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Hydrogen Production from Reformate Gas by a Cyclic Water Gas Shift Reactor

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1 Introduction

Hydrogen plays an important role in today's chemical industry. Also, in many scenarios of future energy supply systems, hydrogen is considered as a main energy carrier. The main path for hydrogen generation is the steam reforming process, based on fossil fuels or on renewable biomass. Applications such as fuel cells, but also some chemical processes, require very pure hydrogen, especially with respect to carbon monoxide. In the classical process scheme, a series of two water gas-shift reactors together with a deep-removal reactor (preferential oxidation, palladium membranes, pressure swing adsorption or methanisation) is used to decrease the concentration of carbon monoxide in the reformat gas to sufficiently low levels. While the reforming process operates at temperatures above 700 °C, this cleaning sequence requires the temperature to be lowered to less than 100 °C. Thus, two drawbacks of this process become obvious: the sequence of three reactors with intermediate heat exchangers and the energy loss due to the necessary cooling of the gas.

The cyclic water gas-shift reactor (CWGSR, Fig. 1) (Messerschmitt, 1911) is an alternative to the classical water gas-shift process. It works at temperatures similar to those used in steam reforming (650-850 °C). Each process cycle is divided into two phases: during the first phase, reformat gas (hydrogen contaminated with carbon monoxide) is fed into a fixed bed of metal oxide. The metal oxide, usually iron oxide, is reduced and the gases are oxidised (Eqs. 1 and 2, forward reaction). After sufficient time, feeds are switched and steam is fed into the reactor. During this second phase, the metal is oxidised again (Eqs. 1 and 2, backward direction), producing a mixture of hydrogen and water which is free of carbon monoxide.



The CWGSR produces pure hydrogen from reformat gases in a single unit.

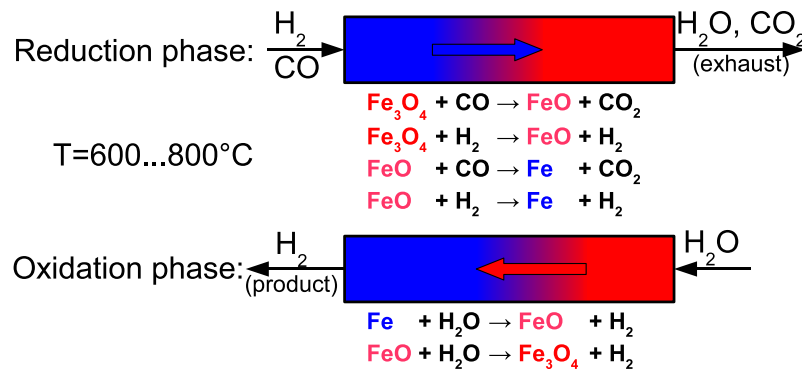


Figure 1: CWGSR working principle.

2 Objectives

The project focuses on the analysis, design and the practical realisation of this reactor. To obtain this goal, the following objectives are pursued:

- Development of a cheap, suitable and stable fixed bed material based on iron oxide.
- Evaluation of reaction kinetics and oxygen capacity.
- Model based analysis, design and control.
- Validation in a pilot plant.

3 Material Development

Pure iron oxide suffers from deactivation in regular CWGSR operations very quickly due to loss of active surface by sintering. Experiments show that additions of CeZrO_2 improve the activity and stability of the material (see Fig. 2). This finding is supported by REM images of new and used material (see Fig. 3) (Galvita et al. 2008).

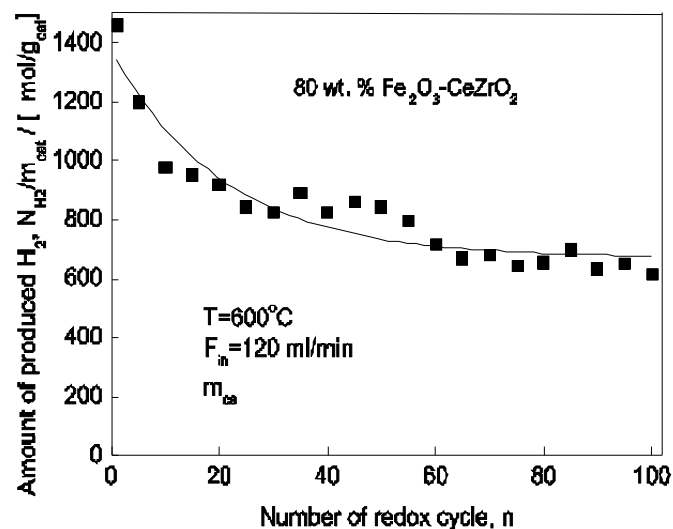


Figure 2: Material activity over 100 cycles.

