

De-centralised hydrogen production by an integrated biomass gasification/sponge iron process

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ABSTRACT

In the paper a new clean process for de-centralised generation of pure hydrogen from bio-mass is presented. By application of microwave radiation with 2.45 GHz frequency, selective heating of iron oxides can be combined with plasma activation of the reducing gas mixture, thus enabling quasi-continuous operation of the reversible oxidation and reduction of an iron sponge. A proprietary microwave assisted sponge iron reactor, MW-SIR is used in order to convert solid bio-mass directly into two gaseous fuels: a lean gas, which can be burned in a domestic boiler and pure hydrogen, which can be used to re-charge the hydrogen tank of a fuel cell car or other de-centralised appliances operated with hydrogen. Benefits of this new process are discussed as compared to state of the art technology for gasification of biomass for large scale production of hydrogen.

Keywords: Bio-mass, hydrogen, sponge iron, plasma, microwave

1 INTRODUCTION

The need to increase the share of hydrogen in the energy market is growing, because the potential of new highly efficient systems for energy conversion, like e.g., fuel cell systems, can be fully exploited only with such a zero-emission fuel [1]. The implementation of hydrogen into the energy market is retarded, because a centralised distribution system for hydrogen is not existing.. Therefore solutions are needed to overcome this drawback with the help of a de-centralised hydrogen generation technology, ideally based on biomass conversion into hydrogen. State of the Art technology for pyrolysis of hydrocarbons or the water gas shift reaction to obtain hydrogen is based on very large installations, because of problems with catalyst activity and the high effort to purify the gas mixtures. Hydrogen can also be obtained by reacting sponge iron with steam [2]. State of the Art sponge iron production is similar to hydrogen production a large scale process, therefore till now no efforts were undertaken to “scale down” this

process and utilise low energy content carbon-containing raw materials as reducing agent.

In the paper a de-centralised production of hydrogen is described via a new, down-scalable technology based on a microwave assisted steam-iron process. In the first step a CO and H₂ containing syngas from bio mass pyrolysis reacts with Fe₂O₃ (hematite), Fe₃O₄ (magnetite) or FeO (wustite) to produce an iron sponge. In the second step the reduced iron is re-oxidised with steam to form a mixture of solid iron oxides and gaseous pure hydrogen. The major problems of existing technology are: 1. the incompatibility of the reaction rate for oxidation and reduction of iron, 2. Sintering of the iron sponge because of the high temperature needed for reduction. Under isothermal conditions at 800°C, the oxidation rate is approximately two times higher than the reduction rate [3]. By the use of pulsed microwave power with a frequency of 2.45 GHz for selective heating of the iron ores and ignition of a microwave plasma at ambient pressure the reaction rate of both reactions is synchronised and a quasi continuous hydrogen production is possible. The flow sheet of the 2-step process is shown in figure 1.

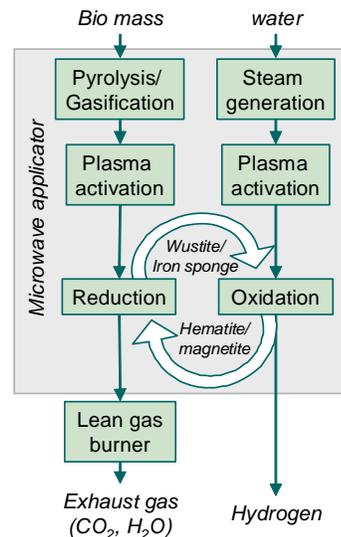


Figure 1: Flow sheet of the 2-step process for hydrogen production from bio mass. 1. step: reduction of iron oxide to iron sponge by the use of gasified bio mass; 2. step: pure hydrogen production by oxidation of iron sponge with steam

The temperature needed for reduction of iron oxides is significantly decreased due to plasma activation of the gaseous species and no sintering of the sponge iron is observed.

The reduction step is incomplete, therefore an exhaust gas with calorimetric values sufficient as low BTU-fuel for a modified domestic boiler is obtained as by-product. The main product hydrogen is obtained during the oxidation step with steam.

Utilisation of such a process for “domestic” hydrogen production in combination with heat generation for e.g., hot water supply is shown in figure 2.

