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USING STEAM REFORMING TO PRODUCE HYDROGEN WITH CARBON DIOXIDE CAPTURE BY CHEMICAL-LOOPING COMBUSTION

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ABSTRACT

In this paper, a novel process for hydrogen production by steam reforming of natural gas with inherent capture of carbon dioxide by chemical-looping combustion is proposed. The process resembles a conventional circulating fluidized bed combustor with reforming taking place in reactor tubes located inside a bubbling fluidized bed. Energy for the endothermic reforming reactions is provided by indirect combustion that takes place in two separate reactors: one for air and one for fuel. Oxygen is transferred between the reactors by a metal oxide. There is no mixing of fuel and air so carbon dioxide for sequestration is easily obtained. Process layout and expected performance are evaluated and a preliminary reactor design is proposed. It is found that the process should be feasible. It is also found that it has potential to achieve better selectivity towards hydrogen than conventional steam reforming plants due to low reactor temperatures and favorable heat-transfer conditions.

Keywords: Hydrogen; Synthesis gas; Steam reforming; Carbon capture; Chemical-looping combustion

1. INTRODUCTION

According to the International Energy Agency, roughly 80% of the primary energy production of the world comes from combustion of oil, coal and natural gas [1]. So, whether we like it or not, our dependence on fossil fuels for electricity, industry, heating and vehicle fuels can hardly be overestimated. When burnt, all fossil fuels emit CO_2 (carbon dioxide) into the atmosphere. Since the work of Arrhenius more than 100 years ago, it has been known that CO_2 is a greenhouse gas that affects the climate of the earth [2]. Today, the CO_2 concentration in the atmosphere is 30% higher than it was before the industrialization era and the annual emissions are still increasing. In the last years, concerns that our emissions of greenhouse gases will lead to disastrous global climate changes have been growing steadily. This anxiety is reflected by the fact that the first international treaty limiting emissions of greenhouse gases, the Kyoto protocol, currently has been ratified by over 140 nations.

One possible way to decrease CO_2 emissions that is receiving increasing interest is CO_2 capture and storage. The idea, in short, is to separate CO_2 from flue gases and store it where it is prevented from reaching the atmosphere. Several methods to do this have been demonstrated or proposed. The area has recently been reviewed by Yamasaki [3] and Anderson et al [4]. CO_2 capture and storage is easiest and most affordable for large point sources, such as power plants and industries. It would be much more complicated and costly

to capture CO_2 from small and numerous contributors such as those in the transportation sector. For this category of applications, other strategies to reduce CO_2 emissions are needed. One option is to replace fossil fuels with H_2 (hydrogen) which contains no carbon and thus can be burnt without CO_2 emissions. H_2 is also the preferred fuel for fuel cells, which is a technology that has made steady progress over the past decades and promises both higher efficiency and lower emissions than conventional engines. Fuels cells are interesting for many applications, including vehicles.

In the future, it might be feasible to produce H_2 directly from sustainable energy sources, for example by electrolysis with sun- and wind power or by gasification of biomass. While this is very appealing, it is evident that it will take decades of purposeful research and development before these production methods could become of any real significance. The prospects for building an energy infrastructure with H_2 as a major energy carrier have been reviewed by Ogden [5], and more recently by Khare et al [6].

Today, the principal raw material for H_2 production are fossil fuels, particularly natural gas. Just as combustion, this results in CO_2 emissions to the atmosphere. Large-scale facilities are used, so H_2 production with CO_2 capture should be feasible just as for power plants. In this paper, a novel way to produce H_2 by steam reforming of natural gas with inherent CO_2 capture by chemical-looping combustion is proposed and examined. The proposed process could be used to reduce CO_2 emissions from existing H_2 plants, or to produce CO_2-free fuel for other applications.

The layout of the paper is as follows. In section 2, chemical-looping combustion is presented. There is also a brief description of H_2 production by steam reforming of natural gas. This section has been included to illustrate the similarities between the process proposed in this paper and existing technologies. In section 3, a basic process scheme capable of taking advantage of the most desirable characteristics of both chemical-looping combustion and steam reforming is outlined. Based on this simplified process scheme, two computer models have been designed. The first model describes the general characteristics of the proposed reformer plant, such as thermodynamic constraints, temperatures, pressure levels, gas flows and required heat transfer operations. The second model describes the properties of one single reformer tube. Data from the models have been used to make a preliminary design of the reactor system, in order to show that the process is feasible. The computer models and the proposed process design are described in section 4. In section 5, the process is discussed and further topics of research are suggested.

2. DESCRIPTION OF USED TECHNOLOGIES

2.1 Chemical-looping combustion

Chemical-looping combustion (CLC) is a novel process for heat and power production with inherent CO_2 capture. It has also been called unmixed combustion since direct contact between fuel and combustion air is avoided. Instead, an oxygen carrier performs the task of bringing oxygen (O_2) from the air to the fuel. Suitable oxygen carriers are small particles of metal oxide such as Fe_2O_3 (hematite), NiO (nickel oxide), CuO (copper oxide) or Mn_2O_3 (manganese oxide). In this paper, the abbreviation Me is used to describe a generic oxygen carrier in its reduced form while MeO is used for the oxidized form. Research related to the development and testing of oxygen-carrier particles have been published by research groups at Chalmers University of Technology in Gothenburg [7, 8, 9], Tokyo Institute of Technology [10, 11], Korean Institute of Energy Research [12, 13], CSIC-ICB in Zaragoza [14], Politecnico di Milano [15] and TDA Inc [16]. A basic chemical-looping combustion system, shown in figure 1, has two reactors, one for air and one for fuel.
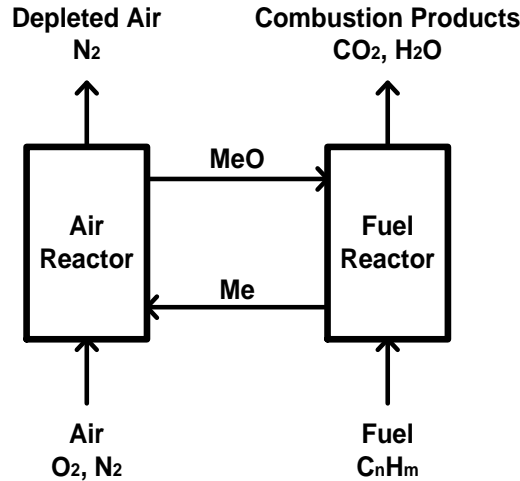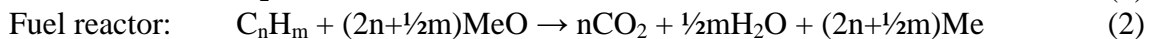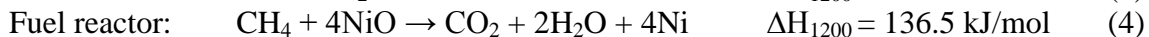
Figure 1. Chemical-looping combustion. The abbreviation Me is used to describe the oxygen carrier in its reduced form while MeO is used for its oxidized form.

The oxygen carrier circulates between the reactors. In the air reactor, it is oxidized with O_2 from the combustion air according to reaction (1). In the fuel reactor, it is reduced to its initial state by the fuel, which in turn is oxidized to CO_2 and H_2O (water vapor) according to reaction (2).

