International Gas Union Research Conference 2014

Development of an Autothermal Biogas Processor for Hydrogen Production

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Keywords: biogas reforming, autothermal reforming, green hydrogen production, reforming plant, CFD simulation of regularly structured catalyst supports

Abstract

In this paper a novel concept for biogas reforming is presented. Major novelties are the utilization of an autothermal or oxidative steam reforming in combination with a subsequent catalytically coated soot trap for soot retention and oxidation as well as enhancement of the water gas shift reaction.

The plant design of the BioRobur (Biogas robust processing with combined catalytic reformer and trap) processor has been realized on the basis of ASPEN PLUS® mass and energy flow modeling. The system efficiency depends on the reforming route (catalytic partial oxidation, steam reforming or autothermal reforming), the level of heat integration, the preheating temperature of the mixed reactants, the steam-to-carbon- and oxygen-to-carbon ratio as well as the usage of the off-gas from pressure swing adsorption (PSA). The highest efficiency is achieved with an autothermal reforming in the first place. Through the energetic usage of the PSA off-gas in an extra burner and a sophisticated heat integration a system efficiency up to nearly 70% is realizable. Without the two mentioned possibilities the efficiency trops down to 50%.

In addition, detailed numerical simulations of the transient gas flow inside the catalyst have been conducted in order to evaluate the performance of different geometries for the catalyst support regarding their ability to support the catalytic conversion process at a moderate pressure loss.

Exemplary results of a sensitivity analysis based on calculations in ASPEN PLUS® are shown. Furthermore, the results of CFD and FEM simulations on different catalyst support geometries are presented. Structures composed of Kelvin cells were found to be the best catalyst support due to their enhanced dispersion coefficient while at the same time featuring lower pressure loss as compared to the modified octet cells. Additionally, the Kelvin cell shows both high effective thermal conductivity and relatively high specific surface area.

1 Introduction

With an increasing global energy demand, the search for an environmentally-friendly and safe fuel is of great importance. The aim of governments and researchers around the world is the achievement of a gradual transition from the current fossil fuel system to a clean and sustainable one. Hydrogen, as a secondary energy carrier, is considered as a reliable fuel, which can be produced in an energy-efficient way and, if produced from renewable primary energy carriers, with very low CO_2 emissions. [1]

Within the framework of the research and development of project “BioRobur”, nine partners from seven european countries are working together on the development and testing of a robust and efficient decentralized system for the production of “green” hydrogen based on autothermal reforming of biogas. Among many possible applications, the prospect of supplying “green” hydrogen for fuel-cell cars, which are presumably going to play a central role in a more and more decarbonizing transportation system, is probably the most promising one.

Main tasks of the work presented in the following are the design, construction and evaluation of a pilot plant for the production of PEM-grade hydrogen (50 Nm^3/h). The major objective is the demonstration of the functionality and the proper interaction of the main components like ATR reactor, steam ejector and soot trap, which together form the innovative plant concept.

To identify the best support structure for the catalyst, three different geometries (cubic cell, modified octet cell, Kelvin cell) were investigated with detailed numerical models regarding effective thermal conductivity, hydrodynamic dispersion coefficient, permeability and maximum mechanical stress.

This article is structured as follows: In the following chapter, the operation and the components of the BioRobur fuel processor are briefly described. Chapter 3 gives details of the numerical investigations for the flow sheet simulation as well as for the detailed simulation of the catalyst support. In chapter 4, the results of these investigations are presented.

2 Description of the BioRobur processor

An overview of the BioRobur processor is given in Figure 1. The first process step includes compression, preheating and mixing of biogas, air as well as steam. After the mixing of steam with air biogas is supported by a steam ejector, which operates with the superheated steam-air mixture. In the second process step the mixture is fed into an autothermal reforming (ATR) unit and catalytically converted to synthetic gas (H_2- and CO-rich mixture). The catalyst is coated on a carrier, which is manufactured using an additive production technique. The ATR unit include a soot trap where emerging soot particles are extracted from the synthetic gas by a catalytically coated ceramic wall flow filter. The subsequent increase of hydrogen concentration is accomplished with high-temperature (HT-WGS) and low-temperature water gas shift (LT-WGS) reactors as well as a downstream pressure swing adsorption (PSA) unit. Before the PSA-unit a compressor increase the pressure of the synthetic gas from 1.5 bar(g) to 20 bar(g).

