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Biologische Wasserstoffmethanisierung in Hochdruck-Rieselbettreaktoren für Power-to-Gas-Konzepte

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BIOLOGISCHE WASSERSTOFFMETHANISIERUNG IN HOCHDRUCK-RIESELBETTREAKTOREN FÜR POWER-TO-GAS-KONZEPTE

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Inhalt

1. Einleitung

1.1. Entwicklung des Energiesystems

Die europäische Union hat sich zum Ziel gesetzt, bis 2050 die Treibhausgasemissionen um mindestens 80 % unter den Stand von 1990 zu senken (European Commission, 2011). Erreicht werden soll eine Begrenzung des anthropogenen Klimawandels und die damit verbundenen Auswirkungen auf die Umwelt (Henning and Palzer, 2013). Weiterhin soll die Wirtschaft weitestgehend dekarbonisiert und unabhängig von fossilen Ressourcen werden, um Versorgungssicherheit und Wettbewerbsfähigkeit auch bei zukünftig sich verknappenden und verteuernden fossilen Ressourcen zu gewährleisten. Da ein Großteil der Treibhausgasemissionen und Nutzung fossiler Ressourcen auf den Energiesektor entfällt, entsteht ein besonderer Druck auf die Energiesysteme (European Commission, 2011; Henning and Palzer, 2013). Aus diesen Gründen wird die Erzeugung von Energieträgern aus erneuerbaren Energiequellen konsequent ausgebaut, wobei vor allem die Stromerzeugung über Windkraftanlagen und Photovoltaik eine dominierende Rolle einnimmt (Götz et al., 2016; Henning and Palzer, 2013; Kapila et al., 2017). So hat sich in den Jahren 2009 bis 2014 die weltweite kombinierte installierte Leistung von Windkraft und Photovoltaik von 183 GW auf 665 GW erhöht (Kapila et al., 2017).

Allerdings ist die Stromerzeugung aus Windkraft und Photovoltaik hochgradig wetterabhängig und somit sehr schwankend und intermittierend. Der Ausbau der auf erneuerbaren Energieträgern basierenden Energieversorgung wird daher auch einen tiefgreifenden Umbau der bestehenden Struktur der Energiesysteme erfordern (Blanco and Faaij, 2018; Boer et al., 2014; Götz et al., 2016). Die traditionelle, zentralisierte Struktur basiert aus wenigen großen Produzenten, wie etwa Kohle- oder Atomkraftwerke, welche die Energie bedarfsgerecht bereit stellen (Montoya-Bueno et al., 2016). Mit der Einführung der erneuerbaren Energien wird sich diese Struktur wandeln und es wird zu einer Dezentralisierung der Produktion kommen (Montoya-Bueno et al., 2016; Payasi et al., 2011). Zudem werden erneuerbare Energien nicht nur in der Versorgung der auch heute schon durch elektrische Energie abgedeckten Sektoren zum Einsatz kommen, auch im Wärme- und Verkehrssektor wird regenerativer Strom eine wichtige Rolle spielen (Henning and Palzer, 2013).

Die Stromnetze jedoch sind nicht für einen großflächigen Ausbau und die Verbindung einer Vielzahl unterschiedlicher dezentraler und schwankender Erzeugungsanlagen ausgelegt (Viral

and Khatod, 2012). Ein weiterer Ausbau dieser Anlagen stellt eine große Herausforderung an die Netzstabilität dar (Kapila et al., 2017). Derzeit wird der Ausgleich schwankender Stromproduktion durch die Speicherung konventioneller Brennstoffe wie Kohle und Erdgas sichergestellt (Beaudin et al., 2010). Mit dem Ausbau regenerativer und dem Rückbau konventioneller Erzeugungsanlagen stellt dies natürlich keine langfristige Lösung dar.

Um diesem Problem zu begegnen ist mit dem Ausbau intermittierender und dezentraler Energiequellen eine zunehmende Ausweitung der Energiespeicherung erforderlich (Götz et al., 2016; Smallbone et al., 2017). Dadurch wird die Flexibilität der Energieversorgungssysteme erhöht und die Integration erneuerbarer Energiequellen erleichtert. Der Speicherung der Energie in Zeiten einer Überschusserzeugung und deren Freisetzung in Zeiten, in denen der Bedarf über der Produktion liegt, wird in Zukunft eine besondere Bedeutung zukommen (Kapila et al., 2017). Vor dem Hintergrund des Ausbaus der erneuerbaren Energien geht man davon aus, dass in den USA, Europa, China und Indien netzgekoppelte Speicherkapazitäten von zusätzlich 310 GW notwendig sein werden (International Energy Agency, 2014).

