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POWER-TO-GAS (P2G) PROCESS: BASICS

ABSTRACT

The explicit tendency to increase the power generation from stochastic renewable resources forces us to look for technological solutions of energy management and storage. In the recent years, the concept of power-to-gas where the excess energy is converted into hydrogen and/or further methanized into renewable methane is gaining high popularity. The concept presented in this article suggests the conversion of CO₂-containing gases into methane in a pressurized reactor using hydrogen produced via electrolysis. The reaction heat released by the exothermic methanation reaction leads to a temperature rise of the gas in reactors. Several different reactor concepts can be used for the methanation reaction.

The conversion of carbon dioxide is limited in accordance to the chemical equilibrium which depends strongly on temperature and pressure. For maximum carbon dioxide conversion, it is convenient to split the methanation process into several stages adding cooling sections in between. Critical aspects of the P2G process are the availability of CO₂ sources and especially economics as well as the efficiency. In opposite, advantages of the system are strategic benefits such as integrated management of electricity and gas networks. The concept brings the possibility of connecting the power grid to different sectors, where CH₄ is needed such as mobility and industry.

Keywords: methanation, electrolysis, catalytic reactor, synthetic natural gas (SNG)

Основе конверзије електричне енергије у природни гас

САЖЕТАК

Тенденција повећања производње електричне енергије из стохастичких обновљивих извора наводи на тражење нових технолошких решења за управљањем и складиштењем енергије. У последњих неколико година популаран је постао концепт конверзије електричне енергије у синтетички природни гас где се вишак енергије претвара у водоник и / или даље поступком метанизације преводи у обновљиви метан (P2G). Концепт представљен у овом раду описује претварање гасова који садрже CO₂ у CH₄ у реактору под притиском користећи водоник произведен електролизом. Топлота ослобођена егзотермном реакцијом метанизације доводи до повећања температуре гаса у реакторима. За реакцију метанизације може се користити неколико различитих реакторских концепата.

Конверзија угљен-диоксида је ограничена у складу са термо-хемијском равнотежом која доминантно зависи од температуре и притиска. За максималну конверзију угљен-диоксида, прикладно је одвојити процес метанизације у неколико фаза уз додаток расхладних делова између њих. Критични аспекти P2G процеса су доступност CO₂ извора, економичност као и ефикасност. Са друге стране, предности система су стратешке користи као што је интегрисано управљање електричном и гасном мрежом. Концепт доноси могућност повезивања електроенергетске мреже у различитим секторима где је потребан природни гас, као што су саобраћај и индустрија.

Кључне речи: метанизација, електролиза, каталитички реактор, синтетички природни гас

INTRODUCTION

Nowadays one of the most significant environmental problems is fossil usage and as a result, increasing carbon dioxide (CO₂) concentration in the atmosphere. Also, technology progress and ever increasing economic activity has stimulated release of CO₂ emissions including global warming. Today, large effort is made towards finding sustainable solutions for solving this problem without interrupting the economic development.

Despite this positive tendency there is an existing storage problem of stochastic electricity from wind and solar PV energy sources: misbalance between generation and consumption can lead to severe consequences or even to blackout of power system. At the present time, one of the options for RES energy storage is to accumulate it by producing hydrogen (H₂) through water electrolysis. Due to the shortage of renewable H₂ infrastructure, methanation where H₂ is combined with CO₂ to produce synthetic methane can be possible solution for recycling of increasing CO₂ and accumulation of non-continues electricity. Synthetic methane (CH₄) production is convenient because of existing natural gas pipe system. CH₄ can also be burned in an existing power generation stations recovering CO₂ (which should be captured and used in the next cycle [1]). Specific energy of CH₄ is also higher than H₂: 40 MJ/m³ versus 12.7 MJ/m³. Thus, methanizing H₂ has several preferences.

POWER-TO-GAS

The Power-to-Gas (P2G) technology might contribute to tackling this issue. The P2G process links the power grid with the gas grid by converting surplus power into a grid compatible gas via a two-step process: H₂ production by water electrolysis and H₂ conversion with an external CO or CO₂ source to CH₄ via methanation. The resulting CH₄, known as substitute natural gas (SNG), can be injected into the existing gas distribution grid or gas storages, used as CNG motor fuel or it can easily be utilized in all other well-established natural gas facilities. The total world storage capacity of natural gas is > 3600 TWh [2] (total world power production from wind and solar power in 2012: 639 TWh [3]).