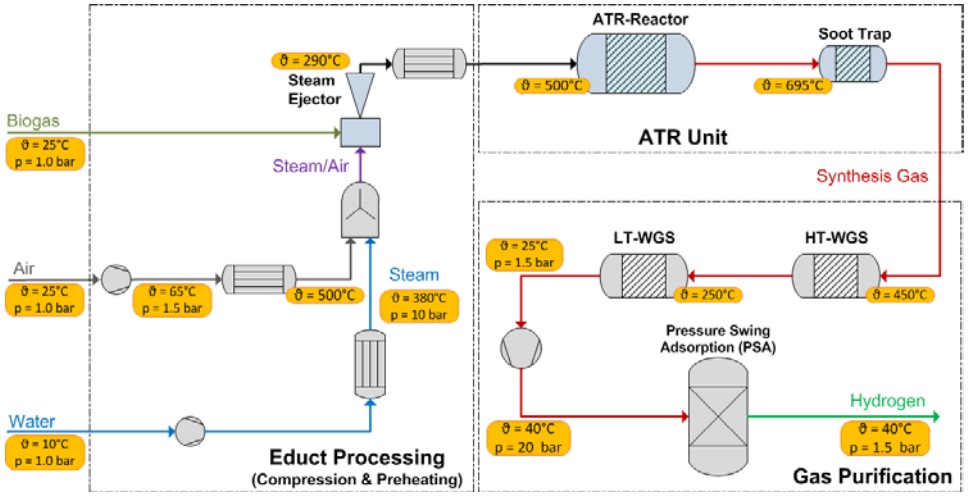

Fig. 1: Block flow diagram of the BioRobur processor (without heat integration)

3 Modeling of the process and the catalyst

3.1 Flow sheet simulation

In order to determine the most suitable reforming process (partial oxidation, steam reforming or autothermal reforming), the optimal system configuration and operating conditions, a detailed flow sheet simulation has been performed.

For the optimization, the plant efficiency η_{plant} has been chosen as objective function, which is defined as:

$$\eta_{plant} = \frac{\dot{n}_{H2} \cdot H_{u,H2}}{\dot{n}_{biogas} \cdot H_{u,biogas} + \dot{Q}_i + P_i} \tag{1}$$

where the chemical energy of hydrogen $H_{u,H2}$ after the pressure swing adsorption process is defined as the energetic input while the fuel enthalpy of biogas $H_{u,biogas}$, the electrical power P_i for compressing the reactants and PSA-feed and the heat Q_i for preheating the reactants are considered to be the input.

A detailed parameter studie identified the S/C- (steam-to-carbon) and O/C- (oxygen-to-carbon) ratio as the most influential parameters. For biogas, the S/C-ratio describes the quantity of water and the O/C-ratio the quantity of atomic oxygen per quantity of methane in the fuel.

$$\frac{S}{C} = \frac{\dot{n}_{H_2O}}{\dot{n}_{CH_4}} \tag{2}$$

$$\frac{O}{C} = \frac{\dot{n}_O}{\dot{n}_{CH_4}} = \frac{2 \cdot \dot{n}_{O_2}}{\dot{n}_{CH_4}} \tag{3}$$

Besides the investigation of the ratios of O/C and S/C, the preheating temperature of the reactants at the inlet of the catalyst have been varied in a range of 500°C to 700°C. Additionally, the benefit of using the PSA-offgas in an additional burner for preheating of the feed streams has been validated.

