CO$_2$-scrubbing and methanation as purification system for PEFC

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Abstract

Hydrogen is usually produced by steam reforming of natural gas in large-scale processes. The reformate consists of hydrogen, carbon dioxide, carbon monoxide, and residues of hydrocarbons. Since the anode catalyst of a polymer electrolyte membrane fuel cell (PEFC) is usually based on platinum, which is easily poisoned by carbon monoxide, the conditioned feed gas should contain less than 100 ppmv CO, and preferably, less than 10 ppmv. Depending on the design and operating conditions of the hydrogen production process, the CO content of a typical reformate gas, even after the CO shift reactor may be in the range of 0.2–1.0 vol.%; this is far higher than a PEFC can tolerate.

A CO management system is required to lower the CO concentration to acceptable levels. In many cases, the CO purification system consists of a combination of physical or chemical processes to achieve the necessary reduction in CO content. A promising alternative for hydrogen purification is a combined process consisting of a carbon dioxide scrubber with subsequent methanation to reduce the carbon monoxide content to an acceptable level of less than 10 ppmv. © 2000 Elsevier Science S.A. All rights reserved.

1. Introduction

Fuel cells are electrochemical systems converting chemical energy directly into electricity. Heat and water are the by-products. These systems work very efficient producing low emissions. Therefore, they are very interesting for decentralised production of electricity and heat. Different fuel cell types, characterized by the electrolyte, are presently being developed and have typical requirements for the operating temperature and fuel gas quality. The fuel cell type with the highest power density and the highest impact on cost reduction is the PEFC, using a polymer electrolyte membrane. Since the anode catalyst of a PEFC is usually based on platinum, which is easily poisoned by carbon monoxide, the conditioned feed gas should contain less than 10 ppmv CO.

In order to provide hydrogen for the PEFC, several methods of gas processing can be selected. In general, there are several ways to produce hydrogen from carbonaceous fuels. For example, natural gas, liquified petroleum gas, gasoline, diesel fuel, coal, biomass or alcohols, like methanol, can be used for hydrogen production. The main

processes employed are steam reforming, partial oxidation, gasification, and thermal, or catalytic cracking. The industrial production of hydrogen is mostly based on steam reforming of natural gas followed by a purification step. A suitable purification system is a carbon dioxide scrubber with subsequent methanation. A small test device for a CO$_2$-scrubber with methanation has been set up for a thermal hydrogen power of about 2 kW. The experimental results will be compared with the results of extensive simulation studies to define optimal operating conditions for the energy demand and to assess the performance of purification.

2. Production of PEFC suitable hydrogen gas

Many households are provided with natural gas, so it may be possible to produce heat and electricity from fuel cells at home; for example, a power range from 1 to 5 kW$_{el}$. The generation of hydrogen by catalytic steam reforming of natural gas has been studied intensely as a method for supplying PEFCs. Natural gas steam reforming is feasible with solid catalysts using nickel as active component in a temperature range from 700°C to 800°C. Due to the principle of Le Chatellier, an increasing system

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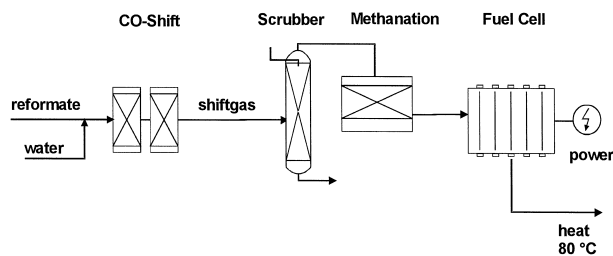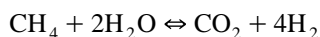*E-mail address:* r.wolters@uni-duisburg.de (R. Wolters).

Fig. 1. Process scheme of reformate treatment with CO_2-scrubber and methanation.

pressure reduces methane conversion. The natural gas reforming process can be characterized by the following stoichiometric reaction of methane:

$$CH_4 + 2H_2O \Leftrightarrow CO_2 + 4H_2$$
$$\Delta_R \overline{H}^{\phi} = 165.02 \, kJ/mol.$$

In addition to this equation, carbon monoxide and methane are components of the product gas. A typical product gas composition of natural gas steam reforming at atmospheric pressure consists of about 55% hydrogen, 6% carbon dioxide, 11% carbon monoxide, 28% water vapor (steam to carbon ratio $S/C = 3$) and traces of methane in thermodynamical equilibrium. The gas purification system selected has, on the one hand, to operate with the gas composition and possible impurities of the feed gas, and on the other hand, accommodate the demands of the fuel cell selected. Generally, the following commercial gas purification procedures can be identified:

- sulphur removal with adsorbents, or in accordance with chemical reactions,
- carbon monoxide conversion by the water–gas reaction (shift reaction),
- selective carbon monoxide methanation,
- selective oxidation of carbon monoxide (PROX),
- pressure swing adsorption (PSA),
- gas absorption with subsequent methanation,
- metal membrane diffusion,
- iron sponge purification.

