

A novel process for stationary hydrogen production: the reformer sponge iron cycle (RESC)

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Abstract

The reformer sponge iron cycle (RESC) is discussed as a new process for stationary hydrogen production. The RESC is based on the sponge iron reaction process in combination with a reformer unit. The sponge iron reaction process is a cyclic process for water splitting, whereby a syngas is consumed. The syngas reacts with iron oxide (magnetite, Fe_3O_4) to produce a reduced form of iron oxide (wuestite or iron). The reduced iron oxide is re-oxidised with steam to form magnetite and hydrogen. This process is now combined with the reformer to enhance the overall efficiency considerably. The reformer is operated with methane or liquid hydrocarbons and carbon dioxide and steam out of the sponge iron reaction process off-gas are used for the reforming reaction. Experimental investigations concentrate on the lifetime analysis of the contact mass of the sponge iron reaction process and the catalyst performance under given temperature conditions, and syngas and off-gas compositions as discussed in this paper.

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1. Introduction

Hydrogen is used world-wide in a number of industrial applications, like ammonia production, oil refining, methanol production, annealing of steel, food processing, especially for the hydrogenation of fats and oil and as a fuel for propelling the US Space Shuttle. The world-wide search for a clean energy carrier has brought hydrogen into the centre of interest of institutions, companies and governments concerned with energy supply and energy technology. Hydrogen is seen as the ideal fuel to replace the fossil energy system in the long term. To replace the fossil energy system, hydrogen has to be produced out of renewable energy, like solar energy, biomass, wind- or hydropower. This visionary energy concept was often discussed in recent literature. A change of the infrastructure of energy supply has to be carefully prepared and will take several decades. Since the production costs of hydrogen out of renewable are still prohibitive for a large scale use, a first step for the introduction of hydrogen is the production out of fossil fuels. This enables the use of the existing infrastructure in parallel to the development of decentralised hydrogen production infrastructure. Hydrogen is produced on-site, and will be offered not as a substitute, but

in addition to the current energy carriers. An area-wide availability of hydrogen will boost the development of energy technologies, like fuel cells for mobile and stationary applications. The first step of a hydrogen economy will include conventional hydrogen production technologies, like production of hydrogen from natural gas. This paper introduces an innovative hydrogen production process, the reformer sponge iron cycle (RESC). The process is a combination of the sponge iron reaction process and a reformer. Currently the process is investigated with natural gas as primary energy. The near term goal is to adapt the process for liquid hydrocarbons, and in the long term, the process should be optimised for synthesis gas, which can be produced, for example, by the gasification of biomass.

2. Hydrogen production processes

Most of hydrogen production is currently obtained from natural gas. The most important process is the catalysed steam reformation in combination with the water gas shift (WGS) reaction. Steam reforming of methane is strongly endothermic and has to be operated at high temperature, low pressure and relatively high steam to carbon ratio [1–3]. Steam reforming will remain a key technology for the production of syngas out of hydrocarbons. The development

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of advanced hydrogen plants has been supported by a better understanding of the reforming reactions, and the key problem is to avoid the formation of carbon [4–7].

In the concept of catalytic decomposition, natural gas is decomposed over a catalyst. Hydrogen is produced and the carbon is formed in the catalytic bed. The catalytic bed is regenerated when it is filled. The advantages of this process are a high purity of hydrogen (over 95%), no carbon monoxide or carbon dioxide in the fuel stream and an overall simpler and less expensive system compared to steam reforming [8].

Partial oxidation (POX) reactions can be divided into catalytic partial oxidation (CPO), non-catalytic partial oxidation and autothermal reforming (ATR). CPO is initiated catalytically (flameless) as opposed to ATR and other POX reactions. For natural gas, conversion beyond 90% may be achieved, but the reaction is complicated and a comprehensive understanding of CPO is currently lacking. The non-catalytic partial oxidation needs high temperature for complete conversion [3]. ATR is a combination of homogenous partial oxidation and steam reforming. The feed streams (steam, methane, oxygen/air) are mixed in a burner operated around 2000 °C. The final steam reforming takes place in the catalyst bed at 1000–1200 °C [9].

By combining a steam reformer with an autothermal reformer, better energy utilisation can be obtained than with either steam or autothermal reforming alone. Depending on the degree of energy integration and the specific operating conditions, the thermal efficiency can be improved by about 1–2% points [10].

Processes in development are coal gasification, thermochemical cycles and steam–iron coal gasification. Other processes, such as photochemical, photoelectrochemical and photobiological processes are being explored [11]. Maturity for commercial exploitation for hydrogen production was also reached for water electrolysis.

3. Reformer sponge iron cycle (RESC)

The reformer sponge iron cycle (RESC) is a process, designed to convert hydrocarbons to hydrogen with a quality that exceeds the requirements of fuel cells. The main advantage of this process is its simplicity—the RESC process consists of a reformer and a sponge iron reaction (SIR) process. The SIR process was already investigated [12]. The SIR process converts synthesis gas to hydrogen, with the advantage that even considerable amounts of impurities in the synthesis gas do not influence the quality of the produced hydrogen. The limitations of the SIR process are given by thermodynamic equilibria, which results in a low overall efficiency when biomass gas (produced by the gasification of wood) was used. A substantial improvement of overall efficiency is possible via application of a higher caloric reduction gas, like synthesis gas from steam reforming of hydrocarbons.

