

## Hydrogen production by steam–iron process

Viktor Hacker <sup>a,\*</sup>, Robert Fankhauser <sup>a</sup>, Gottfried Faleschini <sup>a</sup>, Heidrun Fuchs <sup>a</sup>,  
Kurt Friedrich <sup>a</sup>, Michael Muhr <sup>a</sup>, Karl Kordesch <sup>b</sup>

<sup>a</sup> Innovative Energy Technology, Institute of High Voltage Engineering, Technical University of Graz, Inffeldgasse 18, 8010 Graz Austria

<sup>b</sup> Institute for Chemical Technology of Inorganic Materials, Technical University of Graz, Graz, Austria

Accepted 26 October 1999

### Abstract

The steam–iron process is one of the oldest methods of producing hydrogen. It is a cyclic process for water cleavage, whereby coal is consumed. Coal is gassified to a lean reducing gas, containing carbon monoxide and hydrogen. This gas reacts with iron oxides (haematite Fe<sub>2</sub>O<sub>3</sub>, magnetite Fe<sub>3</sub>O<sub>4</sub>, wuestite FeO) to produce a reduced form of iron oxide (wuestite FeO, iron Fe). The reduced iron oxide is re-oxidised with steam to form magnetite and hydrogen. After studies concerning theoretical limitations, the subsequent practical realisation by construction of a suitable laboratory prototype reactor was performed. Further, the investigation and optimisation of process variables, accompanied by respective chemical analyses, and finally the simulation of the whole process and the design of a demonstration plant for electricity generation system in the range of 10 MW were carried out. The resulting overall efficiency (heat and electricity) of the respective power plant was calculated as 35% and the electrical efficiency at about 25%. The operation of the small scale “Sponge Iron Reactor” (SIR) showed that the hydrogen produced is sufficiently pure for use in any kind of fuel cell (CO < 10 ppm). © 2000 Elsevier Science S.A. All rights reserved.

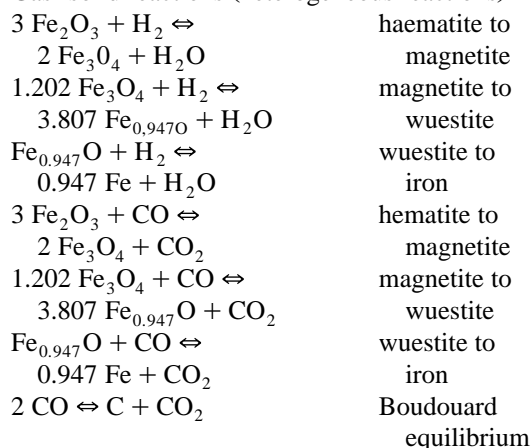
**Keywords:** Hydrogen; Steam–iron process; Water cleavage

### 1. Process principle

The SIR links together research into renewable energy sources and fuel cell technology, as it offers an opportunity to generate pure hydrogen from gasified biomass. The principle of the process is analogous to the old Steam Iron Process, which was developed in the late 19th/early 20th century to produce hydrogen from gasified coal, mainly for use in aerial navigation [1]. The process operates two stages: during the reduction step the iron ores are reduced by synthesis or biomass gas, which is thereby oxidised to a lean gas with low remaining CO (6–8%) and H<sub>2</sub> (ca. 6%) content. In the subsequent oxidation step, the iron ore is re-oxidised by water vapour yielding an hydrogen rich fuel gas. Using a standard biomass gas composition, the iron ore is only reduced as far as the wuestite stage. Depending

on operating temperature, water vapour is converted to about 28% hydrogen during oxidation [2–5].

Gas–solid reactions (heterogeneous reactions)



Gas–gas reactions (homogeneous reactions)



\* Corresponding author. Fax: +43-316-873-7900; e-mail: hacker@hspt.tu-graz.ac.at

## 2. Experimental results

The process was investigated in a laboratory fixed bed reactor in the temperature range of 750–900°C. As contact mass, commercial sponge iron pellets with a high inner surface area and resistant porous structure were selected (filling 1–5 kg). Biomass gas was simulated by mixing synthetic gases.

