Usage of biomass gas for fuel cells by the SIR process

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Abstract

The application of fuel cells in our future energy system depends on a cost-efficient production and supply of hydrogen (H_2) and carbon monoxide (CO). The process cycle iron oxide/iron/hydrogen offers a simple possibility to store the energy of synthesis gases in the form of sponge iron and at the same time to reform and condition these synthesis gases. As 'product' of this energy storage system one receives pure hydrogen. The 'Sponge Iron Reaction' (SIR) process offers some advantages against conventional gas cleaning and conversion processes: (i) low-cost hydrogen by using cheap sponge iron materials; (ii) high-quality hydrogen from low-BTU gases by a two-step operation; (iii) high efficiency compared with competitive technologies and (iv) system versatility and ease of siting. Commercially available iron ore pellets (hematite Fe_2O_3) and self-produced pellets are used as contact mass. © 1998 Elsevier Science S.A.

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1. Theoretical limitations of the sponge iron reactor (SIR)

The iron/iron oxide/hydrogen process is operated in two conditions. In the first step iron oxide is reduced by the gas produced in a gasifier (biomass gas) while this gas is oxidised to a lean gas with low CO and H_2 content. In the second step the reduced iron oxide is oxidised by water vapour whereby the water vapour is reduced to fuel gas, which is a mixture of hydrogen and steam. The possible redox reactions in the SIR are:

Hematite ↔ Magnetite ↔ Wuestite ↔ Iron

$$Fe_2O_3 \leftrightarrow Fe_3O_4 \leftrightarrow Fe_{1-y}O^1 \leftrightarrow Fe$$
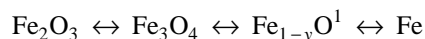
The conversion rate of CO and H_2 during the reduction reactions has been investigated as a function of partial pressure and temperature. Data about oxygen activity represented in the literature at equilibrium wuestite/magnetite are divergent [1–4]. Partly this can be explained by different assumptions of oxygen content in the wuestite $(y)^1$ at equilibrium with magnetite.

The result of equilibrium calculations is shown in Fig. 1

(Baur–Glaessner diagram). Since the partial pressure of H_2 and CO is low in the biomass gas (approx. 50%) and steam is used as oxidant, the redox reactions take place only between magnetite and wuestite phase. The reactions depend mainly on partial pressure of reactants and temperature of reaction. The phase diagram depicts the equilibrium of iron/iron oxide in a CO/CO_2 gas mixture as well as in a H_2/H_2O atmosphere. This shows, that for a reduction to iron the ratio of partial pressures at 800°C has to be at least approx 65% hydrogen (or carbon oxide) to approx 35% steam (or carbon dioxide).

Assuming that the water gas shift reaction (conversion of CO with H_2O to H_2 and CO_2, which may be catalysed by the sponge iron contact mass) is faster than the iron oxide reduction, the whole reduction process would proceed with the higher speed reduction reaction which is reduction by hydrogen. On the contrary, when the water gas shift reaction is slower, the reaction rate of CO determines the reactor length necessary to reach equilibrium.

The rate of reaction, the reactive atmosphere as well as the temperature influence the structure of the reduced pellets [5–7]. These effects are investigated theoretically and practically. Under certain conditions carbon deposition of the biomass gas occurs, which can be calculated from the Boudouard equation. The equilibrium constant K_B defines, for a fixed temperature and pressure, the maximum CO concen-
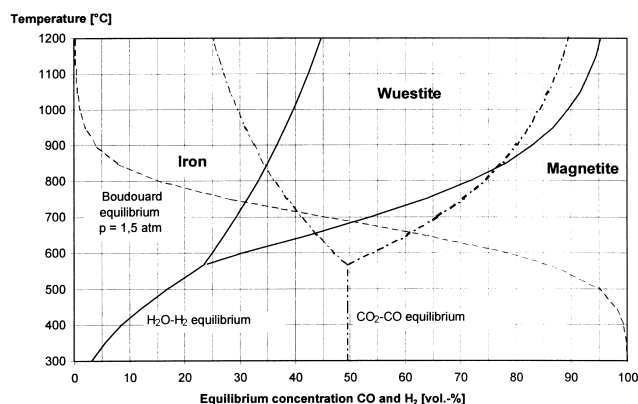

Fig. 1. Baur–Glaessner diagram [8].

tration until carbon deposition starts. According to Fig. 1 carbon is deposited below a temperature of 700°C for biomass gases.

