

Research Article

Thermodynamic Feasibility of Hydrogen-Rich Gas Production Supported by Iron Based Chemical Looping Process

Grzegorz Słowiński¹ and Adam Smoliński²

¹Department of Engineering, Vistula University, 3 Stokłosy Street, 02-787 Warsaw, Poland

²Central Mining Institute, Department of Energy Saving and Air Protection, Plac Gwarkow 1, 40-166 Katowice, Poland

Correspondence should be addressed to Adam Smoliński; smolin@gig.katowice.pl

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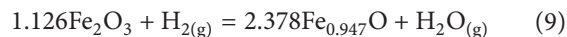
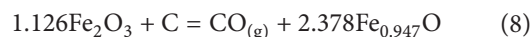
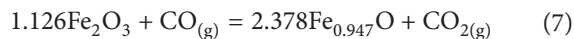
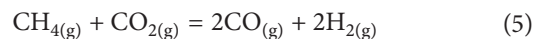
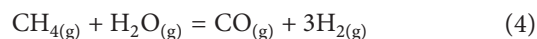
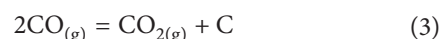
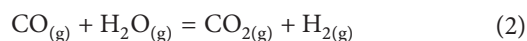
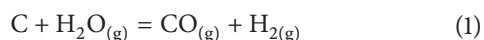
The continuously increasing oil prices as well as stronger environmental regulations regarding greenhouse emissions made the greatest economic powers search a new, price competitive, and environment friendly energy carrier, such as hydrogen. The world research activities in these terms focus on the development of integrated hydrogen and power generating technologies, particularly technologies of hydrogen production from various carbonaceous resources, like methane, coal, biomass, or waste, often combined with carbon dioxide capture. In the paper the thermodynamic analysis of the enhancement of hydrogen production in iron based chemical looping process is presented. In this method, iron oxide is first reduced to iron with a reducing agent, such as carbon oxide, hydrogen, or mixture of both gases (synthesis gas), and then, in the inverse reaction with steam, it is regenerated to iron oxide, and pure stream of hydrogen is produced.

1. Introduction

Nowadays fossil fuel combustion process, particularly combustion of coal, contributes significantly to the increasing, negative environmental impact of a power sector [1–7]. The limited resources of fossil fuels, unstable oil and gas market, and restrictive environmental regulations regarding greenhouse gases emission imply the need for the development of price competitive and environment friendly energy carriers, like hydrogen [8–13]. It is environmentally neutral and may be produced in the process of steam gasification of coal or biomass/waste, reducing the carbon footprint of the power sector and contributing to the development of innovative clean coal technologies.

Hydrogen-rich gas production in gasification process is combined with CO₂ separation, in two main steps [13–19].

(I) The gasification step, in which coal is gasified to syngas and iron oxide is applied to oxidize carbon monoxide present in syngas and to enhance the Boudouard reaction (3) generating carbon dioxide and amorphous carbon:



(II) Capture of carbon dioxide with CaO:



Iron and iron oxide (Fe_{0.947}O) is oxidized in oxygen or in air, and the heat from this exothermic reaction is utilized in calcination of calcium carbonate, generating a sequestration

becomes stable, and the reaction stops. Thus, the possible compositions of gaseous mixture produced during Fe-steam reaction are situated above the borderline dividing Fe-iron oxides region. Similarly, the reduction of iron oxides to Fe is possible by introducing iron oxides to the region of Fe stability, and the composition of the reduction reaction gas product can be found below the borderline dividing Fe and iron oxides regions.

At the temperatures below the triple point, it is possible to produce 1.33 mol of hydrogen per 1 mol of iron (see reaction (12)). The maximum thermodynamically feasible concentration of hydrogen varies from 99.9% vol. at 100°C to 82.8% vol. at 500°C. Above the triple point, it is possible to produce 1.06 mol of hydrogen from 1 mol of Fe in reaction (13) or 1.33 mol of H_2 in reaction (12). In case of reaction (13), the maximum thermodynamically viable hydrogen concentration varies from 78% vol. at 600°C to 64.6% vol. at 1000°C. Performing reaction (12) under the conditions above the triple point would result in the achievable hydrogen concentrations between 62.0% vol. at 600°C and 11.4% vol. at 1000°C. In general, the steam-iron reaction requires possibly low temperature to ensure the potentially highest hydrogen concentration and, at the same time, reasonable process kinetics. The reaction kinetics could be improved by Fe doping with other metals, exhibiting catalytic effects [20, 21]. Applying the lower temperature is also beneficial for Fe structure stability degrading at higher temperatures. However, the elevated temperatures cannot be avoided in the reduction stage. The presence of a few percentages of steam in hydrogen gas should not pose any serious operational problems. In fact, low temperature Polymer Electrolyte Membrane Fuel Cells (PEMFCs), applicable as potential hydrogen consumers, require membrane wetting [12, 26]. If necessary, water can be removed from hydrogen by cooling and condensation.

