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This document appeared in

Detlef Stolten, Thomas Grube (Eds.):

18th World Hydrogen Energy Conference 2010 - WHEC 2010

Parallel Sessions Book 3: Hydrogen Production Technologies - Part 2

Proceedings of the WHEC, May 16.-21. 2010, Essen

Schriften des Forschungszentrums Jülich / Energy & Environment, Vol. 78-3

Institute of Energy Research - Fuel Cells (IEF-3)

Forschungszentrum Jülich GmbH, Zentralbibliothek, Verlag, 2010

ISBN: 978-3-89336-653-8

Versatile Fuel Processor for Oxidative Steam Reforming and Catalytic Partial Oxidation of Various Liquid Fuels

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1 Introduction

Oxidative steam reforming (ATR) and catalytic partial oxidation (CPOX) are reforming processes widely used for on-board hydrogen production in fuel cell systems for off-grid, portable/mobile applications. These reforming processes allow dynamic operation with liquid fuels. Critical challenges in reforming liquid fuels pose the complex nature of the fuels containing various coke precursors, the prevention of combustion in the vaporizer/pre-heater section due to low auto-ignition temperatures, and the creation of homogeneous mixture of air and fuel.

This contribution presents a novel process to transfer a wide range of liquid hydrocarbons and alcohols into the gaseous phase, thus facilitating mixture preparation for reforming and combustion applications. The presented proprietary process transfers any liquid fuel (including diesel) into the gaseous phase and supplies the mixture to the reforming reactor where it is converted into a hydrogen rich gas (synthesis gas) without the formation of carbon or residues. The principle underlying this process is to evaporate the fuel from its surface by radiant heat transferred from a hot metal catalyst coated mesh rather than from a hot heat exchanger wall in contact with the liquid fuel (see Figure 1). For more details please refer to Aicher and Griesser [1]. The vaporized fuel is mixed with additional reforming air and partially oxidized in a CPOX catalyst, as shown in Figure 1. At this point an air/steam mixture can be supplied instead, thus increasing the hydrogen yield of the reforming process by operating it in an oxidative steam reforming mode. The reforming catalyst can be a packed bed or a monolith.

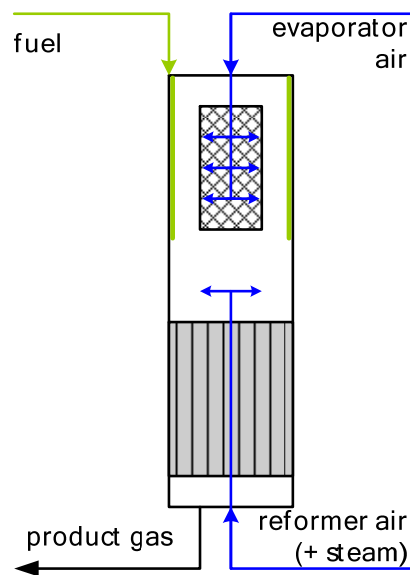


Figure 1: Sketch of the proprietary fuel evaporator reformer.

2 Carbon Formation

During the process design phase carbon formation was considered by investigating the thermodynamic equilibrium of carbon formation. Carbon formation depends on the oxygen-to-steam ratio (O/C) of the feed streams and reactor temperature. We performed process simulations of the CPOX process for hydrocarbons (iso-octane) with the commercial software package ChemCAD[®]. In order to determine critical carbon formation temperatures we calculated the equilibrium gas composition of a CPOX reactor for various oxygen-to-carbon ratios (O/C). By minimizing the Gibbs Free Energy the temperature could be obtained where only trace amounts of solid carbon (mol fraction $> 1\text{e-}6$) are predicted as a possible product. Figure 2 shows predicted minimum carbon formation temperatures in the gas phase over the O/C ratio of the reactor feed.

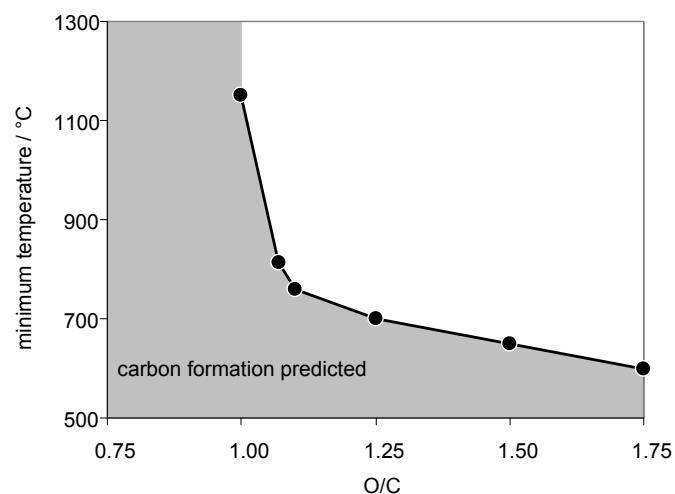


Figure 2: Calculated minimum temperature for diesel CPOX to avoid carbon formation.