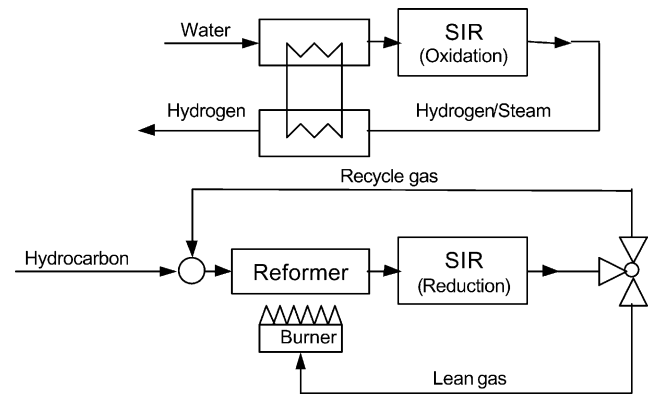


Fig. 1. Concept of the reformer sponge iron cycle (RESC) in oxidation mode (above) and reduction mode (below).

The reformer unit is comparable to the primary reforming step of a hydrogen production plant from natural gas or naphtha. The reformer unit operates at similar temperatures as the SIR, approximately 800–850 °C which eases the system integration of both units. The SIR process replaces the shift conversion as well as the final purification which consists, dependent on the impurities, of a combination of units for carbon dioxide removal, methanation, molecular sieves, purifiers, pressure swing adsorption (PSA) or liquid nitrogen scrubbing.

The process is shown in Fig. 1. A proportion of prospectively 40–55% of the hot off-gas leaving the SIR after iron ore reduction is recycled into the reformer. This off-gas contains CO₂, H₂O as well as non-reacted CO and H₂ (corresponding to the thermodynamic equilibrium in contact with the solid phase, depending on the stage of oxidation of the iron ore). Thus, no or only a slight amount of additional steam is necessary for the reforming process.

The synthesis gas out of the reformer is directly fed to the sponge iron reactor and part of the lean gas is recycled to the reformer. The oxidation step is equal to the conventional SIR

Table 1
Main reactions in the RESC process with heptane as fuel

Reduction	Oxidation
Reformer	
$C_7H_{16} + 3CO_2 \rightarrow 4CH_4 + 6CO$	
$C_7H_{16} + 3H_2O \rightarrow 4CH_4 + 3CO + 3H_2$	
$CH_4 + CO_2 \rightarrow 2CO + 2H_2$	
$CH_4 + H_2O \rightarrow CO + 3H_2$	
$CO_2 + H_2 \rightarrow CO + H_2O$	
SIR process	
$Fe_3O_4 + H_2 \rightarrow 3FeO + H_2O$	$Fe + H_2O \rightarrow FeO + H_2$
$Fe_3O_4 + CO \rightarrow 3FeO + CO_2$	
$FeO + H_2 \rightarrow Fe + H_2O$	$3FeO + H_2O \rightarrow Fe_3O_4 + H_2$
$FeO + CO \rightarrow Fe + CO_2$	
$CO_2 + H_2 \rightarrow CO + H_2O$	

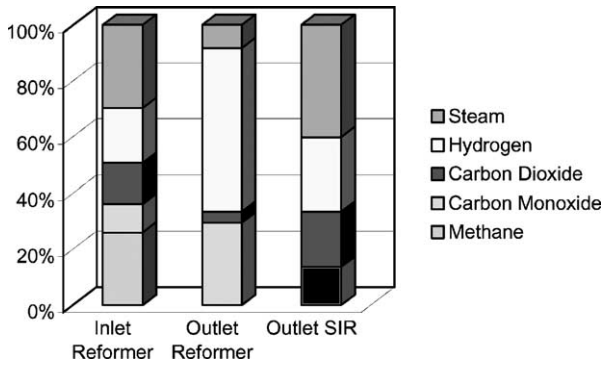


Fig. 2. Gas compositions of RESC process based on equilibrium calculations at the reformer inlet, reformer outlet and sponge iron reaction process outlet at a temperature of 1100 K and a recycle rate of 50%.

process. The main reactions of the process, with heptane as fuel, are shown in Table 1.

The advantage of this process is a high potential synthesis gas that consists mainly of hydrogen and carbon monoxide. The operation of the reformer, the reduction and the oxidation process at these high working temperatures are challenging in respect of the design as well as the process control. Fig. 2 shows the gas compositions of the RESC process based on equilibrium calculations at the reformer inlet, reformer outlet and sponge iron reaction process outlet at a temperature of 1100 K and a recycle rate of 50% (recycle gas).

