HYDROGEN AND POWER PRODUCTION WITH INTEGRATED CARBON DIOXIDE CAPTURE BY CHEMICAL-LOOPING REFORMING

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Abstract

Chemical-looping combustion is a novel combustion technology that can be used for CO_2 capture in power generating processes. Two separate reactors, one for air and one for fuel, are used. Oxygen is transferred between the two by means of an oxygen carrier. Since fuel and combustion air never mix, the combustion products, mostly CO_2 and H_2O, are not diluted with N_2. Consequently, a condenser is sufficient to obtain almost pure CO_2. In this paper, the opportunity to utilize chemical-looping for H_2 production, with CO_2 capture, is examined. The focus is on the thermodynamics and layout of a chemical-looping reformer for natural gas, but system integration for cogeneration of electricity has also been considered. It is found that the proposed reformer systems are very interesting and that their expected performances in several cases are considerably better than for the reference system - a steam reformer with CO_2 capture by amine scrubbing.

1. Introduction

It has been known for more than 100 years that CO_2 is a greenhouse gas that affects the climate of the earth. In the last few years, concerns about increasing emissions of greenhouse gases and looming global warming have been growing steadily. It is also well known that fossil fuels can be used as raw material for H_2 production. This is already in commercial practice, since H_2 is used for a wide range of purposes, such as petrochemical processing and production of ammonia and methanol. These processes, however, emit CO_2 to the atmosphere just like ordinary combustion processes. If the CO_2 is captured and prevented from reaching the atmosphere, H_2 could be used as a CO_2-free fuel for engines, power plants, fuel cells and other applications. In this paper, H_2 production with inherent CO_2 capture based on chemical-looping is examined.

1.1 Chemical-looping combustion

Chemical-looping combustion is a novel combustion technology with inherent CO_2 separation. Direct contact between fuel and combustion air is avoided. Instead, an oxygen carrier performs the task of bringing oxygen from the combustion air to the fuel. A chemical-looping system, shown in figure 1, has two separate reactors, one for air and one for fuel. The abbreviations Me and MeO are used to describe the reduced and oxidized form of the oxygen carrier.

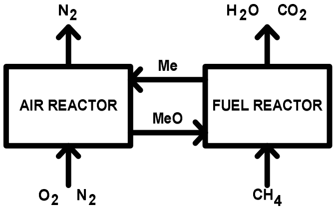

Figure 1: Conceptual chemical-looping combustion with CH_4 as fuel

Suitable oxygen carriers are small particles of metal oxides, with or without an inert binding agent. Oxides of iron, nickel, copper and manganese have been investigated [1, 2, 3]. The oxygen carrier is circulating between the reactors. In the air reactor, it is oxidized with air, according to reaction (1). In the fuel reactor, it is reduced back to its initial state by the fuel, according to reaction (2).

Air reactor: $O_2 + 2Me \leftrightarrow 2MeO$ (1)
Fuel reactor: $C_nH_{2m} + (2n+m)MeO \leftrightarrow nCO_2 + mH_2O + (2n+m)Me$ (2)

The amount of energy released or required in the air and the fuel reactors depends on the nature of the oxygen carrier and the fuel, as well as the reactor temperature. In most cases, reaction (1) is strongly exothermic. Reaction (2) is usually endothermic but can be slightly exothermic, for example if copper oxide is used as oxygen carrier. The sum of the reactions and the total amount of energy released in the reactor system is always the same as for combustion of the fuel with oxygen.

Chemical-looping combustion has several potential benefits compared to conventional combustion. The exhaust from the air reactor is harmless. It consists mainly of N_2 and, if a surplus of air is used, some O_2. In a properly configured system, there should be no formation of thermal NO_X, since regeneration of the oxygen carrier is done without flame and at temperatures well below 1300°C. The gas stream from the fuel reactor

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consists of CO_2 and water vapour, so a condenser is the only equipment needed to obtain almost pure CO_2. This is a very important advantage. 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. In chemical-looping combustion, CO_2 and N_2 are not mixed and, thus, delivered in separate streams.