Der Ausbau der erneuerbaren Energien erfordert somit eine sektorübergreifende Optimierung des Gesamtsystems. Dazu müssen Optionen für die flexible Nutzung und Speicherung der produzierten elektrischen Energie in möglichst vielen Verbrauchssektoren erschlossen werden (Henning and Palzer, 2013).

1.2. Power-to-Gas

Eine technische Lösungsmöglichkeit zur Speicherung großer Mengen elektrischer Energie stellen Power-to-Gas-Konzepte dar. Die Power-to-Gas Technologie (PtG) kann eine zentrale Rolle in zukünftigen Energieversorgungssystemen einnehmen und wird insbesondere in neueren Veröffentlichungen intensiv diskutiert (Blanco and Faaij, 2018; Götz et al., 2016; Hashimoto et al., 2014, 1999; Jentsch et al., 2014; Lecker et al., 2017; Leonzio, 2017; Lewandowska-Bernat and Desideri, 2017; Pleßmann et al., 2014; Simonis et al., 2017).

Mit Hilfe der Power-to-Gas Technologie erfolgt die Transformation von Elektrizität in einen chemischen Energieträger, welcher mit dem Gasnetz kompatibel ist. Das Gasnetz kann anschließend als Speicher- wie auch Transportmedium genutzt und das eingespeiste Gas in vielfältigen Anwendungsgebieten eingesetzt werden (Götz et al., 2016; Lewandowska-Bernat and Desideri, 2017). In begrenztem Umfang ist die Einspeisung von Wasserstoff in Erdgasnetze möglich. Wasserstoff (H_2) kann im Fall einer den Verbrauch übersteigenden Stromproduktion

mittels Elektrolyse produziert werden. Dabei werden Wirkungsgrade von bis zu 77 % erreicht (Jentsch et al., 2014). Die Einspeisung von Wasserstoff ins Gasnetz ist jedoch beschränkt, insbesondere im Hinblick auf die Endverbraucher. So sind Gasturbinen im Bestand auf eine H_2-Konzentration von 1 bis 5 Vol.-% limitiert. Für Gasmotoren ist eine maximale H_2-Zumischung von 2 Vol.-% erlaubt. Unklar ist auch die Eignung von Untergrundspeichern, insbesondere Porenspeichern. Neben der mikrobiologischen Schwefelwasserstoff-Bildung sind die Integrität der Deckgebirge sowie das Verhalten der eingesetzten Werkstoffe und Bauteile der Untertageausrüstung offene Fragen. Auch auf Werkstoffe von Erdgastanks sind Effekte von H_2 zu beachten (Jentsch et al., 2014; Müller-Syring et al., 2013). Der Einsatz von Wasserstoff als Energieträger bedingt zudem auch eine geringere Transport- und Speicherkapazität aufgrund dessen geringerer Dichte (Hashimoto et al., 1999).

Für einen Einsatz von Power-to-Gas im großen Maßstab wird daher die Umwandlung des Wasserstoffs mit Kohlenstoffdioxid in Methan (CH_4) mittels der Sabatier Reaktion favorisiert (Hashimoto et al., 1999). Zwar reduziert sich der Wirkungsgrad durch den weiteren Umwandlungsschritt um weitere 10-15 % (Graf et al., 2014; Jentsch et al., 2014), das daraus resultierende synthetische Erdgas (SNG) kann jedoch flexibel genutzt und nahezu unbegrenzt gespeichert werden (Götz et al., 2016). Weiterhin weist SNG mit 1.200 kWh m^{-3} bei 200 bar auch im Vergleich mit den derzeit modernsten Lithium-Ionen-Speichern (350 kWh m^{-3}) eine sehr hohe spezifische Energiedichte auf (Leonzio, 2017; May et al., 2018). Allein in Deutschland liegt somit die Speicherkapazität von Erdgas bei 260 TWh. Pumpspeicherwerke als die größten elektrischen Speicher weisen lediglich eine Kapazität von 0.05 TWh auf (Lecker et al., 2017). Die weltweite Speicherkapazität von Erdgas liegt sogar bei > 3600 TWh (Götz et al., 2016), welche durch die Power-to-Gas Technologie zugänglich gemacht werden kann.