Another challenge for P2G systems is the temporary storage of hydrogen necessitated by the fluctuating power supply and consequent intermittent operation of the electrolyzer. For the hydrogen storage, the size and necessary peripheral equipment is highly variable and depends on the configuration and the operating parameters of the system.

Several probable methods exist for the hydrogen storage: compressed gas tanks, cryogenic compressed liquid hydrogen tanks, metal hydride storage, physical storage, and underground storage (e.g. salt caverns). Storage of hydrogen as a cryogenic liquid is a technical challenge as well as energetically inefficient [4]. The unstable pressure, continuous leakage of gas, and expensive insulation, make cryogenic liquid hydrogen storage a poor choice for P2G applications. Another option for hydrogen storage is the physical storage of hydrogen in underground caverns.

Although this option is the cheapest option of all storage methods mentioned here, this storage is better suited for high capacity, long term hydrogen storage [5]. Thus, it is not a viable option for P2G systems, which require small scale, onsite, and temporary hydrogen storage.

One possible approach to estimate reactor performance is to compare the Gas Hourly Space Velocity (GHSV) of different reactor concepts. In this case, $F_{V,G,in}$ is the volumetric flow rate of the feed gas without any inert gases and with a stoichiometric H₂/CO₂ ratio. VR is the reactor volume. If the concept is based on a series of reactors, then the sum of all reactor volumes is used [6].

$$GHSV = \frac{F_{V,G,in}}{V_R}$$

The properties of SNG produced in a P2G chain must be similar to the properties of natural gas distributed in the gas grid. Typically, natural gas contains more than 80% CH₄. Further important components are higher hydrocarbons, e. g. ethane, propane, and butane which increase the calorific value compared to pure methane. On the other hand, inert components such as CO₂ or N₂ can be found in natural gas and have a corresponding lowering effect on the calorific value.

The main difference between the methanation technologies is the temperature profile inside the reactor. In principle, there are three types of temperature profiles: adiabatic, isothermal, and polytropic. Kiewidt and Thöming [7] used the Seminov number to distinguish methanation reactors by the heating and cooling rate.

$$Se = \frac{\text{Heat}_{\text{production}}_{\text{rate}}}{\text{Cooling}_{\text{rate}}}$$

- Adiabatic fixed-bed reactors (Se→1)

Fixed-bed reactors without external or integrated cooling typically exhibit an almost adiabatic temperature profile with a distinct hot spot in the bed and high reactor exit temperatures. Since methanation catalysts cannot withstand temperatures above 550-700°C, gas recirculation or steam addition may be necessary [8]. Main advantages are the high reaction rate and the possibility to produce steam at high temperatures. However, the process setup is relatively complex.

- Isothermal reactors (Se→0)

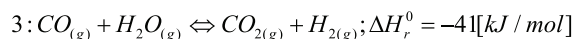
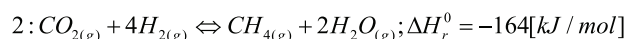
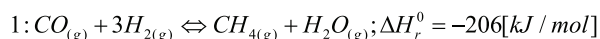
Fluidized-bed reactors and three-phase reactors ideally are isothermal reactors. The process takes place at a temperature ensuring total CO or CO₂ conversion. This leads to a simple process setup and a simple reactor. Furthermore, thermal load acting on the catalyst is low. The limited reaction rates caused by isothermal operation at moderate temperatures are a drawback of such reactors. Another drawback, especially with regard to fluidized-bed reactors, is significant catalyst consumption due to attrition [9].

- Polytropic reactors ($0 < Se < 1$)

Cooled fixed-bed and structured reactors (e.g. micro channel, honeycomb) usually have a hot spot close to the inlet of the reactor. In comparison to adiabatic reactors, however, the hot spot temperature is significantly lower and the product gas leaves the reactor at moderate temperatures (commonly about 300°C). Such polytropic reactors combine the advantages of isothermal and adiabatic reactors. The moderate hot spot leads to increased reaction rates, whereas the lower outlet temperature enables high conversion rates with respect to thermodynamic limitations. In general, polytropic reactors are the most expensive ones [9].

METHANATION

The methanation of CO_2 is a well-researched process that has been in use in chemical industry for a long time. Although many competing reactions take place three of them are considered main reactions.