2. Chemical experiments

2.1. Experiments in a tube furnace device

The tube furnace device consists of two tube furnaces, a gas mixing battery for H_2, CO, CO_2, N_2, He and Ar, a special accuracy weighing machine, flow meters, water evaporator and a gas chromatograph (GC). Pure gases, as well as a gas mixture, according to biomass gas compositions are taken for the reduction, and steam together with N_2 as carrier gas for the oxidation process. Reduction kinetics are measured by on-line monitoring of the gas conversion by gas chromatography of the exhaust gases.

As the oxidation reaction is going much faster, it cannot be followed by GC but by volumetric measurement of H_2 developed throughout the process. Evaluation of the data gives conversion vs. time diagrams for the oxidation and reduction of each cycle, whereby the total conversion is

calculated from the weight difference of the pellets at the beginning and the end of the process. Gas composition data allow to calculate the partial conversion by H_2 and CO.

Evidently, the kinetics within pellets measured in a tube furnace device are much slower and not comparable with the results from thermogravimetric analysis (TGA) (Fig. 4) due to diffusion processes in pellets. Kinetic data are difficult to interpret, as flow conditions in this reactor are not clearly defined and dead zones cannot be avoided. Yet the quality of different pellets, i.e. the conversion rate and the endurance throughout several redox cycles, can be judged from the results. Furthermore, the influence of pellet activation and of catalytic additives may be tested in the tube furnace device. Fig. 2 shows 12 redox cycles of SEK New pellets (commercial pellets from VOEST Alpine Linz GmbH). For the reduction process a $H_2/H_2O/CO/CO_2/N_2$ mixture according to a calculated biomass gas composition, and for the oxidation process a N_2/H_2O gas mixture were used. The mass change of pellets was calculated from data of the GC.

2.2. Selection of material

The goal of the investigations so far has been the selection of pellets with a low sintering tendency and constant high conversion rates (referring to the iron content) resulting from their chemical and structural composition. Different kinds of industrially manufactured pellets have been tested. One of the most essential criteria for the selection of indurated pellets is the long-term usage (high cycle stability) of the pellets in the sponge iron reactor.

The internal surface area as well as the pore size distribution of different particle fractions of pellets in the hematite, magnetite and wuestite phase at the beginning and after varying numbers of redox cycles were determined by BET surface characterisation measurement and Hg porosimetry. The BET surface area is about three times higher in the wuestite than in the hematite phase.
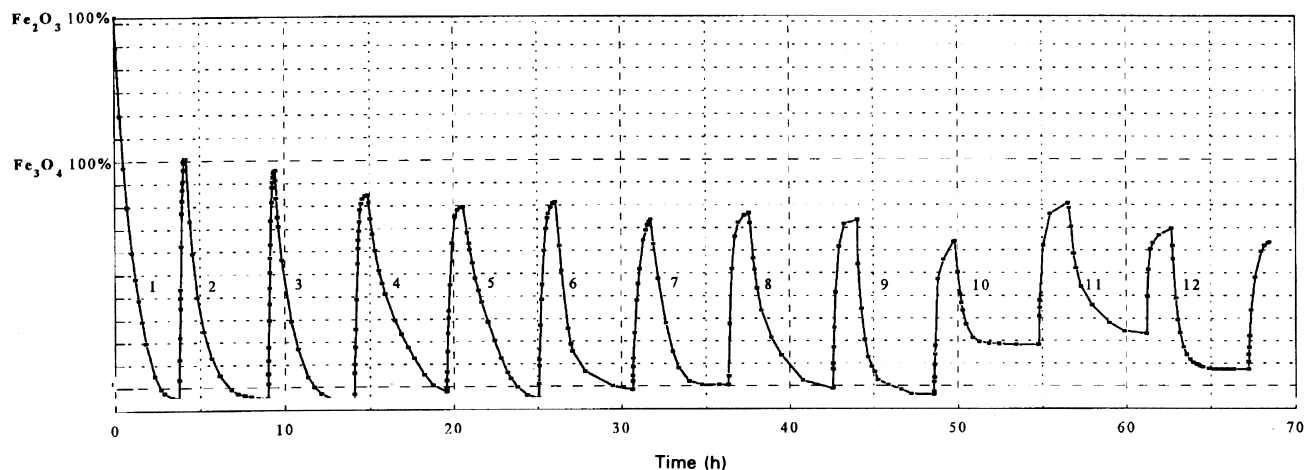

