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Iron carbonate ore beneficiation by direct reduction with hydrogen

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Introduction

Reducing specific carbon dioxide emissions is a high priority task of the industry. The state of the art technology of the iron- and steel industry contributes to carbon dioxide emissions during the iron ore beneficiation [1] to a significant amount. By remodeling the technology, these carbon dioxide emissions can be reduced tremendously [2]. Direct mineral iron carbonate ($FeCO_3$) reduction with hydrogen is an

experimental setup was similar to the one described in Lux et al. [5]. The experiments were performed in a bench scale tubular reactor, Figure 1.. The gas is fed to the reactor on top via mass flow controllers and exits at the bottom of the reactor. For the reduction hydrogen (99.999%) and nitrogen (99.999%) supplied by AirLiquide have been used. The gas stream was between 0.02–0.05 m³ h[-1]. The hydrogen to
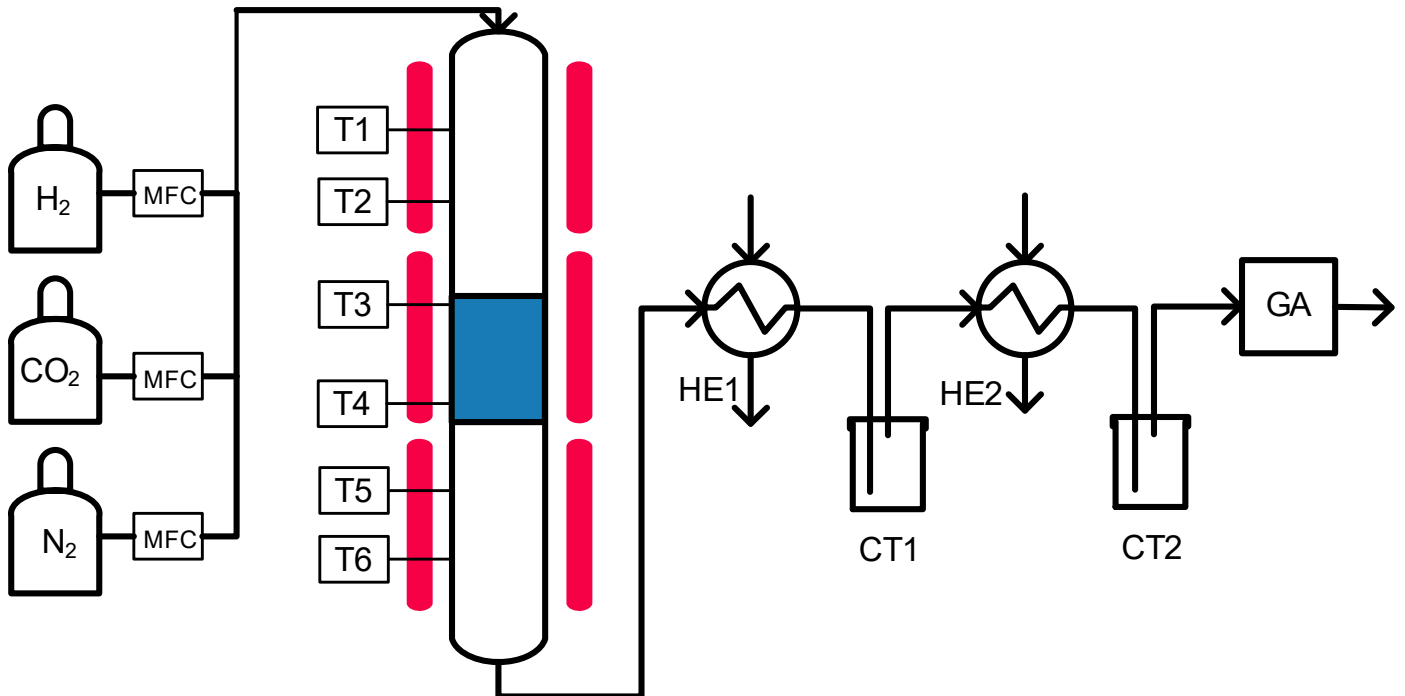

Figure 1: Bench scale tubular reactor, MFC: mass flow controller, Ti: Thermocouple, HE: Heat exchanger, CT: Condensate tank, GA: Gas analyzer.

alternative pathway to state of the art iron ore beneficiation with significantly less specific CO_2 emissions.

In the state of the art process the main reducing agent is carbon based (coke or coal). When substituting carbon based energy carriers with hydrogen reduction of the specific carbon dioxide emissions up to 60% [3] can be achieved. Hydrogen reduces iron carbonate directly to elemental iron (Fe), according to equation 1.

$$FeCO_3 + 2\,H_2 \xrightarrow{Q} Fe + CO + 2\,H_2O \qquad (1)$$
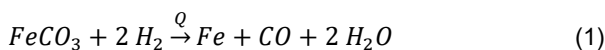
Coke oven gas, which has a high hydrogen content of up to 60 vol.% hydrogen [4], could be a possible hydrogen source for direct ore reduction.

