), see section 1.3.3 below. Dry CO_2 is not corrosive to pipelines, even if it contains contaminants, and most of these pipelines have been operated for decades without any major obstacles [8].

Pipeline transport could be complemented by sea transport. At present there is limited experience with ships for CO_2 transportation, due to lack of demand. The technology should be quite similar to shipping of liquefied petroleum gas however, and there are no known technical barriers. Road and rail tankers also are technically feasible options, but should be uneconomical compared to pipelines and ships.

1.3.3 CO_2 storage

There are several options available for CO_2 storage. At present, geological storage seems to be the preferred choice. Geological storage means that carbon is returned to where it came from, that is back into the earth’s crust. Such technology has been practiced at industrial scale for decades. Huge amounts of CO_2 have been pumped into nearly depleted oil fields in order to boost oil production in a procedure known as enhanced oil recovery. Similar technology could be used to store CO_2 in other geological formations, such as saline aquifers, depleted gas field or deep coal beds. These storage options take advantage of various physical and geochemical trapping mechanisms that would prevent CO_2 from migrating to the surface. Geological formations feasible for CO_2 storage are quite abundant and drilling technology, injection technology, computer simulation of storage reservoir performance and monitoring methods would likely be comparable to methods used for enhanced oil recovery.

Alternatives to geological storage include ocean storage, mineral carbonation and industrial use of CO_2. Ocean storage means that CO_2 is dissolved in ocean water, or stored as homogenous lakes of liquid CO_2 at the sea floor more than 3000 meters below the surface. At present, there are serious concerns about how ocean storage would affect the marine environment and whether the CO_2 stored would actually stay for a sufficiently long time in the ocean, so the concept needs further study. Mineral carbonation means that CO_2 is allowed to react with rocks containing for example magnesium oxides, and in some way mimics the natural weathering process. Under most circumstances such reactions are very slow and the logistics would involve huge amounts of minerals, but if these problems could be solved mineral carbonation would be a way to bind CO_2 in a harmless form that is guaranteed to last for millenniums to come. Industrial use of captured CO_2 as feedstock in chemical processes to produce carbon-containing products is also a possibility, but the expected scale of operations for such processes is too small to be able to contribute significantly to reductions of global CO_2 emissions.

1.3.4 Example of large scale CO_2 capture and storage projects

There are several carbon sequestration projects throughout the world that provides valuable knowledge and experience for future developments. Most of them are at modest scale, but there are some notable exceptions such as the Sleipner CO_2 storage project, see Figure 7, and the In Shala gas project, se Figure 8.

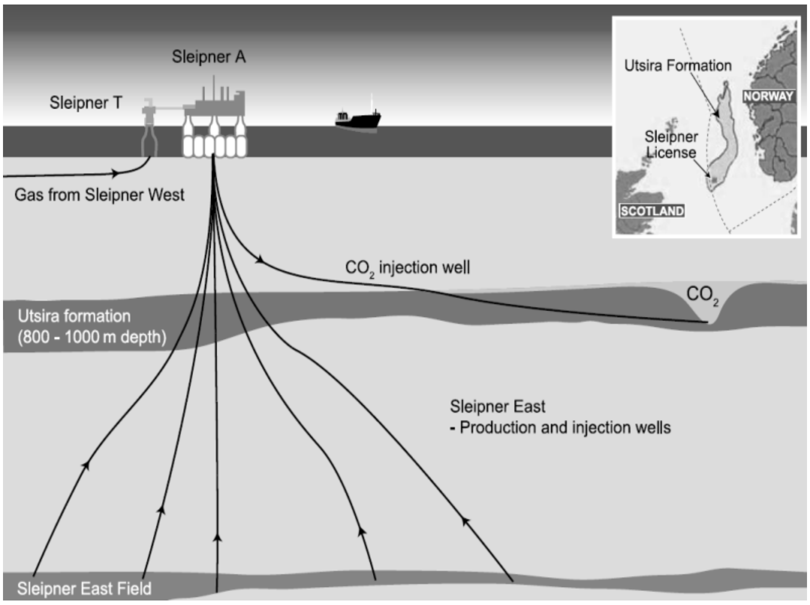

Figure 7. The Sleipner CO_2 storage project. At the Sleipner gas field in the North Sea, 1 million tons of CO_2 per year is removed from natural gas by absorption. The CO_2 is injected into the Utsira formation, which is a deep saline aquifer located 800-1000 meters below the sea floor. The development has been carefully monitored since the start 1996 [8].

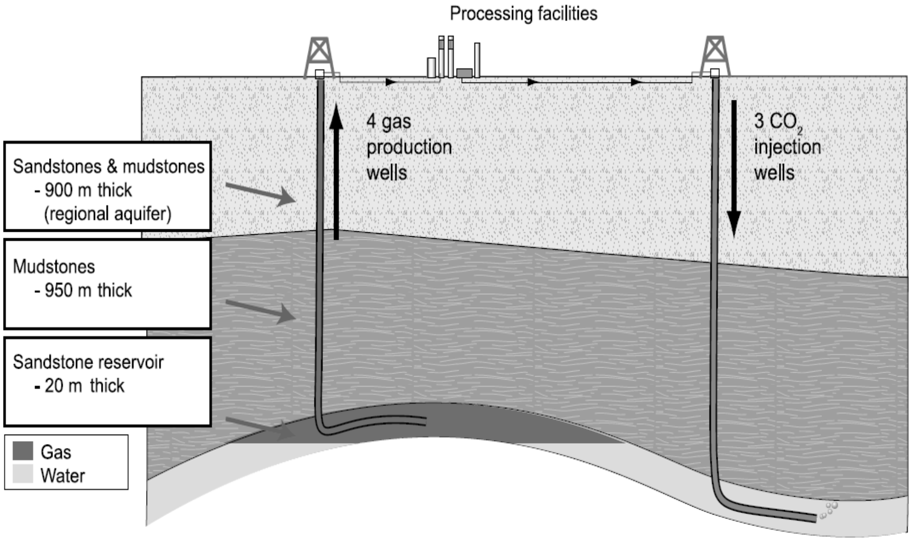

Figure 8. The In Shala gas project. At the Krechba gas field in Algeria, 1.2 million tons of CO_2 annually is captured from natural gas and injected into water-filled parts of the gas reservoir. Injection started 2004 [8].

Another large scale carbon capture and storage operation is the Weyburn project, in which 1.5 million ton CO_2/year is captured from a coal gasification plant in North Dakota and used for enhanced oil recovery in an oil field 330 km away, in Weyburn, Canada [8].

It should also be mentioned that well over 30 million tons of CO_2 is injected into oil wells for enhanced oil recovery each year, only in the United States. Much of this CO_2 is extracted from naturally occurring CO_2 reservoirs, but about 6.5 million ton CO_2/year is captured during upgrading of natural gas [8].

1.3.5 Cost of CO_2 capture and storage

Most evaluators agree that the principal cost for CO_2 capture and storage is associated with the capture step. Transport and storage is generally expected to be much less costly.

Among methods for CO_2 capture, absorption is generally considered to be the most mature. Absorption could be used both for pre combustion CO_2 capture and for post combustion CO_2 capture. If the desired application is a power plant, this would require that a separate absorption facility was constructed, which would increase the investment cost for the power plant considerably. Regeneration of absorbing solvents such as amines also requires considerable amounts of energy, typically in the form of heat. This internal energy demand would reduce the efficiency of the power plant, which means that it would become necessary to burn more fuel in order to produce the same amount of power as in a similar plant without CO_2 capture.

IPCC estimates that carbon capture and storage using commercially available technology would increase the cost of produced electricity with 37-85% in a natural gas fired power plant, and with 43-91% in a pulverized coal fired power plant. The cost to avoid one ton of CO_2 emissions is estimated to \$38-91 for natural gas, and \$30-71 for coal [8]. It should also be noted that the fraction of CO_2 captured in an absorption process will probably not exceed 90%, for practical reasons.

In order to make the CO_2 capture and storage concept more attractive, technologies that reduce the cost for the capture operation and increase the share of CO_2 that is captured would be very helpful. Oxyfuel combustion could reach near 100% CO_2 capture, but requires pure O_2 to operate, which is both capital intensive and power demanding to produce. Chemical-looping combustion, which is described in detail in section 2.4 below, could also provide near 100% CO_2 capture, and could prove to be cheaper and more efficient since there are no major limitations such as cost for production of pure O_2 or heat demand for regeneration of absorbing solvents.

1.4 The use of H_2 as carbon free energy carrier

Carbon sequestration has potential to reduce CO_2 emissions from large point sources such as power plants and industries greatly. However, for some applications this kind of technology will probably not be feasible. It is difficult to imagine CO_2 capture applications for small mobile emission sources such as cars, trucks and airplanes. This is noteworthy since the transportation sector is responsible for a substantial and increasing share of the global CO_2 emissions.

There is an interesting opportunity to address this dilemma that could prove to be positive for other sectors of the society as well. Fossil fuels can be converted into H_2, which is an energy carrier that does not contain carbon. Combustion of H_2 produces only H_2O as waste product. If fossil fuels are converted to H_2, and the resulting CO_2 is sequestrated, an energy carrier that can be utilized without greenhouse gas emissions is obtained.

H_2 is a versatile energy carrier. It can be transported and stored in many ways. It can be utilized as it is or in mixture with other gaseous fuels. It should be possible to use H_2 as fuel both in gas turbines and combustion engines. H_2 is also the ideal fuel in most types of fuel cells, which are applications that promises much higher efficiencies than conventional engines. In recent years several prototype vehicles, using H_2 in fuels cells as propellant, have been taking on the streets of European, Japanese and North American cities, see for example Alvfors et al [14] and Larkins et al [15].

The idea to use H_2 as the main energy carrier in a society is sometimes referred to as the hydrogen economy. The idea is not new. For example, the well known science fiction writer Jules Verne envisioned a world powered by H_2 in his novel *The Mysterious Island* as early as in 1874.

The concept of a hydrogen economy has some very appealing characteristics. Fuel cell vehicles would improve the air quality in cities tremendously since they produce no harmful emissions such as soot, particles, hydrocarbons or NO_X. H_2 could also be useful to improve energy security since it can be produced from a wide range of energy sources. H_2 can be produced for example by gasification of biomass, by reforming of fossil fuels, or by electrolysis of H_2O with electricity from wind, solar, hydro or nuclear power. Iceland, a highly developed nation with about 300 000 inhabitants and 180 000 vehicles, has made the move from petroleum-based fuels to H_2 its official policy, see Maack et al [16]. While an appealing vision, it shall be pointed out that a hydrogen economy could be quite expensive to implement. Existing H_2 technologies such as fuel cells for vehicles, membranes for separation and metal hydrides for storage often utilize rare and expensive materials. H_2 would also require its own distribution infrastructure. Of the many available publications about the possibilities and limitations of H_2 as energy carrier, the review by Ogden [17] is one of the more inclusive.

H_2 production from fossil fuels may appear less attractive than production from truly sustainable energy sources, but it has two advantages. Firstly, H_2 production from fossil fuels is proven technology that has been practiced for decades. Secondly, H_2 from fossil fuels will likely be less costly than H_2 from renewable energy sources, at least in short to medium term. These two factors could be important to obtain public, political and corporate acceptance for H_2 as energy carrier.

1.5 The aim of this work

The research presented in this thesis explores the possibility to produce H_2 from fossil fuel, while taking advantage of chemical-looping technologies to capture CO_2 and increase process efficiency. Both theoretical and experimental studies have been conducted. The findings could be relevant for other applications as well, for example for generation of synthesis gas or for power generation with CO_2 capture.

2

TECHNICAL BACKGROUND

2.1 Synthesis gas generation

The gaseous mixture of H_2 and CO is usually referred to as synthesis gas, or sometimes simply as syngas. It is an important product that has many uses, for example as feedstock for production of ammonia, methanol, synthetic liquid fuels and H_2.

Synthesis gas has a prominent place in the industrial history of Europe and North America. Already in the middle of the 19th century, many major cities had advanced systems for delivering so called town gas to households and industries. Typically, town gas was produced by coal gasification and consisted of H_2, CO and CH_4. It was used for purposes such as lighting, cooking and heating. During the Second World War, the German air force and parts of the German army had to rely on synthetic fuels produced with the so called Fisher-Tropsch process, which used synthesis gas produced by coal gasification.

In the 1950's, coal gasification and its related technologies were largely abandoned, outrivaled by cheap oil and advances in the field of petrochemical processing. There is a notably exception though. The Fisher-Tropsch process was used extensively in South Africa during the apartheid years, when the country was placed under international trade sanctions. Fisher-Tropsch synthesis remains the dominant source for diesel fuels in South Africa today.

As of lately, there has been a recurred interest in the classic technologies from the era of coal gasification. The obvious reasons are the recent increase in the price of crude oil and worries about diminishing oil and natural gas reserves, as well as increased concerns about energy security in many countries. It has also been suggested that H_2 or synthetic fuels produced from synthesis gas could be useful for reducing CO_2 emissions and help mitigate climate change. This would require that biomass was used as feedstock, or that CO_2 capture and storage was applied, see section 2.3 below.

Synthesis gas can be produced from all kinds of hydrocarbon fuels. Steam reforming, reaction (2), is suitable for reforming of light fuels such as natural gas. Partial oxidation, reaction (3), can be used for heavier fuels such as oil, coal and biomass. CO_2 reforming, reaction (4), can be used if synthesis gas with high CO content is wanted. Partial oxidation is slightly exothermic, while steam reforming and CO_2 reforming are highly endothermic.

$$C_nH_m + n\ H_2O \rightarrow n\ CO + (n+½m)\ H_2 \quad (2)$$

$$C_nH_m + ½n\ O_2 \rightarrow n\ CO + ½m\ H_2 \quad (3)$$

$$C_nH_m + n\ CO_2 \rightarrow 2n\ CO + ½m\ H_2 \quad (4)$$

At present, the most important method for synthesis gas generation is catalytic steam reforming of natural gas. Here reforming takes place in reactor tubes packed with a Ni-based catalyst. Typically, the temperature of reforming is 700-950ºC and the pressure is 15-40 bar. The tubes are placed inside a furnace and energy for the strongly endothermic reaction (2) is provided by direct firing.

As mentioned above partial oxidation is suitable for coal gasification. Other possible usages include catalytic partial oxidation of light fuels such as natural gas, and biomass gasification. An obvious drawback with partial oxidation compared to steam reforming is that pure O_2 is required, or else produced synthesis gas will be diluted with N_2, which is undesired in most applications. Production of pure O_2 from air is expensive and also consumes significant amounts of energy.

A third design concept is to combine endothermic steam reforming, reaction (2), and exothermic partial oxidation, reaction (3). Depending on the fuel, process design and amounts of O_2 and H_2O added, this can result in an endothermic, an exothermic or a thermo-neutral process. Reforming of natural gas in a thermo-neutral process is usually referred to as autothermal reforming, and has attracted increased attention in later years. Advantages include less need for heat transfer operations and lower investment cost compared to steam reforming.

It is also possible to use CO_2 reforming, reaction (4), in combination with or as substitute for H_2O in steam reforming or autothermal reforming. In this way, it is possible to produce synthesis gas with comparably high CO/H_2 ratio from a fuel with low C/H ratio, such as natural gas. High CO/H_2 ratio can be desirable for Fisher-Tropsch synthesis and some other petrochemical processes.

The literature dealing with synthesis gas generation is large. Comprehensive reviews include those by Rostrup-Nielsen et al [18, 19], Dybkjær [20] and Ritter et al [21], as well as the sections dedicated to the subject in technical and industrial dictionaries such as Kirk-Othmer's [22] and Ullman's [23].

2.2 Production of H_2 from synthesis gas

As mentioned above, synthesis gas can be used as feedstock for production of H_2. The first step in doing so is to convert CO and H_2O to CO_2 and H_2 via water-gas shift, reaction (5).

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (5)$$

Water-gas shift is slightly exothermic and takes place in a separate reactor vessel. Typically, a reactor temperature in the order of 350-500ºC and an iron/chrome catalyst is used. If the steam content in the synthesis gas is low, additional steam can be added to improve the conversion of CO. Shifted synthesis gas typically has a CO content of 2-4% on dry basis. The water-gas shift reaction is favoured by low temperature. If a very low CO concentration is desired, the first shift reactor is followed by a second and possibly by a third unit operating at lower temperatures and using a more reactive catalyst. In this way it is possible to reduce the CO content to a few tenths of a percentage. Water-gas shift is a classic technology that has been utilized for decades, so the literature dealing with the subject is large. Reviews can be found in the same sources as was mentioned for synthesis gas production [18, 19, 20, 22, 23].

After the water-gas shift, water is removed by cooling and condensation, and a gas mixture consisting mainly of H_2 and CO_2 is obtained. In a steam reforming process there may be substantial amounts of unreformed CH_4 present as well. In order to obtain H_2 of high purity, CO_2, CH_4 and other impurities must be removed.

At present, the most common method for H_2 purification is pressure swing adsorption (PSA). This technology utilizes two basic physical principles. Firstly, volatile compounds with low polarity such as H_2 are more or less nonadsorbable on conventional adsorbents. Secondly, the same adsorbents are capable of adsorbing more CH_4, CO_2, CO and other impurities at a high gas-phase partial pressure than at a lower. In a pressure swing adsorption process, impurities are adsorbed in a bed of solid adsorbent at elevated pressure while H_2 just passes straight through. Although packed beds are used, the pressure drop for H_2 is usually less than 1 bar. When the bed is saturated with impurities it is disconnected from the process and the pressure is decreased, whereby most of the impurities are released. The impurities are usually referred to as offgas, waste gas or purge gas and consist of CO_2, small amounts of CO, unreformed CH_4, and some H_2 that is needed for purging and regeneration of the bed. If the offgas has a substantial heating value it can be used as fuel, for example in a steam reformer furnace. Pressure swing adsorption is a batch process, but by using multiple adsorbers it is possible to provide constant flows. Pressure swing adsorption takes place at about room temperature and requires no compression or other technical work. The only energy penalty is that the offgas needs to be released at atmospheric pressure or lower. The H_2 recovery is limited to about 90% due to the need for H_2 for purging and regenerating the beds. The purity of H_2 produced is very high, most often 99.99% or higher. A useful overview of H_2 purification by pressure swing adsorption can be found in the report by Stöcker et al [24], which is available via UOP, a process design company that has long experience of pressure swing adsorption, while the book by Ruthven et al [25] and the review paper by Ritter et al [21] are comprehensive sources for detailed information.