If CH_4, the primary component in natural gas, is used as fuel and nickel oxide as oxygen carrier, reactions (3-5) will occur:

Air reactor: $4Ni + 2O_2 \rightarrow 4NiO$ $\Delta H_{298} = -959.6$ kJ/mole (3)
Fuel reactor: $CH_4 + 4NiO \rightarrow CO_2 + 2H_2O + 4Ni$ $\Delta H_{298} = 157.3$ kJ/mole (4)
Total reaction: $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ $\Delta H_{298} = -802.3$ kJ/mole (5)

Reaction (3) reveals that 2 moles of NiO are needed to transfer one mole of O_2. Reaction (4) is endothermic and the energy required to reach a suitable temperature of reaction should be provided from the exothermic air reactor by means of the particle circulation. For this reason, the mass flow of oxygen carrier that needs to be circulated is several times more than that required to provide oxygen to the process.

Chemical-looping combustion has recently been demonstrated in a 10 kW prototype using interconnected fluidizing beds [4]. There are several possible ways to use chemical-looping combustion for power production with CO_2 capture. If the system is pressurized, integration with a gas turbine would be favourable [5, 6, 7].

1.2 CO_2 capture and storage

The idea to separate CO_2 from flue gases and prevent it from reaching the atmosphere is receiving increasing interest. In order to be transported and stored, CO_2 needs to be compressed. A pressure in the order of 100 bar would be sufficient. This can be achieved by intercooled multi-stage compression. Electricity demand for this is reported to be in the range of 14-19 kJ/mol CO_2 [8, 9]. If CO_2 is obtained at elevated pressure the required compression work will, naturally, be lower.

Geological storage in depleted oil and gas fields or saline aquifers is the most obvious alternative for CO_2 storage. Lots of research remains to be done, but there is already some experience. At the Norwegian Sleipnir natural gas field, 1 million tonnes of CO_2 is annually separated from raw natural gas and stored in the Utsira aquifer, 800 meters below the sea bed. Similar technology is also used for enhanced oil recovery, which means that compressed CO_2 is pumped into nearly depleted oil fields to increase oil production [10]. In addition to CO_2 storage in geological reservoirs, ocean storage and mineral carbonation are being studied.

1.3 H_2 from fossil fuels

Most processes for H_2 production from fossil fuels involve three principal steps; synthesis gas generation, water-gas shift and H_2 purification, which are shown in figure 2. Synthesis gas is a mixture of H_2 and CO. It is an important product that is used not only for production of H_2, but also as raw material in chemical processes.

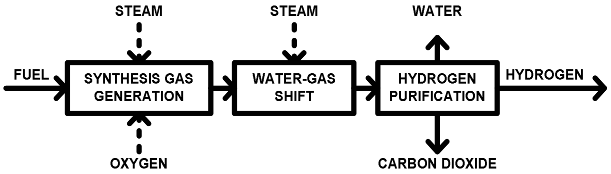

Figure 2: Schematic description of H_2 production from fossil fuels

The endothermic reaction that occurs when light hydrocarbons react with steam and form synthesis gas is called steam reforming. Reaction (6) describes steam reforming of CH_4.

$CH_4 + H_2O \leftrightarrow CO + 3H_2$ $\Delta H_{298} = 206.2$ kJ/mole (6)

In large scale facilities, reaction (6) takes place in bundles of tubes packed with catalyst, typically made up from 15-25 wt% NiO and 75-85 wt% carrier material such as aluminium oxide or magnesia. This makes desulphurization of the fuel necessary, since small amounts of sulphur are enough to poison the catalyst. The reactor temperature is usually 800-900ºC and the pressure 15-30 bars. The required heat is most often provided by direct firing outside the tubes. The efficiency of large-scale steam reforming of natural gas, defined as the ratio of the heating value of produced H_2 to the energy input as fuel and electricity is usually in the order of 65-75%, but higher efficiencies are possible [11, 12].

If synthesis gas with a large fraction of carbon monoxide is needed, steam reforming may not be the best choice. In this case, partial oxidation should be considered. Reaction (7) describes partial oxidation of CH_4

$$CH_4 + \frac{1}{2}O_2 \leftrightarrow CO + 2H_2 \qquad \Delta H_{298} = -35.7 \text{ kJ/mole} \qquad (7)$$

Unlike steam reforming, partial oxidation is used not only on light fuels, but on heavy oil and coal as well. The reactions proceed at elevated pressure, typically 20-70 bars, with or without catalysts. Temperatures as low as 600ºC are used for catalytic processes, while the noncatalytic operate at 1150-1315ºC. Partial oxidation has one obvious drawback. If air is used as oxidizing agent the produced synthesis gas will be diluted with N_2. If pure O_2 is used instead an expensive air separation unit is required. For this reason, partial oxidation is at present only competitive to steam reforming if the price of heavy fuels is much lower than for natural gas or if synthesis gas with a high concentration of CO is wanted [11, 12].