A variety of physical and chemical processes can be used in such a purification system. In many cases, the CO reduction system consists of a combination of several processes to achieve the necessary reduction in CO content, appropriate to the specific demands for stationary or mobile applications. The reformate gas is first purified in a catalytic shift step. Since the CO shift reaction is exothermic and the reaction kinetics decrease with lower temperatures, a combination of a high temperature shift conversion at 400°C on FeCr-catalysts coupled with a low temperature shift conversion at 200°C on CuZn-catalysts is usually necessary. The equation of the shift reaction is given below, in which carbon monoxide reacts with steam to yield hydrogen and carbon dioxide:

$$CO + H_2O \Leftrightarrow CO_2 + H_2 \qquad \Delta_R \overline{H}^{\phi} = -41.14 \, kJ/mol.$$

Depending on the operational conditions, the CO content of the gas mixture after the shift reactors is in the range 0.2–1.0 vol.%, far higher than the PEFC can tolerate. A promising alternative for further hydrogen purification is a combined process consisting of CO_2-absorption with subsequent methanation to reduce the carbon monoxide content to an acceptable level, i.e., less than 10 ppmv. It is necessary to find a suitable process for CO_2-scrubbing, in which the selectivity of the subsequent carbon monoxide methanation can be improved, and the side reaction of carbon dioxide methanation is minimised. Thus, the hydrogen consumption for the methanation step should not exceed a few percent of the hydrogen content of the gas mixture. This process is schematically illustrated in Fig. 1 [1].

The absorption of CO_2 by scrubbing is the most important gas purification technique, which is common to a great number of industrial processes. In general, packed towers are preferred for small installations and applications where a low-pressure drop is desired. Although many packing shapes are available, the most commonly used are rings, saddles, and grids.

The choice of process is determined by the pressure and temperature conditions, at which the reformate gas is available, its composition with respect to major and minor constituents, and the purity requirements of the treated gas. The two amines, which have proved to be of principal commercial interest for gas absorption of CO_2, are monoethanolamine (MEA) and methyldiethanolamine (MDEA) [2,3].

In Fig. 2, the carbon dioxide loading of the amines MEA and MDEA is shown as a function of the partial pressure of carbon dioxide. For a partial pressure increase from 1 to 5 bar, the CO_2 loading of MDEA increases from 0.268 to 0.565 mol CO_2 per mol MDEA, that is, about 100%. In comparison with MDEA, the loading of MEA
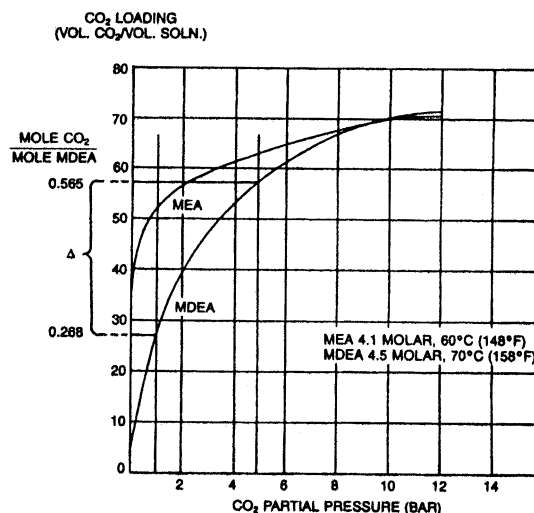