The optimal system configuration has been identified from simulations using a steady-state process model in ASPEN PLUS®. An ideal system without pressure and heat losses has been assumed and a biogas composition of 60% methane and 40% carbon dioxide (mole fractions) was considered.

The heat of the exothermal water gas shift reaction as well as the thermal enthalpy of the synthetic gas can be used for preheating the reactants in order to minimize the heat that has to be supplied to the process externally.

3.2 Modeling of heat transfer, fluid flow and mechanical stress inside the catalyst support

The catalytic carrier employed in the ATR reactor is manufactured with the help of a three dimensional printing technique, enabling the design of structures with improved properties over conventional catalytic carriers, i.e. thermal conductivity, hydrodynamic dispersion, mechanical strength and permeability. In order to find a suitable carrier structure, numerical simulations of fluid flow, heat transfer and the mechanical behaviour have been performed, which are briefly described as follows.

Three different structures, as depicted in Fig. 2, were investigated in this study. All geometries have struts with circular cross section and a porosity of 85%. Since all lattices consist of periodically repeating unit cells and assuming that the catalyst dimensions are large compared to the unit cells, the simulations could be restricted to a single element for the heat transfer and fluid flow calculations, and to a small array of 5x5x5 elements for the stress analysis (FEM). In the present study, this approach allows a full resolution of the strongly transient fluid flow field inside the porous media, making the modeling of small flow structures unnecessary.

a) Cubic cells "CUBE" | b) Modified octet cells "OCTET" | c) Kelvin cells "KELVIN"

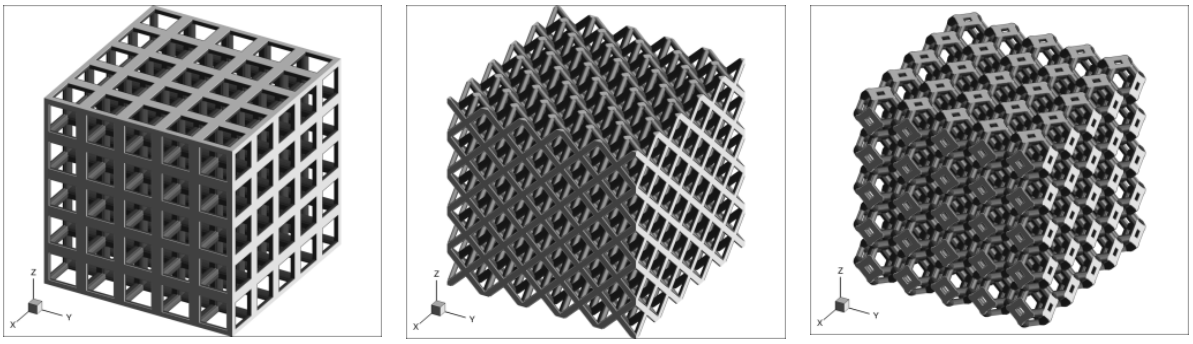

Fig. 2: Investigated structures, consisting of homogenous unit cell lattices.

For the thermal and fluid flow simulations, the different porous media are numerically modeled using Cartesian voxel approximations, where each voxel is either attributed to be solid or liquid. In the present study the computational domain is resolved with a number of 256x256x256 voxels, which was found to be sufficient for grid-independent solutions. In case of the FEM simulations, each strut has been modeled by two vertices and a connection between them. In a second step, the struts were meshed by beam elements with Timoshenko formulations which consider both, shear and bending in

an element. At least four elements have been used for each single strut. Since the octet cell is anisotropic, two orientations were considered, which are termed “x,y” and “z” in the following.