It is also possible to combine steam reforming and partial oxidation in a single reactor. This is most often referred to as autothermal reforming. A catalyst similar to those used in steam reformers is needed, which makes desulphurization of the fuel necessary. If this kind of process is properly configured, the need for external heating and cooling can be reduced or eliminated. In general, autothermal reforming processes have much in common with partial oxidation of light fuels [11, 12].

An alternative design that could prove favourable for catalytic reforming of light fuels is to utilize a fluidized-bed reactor. In this reactor type, it is possible to achieve intensive mixing of fuel and catalyst, as well as a more even temperature distribution [13, 14, 15].

For partial oxidation or autothermal reforming, the need for expensive air separation could be eliminated by using a chemical-looping system build up from interconnected fluidized-beds, as the reformer. This is described in section 2.1 below.

If high purity H_2 is wanted, water-gas shift, reaction (8), can be used to transform CO to H_2.

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H_{298} = -41.2 \text{ kJ/mole} \qquad (8)$$

For industrial purposes, reaction (8) takes place in one or two separate vessels. The first, the high-temperature shift reactor, is operating at temperatures in the region of 350-500ºC and use an iron/chrome catalyst. Steam is added to achieve a H_2O/CO ratio of 1.5-4. If a high conversion of CO is needed, the high temperature shift is followed by a second reactor operating at 180-250ºC. A low reactor temperature is desirable, since the chemical equilibrium of reaction (8) favours H_2 at low temperatures. Unfortunately, a low temperature also means a slow reaction rate, so a copper/zinc catalyst that is sensitive to poisoning is required [11, 12].

The H_2 rich process stream from the water-gas shift reactor is diluted with H_2O and CO_2. Other impurities, such as CO and unreformed fuel, are also present but at low concentrations. H_2O is usually removed first. Since it condenses at much higher temperatures than the other impurities, cooling in a condenser is sufficient. After that, there are several ways to proceed. At present, the dominating technology for production of high purity H_2 is pressure swing adsorption. Absorption, which means that the process stream is scrubbed with a CO_2 absorbing solvent, is also frequently used. The solvent is regenerated by heating in a separate desorber fed with steam, usually of 120-140ºC. The energy required for this varies among different solvents, values from 42.5 kJ/mol CO_2 to 209 kJ/mol CO_2 have been reported [12]. Impurities, such as CO, CH_4 and some CO_2, remain with the H_2, so further purification may be needed. Alternative methods for H_2 purification, such as cryogenic fractionation and membranes, are currently not regarded as competitive for industrial purposes [11, 12].

2. Description of the investigated systems

2.1 Chemical-looping reforming

The systems examined in this paper utilize a chemical-looping process as reformer. Interconnected fluidized-beds are used as fuel and air reactors. The main difference, compared to an ordinary chemical-looping combustion process, is that less air is fed to the air reactor. Complete combustion of CH_4, reaction (5), requires 2 moles of O_2 per mol CH_4. Partial oxidation of the same fuel, reaction (7), needs only a quarter of that. The proposed reformer system uses about 0.7 moles of O_2 per mole CH_4.

Particles, consisting of 25 wt% NiO and 75 wt% support material, e.g. $NiAl_2O_4$, are used as fluidizing bed material, oxygen carrier and catalyst. The inert support material is added to increase the mechanical strength and active area of the particles. The total quantity of particles in circulation is about twenty times higher than that required for the oxidation of Ni in the

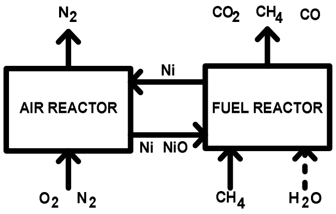

Figure 3: Conceptual chemical-looping reforming

air reactor. This is necessary to maintain the temperature in the reformer, since the overall reaction there is endothermic.

At process start up, fuel added to the fuel reactor will burn to CO_2 and H_2O just like in an ordinary chemical-looping combustion process. Soon, however, all excess NiO will become reduced to metallic Ni, and the lack of oxygen in the fuel reactor will result in partial oxidation rather than combustion. In addition, metallic nickel catalyzes synthesis gas generation.