Air reactor: $O_2 + 2Me \rightarrow 2MeO$ (1)

Fuel reactor: $C_nH_m + (2n+\frac{1}{2}m)MeO \rightarrow nCO_2 + \frac{1}{2}mH_2O + (2n+\frac{1}{2}m)Me$ (2)

The amount of energy released or required in the reactor vessels depends on the nature of the oxygen carrier and the fuel, as well as the temperature of reaction. Reaction (1) is strongly exothermic. Reaction (2) is usually endothermic but for some combinations of fuel and oxygen carrier it is slightly exothermic. In principle, all kinds of fuels can be utilized in a chemical-looping combustor. If CH_4 (methane) is used as fuel and NiO as oxygen carrier reaction (3-4) will occur in the reactors.

Air reactor: $4Ni + 2O_2 \rightarrow 4NiO$ $\Delta H_{1200} = $ -938.2 kJ/mol   (3)

Fuel reactor: $CH_4 + 4NiO \rightarrow CO_2 + 2H_2O + 4Ni$ $\Delta H_{1200} = $ 136.5 kJ/mol   (4)

The total amount of energy released in the reactor system is the same as for combustion of the fuel. The sum of reaction (3-4) is complete combustion of CH_4 with O_2, reaction (5).

Total reaction: $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ $\Delta H_{1200} = $ -802.7 kJ/mol   (5)
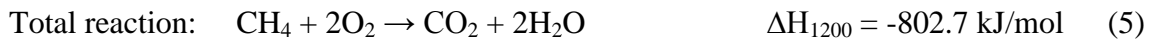
Chemical-looping combustion has several potential benefits compared with conventional combustion. The exhausts from the oxidation reactor are harmless, consisting mainly of N_2 (nitrogen) and, if a surplus of air is used in the oxidation reactor, some O_2. In a well-configured system, there should be no thermal formation of NO_X (nitrogen oxides) since regeneration of the oxygen carrier takes place without flame and at moderate temperatures. The gas from the reduction reactor consists of CO_2 and H_2O, so a condenser is the only equipment 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 this can be avoided completely since CO_2 and N_2 are never mixed.

In practice, a chemical-looping combustion process can be designed in several ways. But circulating fluidized beds are likely to have an advantage over other alternatives since it provides good contact between gas and solids and allows a smooth flow of oxygen carrier between the reactors. Circulating fluidized beds are well known technology that is used for many large scale industrial applications. Chemical-looping combustion has recently been successfully demonstrated by Lyngfelt et al in a 10 kW prototype using circulating fluidized beds. 99.5% fuel utilization at 800 ºC with no detectable leakage between the reactors and very small losses of oxygen-carrier material was achieved [17].

It shall be noted that H_2 production by chemical-looping has been proposed and examined by Rydén et al [18], Mattisson et al [19] and Zafar et al [20]. These papers deal with chemical-looping reforming (CLR), which essentially is partial oxidation or autothermal reforming of natural gas utilizing chemical-looping as a source of undiluted O_2.

2.2 H_2 production by steam reforming

Steam reforming (SR) is a well known industrial process that converts hydrocarbon fuel to synthesis gas, a reactive gas mixture consisting mainly of H_2 and CO (carbon monoxide). Synthesis gas is used for production of ammonia, methanol, synthetic fuels and other chemicals, as well as for production of pure H_2. At present, almost all produced H_2 is used for industrial applications, not as CO_2-free fuel. The largest consumption is in the refining industry but H_2 is also used in metallurgy, for hydrogenation of fats and for manufacturing of high quality electronic components.

Most modern facilities for H_2 production include tubular steam reforming of natural gas followed by a water-gas shift reactor (WGS) and product purification by pressure swing adsorption (PSA). A simplified process scheme for a typical H_2 plant is shown in figure 2.
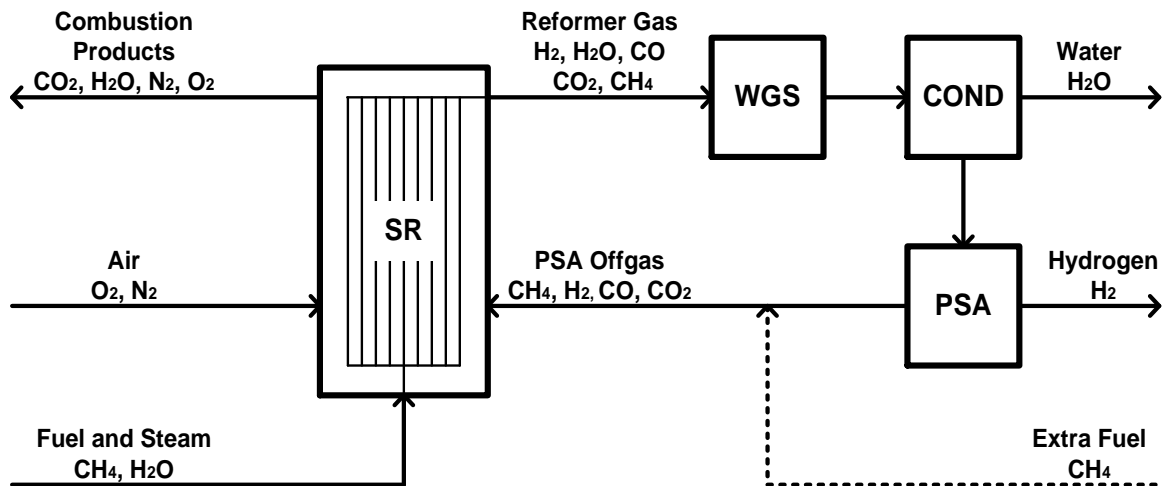

Figure 2. Schematic description of a steam reformer plant for production of high purity H_2. SR is the steam reformer furnace which contains the reformer tubes, WGS is a water-gas shift reactor, COND is a condenser and PSA is a pressure swing adsorption unit. Extra fuel is used if the heating value of the PSA offgas is insufficient to provide the reformer with energy. Heat exchangers, fans and compressors are not shown.

Reaction (6) describes steam reforming of CH_4, the main component of natural gas. Other light hydrocarbons, such as naphtha or liquefied petroleum gas, can also be used as feedstock.

Steam reforming converts stable molecules into reactive ones. Consequently, it is a highly endothermic process.

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad\qquad \Delta H_{1100} = 225.4 \text{ kJ/mol} \qquad (6)$$

In most facilities, steam reforming takes place in tubes located inside a furnace. Reactor design is complex. Heat for the endothermic reformer reactions is provided by direct firing of a fuel in the furnace. Consequently, the reformer tubes are subject to very high thermal stress. There are also unwanted reactions such as formation of solid carbon that needs to be avoided. Much knowledge is required for successful choice of tube dimensions, furnace temperature, operating pressure and heat flux profile. Generally, reformer tubes are made up of some high alloy steel. The diameter of the tubes is in the range of 70 to 160 mm with a wall thickness of 10 to 20 mm. The heated tube length is 6-15 meters, depending on furnace type. The tubes are packed with catalyst material, typically made from nickel and some inert binding agent. The size and shape of the catalyst are optimized to achieve maximum activity and maximum heat transfer while minimizing the pressure drop. Desulphurization of the fuel is necessary since small amounts of sulphur are enough to poison the catalyst. The process parameter varies. In most cases the outlet temperature from the reformer is in the interval 700-950 $^\circ$C, the outlet pressure between 15-40 bars and the steam to carbon ratio in the feedstock 3.0-6.0. The reforming reactions are fast and the resulting product composition is usually close to thermodynamic equilibrium.