1.3. Wasserstoffmethanisierung

Für die Umwandlung von Wasserstoff in Methan stehen zwei unterschiedliche Konzepte zur Verfügung. Die chemisch-katalytische Methanisierung von Wasserstoff findet bei Temperaturen bis 550 °C und Drücken bis 100 bar statt. Metalle wie Nickel, Ruthenium, Rhodium oder Cobalt können als Katalysator verwendet werden, wobei aufgrund der geringen Materialkosten und hohen Selektivität für Methan in der Regel Nickel-Katalysatoren zum Einsatz kommen (Götz et al., 2016; Graf et al., 2014). Aufgrund der hohen Gasdurchsätze, die bei diesem Verfahren möglich sind und der stark exothermen Methanisierungsreaktion liegt die

Herausforderung vor allem in der Abfuhr der Prozesswärme, um etwa das Sintern des Katalysators während der Methanisierung zu verhindern (Götz et al., 2016). Weitere Herausforderungen stellen die für dieses Konzept erforderliche hohe Reinheit der Eduktgase sowie die geringe Flexibilität hinsichtlich Lastwechsel dar (Barbarossa and G. Vanga, 1992; Bartholomew, 2001; Götz et al., 2016; Graf et al., 2014; Ullrich et al., 2018). Aufgrund des komplexen Prozesses der chemisch-katalytischen Methanisierung eignet sich dieses Konzept insbesondere für große Anlagen ab 100 MW Elektrolyseleistung (Götz et al., 2016).

Eine weitere Möglichkeit zur Umwandlung von Wasserstoff und Kohlenstoffdioxid in Methan stellt die biologische Wasserstoffmethanisierung (BHM) dar. Hydrogenotrophe methanogene Mikroorganismen wandeln hierbei die Reaktionsgase Wasserstoff und Kohlenstoffdioxid in Methan und Wasser um (Lecker et al., 2017). Das biologische Konzept zeichnet sich durch „mildere“ Betriebsbedingungen mit Temperaturen bis 70 °C und Drücken bis 9 bar aus (Graf et al., 2014; Ullrich et al., 2018). Als Vorteil gegenüber der chemisch-katalytischen Methanisierung werden ein flexibles Lastwechselverhalten sowie eine ausgeprägte Robustheit hinsichtlich der Eduktgasbeschaffenheit genannt (Bartholomew, 2001; Götz et al., 2016; Liew et al., 2016; Seifert et al., 2013; Strevett et al., 1995). Bezogen auf die eingespeiste Eduktgasmenge am Reaktoreingang steht dem jedoch eine bis zu Faktor 50 geringere Leistungsfähigkeit gegenüber (Götz et al., 2016; Graf et al., 2014).

1.4. Reaktorkonzepte der biologischen Wasserstoffmethanisierung

Die biologische Wasserstoffmethanisierung kann in unterschiedlichen Reaktorsystemen durchgeführt werden. In vielen aktuellen Untersuchungen werden derzeit unterschiedliche Reaktorsysteme getestet und hinsichtlich Prozessenergiebedarf und Methanproduktionsrate hin optimiert.

Untersucht werden zur BHM insbesondere Rührkesselreaktoren (CSTR), welche auch bereits im industriellen Maßstab zum Einsatz kommen. Mikroorganismen und Eduktgase befinden sich bei diesem Konzept in dem mit Prozessflüssigkeit gefüllten Reaktionsraum des Reaktors (Götz et al., 2016; Lecker et al., 2017; Luo and Angelidaki, 2012; Seifert et al., 2013). Um hohe Methanproduktionsraten zu erreichen, ist eine intensive Durchmischung von Mikroorganismen und Eduktgasen in der Prozessflüssigkeit notwendig. Die Methanproduktionsraten hängen dabei wesentlich von den Stoffaustauschraten ab, so dass CSTR-Reaktoren zur BHM über eine

entsprechende Gaseinbringtechnik und hohe Rührwerksdrehzahlen verfügen müssen (Götz et al., 2016; Jochum, 2015). Um hohe Methanmengen zu erreichen, ist bei CSTR-Reaktoren daher mit einem hohen Leistungseintrag zu rechnen (Graf et al., 2014). Auf diesem Weg wurden im Bereich der BHM die bisher höchsten Methanmengen mit einer Methane Formation Rate (MFR) von 137,17 L CH_4 L^{-1} d^{-1} erzielt (Seifert et al., 2014). Dabei beschreibt die MFR die produzierte Methanmenge bezogen auf das Reaktorvolumen und ist ein wichtiger Parameter zur Beurteilung der Reaktorleistung (Götz et al., 2016).