Experimental setup and produce

In our research project the direct mineral iron carbonate reduction with hydrogen has been investigated. The

nitrogen ratio was $H_2:N_2=9:1$. The exit gas is quenched in a heat exchanger, and the condensables are collected in the condensate tanks. Afterwards the gas is analyzed in a gas

analyzer from ABB (Caldos27 thermal conductivity analyzer and Uras 26 infrared photometer).

The iron ore used was mineral iron carbonate from Eisenerz, Austria (Figure 3). The sample size was 100 g. In a design of experiment five factors were tested for their influence on the reduction of a mineral iron carbonate-ore and the composition of gas product: process temperature, particle size, initial mass of the ore, gas flow and hydrogen concentration.

conditions gaseous products vary between methane, carbon monoxide, carbon dioxide and water.

Figure 2 shows the corresponding Gibbs' free energy plot. According to equation 2 CO_2 is formed during formation of wustite (FeO) and iron. The Gibbs' free energy for this reaction is negative.

$$FeCO_3 \xrightarrow{Q} FeO + CO_2 \qquad\qquad (2)$$
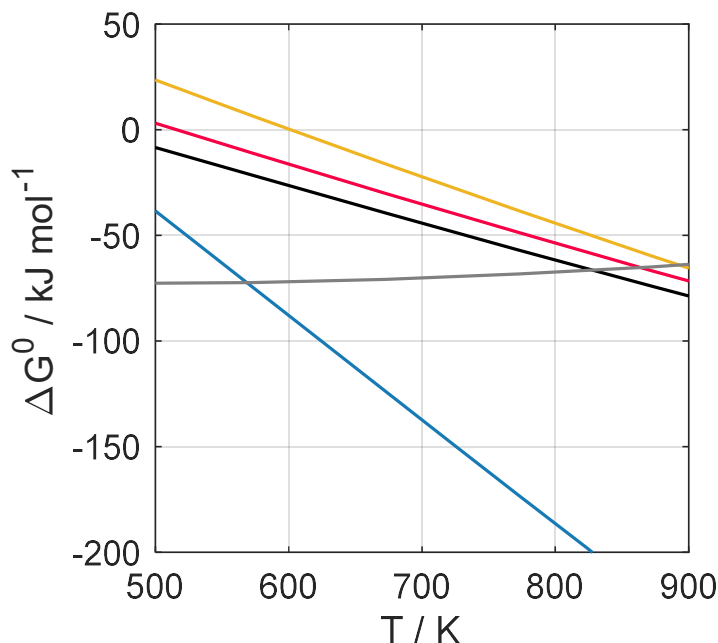
Corresponding to the Gibbs free energy formation of

Figure 2: Gibbs' free energy plot for different solid and gas products formed during iron carbonate reduction with hydrogen (data was calculated with HSC Chemistry 8 [6]).

Results and discussion

Different solid and gas products are formed by iron carbonate reduction with hydrogen.

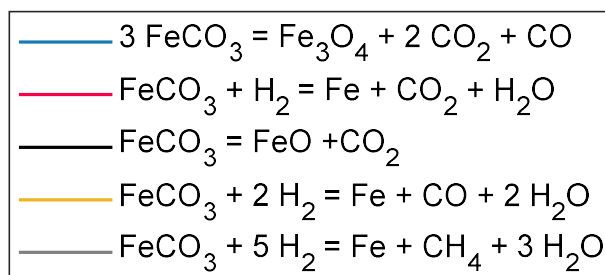Figure 1: Sample of the mineral iron ore from Eisenerz, Austria.

Solid products include elemental iron (Fe), wustite (FeO) and magnetite (Fe₃O₄). Depending on the operation

elemental iron and methane is thermodynamically favored.

Carbon monoxide is formed as a byproduct during conversion of iron carbonate to elemental iron. The Gibbs' free energy of this reaction is negative for temperatures above 600 K.

The outcome of the design of experiments showed that the factors process temperature, particle size, gas flow and the interaction of gas flow*temperature and gas flow*gas flow were identified as strong impact on mineral iron carbonate conversion, as shown in Figure 4.

The major influence on the solid and gaseous products is the temperature. Higher temperatures lead to shorter reaction times for completed conversion at that temperature (marked by reaching feed gas concentration in the exit gas stream).

The conversion of the mineral iron carbonate is constant between 658 K and 753 K varying around 86 % conversion of the whole mineral based on the measured mass loss.

