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High purity hydrogen production with a 10kW$_{th}$ RESC prototype system

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ABSTRACT

The Reformer Steam Iron Cycle (RESC) is suitable to attain high-purity pressurized hydrogen from a broad range of renewables and residues in decentralized on-site applications. This paper introduces a 10 kW$_{th}$ lab prototype system for high purity hydrogen production exceeding 99.999%. The significantly enlarged reactor system comprises of a combined steam reformer and fixed bed chemical looping system within a single unit. A series of experiments was conducted to demonstrate the system applicability for decentralized hydrogen production with an improved process layout. A previously undiscovered hydrogen purity was realized from a fixed-bed chemical looping prototype system. Supplementary, the applied oxygen carrier material was characterized to reveal occurring degradation effects in large-size reactors as a significantly increased thermal stress. A characterization by SEM, EDX, light microscopy and BET methods was performed to exhibit the effects on the pelletised material.

1. Introduction

There is a broad consensus in the scientific community that there is a human-caused greenhouse gas emission increase since the beginning of the industrial revolution in the second half of the 18th century. Since the first utilization of coal in steam turbines, resources as fossil oil, natural gas and coal provided the increasing energy demand for mobility applications and electrical power generation. In their fifth assessment report, the International Panel for Climate Change (IPCC) reported anthropogenic greenhouse gas emissions are extremely likely to be the dominant cause of the current temperature increase since the 19th century [1].

Hydrogen is proposed as a suitable secondary energy carrier to replace fossil hydrocarbons for both mobility applications as well as to face the future demand for volatile renewable energy storage and distribution [2]. More than 95% of today's hydrogen is supplied from industrial scale steam reforming of natural gas or other fossil feedstock in centralized plants [3]. Efficient hydrogen production methods utilizing locally available renewables have to be found to facilitate a sustainable energy system. A widespread use of hydrogen as energy carrier for mobility applications is currently impeded by high logistical efforts and costs to serve decentralized filling stations [4]. Currently compressed or liquid hydrogen has to be shipped over long distances from centralized production sites to local customers. The drawback in shipping hydrogen is the considerably low volumetric energy density of 500 MJ m^{-3} and 1800 MJ m^{-3} for compressed hydrogen at 50 and 200 bar, respectively, compared to conventional diesel fuel with 36,000 MJ m^{-3}.

The environmental sustainability of hydrogen as a secondary energy carrier is highly influenced by the production method. There are several opportunities for a sustainable hydrogen production presented in literature, e.g. from electrolysis using excess power from wind turbines or hydropower as well as to purify syngas from biomass gasification with conventional methods as pressure swing adsorption. Different approaches are discussed for the conversion of biomass into hydrogen like anaerobic fermentation of biomass or production of syngas from biomass or residues as feedstock with pyrolysis or gasification and subsequent gas purification. The chemical looping processes can utilize a wide range of reducible gases to produce hydrogen and are outreaching to utilize renewable bio-based feedstocks for high-purity hydrogen production with integrated carbon dioxide sequestration. Several renewables like gasified biomass, landfill gas, bioethanol or biogas are proposed for hydrogen production from chemical looping systems [5–12].

2. Chemical looping hydrogen production

In chemical looping processes for hydrogen production, an oxygen carrier is reduced from a metal oxide to a metal or a metal oxide with lower oxidation stage with a reductive gas. In the second step, steam reconverts the oxygen carrier to a metal oxide and pure hydrogen is released after a condensation of excess steam. Several materials as iron, copper, cerium or tungsten exhibit suitable thermodynamic properties for chemical looping hydrogen systems regarding the chemical equilibrium [13]. Iron oxide as an easily available, cheap and non-toxic metal

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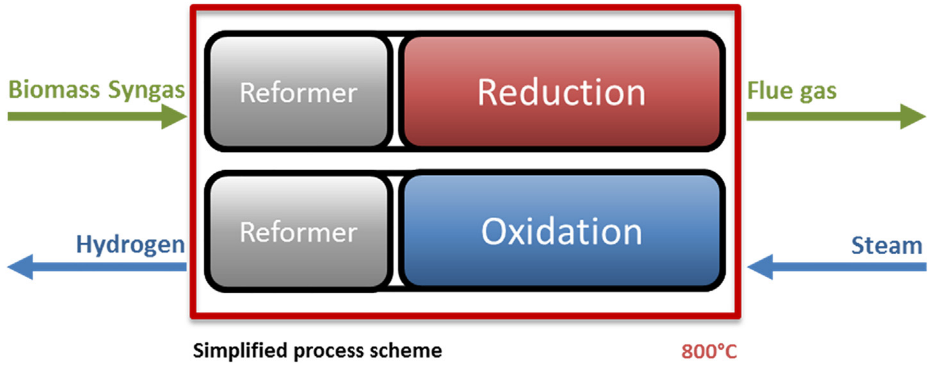

Fig. 1. Schematic process scheme of the RESC-process based on the chemical-looping principle.

has superior properties for this purpose. The stabilization of the iron oxide with different high melting metal oxides as e.g. aluminum oxide, titanium oxide, calcium oxide or cerium oxide is required to preserve the conversion stability and enhances the reactivity in these high-temperature process conditions [14].