3.2. Iron Oxides Reduction with Hydrogen. Iron oxides reduction with hydrogen is reverse to the oxidation, and the thermochemical limitations of the process are given in Figure 2. It can be seen that Fe_3O_4 or $Fe_{0.947}O$ reduction to metallic iron terminates at relatively low concentration of steam in H_2 - H_2O atmosphere. At 100°C it is 0.1% vol. steam, and it grows to 35.4% vol. at 1000°C. Thus, the higher temperatures are favorable for the reduction stage. However, even at higher temperature (of 1000°C), if iron oxides are to be reduced in a flow of hot hydrogen, the flue gas will still contain over 60% vol. of hydrogen. This implies that hydrogen needs to be separated from hydrogen/steam stream and recycled.

3.3. Iron Oxides Reduction with Carbon Monoxide. The iron oxides reduction process may be performed with carbon oxide, according to the following reactions:

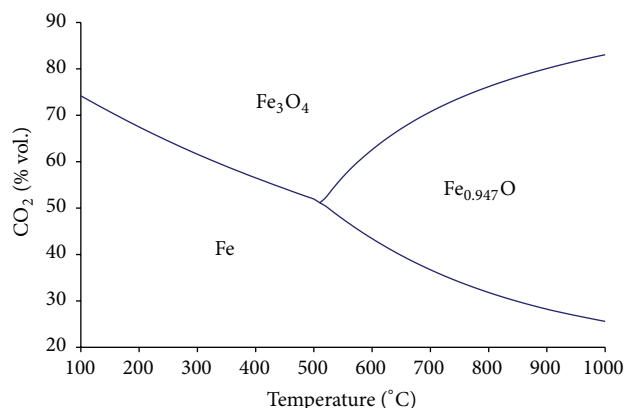
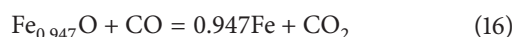
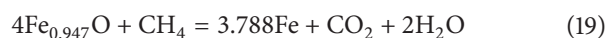
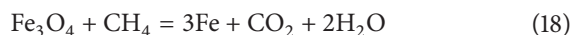


FIGURE 3: The phase stability diagram of Fe, $Fe_{0.947}O$, and Fe_3O_4 phases in CO- CO_2 atmosphere.

Figure 3 presents the phase stability diagram for the system $Fe/Fe_{0.947}O/Fe_3O_4$ in the CO- CO_2 atmosphere. The maximum utilization of CO in Fe_3O_4 reduction decreases from 74% vol. at 100°C to 26% vol. at 1000°C. This means that the reduction should be done at possibly low temperature for the optimal utilization of CO. Three other aspects, however, need to be also considered. First, the reaction kinetics may be insufficient at low temperatures; second, low temperatures are thermodynamically favorable for carbon deposition in the Boudouard reaction [18, 27]; and, third, the reduction may be performed with the application of synthesis gas, rather than with a pure CO stream. As it was shown in Section 3.2, the reduction of magnetite with hydrogen is more efficient at high temperatures.

3.4. Iron Oxides Reduction with Methane. It is assumed that iron oxide reduction with methane goes through the reactions:



H_2 , CO, and C do not constitute the products of the reduction reactions. In Figure 4 the phase stability diagram for the system $Fe/Fe_{0.947}O/Fe_3O_4$ in the CH_4 - CO_2 - H_2O atmosphere is presented. It can be seen that the reaction equilibrium depends strongly on the temperature; high consumption of methane is achieved at relatively high temperatures. Increased pressure moves the equilibrium borders to higher temperatures range.

3.5. Remarks on a Reducing Gas Consumption in the Iron Oxides Reduction Process. The reduction of magnetite at temperatures over the triple point proceeds in the order of magnetite, wustite, and then iron. It could be explained on the example of magnetite reduction with hydrogen at 800°C.

