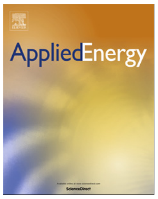
Applied Energy 150 (2015) 176–184

Contents lists available at ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy



A novel reactor type for autothermal reforming of diesel fuel and kerosene

Joachim Pasel [a,*], Remzi Can Samsun [a], Andreas Tschauder [a], Ralf Peters [a], Detlef Stolten [a,b]

[a] *Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research, IEK-3: Electrochemical Process Engineering, 52425 Jülich, Germany*
[b] *Chair for Fuel Cells, RWTH Aachen University, Germany*

HIGHLIGHTS

- Development and experimental evaluation of Juelich's novel ATR reactor type.
- Constructive integration of steam generation chamber and nozzle for water injection.
- Internal steam generator modified to reduce pressure drop to approx. a thirtieth.
- Novel concept for ATR heat management proven to be suitable for fuel cell systems.
- Reaction conditions during shut-down and start-up optimized to reduce byproducts.

ARTICLE INFO

Article history:
Received 13 February 2015
Received in revised form 8 April 2015
Accepted 9 April 2015
Available online 21 April 2015

Keywords:
Autothermal reforming
Diesel
Kerosene
Reactor development
Fuel cell systems
Start-up and shut-down strategies

ABSTRACT

This paper describes the development and experimental evaluation of Juelich's novel reactor type ATR AH2 for autothermal reforming of diesel fuel and kerosene. ATR AH2 overcomes the disadvantages of Juelich's former reactor generations from the perspective of the fuel cell system by constructively integrating an additional pressure swirl nozzle for the injection of cold water and a steam generation chamber. As a consequence, ATR AH2 eliminates the need for external process configurations for steam supply. Additionally, the internal steam generator has been modified by increasing its cross-sectional area and by decreasing its length. This measure reduces the pressure drop of the steam generator from approx. 500 mbar to roughly a thirtieth. The experimental evaluation of ATR AH2 at steady state revealed that the novel concept for heat management applied in ATR AH2 is suitable for fuel cell systems at any reformer load point between 20% and 120% when the mass fractions of cold water to the newly integrated nozzle are set to values between 40% and 50%. The experimental evaluation of ATR AH2 during start-up and shut-down showed that slight modifications of the reaction conditions during these transient phases greatly reduced the concentrations of ethene, ethane, propene and benzene in the reformate. From the fuel cell system perspective, these improvements provide a very beneficial contribution to longer stabilities for the catalysts and adsorption materials.

1. Introduction

According to analyses, the global energy demand is set to grow substantially in most fields over the next 25 years [1,2]. The analyses differentiate between industrial, transportation, residential and commercial sectors. Specchia [2] points out that the growth in energy demand will particularly apply to countries that do not belong to the "Organization for Economic Co-operation and Development" – non-OECD countries – like China or India. The highest growth rates for energy demand in these countries have been forecast for the industrial sector, while those for the transportation sector are anticipated to be slightly lower. In the OECD countries, a slight decrease has been forecast for the energy demand of the transportation sector. This has been attributed to higher fuel efficiencies, particularly in the case of light-duty vehicles. Nevertheless, in the year 2010, a large proportion of the total energy consumed in Germany, namely 29.5%, was spent by the transportation sector [3]. From this perspective, there is thus a great need and substantial potential for the technical and scientific development of efficient energy conversion systems. Among the numerous energy conversion technologies, fuel cell systems represent a promising variant. For example, when applied as auxiliary power units (APUs) in heavy-duty trucks or aircraft for onboard

---

* Corresponding author. Tel.: +49 2461 615140; fax: +49 2461 616695.
E-mail address: j.pasel@fz-juelich.de (J. Pasel).

http://dx.doi.org/10.1016/j.apenergy.2015.04.038
0306-2619/© 2015 Elsevier Ltd. All rights reserved.

power supply, fuel cell systems based on high-temperature polymer electrolyte fuel cells (HT-PEFCs) and autothermal reforming of liquid hydrocarbons have net efficiencies for power generation between 25% and more than 40% [4]. This comparably wide range correlates with the average cell voltage of the fuel cell stack and its hydrogen utilization, respectively. Efficiencies of 25% are due to values for the average cell voltage of 550 mV and 75% for the hydrogen utilization, while the highest system efficiencies of around 40% require an average cell voltage of 750 mV and a hydrogen utilization of 90% [4]. In this respect, 750 mV is regarded as the ultimate goal for HT-PEFC stack development. However, conventional-gas-turbine powered APUs used during ground operation in aircraft for onboard power generation have net efficiencies of only approx. 15% [5]. The efficiencies of APUs in heavy-duty trucks driven by the main diesel engine and operating in the "idling mode" only amount to approx. 11% [6]. A comparison of these values with the efficiency ranges of fuel-cell-based APUs shows the ecological and economic relevance of fuel-cell-based APUs. Recently, three projects on this topic funded by the European Commission's "Fuel Cells and Hydrogen Joint Undertaking" – "Fuel Cell Coupled Solid State Hydrogen Storage Tank (SSH2S)", "Fuel Cell Based Power Generation (FCGEN)" and "Demonstration of first European SOFC Truck APU (DESTA)" – were completed. Samsun et al. [7] have successfully demonstrated the operation of a fuel cell system with HT-PEFC and autothermal reforming of diesel fuel and kerosene with an electric power of 5 kW.