Both carbon sources CO_2 (2) or CO (1) can be hydrogenated to CH_4 via the sabatier process, but they tend to influence each other. The reaction of CO via the sabatier process is preferred and can even inhibit the CO_2 methanation, caused by the far stronger adsorption strength of CO . Depending on catalyst material, the CO_2 conversion contains the formation of CO as reaction intermediate (see Table 1). CO can also be formed during the methanation process in gas preheating devices via the water-gas shift reaction equation 3. Since part of the CO can remain in the product gas, it has to be separated to achieve the requirements of the natural gas grid. Therefore, the reaction conditions should prefer a high CO conversion to minimize its fraction in reaction product [10].

A catalyst is necessary to initiate the reaction 1 and 2. A wide variety of catalyst exists. For methanation, both noble and non-noble metals are used, e.g. Rhodium, Ruthenium, Cobalt, Manganese and Nickel. Some catalysts, especially noble metals, have high costs (Silver, Platinum and Gold); hence, it would not be economically feasible to utilize these metals in pure form. In such cases, it is suitable to use a support material – a less costly material than the catalyst itself, but with a high contact area relative to its size. Various oxide supports exist, e.g. TiO_2 , SiO_2 , Al_2O_3 , CeO_2 , ZrO_2 and CuO . Despite the large variety, Nickel and Ruthenium catalysts are the most used and explored [1].

Catalyst	Intermediate	Reactor type	Ref
Ni/Al-Tube	CO	Tube wall reactor	[10]
Ni/SiO ₂	CO	Tube reactor	[10]
Ni-La ₂ O ₃ /Al ₂ O ₃	CO	Tube reactor	[10]
Ni/Al ₂ O ₃	CO	Tube reactor	[10]
Ru/TiO ₂	CO	Tube reactor	[10]
Ni/ANM	CO	Flow unit	[11]
Ru/TiO ₂	CO, HCOO-	DRIFTS cell	[12]

Table 1 Typically detected reaction intermediates in catalytic conversion of CO_2 to CH_4

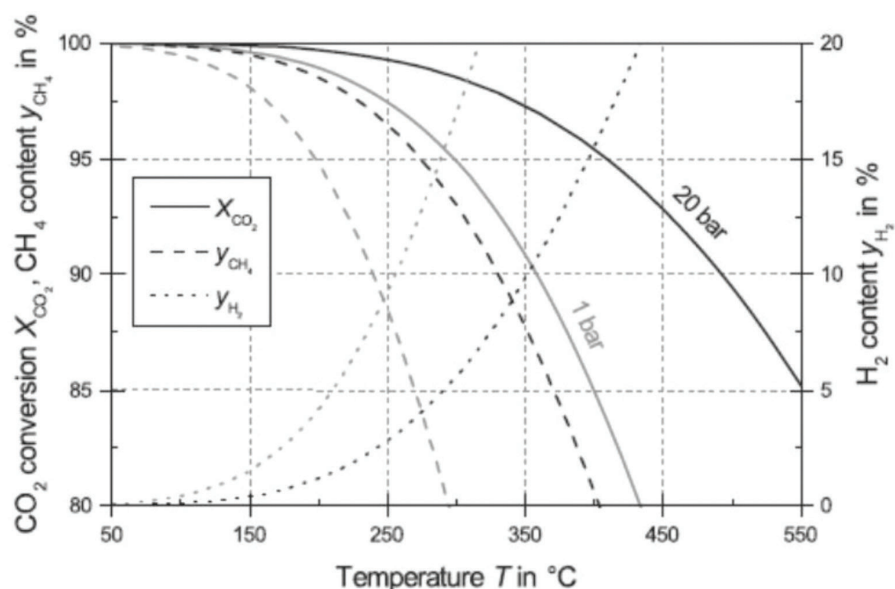


Fig. 1 Conversion Equilibrium

CO and CO₂ hydrogenation are highly exothermic reactions with the consequence that high temperatures limit the CO and especially the CO₂ conversion. As illustrated in Fig. 1, a temperature below 225°C (1 bar) or 300°C (20 bar) is required to reach a CO₂ conversion of at least 98%. Additionally, the positive effect of pressure, as previously addressed, is apparent from the results shown in Fig. 1 [6]. Consequently, an elevated pressure should be used for the methanation.

WATER ELECTROLYSIS

The conversion of electric into chemical energy is the core element of each power-to-gas concept and is performed in the process of water electrolysis. By applying an electric potential to two electrodes, water is split into its components hydrogen and oxygen, which are formed at the cathode and anode, respectively. In addition to the two electrodes, an electrolyzer is composed of an electrolyte, which is capable of conducting ions, and a diaphragm, which is an electric isolator and keeps the evolving gas streams separate in order to avoid a flammable mixture.