In den vergangenen Jahren werden vermehrt auch Rieselbettreaktoren (TBR) untersucht. Hier werden die Mikroorganismen auf Füllkörpern mit hoher spezifischer Oberfläche im gasgefüllten Reaktionsraum des Reaktors immobilisiert. Ein feuchtes Milieu sowie die Nährstoffversorgung werden durch die regelmäßige Berieselung mit der Prozessflüssigkeit erzielt. So werden mit diesem Konzept hohe Mikroorganismen-Konzentrationen mit einer großen Phasengrenzfläche erreicht, um auch ohne den Einsatz von Rührwerkstechnik hohe Stoffaustauschraten zu ermöglichen (Burkhardt and Busch, 2013; Graf et al., 2014; Rachbauer et al., 2016; Strübing et al., 2017). In ersten Untersuchungen mit diesem Konzept wurden MFR von 1.17 L CH_4 L^{-1} d^{-1} erzielt (Burkhardt and Busch, 2013). Jüngste Untersuchungen konnten diese zwar deutlich steigern, mit einer MFR von 15,4 L CH_4 L^{-1} d^{-1} ist sie immer noch um den Faktor 9 niedriger als bei CSTR-Reaktoren (Strübing et al., 2017). Um die Leistung der BHM bei diesem vielversprechenden Reaktorkonzept weiter zu steigern, muss die Gas-Flüssig-Austauschrate verbessert werden (Graf et al., 2014; Lecker et al., 2017; Strübing et al., 2017).

Neben den hohen Mikroorganismenkonzentrationen, die in TBR erreicht werden können, sind hierfür auch hohe Eduktgas-Konzentrationen eine wesentliche Voraussetzung (Jochum, 2015). Im gasgefüllten Reaktorraum von TBR lässt sich dies mit einer Druckerhöhung realisieren (Graf et al., 2014). Diese wirkt sich positiv auf den Transport der Gase in die Flüssigkeit aus, ohne den Metabolismus der Mikroorganismen negativ zu beeinträchtigen (Bär et al., 2015). Weiterhin begünstigt das damit verbesserte Nahrungsangebot eine weitere Steigerung der Mikroorganismenkonzentration (Graf et al., 2014).

Da es sich um einen biologischen Prozess handelt, stellt auch die Erhöhung der Prozesstemperatur eine weitere Möglichkeit zur Steigerung des Gas-Flüssig-Stoffaustausches dar. Denn die Steigerung der Temperatur hat eine Erhöhung der Stoffwechselgeschwindigkeit der Mikroorganismen zur Folge, welche die Konzentrationsdifferenz von Gas- und Flüssigphase erhöht und somit den Stoffaustausch beschleunigt (Benjaminsson et al., 2013). Eine Erhöhung der Temperatur führte zu signifikanten Steigerungen der Methanbildung von

Mikroorganismen bis hin zu einer Vervierfachung (Graf et al., 2014; Guiot and Cimpoia, 2012; Guneratnam et al., 2017; Luo and Angelidaki, 2012).

Eine weitere Möglichkeit zur Leistungssteigerung der BHM in TBR stellt die Anpassung der Berieselung dar. Findet eine Berieselung üblicherweise kontinuierlich mit einem konstanten Flüssigkeitsstrom statt, konnten in petrochemischen Anwendungsfeldern von TBR durch eine periodische Berieselung der Gas-Flüssig-Stoffaustausch signifikant gesteigert werden. Begründet werden die damit einhergehenden Leistungssteigerungen mit einer verbesserten Flüssigkeitsverteilung im Reaktionsraum und einer dünneren den Katalysator umgebenden Flüssigkeitsschicht (Atta et al., 2014; Liu and Mi, 2005; Liu et al., 2009). In petrochemischen Anwendungsfeldern von TBR hat sich die periodische Berieselung als Maßnahme zur Leistungssteigerung bereits mehrfach bestätigt (Banchero et al., 2004; Liu and Mi, 2005; Liu et al., 2008; Stradiotto et al., 1999; Turco et al., 2001; Urseanu et al., 2004).

In wissenschaftlichen Untersuchungen wurden die beschriebenen Maßnahmen der Druck- und Temperaturerhöhung sowie die periodische Berieselung als Möglichkeit zur Leistungssteigerung von TBR im Rahmen der BHM noch nicht untersucht.

1.5. Zielsetzung

Die Leistungsfähigkeit der biologischen Methanisierung stellt eine große Herausforderung zur Umwandlung von regenerativ erzeugtem Wasserstoff im Rahmen von Power-to-Gas Anwendungen dar. Aus diesem Grund sollen in dieser Arbeit Rieselbettreaktoren als das derzeit vielversprechendste Reaktorkonzept zur BHM hinsichtlich ihrer Leistungsfähigkeit optimiert werden.