If H_2 is the desired product, steam reforming is followed by water-gas shift, reaction (7), which is an exothermic reaction that transforms CO and H_2O to CO_2 and H_2.

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad\qquad \Delta H_{600} = -38.9 \text{ kJ/mol} \qquad (7)$$

Water-gas shift takes place in one or two separate reactor vessels. The first one, the high temperature shift reactor, operates at temperatures in the order of 350-500 $^\circ$C and utilizes an iron/chrome catalyst. Additional steam can be added to improve the degree of CO conversion. This is not necessary for reformer gas from steam reforming since it already contains excess steam. A typical CO concentration after high temperature water-gas shift is 3.5 mol% on dry basis. If lower CO concentration is required, the high temperature shift reactor is followed by a second shift reactor operating at lower temperature.

Today, the primary alternative for H_2 purification is pressure swing adsorption. This technology utilizes two basic physical principles. Firstly, highly 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 facility for H_2 purification the impurities are adsorbed at high pressure, while H_2 is just passing through the adsorber vessel. When the vessel is full it is disconnected from the process and the pressure is decreased, thus releasing most of the impurities. A small fraction of the produced H_2 is needed for purging and regeneration of the adsorbers, so the H_2 recovery is limited to about 90%. The offgas from the adsorber vessel consists of CO_2, purge H_2, unreformed CH_4, some CO and minor fractions of other impurities. The offgas has substantial heating value and is generally recirculated and used as fuel in the reformer furnace. Pressure swing adsorption is a batch process, but by using multiple adsorbers it is possible to provide constant flows. The pressure drop for H_2 is usually about 0.5 bar. There is no need for power, heating or chemicals. H_2 with very high purity, 99.9% or higher, is produced.

Large scale steam reforming of natural gas has been practiced for decades and involved technologies can be considered as quite mature. Consequently, the number of papers dealing

with the subject is very large. Informative reviews include those by Rostrup-Nielsen [21] and Dybkjær [22].

3. DESCRIPTION OF THE PROPOSED PROCESS

In this paper, H_2 production by steam reforming with CO_2 capture by chemical-looping combustion is proposed and examined. The process resembles a conventional steam reforming plant but the furnace is replaced with chemical-looping combustion. A schematic description of the examined system is shown in figure 3.
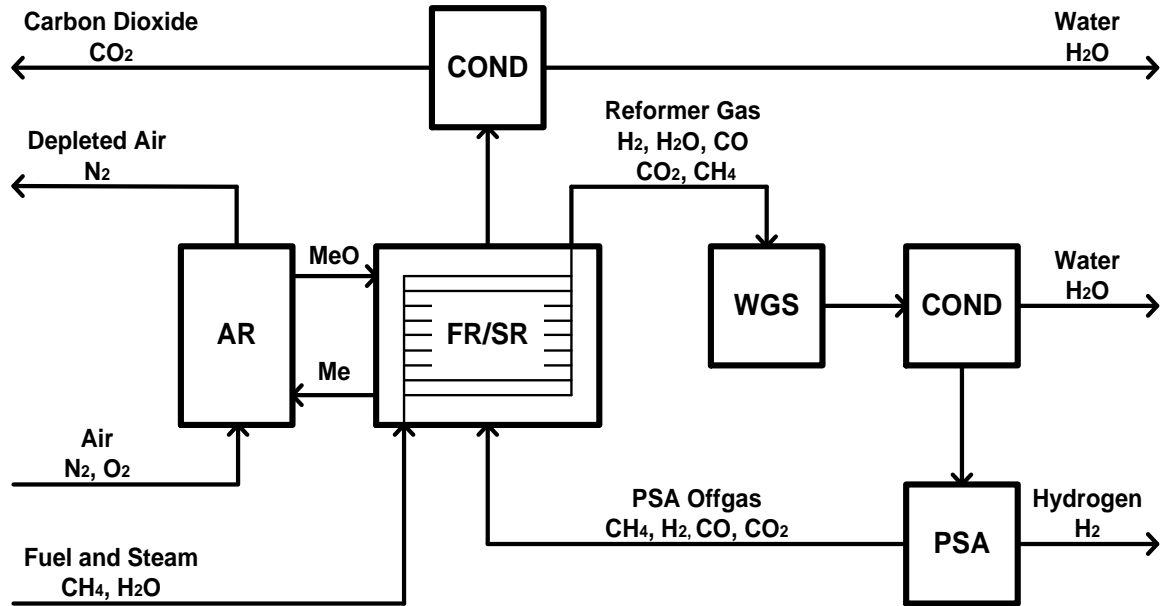

Figure 3. Schematic description of the H_2 plant proposed in this paper. AR is the air reactor, FR/SR is the fuel reactor which also contains the reformer tubes, WGS is a high temperature water-gas shift reactor, COND are condensers for water removal and PSA is a pressure swing adsorption unit. Heat exchangers, fans and compressors are not shown.

Reforming takes place in reformer tubes packed with catalyst, just as in a conventional steam reformer. The tubes are located inside the chemical-looping fuel reactor. This arrangement, which could be compared to a fluidized bed heat exchanger, should be compatible with chemical-looping combustion as proposed and demonstrated by Lyngfelt et al [17, 23]. An overview of the proposed reactor system is shown in figure 4.

The reactor system is composed of two interconnected fluidized beds. The air reactor is a high-velocity fluidized bed working as a riser, while the fuel reactor is a low-velocity bubbling bed. The reformer tubes are placed horizontally inside the fuel reactor. Oxygen carrier is used as bed material. The high gas velocity in the air reactor provides the necessary driving force to obtain a circulation of particles between the beds. Oxidized particles are collected in the cyclone and led to the fuel reactor. Reduced oxygen carrier is transferred back to the air reactor by gravity. Gas leakage between the reactors is prevented by particle-gas locks fluidized with steam. Heat for the endothermic reformer reactions is provided by the exothermic reactions in the air reactor and transferred to the fuel reactor with the particle circulation.
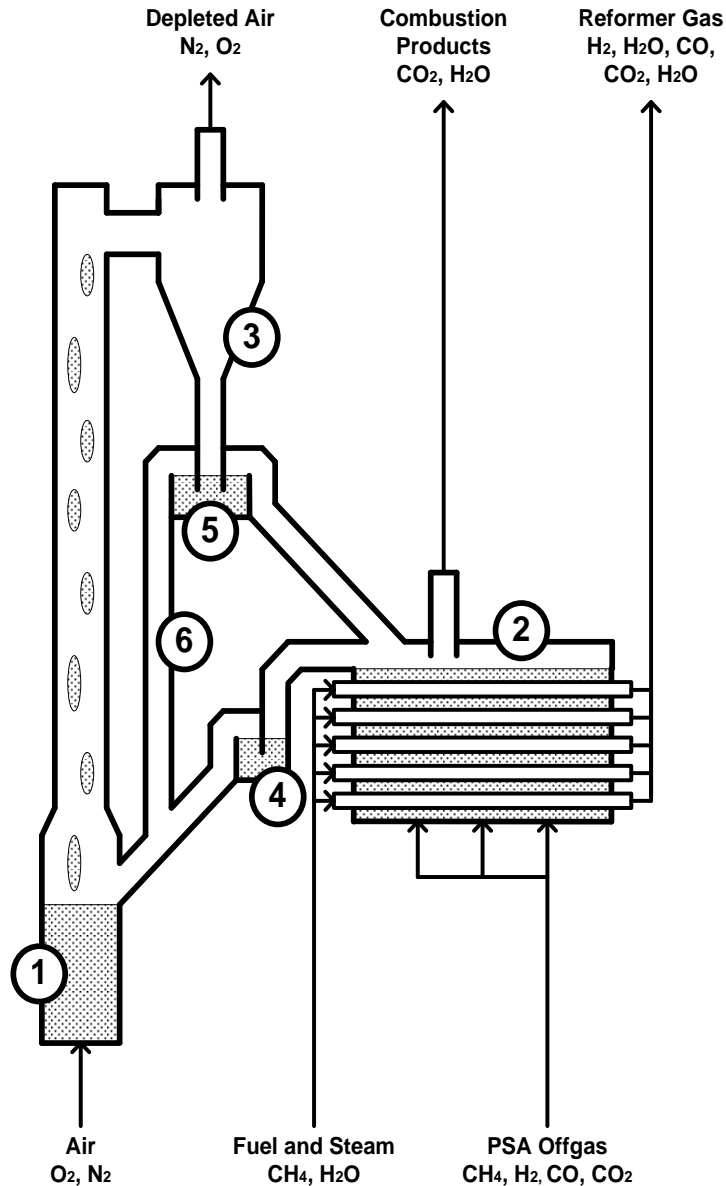
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Figure 4. Visualization of the proposed reactor system. (1) is the air reactor, (2) is the fuel reactor which also contains the reformer tubes, (3) is a cyclone for particle separation, (4) and (5) are particle-gas locks that prevent leakage between the reactors, (6) is an extra recirculation that can be used to control the reactor temperatures while keeping constant flows of air and offgas.

