IBP1054_17

Energy-efficient conversion of green hydrogen and carbon dioxide to methane

Ronny Dietrich, Robert Manig[2], Christoph Birkner[3]
Ronny Erler[4], Hartmut Krause[5]

Abstract

The share of electricity from renewable sources, especially wind and solar, is increasing continuously. The conditionally predictable fluctuating amounts of electricity are major challenges for the energy sector in terms of efficient storage technologies. One way to store a huge amount of fluctuating energy is the conversion of electrical surplus power into the chemical energy carrier hydrogen by power-to-gas-process with subsequent biological methanation. The research project "BioRePow" as part of the lighthouse project "inTebi" at DBI - Gastechnologisches Institut gGmbH Freiberg (DBI) investigates the biological methanation in a bubble column reactor. The biological methanation of green hydrogen and carbon dioxide based on the Sabatier reaction [2], according to equation (1):

$$4\,H_2 + CO_2 \rightarrow CH_4 + 2\,H_2O \qquad \Delta H_R^0 = -253\,\frac{kJ}{mol} \qquad (1)$$

Considering the gas quality requirements according to DVGW - worksheet G260 [3] and G262 [4] the focus is the energy-efficient production of methane at a pressure level sufficient for a subsequent injection into natural gas grid without gas compression systems. In recently conducted test series biological energy conversion of more than 80% were achieved by optimize the fumigation system, main process parameters and renouncement of energy intensive system components such as agitator, circulation or gas separation. The work conditions verified in a wide range of process parameters like pressure, flow rate and composition of the reactant gases.

1. Introduction

The share of electricity from renewable sources, especially wind and solar, is increasing continuously. (31,5 % share of renewable energies in Germany electricity sector in 2015) [5] The conditionally predictable fluctuating amounts of electricity are major challenges for the energy sector in terms of efficient storage technologies. One way to store a huge amount of fluctuating energy is the conversion of electrical surplus power into the chemical energy carrier hydrogen by power-to-gas-process with subsequent methanation [6].
For this purpose, there are two basic methods: catalytic and biological methanation. In the case of catalytic methanation, the conversion takes place at high temperatures (about 300-500 ° C) with the aid of a mostly nickel-based catalyst. This process has already reached common standard. The high-energy requirement in plant operation has a detrimental effect on the overall balance. In contrast, the biological methanation can be realized at much lower mesophilic to thermophilic temperature level. The process control can be carried out at a pressure level, which allows direct feeding into the natural gas grid. In Germany, a gas quality of at least 95% by volume is required [7].

2. Biological methanation

Mechanical Engineer – DBI - Gastechnologisches Institut gGmbH Freiberg
[2]Chemical Engineer – DBI - Gastechnologisches Institut gGmbH Freiberg
[3] Scientific Assistant – DBI - Gastechnologisches Institut gGmbH Freiberg
[4] Economic Engineer – DBI - Gastechnologisches Institut gGmbH Freiberg
[5] Ph.D., Engineer, CEO,– DBI - Gastechnologisches Institut gGmbH Freiberg

Biological methanation is a biochemical metabolic process of microorganisms that convert hydrogen and carbon dioxide into methane and water. The reaction based on the Sabatier-process and could be described by the following chemical formula (1):

$$4\,H_2(g) + CO_2(g) \rightarrow CH_4(g) + 2\,H_2O(l) \qquad \Delta H_R^0 = -253\,\frac{kJ}{mol} \qquad (1)$$

The exothermic process proceeds under anaerobic conditions. The methanogenic archaea act as a catalyst. The methanogenic condition takes place in the last partial process of the fermentation process, in methanogenesis according to figure 1.