Im ersten Schritt wurde diesbezüglich ein praxisnahes, kontinuierliches und weitestgehend automatisiertes Konzept für eine Versuchsanlage an der Universität Hohenheim entworfen und als Versuchsanlage mit drei Reaktoren im Labormaßstab realisiert. Der Fokus der anschließend durchgeführten verfahrenstechnischen Optimierung sollte auf einer Optimierung des Gas-Flüssig-Stofftransports liegen. Die Arbeit untersuchte hierbei Maßnahmen, die in bisherigen wissenschaftlichen Untersuchungen im Rahmen der BHM in TBR noch nicht näher behandelt wurden. Im Einzelnen wurden folgende Punkte untersucht:

(1) Welchen Einfluss haben steigende Betriebsdrücke auf die biologische Wasserstoffmethanisierung?

(2) Ist das Verfahren der periodischen Berieselung auch in biologischen Rieselbettreaktoren eine Möglichkeit zur Steigerung des Gas-Flüssig-Stoffaustausches?
(3) Welche Auswirkungen haben unterschiedliche Betriebstemperaturen auf die Leistungsfähigkeit des Konzepts der biologischen Wasserstoffmethanisierung in Hochdruck-Rieselbettreaktoren?

Die Ergebnisse der Untersuchung wurden in den jeweils folgenden Experimenten berücksichtigt. So ist es möglich, eine gesamte Leistungssteigerung der Optimierungsmaßnahmen zu erfassen. Weiterhin sollte der Einfluss der verschiedenen Betriebsparameter auf die Konversionsrate der Eduktgase und den Methangehalt der Produktgase untersucht werden, um die Praxistauglichkeit des Verfahrens zu beurteilen.

2. Publikation 1: Influence of operating pressure on the biological hydrogen methanation in trickle-bed reactors

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Influence of operating pressure on the biological hydrogen methanation in trickle-bed reactors

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ABSTRACT

In order to investigate the influence of pressures up to 9 bar absolute on the productivity of trickle-bed reactors for biological methanation of hydrogen and carbon dioxide, experiments were carried out in a continuously operated experimental plant with three identical reactors. The pressure increase promises a longer residence time and improved mass transfer of H_2 due to higher gas partial pressures. The study covers effects of different pressures on important parameters like gas hourly space velocity, methane formation rate, conversion rates and product gas quality. The methane content of 64.13 ± 3.81 vol-% at 1.5 bar could be increased up to 86.51 ± 0.49 vol-% by raising the pressure to 9 bar. Methane formation rates of up to 4.28 ± 0.26 $m^3\,m^{-3}\,d^{-1}$ were achieved. Thus, pressure increase could significantly improve reactor performance.

1. Introduction

Power-to-gas technology allows the conversion of electrical energy to synthetic natural gas (SNG) via electrolytic hydrogen production and its subsequent conversion together with carbon dioxide to methane and water (Clegg and Mancarella, 2015). This process is beneficial in many ways. Firstly, a significant quantity of electrical energy, produced by fluctuating renewable energy sources including wind and solar power, is able to be managed and stored (Leonzio, 2017). Another advantage is the high specific energy density of SNG (1.200 kWh m^{-3} at 200 bar). A longer storage period from minutes to months is also possible because of the existing high storage capacities in the gas grid (Kirchbacher et al., 2017). Thus, the well established gas grid can be used as a powerfull energy storage and transportation system for electric energy.

The production of SNG with the power-to-gas technology is a two-step process. First, electrical energy is transformed into oxygen (O_2) and hydrogen (H_2) by electrolysis of water. In the second step, H_2 is converted with an external CO or CO_2 source to methane (CH_4) via methanation (Götz et al., 2016). The methanation reaction can take place either in catalytic or biological reactors. Catalytic processes usually operate at temperatures between 200 and 550 °C, pressures of up to 100 bar and have a very high methane formation rate (MFR), which describes the specific methane yield, calculated as a function of the reactor volume. In order to achieve the same output, significantly larger reactor volumes are necessary for a biological reactor (Barbarossa and Vanga, 1992; Bartholomew, 2001). A typical value for evaluating the performance of a reactor is the gas hourly space velocity (GHSV). It refers to the incoming gases and according to Götz et al. (2016) the efficiency at the same MFR of biological reactors with GHSV of up to 300 h^{-1} is significantly lower than that of catalytic ones with GHSVs up to 5000 h^{-1}.