The amount of carbon monoxide produced shows a different behavior. The total amount of carbon monoxide is higher at 673 K with 147.5 mmol carbon monoxide and sinks till 733 K of 142.7 mmol carbon monoxide.

The selectivity to carbon monoxide however, rises with rising temperature and the selectivity to carbon monoxide is highest at 733 K. The effect, that at 673 K both the carbon

monoxide mmol amount in the exit gas and the total produced carbon based gases (carbon monoxide and carbon dioxide) in the exit gas are highest, marks the temperature were the magnesium carbonate and manganese carbonate start to be reduced.

Furthermore, higher conversion at higher temperatures is influenced not only by the reduction of the carbonates (iron, magnesium and manganese) to oxides (wustite FeO, magnesium oxide and manganese oxide) but also by the reduction of iron carbonate to elemental iron and by the reduction of wustite to elemental iron. This offers opportunity for further reduction of wustite with hydrogen to elemental iron as shown in equation (3).

$$FeO + H_2 \rightarrow Fe + H_2O \qquad (3)$$

In a further investigation of the temperature influence has shown that at higher temperatures again the elemental iron selectivity can be maximized, whereas at temperatures over 500°C no additional benefit for the conversion of iron carbonate can be assumed.

The influence of the interaction of flow*flow was reduced in the further analyzes of the temperature be keeping the gas stream constant at

Acknowledgement

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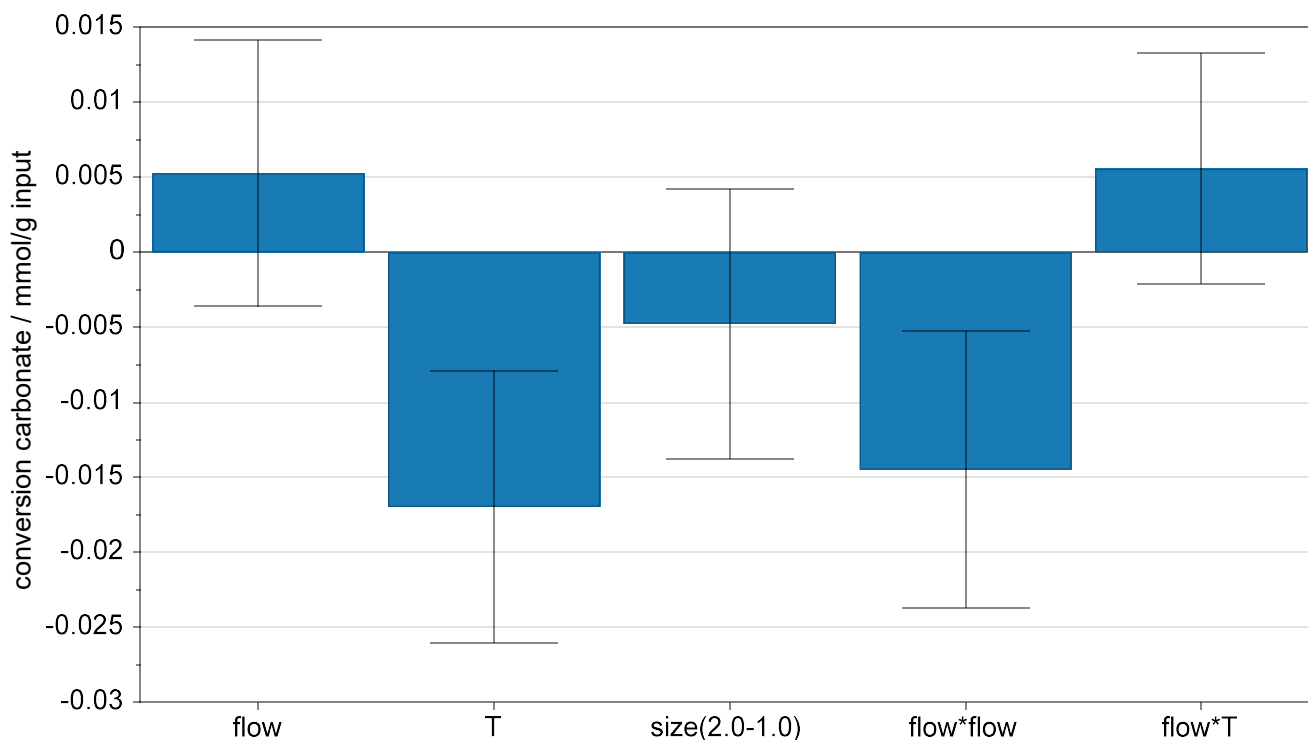

Figure 4: Result of the design of the experiments: Influence of the process parameters on iron carbonate conversion.