In order to obtain the isothermal transient flow field, the conservation equations for mass and momentum are solved using a CFD code based on the Lattice-Boltzmann method (LBM). Details of this method are described by Yu et al. [2] and Aidun and Clausen [3]. For determination of the mixing performance, massless particles are homogenously suspended into the flow and are subsequently tracked in a Langrangian framework. Since the boundaries of the computational domain are assumed to be periodic in all directions and the particles are allowed to re-enter the domain once they crossed the boundary, they experience an infinitely extended domain. From the trajectories of the particles, the transverse dispersion coefficient has been evaluated assuming that the particles are hydrodynamically dispersed following a Gaussian distribution in space. Since at higher Reynolds numbers the nature of the flow is strongly unsteady, all fluid flow computations were continued over a time, sufficient for obtaining converged statistical information.

For evaluating the effective thermal conductivity of the structures, the heat transfer was solved by using the finite volume method (FVM) under the assumption of a non-conducting fluid phase, as described by Mendes et al. [4]. A temperature difference was imposed at two opposite walls while all other boundaries were considered adiabatic. From the obtained temperature field, the averaged heat flux has been evaluated, which allowed to calculate the effective thermal conductivity using the averaged Fourier’s law of heat conduction.

In order to test the mechanical behavior of the supports, an analysis on the basis of the finite element method (FEM) was performed employing the commercial software COMSOL V4.4. In accordance with all other investigations, the porosity of the structures was kept at 0.85 and further, a size of L=7.43 mm of the cubic unit cells was chosen. SiSiC has been used as the material with E=264 GPa, density ρ=2640 kg/m³ and poisson’s ratio ν=0.25. After the structure was loaded by giving a tensile displacement of 0.01 mm to the upper vertices, the maximum stress was determined.

4 Results

4.1 Comparison of reforming process types

The influence of the type of process for the biogas reforming (equal conditions: output of 50 Nm^3/h hydrogen, water gas shift for CO-reduction after main reaction, hydrogen separation by lossy pressure swing adsorption, etc.) on the plant efficiency has been examined, considering maximum heat integration. The results on the comparison of plant efficiencies obtained for autothermal reforming (ATR), steam reforming (SR) and catalytic partial oxidation (CPOX) are summarized in Fig. 3. Calculation of hydrogen separation by lossy pressure swing adsorption has been performed by assuming a hydrogen split fraction of 0.82 as well as an isentropic efficiency of 92% and a mechanical efficiency of 96% for the PSA compressor.

Due to the need for external heat supply for the endothermic reaction, the calculated maximum plant efficiency for SR was found to be the lowest, amounting to 60.4%. The exothermic reaction of the CPOX releases heat, which could be used for reactant preheating. However, there would be an excess of heat that could not be used for the process. The plant efficiency with CPOX is limited to 63.3% due the fact, that the preheating temperature has to be restricted to 600°C to avoid pre-reactions of the fed

flow. With an plant efficiency of 65% the ATR reaches the highes value. Besides that, there are other benefits like lower affinity to soot formation or carbon depositions in long term operation, easier adaptability to changing biogas composition, more compact design, lower material as well as manufacturing costs, faster start-up and shut-down times and last but not least easier process control [5-7].

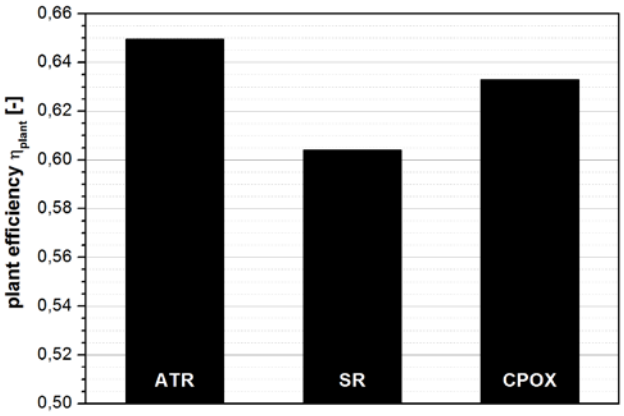

Fig. 3: Maximum plant efficiency for different process types of biogas reforming with maximum heat integration

4.2 Sensitivity analysis of the autothermal reforming

The ideal operating parameters for autothermal reforming of biogas have been determined by a sensitivity analysis. Fig. 4 presents the plant efficiency depending on S/C- and O/C-ratio at a reactant preheating temperature of 600°C.