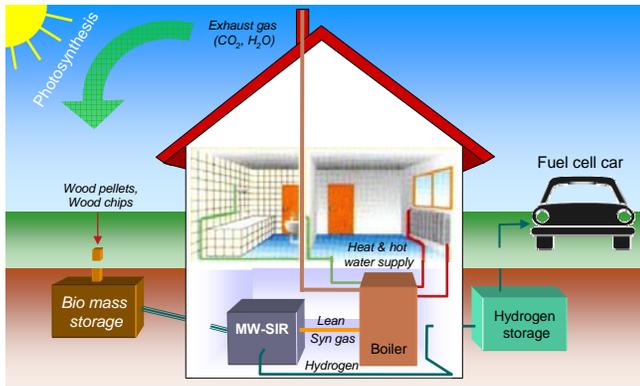


Figure 2: Concept of an integrated domestic hydrogen production with a microwave assisted sponge iron process (MW-SIR).

2 EXPERIMENTAL

The experimental laboratory setup is shown in figure 3. The hematite is placed as a fixed bed in a quartz tube of a 2.45 GHz, 2.8 kW microwave applicator, together with 20 wt.% of wood chips (beech), which are in direct contact with the iron oxide.

After turning on the microwave power, the bio mass is indirectly heated by the hematite bed, because the dielectric losses of the hematite are 10 times higher than the losses of dry beech chips. During the following pyrolysis the bio mass undergoes various reactions resulting in the formation of gaseous products like CO, CO₂, CH₄, H₂, H₂O and tar like products.

Within the fixed bed of hematite the evolved CO and H₂ leads to the formation of sponge iron. When the reduction step is completed a steam argon mixture is introduced to re-oxidise the iron sponge corresponding to the following equations:

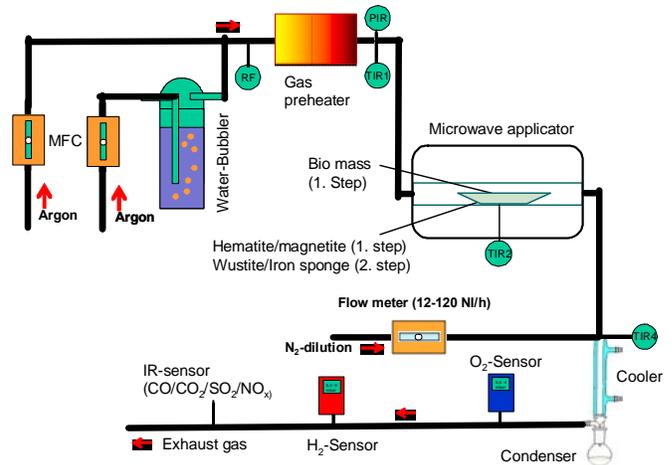


Figure 3: Experimental laboratory setup for bio mass pyrolysis and hematite reduction (1. step) and vapour conversion into Hydrogen and oxidation of the wustite/iron-sponge.

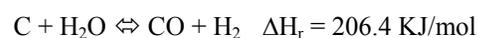
For safety reasons at laboratory scale experiment the produced hydrogen gas is diluted with nitrogen and than the excess of water is condensed in a cooling trap. Process control occurs by on-line measurement of the hydrogen and CO content in the product gas stream, as well as the water content in the exhaust gas. The degree of oxidation and reduction of the iron sponge as well as the iron oxides has been verified by phase analysis (XRD) of the solid in the fixed bed.

3 RESULTS

The results of on-line monitoring the gas composition from the 2 step process are shown in figure 4. Within one hour the biomass is carefully pyrolysed at a microwave power level of up to 800W. After about 35 min the first pyrolysis step is completed and the water gas shift reaction occurs. This is visible from the strong reduction of the CO concentration and a corresponding increase of the Hydrogen concentration:



At the beginning of the oxidation reaction with steam CO concentration is increased because the remaining charcoal reacts with steam according the following equation:



The carbon oxides, CO and CO₂ are unwanted impurities in the hydrogen, especially for fuel cell applications. Therefore the hydrogen produced in the first 10 min of the

oxidation is burned similar to the gasses obtained during reduction of the iron oxides. As soon as no carbon oxides are detectable, the hydrogen is collected in a tank.