It is also possible to separate H_2 and impurities by absorption. Here the synthesis gas is scrubbed with a solvent that interacts physically or chemically with impurities but not with H_2. Amine solvents such as MEA and MDEA are well-suited for separation of H_2 and CO_2. The resulting CO_2 rich solvent is pumped to a separate stripper column where it is regenerated and CO_2 is released. Solvent regeneration consumes considerable amounts of heat and typically takes place at low pressure and temperatures in the order of 100-140ºC. Only CO_2 is captured, so additional purification steps are needed if high purity H_2 is required. The IPCC special report on carbon dioxide capture and storage [8] provides an overview about the subject, while the paper by Veawab et al [26] is a good source for detailed information about solvent regeneration.

2.3 H_2 from natural gas with CO_2 capture

It would be relatively easy to capture CO_2 in H_2 plants that utilize absorption for H_2 purification. In such facilities, the cost and energy penalty for CO_2 capture would be small since almost pure CO_2 is obtained when the absorbing solvent is regenerated. In a steam reforming plant the capture efficiency would be limited though, since only CO_2 present in the process gas is captured and additional fuel must be burnt to provide heat for the endothermic reforming reactions.

Most modern facilities for production of high purity H_2 utilize steam reforming in combination with pressure swing adsorption. Here no CO_2 is provided in separate process streams, so additional gas separation, for example by absorption, would be needed for CO_2 capture. Process studies describing H_2 production by reforming of natural gas with CO_2 capture by amine absorption have been presented by Audus et al [27], Kaarstad et al [28], Feng et al [29], and Consonni et al [30], who also have reviewed some industrial reports about the topic. Reforming of natural gas with CO_2 capture could also be used for power generation with pre-combustion CO_2 capture. There is a wide range of process studies about this topic available. The IPCC special report on carbon dioxide capture and storage [8] provides an overview.

2.4 Chemical-looping combustion

Chemical-looping combustion is an innovative combustion technology that can be used for CO_2 capture in combustion processes. The basic idea can be traced back to the middle of the past century, and there is a patent from 1954 by Lewis and Gilliland [31], which describes a process concept similar to chemical-looping combustion. The stated purpose was production of high purity CO_2, and the process was not commercialized. Early work includes a study from 1983 by Richter and Knoche [32], who suggested a fuel oxidation reaction scheme involving two intermediate reactions with a metal oxide as oxygen carrier. Other pioneers include Ishida et al [33], who in 1987 presented a novel combustion concept they called chemical-looping combustion, which was similar to the idea put forth by Richter and Knoche a few years earlier. Occasionally the concept has been referred to as unmixed combustion, for example by Lyon et al [34].

Chemical-looping combustion requires two separate reactors, one for air and one for fuel. A solid oxygen carrier that performs the task of transporting oxygen between the reactors is also required. Direct contact between fuel and air is avoided and the combustion products are not diluted with N_2, see Figure 9.

Typically, the abbreviation MeO is used to describe the oxygen carrier in its oxidized form, while Me is used for the reduced form. This is because many potential oxygen-carrier materials are metal oxides, for example NiO, Fe_2O_3, Mn_3O_4 and CuO.

The oxygen carrier circulates between the reactors. In the fuel reactor, it is reduced by the fuel, which in turn is oxidized to CO_2 and H_2O according to reaction (6). In the air reactor, it is oxidized to its initial state with O_2 from the combustion air according to reaction (7).

$$C_nH_m + (2n+\tfrac{1}{2}m)\ \mathrm{MeO} \rightarrow n\ CO_2 + (\tfrac{1}{2}m)\ H_2O + (2n+\tfrac{1}{2}m)\ \mathrm{Me} \qquad (6)$$

$$\mathrm{Me} + \tfrac{1}{2}\ O_2 \rightarrow \mathrm{MeO} \qquad (7)$$

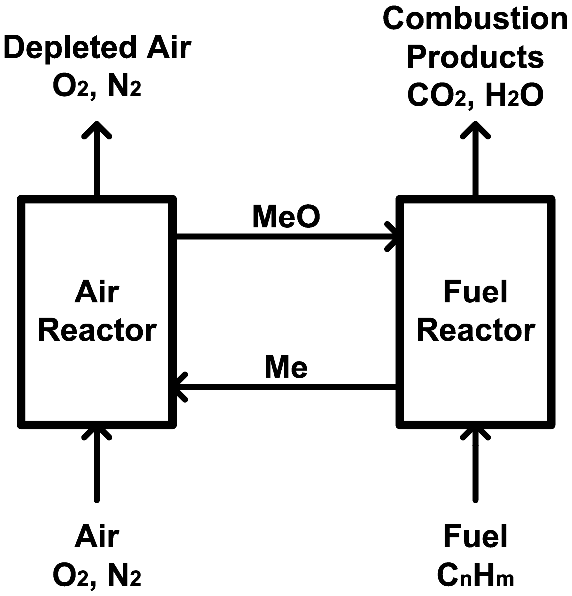

Figure 9. Schematic description of chemical-looping combustion.

The amount of energy released or required in each reactor vessel depends on the nature of the oxygen carrier and the fuel. Reaction (7) is always strongly exothermic. For most oxygen-carrier materials, reaction (6) is endothermic if the fuel is a hydrocarbon. If CO or H_2 is used as fuel or if CuO is used as oxygen carrier, reaction (6) is slightly exothermic. If reaction (6) is endothermic the flow of solid oxygen carrier can be used to transport sensible heat from the air reactor to the fuel reactor. The net energy released in the reactor system is the same as for ordinary combustion. This is apparent since combining reaction (6) and reaction (7) yields reaction (8), which is complete combustion of the fuel with O_2.

$$C_nH_m + (n+\tfrac{1}{4}m)\ O_2 \rightarrow n\ CO_2 + \tfrac{1}{2}m\ H_2O \qquad (8)$$

In principle, all kinds of fuels can be oxidized with chemical-looping combustion. A process using gaseous fuels such as natural gas, refinery gas or synthesis gas would be the easiest to realize, but there is considerable interest in chemical-looping combustion of solid fuels, such as coal, as well.

Compared to conventional combustion, chemical-looping combustion has several potential benefits. The exhaust gas from the air reactor is harmless, consisting mainly of N_2 and possibly some O_2. There should be no formation of thermal NO_X since regeneration of the oxygen carrier takes place without flame and at moderate temperatures. The gas from the fuel reactor consists of CO_2 and H_2O, so cooling in a condenser is all that is needed to obtain almost pure CO_2. This is a major advantage with chemical-looping combustion. About three quarters of the energy required for CO_2 capture and storage with conventional methods, such as amine scrubbing of flue gases, is associated with the separation of CO_2 and N_2. With chemical-looping combustion, fuel and air are not mixed, and therefore there is no energy penalty for separation of CO_2 and N_2.

Possible side reactions include formation of solid carbon in the fuel reactor. This is not desired since solid carbon could follow the oxygen-carrier particles to the air reactor and burn there, which would reduce the degree of CO_2 capture. Solid carbon could be formed either through the Boudouard reaction, reaction (9), or through hydrocarbon decomposition, reaction (10). Formation of solid carbon is well documented from various chemical processes, and it is known that reactions (9-10) can be catalysed by metallic surfaces.

$$2\,CO \rightarrow C + CO_2 \tag{9}$$

$$C_nH_m \rightarrow n\,C + \tfrac{1}{2}m\,H_2 \tag{10}$$

In practice, a chemical-looping combustion process could be designed in different ways, but circulating fluidized beds with oxygen-carrier particles used as bed material are likely to have an advantage over other alternatives since this design is straightforward, provides good contact between gas and solids and allows a smooth flow of oxygen carrier between the reactors. Circulating fluidized beds are conventional technology that is used for a wide range of purposes, for example regenerative catalytic processes and combustion of solid fuels.

In later years, when carbon sequestration has become a widely discussed issue, the interest for chemical-looping combustion has grown. The research has focused on experimental and theoretical investigations of possible oxygen-carriers and on process studies examining how chemical-looping combustion could be used for power generation. A feasible oxygen-carrier material for chemical-looping combustion should:

- Have high reactivity with fuel and oxygen.
- Be thermodynamically capable to convert a large share of the fuel to CO_2 and H_2O.
- Have a sufficiently high oxygen ratio, e.g. the mass fraction of the material that is oxygen which can react according to reaction (6) should be high.

- Have low tendency towards fragmentation, attrition, agglomeration and other kinds of mechanical or thermal degeneration.
- Not promote extensive formation of solid carbon in the fuel reactor.
- Preferably be cheap and environmentally sound.

At present, metal oxides such as NiO, Fe_2O_3, Mn_3O_4 and CuO supported on inert carrier material such as Al_2O_3 or ZrO_2 seem like the most likely candidates to meet those criteria. An overview of the research treating these kinds of oxygen-carriers can be found in the works of Cho [35], Johansson [36] and Adánez et al [37]. Information about additional potential oxygen-carrier materials can be found in the work of Jerndal et al [38], which includes a theoretical examination of 27 different oxide systems.

Continuous chemical-looping combustion of gaseous fuels in circulating fluidized beds has been demonstrated by Lyngfelt et al [39], Ryu et al [40], Johansson et al [41, 42], Abad et al [43, 44], Adánez et al [45], Linderholm et al [46], de Diego et al [47], and Kim et al [48]. Continuous chemical-looping combustion of solid fuels in circulating fluidized beds has been demonstrated by Berguerand et al [49, 50]. Reaction kinetics for various oxygen carriers have been examined by Abad et al [51, 52] and Zafar et al [53, 54]. Carbon formation on oxygen-carrier particles for chemical-looping combustion has been specifically examined by Cho et al [55]. The effects of pressure on the properties of various oxygen-carrier materials have been examined by García-Labiano et al [56]. An overview of various subjects regarding chemical-looping combustion, such as design of experimental reactors, power production with CO_2 capture and more about oxygen carriers can be found in the doctoral theses by Brandvoll [57], Johansson [58], Wolf [59], Kronberger [60] and Naqvi [61].

2.5 Chemical-looping reforming

Chemical-looping reforming, as described in this thesis, was proposed in 2001 by Mattisson and Lyngfelt [62]. The idea is older though. In fact, Conrad Arnold representing the Standard Oil Development Company was granted a patent of a process similar to chemical-looping reforming as early as in 1950 [63].

Chemical-looping reforming utilizes the same basic principles as chemical-looping combustion. The difference is that the products desired are not heat but synthesis gas, a mix of H_2 and CO. Therefore, the air to fuel ratio is kept low to prevent the fuel from becoming fully oxidized to CO_2 and H_2O. Chemical-looping reforming in its most basic form could be described as a process for partial oxidation of hydrocarbon fuels where a solid oxygen carrier is used as a source of undiluted oxygen. This is favourable since it would eliminate the need for expensive and power demanding air separation. The basic principles of chemical-looping reforming are illustrated in Figure 10.

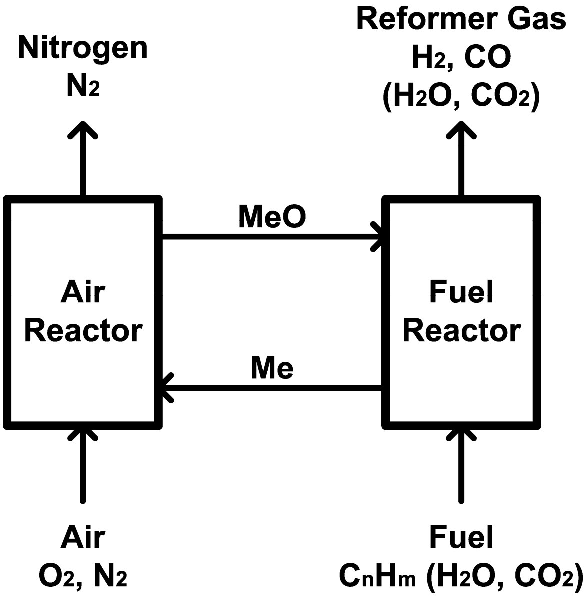

Figure 10. Schematic description of chemical-looping reforming.

In the air reactor, reaction (7) will occur, just as in chemical-looping combustion. In the fuel reactor, some fuel may become completely oxidized to CO_2 and H_2O via reaction (6), but a large share should react according to reaction (11), partial oxidation using oxygen from the oxygen carrier.

$$C_nH_m + n\ MeO \rightarrow n\ CO + \tfrac{1}{2}m\ H_2 + n\ Me \qquad (11)$$

Steam or CO_2 could be added to the fuel to enhance the relative importance of steam reforming, reaction (2), or CO_2 reforming, reaction (4), respectively. This could be useful if synthesis gas with a H_2/CO ratio that does not correspond to the H/C ratio of the fuel is desired.

The overall reaction energy of the reactor system varies as the relative importance between the different possible reactions is altered. When the fuel and oxygen carrier reacts according to reactions (6) and (7), heat corresponding to the lower heating value of the fuel is released. When the fuel reacts according to reactions (11) and (7), heat is released corresponding to the reaction energy for partial oxidation of the fuel. Reaction (2) and reaction (4) are strongly endothermic and do not provide any reduced oxygen carrier to be reoxidized with the exothermic reaction (7). Therefore steam reforming and CO_2 reforming can not be allowed to dominate the process, since this would make the sum of reactions endothermic. External heating at relevant temperatures would likely be unfavourable from a technical point of view, and should be avoided.

The outlet from the fuel reactor consists of H_2, H_2O, CO and CO_2, and could be used as feedstock for chemical processes or for production of H_2, just as synthesis gas from other reforming or partial oxidation processes. Due to reaction kinetics and thermodynamics it is possible that there will be some unreformed CH_4 in the reformer gas if the reactor temperature is not sufficiently high. If thermodynamic equilibrium is assumed, a fuel reactor temperature in the order of 800ºC should be sufficient to achieve at least 99% conversion of CH_4 at atmospheric pressure. At elevated pressure, somewhat higher temperature may be necessary due to less favourable thermodynamics.

Oxygen-carrier materials for chemical-looping reforming would need to have about the same properties as those for chemical-looping combustion. The main difference is that they must be capable to convert the fuel to CO and H_2 when the air to fuel ratio is reduced, rather than produce CO_2, H_2O and unreformed fuel. Furthermore, the oxygen carrier should be resistant towards carbon formation since decomposition of the fuel, reaction (10), could be expected to be a bigger issue for chemical-looping reforming than for chemical-looping combustion.

Oxygen carriers for chemical-looping reforming have been examined by Zafar et al [64], who performed tests in a fluidized-bed reactor with oxygen-carrier particles as fluidizing agent, by Johansson et al [65], who performed pulse experiments in a fluidized-bed reactor with oxygen-carrier particles as fluidizing agent, and by Mattisson et al [66]. These studies indicate high reaction rate and good selectivity towards H_2 and CO for oxygen carriers with NiO as active phase, while oxygen carriers based on Fe_2O_3, Mn_3O_4 and CuO suffered from poor selectivity and produced mostly CO_2, H_2O and unreformed CH_4. Continuously operating chemical-looping reforming in circulating-fluidized bed reactor systems has been demonstrated in Paper III and Paper IV.

In later years, other process concepts sharing attributes with chemical-looping reforming have also been proposed. Stobbe et al [67] have suggested a process involving oxidation and reduction of manganese oxide. Fathi et al [68], Gavalas et al [69] and Jalibert et al [70] have suggested and examined partial oxidation of CH_4 by oxidation and reduction of CeO_2

promoted with various catalysts. Shen et al [71, 72], Zeng et al [73], Li et al [74] and Bjørgum [75] have studied the possibility to generate synthesis gas by cyclic oxidation and reduction of perovskite materials such as $La_xSr_{1-x}Fe_yCo_{1-y}O_{3-\delta}$, in similar fashion as is done in chemical-looping reforming. Perovskite materials have been examined in Paper V.

3

THEORETICAL WORK

3.1 Introduction

When the work presented in this thesis was initiated, chemical-looping combustion was an untested process concept for combustion with inherent CO_2 capture. A few projects had been initiated to examine basic properties of various oxygen-carrier materials. The method of choice for such experiments was reduction and oxidation in batch reactor, typically with CH_4 as fuel. A few process studies had also been conducted, usually describing generation of electricity by using chemical-looping combustion of natural gas as heat source for various power cycles. The option to use chemical-looping technologies for production of synthesis gas and H_2 from natural gas had been suggested by Mattisson et al [62]. The general concept of chemical-looping autothermal reforming had been laid out in a master thesis by Johansson [76]. The option to use chemical-looping combustion as a heat source for steam reforming had not been considered.

Because of the limited knowledge about the subject, the initial focus of the work presented in this thesis was to explore the possibilities of the chemical-looping concept, in order to determine how it could be utilized for production of H_2. This was done in theoretical studies which can be found in Paper I and Paper II, as well as in other studies that at present has not been published in peer reviewed publications.

3.2 Developing process schemes for H_2 production

In order to examine the possibility to use chemical-looping technologies for H_2 production, a comprehensive study was made to investigate possible process concepts, in order to examine if they would be practically feasible and technically beneficial. For each identified possibility, a general assessment of the technical viability was conducted. If the result of this assessment was considered promising, a more detailed investigation of the concept and a thermal analysis were carried out.

In this line of work, thermal analysis is very helpful. It is straightforward and provides a general idea about the potential efficiency of the process concept examined. The results are quantifiable, which makes a comparison between different alternatives comparably simple.

The assumption that needs to be made is that the thermodynamic efficiency of an industrial process should be correlated to its resource consumption, economy and general attractiveness. In most cases, this assumption should be true.

Some of the basic analyses were done with the computer tool HSC Chemistry 5. In order to answer more complex questions, a few program routines describing the expected performance of relevant process operations were written in MATLAB, which is a mathematic programming tool. These programs used thermodynamic data from Barin [77] and Yaws [78]. Typically, the various process operations were assumed to proceed to thermodynamical equilibrium, unless more accurate data from real-world industries were available, see Paper I, Paper II and section 3.6 for details about assumptions used. The program routines could then be connected to simulate various process concepts. A routine for pinch analysis was used to optimize the efficiency of each setup. Pinch analysis is a common and useful method for optimization of heat-transfer operations in industrial processes.

