



The production of pure pressurised hydrogen by the reformer-steam iron process in a fixed bed reactor system



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HIGHLIGHTS

- Carbon monoxide free hydrogen is produced from syngas.
- Hydrogen is generated at elevated pressure.
- Pressurisation of hydrogen by the process itself without an additional compression step.
- Iron oxides are used for hydrogen production.

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ABSTRACT

In this paper a fixed bed chemical looping process for the decentralised production of pure pressurised hydrogen for fuel cell applications is described. CH₄ is converted to a syngas using conventional steam reforming. The syngas is directly used for the reduction of an iron based oxygen carrier. A consecutive oxidation step using steam leads to the formation of pure pressurised hydrogen. A thermodynamic analysis was performed in order to investigate feasible conditions for the syngas generation and reduction step. Experiments using pure hydrogen as well as an artificial syngas mixture showed the feasibility of the process for the production of pressurised hydrogen. A stable hydrogen production at a pressure of 8–11 bar(g) was achieved and only minor impurities of 700 ppm of carbon dioxide but no signs of carbon monoxide were detected in the produced hydrogen. Although the active surface decreased from 7.5 m² g⁻¹ to 0.9 m² g⁻¹ only moderate losses of reactivity were measured in the fixed bed reactor. Thermogravimetric analysis showed a loss of 9% of reactive material over nine cycles, presumably due to sintering effects.

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1. Introduction

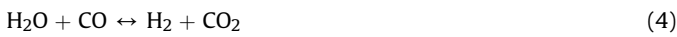
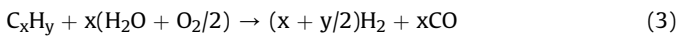
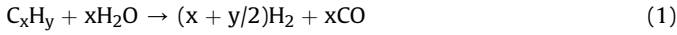
Fuel cells have the potential to make emission free power generation and mobility possible. In order to achieve this goal an area-wide hydrogen supply has to be built up. Today hydrogen is mainly produced for industrial applications and only corresponds to less than 2% of the world's primary energy demand [1]. Therefore major efforts have to be undertaken to increase the capacities for hydrogen production, distribution and storage. One promising approach to achieve a comprehensive supply of hydrogen is its

decentralised production based on an already existing infrastructure. This minimises the efforts needed for hydrogen transportation and long-term storage and enables a continuous growth of the hydrogen production capacity directly connected with the increasing demand for hydrogen. The only already fully commercialised technology for decentralised hydrogen production is electrolysis. But due to its low overall efficiency this process is only to favour in periods of overproduction of electric energy. On the other hand the decentralised conversion of hydrocarbons to a hydrogen rich syngas enables hydrogen production without such limitations. In the beginning this production method will be based on fossil fuels such as natural gas and gasoline. In a long term perspective the conversion of renewable resources such as bio-ethanol,

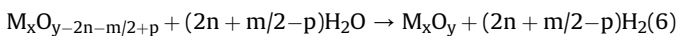
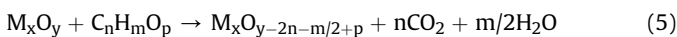
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glycerine, solid biomass or biogas offers a possibility for hydrogen production without net CO₂ emissions. The production of bio-based energy carriers requires large areas and the energy content of these compounds is low. Therefore transportation over long distances needs high amounts of energy and is economically challenging. This favours the decentralised conversion of renewable resources to hydrogen. The common methods for H₂ production based on hydrocarbons are steam reforming (Eq. (1)), partial oxidation (Eq. (2)) and autothermal reforming (Eq. (3)) which is a combination of Eqs. (1) and (2). These methods produce a CO rich syngas and are often combined with the water-gas shift reaction (Eq. (4)) to increase the amount of produced H₂.