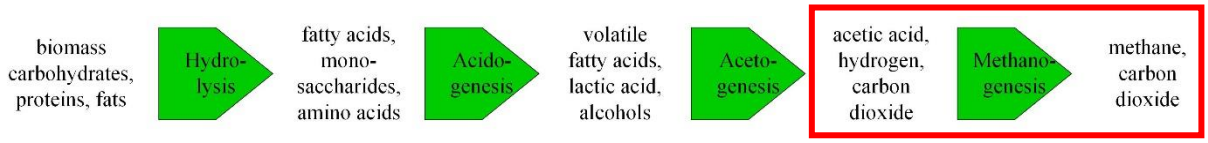

Figure 1: Steps of biological fermentation

Methanogenesis essentially comprises two parallel methane formation paths, the acetoclastic and the hydrogenotrophic methanogenic condition. For the biological methanization, the hydrogenotrophic methane formation by the archaea is targeted. Due to the chemolithotrophic feeding of the archaea, the cellular respiration of carbon dioxide and hydrogen to form methane, no additional carbon sources are required [8]. The preferred anaerobic respiration of hydrogenotrophic methanogens can be set in two process concepts and encouraged principle. Firstly, the methanation can be carried out "in situ". It means that carbon dioxide of the biogas production process reacts directly with hydrogen from external sources to methane. The second process concept is characterized by "ex situ" methanation. The two reactant gases carbon dioxide and hydrogen are fed to fermentation from external sources. The amount of dissolved and biologically available hydrogen in the fermentation substrate has a limited effect in both processes. Relevant process parameters are temperature, pressure or pH. The optimum pH value for methanogenic microorganisms is between six and eight. Some representatives can also achieve good metabolites at pH values of five or nine [9]. The temperature range of methanogenic microorganisms is also widely spread and ranges from mesophilic to hyperthermophilic temperatures. With increasing temperature optimum of the microorganisms usually also, their metabolic rate increases, leading to higher methane formation rates. The microorganisms are insensitive to the prevailing pressure and can be used up to the high-pressure range. An important performance criterion for the methanation process is the methane formation rate (MFR). It describes the amount of methane generated with respect to the amount of the fermentation substrate used and the time formula (2):

$$MFR = \frac{\dot{V}_{CH_4}}{(V_{Substrat} \cdot t)} \qquad [MFR] = \left[\frac{Nm^3}{m^3 \cdot h}\right] = \left[\frac{Nl}{l \cdot h}\right] \qquad (2)$$

3. Hydrodynamics und mass transport

The hydrodynamics and mass transport are the main tools for describing the dependencies for example reactant gas flow, nozzle cross-section, gas pressure, the temperature and viscosity of the liquid, the formation of bubbles in terms of the substance conversion. Hydrodynamics describes the formation of gas bubbles as well as their ascent behavior in an aqueous medium and provides information on the type and quality of the gassing. For example, the bubble formation on a static nozzle is shown in figure 2.

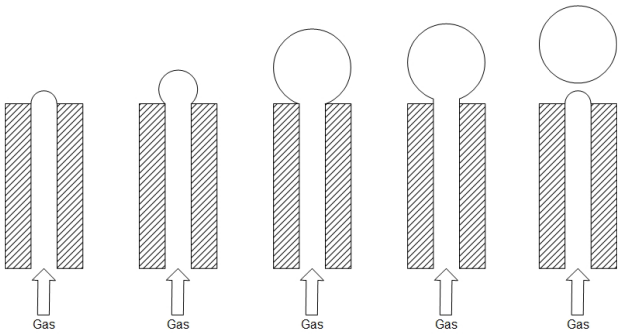

Figure 2: Genesis of bubbles at an injector [10]

The replacement of a gas bubble at an outlet opening is carried out, for example, only when the upward acting lift force exceeds the holding force on the nozzle. Gas bubbles have a nearly ideal spherical shape up to a diameter of 0.7 mm [11]. With increasing bubble size, the flow resistance increases. This leads to a change in the bubble shape and movement. The ascent rate can be calculated by means of a force equilibrium of lift force, weight force and resistance force on individual bubbles. With the help of the correlation, the ascent rate for gas bubbles can be formulated with formula (3):

$$u_a = \sqrt{\frac{4 \cdot d \cdot (\rho_l - \rho_g)}{3 \cdot \rho_l \cdot c_w}} \tag{3}$$