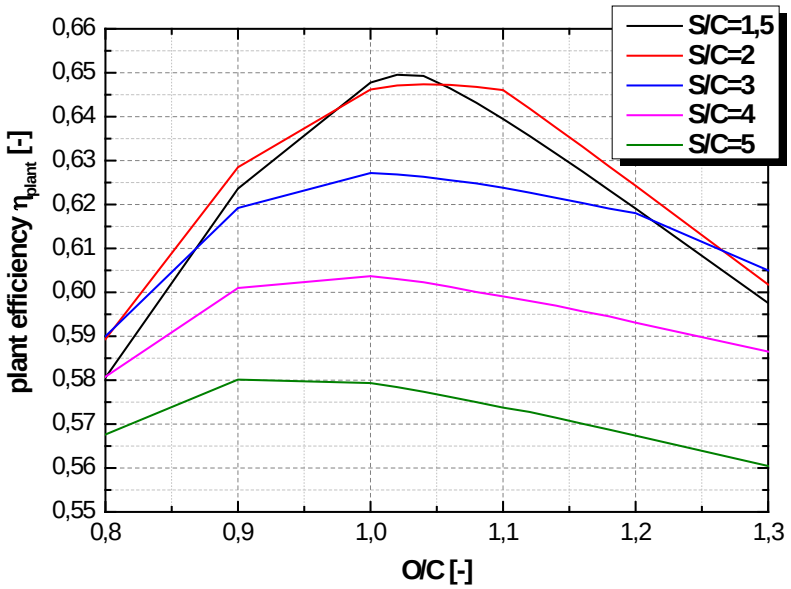

Fig. 4: Efficiency analysis without using PSA off-gas (600°C ATR inlet temperature)

With an increasing S/C-ratio a decrease in plant efficiency has been determined, despite of an increasing yield of hydrogen in the synthetic gas. For high S/C-ratios the heat that is necessary for reactant

preheating and steam generation, cannot be provided solely by heat integration from the product gas cooling. Therefore an additional external heat source would be required. The optimum plant efficiency of 65% was found to be at S/C=1.5 and O/C=1.02.

By thermal integration of the low caloric PSA off-gas in the process, a further increase of the plant efficiency to significantly more than 65% would be possible. The released heat by the combustion of the hydrogen containing off-gas could be used for steam generation and superheating. By this means, the heat supply by an external heat source could be avoided. Hence, higher S/C ratios including higher hydrogen yields could be achieved, while at the same time improving the overall efficiency of the conversion process. As Fig. 5 points out a reverse behaviour regarding the S/C-ratio is visible. This leads to a maximum plant efficiency of 69% with a S/C-ratio of 5 and an O/C-ratio of 0.9.