Both, the oxidation and the reduction step can be accelerated by plasma activation of the gaseous species. A microwave power level of 200 and 1000 W respectively, enables ignition of an atmospheric MW-plasma, as shown in figure 5.

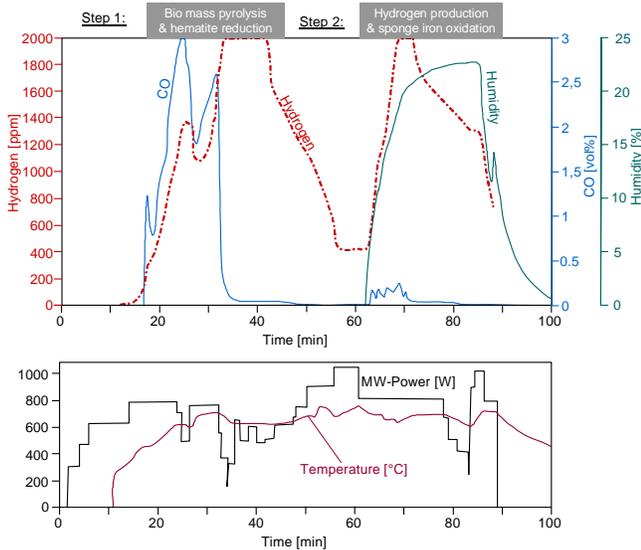


Figure 4: Temperature profile and gas composition versus process time for a 2-step MW-SIR-process



Figure 5: View into the microwave cavity during plasma assisted oxidation of sponge iron (microwave power level: 200W)

For an efficient oxidation as well as reduction step a temperature level between 600 and 700°C is favourable, to avoid sintering of the sponge. From DC-plasma metallurgy it is known, that if ionized hydrogen and hydrogen radicals are used as reductive to reduce the reaction temperature needed [4]. In figure 6 the Gibb's energy as a function of temperature is shown for the conventional reduction of wustite (FeO) and for two types of DC-Plasma assisted reduction.

In this work a microwave plasma has been used because of the selective heating of iron oxides and the high efficiency of the MW-plasma. The observed reduction

behaviour indicates that a MW-plasma effects process comparable to DC-plasma.

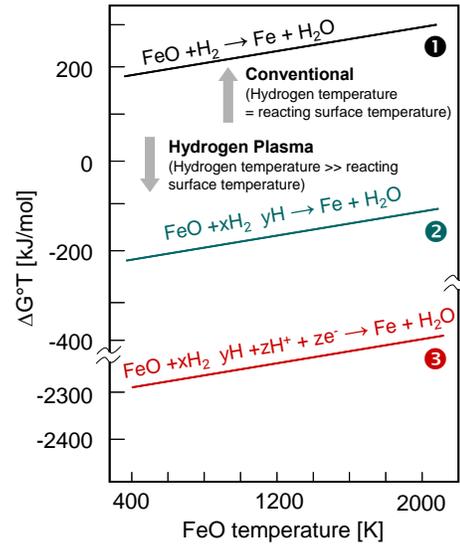


Figure 6: Gibb's energy versus surface temperature for FeO reduction by hydrogen plasma (1) conventional heating, (2) DC-Plasma without a applied electric field, (3) DC-Plasma with negative polarity on the FeO surface [4]

