An experimental investigation of biodiesel steam reforming

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ABSTRACT

Recently, liquid biofuels have attracted increasing attention as renewable feedstock for hydrogen production in the transport sector. Since the lack of hydrogen infrastructure and distribution poses an obstacle for the introduction of fuel cell vehicles to the market, it is reasonable to consider using liquid biofuels for on-board or on-site hydrogen generation. Biodiesel offers the advantage of being an environmentally friendly resource while also having high gravimetric and volumetric energy density.

The present study constitutes an experimental investigation of biodiesel steam reforming, the main emphasis of which is placed on finding optimum operating conditions in order to avoid catalyst deactivation. Temperature was varied from 600 °C to 800 °C, pressure from 1 bar to 5 bar and the molar steam-to-carbon ratio from 3 to 5. Based on the experimental results, coke formation and sintering are identified as the main deactivation mechanisms. Initiation of catalyst deactivation primarily depends on catalyst inlet temperature and feed mass flow per open area of catalyst. By using a metallic based precious metal catalyst, applying low feed flow rates (31 g/h·cm^2) and a sufficiently high catalyst inlet temperature (>750 °C) coking can be minimized, thus avoiding catalyst deactivation. A stable product gas composition close to chemical equilibrium has been achieved over 100 h with a biodiesel conversion rate of 99%.

Introduction

Today, approximately 65 million tons of hydrogen are produced annually worldwide [1]. Steam reforming of natural gas is the prevalent hydrogen production technology. Large quantities of hydrogen are needed in the chemical and petrochemical industry, in particular for ammonia production, oil refining and methanol synthesis. Moreover, hydrogen is increasingly discussed as a fuel for transport applications [2]. Especially production from logistic fuels is considered as a viable option to accelerate market introduction of hydrogen as an alternative energy carrier [1].

Auxiliary power units (APUs) for on-board power generation based on liquid fuels are generally regarded as one important early market for fuel cells (FCs) in transport. Detailed analysis of the market for diesel proton exchange membrane (PEM) fuel cell APUs revealed a market demand for

implementation in long-haul trucks in particular in the United States and elsewhere [3]. On-board APU systems can help reduce greenhouse gas emissions. By coupling fuel processor systems based on liquid fuels with solid oxide fuel cell (SOFC) or PEM based APUs, CO_2 emissions can be reduced by up to 33% [4]. Apart from directly coupling a fuel processor with an FC, reforming of liquid biofuels can be applied for on-site decentralized hydrogen production, for instance by integrating a reformer system into an existing refueling station as currently investigated in the FCH JU project NEMESIS2+ (New Method for Superior Integrated Hydrogen Generation System 2+). Thereby problems related to the lack of hydrogen infrastructure can at least be partly avoided [5].

Recently, biodiesel has been attracting increasing attention as a renewable and environmentally friendly resource for fuel cell applications [6,7]. Currently, biodiesel is produced at a rate of approximately 30 billion liters per year, thus representing 19% of world's biofuel production [8]. Biodiesel is a fatty acid methyl ester (FAME) which is produced from transesterification of vegetable oil with methanol. Glycerol emerges as by-product and can be further used for food industry and pharmaceutical applications.

Hydrogen production from biodiesel by means of reforming can be achieved via partial oxidation (POX), steam reforming (SR) or autothermal reforming (ATR). SR is the most established technology among the available reforming options. A main advantage of SR is the high partial pressure of hydrogen in the reformate gas, which allows the subsequent fuel cell stack to operate with higher efficiency. In contrast, the system complexity of an SR-APU system is higher compared to an ATR-APU system resulting in increased system weight, volume and costs. Regarding net electrical efficiency, simulation studies of Specchia et al. and Martin et al. report comparable values for SR- and ATR-APU systems in the range of 30–39 % [9,10].

Various types of catalysts appear suitable for biodiesel reforming, including noble, non-noble and bimetallic catalysts [1,11]. Rh and Ni catalysts are commonly considered to be most suitable for steam reforming of liquid fuels [12]. The main challenge related to biodiesel reforming is unwanted coke deposition on the catalyst surface, resulting in performance losses. Furthermore, catalyst deactivation can be caused by sintering and/or sulfur poisoning [13]. Taking into account that biodiesel has a relatively low sulfur content of typically <5 ppm, coking and sintering are considered to be the main causes of catalyst deactivation.