The proposed process has some very appealing characteristics. Almost pure CO_2 is delivered in a separate process stream. Due to the relatively low temperature level in the air reactor, there should be no formation of thermal NO_X. The offgas is rich with H_2 which shows high reactivity with chemical-looping oxygen carriers. The heat-transfer coefficient for the outside of the reformer tube is high due to the hot fluidized particles, so it should be relatively easy to obtain and maintain a favorable tube wall temperature profile. Chemical-looping combustion takes place at ambient pressure and modest temperature, so reactor design should be rather straightforward. Steam reforming takes place at elevated pressure which reduces the power consumption for compression of produced H_2. The offgas from the pressure swing

adsorption unit is used as fuel in the fuel reactor. If the offgas is released at sufficient pressure to overcome the pressure drop in the fuel reactor, no separate offgas fan should be needed.

4. MODELING AND PRELIMINARY DESIGN

4.1 Basic process model

In order to evaluate system performance and identify critical process parameters, a computer model was made that calculates flows, temperatures and other properties for the involved process components. It is assumed that the reactions in the reformer and shift reactor proceed to thermodynamic equilibrium. It is also assumed that there is complete conversion of offgas to CO_2 and H_2O in the fuel reactor, that there is no gas leakage between the reactors and that the low-pressure steam needed for fluidization of the particle-gas locks is negligible. Heat losses from reactors and piping have not been considered. The fuel is CH_4, assumed to be delivered at a pressure of 25 bar. The oxygen carrier is assumed to be made of 42 mass-% NiO and 58 mass-% alumina (Al_2O_3), with the later regarded as inert. Thermodynamic data and various physical properties are taken from Barin [24] and Yaws [25]. Process parameters that have been assigned fixed values can be found in table 1.

ΔT_{ar-fr} (K)	50	Temperature difference between air and fuel reactor
$\Delta T_{fr-ref,out}$ (K)	100	Temperature difference between fuel reactor and reformer outlet
$T_{shift,in}$ (°C)	350	Shift reactor inlet temperature
$p_{ref,out}$ (bar)	24.0	Reformer tubes outlet pressure
η_{psa} (%)	90	H_2 recovery in PSA unit
T_{psa} (°C)	40	Temperature in PSA unit
T_{amb} (°C)	20	Ambient temperature
p_{amb} (bar)	1.013	Ambient pressure
$\lambda_{ar-offg}$	1.20	Air ratio compared to stoichiometric combustion of offgas

Table 1. Chosen and assumed process parameters

The reformer tubes outlet temperature is identified as the single most important process parameter. Three cases are presented below in which it is varied from 750 °C to 850 °C. Steam to fuel ratio in the feedstock and preheating of fuel, steam and air has been adjusted to obtain as high H_2 production as possible, under the constraint that no extra fuel or external heating is required. Reformer efficiency is defined as lower heating value of produced H_2 divided by lower heating value of consumed CH_4. It would be possible to produce some low-pressure steam or hot water for district heating as by-product, but this option has not been considered in this work. Process data have been collected and examined by pinch analysis which is a straightforward and useful method to analyze the thermal properties of industrial processes. The key data for the examined cases are presented in table 2.

	A	B	C	
$T_{ref,out}$ (°C)	750	800	850	Reformer tubes outlet temperature
$\lambda_{H2O/CH4}$	4.80	3.80	3.05	Steam to carbon ratio in the feedstock
T_{ar} (°C)	900	950	1000	Air reactor temperature
T_{fr} (°C)	850	900	950	Fuel reactor temperature
$T_{shift,out}$ (°C)	382	402	421	Shift reactor outlet temperature
$T_{preh,out}$ (°C)	448	557	664	Required preheating of fuel, steam, offgas and air
$\lambda_{H2/CH4}$	2.54	2.69	2.80	Moles produced H_2 for each mol consumed CH_4
η_{ref} (%)	76.6	80.9	84.6	Reformer efficiency

Table 2. Process characteristics for three basic cases.

It can be seen that an increase in reformer temperature from 750 ºC to 800 ºC improves the efficiency 4.3%. This is mainly due to reduced steam to fuel ratio. With high reformer temperature, less steam is needed to obtain desired H_2 yield from reaction (6). This means improved reformer efficiency since less steam needs to be produced, heated and cooled for each mole of fuel. Increasing the reformer outlet temperature to 850 ºC increases efficiency further but would require preheating of fuel, steam and air to 664 ºC. This kind of preheating of the fuel could lead to formation of solid carbon, which needs to be avoided. For that reason, case B is chosen for further examination of the process and for dimensioning of the reactor system.

4.2 Reformer tube model

The kinetics for catalytic steam reforming at relevant temperatures is fast. Therefore, the balance between heat input through the tube walls and heat consumption by the endothermic reformer reactions is the central design problem. A change from furnace to fluidized bed will have large impact on the heat transfer characteristics and possibly on the reformer tubes. In order to examine this, a simplified model was made that describes one single reformer tube surrounded by a hot fluidized bed. The model calculates gas composition, heat flux, temperatures and pressure drop along the tube. It is assumed that the reformer gas is perfectly mixed in the radial direction with respect to temperature, pressure and chemical composition and that there is no thermal or chemical mixing in the axial direction. All reactants are considered as ideal gases. Properties of gas mixtures are calculated with the expressions by Wilke [26] and Mason et al [27]. Thermodynamic data and other material properties are taken from Barin [24] and Yaws [25]. The catalyst is raschig rings with the dimension 16×6×16 mm. Physical data for the catalyst and thermal conductivity for the tube material is taken from Gupta et al [28]. Expressions for pressure drop, heat transfer from the reaction mixture to the tube wall, heat transfer through the tube wall and reaction kinetics are taken from Saraf et al [29]. The heat-transfer from the fluidized bed to the outside of the reactor tubes is calculated with Zabrodsky's correlation for Geldart's group B particles. For relevant cases, this correlation is found to give values very close to the average of the heat-transfer according to the correlations by Zabrodsky, Gelperin, Andeen and Glicksman. All these expressions have recently been investigated by Kim et al [30]. Tube dimensions and inlet flow of fuel and steam has been set to values typical for conventional steam reformers. Reactor models by Gupta et al [28], Saraf et al [29], Kvamsdal et al [31] and Xu et al [32, 33] has been consulted, as well as review papers by Rostrup-Nielsen [21] and Dybkjær [22]. Data for one single reformer tube for case B from table 2 above is presented in table 3.

