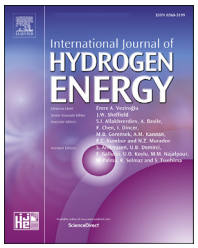
Available online at www.sciencedirect.com

ScienceDirect

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



Water-gas shift reactor for fuel cell systems: Stable operation for 5000 hours

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*

ARTICLE INFO

Article history:
Received 23 March 2018
Received in revised form
9 August 2018
Accepted 20 August 2018
Available online 13 September 2018

Keywords:
Water-gas shift reaction
Reactor development
Long-term stability
Catalyst regeneration
Fuel cell systems

ABSTRACT

The water-gas shift reactor in the fuel processing unit of a fuel cell system has the vital function of reducing the concentration of CO in the reforming reactor's product gas to values of between 1.0 and 1.5 vol% in order to protect the anodic catalyst from becoming irreversibly poisoned. This paper presents Jülich's recent development in this field, specifically the WGS 6 in the 5 kW_e class. The WGS 6 is characterized by a fundamentally new concept for arranging high temperature and low temperature shift stages. Both stages are now coaxially integrated in one joint casing to provide higher values for the power density and specific power, whereas in earlier reactor generations, these stages are arranged in two separate, parallel housings. In addition, this contribution presents results from a long-term experiment for 5000 h on stream with WGS 6 and discusses the temporal trends of the product gas composition and reactor temperatures across this timespan. For this experiment, the inlet gas stream is produced by an autothermal reformer, which is installed upstream of the WGS 6.

Introduction

Energy utilization and environmental degradation are undeniably linked [1]. Depleting fossil fuel resources, high levels of pollution and climate change repeatedly draw attention to this issue and reinforce the need to make energy conversion more sustainable. Energy, largely generated from fossil fuels, enabled the industrial and therefore economic growth of the last 250 years [2,3]. In order to best protect the environment, preventive measures such as making energy generation more sustainable must be taken. In accordance with the notable increase in the service and transport sectors in the last 40 years [4], these account for a high proportion of emissions. The expansion of the transportation network made it significantly easier to move goods, people and information across cities, countries and continents. This enabled industry to shift to locations where production was cheaper and for both goods and people to travel further distances. In 2013, transportation accounted for a third of energy consumption in OECD countries, making it the largest sector by energy consumption, and almost completely reliant on oil [4]. In the transport sector, most vehicles continue to be powered by internal combustion engines (ICEs). These engines are largely fueled by liquid hydrocarbon mixtures, such as crude oil fractions or biodiesel, by which they convert thermal and chemical energy into

* *Corresponding author.*
E-mail address: j.pasel@fz-juelich.de (J. Pasel).
https://doi.org/10.1016/j.ijhydene.2018.08.125