### 2.1. Process stability

Long-term stability of the contact mass and constantly high conversion rates are crucial for economic feasibility of the whole process. Experiments were carried out over a period of about 40 h at average temperatures of 800°C, 850°C and 900°C. As the reduction and oxidation reaction become slow in the vicinity of 100% conversion to magnetite and wuestite, we chose a definite area which is optimally positioned nearer to the magnetite than the wuestite border. So, we utilised 40–60% of the total redox potential of the contact mass between wuestite and magnetite (Figs. 1 and 2). To define the reactive zone, the 100% magnetite and wuestite limits were determined at the beginning of each experiment by complete reduction and oxidation in the first cycle.

Comparing the duration of reduction and oxidation it was found that, at lower temperatures, both conversion rates are less than at higher temperatures over several cycles. At 800°C, reduction times increase about 2.2% and oxidation times about 11% from cycle to cycle, whereas at 850°C, the duration of the reduction increases about 3% and oxidation about 4.5% per cycle. At 900°C, however, the reactivity loss per cycle was only 1% for reduction and less than 1% for oxidation. Originally, it had been supposed that cycle stability became worse with higher working temperatures. Present experimental results, however, show the contrary is true.

### 2.2. Quality of produced hydrogen

Besides long-term stability, the level of gas purification by the Sponge Iron Process is a fundamental parameter for its applicability in fuel cells. Gassified biomass contains

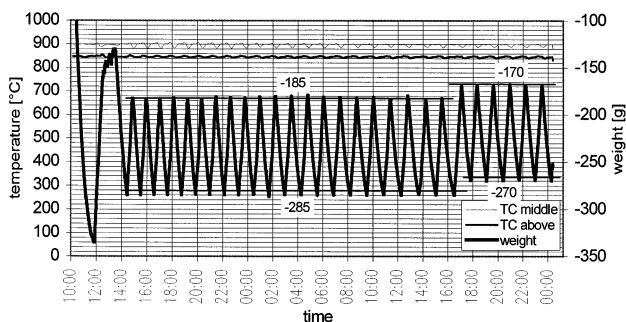


Fig. 1. Redox cycles with SEK-Pellets at 900°C.

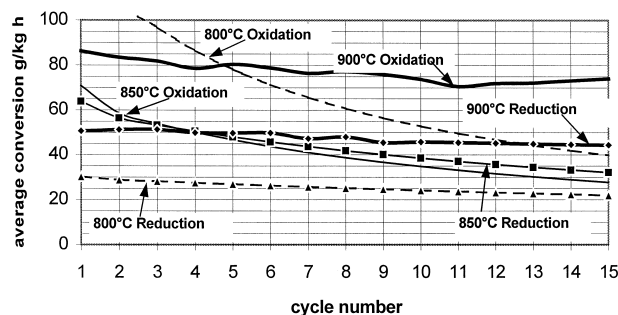


Fig. 2. Average conversion rate (mass difference per kg pellets per hour) at different operation temperatures over 15 redox cycles.

impurities such as amine and sulfur compounds as well as halogenides. For  $\text{H}_2\text{S}$  and  $\text{HCl}$ , an amount of  $0.02 \pm 0.01$  vol.% was estimated. Finally, tar and dust may be troublesome; removal is costly and, therefore, it would be advantageous, if these components could be eliminated in one step in the SIR. Attention was focussed upon the most insidious impurities in hydrogen, namely  $\text{CO}$ ,  $\text{H}_2\text{S}$  and  $\text{HCl}$ . Gas components in the ppm range were measured via a bleed from the flow of the exhaust gases through a Dräger test system.