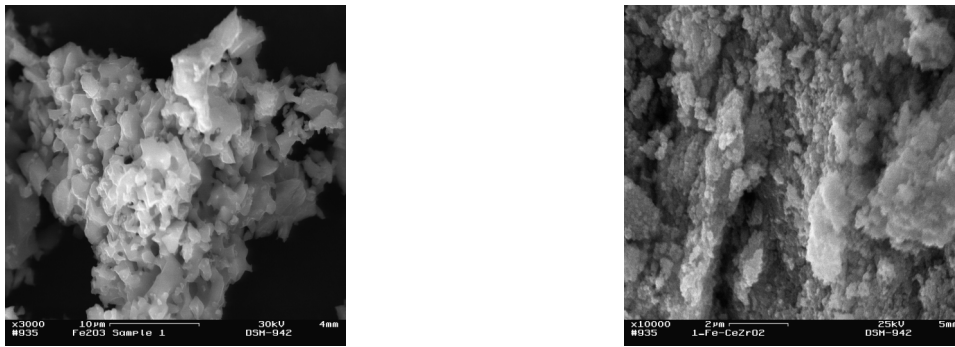


Figure 3: REM pictures of Fe₂O₃ (left) and 80-Fe₂O₃-CeZrO₄ (right) after 4 cycles.

4 Reaction Kinetics

Reaction kinetics were determined by thermo-gravimetric analysis (TGA) under different atmospheres of CO/CO₂. By properly choosing the ratio of CO and CO₂ in the reactant gas, the different reduction/oxidation reactions could be investigated separately. Fig. 4a shows the equilibrium diagram of the iron/iron oxide system in an atmosphere of CO and CO₂. The arrows indicate which gas compositions may be applied in order to obtain reduction of the bed material to a certain oxide species. Fig. 4b shows an exemplary TGA result of a sequence of reduction steps. The final weight reduction corresponds very well with the stoichiometric value, showing that the material can be completely reduced within reasonable time.

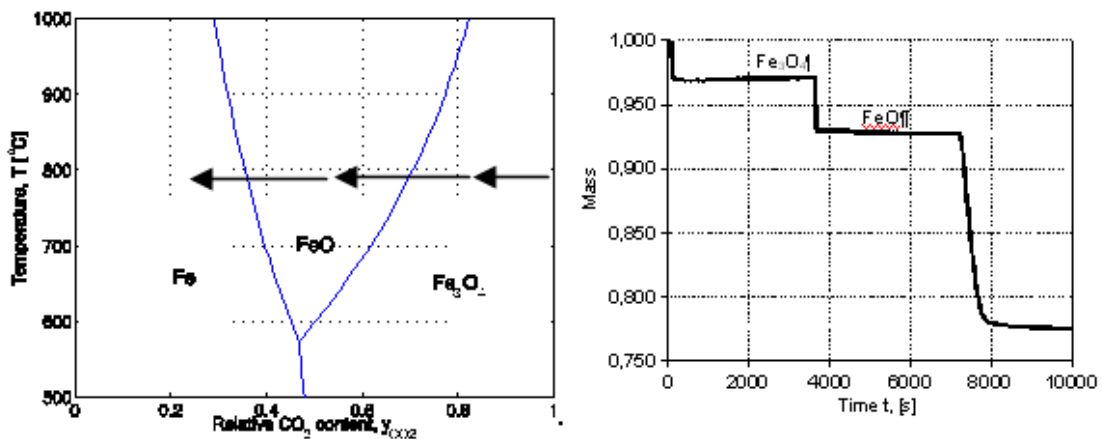


Figure 4a: left: Equilibrium lines of the system Fe/Fe_xO_y + CO/CO₂.
right: TGA measurement curve during stepwise reduction experiment.