Bubble size and ascent rate and ascent behavior are essential influencing factors on the mass transfer from the gas phase into the liquid phase. The mass transport is generally described by the formula (4):

$$\dot{n} = -k_L \cdot A \cdot (c_{A*} - c_{\bar{A}}) \tag{4}$$

The mass flow is a product of mass transfer coefficients k_L, the interface A and the concentration gradient between the interface and the liquid (c_{A*}-$c_{\bar{A}}$). The concentration gradient is essentially determined by the solubility of the reactant gases in the liquid phase as well as the conversion rate of the dissolved gases by the microorganisms. Carbon dioxide has a significantly higher solubility in water with $7{,}8 \cdot 10^{-4}\ \frac{\text{mol}}{\text{l·bar}}$ than hydrogen with $3{,}4 \cdot 10^{-2}\ \frac{\text{mol}}{\text{l·bar}}$. Based on the stoichiometry of equation (1) and the low solubility of hydrogen in comparison to carbon dioxide, hydrogen becomes the limiting factor in biological methanation. Assuming that the dissolved hydrogen is directly converted by the existing microbiology, the term of the concentration gradient is simplified to c_{A*}. The penetration theory of Higbie can be used to describe the transient mass transfer in a bubble column. According to the penetration theory, turbulence during the bubble movement encourages the mass transfer. If a liquid particle comes into contact with the gas phase, the material exchange between the two phases takes place within the contact time τ. With increasing turbulence or high relative velocity between the gas bubble and the aqueous medium, the contact time and the number of fluid particles involved in the material exchange are increased. The contact time τ is calculated from the bubble size and the ascent rate according to the following equation:

$$\tau = \frac{d}{u_A} \tag{5}$$

For mass transfer the formula (6) obtained as a function of the temperature-dependent diffusion coefficient in accordance with equation (7):

$$\dot{n} = 2 \cdot \sqrt{\frac{D_{AB}}{\pi \cdot \bar{\tau}}} \cdot A_B \cdot \left(\bar{c}_A - \bar{c}_M\right) \tag{6}$$

$$D_{AB} = \frac{k_B \cdot T}{6\pi \cdot \eta_F \cdot R_0} \tag{7}$$

The theoretical analyses for hydrodynamics and mass transport show that the bubble size and its distribution in the substrate have a decisive influence on the mass transfer. In order to produce a large phase boundary surface and a high mass transport, many small, finely divided gas bubbles are necessary in the substrate. In essence, such a bubble image dependent on the gas injector and the educt gas volume flow. The mass

conversions or the gas components in the product gas flow can be calculated based on hydrodynamics and mass transport. Figure 3 graphically illustrates this relationship.