Two main options for H_2 production with CO_2 capture were identified and examined in some detail. Chemical-looping autothermal reforming, CLR(a), utilizes chemical-looping reforming to perform a partial oxidation of a fuel. H_2O or CO_2 is added to the fuel to provide a thermo-neutral reactor system, to suppress formation of solid carbon and to enhance the yield of H_2 or CO respectively. CLR(a) is a flexible process concept that could operate at atmospheric or elevated pressure. The second concept, steam reforming integrated with chemical-looping combustion (SR/CLC), utilizes conventional tubular steam reforming at elevated pressure for synthesis gas generation, and chemical-looping combustion at atmospheric pressure for CO_2 capture and generation of heat for the endothermic reforming reactions.

It shall be pointed out that the naming of these two process concepts has undergone some evolution throughout the work. Chemical-looping autothermal reforming was initially referred to only as chemical-looping reforming (CLR). Steam reforming integrated with chemical-looping combustion is referred to as chemical-looping steam reforming, CLR(s), within the ongoing EU-project CACHET.

Chemical-looping autothermal reforming was examined in Paper I, while steam reforming integrated with chemical-looping combustion was introduced and examined in Paper II. An updated process study can be found in section 3.6 of this thesis, where different options for H_2 production with CO_2 capture are compared to each other using similar base assumptions. An updated study is motivated by improvements in the understanding of the chemical-looping autothermal process since Paper I was written, which allows the use of more relevant assumptions and process parameters. The same models have been used as in Paper I and Paper II, with some minor modifications.

The economical potential of these process concepts have not been directly addressed in this work. However, both have been selected for closer examination within the CACHET project, which is contract 019972 under the 6th framework programme funded by the European Commission. In this project they will be further investigated, and a detailed cost analysis will be conducted.

3.3 Chemical-looping autothermal reforming at atmospheric pressure

A schematic description of the suggested process layout for a chemical-looping autothermal reforming process that operates at atmospheric pressure is shown in Figure 11.

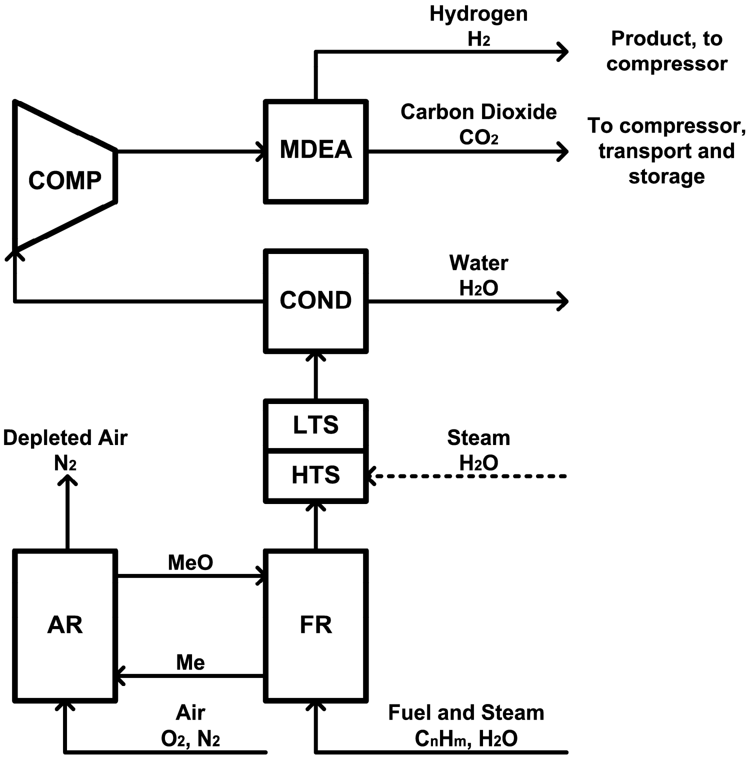

Figure 11. Schematic description of chemical-looping autothermal reforming with synthesis gas compression prior to CO_2 capture. Heat exchangers and possible integration with external steam cycle are not shown.

Prior to entering the fuel reactor (FR), the fuel is mixed with steam in order to prevent decomposition of the fuel into solid carbon. This is not necessary from a thermodynamical point of view, but will likely be needed because Ni-based oxygen carriers catalyze decomposition of the fuel according to reaction (10). The experiments presented in section 4 indicate that 25-30% steam should be sufficient.

Prior to the high-temperature shift (HTS), the gas outlet from the fuel reactor (FR) is cooled to 300-400ºC. If low outlet concentration of CO is desired, some additional steam must be added in order to improve the equilibrium for the shift reaction. Cooling is also needed between the high-temperature shift and the low-temperature shift (LTS), in order to reach the desired temperature of 200-250ºC. After the shift reactors, the gas mix consists of H_2, H_2O, CO_2 and minor amounts of CH_4 and CO. H_2O is removed by cooling in a condenser (COND), while CO_2 is captured by absorption with MDEA solvent (MDEA). CO_2 for sequestration is obtained by regenerating the MDEA solvent in a stripper column.

An atmospheric chemical-looping reforming process would be relatively easy to build and operate, and the reactors would probably not need to work with temperatures above 900ºC since conversion of the fuel is favoured by low pressure. Heat obtained by cooling of the various process streams can be used for preheating of air, fuel and steam. Integration with an external steam cycle should be considered, since there will be excess heat available in the hot gas stream after the air reactor.

The atmospheric process has one obvious drawback. H_2 of atmospheric pressure can not be stored, transported or used in any practical or economical way. So in order to be a valuable product, H_2 must always be compressed to a certain pressure. The power required for compression of a gas is approximately proportional to its volume. Reforming involves an increase in gas volumes by several times, see expressions (2-4). Because of this, any reforming process that operates at atmospheric pressure will have a large inherent efficiency penalty because of the increase in power consumption for compression of H_2 produced.

In Figure 11, a synthesis gas compressor (COMP) has been positioned prior to the amine absorption unit. The compressor pressurizes produced H_2, but also CO_2 that is present in the shifted gas. CO_2 for sequestration is then captured by amine absorption, and since regeneration of the amine solvent needs to take place at close to atmospheric pressure this means that CO_2 for sequestration will have to be compressed twice. While this procedure is power demanding, it is likely the most feasible configuration for chemical-looping autothermal reforming at atmospheric pressure with CO_2 capture. High partial pressure of CO_2 in the gas to the absorption unit means that a comparably weak absorbing solvent such as MDEA can be used, which reduces energy consumption for solvent regeneration greatly.

Other process configurations are possible. It should be feasible to capture CO_2 at atmospheric pressure using a stronger amine solvent such as MEA. This would reduce the power demand for compression since the CO_2 for sequestration only needs to be compressed once. On the other hand, a stronger amine solvent would result in a much larger heat demand for solvent regeneration. If there is excess heat of sufficient temperature available, for example from a nearby industrial process, this could be an appealing option.

Another possible drawback with an atmospheric process configured as in Figure 11 is that the water-gas shift reactors would become quite large, since the gas volumes that need to be treated increase radically as the pressure is reduced. This could be addressed by cooling the produced synthesis gas directly after the fuel reactor, remove H_2O in a condenser and compress the dry gas prior to the water-gas shift. This would increase the need for heat exchange within the process and there would also be a considerable efficiency penalty, since extra H_2O would need to be produced and added directly to the shift reactor, in order to compensate for the H_2O that was removed in the condenser.

The reformer efficiency for the process configuration proposed in Figure 11, calculated according to the definition in expression (12) below and using the parameters from section 3.6 below is 73.5%, with 93.9% CO_2 capture. In Paper I, the corresponding efficiencies were calculated to 69.6-75.9%, depending on chosen process parameters. In Paper I, slightly different process configuration and fairly optimistic assumptions for the amine absorption were used.

3.4 Chemical-looping autothermal reforming at elevated pressure

A schematic description of the suggested process layout for a chemical-looping autothermal reforming process operate at elevated pressure is shown in Figure 12.

The flow sheet presented in Figure 12 is similar to the atmospheric process proposed in Figure 11. The main difference is that the process air is compressed (AC) before entering the air reactor (AR). This makes integration with a gas turbine (GT) logical. Thus the hot pressurized N_2 from the air reactor can be used to generate power, in order to compensate for the power needed for air compression.

Steam is added to the fuel in order to suppress formation of solid carbon. As was mentioned above, 25-30 % steam should be sufficient for a process operating at atmospheric pressure. However, since reactions (9-10) involve a decrease in gas volumes they should be favored at high pressure, according to Le Chatelier's principle. Therefore, carbon formation could possibly be a larger obstacle in a pressurized process. This remains to be examined experimentally.

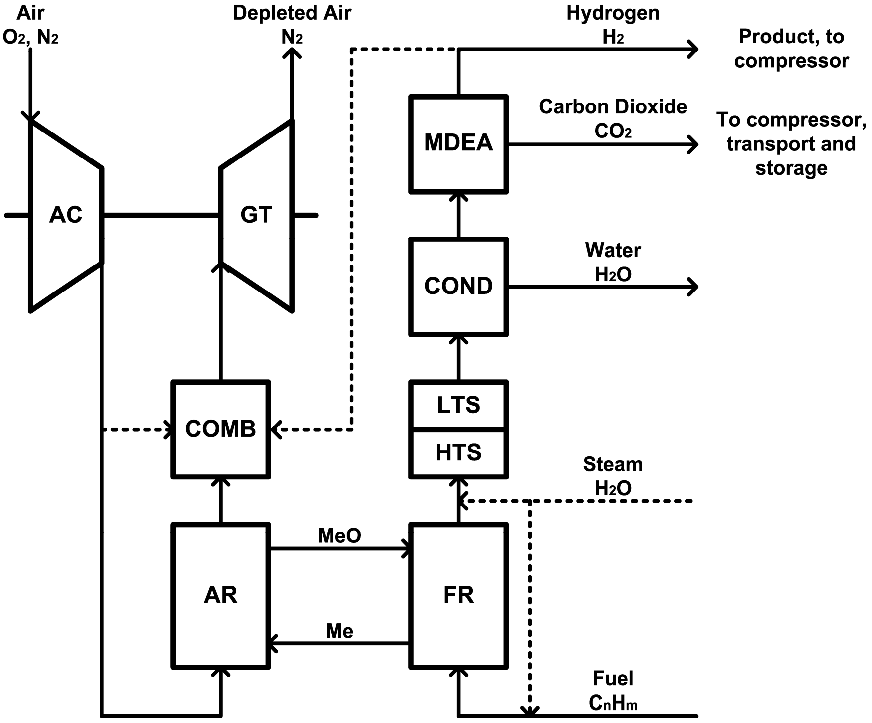

Figure 12. Schematic description of cogeneration of H_2 and power by chemical-looping autothermal reforming at elevated pressure, as proposed in Paper I. Heat exchangers and possible integration with external steam cycle are not shown.

Water-gas shift, water removal by condensation and CO_2 capture by amine absorption are the same as for to the atmospheric process. If desired, some of the H_2 produced could be burnt in a separate combustor (COMB) to increase the power output of the gas turbine.

The heat obtained by cooling of the various process streams is used for preheating of air, fuel and steam. Because of the gas turbine, there is a better match between preheating and process cooling compared to the atmospheric process. Hence no external steam cycle should be needed to obtain good heat utilization.

In order to achieve high conversion of the fuel, a pressurized process would require comparably high fuel reactor temperature. This is because reforming reactions involve a large volumetric increase, see reactions (2-4), which is not favoured by elevated pressure. Therefore a fuel reactor temperature in the order of 1000ºC would be necessary to achieve 99% conversion of CH_4 at a pressure 10 bar, if thermodynamic equilibrium is considered. High air reactor temperature is also desired in order to maximize the output of the gas turbine.

Chemical-looping autothermal reforming at elevated pressure involves a few technical obstacles, which would need to be addressed in order to make the process practically feasible.

Pressurized circulating fluidized beds are not commonly used technology, at least not for the pressures and temperatures needed for CLR(a). Therefore it is not clear if or when the necessary reactor system could be technically and economically available. Additionally, dust or elutriated particles from the oxygen carrier could possibly be harmful to the gas turbine. While hardly unsolvable, these difficulties need to be carefully considered.

The reformer efficiency for the process configuration proposed in Figure 12, calculated according to the definition in expression (12) below and using the parameters from section 3.6 below is 81.1%, with 92.6% CO_2 capture. In Paper I, the efficiencies were calculated to 79.0-81.1%, depending on chosen process parameters.

3.5 Steam reforming integrated with chemical-looping combustion

In Paper II, a process concept that utilizes tubular steam reforming at elevated pressure for synthesis gas generation and chemical-looping combustion at atmospheric pressure for CO_2 capture and heat generation, was proposed an examined. To avoid confusion, this process concept is referred to as steam reforming integrated with chemical-looping combustion, (SR/CLC), in this thesis. In upcoming work within the CACHET-project, the same process will be referred to as chemical-looping steam reforming, CLR(s).

Steam reforming integrated with chemical-looping combustion resembles steam reforming with H_2 purification by pressure swing adsorption, which at present is the dominating technology for H_2 production. In a conventional steam reforming plant, the energy needed for the highly endothermic steam reforming, reaction (2), is provided by combustion of pressure swing adsorption offgas and natural gas in a furnace. The reformer tubes are located inside the furnace and heat transfer is due to radiation. In the proposed process, the furnace is replaced by chemical-looping combustion in a circulating fluidized-bed reactor. The reformer tubes can be located either inside the fuel reactor or in a separate fluidized bed heat exchanger connected to the air reactor.

In Paper II, it was assumed that the tubes would be located inside the fuel reactor. A schematic description of the reactor system proposed in Paper II is found in Figure 13.

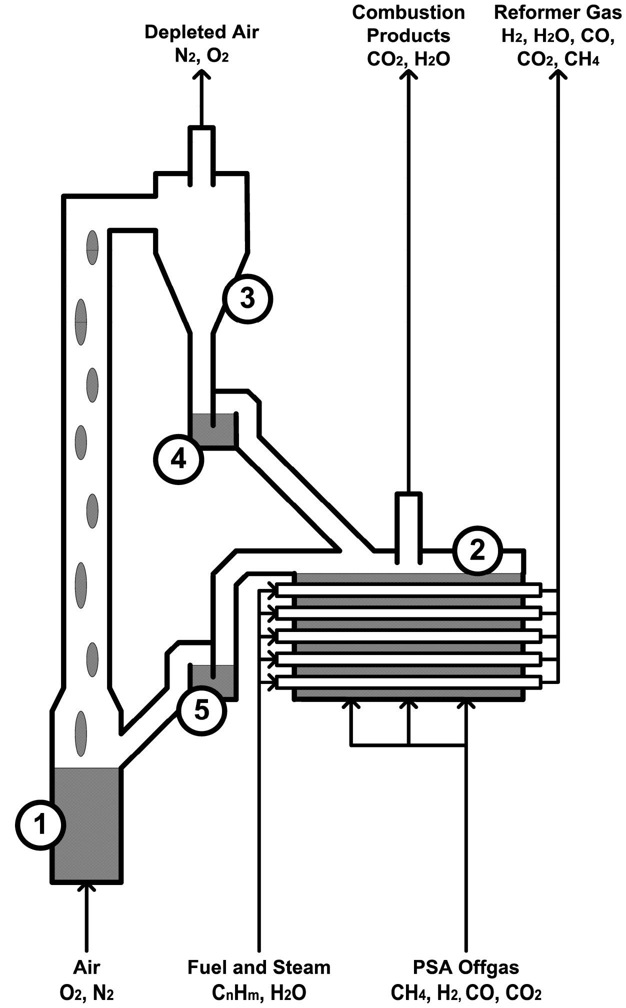

Figure 13. Reactor system for steam reforming of natural gas with CO_2 capture by chemical-looping combustion. (1) is the air reactor, (2) is the fuel reactor which also contains the reformer tubes, (3) is a cyclone for particle separation, (4) and (5) are loop seals that prevent leakage between the reactors. The loop seals are fluidized with small amounts of steam.

Steam reforming integrated with chemical-looping combustion would provide three advantages compared to conventional steam reforming. Firstly, it would provide close to 100% CO_2 capture. Secondly, it would eliminate the problem with formation of thermal NO_X in the reformer furnace, since chemical-looping combustion operates without flame and at temperatures below 1000ºC. Thirdly, it would make it possible to reduce the flue gas temperature compared to conventional steam reforming without increasing the length of the reformer tubes. This would be possible since fluidized-bed heat transfer results in very high convective heat transfer coefficient on the outside of the reformer tubes. This could be a significant advantage. In a conventional steam reforming furnace, the heat transfer from the flue gas to the reformer tube surface is mostly due to radiation. Hence very high furnace temperature is needed and most often more heat is bound in the flue gases than what can be utilized within the process for preheating of fuel and steam. Typically, this spare heat is used for production of export steam, which is a much less desirable product than H_2. Reduced flue gas temperature would mean that H_2 production could be increased at the expense of reduced steam export.

The possibility that the fluidized bed could cause erosion on the reformer tubes would need to be examined. Such tubes are large and expensive devices made from comparably exclusive materials, which must be capable of withstanding large temperature gradients and extreme thermal stress. Fluidized-bed heat exchangers are rather conventional technology though, so it seems reasonable to believe that these difficulties could be contained.

An integrated process that utilizes pressure swing adsorption for H_2 purification is the logical choice. This would provide H_2 with very high purity to a comparably low separation cost. The offgas from the pressure swing adsorption unit could be used as fuel in the chemical-looping combustor. A schematic description of the process proposed in Paper II can be found in Figure 14.

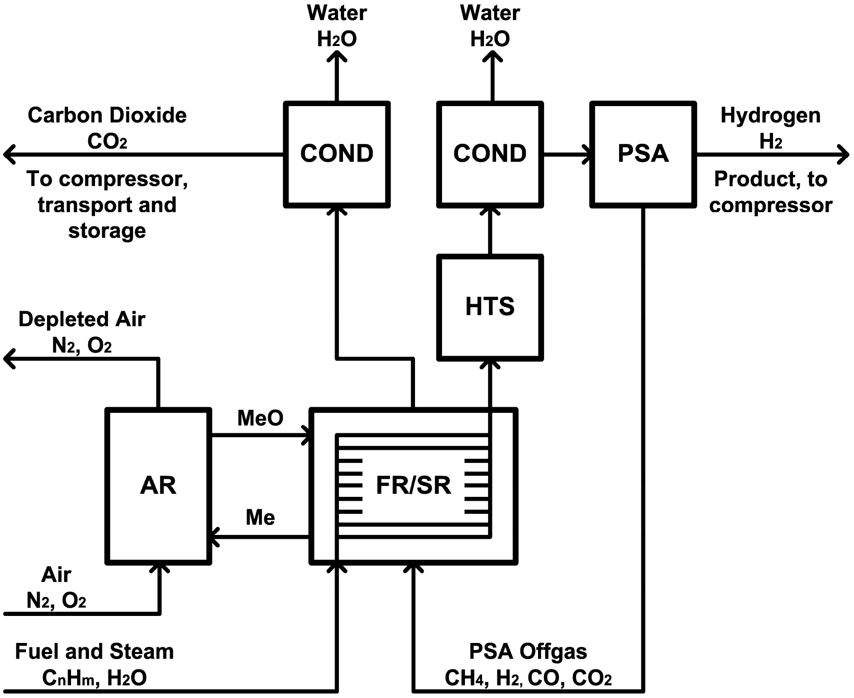

Figure 14. Schematic description of the H_2 plant proposed in Paper II. Heat exchangers, fans and compressors are not shown.

