

Investigations on Mixed CO₂- and Steam Reforming of Liquid Hydrocarbons for the Decentralized Production of Hydrogen

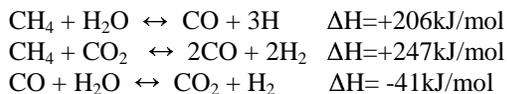
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For the mid term market introduction of FC vehicles decentralized hydrogen production may become an important issue. The reformer sponge iron process is an innovative process for the production of pure hydrogen suitable for all kind of fuel cells. As feedstock liquid hydrocarbons can be used, thus this process is well suited for the decentralized production of hydrogen e.g. at filling stations. In this presentation results on practical and theoretical investigations on mixed CO₂- and steam reforming of liquid hydrocarbons for the production of synthesis gas to be used in the reformer sponge iron process (the second step in the total RESC-process) are presented.

The Reformer Sponge Iron Cycle (RESC) is a process to convert gaseous and liquid hydrocarbons into pure hydrogen. It is based on the combination of the reduction / oxidation reaction of iron ores (Sponge Iron Reaction, SIR) [1] with mixed steam- and CO₂-reforming of hydrocarbons.

Sponge Iron, generated by the reduction of iron ores, is oxidized with steam to produce pure hydrogen and afterwards again reduced with synthesis gas. Reforming of hydrocarbons produces this synthesis gas. In this reforming process, a part of the lean gas containing H₂O and CO₂ is feed to the reactor as shown in Figure 1, thus a combined steam and CO₂-reforming will take place. The operating temperatures are 800°C-850°C for the SIR-process and the reforming of methane, and approx. 500°C for the pre-reforming of higher hydrocarbons. In detail the process is described in [2].

General reviews on steam reforming have been written by Rostrup-Nielsen [3] and others. This study concentrates on the reforming of hydrocarbons with simulated lean gas. Using the off-gas of the oxidizing step of the SIR-reaction simultaneously a carbon dioxide and a steam reforming takes place [4]. Parallel several reactions run off such as steam reforming, thermal cracking, methanisation, water gas shift reaction etc. The most important reactions (e.g. for methane) are:



The experimental setup is shown in Figure 2. According to theoretical calculations a gas mixture equal to the outlet of the oxidizing step in the steam iron reaction is mixed. Liquid hydrocarbons and water for the reforming reactions are evaporated and mixed with the preheated gas mixture and feed to the reactor. The reactor tube (inner diameter 24mm) is electrically heated. In the middle of the reactor tube 30g of industrial nickel based steam reforming catalyst are placed.

Besides the on-line gas analysis on H₂, CO, CO₂, and CH₄ using Hartman&Braun Advance Optima System of the outlet after condensing water, gas-chromatographic analysis (µGC) are carried out to be able to prove on

higher hydrocarbons (> to C₂) in the reformer's gas.

First results for the steam reforming of different feedstocks are summarised in the figure 3. In this experiments 0.2 mol/h hydrocarbon is reacted with steam using a steam to carbon ratio of 3:1. With increasing temperature the outlet concentration of methane degrades while hydrogen in the reformer's gas increases.

Gas chromatographic measurements shows that for the investigated hydrocarbons at catalyst temperatures above 500°C only methane can be found in the outlet, while for temperatures below 500°C traces of higher hydrocarbons can be determined.

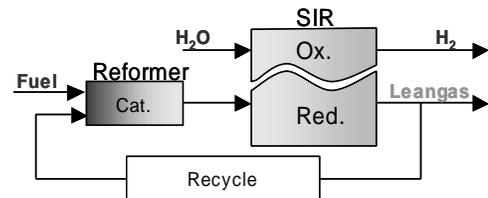


Figure 1: schematic representation of the RESC process to produce pure hydrogen from different hydrocarbons

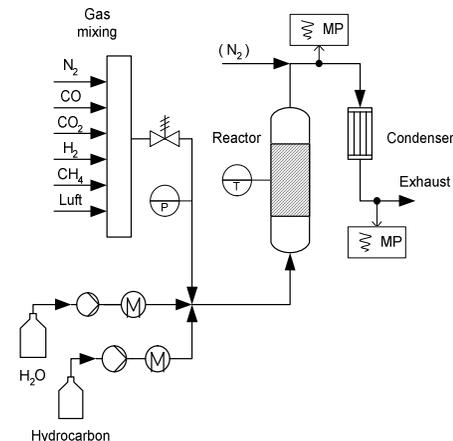


Figure 2: experimental setup

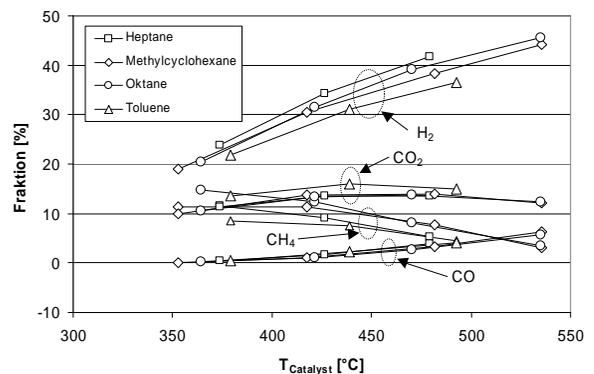


Figure 3: Reformer outlet gas composition for different feedstocks

Acknowledgements

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