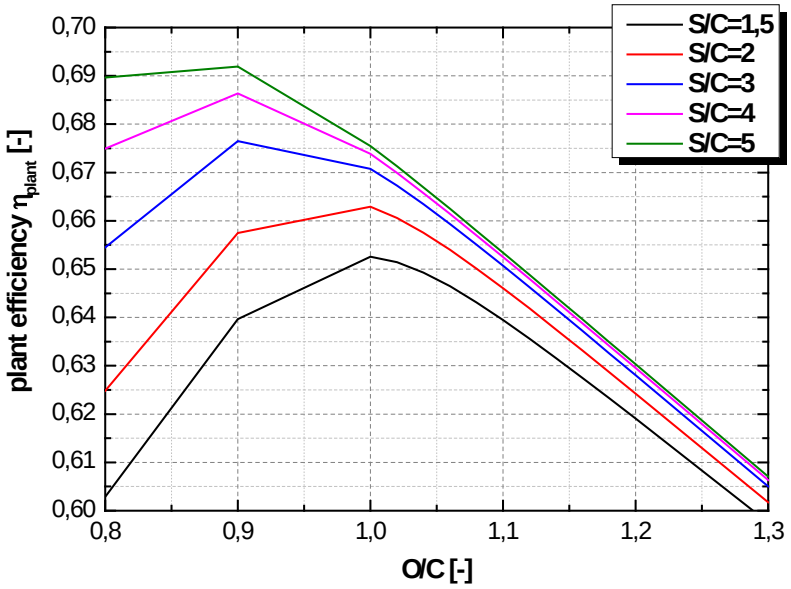

Fig. 5: Efficiency analysis with using PSA off-gas (600°C ATR inlet temperature)

4.3 Thermal, fluid flow and stress simulation of the catalyst support

Selected results from the simulations on the different lattice structures, as described in Chapter 3.2, are presented qualitatively in Fig. 6 for various characteristic properties along with the specific surface area. For the sake of brevity, all data were normalized with respect to the results for the Kelvin cell (100 %), and are discussed as follows:

a) Effective thermal conductivity

The effective thermal conductivity serves as an indicator regarding the ability of the structures to spread locally released heat and hence for the avoidance of hot spots, which can result in a deactivation of the catalyst. While the lattices composed of Kelvin and cubic cells perform similar and do not show any directional dependency, the modified octet cell offers an increased conductivity along the z-axis at the cost of the other two directions. This behaviour, however, does not appear as an advantage since enhanced heat transfer would be required especially perpendicular to the flow, i.e. in the two spanwise directions.

b) Hydrodynamic dispersion coefficient

Hydrodynamic mixing is crucial for the catalytic conversion and can also prevent from hot spots. As an indicator for the mixing performance of the different lattices, the transverse dispersion coefficient has been evaluated for a range of different Reynolds numbers (Re), where Re is based on the size of a unit cell. For the sake of brevity, only the results for Re=1000 are presented, which suggest the Kelvin cell as most suitable structure. At lower values of Re, where the flow becomes steady-state, the simulations showed that the hydrodynamic component of dispersion almost vanishes for all structures.

c) Permeability

A high permeability is desirable to reduce the pumping power required for plant operation and the overall pressure upstream of the catalyst. As clear from the figure, the structure of cubic cells shows the highest permeability (265 % with respect to the Kelvin cell), while Kelvin and octet cells follow with huge distance. This picture also remains for high values of Re, where the pressure loss increases additionally due to inertial effects. Nevertheless, it is expected that the estimated total pressure loss for the whole catalyst of 300 mm length stays well below the design constraint of 100 mbar for all structures at a cell size of 5 mm.

d) Maximum mechanical stress

As a result of the linear FEM simulations the maximum stress was calculated based on Mohr Coulomb failure criterion for each structure. The results of this analysis show the poor mechanical strength of the Kelvin cell lattice on the one hand and high strength of the octet cell lattice on the other hand. The maximum mechanical stress resisted by the cubic cell lattice ranks in between the other structures.

On the basis of this discussion and the detailed results, a structure composed of Kelvin cells is proposed as catalyst carrier. The Kelvin cell lattice features the highest dispersion coefficient over the entire range of Reynolds numbers at a lower pressure loss as compared to the modified octet cells. Furthermore, the Kelvin cell is characterized by a high effective thermal conductivity in all directions as well as a relatively high specific surface area. Although the maximum mechanical stress is higher in comparison to the other two cell types, it is expected that it can handle the loads exerted on the carrier structure. Regarding the constraints imposed by the manufacturing process, a cell width of 5 mm is suggested.