On the other hand, the catalytic processes has some disadvantages compared to the biological pathway. For example, nickel catalysts which are commonly used in the thermochemical power-to-gas technology, demand high purity standards of the feed gases (Barbarossa and Vanga, 1992; Bartholomew, 2001). Sulphur and sulphur-containing components are known catalyst poisons for the nickel catalysts used in catalytic methanation (Bartholomew, 2001; Götz et al., 2016). For many applications, the feed gas must be cleaned before injection into the methanation reactor (sulphur content ≪ 1 ppm) (Götz et al., 2016). In contrast, the biological methanation process appears to be very robust, meaning that it will not be affected by impurities of the feed gases or infections with foreign organisms (Götz et al., 2016; Liew et al., 2016; Seifert et al., 2013). Even minor disruptive components such as sulphur and oxygen were found to have no effect on the biological methanation (Bartholomew, 2001; Götz et al., 2016). Seifert et al. (2013) investigated the conversion of real gases (synthesis gas, biogas and flue gas) by *methanothermobacter marburgensis*. Methane formation

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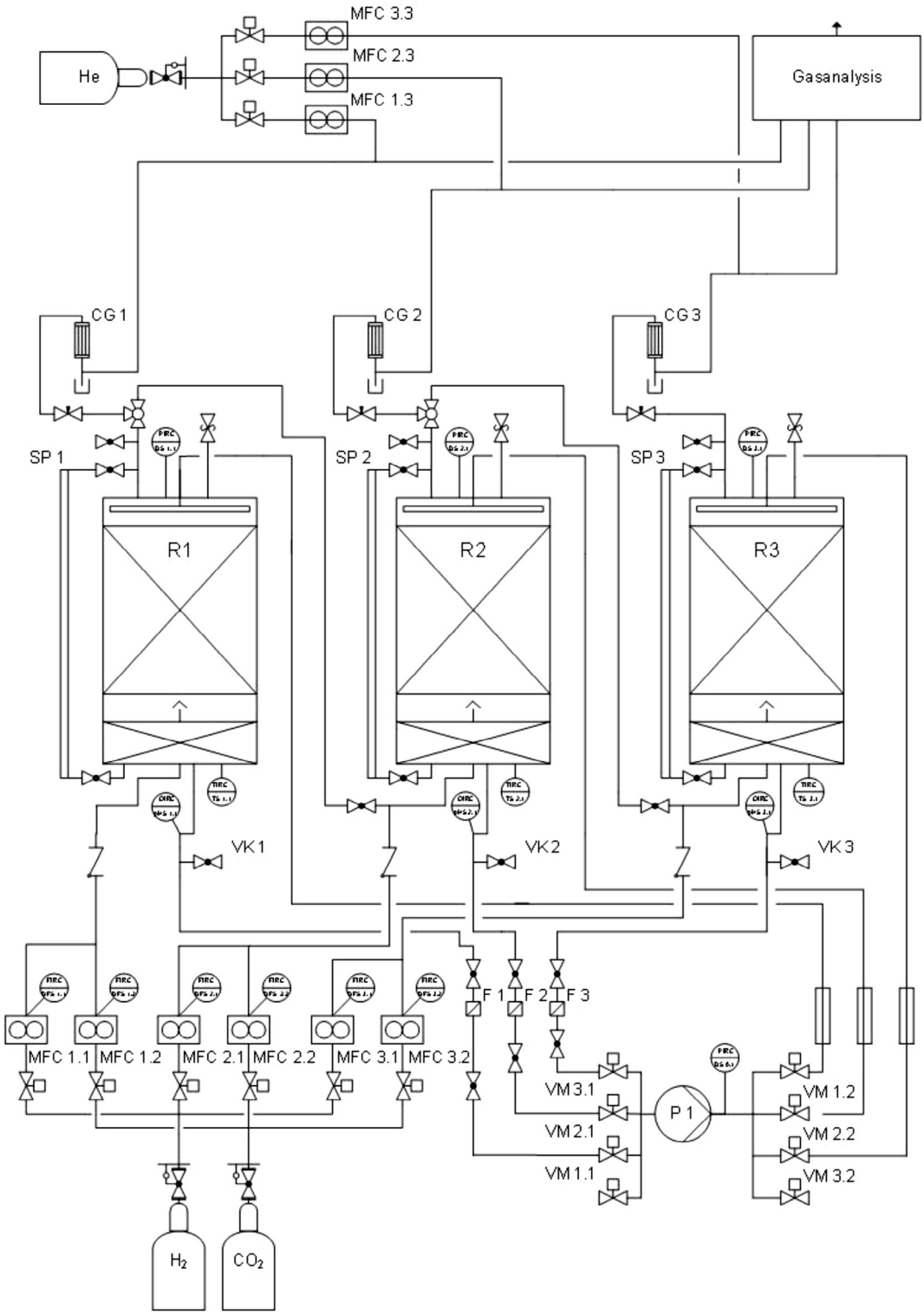

Fig. 1. Piping and instrument diagram of the test facility with the three trickle-bed reactors (R1–R3), the injection of the educt gases CO_2 and H_2 (MFC 1.1–MFC 3.2), the circulation unit of the nutrient solution (P 1, VM 1.1–VM 3.2), the gas analysis and the gas quantity measurement (MFC 1.3–MFC 3.3) with He as the tracer-gas.

was not affected by the presence of sulfur components or short chain hydrocarbons. Furthermore, some of these components can be partly removed by biological methanation (Bartholomew, 2001; Götz et al., 2016). For example, Strevett et al. (1995) investigated the reaction behavior of hydrogen-sulfite (H_2S) containing biogas and showed that even H_2S was also degraded.