D_i (m)	0.10	Inner diameter of reformer tube
D_o (m)	0.12	Outer diameter of reformer tube
$F_{CH4,in}$ (mol/s)	1.034	CH_4 flow in tube inlet
$F_{H2O,in}$ (mol/s)	3.931	Steam flow in tube inlet
T_{fr} (ºC)	900	Temperature of fuel reactor bed
$T_{ref, in}$ (ºC)	557	Reformer tube inlet temperature
$T_{ref,out}$ (ºC)	800	Reformer tube outlet temperature
$p_{ref,in}$ (bar)	24.9	Reformer tube inlet pressure
$p_{ref,out}$ (bar)	24.0	Reformer tube outlet pressure
d_{cat} (mm)	17.41	Equivalent diameter of catalyst pellet
$ø_{cat}$	0.656	Sphericity of catalyst pellet
ρ_{cat} (kg/m^3)	2397	Density of catalyst pellet
ε_{ref}	0.605	Void fraction for the catalytic bed
$T_{wall,max}$ (ºC)	866	Maximum tube wall temperature
L_{ref} (m)	11.4	Heated tube length

Table 3. Data for one single reformer tube.

The heated tube length should be 11.4 m. This is in the same order as for conventional steam reforming. The tube wall temperature varies less along the reactor tube than it would do in a conventional side-fired furnace. This is due to lower surrounding temperature and higher heat-transfer coefficient for the outside of the tube wall. In the end of the reactor, the outside temperature of the reformer tube is 866 ºC, which is lower than for a conventional side-fired reformer tube operating with the same outlet temperature.

4.3 Dimensioning of reactor vessels and oxygen-carrier flow

In order to check the practical feasibility of the process, a preliminary reactor design has been made. A production of 1000 moles H_2 per second has been assumed. This corresponds to approximately 300 MJ/s of added fuel. The fuel reactor is fluidized with offgas from the pressure swing adsorption unit. The reformer tubes are placed horizontally inside the fuel reactor. The assumptions from table 1, 2 and 3 have been used, as well as additional assumptions that can be found in table 4. Data for the air and fuel reactor are presented in table 5 and 6.

F_{CH4} (mol/s)	372.4	CH_4 to plant
F_{H2} (mol/s)	1000	H_2 product
Hi_{CH4} (MJ/s)	299	Lower heating value of the feedstock
Hi_{H2} (MJ/s)	242	Lower heating value of the product
ε_{fr}	0.6	Void fraction in the fuel reactor bed
u_{fr} (m/s)	0.47	Fluidizing velocity in the bottom of the fuel reactor
T_{ar} (ºC)	950	Air reactor temperature
T_{fr} (ºC)	900	Temperature in the fuel reactor
d_{oxc} (µm)	200	Mean diameter of the oxygen-carrier particles
ρ_{oxc} (kg/m^3)	1800	Density of the oxygen-carrier particles

Table 4. Chosen and assumed parameters for preliminary reactor design.

M_{ar} (kg/s)	40.4	Air flow
V_{ar} (m^3/s)	135.9	Volume flow in the bottom of the air reactor
$m_{bed,ar}$ (metric tons)	9.8	Air reactor bed mass
Δp_{ar} (bar)	0.035	Pressure drop over the air reactor
$M_{oxc,ar,out}$ (kg/s)	1860	Particle flow from the air reactor

Table 5. Data for air reactor

M_{offg} (kg/s)	13.7	Offgas flow to the fuel reactor
$x_{H2,offg}$	0.230	Mol fraction of H_2 in offgas
$x_{CH4,offg}$	0.181	Mol fraction of CH_4 in offgas
$x_{CO,offg}$	0.057	Mol fraction of CO in offgas
$x_{CO2,offg}$	0.532	Mol fraction of CO_2 in offgas
Hi_{offg} (MJ/s)	105	Lower heating value of the offgas
$M_{oxc,fr,out}$ (kg/s)	1852	Particle flow from the fuel reactor
$V_{fr,in}$ (m^3/s)	39.5	Volume flow in the bottom of the fuel reactor
A_{fr} (m^2)	84.4	Cross section base area of the fuel reactor
L_{fr} (m)	11.4	Fuel reactor length
W_{fr} (m)	7.4	Fuel reactor width
$H_{bed,fr}$ (m)	2.5	Fuel reactor bed height
N_{tube}	360	Number of reformer tubes
ΔL_{tube} (m)	0.24	Distance between reformer tube centers
$m_{bed,fr}$ (metric tons)	118.5	Fuel reactor bed mass
Δp_{fr} (bar)	0.177	Pressure drop over the fuel reactor

Table 6. Data for fuel reactor

The oxygen carrier flow rate should depend mainly on the size and density of the oxygen carrier and the fluidizing velocity in the air reactor. Since fluidizing velocity in the air reactor can be adjusted freely by changing the cross section area, air reactor design should cause no major problems. The flow rate of oxygen carrier in the riser is 1860 kg/s. The mass of the particles in the air reactor has been set to 9.8 metric tons and the pressure drop to 0.035 bar. With a fluidizing velocity in the order of 5 m/s this should corresponds to a particle flow of about 50 kg/s m^2, which is similar to what is reported for a 12 MW circulating fluidized bed boiler operating with a fluidizing velocity of 5 m/s, a pressure drop of 0.07 bar over the bed and silica sand particles with a diameter of 320 μm [34].

The necessary oxygen-carrier conversion corresponds to 54% of the active NiO phase per minute in the air reactor and 4.5% of the active NiO phase per minute in the fuel reactor. Experimental data from Cho et al [9] and Adánez et al [14] suggests that this could be achieved with the assumed oxygen carrier. The total amount of oxygen-carrier particles corresponds to 345 kg for each mol/s processed CH_4.

In the fuel reactor, 360 reformer tubes are needed. They are placed in a triangular pitch with twelve layers, each consisting of 30 tubes. The distance between the tube centers is twice the tube diameter. The total bed height is 2.5 meters, which corresponds to a pressure drop of 0.177 bar. If the offgas from the pressure swing adsorption unit is released at a pressure of 1.2 bar, the ratio between inlet pressure and outlet pressure in the pressure swing adsorption unit is 20, which should be sufficient to obtain 90% recovery of H_2. If lower outlet pressure is desired, or if a bottom plate with significant pressure drop is needed to achieve good fluidization, a separate offgas fan might be needed.