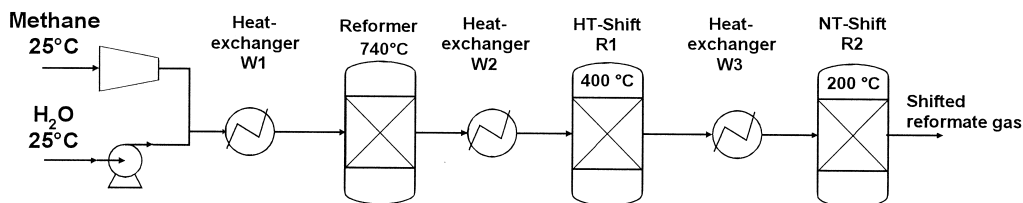Fig. 2. CO_2-loading for MEA and MDEA in dependence on carbon dioxide pressure [1].
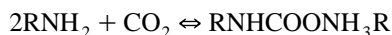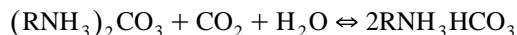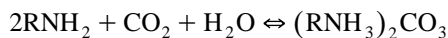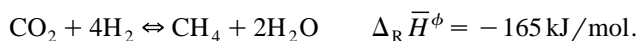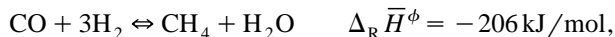
Fig. 3. Flowsheet of methane reforming and purification by shifting.

increases only about 20%. On the other hand, the loading of MEA shows high loading values at low partial pressures. Therefore, MEA has an excellent performance for the purification step and is still the preferred solvent for gas streams containing relatively low concentrations of carbon dioxide. This is especially true when the gas is at low system pressures and maximum removal is required.

The principal reactions occurring when solutions of a primary amine, such as MEA $(R_{MEA} = C_2H_4OH)$, are used to absorb CO_2, may be represented as follows:

$$2RNH_2 + CO_2 + H_2O \Leftrightarrow (RNH_3)_2CO_3$$

$$(RNH_3)_2CO_3 + CO_2 + H_2O \Leftrightarrow 2RNH_3HCO_3$$

$$2RNH_2 + CO_2 \Leftrightarrow RNHCOONH_3R$$

The CO concentration can be reduced further to a suitable level for the PEFC by a methanation step over a Ni-catalyst. In the methanation reactor, which works at about 300°C, the carbon monoxide and residues of carbon dioxide react as follows:

$$CO + 3H_2 \Leftrightarrow CH_4 + H_2O \qquad \Delta_R \overline{H}^\phi = -206\,kJ/mol,$$

$$CO_2 + 4H_2 \Leftrightarrow CH_4 + 2H_2O \qquad \Delta_R \overline{H}^\phi = -165\,kJ/mol.$$

The carbon dioxide methanation is negligible, provided that most of the carbon dioxide has been absorbed. The remaining carbon monoxide reacts with hydrogen to yield methane and water. The removal of CO from a hydrogen-rich gas by methanation is a well-known technology that leads to a CO content of less than 10 ppmv.

3. Simulation of fuel cell systems

Hydrogen production for differing fuels and the subsequent purification process, consisting of absorption, desorption, and methanation, has been analysed by an extensive simulation study to define optimal operating conditions for the energy demand and purification performance. The main parameters are gas pressure, gas temperature, the mole fraction of the amine in the scrubbing solution, the mole ratio of amine to CO_2, and the degree of regeneration of the desorption step. The simulation program, Aspen Plus® from Aspen Technology (Cambridge, MA, USA) is used for the process simulation of the fuel cell system. The simulation code predicts the behaviour of a process using basic engineering relationships such as mass and energy balances, phase and chemical equilibrium, or reaction kinetics. With reliable thermodynamic data, realistic operation conditions, and the equipment models given by the simulation program, actual plant behaviour can be simulated, calculated, and optimized. The program contains data, properties, unit operation models, and other features for specific industrial applications.

The simulations were performed for three different hydrogen production processes in order to demonstrate the
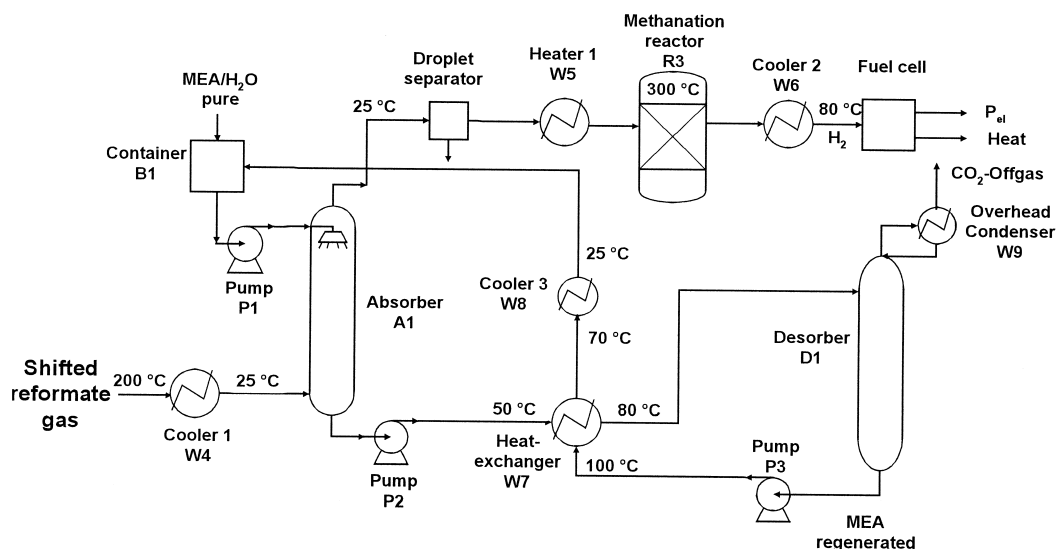