#### 2.2.1. Carbon monoxide

For use in polymer electrolyte fuel cells, PEFC, the  $\text{CO}$  content has to be well below 30 ppm. Two redox cycles were performed with a bottoming of 4.6 kg pellets at 800°C. After reduction, the purity of the oxidation gas was measured by a Dräger tube for carbon monoxide (8/a measuring range 8–150 ppm  $\text{CO}$ ). Directly after switching from reduction to oxidation, 20 ppm  $\text{CO}$  was found. In the second cycle,  $\text{N}_2$  was flushed through the reactor for 10 min between the reduction and oxidation process, in order to remove the reduction gas mixture from the reactor as well as from the condenser coils. After this procedure a residual  $\text{CO}$  content of 4–8 ppm was found in the dry oxidation exhaust gas. Consequently, the hydrogen produced meets the requirements of a PEFC. As  $\text{CO}$  is soluble in water to an extent of 0.022 l/kg at 20°C, in practise it might be advisable to use a separate gas condenser for the oxidation and for the reduction gas, or, alternatively, not to condense the water in the off-gas after reduction.

#### 2.2.2. Hydrogen chloride

Five cycles with addition of  $\text{HCl}$  (0.06 mol/l in water, corresponding to 0.021 vol.% in the reduction gas mixture) were studied with 4.6 kg SEK pellets at 900°C. Between reduction and oxidation, the reactor was flushed with  $\text{N}_2$  for 3 min for the reasons mentioned above. In the dry oxidation gas stream, (after  $\text{CaCl}_2$ ),  $\text{HCl}$  was only detected in traces after 10-fold extension of the measuring range of a Dräger  $\text{HCl}$  1/a Tube (normal range: 1 to 10 ppm). Then, after condensation, the product gas was bubbled through a receiver flask filled with concentrated  $\text{NaOH}$ .

Analysis of condensed waters and the receiver solution was carried out by titration with  $\text{AgNO}_3$  following the method of Mohr. According to these calculations, virtually no HCl is retained by the contact mass, being removed during oxidation by steam. Clearly, HCl in the product gas is bound mainly to water and is removed from the hydrogen by condensation. Depending on the HCl sensitivity of the chosen fuel cell, a more or less complete condensation of water will be necessary. No influence of HCl on reaction kinetics was detected.

### 2.2.3. Hydrogen sulfide

The oxidation gas stream was analysed by a Dräger tube for hydrogen sulfide 0.5/a (normal range 0.5 to 15 ppm, extension of range by more pump strokes possible) after passing through a  $\text{CaCl}_2$ -filled drying tube which is necessary, as a too high moisture interferes with the analysis. The individually collected condensed waters, after reduction and oxidation, were qualitatively analysed by reaction with lead acetate, as well as by the iodine/azide reaction. As  $\text{H}_2\text{S}$  is an intensely odorous substance (threshold ca.  $0.2 \mu\text{g H}_2\text{S}$ ), the odour was also taken as indication of its presence. Quantitative analysis of  $\text{H}_2\text{S}$ -waters were carried out by iodometric titration. Solid contact mass, as well as samples of condensed waters drawn from the long-term experiment described below, were analysed by inductively-coupled argon plasma mass spectrometer, ICPMS. Initially,  $\text{H}_2\text{S}$  was fed to the reduction gas as  $\text{H}_2\text{S}$ -water, however, only  $\text{H}_2\text{S}$  concentrations of 0.005 vol.% could be attained in the reduction gas stream. In order to judge the process behaviour under elevated  $\text{H}_2\text{S}$  stress,  $\text{H}_2\text{S}$  was introduced during reduction as a 3% gas mixture in  $\text{N}_2$ . In the condensed waters of the reduction reaction,  $\text{H}_2\text{S}$  was perceptible by odour after the 3rd reduction cycle. The 4th and 5th cycle condensed water samples after reduction gave a positive reaction with iodine/azide. In the condensed water specimens after the (hydrogen generating) oxidation, a slightly positive reaction with iodine/azine and a detectable smell was only found after the 5th oxidation cycle. However, in the dried hydrogen produced no  $\text{H}_2\text{S}$  could be detected by Dräger tubes.