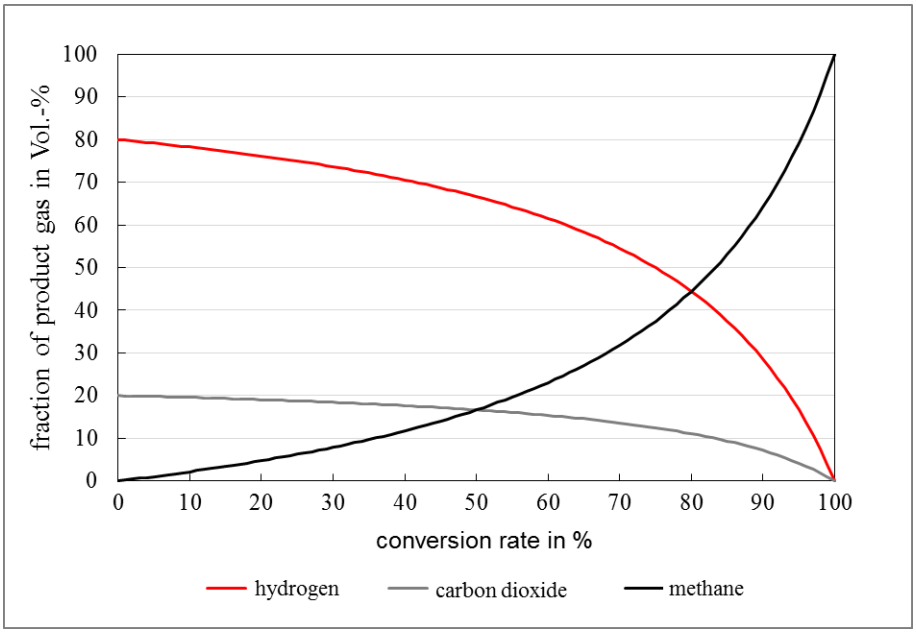

Figure 3: Composition of product gas as a function of conversion rate

4. Pilot plant in laboratory scale

At the DBI, experiments on biological methanation are carried out on a pressurized bubble column in the laboratory scale. The relevant process and design parameters, such as pressure, reactant gas flow and stoichiometry, reactor dimensions as well as the desired range of variations as in table 1, were determined based on a literature study and theoretical considerations.

Table 1: Relevant process and design parameters of biological pressure methanation

Parameter	**range**
temperatur	thermophilic (55 °C)
reactor capacity	5,2 l
reactor height	1,6 m
reactor pressure	1 … 10 bar
reactant gas flow	50 … 200 ml/min
stoichiometry (H_2 : CO_2)	3:1 … 8:1
porositiy of injektionsystem	1… 400 µm
inoculum	sewage sludge

The pilot plant based on the method principle of a bubble column. The reactor was designed in such way that experiments up to 38 bar in mesophilic to thermophilic temperature range can be carried out. The reactant gases are metered through the Mass Flow Controller (MFC) and fed to the process. There is a continuous analysis of the product gas in terms of quality and quantity, as well as the process parameters pH, redox, temperature and pressure. Energy-intensive system components such as agitator, agitation or gas separation was deliberately omitted in the process engineering concept. The basic principle is shown in the flow chart in figure 4 and a section of the pressurized bubble column in figure 5.