Fig. 4. Flowsheet of carbon dioxide scrubbing with subsequent methanation.

Table 1
Gas composition for hydrogen production and scrubbing/methanation as purification system

	Biomass gasification; autothermal $\lambda = 0.35$; $T_{\text{Gasifier}} = 800°C$		CH_4 steam reforming; $S/C = 3$; $T_{\text{Reformer}} = 800°C$		Methanol reforming; $S/C = 4$; $T_{\text{Reformer}} = 300°C$	
	Shifted gas	Purified gas	Shifted gas	Purified gas	Shifted gas	Purified gas
p [bar]	1	1	3	3	7	7
T [°C]	200	80	200	80	200	80
H_2 [vol.%]	32.5	47.1	78.7	97.8	74.2	99.1
N_2 [vol.%]	30.1	44.8	–	–	–	–
CO [vol.%]	0.2	traces	0.3	traces	0.1	traces
CO_2 [vol.%]	24.0	traces	19.4	traces	24.8	traces
CH_4 [vol.%]	traces	0.5	0.4	0.8	0.3	0.4
H_2O [vol.%]	13.2	7.6	1.1	1.4	0.6	0.6

suitability of the scrubbing process and to compare the efficiencies of the total systems. The comparison was carried out for hydrogen production by means of autothermal biomass gasification, methane steam reforming, and methanol steam reforming, with scrubbing and methanation as the purification step. In Fig. 3, the methane steam reforming and shift processes are illustrated.

The flowsheet of the carbon dioxide absorption process and the carbon monoxide conversion with hydrogen to methane for all hydrogen generation processes is given in Fig. 4. After the low temperature shift (NT-Shift), the reformate from the biomass gas is cooled down to 25°C and is fed into the absorber to reduce the CO_2-content. Then, the gas stream leaves the head of the absorber with a temperature of nearly 25°C, and a CO_2 content of less than 100 ppmv. In the methanation reactor, working at a temperature of 300°C, the carbon monoxide and the residues of carbon dioxide, react to produce methane. After cooling down to 80°C, the hydrogen-rich gas is suitable for a PEFC. The scrubbing solution is heated to nearly 50°C by the absorption heat in the absorption column. Then, the fluid is pumped to the internal heat exchanger, where it is heated up to 80°C. After taking up the desorption heat, the carbon dioxide is removed in the desorber from the alkanolamine solution at temperatures above 100°C.

If a suitable absorbent is chosen, the carbon dioxide is selectively and nearly complete removed. For carbon dioxide removal, alkanolamines are mainly chosen in industrial applications. The absorbent choice for the simulation is 10

mol% MEA in water, resulting from an extensive simulation study with electrolyte reactions. A higher MEA concentration engenders a disadvantage of lower corrosion-resistance and should not be employed. At a lower mole concentration, a higher energy demand for desorption is necessary because of the additional water content, which has also to be heated. As a result of energy optimisation for 10 mol% MEA, the optimal mole-proportion for the amine purification process amounts to approximately 4 mol amine per mole carbon dioxide. In Table 1, the simulation results are shown for the gas compositions for methane steam reforming, biomass gasification, and for methanol reforming after shifting and scrubbing with subsequent methanation.