### 2.3. Results of the experimental phase

- Pellets with the lowest iron content best matched the requirements for mechanical and cycle stability.
- High working temperatures are favoured for good hydrogen productivity. Increasing the temperature results in a better redox potential of biomass gas and oxidation, which though not favoured thermodynamically, yielded approx. similar  $\text{H}_2:\text{H}_2\text{O}$  ratio as with lower temperatures.
- For biomass gas utilisation, in general, an approximation to thermodynamic conversion is possible.
- Hydrogen productivity, expressed in terms of mass of iron ore material utilised, is best in a narrow reactive regime. In these experiments, 22–28 nl hydrogen per kg pellets per hour is produced.
- Cycle stability of the material used was most satisfactory at  $900^\circ\text{C}$ . Cycle stability is a parameter to be optimised for process performance. An average life-time of the contact mass of 3 months has to be achieved. The addition of  $\text{H}_2\text{S}$  had no influence on cycle stability.
- Purity of produced hydrogen ( $\text{CO} < 8 \text{ ppm}$ ,  $\text{HCl} < 4 \text{ ppm}$ ,  $\text{H}_2\text{S} < 1 \text{ ppm}$ ) is sufficient for application in any fuel cell [6,7].

### 3. Simulation SIR

The software Sponge Iron Bed Calculation (SIBCalc) was generated at the Institute for Apparatus Design, Particle and Combustion Technology (Prof. G. Krammer, Technical University of Graz). This program uses the existing software “ReaSim 4.3” [9] which was developed at the same institute. ReaSim 4.3 enables the calculation of chemical reactions of gas flows in packed beds. Therefore, a one-dimensional (considering only time and a length axis), pseudo-heterogeneous (two separated phases considered, gas and solid phase, without a priori separation in the calculation box), model is applied.

The temperature distribution during reduction from haematite to wuestite by hydrogen was calculated. The temperature is represented as a function of reactor length (0.5 m) and duration of the reaction (15000 s). This is shown in Fig. 3. The gas phase temperature (solid line) and the temperature of the solid phase (dashed line) are depicted in this diagram. These temperatures are calculated for individual durations of reactions of 0, 2000, 4000, 6000, 8000 and 10000 s. The temperature at time 0 s has a constant value of 1073 K over all the reactor length. At a time of 2000 s there is a minimum in temperature (about

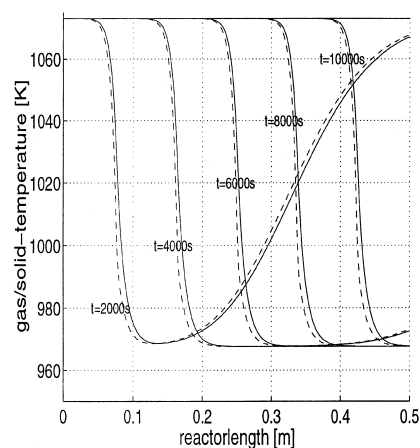


Fig. 3. Gas and solid phase temperature as a function of the reactor length and time [10].

970 K) at a length of 0.14 m. Afterwards, the temperature increases, since the reaction is not completed over the entire reactor. The reactor has an initial temperature of 1073 K. For all subsequent times, the temperature minimum moves to positive abscissa. The highest temperatures in the reactor are limited by the temperature of the reduction gas at the entrance of the retort. The minimum temperature results from the chemical equilibrium of the endothermic reaction.

#### 4. Design of a SIR demonstration plant

The operation temperature of the SIR favours the usage of a high temperature fuel cell for electricity generation. A Solid Oxide Fuel Cell, SOFC, was chosen. The power plant consists of a gasifier, SIR and SOFC. The 2-fold amount of retorts for the reduction step than for the oxidation is necessary since the oxidation rate is approx. two times faster than the reduction rate at the temperature of 800°C [8]. The sponge iron process requires re-heating after the oxidation to raise the temperature to about 800°C, as reduction is an exothermic process. The heat is supported by lean gas combustion.