The air reactor (AR) and fuel reactor (FR) are operating at atmospheric pressure. Steam reforming (SR) takes place at elevated pressure in reformer tubes packed with catalyst. In Figure 14, the tubes are located inside the fuel reactor, but they could as well be placed in a separate fluidized-bed heat exchanger. A single water-gas shift reactor operating at moderate temperatures (HTS), is sufficient. There is no point in reducing the CO concentration to very low values, since CO can be used to produce process heat, which is needed for the endothermic steam reforming reaction. Water is removed from the shifted gas by cooling in a condenser (COND) before it enters the pressure swing adsorption unit (PSA). H_2 is delivered at elevated pressure, but a fraction of it is needed for purging and regenerating the adsorbers. The resulting pressure swing adsorption offgas consists of CO_2, H_2 used for purging and regenerating the adsorbers, unconverted CH_4 and minor amounts of CO. The offgas is delivered slightly above atmospheric pressure and is used as fuel and fluidizing gas in the chemical-looping fuel reactor. High purity CO_2 for sequestration is obtained by chemical-looping combustion.

In Paper II, a model that describes H_2 production with CO_2 capture by chemical-looping combustion and H_2 purification by pressure swing adsorption according to Figure 14 was made. The model calculated key parameters such as temperatures, gas compositions, gas flows, heating and cooling throughout the process. In addition to the thermodynamical model, a second model describing the properties of one single reformer tube surrounded by a hot fluidized bed was also made. The two models were combined and used to make a tentative design of a reactor system and a heat-exchanger network for a plant with a H_2 production of 1000 mol/s, which corresponds to a fuel flow of roughly 300 MW. It was found that the reactor dimensions, particle flows, gas flows, pressure drops and temperature levels seemed reasonable. The offgas produced would be sufficient for fluidization of the fuel reactor. Setting up a suitable heat exchanger network was found to be straightforward. The amount of oxygen-carrier particles required was quite high, 345 kg for each mol/s processed CH_4 for the base case. This should be more than enough to obtain complete conversion of the fuel with many types of oxygen carriers. If desired, the necessary amount could be reduced by decreasing the distance between the reformer tubes in the fuel reactor, or changing the geometry of the fuel reactor.

The reformer efficiency for the process configuration proposed in Figure 14, calculated according to the definition in expression (12) below and using the parameters from section 3.6 below is 80-82%, with 100% CO_2 capture. In Paper II, the corresponding efficiencies were calculated to 76.7-84.6%, excluding power for CO_2 compression which amounts to an efficiency penalty of approximately 2%-points. The efficiency was found to be strongly correlated to the outlet temperature of the reformer tubes. High temperature here improves the conversion of CH_4, so that less H_2O needs to be produced and added to the CH_4 to obtain desired product composition.

3.6 Comparative process study of H_2 production with CO_2 capture

In order to make a comparison between chemical-looping autothermal reforming and steam reforming integrated with chemical-looping combustion, an updated process study examining the different concepts has been made. The same programs and models were used here as in Paper I and Paper II, with some minor modifications.

The purpose is to show how the efficiency of different process concepts can be compared to each other, how the thermodynamical studies have been conducted, and to highlight important characteristics of each process alternative. The study is similar to the one previously presented in the licentiate thesis by Rydén [79]. The following process alternatives have been included in the study:

1. Chemical-looping autothermal reforming at atmospheric pressure integrated with a steam cycle, where synthesis gas is compressed prior to CO_2 capture by absorption with MDEA solvent, as in Figure 11.
2. Chemical-looping autothermal reforming at elevated pressure integrated with a gas turbine, with CO_2 capture by absorption with MDEA solvent, as in Figure 12.
3. Steam reforming integrated with chemical-looping combustion, as in Figure 14.

The processes have been considered as stand-alone plants optimized for H_2 production. Aside from the chemical-looping reactors, all other components are conventional technology operating at conservative process parameters. The following assumptions have been used:

- The fuel is CH_4, which is delivered to the plant at a suitable pressure and a temperature of 20°C.
- For chemical-looping autothermal reforming, the fuel is mixed with one third steam, which is assumed to prevent carbon formation in the fuel reactor.
- The desired product is H_2 at a pressure of 20 bar. If amine absorption is used for CO_2 capture the produced H_2 will also contain impurities such as CH_4, CO and

CO_2, so further purification would be needed for some applications. This has not been considered.

- The gases from the reforming step and the water-gas shift reactors are assumed to be at thermodynamic equilibrium.
- Complete conversion of the fuel to CO_2 and H_2O is assumed for the chemical-looping combustion part of the chemical-looping steam reforming process.
- No heat losses have been considered. Therefore a real-world H_2 plant would have slightly different process parameters and efficiency. Steam reforming plants generally have very high thermal efficiency, 95% or higher [18], so the difference should be small.
- Preheating of fuel, steam and air proceeds to a fixed temperature, for each examined case.
- The power demand in pumps for feed-water and amine solvent, which is very small compared to the power consumption for gas compression, has been neglected.
- Amine absorption captures 95% of the CO_2 available in the process stream. Regeneration of the amine solvent takes place in a stripper column at 130ºC and atmospheric pressure. Heat demand for the regeneration of MDEA is set to 60 kJ/mol CO_2. Reported heat demand for amine regeneration varies much between different sources. The number used has been selected after consulting the work of Veawab et al [26] and IPCC:s special report on carbon dioxide capture and storage [8].
- Pressure swing adsorption produces pure H_2 and the recovery rate is limited to 90%. The offgas is released at atmospheric pressure.
- 10% excess air is used for combustion and chemical-looping combustion.
- CO_2 for sequestration is compressed to 100 bar. Transport and storage of CO_2 has not been considered.
- Multi-stage compression with intercooling is assumed. CO_2 compression takes place in three steps while air, H_2 and synthesis gas is compressed in two steps.
- The oxygen-carrier particles consist of 50% NiO and 50% Al_2O_3. The mass flow of oxygen carrier is set to a value so that the temperature difference between the fuel reactor and air reactor becomes 50 K.

- The isentropic efficiency of fans, pumps, compressors and turbines has been set to 85%, while the mechanical efficiency has been set to 99%.
- Ambient temperature is 20ºC.
- Ambient pressure is 1 bar.
- The minimum temperature difference for heat exchange is 20 K.
- The pressure drops has been set to 1.0 bar for reformer tubes, 0.5 bar for water-gas shift, absorption and pressure swing adsorption and 0.1 bar for fluidized-bed reactors.

Process data for the base cases in the comparative study are summarized in Table 1 below. The efficiency of a reforming process can be defined in numerous ways. In this thesis, the reformer efficiency, η_{ref}, has been calculated with expression (12). η_{ref} expresses the efficiency of conversion of CH_4 into H_2, and adjusts the result for net power demand, which includes compression of H_2 to 20 bar.

$$n_{ref} = \frac{\{(n_{H2,out} / n_{CH4,in}) + E_{net} / (Hi_{H2} \times \eta_{el})\} \times Hi_{H2}}{Hi_{CH4}} \tag{12}$$

$(n_{H2,\ out}/n_{CH4,\ in})$ = Moles H_2 produced per mole CH_4 in the feedstock
E_{net} = Power surplus/demand (J/mol CH_4)
Hi_{CH4} = Lower heating value for CH_4 (802 300 J/mol)
Hi_{H2} = Lower heating value for H_2 (241 800 J/mol)
η_{el} = Reference efficiency for power generation with H_2, set to 0.58

The other abbreviations and notations used in Table 1 are explained in section 7 below.

	CLR(a) (SC)	**CLR(a) (GT)**	**SR/CLC (base)**	**SR/CLC (improved)**
$p_{reforming}$ (bar)	1.0	10.0	21.0	21.0
$T_{air\ reactor}$ (°C)	950	1050	960	990
$T_{fuel\ reactor}$ (°C)	900	1000	910	940
$T_{reformer,\ out}$ (°C)	-	-	810	840
$T_{reformer\ furnace}$ (°C)	-	-	-	-
CH_4 conversion (%)	99.9	99.0	79.0	81.3
$T_{preheating}$ (°C)	500	600	600	670
(H_2O/CH_4) in fuel mix	0.50	0.50	3.50	3.00
(O_2/CH_4) for CLR	0.60	0.60	-	-
(H_2O/CO) in HTS	2.3	2.5	-	-
T_{HTS} (°C)	310	380	400	380
T_{LTS} (°C)	200	230	-	-
H_2 recovery in PSA (%)	-	-	90.0	90.0
$p_{CO2,\ ABS}$ (bar)	5.35	2.47	-	-
$H_{REG,\ ABS}$ / $Hi_{CH4,\ in}$ (%)	-7.02	-6.93	-	-
$E_{(GT/SC)}$ / $Hi_{CH4,\ in}$ (%)	+2.95	+4.60	-	-
$E_{COMP,\ air}$ / $Hi_{CH4,\ in}$ (%)	-0.10	-2.87	-0.11	-0.11
$E_{COMP,\ syngas}$ / $Hi_{CH4,\ in}$ (%)	-7.14	-	-	-
$E_{COMP,\ H2}$ / $Hi_{CH4,\ in}$ (%)	-	-0.87	-	-
$E_{COMP,\ CO2}$ / $Hi_{CH4,\ in}$ (%)	-1.81	-1.78	-1.93	-1.93
E_{net} / $Hi_{CH4,\ in}$ (%)	-6.10	-0.93	-2.04	-2.04
$n_{H2,\ out}$ / $n_{CH4,\ in}$	2.79	2.74	2.77	2.84
$p_{H2,\ out}$ (bar)	20	20	20	20
$Hi_{H2,\ out}$ / $Hi_{CH4,\ in}$ (%)	84.1	82.7	83.4	85.5
Produced H_2 purity (%)	97.9	97.4	100	100
CO_2 capture (%)	93.9	92.6	100	100
η_{ref} (%)	73.5	81.1	79.8	82.0

Table 1. Process data for the base cases in the comparative process study.

3.6.1 Conclusions about atmospheric CLR(a)

The simplest possible chemical-looping autothermal reforming system for H_2 production would be an atmospheric process, in accordance to the process proposed in Figure 11 above.

In the case presented in Table 1 above, produced syntheses gas is compressed to slightly above 20 bar prior to the amine absorption unit. Integration with a single steam turbine operating with a maximum temperature of 600ºC, a top pressure of 100 bar and a back pressure of 4.8 bar have been considered. The back pressure is chosen so that the heat from the condensers is delivered at a temperature suitable for regeneration of the MDEA solvent. Excess heat is used for preheating of fuel, steam and air.

The reformer efficiency of the process configuration proposed in Table 1 is 73.5 %, with 93.9% CO_2 capture. This is lower than the other CLC process alternatives examined in this thesis, but compares well with conventional steam reforming with CO_2 capture, see section 3.6.4 below. It should be noted that there is a considerable external power demand, despite the steam cycle. This is due to the extensive need for gas compression.

3.6.2 Conclusions about pressurized CLR(a)

Pressurized chemical-looping reforming has potential to achieve much higher overall efficiency compared to the alternative operating at atmospheric pressure. The energy penalty for H_2 compression is reduced dramatically, as is explained in sections 3.3-3.4 above. Further, CO_2 is obtained at decently high partial pressure without the use of an extra synthesis gas compressor, so the need to compress CO_2 for sequestration twice is eliminated.

Integration with a gas turbine is important to achieve high overall process efficiency. As can be seen in the case presented in Table 1, there is a considerable efficiency penalty for air compression, but much of this is regained by expanding the depleted air in the gas turbine. There is a small external power demand. If 1-2% of produced H_2 is burned in a separate combustor as is shown in Figure 12, the process would become self sufficient with electricity.

The reformer efficiency for the base case is 81.1%, with 92.6% CO_2 capture. Increasing the reactor temperatures could improve the efficiency slightly because of better conversion of CH_4 and increased output from the gas turbine. This would require preheating to very high temperatures or integration with a steam cycle, otherwise the process would produce excess heat. Further improvements could involve increased pressure or use of an absorbing solvent that require less energy for regeneration.

3.6.3 Conclusions about SR/CLC

Steam reforming integrated with chemical-looping combustion, as described in Figure 14 above, would provide some obvious advantages. CO_2 is captured by chemical-looping combustion. Integration with pressure swing adsorption for production of H_2 with very high purity would be straightforward, since the low-pressure offgas can be used as fuel in the chemical-looping combustor. There is no need for gas turbine, steam cycle, air compression, amine absorption or low-temperature shift reactor. The reforming reactions take place at elevated pressure so there is no large energy penalty for H_2 compression. Chemical-looping combustion would take place at atmospheric pressure, which would be comparably easy to realize and operate.

For the base case presented in Table 1, the reformer efficiency is 79.8%, with 100% CO_2 capture. The efficiency could be improved further by increasing pressure, temperature and preheating, while reducing the H_2O/CH_4 ratio. Increasing the temperature of reforming by 30ºC improves the efficiency to 82.0%, as can be seen in Table 1. This is mostly because less H_2O needs to be added in order to obtain sufficient conversion of the fuel. Steam reforming at 950 ºC and 40 bar with preheating of steam and fuel up to 670 ºC is commercially available, so even better efficiency could be possible.

3.6.4 Comparison with conventional steam reforming

The numbers in Table 1 could be compared to the expected efficiency for production of H_2 with CO_2 capture using conventional methods. Process studies describing steam reforming with CO_2 capture by amine absorption located after the water-gas shift reactors has been presented for example by Consonni et al [30] and Audus et al [27]. In both these studies an overall efficiency of about 73% with 85% CO_2 capture are reported. Consonni et al [30] also cites a few industrial studies that report efficiencies in the range of 69-73%, with 85-87% CO_2 capture. In the licentiate thesis by Rydén [79], a reformer efficiency of 73.3% with 87.6% CO_2 captured was reported for this option, while using similar assumptions as for the study presented in this thesis. It can be concluded that while all these studies use slightly different process setups and base assumptions, the results are pretty similar. The expected efficiency is in the order of 69-73%. The level of CO_2 capture is limited to ≈85% because of the extra natural gas that needs to be burnt in the reformer furnace.

If higher degree of CO_2 capture is wanted, a different process configuration is needed. One option would be to capture CO_2 by absorption in the flue gas from the reformer furnace. This would require a comparably strong amine solvent such as MEA, due to the low partial pressure of CO_2. This option has been examined in the licentiate thesis by Rydén [79]. An efficiency of 70.7% with 95% CO_2 capture was reported.

Also in Paper I, brief calculations for a reference process consisting of steam reforming with CO_2 capture were presented. However, in this study the temperature difference between the heating media and the reformer tubes had been set to a very low value, which resulted in a comparably high efficiency of 75%. While such a process could be realized by so called heat-exchange reforming, it is questionable whether this kind of technology is commercially attractive [18, 20, 80].

3.6.5 Comments on the comparative study

The comparative study presented above should not be seen as an exercise in technological stretch with the aim to obtain as high theoretical efficiencies as possible, but as a tool to examine strengths and weaknesses of novel process concepts for H_2 production with CO_2 capture. It is possible that the process parameters such as reactor temperature could have been improved slightly. Integration with several steam cycles operating at different pressure levels could have resulted in slightly better heat integration, which could reduce exergy losses.

In Table 1, it can be seen that atmospheric chemical-looping autothermal reforming has about 7.5%-points lower η_{ref}, compared to the alternatives that is operating at elevated pressure. This loss in efficiency can be almost entirely attributed to the penalty for H_2 compression and the need to compress CO_2 twice. It shall be noticed that it was assumed that the fuel was CH_4. If there would have been higher hydrocarbons present in the fuel, the energy penalty for H_2 compression would have been even larger, because of the even larger volume increase. This highlights the importance of operating reforming processes at elevated pressure.

Process alternatives involving pressure swing adsorption should be attractive if high purity H_2 is the desired product. The option to use pressure swing adsorption has not been considered for chemical-looping autothermal reforming. For this to be feasible, a reactor system operating at elevated pressure or gas compression prior to the gas separation unit would be needed. More importantly, the pressure swing adsorption offgas would contain at least 10% of the H_2 produced, and there is no obvious way to utilize it the within a chemical-looping autothermal reforming process.

In section 3.6.4, it is shown that most process studies describing H_2 production with CO_2 capture using conventional technologies ends up with efficiencies in the range of 69-73%, with a CO_2 capture rate below 90%. Steam reforming integrated with chemical-looping combustion and chemical-looping autothermal reforming at elevated pressure have potential to do better than this. Steam reforming integrated with chemical-looping combustion would also provide nearly 100% CO_2 capture.

If the H_2 produced is to be used directly for power generation in a combined cycle, high purity H_2 would not be needed and CO_2 capture by absorption would be appropriate. Process studies concerning power generation by reforming of natural gas to H_2 with pre-combustion

CO_2 capture by absorption have been presented by various authors, for example by Lozza and Chiesa [81, 82], Corradetti et al [83], Ertesvåg et al [84] and Undrum et al [85]. In these studies, the efficiency for power generation typically was found to be 45-49% with 88-90% CO_2 capture. These numbers should not be compared directly with those presented in Table 1, since close integration between reforming and power generation has not been considered. But since pressurized chemical-looping autothermal reforming and steam reforming integrated with chemical-looping combustion show considerably better potential than steam reforming with CO_2 capture by conventional means, it seems reasonable to believe that chemical-looping technologies should be interesting not only for H_2 production, but for power generation with pre-combustion CO_2 capture as well.