The efficiency of the total process η_{Total}, including scrubbing and methanation purification, can be determined as the product of the separate efficiencies of the process chain:

$$\eta_{\text{Total}} = \prod_t \eta_t$$
$$= \eta_{\text{Ref/Gas}} \cdot \eta_{\text{Absorption}} \cdot \eta_{\text{Methanation}} \cdot \eta_{\text{Internal}} \cdot \eta_{\text{Fuel Cell}}$$

The separate efficiencies, each related to their energy input, are defined as follows:

$\eta_{\text{Ref/Gas}}$: hydrogen production by means of reforming or gasification after NT-Shift

$\eta_{\text{Absorption}}$: carbon dioxide scrubbing, including absorption and desorption

$\eta_{\text{Methanation}}$: methanation process

Table 2
Efficiencies for hydrogen production, scrubbing/methanation and electricity generation

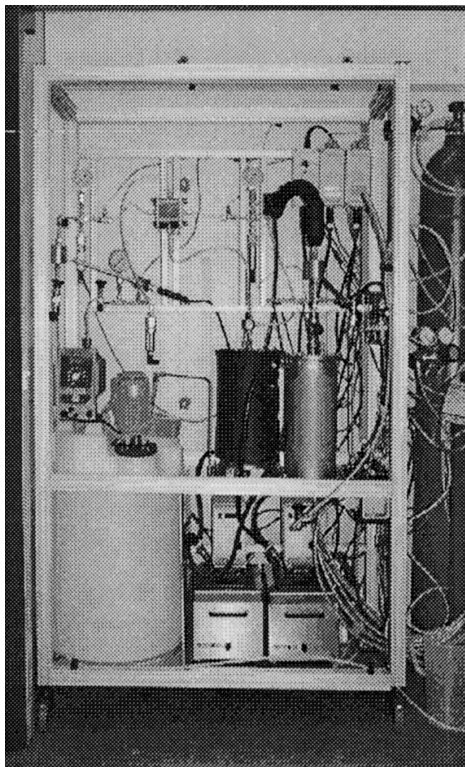| Efficiencies	Biomass gasification (%)	CH_4 steam reforming (%)	Methanol reforming (%)
$\eta_{\text{Gasification/Reforming}}$	81.72	77.78	82.87
$\eta_{\text{Absorption}}$	87.92	87.89	84.09
$\eta_{\text{Methanation}}$	96.97	98.85	99.36
η_{Internal}	≈ 100	98.81	≈ 100
$\eta_{\text{Fuel cell}}$	37.50	50.00	50.00
$\eta_{\text{Total}} = \Pi \eta_i$	26.13	33.39	34.62

Fig. 5. Experimental plant.

$\eta_{Internal}$: energy demand for processes under pressure, e.g., for compressor

$\eta_{Fuel\ Cell}$: electricity generation in the fuel cell

It must be recognized that fuel cell efficiency is dependent on the utilisation factor of hydrogen. Because of the nitrogen content in the biomass gas, the hydrogen content is only 50%, and fuel cell efficiency is set to 37.5%. After scrubbing and methanation, the hydrogen content for methane and methanol reforming is nearly 100%, and so a fuel cell efficiency of 50% is acceptable.

The efficiency of the total process, η_{Total}, is listed with respect to hydrogen production in Table 2. The efficiency for steam reforming is nearly 78%, for biomass gasification, 82%, and for methanol reforming, 83%. The efficiency for the purification during hydrogen production is about 88% for the scrubbing process, and 98% for the methanation step.

The ideal efficiency for the total process is 26.13% for biomass gasification, 33.39% for methane steam reforming, and 34.62% for methanol reforming. Including the heat requirement of the fuel cell, the overall efficiency, electricity generation plus heat utilisation, may be twice these values. This implies that the utilisation efficiency, for example, for methane steam reforming, could achieve nearly 67% and 70% for methanol reforming.

4. Experimental investigations

A small test device, a CO_2-scrubber with methanation has been set up with a thermal hydrogen power of about 2 kW. The experimental results are compared with the results of the simulation. The experimental investigations of the purification system with scrubbing and methanation for typical reformate gases or gasified biomass have been performed with the test stand shown below in Fig. 5. The gas composition of the purified gas can additionally be analysed with measuring instruments.