Different types of electrolyzers can be distinguished according to their utilized electrolyte. Among these are alkaline water electrolysis with a liquid alkaline electrolyte, acidic proton exchange membrane (PEM) electrolysis with a proton conducting polymer electrolyte membrane, and high temperature electrolysis with a solid oxide electrolyte [13]. The respective technical principles as well as their characteristics will be described in the following subsections.

Alkaline water electrolysis has been commercially available for several decades with modules up to 2.5 MWe and operating pressures up to 30 bar [14]. The electrolyte consists of aqueous potassium hydroxide with a concentration of 20-40 % KOH and conducts OH ions. The electrodes are made of perforated steel with catalysts based on nickel, cobalt or iron. They are separated by a highly insulating diaphragm. Typical operating temperatures are around 80°C with relatively low current densities of 0.2-0.4 A/cm².

PEM electrolyzers have been developed for about 20 years and are only available on a small scale. The technology is based on the utilization of a proton-conducting polymeric membrane as the electrolyte and diaphragm combined in one element. The membrane is directly connected to the electrodes in the membrane electrode assembly (MEA). Operating temperatures are limited to about 80°C due to the polymeric material [15]. The membrane allows for high current densities of 0.5 A/cm²; as well as for very low part loads due to its impermeability for gases.

Hydrogen can be produced at pressures up to 100 bars, while it is possible to simultaneously produce the oxygen at atmospheric pressure, thus avoiding the safety issue of handling pressurized oxygen and also increasing efficiency. The cell efficiency is of the same magnitude as that of alkaline electrolyzers, but stack efficiency is lower. This effect will be minimized when PEM electrolyzers reach the same sizes as alkaline electrolyzers [16].

High-temperature steam electrolysis was first developed in Germany between 1975 and 1987 and is still at the stage

of basic research. The electrolyte is a solid oxide (solid oxide electrolysis cell - SOEC), which usually consists of conducting stabilized zirconium oxide. The cell is operated at temperatures of about 700-1000°C with steam instead of liquid water and it functions using the reverse process of the solid oxide fuel cell. The unique potential of the SOEC is the thermodynamic effect, which occurs when the water-splitting reaction is carried out at elevated temperatures. Here, only part of the total amount of required enthalpy has to be supplied in the form of electric energy. The rest can be provided by a high-temperature heat source. The electric efficiency, as the ratio of chemically bound energy output to electric input, can therefore even exceed 100%. Due to the high temperatures, the SOEC can also be utilized for co-electrolysis, where the reactions of CO₂ to CO and H₂O to H₂ take place simultaneously, thus leading to the production of syngas. This process can be used for the CO₂-neutral production of all kinds of hydrocarbons in the chemical industry. Since this technology is still at an early development stage, many characteristics have to be investigated and improved, such as total system development, part-load behavior and long-term stability. In general, typical applications for the SOEC are seen in combination with processes which can provide the required heat for the reaction [17].

REACTORS

The methanation is a relatively high exothermic reaction. Significant heat flow will be dissipated in methanation process as function of CO₂ conversion at different gas hourly space velocities (GHSV) and initial molar composition of H₂ and CO₂. However, it must be noted that heat dissipation gradients are formed inside reactors. Their variations depend on the catalyst activity. As a consequence, heat management is very important in reactor design. On the other hand, the methanation is thermodynamically limited at elevated temperature while it is kinetically limited at low temperature as discussed above. In summary, heat dissipation and temperature control are the key parameters in designing methanation reactors [18].

Various reactor types have been adapted for the methanation. In this subsection, the most relevant ones, namely fixed-bed, monolith, microchannel, membrane and sorption-enhanced reactors, are discussed.

The fixed-bed reactors are most used for the methanation. They are characterized by the advantages that the contacting of the catalyst particles by the gas tends to be quite uniform, and long contact times are possible. They are designed adiabatic or polytropic.

The adiabatic version is a cascaded process, in which multiple adiabatic reactors are used that operate in series and use heat exchangers between each reactor to the next downstream reactor to cool the process gas to the desired inlet temperature in order to obtain high CO₂ conversion [19]. In the reactors, the catalysts are packed in static beds, and the process reacting gas is then passed through the beds, where the reactions are induced as the gases contact the catalyst. The adiabatic reactors are relatively simple and cost-effective systems. Additionally, in the systems, the methanation

process can be carried out with high GHSV and steam can be produced with high temperatures in the intercoolers. The main disadvantages of such reactors are the hot spots and the poor flexibility with respect to the load.