4

EXPERIMENTS IN CIRCULATING FLUIDIZED-BED REACTOR

4.1 Introduction

Once it was established that chemical looping could indeed be useful for H_2 production with CO_2 capture, the focus was shifted from theoretical work towards experiments. Paper III and Paper IV deals with chemical-looping reforming experiments conducted in small-scale circulating fluidized bed reactor. In Paper IV, the option to use the examined oxygen carriers for chemical-looping combustion has also been examined. Paper III and Paper IV used similar methodology, measurement methods and equipment. In both cases, desulphurized natural gas with high CH_4 content was used as fuel. In addition to the different oxygen carriers, the main differences is that the overall procedure was more refined in Paper IV compared to Paper III, and that the important lower part of the reactor system, which is where the chemical reactions and circulation of solids take place, had been improved.

4.2 Reactor system

The reactor used in Paper III had previously been used for continuously operating chemical-looping combustion experiments by various authors [41, 42, 43, 44, 58]. The reactor was designed based on results obtained with a cold-flow model, see Johansson [58] and Kronberger [60] for details. A schematic description of the reactor can be found in Figure 15.

The reactor used in Paper IV is basically an improved and slightly altered version of the reactor used in Paper III. It was designed and constructed specifically for the study conducted in Paper IV, and was based on a cold-flow model constructed and tested by at Vienna University of Technology. A schematic description can be found in Figure 16.

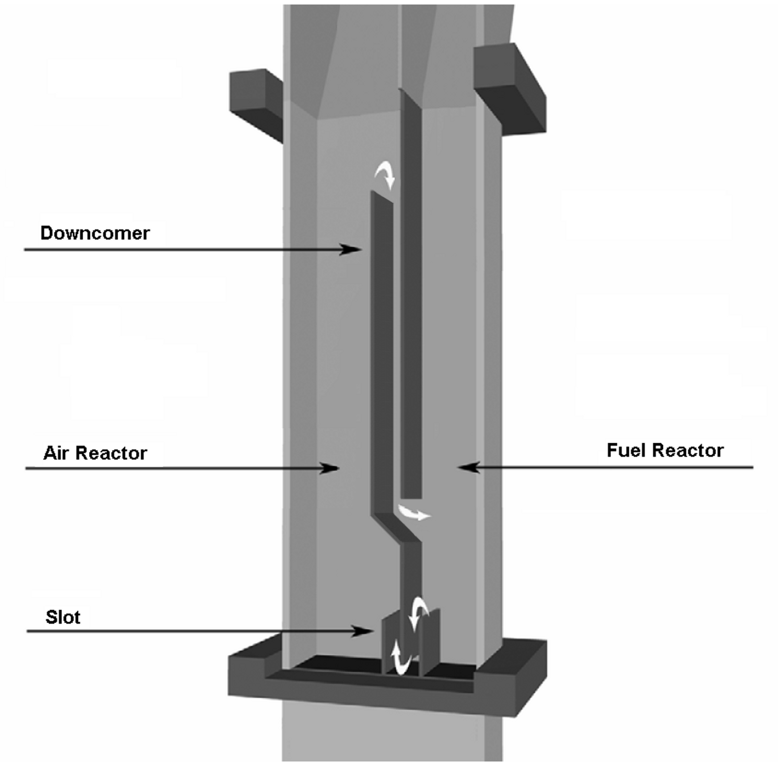

Figure 15. Schematic description of the lower reactor part used for the experiments presented in Paper III.

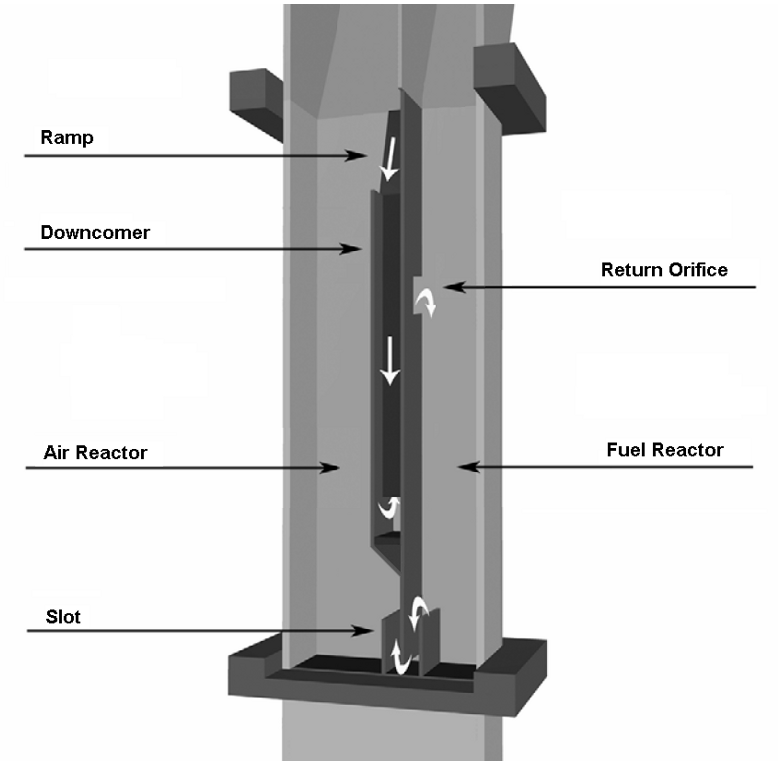

Figure 16. Schematic description of the lower reactor part used for the experiments presented in Paper IV.

Both reactors are designed for gaseous fuels. Suitable flows for chemical-looping combustion experiments are 0.15-0.75 L_n/min natural gas and 3-10 L_n/min air, which corresponds to 100-500 W thermal power. Chemical-looping reforming experiments can be performed by increasing the natural-gas flow to 0.6-1.5 L_n/min, while using a suitable air flow.

Both reactors are 200 mm high. The base of the fuel reactor measures 25×25 mm. The air reactor is 25×40 mm in the bottom and 25×25 mm in the upper narrow part. The oxygen carrier consists of particles, typically with a diameter of 90-250 µm. The necessary amount of oxygen carrier depends on factors such as density, porosity, reactivity and oxygen transfer capacity. Fuel and air enter the system through separate wind boxes, located in the bottom of each part. Porous quartz plates act as gas distributors. In the air reactor section the gas velocity is sufficiently high for oxygen-carrier particles to be thrown upwards. A fraction of these particles falls into the downcomer, which is an open shaft for the reactor used in Paper III, and a J-type loop-seal for the reactor used in Paper IV. In both cases, the downcomer is fluidized with small amounts of inert gas such as N_2 or Ar. The downcomer leads the oxygen-carrier particles to the fuel reactor section, where they are reduced by the fuel. The reduced oxygen carrier is returned to the air reactor via a slot located in the bottom of each reactor, where it is reoxidized with air. Slightly different slot sections were used in the investigations presented in Paper III and Paper IV. The slot was fluidized with small amounts of inert gas, which was added via a horizontal pipe with three 1-mm holes directed downwards.

The open downcomer used in the reactor configuration shown in Figure 15 results in some gas leakage between the air reactor and the fuel reactor. In the improved reactor, this has been addressed by including a J-type loop seal in the downcomer. There are also some other improvement, such as the possibilities to use lower bed height in the fuel reactor.

Above the lower reactor part is a separate vessel for particle separation. Here the same part was used in all investigations, see Figure 17.

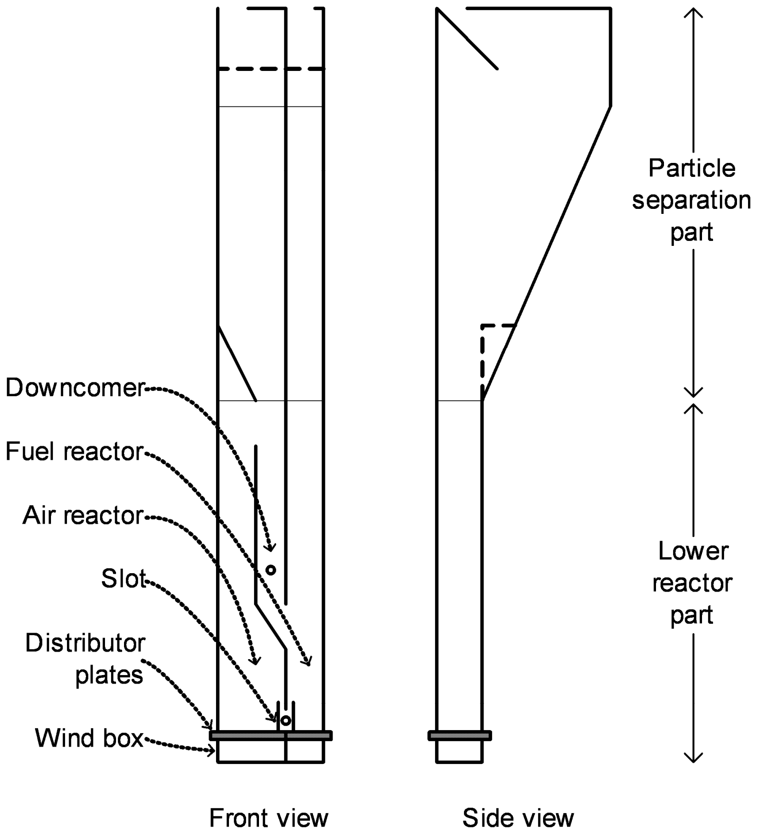

Figure 17. Schematic description of the reactor used in Paper III.

In the particle separation part, the reactor depth expands to decrease the gas velocity and allow particles to fall back into the reactor beds. It is 240 mm high, and in the first 180 mm the reactor depth expands from 25 mm to 105 mm. The last 60 mm has a constant cross-section area. The particles falling down in the sloping section above the air reactor are led to the downcomer by a leaning wall.

In order to make it possible to reach suitable temperature levels, the whole reactor is placed inside an electrically heated furnace. This means that the temperature balance of the reactor does not need to be fulfilled. The temperature of the furnace is controlled with thermocouples located inside the furnace, just outside the reactor.

Downstream from the fuel reactor exit is a water seal that makes it possible to increase the pressure in the fuel reactor by altering the height of the water column. This is done in order to prevent dilution of the fuel reactor gas with air leaking from the air reactor.

4.3 Oxygen-carrier materials

In Paper III, one oxygen carrier particle was examined. In Paper IV, three different oxygen carriers were examined. All four oxygen carriers had NiO as active phase, see Table 2.

Paper	Oxygen carrier	Chemical composition	Production method	Size (μm)	Solids inventory (g)
III	N6AM1400	60% NiO on $MgAl_2O_4$	Freeze granulation	90-212	350
IV	N2AM1400	20% NiO on $MgAl_2O_4$	Freeze granulation	90-212	250
IV	Ni18-αAl	18% NiO on α-Al_2O_3	Impregnation	90-212	180-250
IV	Ni21-γAl	21% NiO on γ-Al_2O_3	Impregnation	90-250	170

Table 2. Basic properties of examined oxygen-carrier materials.

N2AM1400 and N6AM1400 were produced by freeze granulation with $MgAl_2O_4$ as support material, and were sintered for 6 hours at 1400ºC. This resulted in spherical particles with rather high density. The particles Ni18-αAl and Ni21-γAl were prepared by CSIC in Zaragoza by dry impregnation of $Ni(NO_3)_2 \times 6H_2O$ onto Al_2O_3, calcination at 550ºC for 30 minutes and sintering at 950ºC for 60 minutes. This procedure resulted in more porous and somewhat less spherical particles than freeze granulation. Ni18-αAl and Ni21-γAl are patent pending.

Due to the higher porosity of Ni18-αAl and Ni21-γAl, a lower bed mass was used compared to N2AM1400 for some of the experiments. Otherwise the volume of oxygen carrier would have become too large. For Ni18-αAl, experiments were done using two different bed masses. The reason for the comparably large solids inventory used for N6AM1400 is the differing design of the downcomer in the reactor used in Paper III, which required a certain particle level in the fuel reactor. In all cases, the solids inventory corresponds to unfluidized bed heights between 8.4 and 12.0 cm for fresh particles.

4.4 Experimental procedure

Prior to the experiment, the overpressure in the fuel reactor was set to 10-30 Pa by adjusting the level in the water seal. The furnace was heated to a temperature slightly above the desired fuel reactor temperature, which was 800-950°C. During this period both reactor sections were fluidized with air. When sufficiently high temperature was reached, the air to the fuel reactor was replaced by N_2, and after a minute or two, by fuel. Steady-state conditions were reached after a few minutes, depending on the fuel flow and the oxygen carrier. The experiments could be divided into one out of four subcategories:

- ***CLC - Chemical-looping combustion***
  The aim of a CLC experiment was to convert as large share of the fuel as possible to CO_2 and H_2O. This was achieved by using low or modest fuel flow (0.2-0.75 L_n/min) and high air flow (7-10 L_n/min).

- ***$CLR_{(ng)}$ - Chemical-looping reforming***
  The aim of a $CLR_{(ng)}$ experiments was to convert the fuel to CO and H_2. This was achieved by using high fuel flow (0.6-1.5 L_n/min) and moderate to high air flow (3.8-10 L_n/min).

- ***$CLR_{(H2O)}$ - Chemical-looping reforming with steam***
  A chemical-looping reforming experiment where 25-30% steam was added to the natural gas. Adding steam is believed to hamper formation of solid carbon in the fuel reactor, and also increase the production of H_2 via reaction (2). Steam was added by bubbling natural gas through hot water with a temperature of 90-95°C. The gas mixture was then cooled in a cooling column and the resulting condensate was removed, until the desired gas composition was achieved.

- ***$CLR_{(CO2)}$ - Chemical-looping reforming with CO_2***
  A chemical-looping reforming experiment where 30% CO_2 was added to the natural gas. Adding CO_2 is believed to reduce the formation of solid carbon, and would also increase the production of CO via reaction (4). This concept has been tested to improve the general understanding of chemical-looping reforming and could be useful for example to produce synthesis gas with high CO content.

Experiments were conducted in different ways. Most often, the process parameters were held constant for 1-4 hours so that the process was operated at as stable conditions as possible. Experiments with variable process parameters have also been conducted, and while this procedure has its advantages, it makes evaluation and comparison of data less straightforward.

At the end of each experiment, the oxygen-carrier particles were reoxidized. This was done in two steps. Firstly, fuel and air were replaced with N_2. Flows in the order of 1 L_n/min were used. This resulted in a gas velocity in the air reactor that was below the terminal velocity of the oxygen carrier, so the solids circulation stopped. After a few minutes N_2 was replaced with air in both reactor sections. If there was solid carbon present in the fuel reactor, it showed up as CO_2 during the reoxidation. The reoxidation also provided some information about the degree of reduction of the particles in each reactor section, as well as the magnitude of the solids circulation.

In total, around 200 hours of continuously operating experiments with fuel have been recorded, distributed among the experiment types and oxygen carriers as is shown in Table 3.

Oxygen Carrier	**Paper**	**CLC (h)**	**$CLR_{(ng)}$ (h)**	**$CLR_{(H2O)}$ (h)**	**$CLR_{(CO2)}$ (h)**
N6AM1400	III	-	24	17	-
N2AM1400	IV	10	7	35	7
Ni18-αAl	IV	21	4	27	5
Ni21-γAl	IV	5	11	24	2

Table 3. Hours of operation with fuel for each type of experiment and oxygen carrier.

Not included in Table 3 are experiments that lasted for less than 30 minutes. These short experiments amount to perhaps 10 hours totally. Another 100 hours or so of operation have been recorded with other oxygen-carrier materials, but since these results have not yet been published they are not included in this thesis. The total time each oxygen carrier has been fluidized at hot conditions is roughly 50% greater than the total time with fuel.

4.5 Measurements

Prior to analysis, the gas from the reactor halves passed through particle filters, coolers and water traps. Therefore, all measurements were made on dry gas. CO_2, CO and CH_4 were measured using infrared analyzers, while O_2 was measured with paramagnetic sensors. The gas from the fuel reactor was also examined with a Varian Micro-Gas Chromatograph CP4900 equipped with Molsieve 5A and PoraPLOT Q columns, which primarily was used to measure H_2 and high concentrations of CO, but also measured CO_2, CH_4, N_2 and O_2. H_2O was not measured directly, but could be calculated by a species balance. Most often, the composition of the fuel reactor gas was found to be reasonably close to thermodynamic equilibrium for the water-gas shift reaction.

Along the reactor, there was a number of pressure measuring taps. By measuring pressure differences between these taps, it would have been possible to estimate the distribution of solids within the system, and to detect problems such as defluidization and agglomerations. In practice, this did not work out very well for most experiments. The pressure measuring taps located in the bottom of the fuel reactor had a tendency to fill with oxygen-carrier particles and possibly also with small amounts of solid carbon, hence proper measurements of the pressure was not possible. The pressure measurements still provided some information though, since measurements in the air reactor, downcomer and above the particle bed in the fuel reactor generally worked well.

The temperature in each reactor section was measured with thermocouples located 70 mm above the distributor plates. In most cases, this should have been close to the centre of the particle bed.

4.6 Results from chemical-looping combustion experiments

For chemical-looping combustion, the desired reaction is conversion of as much as possible of the fuel to CO_2 and H_2O. The performance can be expressed with the CO_2 yield, γ_{CO2}, which is defined in expression (13).

$$\gamma_{CO2} = x_{CO2,fr} / (x_{CH4,fr} + x_{CO2,fr} + x_{CO,fr}) \tag{13}$$

N6AM1400 was not examined specifically for chemical-looping combustion applications, since this has been done earlier by Johansson et al [41, 42, 58]. For the other three oxygen carriers, no CH_4 was detected in the outlet from the fuel reactor, so the conversion of natural gas was very close to 100%. Unfortunately, the selectivity towards CO_2 and H_2O was not equally good, and significant amounts of CO and H_2 were formed. Here it shall be pointed out that the examined oxygen-carrier materials were chosen for testing because they had shown promise for chemical-looping reforming applications in early screenings using batch-fluidized bed reactors. For chemical-looping reforming, CO and H_2 are the desired products, so perhaps this was not that surprising. An example of the composition of the fuel-reactor gas for a CLC experiment is shown in Figure 18.