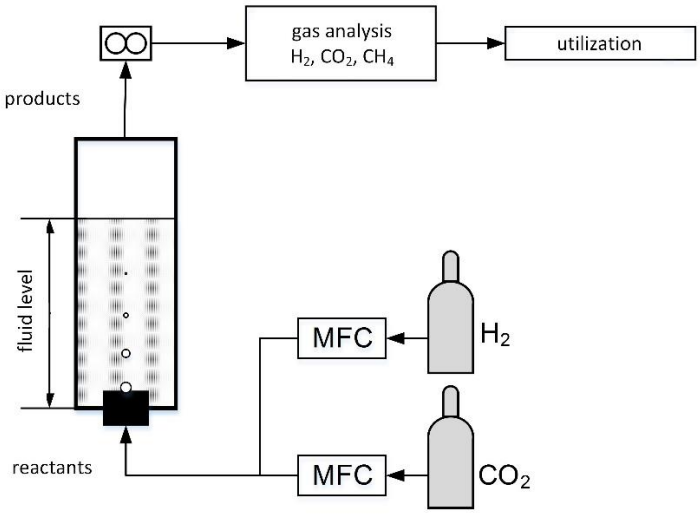

Figure 4: simplified flow chart for biological methanation

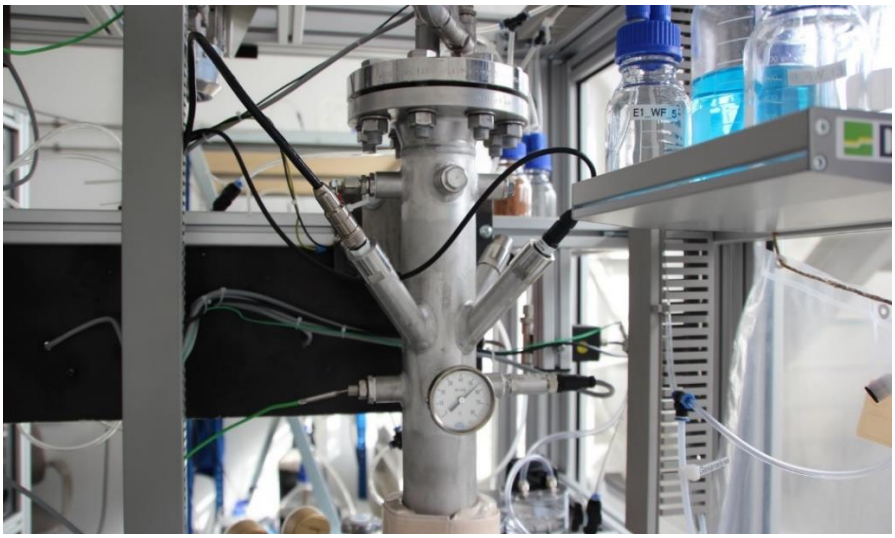

Figure 5: section of the pressurized bubble column

5. Results

The influence of the process parameters pressure, temperature, educt gas flow, educt gasstoichiometry of biological methanation using different gas injectors was investigated in tests on the pressure-forced bubble column. Approximately 90 experiments were carried out for biological methanation. The approach of continuous process control without agitation or recirculation could be demonstrated as a stable method.

The following results were obtained:

- Specific methane formation rate (MFR) of 0.21 l / (l * h)
- Material conversion of approx. 82% in the current plant setup (corresponds to approx. 47% by volume of methane)
- Increase methane formation rates and methane levels by reducing the nozzle / pore size of the gas injector (cf. figure 6)
- Low influence of reactor pressure on gas quality and quantity
- Low influence due to over or substoichiometric addition of hydrogen to gas quality
- No recognizable limitation of biological methanation by microorganisms

The relationship between the gas injector, in particular the pore size, and the methane yield or the methane formation rate must be emphasized. It has been shown that a higher methane yield is achievable by smaller pores and finely divided gas bubbles. This effect has been demonstrated by means of various porous materials. Figure 6 shows a selection of gas injectors with the associated bubble image.