4.4 Design of heat exchanger network

H_2 production by steam reforming involves several heat transfer operations. Therefore, it is relevant to examine the proposed process more closely and set up a scheme for a viable heat exchanger network. This has been done, using data from case B presented in table 2 above, as well as data for the reactors, found in table 4, 5 and 6. A minimum temperature difference of 20 ºC between hot and cold streams has been assumed. The proposed layout is shown in figure 5.
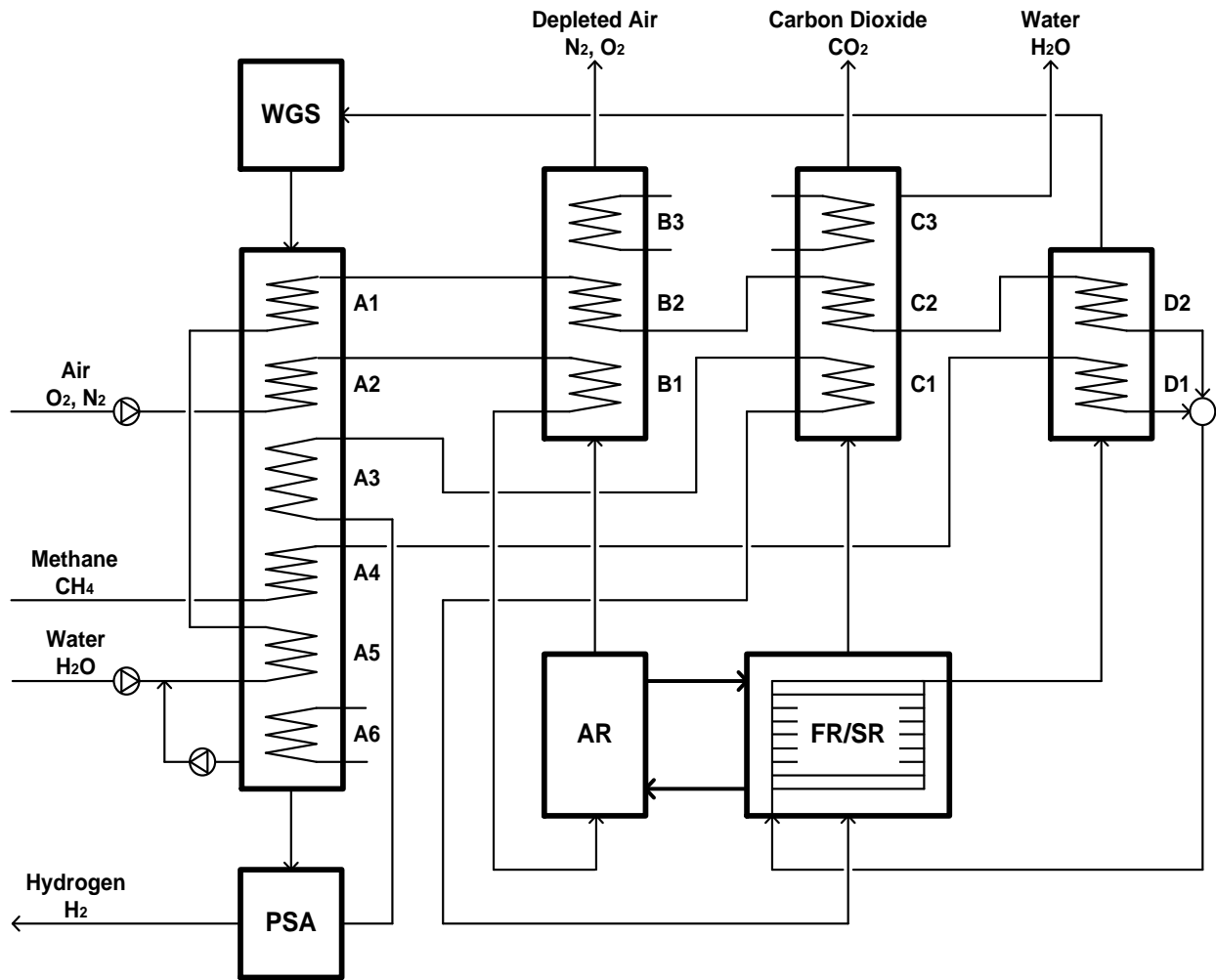
Figure 5. Schematic process layout for the H₂ plant proposed and examined in this paper, including heat exchangers, pumps and fans. The CO₂ compressor is not shown.

The heat exchanger network is pretty straightforward. A large amount excess heat is provided by condensation of the steam in the shifted reformer gas, which takes place at 24 bar and 222 °C. This heat is used for initial preheating of fuel, offgas, air and water. Final preheating to 557 °C is made by heat exchanging with hot gases directly from the reactors. Generation of process steam requires a lot of energy and takes place in several steps, utilizing intermediate temperature levels. Stream data for the heat exchangers can be found in table 7 and 8.

	T_{in} (°C)	T_{out}(°C)	Q (MJ/s)	
A1-A6	402	40	65.2	Shifted reformer gas
B1-B3	950	244	26.0	Air reactor exhaust
C1-C3	900	40	37.5	Fuel reactor exhaust
D1-D2	800	350	38.9	Reformer gas

Table 7. Heat exchanger data for hot streams.

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	T_{in}(°C)	T_{out}(°C)	Q (MJ/s)	
A1	202	224	14.3	Vaporization
A2	23	202	7.5	Initial preheating of air
A3	40	202	2.9	Initial preheating of offgas
A4	20	202	2.7	Initial preheating of fuel
A5	32	202	18.1	Preheating of water
A6	-	40	19.7	External cooling
B1	202	557	14.5	Final preheating of air
B2	224	224	11.5	Vaporization
B3	-	-	-	-
C1	202	557	7.6	Final preheating of offgas
C2	224	224	11.1	Vaporization
C3	-	40	18.8	External cooling
D1	202	557	7.4	Final preheating of fuel
D2	222	557	31.5	Vaporization and superheating

Table 8. Heat exchanger data for cold streams.

External cooling is required for A6 and C3. B3 does not need cooling, but has been included since it could be used for production of some low-pressure steam or hot water. The external power demands for the proposed H_2 plant are summarized in table 9. An air fan is needed to overcome the pressure drop in the air reactor. Two pumps are required, one for pressurization of process feed water to 25 bar and one to raise the pressure of recirculated water from condenser A6. The efficiency of the fan and the pumps has been set to 85%. It shall also be noted that CO_2 needs to be compressed to about 100 bar, in order to be transported and stored. The power demand for this is in the order of 0.12 kWh/kg CO_2. The total power consumption corresponds to about 2.4 % of the lower heating value of the feedstock.

P_{fan} (MW)	0.15	Power demand, air fan
P_{pump} (MW)	0.03	Power demand, water pumps
P_{comp} (MW)	7.07	Power demand, CO_2 compressor

Table 9. External power demands.

5. DISCUSSION

Chemical-looping combustion is still at an early stage of development. The prospects, however, are very promising. The process proposed in this paper involves a few elements that distinguish it from the standard case. Firstly, offgas from pressure swing adsorption is used as fuel. The offgas is rich with highly reactive H_2 and free from sulphur and other components that could poison the oxygen carrier. Consequently, the fuel is not believed to cause any problems. Secondly, the fuel reactor will need to be much larger for the proposed process than for ordinary chemical-looping combustion. The reason for this is obvious; the fuel reactor bed must be large enough to contain the reformer tubes. This design may have impact on fluidization characteristics and should be investigated further, but there is no reason to believe that it will hamper the conversion of the offgas.