In figure 3, adding steam to the fuel reactor is an option. This would be favourable under most circumstances. Steam reforming, reaction (6), is endothermic, so it can be used to control the overall system temperature. It also results in higher H_2 yield per mole CH_4 than partial oxidation, reaction (7). Another option to control the system temperature is cooling of the air reactor. This could be implemented by integrating a fluidized-bed heat exchanger, similar to those used for circulating fluidized-bed combustion.

The fuel is considered to be CH_4. Natural gas typically consists of 80-95% CH_4. Fluidized particle locks prevent gas leakage between the reactors. It is assumed that these locks are ideal, so no gas leakage between the reactors has been considered.

2.2 System 1 – Atmospheric chemical-looping reformer system

A process scheme for H_2 production by chemical-looping at atmospheric conditions is shown in figure 4.

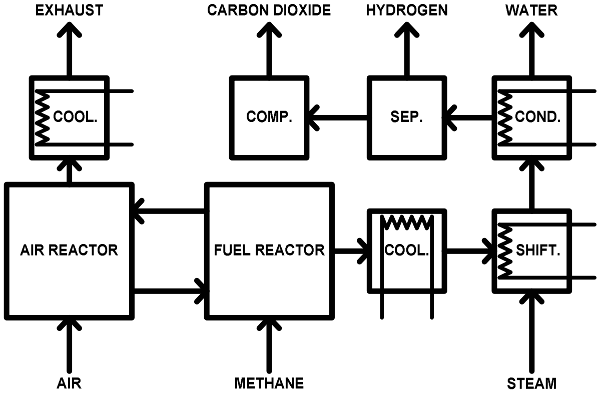

Figure 4: Simplified process scheme for system 1, case 1A. Preheating of fuel, air and steam is not shown.

The exhaust from the air reactor is harmless and consists of almost pure N_2. For the cases considered, it will have a temperature about 900ºC. The air reactor is followed by a heat exchanger that cools the exhaust.

The gas stream from the fuel reactor, which consists of a mixture of H_2, CO, H_2O, CO_2 and CH_4, is also followed by a heat exchanger. This stream has a temperature similar to that from the air reactor. In this case, however, cooling proceeds only to 250ºC. After that, the reformer stream enters a water-gas shift unit. Steam is added to obtain a H_2O/CO ratio of 3. The shift temperature is assumed to be 250ºC and the final CO concentration 0.3 mol% on dry basis. These numbers are typical for an industrial low-temperature shift reactor [11, 12, 16].

After the shift reactor, the product stream will contain mainly H_2, CO_2 and H_2O, with small amounts of CO and CH_4 also present. The water vapour is removed in a condenser, in which cooling is assumed to proceed to ambient temperature. Following the condenser is a separation unit in which CO_2 is removed from the product by absorption. The regeneration of the absorbing solvent is assumed to be made in a desorber, fed with a steam flow of 50 kJ/mol CO_2 and a temperature of 140ºC. This is based on the assumption that a tertiary amine, such as methyldiethanolamine (MDEA), can be used in the absorbing solvent [11, 12]. Finally, the captured CO_2 is compressed to 100 bar. The electricity required for this is assumed to be 15 kJ/mole CO_2. The energy cost for transport and storage of CO_2 has not been considered.

Excess energy can be used within the process for preheating air, steam and fuel or for steam generation. It is also possible to generate steam to a multi-pressure steam cycle for power production. This is done in case 1C, described later in this paper. For this case, the isentropic efficiency for pumps and steam turbines has been set to 90% and the corresponding mechanical efficiency to 99%.

H_2 with a purity of roughly 99% is obtained as product. The impurities are mostly CO and some CH_4. Complete separation of CO_2 is assumed, but a few percent left in the product stream would not alter the overall thermal performance of the system in any significant way. The H_2 is delivered at atmospheric pressure, which limits its usefulness. To make a fair comparison with the reference system, a second efficiency is included in the results that takes H_2 compression to 20 bar into account. The electricity required for this is assumed to be 13 kJ/mole H_2.

2.3 System 2 – Pressurized chemical-looping reformer system

If the whole system is pressurized, as is shown in figure 5, it is possible to integrate a gas turbine for increased power generation. This would add some other benefits as well. It would lower the cost for compression of CO_2 and the H_2 product. H_2 purification is also likely to be cheaper and easier, due to smaller gas volumes and more options available.