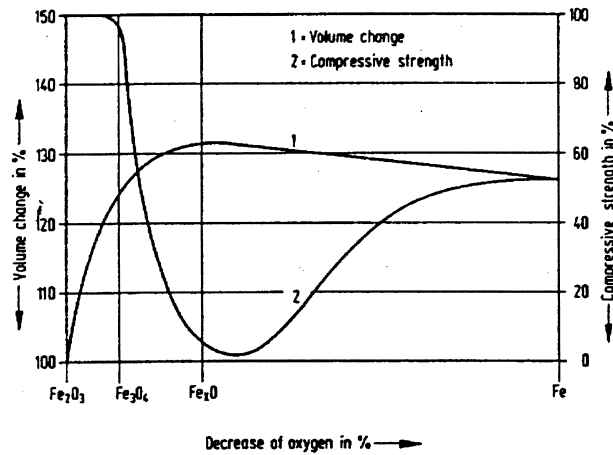Fig. 2. Cycle behaviour of SEK pellets.

Fig. 3. Change of volume and compressive strength during the reduction process of hematite [9].

By increase of porosity, the resistance to fracture is decreasing. After several cycles, surface area and porosity tend to decrease, especially when CO/CO_2 is used as reaction medium. By means of X-ray diffraction spectra of pulverised samples the identity and uniformity of the crystalline phases was determined.

According to Fig. 3, the compressive strength of wuestite is much lower compared to iron, hematite and magnetite. The compressive strength of SEK New pellets in the hematite phase is according to tests approx. 2000 N/pellet. To determine the compressive strength of SEK New pellets in wuestite phase, the hematite pellets were kept approx. 280 min at 800°C in a H_2/water vapour = 50:50 atmosphere. Thereafter, the compressive strength was tested according to ISO 4700, with the result that the mean value of a number of 18 pellets was 461 N/pellet with a SD of 197 N/pellet. This compressive strength of 461 N/pellet of the pellets in the wuestite phase is expected to be high enough to withstand the pressure in the reactor.

2.3. TGA analysis of commercial sponge iron materials

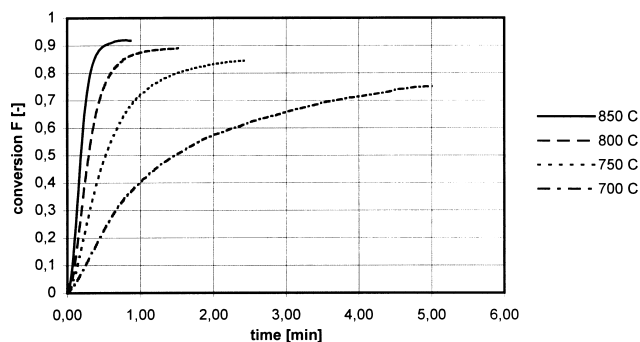For the modelling of a sponge iron reactor the kinetic

Fig. 4. Conversion/time diagram obtained from TGA for the reduction reaction: $Fe_3O_4 + H_2(3FeO + H_2O$ conditions: SEK NEW, 12 l/h (STP), $H_2/H_2O = 50/50$, particle size <10 μm.
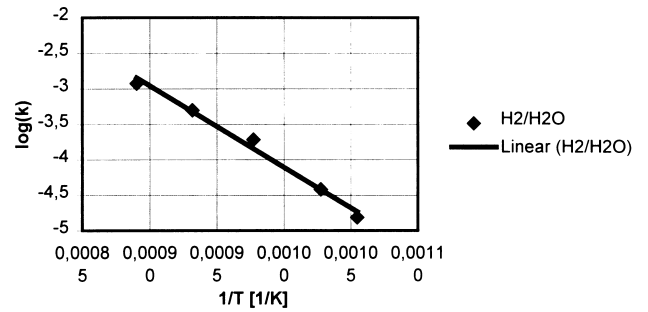

Fig. 5. Arrhenius plot for the determination of the activation energy for the reduction of magnetite with H_2.

parameters of the basic chemical reactions are required. Reduction and oxidation processes of commercial sponge iron materials are monitored by TGA. Pellets are pulverised and about 10–20 mg of fractions <10 μm are applied for TGA.

