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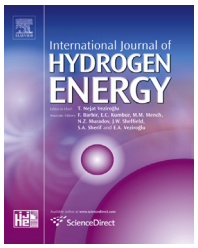

Evaluation of on-site hydrogen generation via steam reforming of biodiesel: Process optimization and heat integration

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ABSTRACT

The present simulation study investigates on-site hydrogen generation (50 Nm^3/h) via steam reforming of biodiesel. The system comprises a steam reformer, a water gas shift stage, a pressure swing adsorption unit and a dual fuel burner. Sensitivity analysis with Aspen Plus shows a positive effect on overall system efficiency for high pressure and low steam-to-carbon ratio. A theoretical maximum efficiency (based on lower heating value) of 78.2% can be obtained requiring a complex and costly heat exchanger network. Consequently, a system simplification is proposed resulting in a novel fuel processor concept for steam reforming of biodiesel based on a fully heat integrated system. A thermal system efficiency of 75.6% is obtained at S/C = 2.53, p = 13 bara and T = 825 °C. The techno-economic evaluation reveals hydrogen production costs ranging from 5.77 €/kg to 11.15 €/kg (depending on the biodiesel market price).

Introduction

Today, hydrogen is predominantly produced by steam reforming of natural gas in large-scale, central production plants. However, with an increasing share of fuel cell vehicles (FCVs) in the market, central hydrogen production will suffer from additional costs associated with the distribution of gaseous-phase hydrogen by trailer over long distances [1]. In contrast, distributed hydrogen generation (DHG) at fueling stations offers the advantage of using readily available liquid fuels such as diesel and biodiesel with high energy densities and already existing infrastructure. DHG is widely seen as a promising alternative in the transition phase towards a fully renewable hydrogen production economy [2–4]. DHG is applicable but not limited to decentralized hydrogen production at fueling sites. There is an increasing demand for annealing applications, in particular for the steel industry and the production of high quality flat glass. According to Neumann et al. [5] conventional hydrogen generation processes up to 300 Nm^3/h H_2 are being increasingly substituted with advanced steam reforming technologies.

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Steam reforming (SR) offers the advantage of a high partial pressure of hydrogen in the product gas (70–80 vol.%, dry basis) compared to 40–50 vol.% for autothermal reforming (ATR) and partial oxidation (POX). Taking further into account that compressing liquid fuels is less energy intensive than compressing gaseous feeds, SR of liquid fuels is widely considered to be the preferred reforming option for stationary hydrogen generation [3,6,7].

Amongst the available logistic fuels, biodiesel, which is a fatty acid methyl ester (FAME) produced from transesterification of vegetable oil with methanol, appears to be a promising feedstock for DHG by means of SR [8,9]. Biodiesel is a renewable, non-polluting resource with a low sulfur content (typically below 5 ppmw). This renders biodiesel a favorable feedstock for catalytic applications since sulfur is known to be a strong catalyst poison [10].

In the past years, several experimental studies have been conducted shedding light on biodiesel steam reforming [11–14]. Recently, Martin et al. [15] presented a study, the main emphasis of which was placed on finding suitable operating conditions for SR of biodiesel. A stable product gas composition has been achieved over 100 h of operation by using a metallic based precious metal catalyst, applying low feed mass flow rates and a sufficiently high catalyst inlet temperature (>750 °C). Catalyst deactivation was not observed. A preceding parametric study revealed a detrimental effect of low catalyst inlet temperatures on catalyst deactivation by coking whereas the effect of varying steam-to-carbon (S/C) ratio in the considered range [3–5] was negligible. Concurrently, Lin et al. [16] observed increasing carbon formation with decreasing reforming temperature. Regarding the minimum allowable S/C ratio in order to ensure coke-free operation, there is evidence from literature data that stable operating conditions with complete biodiesel conversion can be achieved at S/C ratios as low as 2 [11,13].

Moreover, several research groups have carried out theoretical and experimental studies in order to find optimum operating conditions for small-scale hydrogen production systems targeting high system efficiency and low hydrogen production costs.