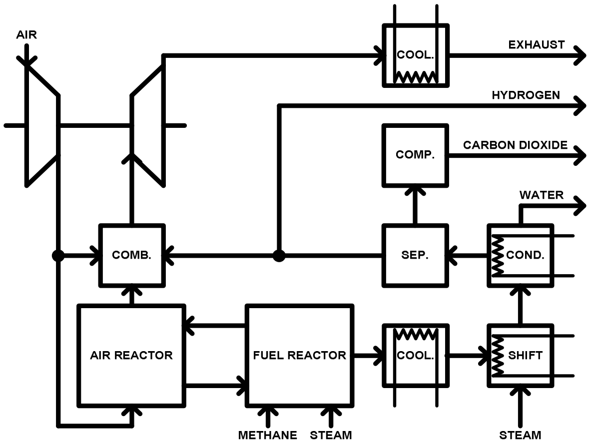

Figure 5: Simplified process scheme for system 2, case 2A. Preheating of fuel and steam is not shown.

A pressurized process would, however, also add a few disadvantages. A more robust construction will be needed. The thermodynamic equilibrium for the reformer reactions is less favourable at elevated pressure and needs to be countered with higher fuel reactor temperature. There will also be an increased need for fans and compressors. In addition, a pressurized system would need significantly more technical development before it could be commercially available.

The exhaust from the air reactor is allowed to expand in a gas turbine before it is cooled to ambient temperature in a heat exchanger. The temperature in the air reactor needs to be 1000ºC or higher. If desired, some H_2 can be taken from the product stream and burnt in a separate combustor to increase the temperature before the gas turbine, thus increasing the power output. This is done in case 2A, shown in figure 5.

The system pressure is 15 bar, which should be appropriate for both the gas turbine and the reformer. The combustion air is pressurized with a compressor before the air reactor. The steam is assumed to be generated by vaporisation at elevated pressure. The isentropic efficiency for compressors, pumps, fans and turbines is set to 90% and the mechanical efficiency to 99%.

The stream from the fuel reactor is treated the same way as described for the atmospheric process above. The main difference is that everything takes place at elevated pressure. This means that the condenser delivers energy at higher temperature, roughly 200ºC, and that the energy required for CO_2 compression drops to a third, 5 kJ/mole CO_2.

The H_2 purification is assumed to have the same characteristics as for the atmospheric process. In reality, there will be more options available in a pressurized system, for example pressure swing adsorption, but this has not been considered. Any excess energy can, of course, be used to produce steam for a steam cycle. The H_2 product is of similar quality as in the atmospheric process. Since it is delivered at elevated pressure, compression to 20 bar requires only 0.8 kJ/mole H_2.

2.4 Reference system – steam reforming

In order to compare the investigated systems with conventional methods for H_2 production, calculations for a steam reformer are included as reference. The reference system, shown in figure 6, is operating at 20 bar, 800ºC and uses similar assumptions as the chemical-looping reformers.

Four moles of steam are fed to the reformer for each mole of CH_4. The reformer is followed by a heat exchanger, a low temperature water-gas shift and a condenser. These components are operating under the same assumptions as in the processes described above. H_2 and CO_2 are separated in a pressure swing adsorption facility. H_2 is delivered at the top pressure, 20 bar. Unreformed CH_4 and 23.5% of the H_2 product remain in the low pressure purge stream from the pressure swing adsorption unit, and are burned to provide energy for the endothermic reforming reactor. CO_2 is captured from the flue gas by absorption, assumed to have the same characteristics as described above. The CO_2 concentration in the flue gas is 20%, which should be compared to H_2 purification for systems 1 and 2, where it is 27-30%.

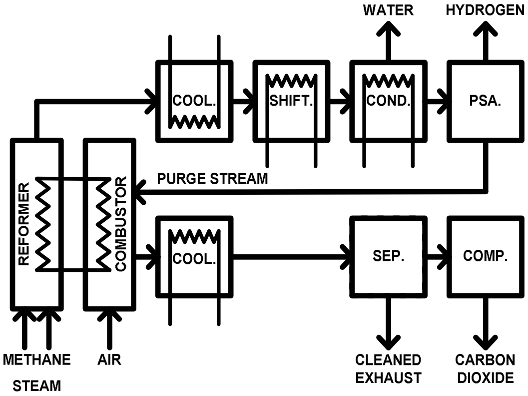

Figure 6: Process scheme for the reference system. Preheating of fuel and steam is not shown.