The core component of any fuel cell system operating on liquid fuels such as kerosene or diesel fuel – apart from the fuel cell itself – is the reformer. There are many different reforming routes and, of these, partial oxidation (POX), heated steam reforming (HSR) and autothermal reforming (ATR) are the most widespread and mature. At Juelich, priority is given to autothermal reforming because it is has been experimentally proven to be the most dynamic, robust and simple variant. The following reactions occur during autothermal reforming.

$$C_nH_m + nH_2O \leftrightarrow nCO + (m/2 + n)H_2 \quad \text{endothermic} \tag{1}$$

$$C_nH_m + n/2O_2 \leftrightarrow nCO + m/2H_2 \quad \text{exothermic} \tag{2}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \text{exothermic} \tag{3}$$

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \quad \text{exothermic} \tag{4}$$

According to the reaction equations, the main products of the autothermal reforming of diesel fuel and kerosene are H_2, CO, CO_2, and CH_4. H_2 and CO are formed by the steam reforming (Eq. (1)) and partial oxidation (Eq. (2)) of the hydrocarbon molecules. CO_2 and CH_4 are products of the water–gas-shift reaction (Eq. (3)) and the methanation reaction (Eq. (4)), respectively.

This paper describes the development and the experimental evaluation of Juelich's novel reactor type for autothermal reforming of diesel fuel and kerosene for fuel cell systems.

2. Experimental

The experiments at steady state and during start-up and shut-down of the autothermal reformer were performed with Juelich's reactor generation ATR AH2. It delivers a molar flow of hydrogen with a thermal power of 28 kW at maximum load. For ATR AH2, the volume of the catalytically coated monolith ($RhPt/Al_2O_3$–CeO_2 catalyst from Umicore AG & Co. KG) was calculated to achieve 100% reformer load at a gas hourly space velocity (GHSV) of approx. 30,000 h^{-1}, an O_2/C molar ratio of 0.47, and a H_2O/C molar ratio of 1.9. For the experiments, NExBTL diesel from Nesteoil in Finland was used. Its final boiling point is at 321 °C. NExBTL diesel does not contain any significant mass fractions of aromatics or sulfur either. Its molecular formula was derived from gas chromatographic analyses and reads $C_{17}H_{36}$ [8].

In all of the catalytic experiments with respect to autothermal reforming, the product gas was analyzed by a mass spectrometer (Prima 600 S, Thermo Electron Corporation) and by a Fourier Transform Infrared Spectrometer (Multigas 2030 FT-IR Analysator, MKS Instruments Deutschland GmbH). The concentrations of the following gases were determined: H_2, CO, CO_2, CH_4, N_2, O_2, Ar, ethane, ethene, propene and benzene.

3. Reactor development

At Juelich, several reactor generations for autothermal reforming have been developed and experimentally validated in recent years. Their fundamental design is shown in Fig. 1 and some pictures of them are presented in Fig. 2.

At steady state, liquid fuel is injected at room temperature into the evaporation chamber. There, fuel is completely evaporated using the enthalpy flow from a mixture of steam and air (as carrier gas), which enters the evaporation chamber at an elevated temperature in the range of 420–460 °C. Steam at these temperatures is provided by feeding a stream of cold water and air through the internal steam generator of the ATR and then by passing the mixture of steam and air through an external heating cartridge. An additional flow of air is injected behind the fuel evaporation chamber. The educt mixture consisting of steam, air and evaporated fuel enters the catalyst where the autothermal reforming reactions take place. The waste heat from these reactions is used in the internal steam generator as mentioned above.

Several publications [8–11] by our group describe the achievements of these reactors with established designs. In [8], the outstanding long-term stability of ATR 9.2 for 10,000 h of time on stream when operating with GTL kerosene and BTL diesel fuel was described and discussed. All reactors possess high power densities in the range of 2.8–3.6 kW/l as well as high mass specific powers with values between 2.2 kW/kg and 3.3 kW/kg [10]. In [11], the ATR 13, which was specifically designed for fuel cell systems for applications in trucks, was operated with a commercial standard diesel fuel for trucks at very high carbon conversions of at least 99.95%. Great effort was invested to identify optimum reaction conditions with respect to the H_2O/C and O_2/C molar ratios and to select the best available nozzle for fuel injection with excellent spray characteristics over the whole load range.

However, these reactor generations with established designs have some critical disadvantages from the fuel cell system perspective. They all require an external process configuration for water and steam mixing and external tubing for steam supply to the fuel evaporation chamber of the reformer. The system configuration is therefore more complex and there are higher heat losses to the environment. Additionally, the established design of the steam generator causes high pressure drops in the range of 500 mbar when it is fed with air and water or steam. This leads to high parasitic losses for the whole fuel cell system due to a relatively high power consumption of the compressor for air supply. These issues together cause a decreased efficiency of the fuel processor section and, of course, reduce the overall system efficiency.

For the design and construction of Juelich's novel reactor type for autothermal reforming, ATR AH2, as shown in Fig. 3 these drawbacks were considered and overcome. Firstly, an additional pressure swirl nozzle for the injection of cold water and a steam generation chamber were incorporated. As a consequence, ATR AH2 eliminates the need for external process configurations for steam supply. Secondly, the steam generator was modified by increasing its cross-sectional area and by decreasing its length.