Katikaneni et al. [17] carried out a detailed performance study comparing on-site hydrogen generation from liquid fuels by different process routes. Calculations were based on a 1000 kg/d hydrogen filling station (approximately 250 FCVs per day). The hydrogen generation efficiency was found to be highest for a concept based on SR with upstream hydrodesulfurization. For diesel fuel a thermal H_2-efficiency of 65.2% was calculated. In terms of hydrogen production costs, the authors conclude that on-site diesel SR is competitive with centralized hydrogen production from natural gas with pipeline transport ($ 6.72 per kg vs. $ 6.23 per kg). Finally, the authors present a hydrogen roadmap starting with a small-scale 50 Nm^3/h H_2 generation system ($ 28.8 per kg H_2), the costs of which can be reduced dramatically by design optimization and heat integration.

Persson [18] investigated an integrated 20 kW hydrogen production system based on feedstock methane using a catalytic converter (steam reformer, water gas shift reactor, catalytic burner) and a pressure swing adsorption (PSA) unit. The Aspen Plus calculations were carried out at a pressure of 4 bara assuming a reformer catalyst inlet temperature of 550 °C and an outlet temperature of 850 °C. In the downstream WGS reactor the carbon monoxide content was reduced to below 1.5 vol.%. The PSA off-gas and methane were burned with air at 900 °C in order to provide the necessary heat for the endothermic steam reforming reaction. Parasitic power consumption amounted for 520 W with estimated heat losses of 710 W. The S/C ratio and the system pressure were identified to be crucial parameters for achieving a high system efficiency. A maximum theoretical efficiency (based on lower heating value LHV) of 79.1% is reported at an S/C ratio of 2.2.

Hulteberg et al. [3] carried out an experimental investigation based on a similar system using Fischer-Tropsch-Diesel for the production of 7 Nm^3/h H_2. The catalytic converter was operated at a pressure of 5 bara and an S/C ratio of 3.1–4.1. Reforming catalyst temperature ranged from 650 °C at the catalyst inlet to 750–800 °C at the catalyst outlet. High heat and mass transfer was ensured by using a noble metal catalyst supported on a patented thermally sprayed woven wire mesh system. With the given experimental set-up, a maximum system efficiency of 58% (based on LHV) was achieved assuming a parasitic power consumption of 500 W.

Although considerable progress has been made in terms of reformer durability and system performance, the development of efficient, low-cost DHG systems based on liquid fuels is still in an early stage leaving room for further development [19,18]. It is well known that hydrogen production costs based on reforming technology depend heavily on the feedstock price [20,1]. Thus, improving reforming efficiency is essential in order to make DHG competitive with other hydrogen production technologies such as central production and distribution by trailer. Moreover, there is a need to substantially reduce investment costs by reducing system size and complexity [4,21].

Regarding SR of biodiesel, there is no literature data available for heat integrated on-site hydrogen production systems including PSA in the kilowatt range. A PSA unit is necessary in order to obtain high purity hydrogen. Preferential oxidation (PrOx) is not applicable in the given case since CO_2 remains in the product gas stream.

The aim of the present paper is to evaluate a 50 Nm^3/h hydrogen generation system based on SR of biodiesel. The chosen capacity arises due to the current market demand for decentralized hydrogen production plants reported by the National Hydrogen Association [22] and the U.S. Department of Energy [23]. Accordingly, most fueling stations with on-site hydrogen production have a hydrogen generation unit in the range between 30 and 100 Nm^3/h. In line, Katikaneni et al. [17] present a roadmap for on-site hydrogen generation at commercial scale, starting with a small size hydrogen refueling station of 50 Nm^3/h. The main emphasis of the current simulation study is placed on maximizing system efficiency by an extensive parameter variation (including system pressure and S/C ratio) and setting up a heat exchanger network with a maximum internal heat recovery and a minimum external heating/cooling demand. A novel fuel processor concept is proposed based on a fully heat integrated biodiesel SR system. Further economic analysis is provided.