The polytropic design is a cooled tube-bundle system. In this variant, a multitude of tubes of relatively small diameter are placed in parallel. While the number of parallel tubes is determined by the required production rate, the diameter of the tubes is chosen to match the required heat exchange area. However, the diameter size is limited towards smaller sizes. In comparison to adiabatic reactors, the polytropic reactors exhibit lower temperature gradients that lead to an increased lifespan of the system, and a certain degree of flexibility [20]. However, the polytropic reactors are more expensive and relatively complex.

The monolith reactors have the advantages of high specific catalyst surface area, small pressure drop and short response time. They have been widely used in exhaust gas cleaning [21]. Monolith reactors have also disadvantages: potential non-uniform gas distribution and thus lower effectiveness, and difficulty in installation of large industrial scale. The monoliths are made from ceramic or metallic materials. However, the ceramic type is brittle and cannot stand mechanical tensions. If the metallic type is chosen, its coating with the catalyst is a challenging issue (relatively short life-time).

The microchannel reactors have the advantage of the improved hydrodynamics that suppresses the formation of hot spots and thereby the deactivation of catalysts. In addition, their high catalyst-surface to reactor-volume ratio offers a relatively small reactor volume. However, the microchannel reactors are single-use systems. In other words, if the catalyst is deactivated irreversibly, the whole reactor has to be replaced because the catalyst is fixed on the inner surface of the reactor. Moreover, their scaling-up is limited [18].

CONCLUSION

The article focuses on the methanation process as one of the crucial steps in the conversion of electric energy from renewable sources to synthetic natural gas (power to gas). The second part then addresses the gas hourly space velocity (GHSV), the reactor inlet gas temperature, and the reaction temperature. If energy integration is strictly applied excess thermal energy can be used in various ways (e.g., electricity generation via steam turbine, district heating, etc. [22]).

The microeconomic evaluation shows that SNG from P2G processes is not competitive with natural gas or even biomethane (~7€/kWh). For economic feasibility, different business cases such as mobility, balancing services, and CO₂ certificates have to be combined. With respect to a macroeconomic consideration, it has to be taken into account that P2G can contribute to minimize the expansion of the electricity grid infrastructure and to increase the share of renewable energy in the transport and the heating sectors. Therefore, P2G can play a major role in the realization of the ambitious transition of the energy system [6].

Methanation research looks back on a history of more

than 100 years and is presently attracting new attention because of climate change, finiteness of fossil fuels, and a changing energy system with a high share of renewables. CO₂ methanation projects generally focus on Europe and especially Germany, the objective being to contribute to a flexible energy system. For this reason, they are combined with electrolysis units for the production of hydrogen. For both, CO and CO₂ methanation processes, the management of the heat of reaction is a difficult task. A multitude of methanation concepts were brought to pilot and commercial scale in the past. Only a few of them are currently available on the market [9].

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REFERENCES

- [1] Aleksandrs Lazdāns, Elina Dace, Julija Gusca, Development of the experimental scheme for methanation process, CONECT 2015, 14-16 October, Riga, Latvia
- [2] J. Wallbrecht, International Gas Union Triennium 2003-2006 Working Committee 2: Underground Gas Storage, Amsterdam, 2006. <http://members.igu.org/html/wgc2006/WOC2database/>
- [3] Observ'ER, Electricity Production in the World: General Forecasts, Worldwide Electricity Production from Renewable Energy Sources - Stats and Figures Series, 2013. <http://www.energies-renouvelables.org/observ-er/html/inventaire/pdf/15e-inventaire-Chap01-Eng.pdf>
- [4] A.L. Roes, M.K. Patel, Ex-ante environmental assessments of novel technologies - Improved caprolactam catalysis and hydrogen storage, J. Clean. Prod. 19 (2011) 1659-1667 <http://dx.doi.org/10.1016/j.jclepro.2011.05.010>
- [5] S. Schoenung, Economic analysis of large-scale hydrogen storage for renewable utility applications, in: International Colloquium on Environmentally Preferred Advanced Power Generation, 2011, pp. 8-10.
- [6] Manuel Goetz, Jonathan Lefebvre, Friedemann Moers, Amy McDaniel Koch, Frank Graf, Siegfried Bajohr, Rainer Reimert, Thomas Kolb, Renewable Power-to-Gas: A technological and economic review, Renewable Energy <http://dx.doi.org/10.1016/j.renene.2015.07.066>
- [7] Kiewidt L, Thöming J. Predicting optimal temperature profiles in single-stage fixed-bed reactors for CO₂-methanation Chem Eng Sci 2015;132:59-71
- [8] Haldor Topsoe: From solid fuels to substitute natural gas (SNG) using TREMP, http://topsoe.ru/business_areas/gasification_based/Processes/Substitute_Natural_Gas.aspx
- [9] Stefan Rönsch, Jens Schneider, Steffi Matthischke,