The reaction rates were described by a modified Avrami-Erofeyev kinetic, which accounts for temperature, gas partial pressures and the thermodynamic equilibria (see Fig. 5). Typical reaction orders are approximately 1.8 with regard to the gas phase and 0.2 w.r.t. to the solid,

which can be interpreted as 1...2 dimensional product growth from already present nuclei at reaction start.

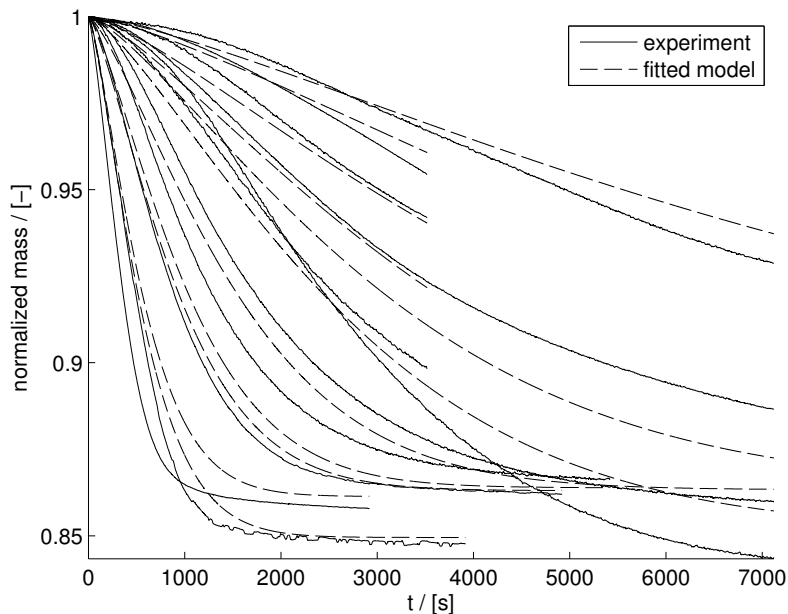


Figure 5: Measured and simulated TGA curves for the reaction $\text{FeO} + \text{CO} \rightarrow \text{Fe} + \text{CO}_2$ subject to different temperatures and partial pressures of CO and CO_2 .

5 Model Based Analysis

First simulations showed a significant advantage of the counter-current flow operation as shown in Fig. 1, as opposed to the straightforward co-flow operation (Heidebrecht et al. 2007). By switching the inlet and outlet ports, the fixed bed's oxidation gradient can maintain its orientation, which leads to less gas loss during phase switching, and higher fuel gas utilisation. Furthermore, regenerative heat exchange can be utilized to ease thermal integration of the reactor.

For a thermodynamic analysis, a mathematical model was used where equilibrium between gas and solid was assumed. Reaction zones then move as fronts through the reactor which then rest, on average, at one of the reactor ends (Heidebrecht et al. 2009). The positions depend on the relative duration of the reduction phase, S^l , and temperature, T . This leads to the formation of different operating regimes (see Fig. 6), which differ in fuel gas utilisation η_{fuel} and product concentration $x_{H_2,out}$. For example long reduction phases at high temperatures cause both reaction fronts to be located at the right end of the reactor, leading to low efficiencies but high hydrogen concentrations (see Fig. 7).

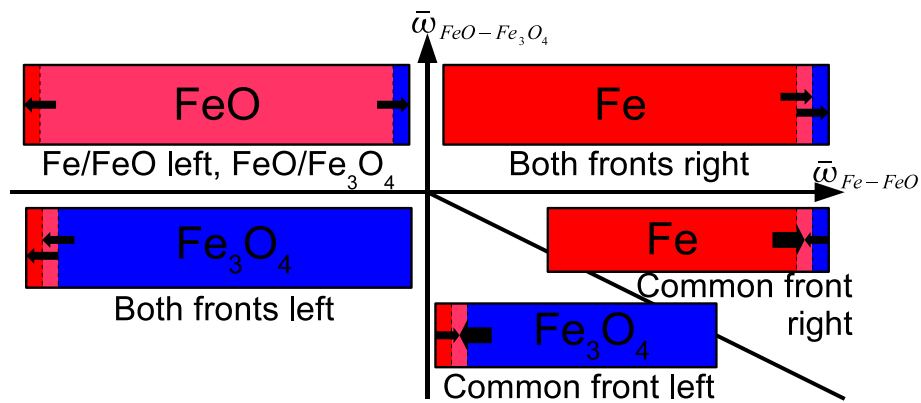


Figure 6: CWGSR operating regimes in reverse-flow mode.