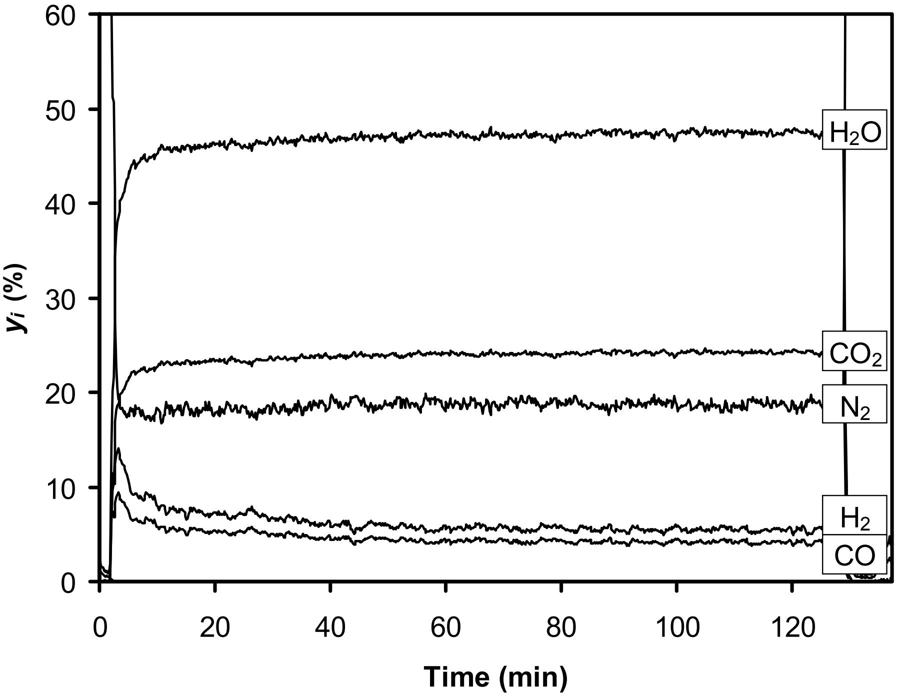

Figure 18. Wet-gas concentration for a 2-hour CLC experiment using 250 g N2AM1400 as oxygen carrier with T_{fr}*=948ºC,* γ_{CO2} *=84.8% and* F_{ng}*=0.49* L_n*/min. The* N_2 *is fluidization gas for the slot and the downcomer.*

Two factors were found to be of importance to achieve high γ_{CO2}, namely fuel reactor temperature and oxygen-carrier loading, see Figures (19-20) below. The air to fuel ratio may have had some influence on the results as well. For Ni18-αAl, four hours of experiment were made where the air flow was changed stepwise between 5 L_n/min and 9 L_n/min, while the fuel flow was held constant at 0.53 L_n/min. Here γ_{CO2} increased from about 86% to 88%. This could have been due to increased solids circulation and increased availability of oxygen in the fuel reactor, but the interpretation is uncertain.

The oxygen carrier Ni18-αAl was used for 21 hours of CLC experiments. In Figures (19-20), it can be seen that this was the oxygen carrier that provided the highest CO_2 yield, among those tested in Paper IV. It also showed some unexpected drawbacks. Firstly, there was some formation of solid carbon in the fuel reactor, which was evident because small amounts of solid carbon accumulated here. Secondly, Ni18-αAl changed reactivity during and in between different experiments. Fresh particles provided remarkably high selectivity towards CO_2. With fresh particles, γ_{CO2} was over 99% with 0.45 L_n/min fuel at 900ºC, which roughly corresponds to the thermodynamic boundary for NiO at that temperature.

However, the gas yield declined rapidly. Some kind of steady-state condition was reached after a few hours, but at a considerably lower gas yield. The particles could be partially regenerated by performing CLR$_{(H2O)}$ experiment with high H_2 and CO concentration, only to lose reactivity again after an hour or so of CLC experiments. The reason for this phenomenon is not known, but the deactivation and regeneration behaviour have been demonstrated in lab scale as well, using a batch fluidized-bed reactor. The numbers presented in Figures (19-20) are for steady-state operations, i.e. when the gas yield deviated considerably compared to the fresh particles for this particular carrier.

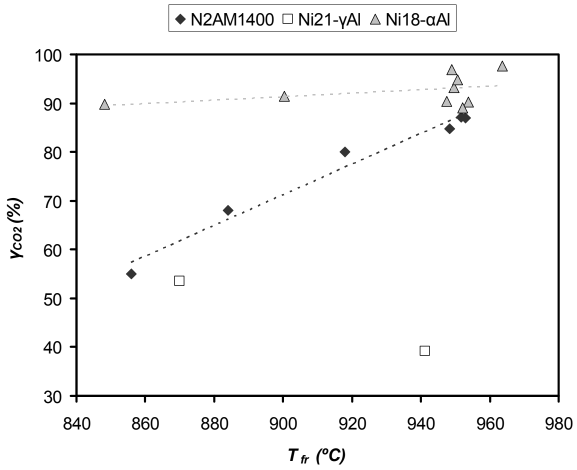

Figure 19. γ_{CO2} as function of the fuel reactor temperature. Each dot represents average values for 30-120 minutes of experiments with stable process parameters and F_{ng}≈0.5 L_n/min.

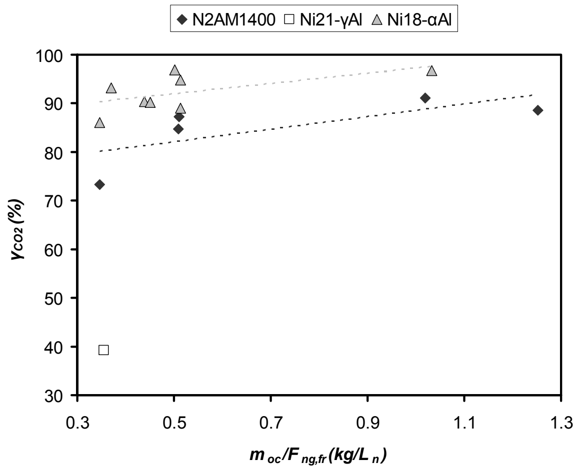

Figure 20. γ_{CO2} as function of the ratio of oxygen-carrier to fuel. Each dot represents average values for 30-120 minutes of experiments with stable process parameters and T_{fr}≈950°C.

The oxygen carrier N2AM1400 was used for 10 hours of CLC experiments. N2AM1400 provided predictable and stable results. No carbon accumulation was detected, so there was most likely no formation of solid carbon in the fuel reactor. γ_{CO2} was low compared to Ni18-αAl, and the results were also very sensitive to fuel reactor temperature, as can be seen in Figure 19.

The oxygen carrier Ni21-γAl was used for 5 hours of CLC experiments. This oxygen carrier provided very low γ_{CO2} and there was also carbon formation, approximately at the same extent as for Ni18-αAl. This oxygen carrier is clearly not suitable for chemical-looping combustion applications.

N6AM1400 has not been examined extensively for chemical-looping combustion within the work included in this thesis, but it is worth citing the work of Johansson et al [41, 42, 58], who examined chemical-looping combustion of natural gas with N6AM1400 as oxygen carrier using a similar experimental setup as the one used here. With 340 g particles, the resulting γ_{CO2} was above 98.5% for most fuel flows and reactor temperatures that were examined. No formation of solid carbon in the fuel reactor was reported. This could be because the methodology and reactor setup used in these experiments made it hard to detect carbon formation though.

4.7 Results from chemical-looping reforming experiments

For chemical-looping reforming, the desired reaction is conversion of as much as possible of the fuel to a mix of CO, H_2, CO_2 and H_2O. The performance can be expressed with the Ψ number, which describes the amount of oxygen that has been transferred to the fuel via the circulating solid particles. Ψ can be calculated via Expressions (14-17), using the measured oxygen to carbon ratio in the exit gas from the fuel-reactor, $(O/C)_{fr}$, the oxygen to carbon ratio of the fuel mix, $(O/C)_{fm}$, corrected for any added H_2O and CO_2, and the oxygen to carbon ratio for complete combustion of the fuel mix, $(O/C)_{cc}$.

In Expressions (16-17), 0.01 represents the amount of O in one unit of the natural gas that has been used as fuel, while 1.14 is the amount of C, and 4.41 is the O demand for complete combustion. For CH_4 the corresponding numbers would be 0, 1 and 4.

$$\Psi = \frac{(O/C)_{fr} - (O/C)_{fm}}{(O/C)_{cc} - (O/C)_{fm}} \tag{14}$$

$$(O/C)_{fr} = \frac{y_{CO2,fr} \times 2 + y_{H2O,fr} + y_{CO,fr}}{y_{CO2,fr} + y_{CO,fr} + y_{CH4,fr}} \tag{15}$$

$$(O/C)_{fm} = \frac{(1 - y_{H2O,fm} - y_{CO2,fm}) \times 0.01 + y_{H2O,fm} + y_{CO2,fm} \times 2}{(1 - y_{H2O,fm} - y_{CO2,fm}) \times 1.14 + y_{CO2,fm}} \tag{16}$$

$$(O/C)_{cc} = \frac{(1 - y_{H2O,fm} - y_{CO2,fm}) \times 4.41 + y_{H2O,fm} + y_{CO2,fm} \times 2}{(1 - y_{H2O,fm} - y_{CO2,fm}) \times 1.14 + y_{CO2,fm}} \tag{17}$$

A Ψ number of 1.0 means that sufficient oxygen has been added to the fuel mix via the solids circulation to oxidize the fuel completely into CO_2 and H_2O. For the natural gas used as fuel for the experiments presented in this thesis, a Ψ number of 0.26 represents partial oxidation to CO and H_2. In Paper V, a corresponding $\Psi_{(V)}$ number is calculated, see expression (22). Here a different approach was used due to different experimental setup. In Paper III, the corresponding number was called the oxygen ratio, which also included oxygen added via steam.

In order for Ψ calculated via Expressions (14-17) to be useful in evaluating the results of a chemical-looping reforming experiment, there should be very high conversion of natural gas and no or little formation of solid carbon, and the gas composition should be reasonably close to thermodynamic equilibrium. These criteria were fulfilled for most of the experiments presented in this thesis.

The desired Ψ value for a chemical-looping reforming process depends on factors such as reactor temperature, desired product composition and amounts of H_2O or CO_2 added to the fuel. For chemical-looping autothermal reforming with the aim to produce as much H_2 as possible operating at 950°C and with 30% steam added to the fuel, a Ψ in the order of 0.30-0.35 seems reasonable, see Paper I and section 3.6 above. Reducing the Ψ number further would increase H_2 production but result in a process that would require extensive preheating or external heating.

In general, the results for the chemical-looping reforming experiments were highly encouraging. The experiments presented in Paper IV ran smoothly and with some steam or CO_2 added to the fuel it was possible to operate the reactor at very low Ψ values with no carbon accumulation, and seemingly no or very little carbon formation. It was even possible to use Ψ values below the stoichiometric ratio for partial oxidation by supplying excess oxygen with H_2O or CO_2. The conversion of natural gas into reagents was very high for all four materials. For low Ψ values and temperatures, minor amounts of CH_4 were slipping through the reactor bed, but this could be expected due to thermodynamical constraints. The oxygen carrier N6AM1400, which was tested in Paper III, was not examined at as low Ψ numbers as the oxygen carriers examined in Paper IV. There are no indications that this would not have been possible, as the experiments at higher Ψ numbers worked fine. An example of the composition of the fuel-reactor gas for a typical $CLR_{(H2O)}$ experiment is shown in Figure 21.

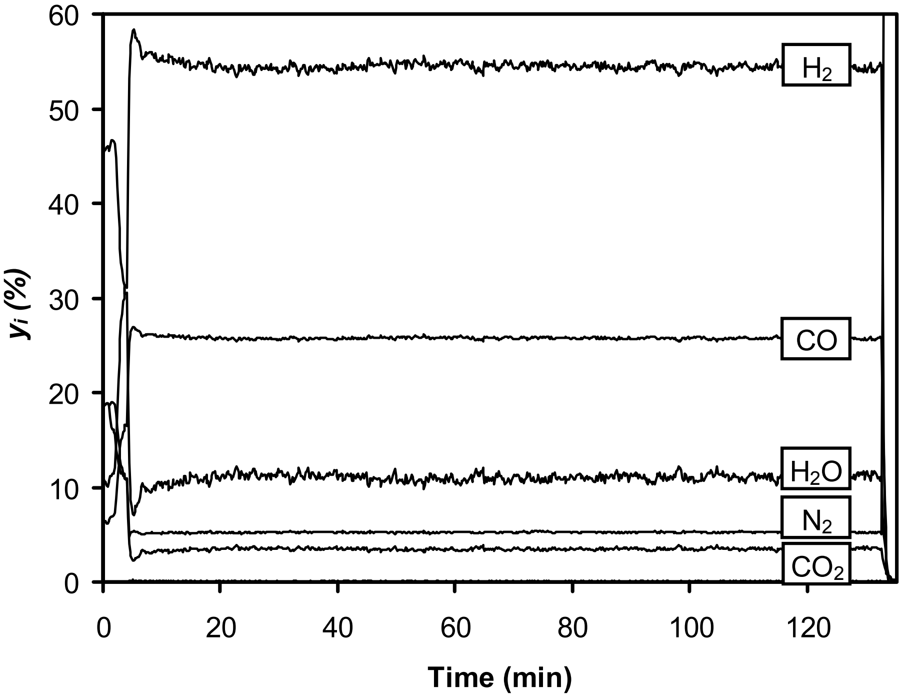

Figure 21. Wet-gas concentration for a 2-hour CLR$_{(H2O)}$ experiment using 170 g Ni21-γAl as oxygen carrier with T_{fr}=951°C, Ψ=28.8% and F_{ng}=1.36 L_n/min. The N_2 is fluidization gas for the slot and the downcomer.

The N2AM1400 particles were used for 35 hours of CLR$_{(H2O)}$, 7 hours of CLR$_{(CO2)}$ and 7 hours of CLR$_{(ng)}$ experiments. The experiments worked well and with 30% H_2O or CO_2 added to the fuel, there was no or very little carbon accumulation in the fuel reactor. There were no problems operating at Ψ values of 0.30-0.35 or even lower, which was the aim of the experiments. The CH_4 concentration was slightly above thermodynamic equilibrium at lower temperatures, but barely detectable above 900°C. The H_2 concentration often was 2-3%-points below equilibrium. One possible reason for the mismatch between calculated and measured H_2 values for N2AM1400 could be that the water-gas shift reaction did not quite reach equilibrium. It could also have been some kind of measuring difficulty, perhaps related to temperature gradients in the fuel reactor.

The Ni21-γAl particles were used for 24 hours of CLR$_{(H2O)}$, 2 hours of CLR$_{(CO2)}$ and 11 hours of CLR$_{(ng)}$ experiments. In most aspects, the results were comparable to those obtained with N2AM1400. With 30% H_2O or CO_2 added to the fuel, there was no or very little carbon accumulation in the fuel reactor. There were no problems doing experiments at Ψ values of 0.30-0.35 or lower. The CH_4 concentration was slightly above thermodynamic equilibrium at lower temperatures, but barely detectable above 900ºC. The H_2 concentration was very close to thermodynamic equilibrium

The oxygen carrier Ni18-αAl was used for 27 hours of $CLR_{(H2O)}$, 5 hours of $CLR_{(CO2)}$ and 4 hours of $CLR_{(ng)}$ experiments. It was possible to use as low Ψ values as for any of the other examined oxygen carriers, and there was no accumulation of carbon in the reactor for any of the $CLR_{(H2O)}$ experiments where the fuel reactor temperature was 870ºC or above. For some reason the leakage of carbon to the air reactor varied greatly when this oxygen carrier was used though.

N6AM1400 was used for 17 hours $CLR_{(H2O)}$ and 24 hours $CLR_{(ng)}$ experiments. These results were obtained using the reactor system with open downcomer, see Paper III. Complete conversion of natural gas was achieved and the selectivity towards H_2 and CO was good. Formation of solid carbon was identified as a potential problem and was apparent for some of the experiments with dry natural gas. For most experiments with natural gas and 25 % steam there was no accumulation of carbon in the reactors, which indicates that there was no or very little carbon formation. The composition of the gas produced was close to thermodynamic equilibrium.

4.8 Characterisation of oxygen carrier particles

Of the tested oxygen-carrier materials, N2AM1400 was the one that provided most consistent results. There were no problems with agglomerations or defluidization, and it seems to have been very stable. The used particles were examined with microscope, scanning electron microscope and x-ray diffraction. No changes in the surface or the phase composition could be detected, compared to fresh particles. The density, porosity and size distribution of the particles did not change in any measurable way.

Ni18-αAl also seems to have been stable. The used particles were intact but looked slightly less porous than the fresh, both in the scanning electron microscope and in conventional microscope. The apparent density of the particles had increased by 9%. According to the x-ray diffraction analysis, no new phases were identified in the used particles.

Ni21-γAl changed considerably during operation. The fresh particles were comparably large and porous, while the used ones were less so. The apparent density of the used particles had increased 40%. The particles remained highly reactive, so whatever happened to them did not deactivate them. It was not possible to verify any changes on the particles with x-ray diffraction analysis.

N6AM1400 also remained highly reactive, but formed lumps with a diameter of up to 20 mm in the fuel reactor. The lumps were soft and only a small force was needed to break them apart. It seems reasonable to believe that these lumps would not have survived for long in a real-word system, where considerably higher gas velocities would have been used. Aside from the lumps, this oxygen carrier maintained its physical properties with respect to fresh material.

5

BATCH EXPERIMENTS IN FIXED-BED REACTOR

5.1 Introduction

Paper V treats reduction and oxidation experiments conducted in a fixed-bed reactor. The aim of these experiments was to examine some novel options for oxygen-carrier materials, such as $La_xSr_{1-x}Fe_yCo_{1-y}O_{3-\delta}$ perovskites and mixed-metal oxides, and compare them to some more well known metal-oxide materials.

5.2 Oxygen-carrier materials

$La_xSr_{1-x}Fe_yCo_{1-y}O_{3-\delta}$ perovskites were synthesized with the glycine-nitrate combustion method and spray drying, ball-milled in ethanol, calcined and sieved to particles with a suitable size. $La_xSr_{1-x}Fe_yCo_{1-y}O_{3-\delta}$ are ceramic materials of perovskite structure which are interesting for many applications, notably as oxygen permeable membranes, for manufacturing of various high temperature electrochemical devices, and as catalyst for oxidation reactions. They have very high thermal stability and decent mechanical properties. The doctoral theses by Fossdal [86] and Lea Lein [87] are good sources for general information about this kind of materials.