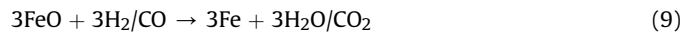
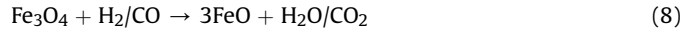
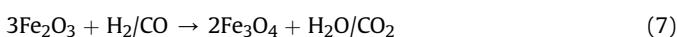
Since the water gas shift reaction is thermodynamically limited at high temperatures and kinetically limited at low temperatures a two-stage process at different temperatures is required to maximise the amount of H₂ in the syngas. In order to remove the CO₂ as well as unreacted CO and C_xH_y an additional purification step is necessary. This final gas clean up can be done by pressure swing adsorption (PSA), monoethanolamine scrubbing (MEA) or membrane based processes. For large scale hydrogen production PSA and MEA are technologically mature and show a good overall efficiency but are difficult to downscale. Membrane based hydrogen production on the other hand shows advantages in decentralised hydrogen production since it enables compact system design and low operation temperatures [2,3]. Though it suffers from high material costs and need further research. Therefore, up to now no technology can completely fulfil the requirements for cost effective and efficient decentralised production of pure hydrogen. An alternative approach for filling this gap is chemical looping hydrogen production (CLH) according to Eqs. (5) and (6).



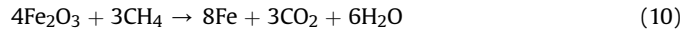
Chemical looping processes such as chemical looping combustion (CLC) and chemical looping reforming (CLR) have gained much interest during the last years as an efficient technology for CO₂ capture and storage applications [4–8] as well as for hydrogen production and purification [9–13].

2. The reformer-steam iron process

We propose the reformer-steam iron process as an innovative process for the decentralised production of pure pressurised hydrogen. The process is based on the *steam iron process* and the *reformer sponge iron cycle* published by Hacker et al. [14,15] which in turn are based on the historic *Messerschmitt-process* [16]. It features production purification and storage of hydrogen based on methane, biogas or higher hydrocarbons in one compact unit. In the first step a catalytic steam reforming reaction according to Eq. (1) is performed. This leads to the formation of a syngas which is rich in CO and H₂ and is used in a consecutive step for the reduction of a haematite-based (Fe₂O₃) oxygen carrier according to Eqs. (7)–(9).



Beside these reactions also direct reduction of haematite with methane following Eq. (10) is possible.



The reduction reactions (7)–(9) are performed at the same temperature as the reforming reaction which allows the realisation of a very simple and compact unit that works without heat exchanging steps between reforming and reduction. After the reduction step the iron is re-oxidised with steam (Eqs. (11) and (12)).



As long as the formation of solid carbon is prevented during the reduction step pure hydrogen for applications such as low temperature fuel cells is generated. After a cooling step to remove unreacted steam from the product, pure hydrogen is obtained. If this process is operated at elevated pressure it is possible to produce pressurised hydrogen without the usage of an additional gas compression step. After the steam-oxidation step an additional oxidation step using air can be used to regenerate magnetite to haematite (Eq. (13)) or the following reduction cycle starts with magnetite.



Different reactor concepts have been investigated but most chemical looping plants operating nowadays use a configuration of two interconnected or circulating fluidised beds [6,12]. Such a configuration offers advantages at large scale applications but for decentralised hydrogen production we propose a system of periodically operated fixed bed reactors where generation of syngas, reduction and oxidation are performed in one compact unit. Instead of moving the solid between two reactors the gas streams are switched between reduction and oxidation. For decentralised hydrogen production this configuration is expected to show three major advantages. The most obvious one is that compared to interconnected fluidised bed technology the fixed bed operation is less complex and more compact. Therefore it represents a simple and cost efficient process for hydrogen production. Furthermore it enables a discontinuous operation and can be used as a hydrogen storage system. By keeping the iron in its reduced state storage of hydrogen without any losses by diffusion or hydrogen boil-off is achieved. A simple steam treatment leads to the re-oxidation of the iron and releases the hydrogen. Based on Eqs. (11) and (12) a calculated mass based storage density of 4.8 wt% is possible [17–19]. The third advantage is that the periodically operation of the reactor enables the production of pressurised hydrogen without an additional gas compression step. State of the art fuel cell powered vehicles store hydrogen in pressure cylinders at a level of 350–700 bar. Therefore, after its generation an additional hydrogen compression step is necessary. This step significantly reduces the efficiency of the whole process and increases the costs of a small-scale hydrogen production unit. The amount of consumed energy as well as the complexity of the compression step can be decreased significantly by increasing the production pressure of the produced hydrogen. Ahluwalia, Hua and Peng calculated the energy demand for the compression of hydrogen from 20 bar to 425 and 850 bar

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