The oxidation of wuestite to magnetite has been investigated under the following conditions:

1. oxidation with H_2O at temperatures from 500 to 800°C, with CO_2 from 400 to 600°C;
2. variation of proportion of inert gas (N_2) in the reaction medium.

The reduction reaction (magnetite to wuestite) is carried out as follows:

1. reduction with H_2 in a H_2/H_2O = 50:50 mixture at temperatures from 700 to 850°C;
2. reduction with CO in a CO/CO_2 = 50:50 mixture at temperatures from 700 to 800°C.

As a result, conversion vs. time diagrams are obtained (Fig. 4) by which reaction rate constants at different temperatures, activation energies and Arrhenius coefficients (Fig. 5) are calculated. For this purpose, the best fitting model equation has to be found, referring to model functions for solid/gas reactions reported in literature [10,11]. The calculated parameters should reflect merely the chemical reaction at the phase border, disregarding any diffusion processes.

The energy of activation for the oxidation of wuestite with steam was found to be ~29 kJ/mol, while the activation energies for the reduction magnetite → wuestite were calculated to be 95 kJ/mol for H_2 and 98 kJ/mol for CO as reducing gas. These findings coincide well with published data [13,14].

Further parameters under investigation, influencing the reaction kinetics respectively the result of TGA, are the following:

1. the quality and pre-treatment of the iron ore material;
2. the number of redox cycles;
3. experimental parameters (particle size, sample size, gas flow, heating rate in the TGA).
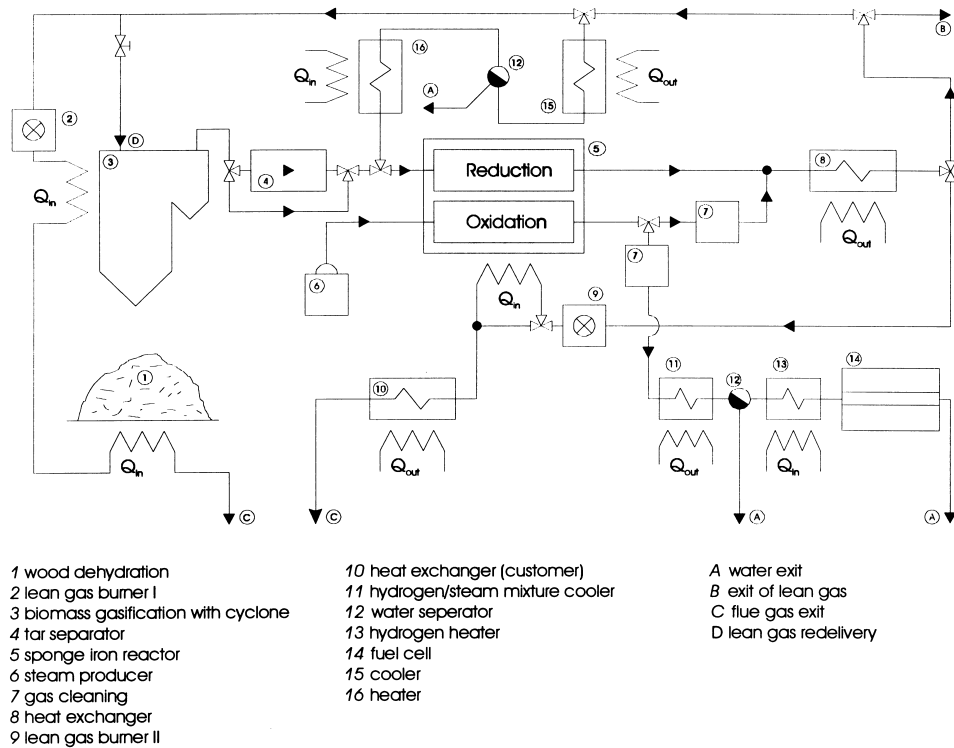
Fig. 6. Concept of integration of SIR into a complete energy system.