The δ-factor in $La_xSr_{1-x}Fe_yCo_{1-y}O_{3-\delta}$ perovskites describes the oxygen deficiency in the material, compared to an ideal perovskite structure. The δ-factor can be reduced or increased by altering factors in the surroundings such as temperature or O_2 partial pressure. The environment in a chemical-looping air reactor is oxidative. Hence δ_{ar} will be small. In the fuel reactor, the environment is reductive, so δ_{fr} will be large. The amount of O_2 available for oxidation of fuel can be written as $(\delta_{ar} - \delta_{fr})$, see expression (18).

$$La_xSr_{1-x}Fe_yCo_{1-y}O_{3-\delta ar} \rightarrow La_xSr_{1-x}Fe_yCo_{1-y}O_{3-\delta fr} + (\delta_{ar} - \delta_{fr}) \times \tfrac{1}{2}\, O_2 \qquad (18)$$

Blom et al [88] have proposed and examined the possibility to use $La_xSr_{1-x}Fe_yCo_{1-y}O_{3-\delta}$ perovskites as oxygen carriers for chemical-looping combustion. Shen et al [71, 72], Zeng et al [73], Li et al [74] and Bjørgum [75] has studied the possibility to generate synthesis gas by cyclic oxidation and reduction of perovskites such as $La_xSr_{1-x}Fe_yCo_{1-y}O_{3-\delta}$, in similar fashion as is done in chemical-looping reforming. Data for examined perovskite materials can be found in Table 4.

Sample	**Material**	**Particle Size (µm)**	**Calcination (T/time)**
1	$La_{0.5}Sr_{0.5}Fe_{0.5}Co_{0.5}O_{3-\delta}$	150-250	900ºC/24 hours
2	$LaFeO_{3-\delta}$	150-250	900ºC/10 hours
3	$La_{0.8}Sr_{0.2}FeO_{3-\delta}$	150-250	900ºC/10 hours
4	$La_{0.5}Sr_{0.5}FeO_{3-\delta}$	150-250	900ºC/10 hours

Table 4. Produced perovskite materials

Metal-oxide particles were produced by freeze granulation, dried in a freeze-drier, sintered and sieved to a suitable size range. Data for produced metal-oxide materials can be found in Table 5.

Sample	**Material**	**Designation**	**Particle Size (µm)**	**Sintering (T/time)**
5	60% NiO on $MgAl_2O_4$	N6AM1400	90-150	1400ºC/6 hours
6	40% Fe_2O_3 on $MgAl_2O_4$	F4AM1100	90-125	1100ºC/6 hours
7	40% Mn_3O_4 on Mg-ZrO_2	M4MZ1150	90-125	1150ºC/6 hours

Table 5. Produced metal-oxide materials

In addition to the pure samples, a few oxide mixtures were also examined. These were prepared simply by mixing particles of the oxygen-carriers in Table 5 in different proportions. Combining different oxygen-carrier materials may create positive synergy effects. During operation, NiO is reduced directly to metallic Ni. Metallic surfaces catalyze decomposition of CH_4, so once some Ni is obtained the conversion of CH_4 to other components is rapid. Fe_2O_3 and Mn_3O_4 are reduced to new oxide phases rather than to metals, and are less reactive with CH_4. But Fe_2O_3 and Mn_3O_4 have the advantage of being cheaper and more environmentally benign compared to NiO, and have also proven to be highly reactive with CO and H_2. Therefore it seems reasonable to believe that if small amounts of metallic Ni could be sufficient to catalyze decomposition of CH_4 into more reactive components such as CO and H_2, the bulk of the oxygen could as well be provided with another material.

The option to use mixtures of NiO and Fe_2O_3 as oxygen-carrier for chemical-looping combustion has been demonstrated by Johansson et al [89], who found that small amounts of NiO increased the reaction rate of the Fe-based oxygen carrier considerably. Data for examined mixed-oxide samples can be found in Table 6.

Sample	Designation	Composition
8	Fe99Ni1	99% F4AM1100 and 1% N6AM1400
9	Fe90Ni10	90% F4AM1100 and 10% N6AM1400
10	Mn97Ni3	97% M4MZ1150 and 3% N6AM1400
11	Mn90Ni10	90% M4MZ1150 and 10% N6AM1400

Table 6. Examined mixed-oxide materials

5.3 Experimental setup

The experiments were carried out in a quartz reactor with a diameter of 15 mm and a height of 350 mm. The reactor was located inside a vertical electrically heated furnace. The temperature of the furnace was controlled with a thermocouple located inside the reactor. In the centre of the reactor there was a porous plate, on which a sample of particles could be located. The top of the reactor was connected to a gas feeding system, capable of handling CH_4, air, Ar, CO_2 and calibration gas. The bottom of the reactor was connected to an outlet pipe. The products were analyzed with a mass spectrometer. Between the reactor outlet and the mass spectrometer, the pipe was heated with an electric heating strip to prevent condensation of H_2O prior to analysis.

5.4 Experimental procedure

A sample of 1.00 gram of the chosen material was added to the reactor. Then the reactor was heated to 900ºC. During this time Ar was used to provide the necessary gas flow through the reactor and the mass spectrometer. When 900ºC was reached, the sample was reduced with CH_4. Ar was used as carrier gas so that the total gas flow into the reactor was 60 ml/min. This was done to provide reasonable response time for the lower CH_4 flows.

Following the reduction of the sample was an inert period of about one minute, during which Ar was fed to the reactor. Then the sample was reoxidized with 60 ml/min air. The reoxidation was aborted when the measured signals of N_2 and O_2 in the reactor outlet were stable. Then there was another short inert period, lasting about 30 seconds. This was necessary to prevent mixing of CH_4 and air prior to the reactor. After this short period of time a new reduction cycle was initiated.

The procedure described above was repeated for 10 cycles for each perovskite, in which the CH_4 flow was varied between 9 ml/min and 33 ml/min. For metal oxide samples, 5 cycles with CH_4 flows between 15 ml/min and 27 ml/min were used.

The most interesting data is the outlet concentration of CH_4, CO_2, H_2, H_2O and CO from the reactor during reduction with CH_4. The method of choice for gas analysis was mass spectroscopy. Compared to the alternatives, mass spectroscopy has the advantage of being capable to measure all relevant gas components continuously, including H_2 and H_2O.

The mass spectrometer provided the actual gas concentrations including inert Ar, which was present as carrier gas. To make it easier to compare experiments with different flows of CH_4 and Ar, the gas composition was converted to a product composition that excluded Ar, see expression (19). Here z is the calculated product composition excluding inert gas and y is the measured wet gas concentration of each component.

$$z_i = y_i / (y_{CO2} + y_{CO} + y_{CH4} + y_{H2O} + y_{H2}) \tag{19}$$

Since all relevant gas components were measured during reduction and the hydrogen to carbon ratio for CH_4, $(H/C)_{CH4}$, is known, formation of solid carbon on the particles, c, could be calculated with a species balance, see expression (20). Here c is expressed as a fictitious gas concentration.

$$(H/C)_{CH4} = 4 = \frac{z_{H2O} \times 2 + z_{H2} \times 2 + z_{CH4} \times 4}{z_{CO2} + z_{CO} + z_{CH4} + c} \tag{20}$$

The formation of solid carbon in the reactor can be expressed as a percentage of the total amount of carbon added with the CH_4, c/c_{tot}, see expression (21).

$$c/c_{tot} = c / (z_{CO2} + z_{CO} + z_{CH4} + c) \tag{21}$$

When evaluating the results of the fixed-bed experiments, parameters of importance include the conversion of CH_4, γ_{CH4}, which is defined in expression (22), the CO_2 yield, $\gamma_{CO2(V)}$, which is defined in expression (23), the degree of oxidation of the gas products, $\Psi_{(V)}$, which is defined in expression (24) and the amount of oxygen that has been removed from the sample, $\Delta\omega$, which is defined in expression (25).

$$\gamma_{CH4} = \frac{z_{CO2} + z_{CO} + c}{z_{CH4} + z_{CO2} + z_{CO} + c} \tag{22}$$

$$\gamma_{CO2(V)} = z_{CO2} / (z_{CH4} + z_{CO2} + z_{CO} + c) \tag{23}$$

$$\Psi_{(V)} = \frac{z_{CO2} \times 2 + z_{H2O} + z_{CO}}{z_{CO2} + z_{CO} + c} \times \frac{1}{4} \tag{24}$$

$$\Delta\omega = 1 - \omega = (m_{ox} - m) / m_{ox} \tag{25}$$

Compared to the γ_{CO2} in section 4, solid carbon is included in the definition of $\gamma_{CO2(V)}$. This is because in these experiments solid carbon could easily be calculated with a species balance, see expression (20). Compared to the Ψ in section 4, z_{CH4} is not included in the definition of $\Psi_{(V)}$. Hence $\Psi_{(V)}$ can be said to describe the selectivity to partial oxidation reactions, independent of the conversion of CH_4.

5.5 Results of experiments with $La_xSr_{1-x}Fe_yCo_{1-y}O_{3-\delta}$ perovskites

$La_{0.5}Sr_{0.5}Fe_{0.5}Co_{0.5}O_{3-\delta}$ was found to have properties that make it potentially well suited for chemical-looping combustion applications. There was high conversion of CH_4 into H_2O and CO_2 in the beginning of each reduction period, see Figure 22. When $\Delta\omega$ was in the order of 2%, the conversion of CH_4 decreased rapidly and the reduction produced H_2O, CO_2 and minor amounts of H_2 and CO. When $\Delta\omega$ reached about 6%, CH_4 started to decompose into H_2 and solid carbon. $La_{0.5}Sr_{0.5}Fe_{0.5}Co_{0.5}O_{3-\delta}$ responded well to increased CH_4 flow. The conversion of CH_4 remained high and $d\omega/dt$ for the chemical-looping combustion period was found to be approximately proportional to the CH_4 flow for flows up to 21 ml/min. The tenth reduction cycle was about as good as the two first. Following the experiments, the sample was examined with XRD and it was found that it had maintained its perovskite structure.

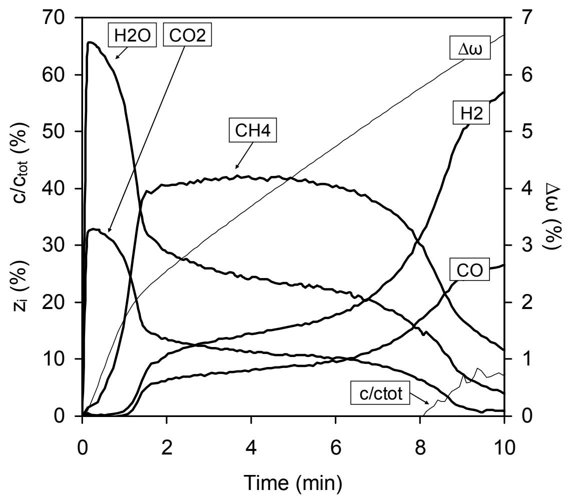

Figure 22. Reduction of $La_{0.5}Sr_{0.5}Fe_{0.5}Co_{0.5}O_{3-\delta}$ *with 9 ml/min* CH_4*, second cycle.*

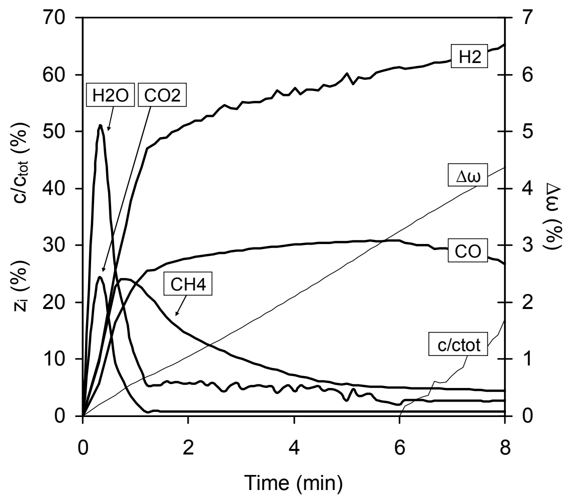

Figure 23. Reduction of $La_{0.8}Sr_{0.2}FeO_{3-\delta}$ *with 9 ml/min* CH_4*, second cycle.*

For the perovskites that did not contain Co, the reduction could also be divided into three distinct periods. First there was a combustion period, where part of the CH_4 was oxidized to H_2O and CO_2. For $LaFeO_{3-\delta}$ this period was very short, while it was more pronounced for $La_{0.8}Sr_{0.2}FeO_{3-\delta}$, and even more so for $La_{0.5}Sr_{0.5}FeO_{3-\delta}$. Following this was a period of partial oxidation where CH_4 was converted mostly into CO and H_2. The CH_4 conversion improved as more O_2 was drained from the sample. Finally, CH_4 started to decompose into H_2 and solid carbon. After the experiments the used samples were examined with XRD, and it could be concluded that all materials had maintained a perovskite structure and that there was no sign of decomposition into metals or metal oxides. An example of a reduction curve for $La_{0.8}Sr_{0.2}FeO_{3-\delta}$ can be found in Figure 23.

In Figure 24, γ_{CH4} has been plotted as a function of $\Psi_{(V)}$, and in Figure 25, $\gamma_{CO2(V)}$ has been plotted as a function of $\Delta\omega$, for the examined perovskites.

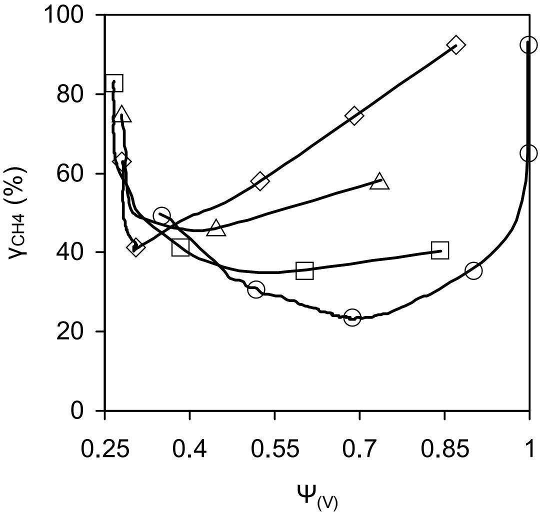

Figure 24. γ_{CH4} as a function of $\Psi_{(V)}$ for examined perovskites, for periods where no carbon was formed. The data is for the third reduction cycle and the symbols correspond to: (○) $La_{0.5}Sr_{0.5}Fe_{0.5}Co_{0.5}O_{3-\delta}$, (□) $LaFeO_{3-\delta}$, (△) $La_{0.8}Sr_{0.2}FeO_{3-\delta}$, (◇) $La_{0.5}Sr_{0.5}FeO_{3-\delta}$.

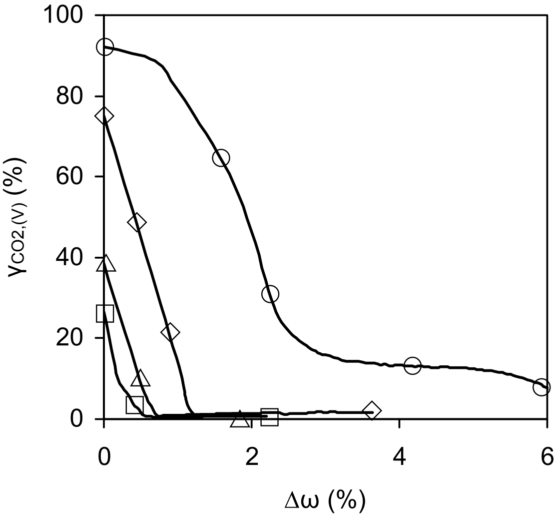

Figure 25. $\gamma_{CO2(V)}$ as a function of Δω for examined perovskites, for periods where no carbon was formed. The data is for the third reduction cycle and the symbols correspond to: (○) $La_{0.5}Sr_{0.5}Fe_{0.5}Co_{0.5}O_{3-\delta}$, (□) $LaFeO_{3-\delta}$, (△) $La_{0.8}Sr_{0.2}FeO_{3-\delta}$, (◇) $La_{0.5}Sr_{0.5}FeO_{3-\delta}$.

In Figure 24 and Figure 25 it can be seen that none of the $La_xSr_{1-x}FeO_{3-\delta}$ perovskites provide high selectivity towards CO_2 and H_2O during reduction. What makes these materials interesting is the second period of the reduction where partial oxidation of the fuel with very high selectivity towards H_2 and CO occurred. In Figure 24 it can be seen that all examined $La_xSr_{1-x}FeO_{3-\delta}$ perovskites reached $\Psi_{(V)}$ well below 0.35 with high conversion of CH_4 and with no carbon formation, so these materials could be interesting for chemical-looping reforming applications.

Of the perovskites, $La_{0.5}Sr_{0.5}Fe_{0.5}Co_{0.5}O_{3-\delta}$ and $La_{0.5}Sr_{0.5}FeO_{3-\delta}$ provided the most stable results. For these two materials, the tenth reduction cycle was similar to the first. For $LaFeO_{3-\delta}$ and to a lesser extent $La_{0.8}Sr_{0.2}FeO_{3-\delta}$, the performance declined as a function of the number of reduction cycles and the CH_4 flow. The period with good selectivity towards H_2 and CO became shorter and carbon formation occurred earlier in the reduction period. The reason for this could have been due to deactivation of the material by solid carbon. It could also have been an effect of agglomerations. The perovskite particles stuck to each other and formed a cake following reduction and oxidation. This could be observed when the particle sample was to be removed. When the reactor was turned upside-down the perovskites did not just fall out of the reactor, but some mechanical force was necessary. Typically the majority of the particles in the used sample were found in a cake of agglomerated particles. The cake was quite hard and did not break up when shaken in a glass jar, but it could easily be pierced with a spoon. The agglomeration could have resulted in reduced effective surface area of the particles, and perhaps in formation of channels through the sample bed that could reduce the amount of active oxygen-carrier material.

5.6 Results of experiments with NiO- and Fe_2O_3-based samples

The oxygen carrier N6AM1400 was found to be very reactive with CH_4, but also propagated early formation of solid carbon. This is most likely an effect of the catalytic properties of metallic Ni in combination with lack of mixing in the fixed-bed reactor. Because of the severe carbon formation, the interpretation of the experiments conducted with only N6AM1400 as oxygen carrier is uncertain. In connection with this, it should be mentioned that in a comparison of the oxygen carrier N6AM1400 with N4AN1600, it was found that the former had lesser tendency of carbon formation [65] while the latter has been used successfully in operation in 10 kW CLC combustion without any detectable leakage of carbon from fuel to air reactor [39].