We established the number of retorts as follows:

- four retorts for the reduction,

Table 1

Parameters for SIR (10 MW<sub>th, Biomass</sub>)

Biomass input [MW]	10
Number of retorts	7
Retorts in oxidation stage	2
Retorts in reduction stage	4
Arrangement of retorts	in parallel
Diameter of retorts [m]	1.25
Height of retorts [m]	3.12
Pellet mass per retort [kg]	7500
Gas velocity, reduction [m/s]	1.02
Gas velocity, oxidation [m/s]	2.36
Electricity output [MW]	2.5
Heat output, 200°C, SOFC [MW]	1

- two retorts for the oxidation,
- one retort for heat exchange.

Working principle with a switching time of 5 min: All retorts have a temperature of 800°C. Retort 1 starts at time 0:00 h with the reduction. After 5 min retort 2 starts with reduction. Retort 3 begins after 10 min. Retort 4 starts after 15 min. Then the reduction process is in the stationary phase. Then every 5 min the reduction retorts change. At time of 0:20 retort 1 starts with the oxidation, whereby retort 5 begins with the reduction. At the same time 4 retorts are in the reduction step. At 0:30 h retort 1 begins with heating phase to reheat the retort to a temperature

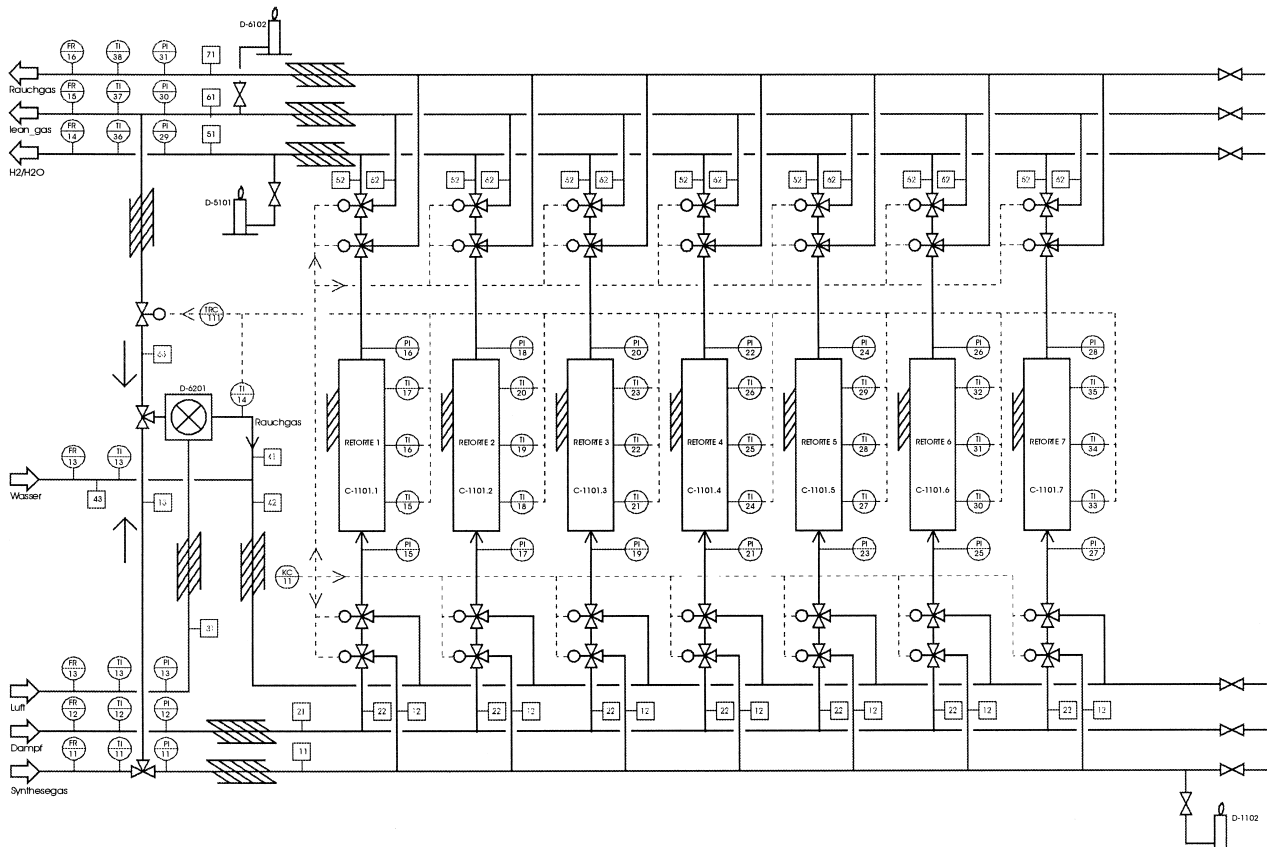


Fig. 4. Sponge iron reactor with seven retorts.

level of 800°C. After 35 min one cycle in retort 1 is completed. Then this retort starts again with the reduction step (Fig. 4 and Table 1).

### Acknowledgements

The authors thank the Austrian Science Fund (FWF P13030-TEC) and the European Commission for their financial support of the project.

### References

- [1] Messerschmitt, Verfahren zur Erzeugung von Wasserstoff durch abwechselnde Oxidation und Reduktion von Eisen in von außen beheizten, in den Heizräumen angeordneten Zersetzern, DE 266863, Germany, 1911.