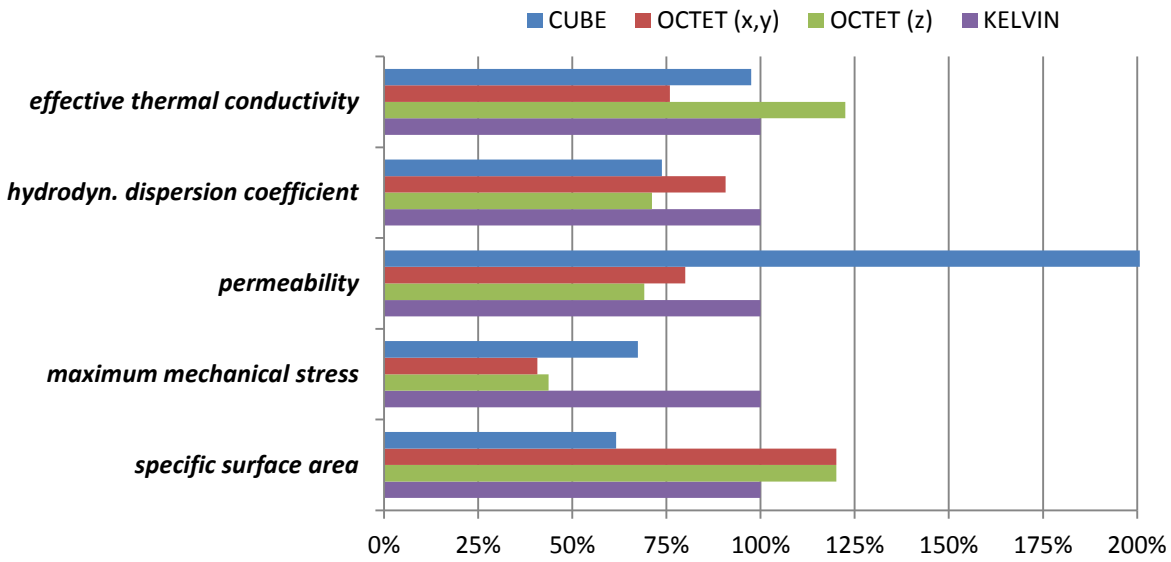

Fig. 6: Summary of the detailed numerical simulations on the different catalyst support structures. Results are displayed normalized with respect to the results of Kelvin cell.

5 Summary and outlook

Autothermal reforming of biogas represents an efficient and robust process for the generation of renewable hydrogen. Compared to steam reforming (SR) and catalytic partial oxidation (CPOX), the autothermal reforming (ATR) features the highest plant efficiency.

Results of the simulation on the basis of ASPEN PLUS® mass and energy flow modeling have shown the positive effect of heat integration on plant efficiencies. A preheating temperature of 600°C and a reactants mixture of S/C=1.5 and O/C=1.02 provide a maximum plant efficiency of 65%. Through the usage of the low caloric PSA off-gas for steam generation and superheating, a further increase in plant efficiency up to 70% would be possible, due to higher hydrogen yields in the synthetic gas resulting from an enhanced steam-to-carbon ratio.

Besides the investigation on plant efficiency, detailed numerical simulations based on CFD and FEM models were performed. Purpose of this task was an evaluation of the suitability of different catalyst carrier geometries regarding their ability to support the catalytic conversion process at a moderate pressure loss. Structures composed of Kelvin cells were found to be the best catalyst carrier due to their enhanced dispersion coefficient while at the same time featuring lower pressure loss as compared to the modified octet cells. Additionally, the Kelvin cell shows both high effective thermal conductivity and relatively high specific surface area. Regarding the results of the numerical simulation and the expected constrictions imposed by the manufacturing process, a size of 5 mm is suggested for the Kelvin cell.

The BioRobur plant will be tested at a scale of nearly 50 Nm^3/h hydrogen generation in order to demonstrate the feasibility of producing renewable hydrogen from biogas. Further, it is planned to compare the optimal operating conditions determined by simulations with experimental data.

Acknowledgments

The authors thank the European commission for the financial support of the investigations in the project BioRobur funded by the 7th European research framework.

Two of the authors, Eric Werzner and Dimosthenis Trimis, would also like to thank the German Research Foundation for supporting the Collaborative Research Center CRC 920, subproject B02, in which numerical tools used for this study were developed.

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