Three different oxygen-carrier samples based on F4AM1100 were evaluated, pure F4AM1100 and the same material with 1% and 10% N6AM1400 respectively. Reduction of Fe_2O_3 takes place in 3 steps. Firstly, Fe_2O_3 is reduced to Fe_3O_4. This is the desired reaction for chemical-looping combustion applications. If the reduction proceeds further, FeO and finally metallic Fe are obtained. These reduction steps can not be used for chemical-looping combustion since there are thermodynamical constraints that limit the conversion of CH_4 to CO_2 and H_2O. They may be useful for chemical-looping reforming applications though.

F4AM1100 with or without added N6AM1400 was found to have properties that make it interesting both for chemical-looping combustion and chemical-looping reforming. Initially, when Fe_2O_3 was reduced to Fe_3O_4, there was high conversion of CH_4 into CO_2 and H_2O. Later during the reduction there was a period with decent selectivity towards CO and H_2, which possibly could be utilized for chemical-looping reforming. See Figure 26 for an example of a reduction curve for F4AM1100 with 1% N6AM1400, which describes a principal appearance of the other reduction curves involving F4AM1100 as well. In Figure 27, γ_{CH4} has been plotted as a function of $\Psi_{(V)}$. In Figure 28, $\gamma_{CO2(V)}$ has been plotted as a function of $\Delta\omega$.

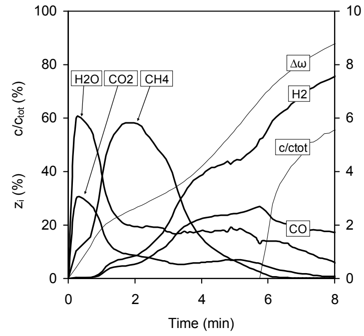

Figure 26. Reduction of 0.99 g F4AM1100 and 0.01 g N6AM1400 with 15 ml/min CH_4, first cycle.

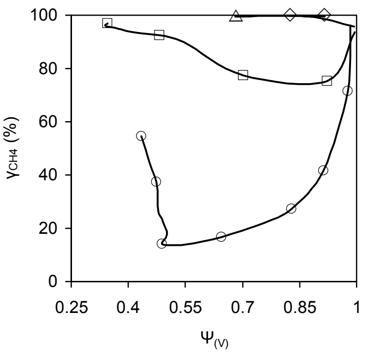

Figure 27. γ_{CH4} as a function of $\Psi_{(V)}$, for periods with no carbon formation. The data is for the third reduction cycle and the symbols correspond to: (○) Fe100, (□) Fe99Ni1, (△) Fe90Ni10, (◇) Ni100.

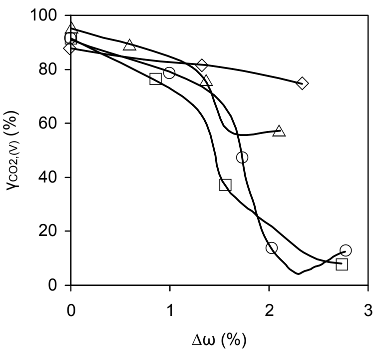

Figure 28. $\gamma_{CO2(V)}$ as a function of $\Delta\omega$, for periods with no carbon formation. The data is for the third reduction cycle and the symbols correspond to: (○) Fe100, (□) Fe99Ni1, (△) Fe90Ni10, (◇) Ni100.

In Figure 27, it can be seen that adding 1% NiO to the sample increased both reactivity and selectivity towards CO and H_2 greatly in this period. $\Psi_{(V)}$ could be 0.35 or lower, and $d\omega/dt$ was more than twice as high compared to the $La_xSr_{1-x}FeO_{3-\delta}$ perovskites.

All samples that contained F4AM1100 changed properties following the first reduction cycle. The reactivity increased and the amount of available oxygen, $\Delta\omega$, seemingly decreased. The changes could be an effect of changes in the surface and pore structure of the materials, following the first redox cycle. Unlike some of the perovskite particles the iron based samples did not form any kind of hard agglomerations.

5.7 Results of experiments with Mn_3O_4-based samples

Three different oxygen-carrier samples based on M4MZ1150 were evaluated, pure M4MZ1150 and the same material mixed with 3% and 10% N6AM1400 respectively. During operation, Mn_3O_4 is reduced to MnO. Under the conditions used, further reduction to metallic Mn should not be possible from a thermodynamic point of view. While oxidation to Mn_2O_3 in the air reactor is thermodynamically possible, this reaction is not believed to happen to any larger extent.

All experiments performed with Mn_3O_4, with or without added NiO, produced similar results. In the beginning of each reduction period, CH_4 was converted to CO_2 and H_2O. When

$\Delta\omega$ was in the order of 2.5-3.0%, which corresponds reasonably well to the amount of available oxygen in the M4MZ1150, this reaction stopped abruptly. See Figure 29 for an example of a reduction curve, which describes a principal appearance of the other reduction curves as well. In Figure 30, γ_{CH4} has been plotted as a function of $\Psi_{(V)}$. In Figure 31, $\gamma_{CO2(V)}$ has been plotted as a function of $\Delta\omega$.

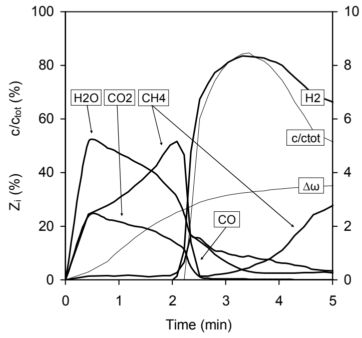

Figure 29. Reduction of 97% M4MZ1150 and 3% N6AM1400 with 15 ml/min CH_4, first cycle.

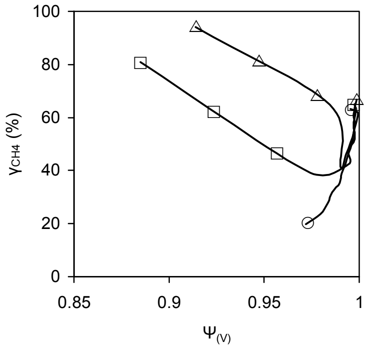

Figure 30. γ_{CH4} as a function of $\Psi_{(V)}$, for periods with no carbon formation. The data is for the third reduction cycle and the symbols correspond to: (○) Mn100, (□) Mn97Ni3, (△) Mn90Ni10.

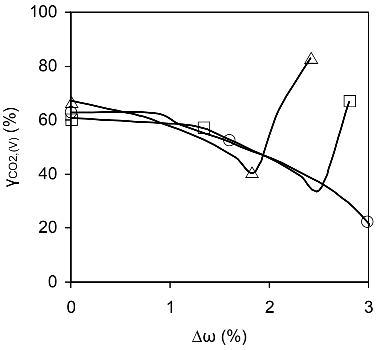

Figure 31. $\gamma_{CO2(V)}$ as a function of $\Delta\omega$, for periods with no carbon formation. The data is for the third reduction cycle and the symbols correspond to: (○) Mn100, (□) Mn97Ni3, (△) Mn90Ni10.

For these oxygen carriers, formation of CO and H_2 was always accompanied by formation of carbon. So there was no indication that M4MZ1150 could be suitable for chemical-looping reforming applications. It could not be verified that adding NiO to the sample created any positive effects. As can be seen in Figures (30-31), the reactivity is very similar for all samples for low values of $\Delta\omega$. At least as long as $\Delta\omega$ was below 2%. After this period, there was severe carbon formation for the samples with NiO present, while the sample without NiO lost reactivity so that most of the CH_4 just passed right through the reactor without any reaction. $d\omega/dt$ was in the same order of magnitude as for F4AM1100. The reactivity also increased considerably after the first reduction cycle, just as for the samples based on F4AM1100. No agglomerations were formed.

6

SUMMARY AND CONCLUSIONS

6.1 Summary

The work in this thesis deals mainly with production of hydrogen using chemical-looping technologies. At the start of the project, only limited work had been conducted in this area, and there was no experimental data from continuous operation. This thesis includes both theoretical and experimental investigations of chemical-looping technologies, and has taken the concept to a new level of development. Among the major achievements within the thesis is the presentation of a new, highly promising technology for hydrogen production, i.e. steam reforming integrated with chemical-looping combustion, in addition to providing proof-of concept of chemical-looping autothermal reforming. The main conclusions from the work will be presented below.

6.2 Conclusions from theoretical work

Two different process approaches for H_2 production with CO_2 capture utilizing chemical-looping technologies have been developed and examined. Steam reforming integrated with chemical-looping combustion means that chemical-looping combustion is used for CO_2 capture and as heat source for generation of H_2 via the endothermic steam reforming reaction. In chemical-looping autothermal reforming, a solid oxygen carrier is used as a source of oxygen undiluted with N_2, in order to perform a partial oxidation of a fuel. The focus has been on thermodynamics, potential process efficiency and practical constraints, and it can be concluded that both approaches seem to be technically feasible and have potential to provide important advantages compared to conventional technologies.

Chemical-looping autothermal reforming could be useful for production of H_2, for production of synthesis gas or for cogeneration of H_2 and power. H_2O or CO_2 can be added to the fuel in order to hamper formation of solid carbon in the fuel reactor, to obtain a thermo-neutral process or to alter the proportions between H_2 and CO in the synthesis gas produced. If CO_2 capture is desired, a separate gas separation step, such as amine absorption, is required.

For chemical-looping autothermal reforming at atmospheric pressure, integration with a steam cycle or other nearby industrial processes would be favourable. For such a process, the reformer efficiency could be in the order of 73-74%, including CO_2 capture, CO_2 compression and H_2 compression to 20 bar.

Pressurized chemical-looping autothermal reforming has better potential. Here integration with a gas turbine would be beneficial, or there would be a considerable energy penalty for air compression. The reformer efficiency could be in the order of 81%, including CO_2 capture and CO_2 compression. The main reasons why pressurized chemical-looping reforming has higher overall efficiency than the alternative operating at atmospheric pressure is that it reduces the energy penalty for compression of H_2. It would also reduce equipment size and make it convenient to use a weaker absorbing solvent for CO_2 capture. The pressurized process involves more complex technology, however. A reactor temperature over 1000ºC is needed due to less favourable thermodynamics. Further, dust and elutriated particles from the oxygen carrier could possibly be harmful for the gas turbine. It shall also be noted that pressurized circulating fluidized beds are at present not widely used technology.

Steam reforming integrated with chemical-looping combustion is a quite different process concept, which could be useful for production of H_2 with high purity. The process scheme is similar to conventional steam reforming, but with a chemical-looping combustion reactor replacing the steam reformer furnace. A fluidized-bed heat exchanger is used to provide heat for the endothermic steam reforming reactions, and chemical-looping combustion provides inherent CO_2 capture. Pressure-swing adsorption is used for H_2 purification. Chemical-looping steam reforming has some very attractive characteristics. Reactor dimensions, particle flows, gas flows, pressure drops, heat transfer operations and temperature levels all seem reasonable. Compared to conventional steam reforming, it would provide 100% CO_2 capture, make it possible to increase H_2 production at the expense of export steam and eliminate formation of thermal NO_X in the reformer furnace. The reformer efficiency could be in the order of 80-82%, including CO_2 capture and CO_2 compression. The reforming reactions take place at elevated pressure, while the chemical-looping combustion takes place at atmospheric pressure.

The expected efficiency for H_2 production with 85% CO_2 capture using conventional technology is in the order of 73% [27, 30, 79]. Pressurized chemical-looping autothermal reforming and chemical-looping steam reforming have potential to achieve considerably higher efficiency than this. Chemical-looping steam reforming also has potential to achieve nearly 100% CO_2 capture. So while the examined process concepts involve some technological challenges, they definitely deserve to be studied further.

6.3 Conclusions from experiments in circulation fluidized-bed reactor

The general conclusion from of the experiments in circulation fluidized-bed reactor is that chemical-looping reforming is practically feasible. Paper III and Paper IV include over 160 hours of continuously operating chemical-looping reforming experiments in small circulating fluidized-bed reactors using 4 different nickel-based oxygen carrier materials. N2AM1400, Ni18-αAl and Ni21-γAl were examined in Paper IV, while N6AM1400 was examined in Paper III. The reactor has been operated at atmospheric pressure and at temperatures in the range of 800-950°C. Natural gas has been used as fuel. The conversion of CH_4 into products was 96-100%, depending on temperature, oxygen carrier and experimental conditions. Typically, there was no measurable CH_4 in the outlet gas if the fuel reactor temperature was 930ºC or above. The gas composition after the fuel reactor was reasonably close to thermodynamical equilibrium. Operating the reactor at the desired process parameters of T_{FR}=950ºC and Ψ=0.30-0.35 with 30% steam added to the natural gas was possible with all of the three oxygen-carrier materials that were tested in Paper IV. N6AM1400, which was examined in Paper III, also worked fine but was not tested at as low air factors. It was possible to substitute the steam for CO_2 and still have a smooth running process with no or very small formation of solid carbon. This verifies that chemical-looping reforming is a feasible concept for production of synthesis gas and H_2. Without addition of H_2O or CO_2 to the fuel, there was formation of solid carbon on all examined oxygen carriers. This was especially true for the impregnated particles Ni21-γAl and Ni18-αAl.

About 40 hours of chemical-looping combustion have also been conducted. For chemical-looping combustion experiments, there was no or barely measurable amounts of CH_4 in the fuel reactor gas at any temperature in the examined span of 800-950ºC. Ni21-γAl provided poor selectivity towards CO_2 and is probably not suitable for chemical-looping combustion. N2AM1400 was slightly better, but the results were highly sensitive to the temperature in the fuel reactor. Ni18-αAl initially provided excellent results, but after a few hours of operation the selectivity towards CO_2 had declined significantly. Ni21-γAl and Ni18-αAl propagated carbon formation in the fuel reactor, unless some H_2O or CO_2 was added to the fuel. All three oxygen carriers that were examined in Paper IV provided low γ_{CO2} compared to N6AM1400, which have been extensively examined for chemical-looping combustion by Johansson et al [41, 42, 58]. The NiO content of N6AM1400 is much higher compared to those oxygen carriers though.

N2AM1400 and Ni18-αAl seem to have retained their physical structure well over the course of the experiments. Ni21-γAl displayed a large reduction in porosity, while

N6AM1400 formed soft lumps in the fuel reactor. Both these oxygen carriers remained highly reactive though. No changes in the chemical-structure could be verified for any of the oxygen carriers examined.

6.4 Conclusions from experiments in fixed-bed batch reactor

It was shown that reduction of $La_xSr_{1-x}FeO_{3-\delta}$ perovskites can provide high selectivity towards CO and H_2 without formation of solid carbon. It was possible to produce gas with $\Psi_{(V)}$ lower than 0.30 without carbon formation, which should be appropriate for most chemical-looping reforming applications. By contrast, $La_{0.5}Sr_{0.5}Fe_{0.5}Co_{0.5}O_{3-\delta}$ had properties that make it feasible for chemical-looping combustion applications. It can be concluded that $La_xSr_{1-x}Fe_yCo_{1-y}O_{3-\delta}$ perovskites has some interesting properties, and might be useful as oxygen-carrier materials.

When used in a fixed-bed reactor, N6AM1400 was found to propagate early formation of solid carbon, likely due to the catalytic properties of metallic Ni. The particles composed of Fe_2O_3 and $MgAl_2O_4$, F4AM1100, was found to have properties that could be useful both for chemical-looping combustion and chemical-looping reforming either in pure form or combined with a nickel-based oxygen carrier. Initially there was high conversion of CH_4 into CO_2 and H_2. This was most likely the reaction when Fe_2O_3 was reduced to Fe_3O_4. Later during the reduction there was a period with good selectivity towards CO and H_2 that could be utilized for chemical-looping reforming. Here adding 1% N6AM1400 to the sample increased both reactivity and selectivity towards CO and H_2 greatly. $\Psi_{(V)}$ could be 0.35 or lower.

The oxygen carrier based on Mn_3O_4, i.e. M4MZ1150 was found to be suitable only for chemical-looping combustion applications, alone or as a mixed oxide with NiO.

7

NOTATIONS

7.1 Abbreviations, symbols and subscripts

ABS	Absorption
AC	Air compressor
ar	Chemical-looping air reactor
AR	Chemical-looping air reactor
c	Solid carbon
c/c_{tot}	Degree of carbon formation
cc	Complete combustion
CLC	Chemical-looping combustion
CLR	Chemical-looping reforming
CLR(a)	Chemical-looping autothermal reforming
CLR(s)	Chemical-looping steam reforming, here referred to as SR/CLC
C_nH_m	Generic hydrocarbon fuel
COMB	Combustor
COMP	Compressor
COND	Condenser
CSIC	Consejo superior de investigaciones científias
CSS	Carbon capture and storage
$d\omega/dt$	Rate of mass conversion
E	Power surplus/demand
EOR	Enhanced Oil Recovery
F	Flow
fm	Fuel mix
fr	Chemical-looping fuel reactor
FR	Chemical-looping fuel reactor
GT	Gas turbine
H	Heat surplus/demand
Hi	Lower heating value

(H/C)	Hydrogen to carbon ratio
HTS	High temperature water-gas shift
IPCC	Intergovernmental panel on climate change
L_n	Normal litre
LTS	Low temperature water-gas shift
m	Mass
MDEA	Methyldiethanolamine / absorption with MDEA solvent
Me/MeO	Generic oxygen-carrier material, reduced/oxidezed
MEA	Monoethanolamine / absorption with MEA solvent
min	Minutes
m_{ox}	Mass of completely oxidized oxygen carrier
n	Number of moles
ng	Natural gas
(O/C)	Oxygen to carbon ratio
p	Pressure/partial pressure
PSA	Pressure swing adsorption
REG	Regeneration of absorbing solvent
SC	Steam cycle
SR	Steam reforming
SR/CLC	Steam reforming integrated with chemical-looping combustion
T	Temperature
syngas	Synthesis gas
WGS	Water-gas shift
x	Dry gas concentration
XRD	X-ray diffraction
y	Wet gas concentration
z	Normalized gas concentration, excluding inert carrier gas
η_{el}	Reference efficiency for power generation with H_2
η_{ref}	Reformer efficiency
γ	Yield
Ψ	Oxygen ratio / degree of oxidation of gas products
ω	Mass-based degree of reduction of an oxygen carrier

8

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