1 wood dehydration
2 lean gas burner I
3 biomass gasification with cyclone
4 tar separator
5 sponge iron reactor
6 steam producer
7 gas cleaning
8 heat exchanger
9 lean gas burner II

10 heat exchanger (customer)
11 hydrogen/steam mixture cooler
12 water seperator
13 hydrogen heater
14 fuel cell
15 cooler
16 heater

A water exit
B exit of lean gas
C flue gas exit
D lean gas redelivery

2.4. Experiments in lab-scale sponge iron reactor

The most suitable pellets shall be applied in a new sponge iron reactor which is constructed at the Technical University Graz. In this reactor the pellets are filled in a horizontal baseplate. Redox processes can be followed by on-line weight measurement providing accurate kinetic data. The composition of the inlet and outlet gases will be determined by GC. The reaction rate is accelerated by turbulent flow conditions in the bulk of the reactor. In principle, similar experiments will be performed as in the tube furnace. Reaction kinetics found in this reactor will be compared with TGA results intending to quantify the diffusion processes which will probably play a decisive role in total reaction kinetics. This laboratory reactor shall also provide all information necessary for a scale-up.

2.5. Concept SIR process (Fig. 6)

The biomass gas produced in the gasifier (3) is prepurified in a tar extractor (4) and the gas oxidised in the SIR (5). The resulting lean gas will be further used in the process after combustion in (9) or (2), or it can be supplied to a second electricity generation system (B). The heat from burning the lean gas is used in the SIR (5), the gasifier (3) and for wood dehydration (1). Optionally the lean gas can be reused in the SIR after lowering the water content of the lean gas in the condenser (15).

In the case that at the beginning of the oxidation process the hydrogen/water steam gas mixture is polluted by impu-

rities which were deposited during the reduction process, this initial gas will be mixed and burnt together (7,8) with the lean gas. After this short purification step the fuel gas will be fed to the gas cleaner and subsequently to the fuel cell (14).

2.6. Energy balance

The energy balance of an isothermal reduction and oxidation process at a temperature of 800°C was calculated. Heat content of 1 kg biomass gas at 800°C amounts to 1190 kJ, the lower heating value (LHV) to 4162 kJ (biomass gas). The lean gas leaves the reactor (800°C) with a heat content of 1253 kJ and a LHV of 2372 kJ (lean gas). For oxidation water steam with a heat content of 411 kJ is fed. For an isothermal reaction 404 kJ heat has to be removed. The LHV of the fuel gas amounts to 1712 kJ (LHV hydrogen), based on 1 kg biomass gas.

2.7. Energy density

In the equilibrium state with biomass gas the chemical formula of wuestite amounts to $Fe_{0.925}O$ [12]. Based on this oxygen content the energy density was calculated:

$$4.286 Fe_{0.925}O + H_2O \rightarrow 1.321 Fe_3O_4 + H_2$$
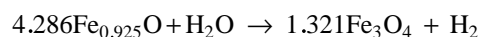
Energy density of SIR results with:

1. hydrogen per kg pellet: 575 kJ_{H_2}/kg_{pellet} (0.16 kW_{H_2}/kg_{pellet});
2. pellets per kg biomass gas: 225 $kg_{pellets}$/effic. SIR 45%).

3. Conclusions

The experiments carried out confirm the possibility of using the SIR process as a base for the production of hydrogen, which is suitable for all types of fuel cells.

According to thermodynamic calculations the application of biomass gas in the sponge iron process enables the reduction of iron ore material to the wuestite stage which is re-oxidised by steam to magnetite. For the concept of a sponge iron reactor, iron ore pellets of varying composition are used as contact mass in a fixed bed. Various pellets were characterised and their suitability and cycle stability tested in a tube furnace. Kinetic studies of powdered pellet material were carried out via TGA in order to gain information about the basic chemical processes. Experiments to follow are the investigation of catalytic as well as structure stabilising additives to achieve better reaction rates and mechanical strength of pellet material. The monitoring of pellet cycle behaviour in a new laboratory scale sponge iron reactor (which is in construction by now) and the comparison and interpretation of kinetic data will provide the basis for a scale up so that the integration of the SIR process into a complete energy system can be calculated.

Acknowledgements

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