- [2] G. Jannach, G. Krammer, G. Staudinger, K. Friedrich, Hydrogen From Biomass Gasification for Fuel Cell System by Application of the Sponge Iron/Iron Oxide Process Cycle, Technische Universität Graz, 1996.
- [3] L.V. Bogdandy, H.J. Engell, Die Reduktion der Eisenerze, Wissenschaftliche Grundlagen und technische Durchführung, Düsseldorf, 1967.
- [4] E. Schürmann, Die Grundlagen der Reduktionsvorgänge in: Physikalische Chemie der Eisen- und Stahlerzeugung, Vorträge einer vom Verein Deutscher Eisenhüttenleute durchgeführten Berichtreihe; Herausgegeben vom Verein Deutscher Eisenhüttenleute; Verlag Stahleisen, Düsseldorf, 1964.
- [5] V. Hacker, G. Faleschini, H. Fuchs, R. Fankhauser, G. Simader, M. Ghaemi, B. Spreitz, K. Friedrich, Usage of biomass gas for fuel cells by the SIR process, J. Power Sources 71 (1998) 226–230.
- [6] A. Heinzl, Fuel Cell Demands, JOR3-CT96-105, 2nd periodic report, 1997.
- [7] K. Kordesch, G. Simader, Einsatz der Brennstoffzellentechnologie für die Verwendung von technischen Gasen aus Abfallholz, project study at the Institute for Chemical Technology of Inorganic Compounds, University of Technology Graz, 1993.
- [8] J.J. Heizmann, P. Becker, R. Baro, Kinetik und Strukturumwandlung bei der Reduktion von Hämatit in Magnetit, Arch. Eisenhüttenwes. 45 (1974) 765–770.
- [9] P. Hartner, Entwicklung eines Computerprogrammes zur eindimensionalen Simulation von heterogenen Festbett und Vorschubreaktoren, Thesis, Technical University Graz, 1996.
- [10] G. Krammer, G. Staudinger, J. Wurzenberger, Simulation der Eisenschwamm-Reaktoren, Internal report, EU-Project, Technical University Graz, 1999.