4. Sponge iron reaction (SIR) process

Hydrogen generation via a redox process, known as the sponge iron reaction process [13,14], was investigated at the institute. The process is based on the reduction of a contact mass by a synthesis gas and the oxidation of the contact mass by steam for the production of pure hydrogen (Fig. 3). Industrial iron ore pellets with an enduring porous structure were selected as contact mass and operation conditions were determined where the process was stable yielding hydrogen sufficiently pure for application in any kind of fuel cell. As the process is basically working in a discontinuous manner, a concept for quasi-continuous performance was worked out. Fuel gas utilisation of synthesis gases and conversion rate of the iron largely depends on the reduction potential of the inlet gas and the process temperature. The reduction potential is defined by the relation of outlet gas composition to inlet gas composition. The theoretical thermal efficiency calculated by the ratio of heating values of generated

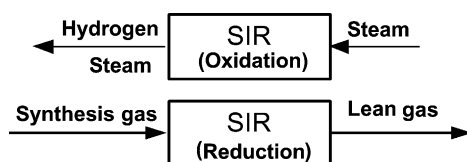
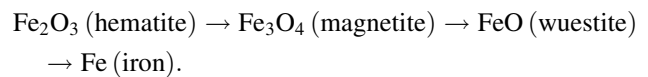


Fig. 3. Concept of the sponge iron reaction process.

hydrogen and input gas results in approximately 45% for very low BTU gases (e.g. synthesis gas produced by the gasification of wood), a value which was also proven by experimental investigations of the process. In addition, direct conversion of hydrocarbons in the SIR process was investigated. The methane conversion principally takes place either by direct reduction or by steam reforming on the iron surface. Experiments showed that the direct methane conversion in the SIR is generally not satisfactory and that the process is strongly temperature dependent and slow at 800 °C. Due to methane conversion carbon decomposition cannot be avoided, which depends on the carbon to water ratio of the synthesis gas. First investigations of *n*-heptane were made to investigate the use of liquid hydrocarbons. Conversion of *n*-heptane was approximately 60%, however, in the drain gas a methane rate of 17% was detected. The methane is a crack product from *n*-heptane, can hardly be converted and cannot be recycled (like liquid products could). Also, as in the direct methane application, carbon deposition took place.

4.1. Conversion rate

The conversion of the contact mass depends on the ratio of hydrogen to steam and carbon monoxide to carbon dioxide in the synthesis gas of the SIR. During the reduction, first the synthesis gas reacts with magnetite. Magnetite is converted into wuestite (the content of oxygen in the wuestite varies through the wuestite phase) and finally to iron:



Steam is used as oxidant. The reaction starts with wuestite or iron. The off-gas consists of steam and hydrogen. Higher temperature results in a higher concentration of hydrogen rate in the off-gas. With the enhancement of the synthesis gas, increased gas utilisation is feasible. The entire process is endothermic. In the RESC process, the deployed feed heat value per mole of methane is approximately equal to the lean gas heat demand per mole of methane. The theoretical outcome supplies thermal efficiencies of the RESC up to 95% in relation to a maximum of 55% in the SIR process.

The maximum hydrogen production depends on the slower process step, which is the reduction of iron oxide to iron. Reduction tests showed an oxygen removal value of approximately 70 g/(kg iron h) between the magnetite and the wuestite phase. Based on this value, 1 kg of iron would produce approximately 9 g hydrogen/h (100 dm³/h) (oxidation time equals zero) which is equal to a higher heating value of the hydrogen produced of 354 W.

5. Reformer

The objective is the development of a system, that works with a minimum amount of recycled SIR off-gas, possibly

without additional steam, at low pressures and temperatures around 800–850 °C to gain a synthesis gas of high reduction potential.

Numerous reforming processes of methane and other hydrocarbons using steam and/or CO₂ are described in literature [15–21]. The formation of carbon during the methane reformation with CO₂ deactivates conventional reformer catalysts, like Ni whereas noble metals (Rh, Ru, Pt) do not cause carbon deposition. The steam to carbon dioxide ratio influences the carbon formation on the catalyst and is currently investigated for selected gas compositions of the RESC process in an electrically heated catalyst test facility consisting of a small (diameter 20 mm) tubular retort providing on-line temperature measurement by PC connected thermocouples as well as off-gas analysis (Caldos and Uras gas analyser as well as GC). For tests of catalyst combinations, the retort is equipped with three separate exchangeable catalyst beds. This test unit provides data for the construction of a small demonstration unit.

6. Summary

The central advantages of the RESC can be summarised as follows:

- The recycle stream out of the off-gas of the reduction reaction is fed to the reformer. Therefore, no (or less) additional steam or carbon dioxide for the conversion of the fuel and the generation of synthesis gas for the hydrogen production in the reformer is needed.
- The high steam to carbon ratio and the relatively low CO₂ to carbon ratio is advantageous for the avoidance of carbon deposition.
- Direct connection of reformer and fine purification (SIR) due to the same working temperature, no intermediate heating or cooling necessary.
- Good product gas quality with very low CO and CO₂ levels.
- With conventional synthesis gas, the contact mass of the SIR process reacts between wuestite and magnetite. With the RESC process, it will be feasible to operate from magnetite to iron. Consequently the utilisation of synthesis gas is higher and the efficiency increases.

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