When looking at the data you notice two contrary effects. From an operations standpoint you would like to reduce the amount of air supplied to the reactor in order to increase your reformer efficiency – the less fuel you combust and the better your reactor is insulated the higher the fuel efficiency. On the other hand, lowering the O/C increases the minimum temperature required to avoid carbon formation posing extra strains on the materials. Therefore, a happy medium has to be established, which lies somewhere between 1.1 and 1.3.

3 Experimental Results

Experimental investigations of the novel evaporator reformer reactor were performed. Test runs with commercial diesel (containing 16 ppm_w sulfur) and kerosene (5 ppm_w sulfur) will be presented for CPOX and ATR operation.

As an example, Figure 3 presents measured gas composition and reactor temperatures for operation of the reactor with diesel flow rates of 0.5 to 5.0 kW (based on the LHV of diesel). With increasing load, O/C was lower because heat losses became less dominant. With decreasing O/C, hydrogen and carbon monoxide concentration increase, while the carbon dioxide concentration decreases. In all cases the measured gas compositions are in close agreement with the thermodynamic equilibrium (not shown in Figure 3). Carbon deposits were never observed during inspection of the reactor internals after each test run. In addition, the concentration of unsaturated hydrocarbons, for instance ethylene, is very low (not shown in Figure 3). This implies that in the reforming catalyst no carbon was formed or deposited.

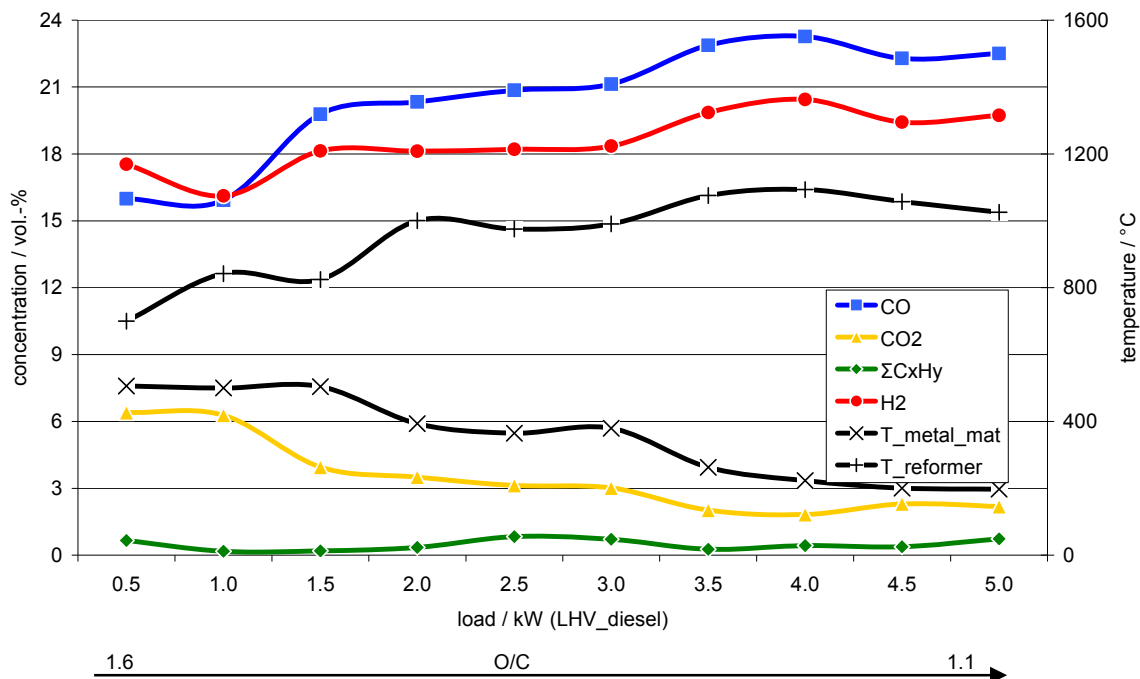


Figure 3: Gas composition and reactor temperatures measured for reactor loads between 0.5 and 5.0 kW (LHV_{diesel}).