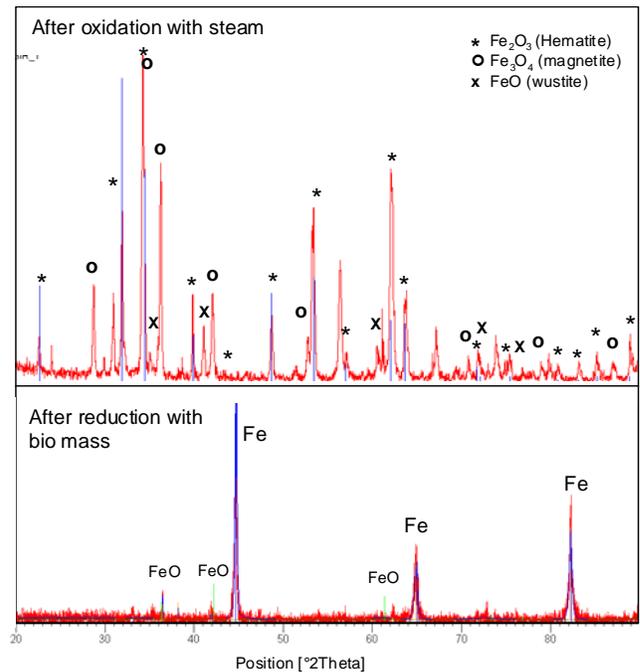


Figure 7: Phase analysis after reduction of iron oxide in direct contact with bio mass and after re-oxidation with steam

In figure 7 the phase analysis of the fixed bed material after reduction with bio mass and after re-oxidation with

steam is shown. It is worth mention, that during the re-oxidation with steam (diluted with argon) no desintegration of the porous sponge occurs although a mixture of different iron oxides (mainly magnetite and hematite) is obtained. After reduction with bio mass the sponge consists mainly of iron (ferrite microstructure with minor content of perlite) with small amounts of wustite.

4 CONCLUSION

Application of microwave radiation for heating and plasma processing of gasses enables a fast and efficient volume heating of a fixed iron oxide bed and conversion of steam into hydrogen at low temperature. as shown at laboratory scale within a small size microwave assisted sponge iron reactor (MW-SIR).

Microwave plasma processing conditions are crucial for the process, to achieve high reaction rates in both steps of the SIR-process and, at the same time, prevent sintering effects. The microwave assisted process is easy controllable, due to the synergetic effect of volumetric heating and atmospheric plasma activation of gasses.

The bio mass can be completely pyrolysed and gasified and the produced syngas enables a efficient reduction of the iron oxide bed combined with simultaneous production of a low BTU-gas that can be used in a domestic boiler for heat and water supply.

Within the re-oxidation step of the sponge iron hydrogen is produced from steam at temperatures as low as 600°C to 700°C.

The concept of an integrated MW-SIR module for domestic application is shown in figure 8. The reactor consists of two switchable chambers filled with the fixed bed material heated by microwave. Instead of waveguides the microwaves are introduced into the fixed bed by rod antennas [5,6]. Low power 2.45 GHz magnetrons as used in kitchen microwave ovens can be applied.

The biomass is continuously fed into an indirectly heated coaxial shaft like reaction chamber for pyrolysis and gasification. The syngas enters in alternating steps the fixed bed cambers for reduction of the iron oxide.

The compact MW-SIR module with a size smaller than a domestic boiler enables a quasi continuous production of hydrogen for mobile and stationary fuel cell applications.

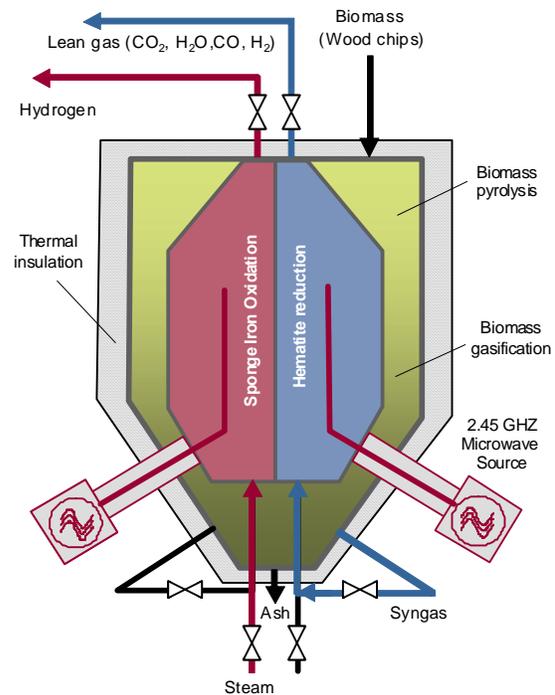


Figure 8: Scheme of the microwave assisted sponge iron reactor (MW-SIR). When the sponge iron in the left chamber is oxidized and the hematite/magnetite in the right chamber is reduced, the valves are switched in the opposite direction.

5 REFERENCES

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