Biological methanation is not only more robust against impurities than the catalytic reaction; it is also more flexible in relation to load changes. Immediate load changes from 100% to 0% were achieved as well as re-start after standstill times of up to 23 days. In contrast, a minimum load is often required for catalytic processes (Götz et al., 2016).

Besides these advantages, the biological methanation has the disadvantage, that large reactors are required due to the low volume related productivity (Götz et al., 2016). The literature indicates a limitation of the MFR due to slow transition of the feed-gases into the

liquid phase containing the microorganisms. Especially H_2 is limiting this essential mass transfer due its nearly 23 times lower solubility compared to CO_2 in water or similar liquids (Barik et al., 1988; Guiot and Cimpoia, 2012; Klasson et al., 1990; Wise et al., 1978). Therefore, the enhancement of the gas-liquid mass transfer is the key parameter to improve the volumetric productivity of the biological hydrogen methanation (BHM) (Seifert et al., 2014). Consequently, the biggest technical design challenge of a BHM reactor is to increase the microbial availability of the gaseous substrates H_2 and CO_2.

In continuously stirred tank reactors, mechanical agitation and stirring are the most common methods used to enhance the transfer of gases and other substances. However, the required amount of electrical energy is expensive (Alitalo et al., 2015). The achievable retention times of the gas in these reactors are remarkably short. After injecting the source gases into such reactors, gas bubbles are formed immediately, which rise to the surface within seconds. Due to the low surface area of these bubbles, the mass transfer and the metabolic rates are severely reduced (Burkhardt and Busch, 2013). Process optimization should therefore improve the gas-liquid mass transport and, at the same time, enable high concentrations of microorganisms (Klasson et al., 1992, 1991; Vega et al., 1990).

Burkhardt et al. (2015) used a trickle-bed reactor for biological methanation, where microorganisms are immobilized in a biofilm on the surface of a packed bed and sprinkled by a process liquid (Alitalo et al., 2015). Using gaseous substrates, trickle-bed reactors have significantly higher phase contact surfaces compared to fixed-bed reactors like anaerobic filters. In this way, mass transport is improved which increases the final productivity of the whole system (Burkhardt et al., 2015). Another advantage of this reactor type is, that nearly no additional mechanical power input is needed and the pressure drop is relatively low (Rachbauer et al., 2016). Trickle bed reactors also enable high conversion rates in biological methanation, thus leading to methane concentrations in the product gas of more than 98% even at higher hydrogen loading rates compared to other biological methanation systems (Burkhardt et al., 2015).

In principle, the mass transfer from the gaseous to the liquid phase can also be enhanced by elevating the operating pressure of the reactor (Klasson et al., 1992, 1991; Vega et al., 1990). High pressure is not expected to influence methanation. Chen et al. (2014) and Merkle et al. (2017) investigated the two-stage anaerobic digestion process in a continuous experimental plant with operating pressures of up to 9 and 50 bar, respectively. Lindeboom et al. (2011) and Merkle et al. (2017) examined the influence of operating pressures up to 100 bar on the biological conversion efficiency in batch systems. Even at these high pressures, no biological process disturbances is reported.

The aim of this study is to investigate the influence of high operating pressures on the productivity of trickle-bed reactors used for biological power-to-gas technology. For this purpose, a continuously operated and completely automated test facility was developed and built up at the University of Hohenheim. In test series, the influence of the operating pressure on gas quality, methane formation rate and retention time was explored.

2. Methods

2.1. Experimental setup

The experimental-plant was realized with three identical trickle-bed reactors, which can be operated up to a pressure of 10 bar absolute. A single reactor consisted of a 1 m long stainless steel pipe with an inner diameter of 0.15 m and a volume of 22.5 L. The structure of the plant is shown as a piping and instrumentation diagram in Fig. 1.