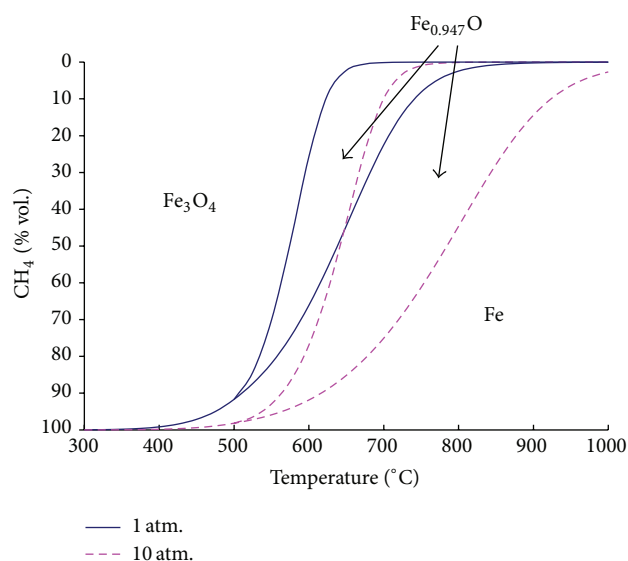


FIGURE 4: The phase stability diagram of Fe, $\text{Fe}_{0.947}\text{O}$, and Fe_3O_4 phases in the $\text{CH}_4\text{-CO}_2\text{-H}_2\text{O}$ atmosphere.

10 mol of Fe_3O_4 can be reduced at 800°C in a single stage by blowing with pure hydrogen. The necessary amount of H_2 is given by the following equation:

$$N_{\text{H}_2} = \frac{4 \cdot 10 \text{ mol}}{29.43\%} = 135.92 \text{ mol} \quad (21)$$

The process consumes 135.92 mol of pure H_2 . The flue gas produced contains 40 mol of H_2O (29.43% vol.) and 95.92 mol of H_2 (70.57% vol.). The same process could be conducted in two stages. In the first one magnetite is reduced to wustite in reversed reaction (14). The hydrogen consumption is

$$N_{\text{H}_2}^1 = \frac{10 \text{ mol}}{1.202 \cdot 74.07\%} = 11.23 \text{ mol} \quad (22)$$

The reaction produces $(10 \cdot 3.807)/1.202 = 31.67 \text{ mol}$ $\text{Fe}_{0.947}\text{O}$. The flue gas is composed of 8.32 mol of H_2O (74.07% vol.) and 2.91 mol of H_2 (25.93% vol.).

In the second stage wustite is reduced to iron in reversed reaction (16). The hydrogen consumption is

$$N_{\text{H}_2}^2 = \frac{31.67 \text{ mol}}{29.43\%} = 107.61 \text{ mol} \quad (23)$$

The flue gas contains 31.67 mol of H_2O (29.43% vol.) and 75.94 mol of H_2 (70.57% vol.).

In total, in the second case of reduction (two-stage process) 118.83 mol of H_2 is consumed, which is 17.69 mol less than in the single-stage process. The flue gas from the reduction of wustite to iron contains enough H_2 to transform magnetite to wustite. This creates an additional opportunity for improved gas management in case that several iron containing reactors are applied. The flue gas from the $\text{Fe}_{0.947}\text{O}/\text{Fe}$ stage in one reactor may be utilized for driving the $\text{Fe}_3\text{O}_4/\text{Fe}_{0.947}\text{O}$ reaction in the next reactor.

4. Summary and Conclusions

On the basis of the thermodynamic analysis of the enhanced hydrogen production in iron based chemical looping process it may be concluded that the steam-iron reaction should be carried out at possibly low temperature, ensuring the potentially highest hydrogen concentrations and, at the same time, reasonable process kinetics.

Analysis of the phase stability diagram of Fe, $\text{Fe}_{0.947}\text{O}$, and Fe_3O_4 phases in $\text{H}_2\text{O-H}_2$ atmosphere allowed concluding that, at temperatures below the triple point, it is feasible to produce 1.33 mol of hydrogen per 1 mol of iron. The maximum thermodynamically feasible concentration of hydrogen varies from 99.9% vol. at 100°C to 82.8% vol. at 500°C .

Above the triple point of the phase stability diagram of Fe, $\text{Fe}_{0.947}\text{O}$, and Fe_3O_4 phases in $\text{H}_2\text{O-H}_2$ atmosphere, it is possible to produce 1.06 mol of hydrogen from 1 mol of Fe (in the reaction $0.947\text{Fe} + \text{H}_2\text{O} = \text{Fe}_{0.947}\text{O} + \text{H}_2$) or 1.33 mol of hydrogen (in the reaction $0.75\text{Fe} + \text{H}_2\text{O} = 0.25\text{Fe}_3\text{O}_4 + \text{H}_2$), respectively. The maximum thermodynamically feasible hydrogen concentration varies from 78.0% vol. at 600°C to 64.6% vol. at 1000°C .

Competing Interests

The authors declare that they have no competing interests.

Acknowledgments

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