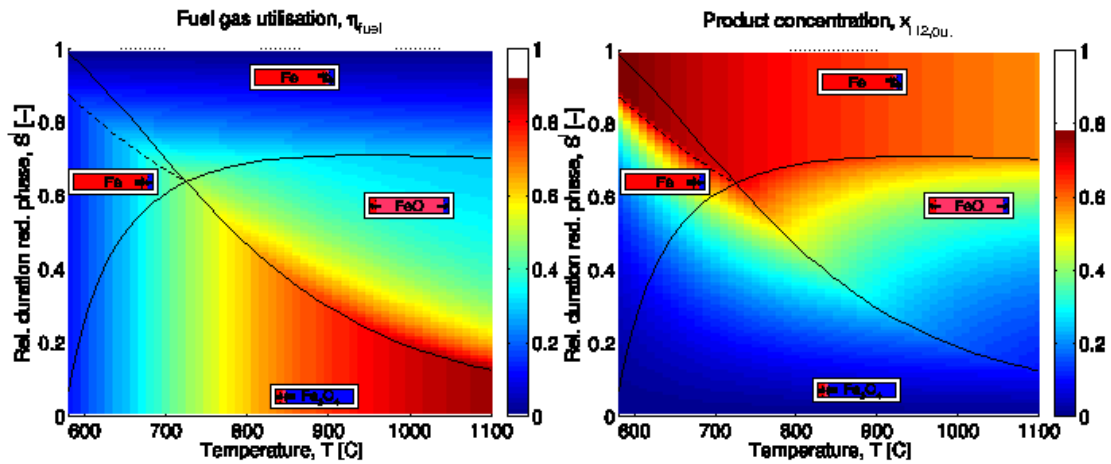


Figure 7: Fuel gas utilisation and H₂ product concentration in different regimes, depending on temperature and relative reduction phase duration.

Other, more complex models are currently under development. They will be applied to optimise design and operating parameters.

6 Pilot Plant

A pilot plant with a CWGSR bed length of 70 cm, inner diameter of 20 mm and bed mass of 200 g has been built (see Fig. 8a). Typical flow rates are several NI/min.

In Fig 8b, a first proof of concept is shown: The exhaust gas compositions during several reduction phases (CO, CO₂) and the product concentration (H₂) during the oxidation phase.

The plant will be used to validate the developed models and support derived results.



Figure 8a: Pilot Plant with a 70 cm · Ø 20 mm fixed bed, several NI/min flow.

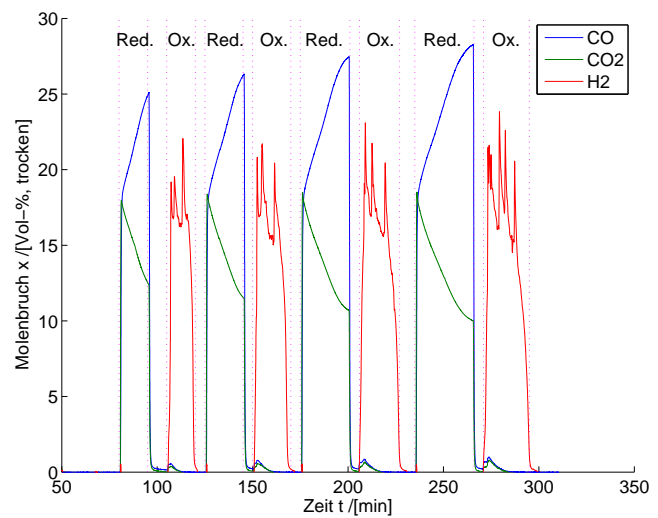


Figure 8b: Outlet measurements: CO, CO₂ and H₂ concentrations during repeated reduction and oxidation steps.

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