- Michael Schlüter, Manuel Götz, Jonathan Lefebvre, Praseeth Prabhakaran, Siegfried Bajohr, Review on methanation – From fundamentals to current projects, *Fuel* <http://dx.doi.org/10.1016/j.fuel.2015.10.111>
- [10] Florian Kirchbacher, Philipp Biegger, Martin Miltner, Markus Lehner, Michael Harasek, A new methanation and membrane based power-to-gas process for the direct integration of raw biogas e Feasibility and comparison, *Energy* (2017) 1-13 <http://dx.doi.org/10.1016/j.energy.2017.05.026>
- [11] Lapidus AL, Gaidai NA, Nekrasov NV, Tishkova LA, Agafonov YA, Myshenkova TN, The mechanism of carbon dioxide hydrogenation on copper and nickel catalysts, *Pet Chem* 2007;47(2):75-82.
- [12] Marwood M, Doepper R, Renken A, In-situ surface and gas phase analysis for kinetic studies under transient conditions the catalytic hydrogenation of CO₂, *Transient Kinet* 1997;151(1):223-46
- [13] Mergel J, Carmo M, Fritz D, Status on technologies for hydrogen production by water electrolysis, *Transition to renewable energy systems*, Weinheim, Germany: WILEY-VCH; 2013
- [14] Mergel J. Hydrogen production by water electrolysis: current status and future trends, AGEF seminar, Ruhr University Bochum; 2013. p. 104.
- [15] Smolinka T, Gunther M, Garcke J. NOW-Studie: Stand und Entwicklungspotenzial der Wasserelektrolyse zur Herstellung von Wasserstoff aus regenerativen Energien, Fraunhofer ISE & FCBAT; 2011.
- [16] FCHJU, Development of water electrolysis in the European Union. Fuel cells and hydrogen-joint undertaking, 2014.
- [17] Sebastian Schiebahn, Thomas Grube, Martin Robinius, Vanessa Tietze, Bhunesh Kumar, Detlef Stolten, Power to gas: Technological overview, systems analysis and economic assessment for a case study in Germany, *International journal of hydrogen energy* 40 (2015) 4285-4294
- [18] Karim Ghaiba, Fatima-Zahrae Ben-Fares, Power-to-Methane: A state-of-the-art review, *Renewable and Sustainable Energy Reviews* 81 (2018) 433–446 <http://dx.doi.org/10.1016/j.rser.2017.08.004>
- [19] Kopyscinski J, Schildhauer TJ, Biollaz SMA, Production of synthetic natural gas (SNG) from coal and dry biomass – a technology review from 1950 to 2009, *Fuel* 2010; 89(8), [1763–83], [http://refhub.elsevier.com/S1364-0321\(17\)31134-6/sbref188](http://refhub.elsevier.com/S1364-0321(17)31134-6/sbref188)
- [20] Hagen J. *Chemiereaktoren*, 1st ed. Weinheim: Wiley-VCH; 2004. [http://refhub.elsevier.com/S1364-0321\(17\)31134-6/sbref192](http://refhub.elsevier.com/S1364-0321(17)31134-6/sbref192)
- [21] Sadeghi F, Tirandazi B, Khalili-Garakani A, Nasseri S, Nodehi RN, Mostouf N, Investigating the effect of channel geometry on selective catalytic reduction of NO_x in monolith reactors, *Chem Eng Res Des* 2017;118:21–30. [http://refhub.elsevier.com/S1364-0321\(17\)31134-6/sbref196](http://refhub.elsevier.com/S1364-0321(17)31134-6/sbref196)
- [22] Tanja Schaaf, Jochen Grünig, Markus Roman Schuster, Tobias Rothenfluh, Andreas Orth, Methanation of CO₂ - storage of renewable energy in a gas distribution system, *Energy, Sustainability and Society*, DOI 10.1186/s13705-014-0029-1