Prototype reactor systems were implemented as circulating fluidized bed systems with separate reactors for each reaction step or in a fixed bed configuration [15–17]. The fluidized bed process scheme is well suitable for continuous hydrogen production in large-scale plants [18], for small-scale decentralized hydrogen production, a more simple process design without moving parts would be preferred.

Hacker et. Al. proposed a process scheme with cyclic reduction and oxidation of an iron based oxygen carrier for hydrogen production (Fig. 1) [19]. In a single tubular fixed-bed reactor, a conventional steam-reformer for the conversion of various hydrocarbons is combined with an oxygen carrier bulk for hydrogen purification [20]. In the reduction step, a reducible syngas is produced from a hydrocarbon feedstock, i.e. bioethanol or methane, via steam reforming. Subsequently, the syngas reduces the present magnetite in the reactor to wuestite and iron (Eqs. (3) and (4)).

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \Delta H_{R,298} = +205.9\,\text{kJ mol}^{-1} \tag{1}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H_{R,298} = -41.1\,\text{kJ mol}^{-1} \tag{2}$$

$$Fe_3O_4 + H_2/CO \rightarrow 3FeO + H_2O/CO_2 \qquad \Delta H_{R,298} = +74.7/+33.6\,\text{kJ mol}^{-1} \tag{3}$$

$$FeO + H_2/CO \rightarrow FeO + H_2O/CO_2 \qquad \Delta H_{R,298} = +25.4/-15.7\,\text{kJ mol}^{-1} \tag{4}$$

In the oxidation step, steam reconverts the iron-based oxygen carrier to magnetite (Eqs. (5) and (6)). The oxygen atom bonds within the metal lattice and hydrogen is released. The direct allocation of a pre-pressurized product gas from this reactor system is feasible by compressing the liquid water before vaporizing, as this would result in considerable energy savings for hydrogen pressurization [21,22]. As already presented by our research group, direct high-pressure hydrogen production within a small-scale test bench has already been published with synthetic gas mixtures, constituting like syngas from different renewable feedstock [23,24].

$$3FeO + H_2O \rightarrow Fe_3O_4 + H_2 \qquad \Delta H_{R,298} = -74.7\,\text{kJ mol}^{-1} \tag{5}$$

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2 \qquad \Delta H_{R,298} = -151.1\,\text{kJ mol}^{-1} \tag{6}$$

Due to the combined fixed-bed reactor system, the required space can be minimized to the bulk density of the oxygen carrier. Fixed-bed operation is ideal for the decentralized conversion of renewable gases, since the reactor operation does not demand for a continuous fluidization and is able to handle strongly fluctuating renewable resources. Therefore, the layout of a very compact and highly integrated system design is feasible for small- and medium scale applications by periodically shifting the input gas. In contrast to fluidized bed operation, a fixed-bed reactor system would allow the permanent storage of reduced iron in the reactor with a volumetric storage density even exceeding a 700 bar pressure vessel. This is especially of interest in future renewable energy systems, if a varying feedstock availability and a discontinuous hydrogen withdrawal i.e. at fueling stations has to be balanced. The process-integrated storage of a chemically bonded energy can therefore contribute to a higher uptime to utilize a continuous biogas stream but offering a discontinuous on-demand hydrogen production.

The objective of this study is to demonstrate high purity hydrogen production from methane and the impact of important process parameters within a 10 kW fixed-bed chemical looping prototype based on the RESC process.

3. Experimental

3.1. Oxygen carrier synthesis

The applied oxygen carrier material was made from 80% Fe_2O_3 and 20% Al_2O_3 powder (Alfa Aesar). The materials were dry mixed and pelletized using an intensive mixer (Eirich EL1). Afterwards, the pellets were calcined in air at 900 °C for 6 h. The particle size distribution of the pelletized sample was analyzed with an image scanner and evaluated with the program ImageJ.

3.2. Oxygen carrier stability evaluation

The pelletized oxygen carrier was analyzed in a thermogravimetric device (Netzsch STA449 C) to determine the conversion stability of single pellets. Hydrogen was used as reductive gas (50 NmL min^{-1} H_2, 50 NmL min^{-1} N_2) and steam from an external vaporizer (ADrop DV-2) oxidized the oxygen carrier material (3.6 g h^{-1} H_2O, 50 NmL min^{-1} N2). The furnace temperature was set to 800 °C and the powder temperature was measured on the sample holder beneath the iron-oxide pellet.

A thermogravimetric lab-scale test bench was assembled to determine the conversion stability of the pelletized oxygen carrier material in a packed bed (Fig. 2). An external heated reactor system with an inner diameter of 44 mm filled with 250–500 g of pelletized oxygen carrier (red shaded area) was cyclic reduced and oxidized with pure hydrogen (15 NL min^{-1}) and steam (10 g min^{-1}). The reactor was purged with nitrogen between reduction and oxidation phases to determine the mass difference. A digital scale (Kern ILS 30 K/4C) with a precision of ± 1 g measured the mass change of the whole reactor system to evaluate the oxygen carrier conversion. Inert aluminum oxide pellets (grey shaded area, Alfa Aesar) were used to preheat the gas feed on both sides.

The temperature of the furnace was set to a specific value, the temperature inside the packed bed was measured with a single thermocouple to determine the temperature change by the exothermic and