3. Calculations

3.1 Gas composition after the reformer

The reactions that take place in a reformer usually lead to a product composition very close to thermodynamic equilibrium [12, 13]. In a fluidized bed, the mixing of solids and gases is intense. Almost uniform temperature can be achieved, and deactivated catalyst can easily be replaced. Consequently, it is assumed that the synthesis gas composition after the fuel reactor will be at equilibrium. Successful reforming in fluidizing-beds has been performed at an experimental scale [13, 14].

A study of the equilibrium for different temperatures, pressures and feedstock compositions, highlights suitable operating conditions for the reformer system. If, for example, 0.7 moles O_2 per mole CH_4 is fed to the system, almost full conversion of CH_4 is achieved at 800ºC and 1 bar. But if the reformer pressure is 15 bar, the same conditions result in a CH_4 conversion of only 78%. With a system pressure of 15 bar, a reformer temperature over 1000ºC is needed. It is also found that a little steam added to the fuel reactor has positive effects on the conversion of CH_4 and on H_2 production.

3.2 Carbon formation

Reactions (6) and (7) indicate that 0.5 mole of O_2, or 1 mole H_2O, is needed to reform one mole CH_4. For practical purposes, however, additional oxygen is likely required to prevent formation of solid carbon, which needs to be avoided, since carbon on the particles would circulate to the air reactor and burn there, with CO_2 emissions as a result. There should be no carbon formation, if the ratio O/CH_4 is over 1.2 [17]. For the processes examined in this paper, there is no reason to use such low amounts of oxygen. Consequently, carbon formation is not believed to be a problem. This, however, would need to be verified experimentally.

3.3 System performance

The expected performance of the processes examined has been calculated through pinch analysis. In short, this means that data have been collected from all streams that require heating or cooling. The data are used to produce so called composite curves, which are graphical representations of heating and cooling demands plotted against temperature. This is a straightforward but powerful method to analyze the thermodynamic performance of a process. No actual heat exchanger networks have been proposed. That would require practical considerations that would go beyond the purpose of this paper.

A term named H_2 equivalent, equation (9), is used to define reformer efficiency, equation (10). The H_2 equivalent describes the amount H_2 that will be left per mole CH_4 fed to the process if external heat and power demands are met using part of the H_2 produced for heating or power production. If the process produces excess heat or power, the H_2 equivalent becomes higher than the actual H_2 product.

$$H_{2\,eq} = H_{2\,pr} + h_e/(h_{i,H2} * \eta_h) + P_e/(h_{i,H2} * \eta_{el}) \qquad (9)$$
$$\eta_r = (H_{2\,eq} * h_{i,H2}) / h_{i,CH4} \qquad (10)$$

h_e = Heating excess/demand/ (J/mole CH_4)
P_e = Power excess/demand/ (J/mole CH_4)
$H_{2\,pr}$ = H_2 product (mole/mole CH_4)
$H_{2\,eq}$ = H_2 equivalent (mole/mole CH_4)

η_{el} = η external electricity (0.58)
η_h = η steam generation (0.90)
η_r = η reformer
$h_{i,CH4}$ = LHV for CH_4 (802 300 J/mole)
$h_{i,H2}$ = LHV for H_2 (241 800 J/mole)

4. Results

The performance of the chemical-looping reformer systems has been examined for a wide range of cases. Presented below are a few particularly interesting ones. All have been configured to maximize H_2 production. In practice, this means that a sufficient temperature of reduction has been achieved by adding as little air to the air reactor as possible. For the atmospheric processes, a reformer temperature around 870ºC has been used. The pressurized processes require a higher temperature, about 1000ºC. For case 2C, it is assumed that the maximum temperature is determined by the gas turbine rather than the reformer system, so it is set to 1200ºC.

In addition, all cases have been configured to be self-sustaining with heat. All energy needed for steam generation, desorbtion of the absorbing solvent used in the separation unit and preheating of air, steam and fuel is delivered through heat exchanging within the process. Excess heat is used to produce steam, which is used to generate electricity in a separate steam cycle. Thus, a comparison between the different cases through equation (9) is possible.