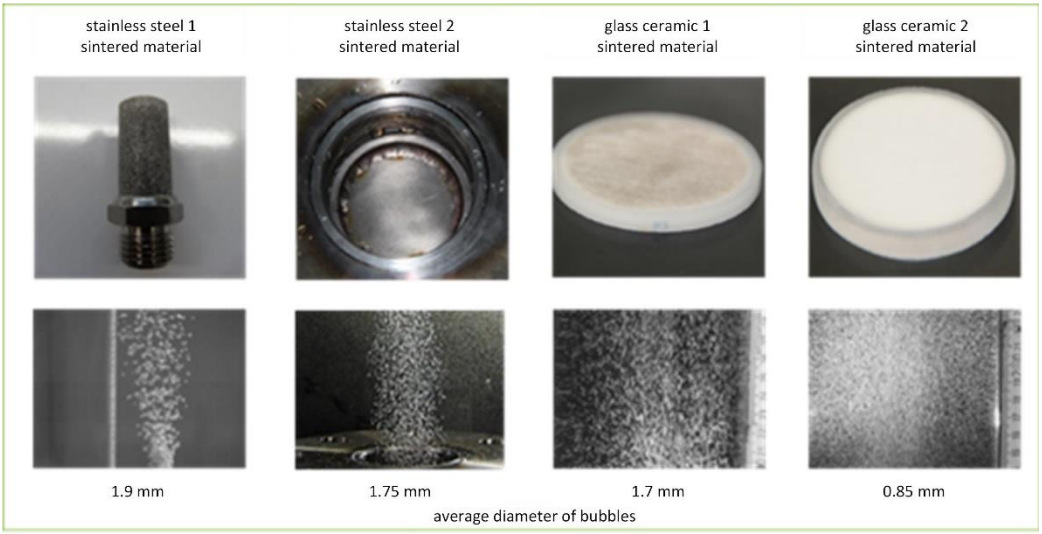

Figure 6: bubble images and average diameter for different gas injectors

The gas bubbles were generated by means of air in water. Using a high-speed camera, the bubble images could be recorded and evaluated. In the experiments, the glass ceramic '2' exhibited the best dispersing behavior and produced the smallest gas bubbles with a diameter of less than 0.85 mm. The low mechanical loadability repeatedly led to the breakage of the glass ceramic. By replacing the glass ceramic with stainless steel sintering materials, a clearly simplified and more stable gas injector could be constructed. The stainless steel sintered material '2' produced a comparable bubble image to the glass ceramic '1'. This result is also reflected in the achieved conversion and methane formation rates of the methanation tests in the pressure-forced reactor. Figure 7 shows the methane concentrations and methane formation rates obtained, varying the educt gas volume flows and gas injectors.

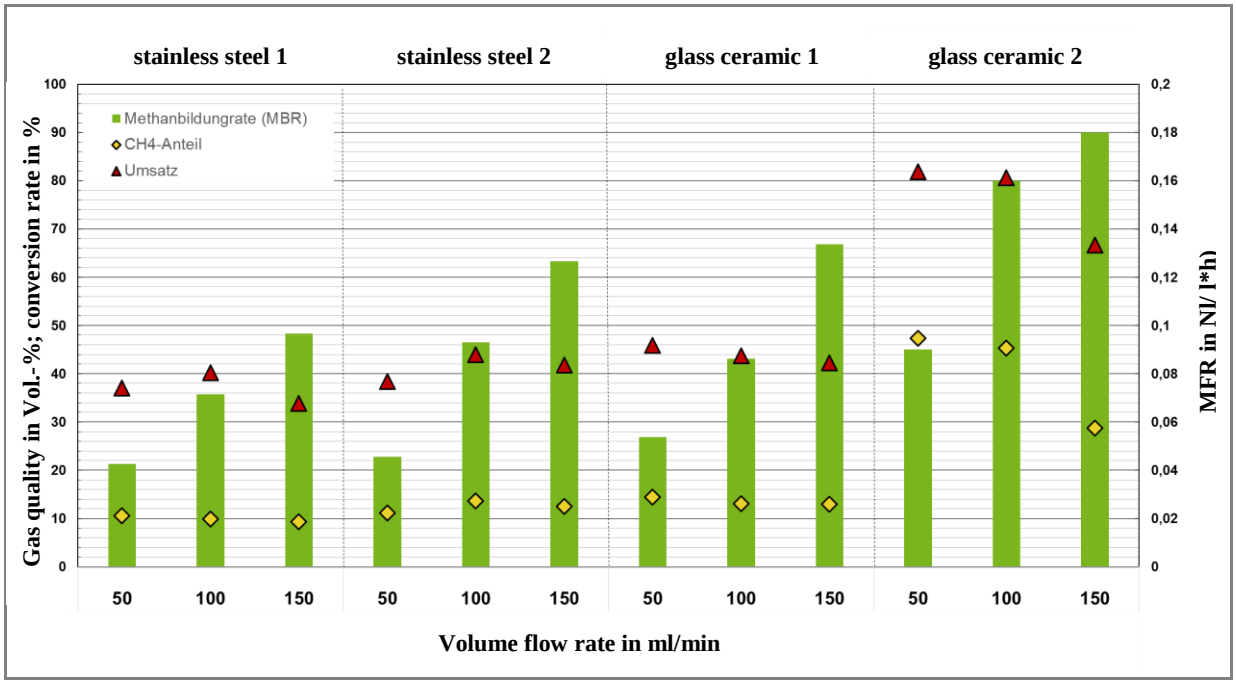

Figure 7: Conversion rate, proportion of methane and methane formation rate according to Gas injection system and volume flow rate

