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Hydrogen safety risk assessment methodology applied to a fluidized bed membrane reactor for autothermal reforming of natural gas

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A B S T R A C T

The scope of this paper is the development and implementation of a safety risk assessment methodology to highlight hazards potentially prevailing during autothermal reforming of natural gas for hydrogen production in a membrane reactor, as well as to reveal potential accidents related to hydrogen under certain conditions. The newly developed methodology is able to cover all possible risk scenarios. The methodology was applied to a novel autothermal membrane fluidized bed reactor integrated within a micro-CHP system of 5 kWel with a PEM fuel cell. The system modelled is based on a prototype developed within the European ReforCELL project. A thorough safety risk assessment methodology was applied examining and evaluating the final outcomes of hydrogen release accident scenarios. The main conclusion of this analysis is that hydrogen may lead to a series of accident types that may pose a threat to the public safety, however, all considered scenarios fall well within the standard criteria, which indicates the adequate safety of this novel technology.

Introduction

In recent years a great effort has been dedicated to the gradual substitution of ordinary fossil fuels by new energy carriers, primarily because of the simultaneous depletion of natural resources, rapid increase in the worldwide energy demand and impact of anthropogenic CO_2 emissions on climate change. Hydrogen is emerging as a future alternative for mobile and stationary energy conversion systems in addition to its use in chemical and petrochemical applications, mainly because it is an energy-efficient and low-polluting fuel [1]. Alternatively, aiming at environmental benefits, the use of hydrogen combined with other gaseous fuels (i.e. natural gas) to increase the conversion efficiency is under consideration [2].

At the moment most of the hydrogen consumed worldwide is being produced by dehydrogenation of fossil fuels or by water splitting using electricity generated with fossil fuels [3]. On one hand, there are different studies assessing how to increase the efficiency of different methods for hydrogen production using either fossil sources or renewable sources [4,5].

On the other hand, a full deployment of hydrogen as the preferred energy carrier will surely be influenced by the public acceptance of hydrogen mainly based on safety concerns for

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both production (centralized or distributed) [6,7] and utilization (automotive or residential) [8]. The public perception is definitely influenced by past circumstances of severe accidents with significant economic and societal costs [9]. While the causes of these accidents should be better evaluated, surely better safety measures related to hydrogen are required. To this end, a better knowledge of potential hazards and ways to better evaluate risk zones around hydrogen installations are required [10].

In recent years different papers have been proposed assessing the risks associated with hydrogen production and hydrogen utilization [11–15].

In this paper, a thorough safety risk assessment methodology has been developed and applied to the case of hydrogen production through an autothermal membrane reformer (ATR-MR) integrated within a micro-CHP system of 5 kW_{el} based on a PEM fuel cell. The system under investigation is based on a prototype developed within the ReforCELL European project. The safety risk assessment analysis covers the hazard identification, frequency assessment, consequence assessment and risk characterization. In particular, a systematic approach is applied, which measures risk through risk analysis methods and relates it to established acceptance criteria for the identification of design specifications or need for risk mitigating measures.

First the membrane reactor concept and system design will be described, followed by the description of the risk identification strategy and finally the risk evaluation will be carried out.

Autothermal reforming of NG in a fluidized bed membrane reactor concept

Fuel cell development has seen remarkable progress in the past decade because of the increasing need for further improvements in energy efficiency and the possibility of clean energy conversion, two main pillars of the H2020 European research agenda. Because of the direct transformation of chemical energy into electrical energy, the fuel cells are not limited by the Carnot cycle efficiency, resulting in a higher energy efficiency than can be achieved with any other current energy conversion cycle. Small scale applications (up to 100 kW) include primary propulsion for light duty vehicles, auxiliary power units, and portable power for residential applications (combined heat and power application, CHP) [16].

Polymer electrolyte membrane fuel cells (PEMFCs) are primarily suited for residential, commercial and transportation applications. While PEMFCs offer a higher power density compared with other fuel cell systems, they require ultrapure H_2 (<10 ppm CO) because of extreme sensitivity of the anode catalyst towards CO poisoning. This has essentially raised the need to develop reactor (and separation) technologies for the production of ultrapure H_2 from fossil fuels with very high energy efficiency [17], especially when small scale hydrogen production applications are concerned.

Indeed, on an industrial scale, most of the hydrogen is currently produced via steam reforming of natural gas. The conventional process involves feed gas preheating and pretreatment (such as hydro-desulphurization), primary and secondary reformers (often multi-tubular fixed-bed reactors) and high and low temperature shift converters, CO_2 removal and methanation units. Often a PSA (Pressure Swing Adsorption) unit is used to achieve the desired hydrogen purity. In view of thermodynamic limitations and the high endothermicity of steam reforming, heat transfer at high temperatures (850–950 °C) is required, whereas excess of steam is used to avoid carbon deposition (typical feed H_2O/CH_4 molar ratios are 2–5) [18,19].

For the production of ultra-pure hydrogen for small scale applications, this route is not attractive because of the large number of process units required, which makes downscaling uneconomical, especially because of the difficulties in heat integration. A high degree of process integration and process intensification can be accomplished by integrating hydrogen perm-selective membranes in the steam reformer [20,21] [22]. Via the integration of hydrogen perm-selective membranes, the number of process units can be drastically reduced while the total required reactor volume can be largely reduced. At the same time higher methane conversions and hydrogen yields beyond thermodynamic equilibrium limitations can be achieved, at lower temperatures and with higher overall energy efficiencies [23–27].

Autothermal operation without external or internal heat exchange can be accomplished through a combination of steam reforming and oxidation, which together with the membrane integration inside a fluidized bed reactor allows to combine the benefits of both separation and purification via the membranes and benefits derived from fluidization, viz. good heat and mass transfer, uniform temperature and low pressure drop [28].

System description

In order to assess the hydrogen production process through an ATR-MR system, a fluidized bed membrane reactor was considered, as designed by the Chemical Process Intensification group at the Eindhoven University of Technology which was used as a base case for a prototype developed within the European ReforCELL project.

The process flow diagram (Fig. 1) shows that the setup consists of six sections: a feed section, a steam feed section, a reactor section, a permeate side, a retentate side and an analysis section.

The feed section consists of the feed gases supply from gas cylinders (mainly CH_4, Air/O_2 and N_2) and mass flow controllers to set the desired flow rate and gas composition. All gas supply lines are additionally protected with pneumatically operated shut-off valves to cut-off gas supply in case of an emergency shutdown. For the steam feed section, a Controlled Evaporator Mixer (CEM) system is used to generate steam. The steam supply lines (connected to the reactor exhaust lines) are insulated and covered with electrical tracing to keep the temperature sufficiently high (~200 °C) to avoid water condensation and pressure fluctuations in the reactor due to droplet formation.

The reaction section consists of the fluidized bed membrane reactor which is heated by three electrical furnaces in order to overcome unavoidable heat losses. The reforming