In a basic chemical-looping reformer system, such as case 1A, most of the energy available for heat exchanging is delivered at high temperature. The largest energy demands within the process, steam production and desorption requires only modest temperatures, 110-150ºC. Consequently, substantial exergy losses are inevitable. This can be addressed by adding a gas turbine or a steam cycle to the system, so that available energy can be utilized at higher temperatures. If a gas turbine is included, the turbine exhaust, which still has considerable temperature, should be used for steam heating to a separate steam turbine. With this kind of process layout, most of the energy available at high temperatures is used to produce electricity. An increased amount for energy available at lower temperatures will be needed. This should be met by extracting steam, of fitting pressure, from the steam cycle. Since some energy is used to produce electricity, an increased amount of air to the air reactor, which changes the composition of the gas from the fuel reactor towards CO_2 and H_2O rather than CO and H_2, will be required. Otherwise, the energy released in the reactor system will not be enough to sustain the process.

4.1 Examined cases

Case 1A – Partial oxidation in adiabatic reformer, atmospheric process. This case, described in figure 4, is the most straightforward process examined in this paper. All oxygen is fed to the system with the oxygen carrier. The overall system performance is lower than for the other examined cases. This is not surprising, since this configuration lacks options to reduce exergy losses within the process. The overall reformer efficiency is 76.9%, or 69.6% if the H_2 is compressed to 20 bar.

Case 1B – Autothermal reforming in adiabatic reformer, atmospheric process. The only difference between this case and case IA is that a little steam is added to the fuel reactor. This makes it possible to increase the preheating slightly without increasing the reactor temperatures. This does not increase the total steam consumption in any significant way, since a fixed H_2O/CO ratio is used in the water-gas shift reactor. In addition to this, a small amount of steam has a positive effect on CH_4 conversion and, thus, on the H_2 yield. Case 1B has the highest net H_2 production of all examined cases, 2.68 moles per mole CH_4. The reformer efficiency is 77.5%. Just like in case 1A, the efficiency drops dramatically if the H_2 produced is compressed to 20 bar.

Case 1C – Atmospheric reformer with integrated steam cycle. Case 1C is basically case 1B integrated with a steam cycle. Two steam turbines are considered, working with 120/20 and 20/4 bar inlet/outlet pressure. Maximum inlet temperature for the turbines is set to 600ºC. The reason for not adding a third turbine, working at even lower pressures, is the energy demand at temperatures between 100 and 140ºC within the process. This makes expansion to lower pressures than 4 bars inappropriate. Case 1C has a net production of electricity and the reformer efficiency becomes 83.2%, which is considerably higher than for cases 1A and 1B. If H_2 is compressed to 20 bar, the efficiency drops to 75.9%, which is in the same order as the reference system.

Case 2A – Autothermal reformer with internal H_2 combustion, pressurized process. This case, described in figure 5, is a pressurized chemical-looping reformer, integrated with a gas turbine and a single steam turbine. The steam turbine is working with 120/20 bar inlet/outlet pressure and a maximum inlet temperature of 600ºC. The reason for only using one steam turbine is the heat needed in the process at temperatures between 140 and 200ºC, so expansion to lower pressures than 20 bars would not be favourable. A small fraction of the H_2 product is used in an internal combustor to raise the temperature before the gas turbine inlet to 1200ºC. This makes it possible to increase the power output, while sacrificing some H_2. The reformer efficiency is 80.2% which is almost 4% higher than for the reference system.

Case 2B – Autothermal reforming in adiabatic reformer, pressurized process. This case is similar to 2A, but there is no H_2 combustor. Instead, the gas stream from the air reactor goes straight to the gas turbine. Consequently, there will be even less heat available for heat exchanging within the process than in case 2A. So, there is no preheating whatsoever. The steam cycle is configured as in case 2A. Case 2B has slightly higher H_2 production than 2A, but generates less electricity. The reformer efficiency is 79.3%.

Case 2C – Autothermal reforming at high temperature, pressurized process. This is basically case 2B, but the temperature in the air reactor is raised to 1200ºC by adding more oxygen. This results in higher reformer efficiency since the CH_4 conversion and electricity output increases. It would, however, require construction materials and oxygen carrier highly resistant to thermal wear. For case 2C, the reformer efficiency becomes 81.4%, almost 6% better than the reference system. The steam cycle is configured as in case 2A.

Reference system – steam reforming with CO_2 capture by amine scrubbing. Without CO_2 capture, the reference system has an efficiency of 78.7%. In addition, steam with a temperature of about 200ºC that can be used for amine scrubbing is obtained as a by-product. With CO_2 compression to 100 bar, the reformer efficiency drops to 75.3%.