In another set of experiments the impact of load changes on the reactor performance as well as the influence of higher sulfur concentrations in the diesel fuel was investigated. During load changes the air flow to the reactor has to be controlled in order to keep the CPOX reactor temperature below a maximum value of about 1000-1050 °C to avoid sintering of the catalyst. The investigations show that the system reacts immediately to load changes of 1.5 kW.

To elucidate the influence of sulfur on the evaporator reformer performance, two test series were conducted. First, three different diesel feeds with 16, 50 and 100 ppm_w sulfur were prepared and supplied to the reactor. The tests were done for two different diesel flow rates (1.5 and 3.0 kW). While the impact on the reformer temperature is negligible, the increase in sulfur reduces the concentration of carbon monoxide and hydrogen by approximately 10 % when increasing sulfur content from 16 to 100 ppm_w. The concentrations of methane and higher hydrocarbons show a slight increase. These effects are less pronounced at the higher diesel flow rate, i.e. 3.0 kW (see Fig. 4).

For the lower diesel flow rate the impact of sulfur on the performance over an extended period of time was investigated as well. Therefore, diesel with about 100 ppm_w sulfur was fed to the reactor for about 10 hours (see Fig. 4). Hydrogen and carbon monoxide concentration decline significantly from about 17.1 and 20.3 mol-% to about 15.3 and 18.7 mol-%, respectively. It was surprising that this deterioration in performance disappeared after purging with air for half an hour during shut down to ensure that no liquid hydrocarbons gather on the evaporator catalyst.

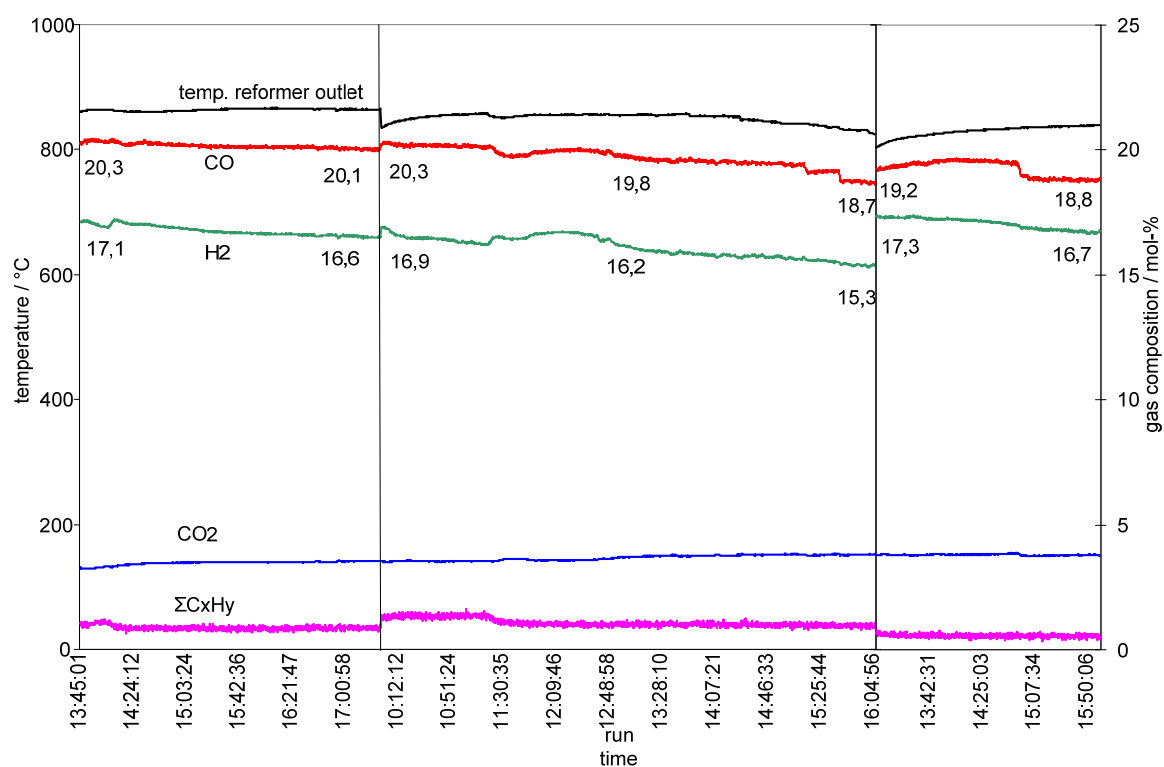


Figure 4: Impact of sulfur on diesel CPOX operation with 1.5 kW (LHV_diesel).

References

- [1] T. Aicher, L. Griesser, J. Power Sources, 165 (2007) 210-216