The reported literature treating hydrogen production from biodiesel is almost entirely related to the ATR of biodiesel for fuel cell applications [14–21]. Although promising concepts have been identified, challenges remain with regard to incomplete biodiesel conversion, formation of higher hydrocarbons, catalyst coking and poor mixing of reactants. In contrast, hydrogen production from biodiesel by means of steam reforming is very recent and offers significant room for further development [6,7].

Nahar carried out a thermodynamic analysis of biodiesel SR and ATR using Gibbs free energy minimization method [22]. The water-biodiesel molar feed ratio (WBFR) was varied between 3 and 12, oxygen-biodiesel molar feed ratio (OxBFR) between 0 and 4.8 and reaction temperature between 300 °C and 800 °C at atmospheric pressure. Hydrogen yield and selectivity were found to be highest for SR conditions with a maximum hydrogen yield at WBFR = 12 and T = 800 °C. Increased coke selectivity is reported for SR compared to ATR conditions.

Martin and Wörner report a plateau for thermal hydrogen efficiency for a heat integrated biodiesel SR system (including water gas shift and burner) of 76% at S/C = 3 in the temperature range 700 °C–850 °C [10].

Abatzoglou et al. investigated biodiesel steam reforming using a newly developed Al_2O_3/YSZ supported $NiAl_2O_4$ spinel catalyst [23]. Work was performed in a fixed-bed isothermal reactor. Biodiesel/water was emulsified prior to being injected at room temperature into the reactor preheating zone maintained at 550 °C. The molar steam-to-carbon ratio (S/C) was varied between 1.9 and 2.4, the temperature between 700 °C and 725 °C and space velocity (SV) between 5500 and 13 500 $cm^3_{reac}g^{-1}_{cat} h^{-1}$ at atmospheric pressure. Results show that complete biodiesel conversion is achieved during 4 h of operation at S/C = 1.9, SV = 5500 and T = 725 °C. Coke deposition and catalyst deactivation were not observed.

Shiratori et al. evaluated paper structured catalysts (PSCs) for steam reforming of biodiesel [24]. Catalytic activity of the Ni-PSC could be significantly improved by Ni–MgO loading and introducing Cs as an inorganic binder. The inorganic fiber network of the PSC with a mean pore size of 20 μm leads to an effective three-dimensional diffusion and a good dispersion of the metal catalyst particles, resulting in efficient biodiesel conversion. 50 h of biodiesel steam reforming was achieved using a Ni–MgO loaded PSC at 800 °C and S/C = 3.5 with 90% fuel conversion. Although formation of C_2H_4 could be avoided, CH_4 levels started to rise after 28 h of operation, indicating the onset of catalyst deactivation. However, Ni agglomeration and carbon deposition on the PSC were not observed. In a follow-up study, the authors evaluated SOFC performance connected with PSC in the direct feed of wet oleic fatty acid methyl ester ($C_{19}H_{36}O_2$). By application of two PSCs in series (Ni–MgO loaded and Ru-loaded $BaTiO_3$ containing PSC) prior to a single cell SOFC, stable cell voltage has been observed for 100 h at 800 °C and S/C = 2. Carbon formation was not observed on the SOFC anode surface nor on the PSCs. Data on reformate gas composition prior to the SOFC is not available [25].

Nahar and Dupont reviewed the use of steam reforming to convert liquid bio-feedstock to hydrogen-rich product gas. They consider liquid fuels to be a promising option for hydrogen production, offering a range of advantages such as existing infrastructure and high volumetric and gravimetric energy density. According to the authors, biodiesel is among the least explored liquid feedstocks for hydrogen production [6].

The objective of this paper is to evaluate biodiesel steam reforming at various operating conditions using a proprietary precious metal based catalyst. The experimental study includes variation of the reforming temperature, pressure, steam-to-carbon ratio, feed mass flow and catalyst substrate. The main emphasis is placed on finding optimum conditions for coke-free operation, thus avoiding catalyst deactivation. The initiation of catalyst deactivation is evaluated in detail including measurement of carbon deposition on the catalyst