TABLE 1: PROCESS DATA FOR EXAMINED CHEMICAL-LOOPING REFORMER SYSTEMS

	Case 1A	Case 1B	Case 1C	Case 2A	Case 2B	Case 2C	Ref.
CH_4 to fuel reactor (kmole)	1.00	1.00	1.00	1.00	1.00	1.00	1.00
O with oxygen carrier (kmole)	1.32	1.31	1.42	1.39	1.45	1.50	-
O with H_2O (kmole)	-	0.20	0.20	0.25	0.25	0.25	4.00
Reformer pressure (bar)	1	1	1	15	15	15	20
Temperature of reforming(ºC)	884	888	872	1000	1017	1172	800
Air reactor temperature (ºC)	913	918	898	1029	1036	1200	-
Preheating of air, steam and fuel (ºC)	260	300	550	200	-	480	800
Air reactor cooling (kJ)	-	-	70000	-	-	-	-
CH_4 conversion (%)	99.8	99.9	99.9	98.8	99.2	99.9	85.8
H_2 total (kmole)	2.66	2.68	2.57	2.55	2.51	2.49	3.04
H_2 to internal combustor	-	-	-	0.11	-	-	0.43
H_2 product (kmole)	2.66	2.68	2.57	2.44	2.51	2.49	2.61
$h_{i,H2\ product} / h_{i,CH4}$ (%)	80.2	80.8	77.5	73.5	75.6	75.0	78.7
Net electricity (kJ)	-15000	-15000	27000	31500	16300	29400	-15000
Net electricity, H_2 compressed to 20 bar (kJ)	-49600	-49800	-6400	29500	14300	27400	-15000
η Reformer (%)	76.9	77.5	83.2	80.2	79.3	81.4	75.3
η Reformer, H_2 compressed to 20 bar (%)	69.6	69.9	75.9	79.9	79.0	81.1	75.3

5. Discussion

The atmospheric process is rather straightforward and has some advantages. It has large H_2 production and can be built with well-known technology. It is possible to achieve almost full conversion of CH_4 at rather low temperatures.

Integration with a steam cycle, such as is done in case 1C, improves the efficiency substantially. There are two reasons for this. First, more energy can be utilized at high temperatures within the process. Second, steam at pressure and temperature suitable for regeneration of the absorbing solvent, water-gas shift and fuel reactor can be extracted directly from the turbines. Consequently, integration with a steam cycle makes it possible to reduce the exergy losses in the system considerably.

H_2 production at atmospheric pressure is unfavourable if pressurized H_2 is wanted as product. Reforming involves a substantial increase of gas volume. Thus, compression of the fuel requires less energy than compression of the products. Despite this, case 1C has higher reformer efficiency than the reference system, even if H_2 is delivered at a pressure of 20 bar.

The pressurized processes are not as uncomplicated as the atmospheric ones. The energy available for internal heat exchange is smaller because of the gas turbine. In addition, the vaporization of process steam needs higher temperatures. Despite this, the pressurized systems show very good performance. This is because integration with both a gas and a steam turbine has been considered for all cases, which reduces exergy losses.

For a process working at a pressure of 15 bar, a reactor temperature over 1000ºC is necessary to reach good CH_4 conversion. This is not believed to cause difficulties for an oxygen carrier based on NiO, although this needs to be verified experimentally. In general, a pressurized chemical-looping reformer integrated with a gas turbine should operate at as high a temperature as possible, as in case 2C. Whether it will be the gas turbine, the oxygen carrier or some other factor that will set the high temperature limit is too early to say.

As for product quality, the proposed systems do not separate CO and CH_4 from the H_2 product. In practice, all CO_2 would not be removed either. A H_2 concentration of 97-98% would, however, be sufficient for most applications, including many kinds of fuel cells. This would reduce the CO_2 emissions by 97-98%. If higher purity is needed, further purification steps could, of course, be added.

6. Conclusions

A thermodynamic analysis has been conducted to investigate the characteristics of some novel processes that utilize chemical-looping for production of H_2. The atmospheric processes have large H_2 production, but the electricity needed to compress the product is considerable. The pressurized processes are less straightforward, but have very good overall efficiency, even if pressurized H_2 is desired. The efficiency could be at least 4% higher than for the reference system, a steam reformer with CO_2 capture by amine scrubbing. With an oxygen carrier resistant to thermal wear, a reformer efficiency above 81% is possible.

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