The absorber in the experimental plant is 1 m in length and 30 mm in diameter. It consists of many small packed rings. The methanation reactor, with a volume of 0.05 l, filled with a nickel catalyst, is heated by electricity. The volume flow of the amine solution is variable between 0
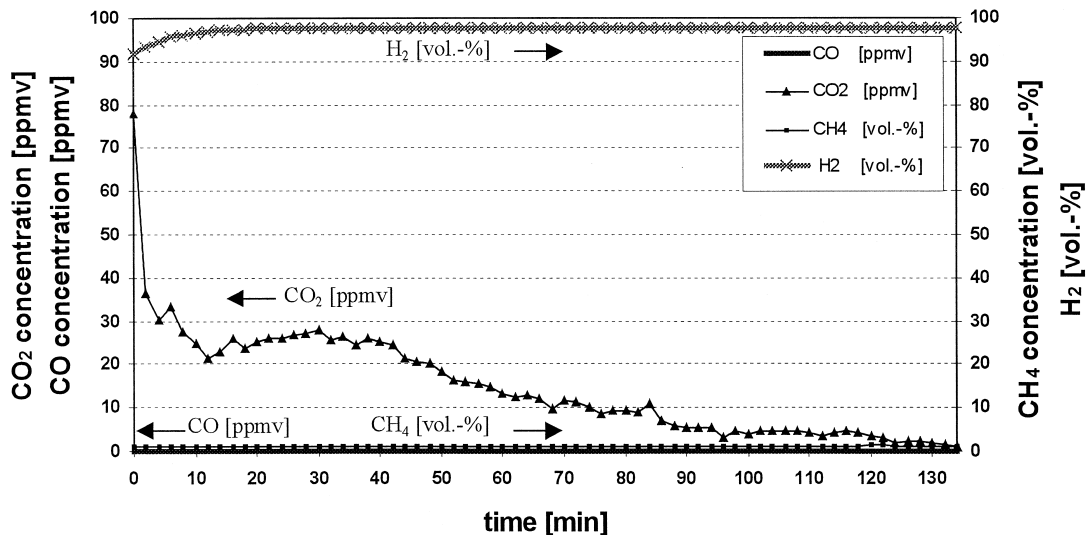

Fig. 6. Purification of reformate gas with absorption and methanation (long-term test).

and 17.5 l/h; in these experiments, a volume flow of 3.5 l/h was sufficient. The concentration of MEA in water amounts to 10 mol%, resulting from extensive simulation results. The absorption medium is pumped into the head of the absorber, reacts with the carbon dioxide, and is fed from the bottom to the desorber for regeneration. The variable operating parameters for the experimental are the system pressure in the range from 1.0 and 4.0 bar, the carbon monoxide, carbon dioxide, and hydrogen volume flow and concentration, the concentration and volume flow of the amine solution, as well as the system temperature. The temperature of the methanation step is between 300°C and 350°C, limited by the thermal stability of the methanation catalyst (maximum value 400°C).

In Fig. 6, the purification results of the system absorption and methanation for a typical reformate gas are shown. The experiments were carried out for a system pressure of 1400 mbar. For a total volume flow of 5 l_N/min, a carbon dioxide flow of 1 l_N/min, (20 vol.%) is totally removed in the absorption stage. A carbon monoxide flow of 0.05 l_N/min (1 vol.%) is converted with 0.15 l_N/min hydrogen (3 vol.%) into methane in the methanation reactor at a temperature of nearly 350°C. The impurities in the purified hydrogen gas include only traces of carbon monoxide and carbon dioxide. The decreasing carbon dioxide content, from nearly 50 down to 5 ppmv, is caused by impurities of carbon dioxide in the pipes, in the absorber, and in the measuring instruments. For a low temperature fuel cell, this carbon monoxide content is satisfactory. The purified hydrogen gas, after absorption and methanation, contains only traces of carbon monoxide and is suitable for low temperature fuel cells. Furthermore, the hydrogen content of the purified gas is nearly 98.5 vol.%, ideal for electricity generation in fuel cells. The methane content resulting from the methanation of carbon monoxide and the remaining carbon dioxide amounts to only 1.5 vol.%. This data show good correspondence with the simulation results for the thermodynamical equilibrium above, especially as the gas samples analysed proved water free. This laboratory demonstration shows the feasibility of the purification system for PEFC; an evaluation of the desorption process for electric power generation will now be investigated.

5. Conclusions

In order to provide hydrogen for a PEFC, the processes of steam reforming of natural gas and of methanol or biomass gasification combined with CO_2-scrubber and subsequent methanation have been studied by theoretical and experimental investigations. Extensive simulations with Aspen Plus® have been performed for the different hydrogen production processes, including gas purification and internal heat integration. Important results for energy optimisation indicate optimal operating conditions of 10 mol% MEA in water, and approximately 4 mol amine per mol carbon dioxide. The purified hydrogen gas is suitable for a PEFC and contains only traces of carbon monoxide and carbon dioxide. Selecting optimal operating conditions, the efficiency of the purification process consisting of absorption, desorption, and methanation, can achieve more than 80%. The experimental setup confirms the feasibility of the process for a small power range of 1–2 kW.

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