6. Conclusion and outlook

An effective and energy-efficient process for biological methanation in the laboratory scale was established based on investigations on the pressure-forced bubble column. The gas injection system, respectively the predominant hydrodynamic states in the bubble column, are crucial for high conversions in biological methanation. In a comprehensive experimental program, the relationships of hydrodynamics, mass transfer and resulting conversion rates were investigated and the stability of the microorganisms test. The shape and size of the bubbles, the rate of ascent and the feed gas volume flow have a decisive effect on the conversion, the methane formation rate and product gas quality. The methane yield correlates disproportionately with the reactor height.

In the next steps, the process will be optimized and upscaling will be done. Therefore studies for the needed reactor height and the gas injection are realized. The analyses of the influence of mixed biological cultures on methanation is also part of the further research program.

7. Acknowledgement

The IGF project 22 LBG "Biologisches Repowering zur Erhöhung der Biogasanlagenleistung - BioRePow " of the Research Association DVGW - Deutscher Verein des Gas- und Wasserfaches e.V. was funded by the AiF under conditions of the program for the promotion of industrial joint research (IGF) by the Federal Ministry of Economics Affairs and Energy (BMWi) based on a decision of the German Bundestag. The authors would like to thank the financial support.

8. References

[1] F. Graf, A. Krajete, U. Schmack, *DVGW-1658 Abschlussbericht G 3-01-13 biologischen Methanisierung* **2014**.
[2] P. Sabatier, J. B. Sendness, *Nouvilles synthéses des méthane*, C. R. Acad. Sci. Paris **1902**.
[3] DVGW - Deutscher Verein des Gas- und Wasserfaches e.V., *Gasbeschaffenheit* **2013** *(G 260)*.
[4] DVGW - Deutscher Verein des Gas- und Wasserfaches e.V., *Nutzung von Gasen aus regenerativen Quellen in der öffentlichen Gasversorgung* **2011** *(G 262)*.
[5] Bundesministerium für Wirtschaft und Energie, *Bruttostromerzeugung in Deutschland 2016: vorläufige Zahlen, z.T. geschätzt; ** regenerativer Anteil; Stand: Februar 2017*.
[6] F. Graf, M. Götz, M. Henel, D. T. Schaaf, D. R. Tichler, *DVGW - Technoökonomische Studie von Power-to-Gas-Konzepten Teilprojekte B-D Abschlussbericht*.
[7] Deutscher Verein des Gas- und Wasserfachs (DVGW), *Gasbeschaffenheit; Technische Regeln - Arbeitsblatt: DVGW G260* **2013**.
[8] H. D. Janke, *Umweltbiotechnik*, 2nd ed., Verlag Eugen Ulmer Stuttgart, Stuttgart **2008**.
[9] H. Huber, in *Biologische Methanisierung* (Eds: Ostbayrisches Technologie-Transfer-Institut e.V.). Regensburg **2015**.
[10] R. Kumar, N. R. Kuloor, *Blasenbildung in Flüssigkeiten niedriger Viskosität unter konstanten Strömungsbedingungen*, Chemie Technik **1967**.
[11] N. Fries, Experimentelle Untersuchungen zum Aufstiegsverhalten kleiner, fluider Kugeln in einer Drehkammer, Ruhr-Unsiversität Bochum **2006**.
[12] M. Kraume, *Transportvorgänge in der Verfahrenstechnik: Grundlagen und apparativeUmsetzungen*, Springer-Verlag, Berlin Heidelberg New York **2013**.