The size of the fuel reactor has some possible downsides. Firstly, the pressure drop over the fuel reactor bed may become quite large. The pressure drop is proportional to the density of the oxygen carrier and to the bed height. Therefore, an oxygen carrier with low density and a low bed height should be desirable. These parameters, however, are put under constraints. The oxygen-carrier density needs to be balanced with other desired characteristics such as

high reactivity, long life span and a low price. One way to reduce the bed height could be to increase the cross-section area of the fuel reactor. This would make it possible design a broader and flatter reactor. However, increased cross-section area would also lead to reduced fluidizing velocity since the amount of available offgas is fixed for each process configuration.

Secondly, a big fuel reactor also means that the required amounts of oxygen-carrier particles becomes quite large. Naturally, the necessary bed mass is proportional to the density of the oxygen carrier. It shall be noted, however, that it is also a function of the reactor design. One way to reduce both required bed mass and pressure drop over the fuel reactor is to reduce the tube pitch, which is the distance between the tubes in the reactor. This would result in a much more compact fuel reactor design. For the case examined in this paper, a decrease of the distance between the reactor tube centers from 0.24 m to 0.20 m would decrease the total amount of oxygen-carrier particles by 35%, see figure 6.
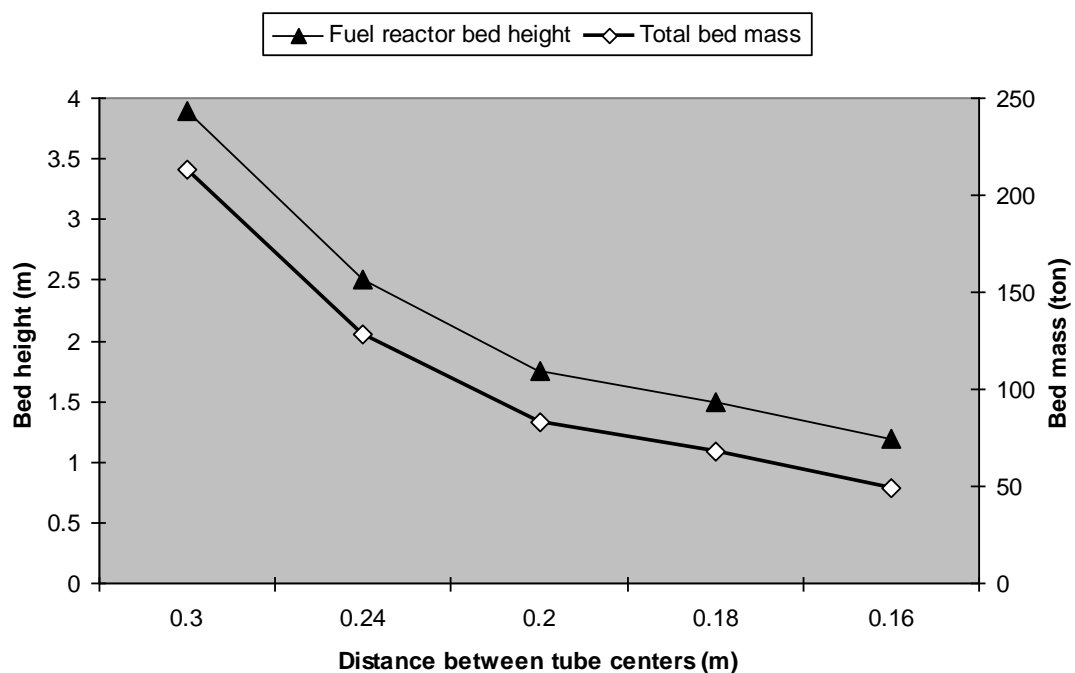
Figure 6. Total bed mass and fuel reactor bed height for the case examined in this paper as a function of tube pitch in the fuel reactor. The pressure drop is proportional to the bed height.

In general, high reactor temperatures are desirable. Increased reformer temperature reduces the required steam to carbon ratio and thus increases reformer efficiency. Increasing temperature in the fuel reactor improves heat transfer through the tube walls. This reduces the necessary length of the reactor tubes which reduces tube-side pressure drop. Shorter reactor tubes would also make it possible to design a flatter fuel reactor, with reduced pressure drop over the fluidized bed, as described above. Increasing reformer pressure could also be interesting since it would lead to a more compact reformer, higher H_2 pressure and possibly improved H_2 recovery in the pressure swing adsorption unit. Increased reformer pressure will, however, require increased reformer temperature due to less favorable thermodynamics.

While it is tempting to propose high temperature processes, one should be aware that a fluidized bed is a rather harsh environment. At high temperatures, erosion of the reformer tubes might become a problem. The proposed fuel reactor somewhat resembles fluidized bed heat exchangers used for steam production in fluidized bed coal combustion. Unfortunately, direct comparison is not possible. This kind of heat exchanger tubes are not placed inside the

combustion chamber. Instead, an external vessel fluidized with recirculated flue gases is used due to problems with erosion and corrosion. For coal combustion, high gas velocities are needed in the combustion chamber which promotes erosion. In addition, coal contains highly corrosive components such as sulphur and chlorine. For the case proposed in this paper, the feedstock is desulphurized natural gas so there will be essentially no corrosive components present at all and the gas velocity can be set to low values. Therefore, it seems reasonable to assume that the reformer tubes could be placed directly inside the fuel reactor. However, the option to use an external fluidized bed heat exchanger should not be ruled out. Neither should other principles for highly efficient heat exchange between chemical-looping flue gases and reforming reactions.

The heat-transfer coefficient for the outside of a tube in a fluidized bed is much higher than for a tube in a furnace, so it should be relatively easy to obtain and maintain desired reformer temperature. If a certain temperature profile is desired, the bed could be divided into segments set to operate at different temperatures. This could be interesting, for example to reduce thermal stress, optimize heat transfer or hamper formation of solid carbon.