mechanical energy. However, the combustion of these hydrocarbon fuels produces high amounts of harmful and environmentally-potent by-products, including carbon oxides, sulfur components and fine particulates. An ideal fuel alternative is hydrogen. It is the most abundant element in the universe and also has the highest specific energy, namely: 122 kJ g^{-1}, which is 2.75 times greater than that of any other conventional fuel [5,6]. As water is the only product of hydrogen combustion, utilizing it reduces greenhouse gas emissions and eliminates pollutant emissions from both mobile and stationary sources, as well as increases fuel efficiency [1]. However, the largest limitation of using hydrogen as a transport fuel is the lack of sufficient infrastructure [7]. In this respect, a suitable route for hydrogen production is onboard fuel reforming. Thereby, hydrogen can be produced in transit from conventional fuels such as diesel, removing issues of storage and logistics [8]. The most promising technology for enabling the use of hydrogen as an energy carrier is fuel cells. An auspicious means to introduce hydrogen fuel cells into the transportation sector is through specialized technologies such as auxiliary power units (APUs) [9]. APUs can be used in large vehicles, aircraft and leisure transportation to provide energy for functions such as heating, refrigeration and lighting. At present, commercial aircraft APUs have an efficiency of 15–20% in ground operation [10,11], while idling truck engines operate at only 3–11% efficiency [12–14]. The current Department of Energy (DoE) 2020 efficiency targets for APUs in trucks and planes are 40% [10,15]. According to Samsun et al. [16], fuel cell-based APUs offer the potential to reach this efficiency goal. Specchia [17] published an interesting overview about research and development at a European level on fuel processor units, commercially available APUs and combined heat and power systems (CHPs). A large variety of fuels such as natural gas, biogas, low sulfur road diesel, propane, butane, liquefied petroleum gas (LPG), methanol and ethanol can be used for these systems. Doucet et al. present a system for the co-generation of heat and electricity using a polymer-electrolyte fuel cell (PEFC) for e.g. domestic applications [18]. Thereby, hydrogen can be produced by water electrolysis and stored in hydride tanks. The three principal methods of reforming for hydrogen generation are steam reforming (SR), partial oxidation (POX) and autothermal reforming (ATR) [19]. These account for 96% of industrial hydrogen production [6] and can also be conducted in trucks and aircraft. Within the European project BIOFEAT aiming at the development of a biodiesel fuel processor for a PEFC, Specchia et al. [20] performed a conceptual design study with three fuel processing routes: (i) ATR with high-temperature (HTS) and low-temperature shift stage (LTS), (ii) ATR with one medium-temperature shift stage (MTS) and (iii) a thermal cracker with HTS and LTS. As a result of their simulations, they identified the combination of ATR with HTS and LTS as most appropriate with an overall APU system efficiency of approximately 29%. Severin et al. [21] address the important aspect of system size and present a packaging concept for a fuel cell-based APU with an electric power of 3 kW and a volume of the fuel processor unit of 25 L. Apart from the desired hydrogen, the product gases of the reforming reactions (reformate) contain considerable amounts of CO_2, CO and CH_4 as additional main products, with CO concentrations being in the range of 7–10 vol% [22,23]. Unfortunately, CO poisons the anode reaction in PEFCs working at 80 °C due to preferential adsorption and blocking of the active sites. This should be avoided, as reversing the effect of the CO on the catalyst often requires different operating conditions and is therefore not instantaneous, resulting in a substantial performance decrease [24]. Current high-temperature polymer-electrolyte fuel cells (HT-PEFCs) operate at temperatures in the range of 120–200 °C [25]. The increased temperature range is beneficial, as it enhances the anode and cathode kinetics, simplifies stack cooling and water management, but most importantly, the increase in CO tolerance up to 3 vol% is crucial [26,27]. As a consequence, the type of fuel cell greatly influences the extent of the gas clean up necessary to decrease the above-mentioned CO concentrations. If a PEFC (80 °C) is used, CO concentrations must be reduced to 50 ppm, which makes the combination of a water-gas shift (WGS) reactor with a methanation reactor or a reactor for the preferential CO oxidation (PROX) mandatory [22,28,29]. However, if the APU operates with an HT-PEFC, it is sufficient to reduce the CO concentration to values of below 3 vol% [26], whereby a reduction of the CO concentration to the range of 1.0–1.5 vol% is highly preferable. In this case, it is adequate to include a WGS reactor in the fuel processing unit of the APU. For the WGS reaction, as with other chemical processes, central significance is attached to the catalyst (for lowering the activation energy) and issues relating to its activity and stability. Krekel et al. [30] summarize a large number of scientific contributions that deal with possible routes for WGS catalyst deactivation. These are carbonate/formate formation on the catalyst surface [31–40], over-reduction of the washcoat [37,41–43], washcoat particle growth [44–46], loss of interaction between the catalyst and washcoat [47–49], sintering of catalyst particles [38,42,50–57], the influence of unsaturated alkenes, such as ethene, propylene and butene in the reformate [19,45,58,59] and the formation of sulfur species on the catalyst surface [60,61]. In this paper, the development of reactors for the water-gas shift reaction conducted in recent years at Jülich is described with a focus on technical advances in actual reactor generation denoted as 'WGS 6'. In addition, this contribution presents experimental results from a long-term experiment for 5000 h on stream with WGS 6 and discusses the temporal trends of product gas composition and reactor temperatures within this timespan. The educt gas mixture for the WGS 6 was generated in an autothermal reformer (ATR). The reaction conditions under which the ATR was operated are also described in detail in this contribution.

Reactor development WGS

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H = -41.2\ \text{kJ mol}^{-1} \tag{1}$$

For the water-gas shift reaction (see Eqn (1)), four reactor generations (WGS 3-WGS 6) were designed and manufactured at Jülich in recent years. Their thermal powers, power densities and specific powers are summarized in Table 1 (WGS 1 and WGS 2 are not included in this list as they were immature, bulky and simple proofs of concept). The development of these reactor generations is based on earlier investigations