Finally, it should be noticed that conventional steam reformer furnaces usually operate with very high outlet temperatures. This is necessary since heat transfer from the flue gases to the reformer tubes is mainly due to radiation. In a typical reformer furnace, about 50% of the heat produced by combustion is transferred through the tube walls and absorbed by the process [21, 22]. The other half is bound to the hot flue gases and transferred to a waste heat recovery section, where it is used for preheating and for generation of export steam. The overall thermal efficiency for a steam reforming plant can be as high as 95% but the reformer efficiency, if defined as the lower heating value of produced H_2 divided by lower heating value of consumed fuel, is often not more than 60-75%. If a larger share of the combustion heat was used for steam reforming rather than for production of export steam, it would be possible increase the H_2 production. This can be achieved either by increasing the preheating or by reducing the outlet temperature of the furnace, see figure 7.
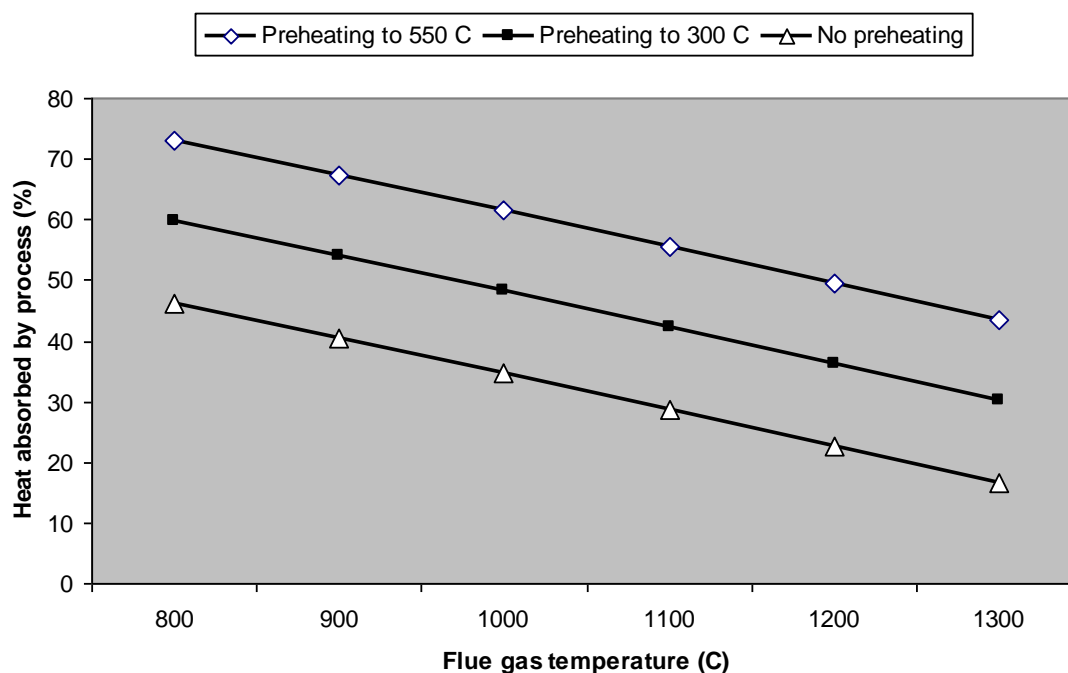

Figure 7. Heat absorbed by a steam reforming process as function of flue gas temperature. The fuel is offgas consisting of 23% H_2, 18% CH_4, 6% CO and 53% CO_2, and it is assumed that it is burned in a furnace with 10% excess air.

The reformer process proposed in this paper utilizes added offgas so well that there is no need for any steam export. This is possible due to the high heat-transfer coefficient on the outside of the reformer tubes, which makes it possible to operate the reactors at moderate temperatures. This opens an opportunity to design processes with improved selectivity towards H_2 and higher reformer efficiency than conventional steam reformers, with the added feature of CO_2 capture.

6. CONCLUSION

A novel process for production of H_2 by steam reforming of natural gas with inherent CO_2 capture by chemical-looping combustion is proposed. The reformer efficiency is the same as for H_2 production by steam reforming with comparable process parameters. A preliminary reactor design has been made in order to demonstrate the feasibility of the process. The reactor dimensions, particle flows and pressure drops seems reasonable. The temperature in the reactors can be kept well below 1000 ºC, possibly below 900 ºC. In addition to CO_2 capture, the proposed process has potential to achieve higher selectivity towards H_2 than conventional steam reforming plants. This is because of the low temperature in the reactors and the high heat-transfer coefficient on the outside of the reformer tubes, which makes it possible to utilize more of the energy provided with the fuel for reforming, rather than for production of export steam.

7. ACKNOWLEDGEMENTS

8. APPENDIX

8.1 Nomenclature

A = Surface area (m^2)
Cp = heat capacity (J/mol K)
D = Tube diameter (m)
d = Particle diameter or catalyst pellet equivalent diameter (m)
F = molar flow (mol/s)
G = superficial mass velocity (kg/m^2 s)
H = height (m)
Hi = lower heating value (J/mol)
K = equilibrium constant
k = thermal conductivity (W/m K)
L = length (m)
m = mass (kg)
M = mass flow (kg/s)
N = generic number
P = Power (W)
p = pressure or partial pressure (Pa)
Pr = Prandtl number
Q = heat transfer (J/s)

q = heat flux (W/m^2)
R = universal gas constant (J/mol K)
Re = Reynolds number
r = rate of reaction (mol/s bar kg of catalyst)
T = Temperature (K)
u = superficial gas velocity (m/s)
V = volume flow (m^3/s)
W = width (m)
x = mol fraction
α = heat transfer coefficient (W/m^2 K)
ε = void factor
η = efficiency
ø = sphericity
ρ = density (kg/m^3)
μ = kinematic viscosity (kg/m s)
λ = generic ratio

8.2 Subscripts

amb = ambient
ar = air reactor
bed = fluidized bed
cat = catalyst particle
comp = compressor
fan = air fan
fr = fuel reactor
g = gas
i = inside
in = inlet
max = maximal
min = minimal
o = outside
out = outlet
offg = pressure swing adsorption offgas
oxc = oxygen carrier particles
ref = reformer reactor or reformer tube
preh = preheater
psa = pressure swing adsorption unit
pump = water pump
shift = water-gas shift reactor
wall = tube wall

8.3 Expressions used in the reformer tube model

Heat transfer from the fluidized bed to the reformer tube, from Kim et al [30].

$$\alpha_{wall,o} = 35.8 \times \rho_{oxc}^{0.2} \times k_{g,fr}^{0.6} \times d_{oxc}^{-0.36}$$
$$q_{wall,o} = \alpha_{wall,o} \times (T_{fr} - T_{wall,o})$$

Heat transfer from the inside of the reformer tube to process gas, from Saraf et al [29].

$$\alpha_{wall,i} = (k_{g,ref}/d_{cat}) \times [2.58 \times (Re_{cat})^{1/3} \times (Pr_{g,ref})^{1/3} + 0.094 \times (Re_{cat})^{0.8} \times (Pr_{g,ref})^{0.4}]$$
$$Re_{cat} = (d_{cat} \times G_{ref})/\mu_{g,ref}$$
$$Pr_g = (Cp_{g,ref} \times \mu_{g,ref})/K_{g,ref}$$
$$q_{wall,i} = 0.4 \times \alpha_{wall,i} \times (T_{wall,i} - T_{gas})$$

Heat transfer through the tube wall, from Saraf et al [29].

$$q_{wall} = [2 \times k_{wall} \times (T_{wall,o} - T_{wall,i})]/[D_o \times \ln(D_o/D_i)]$$
$$q_{wall} = (D_i \times q_{wall,i})/D_o$$

Rate equations, from Saraf et al [29].

$$r_1 = A_1 \times \exp[-E_1/(R \times T)] \times [p_{CH4} - (p_{H2}^3 \times p_{CO})/(K_{eq6} \times p_{H2O})]$$
$$r_2 = A_2 \times \exp[-E_2/(R \times T)] \times [p_{CO} - (p_{H2} \times p_{CO2})/(K_{eq7} \times p_{H2O})]$$
r_1 = rate of reaction for reaction 6 (mol/s bar kg of catalyst)
r_2 = rate of reaction for reaction 7 (mol/s bar kg of catalyst)
A_1 = 34.8 (mol/s bar kg of catalyst)
A_2 = 833.7 (mol/s bar kg of catalyst)
E_1 = 36751 (J/mol)
E_2 = 58150 (J/mol)

Pressure drop, Ergun's equation from Saraf et al [29].

$$dp/dL = -[150 \times (1-\varepsilon_{ref})/Re_{cat} + 1.75] \times (G_{ref}^2/\rho_{g,ref}) \times (1/d_{cat}) \times [(1-\varepsilon_{ref})/\varepsilon_{ref}^3]$$

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