The reaction space of each reactor was equipped with a fixed bed and a trickle-bed to immobilize the microorganisms. The trickle-bed was in the gas-filled compartment of the reactor and had a volume of 13 L and a hight of 0.74 m. The 1.5 L fixed-bed conduced the microorganisms in the sump of the reactor in the liquid phase as a settling area. The idea of this additional fixed-bed beneath the trickle-bed was to ensure that the gaseous reactants dissolved in the circulated process liquid were converted rapidly and almost completely, too. The packing elements used in this experiment are HX09 and are from Christian Stöhr GmbH & Co. KG, Germany. They are made of HDPE recyclat, and have a diameter of 9 mm, a length of 7 mm and a surface area of 861 $m^2\,m^{-3}$. Thus, a surface of 11.193 m^2 and 1.296 m^2 is available in the trickle-bed and the fixed-bed of each lab-scale reactor, respectively.

The reactors were sealed with blank flanges, to which the reactor-peripherals as well as the sensors were attached. The operating pressure of each reactor was measured using the 261AS absolute pressure transmitter from ABB Ltd., Switzerland. Due to the use of highly volatile and corrosive hydrogen, the pressure sensors were equipped with gold-coated membranes. Temperature and pH-value were recorded using Easytemp TMR31 compact thermometers and Memosens CPS16D combined pH/redox electrodes from Endress + Hauser Messtechnik GmbH + Co.KG., Germany. Since the pH/redox combined electrodes must be removed for periodic calibration, they were installed in the reactor-periphery near VK 1, VK 2 and VK 3 in Fig. 1.

In addition to CO_2 and H_2, the methanogenetic microorganisms need a wide variety of nutrients to achieve high metabolic rates (Vintiloiu et al., 2013). These nutrients were presented with the process liquid, which was gained from the hydrolysate produced with the first stage (hydrolysis-acidification step) of a two-stage biogas process operated with maize silage (Merkle et al., 2017). It contained the necessary nutrients and trace elements that the microorganisms needed. Remaining organic acids and alcohols in the process liquid had been converted quite fast in the reactor and are not responsible for the high quantity of methane produced. Nevertheless, the gas and methane yield resulting from the degradation of the acids and alcohols was calculated and the product-gas is adjusted accordingly to Lemmer and Krümpel (2017).

In order to improve the mass transfer of the gases, the nutrient solution for the microorganisms was sprinkled over the fixed bed in countercurrent with the gases. As the solution passed through the fixed bed, the nutrients were absorbed by the attached microorganisms and accumulated in the reaction chamber in the sump. The sighting tubes SP 1, SP 2 and SP 3 (Fig. 1) outside the reactor were used to control the filling level inside the reaction chamber. Liquid filters (F 1, F 2, F 3) with a pore size of 25 µm protected the central gear pump P 1 against particles. Because a central pump (P 1) was used for circulation in all three reactors, it was possible to switch between various closed circuits by using magnetic valves VM 1.1–VM 3.2 (Bürkert Type 6240 – Servo-assisted 2/2 way piston valve). The circuits were changed every 60 s, resulting in an overall "trickling time" of 20 min per hour and reactor, which corresponds with a recirculation flow of 50 $L\,h^{-1}$ to a liquid quantity of 16.7 $L\,h^{-1}$.

Water is a by-product of the methanation of hydrogen and carbon dioxide and dilutes the nutrient solution. For this reason, half of the nutrient solution was removed and replaced with a fresh one before starting a new run.

For a constant and adjustable temperature level, the reactors were installed in individual heated water baths, which were insulated with 40 mm PU foam mats. In order to ensure a constant temperature distribution, they were heated parallel with a quad distributing adapter and an SE-26 Heating Circulator from Julabo GmbH.

The process gases were provided from gas bottles, which were obtained from the Westfalen AG. H_2 and CO_2 were used in quality 3.0. With mass flow controller (MFC) MFC 1.1–MFC 3.2 of the type 8742 from Bürkert GmbH & Co. KG, the gases could be injected into the reactors at volumes from 1.2 to 60 $L\,h^{-1}$ (H_2) and 0.3 to 15 $L\,h^{-1}$ (CO_2). The product gases were released from the reactors by a mechanical pressure control valve. Subsequently, the product gases flowed through the gas coolers CG 1, CG 2 and CG 3 for condensate removal.

2.2. Experimental procedure

Prior to the start of the experimental procedure, the reactors were filled with already overgrown packing elements taken from a working methane reactor of a two-stage anaerobic fermentation system described by Merkle et al. (2017). After a start-up period and preliminary testing phase of six months, a steady state was reached.

An increase in the operating pressure promises to improve the mass transfer and increase the availability of the reactant gases. Therefore, various pressure stages were tested at 9, 5 and 1.5 bar absolute. The pressure levels were set parallel in each reactor. For a clear representation, the results of the reactors were calculated as an arithmetic average.

The flow rates of the mass flow controllers were adjusted to a H_2/CO_2 ratio of 4, resulting in a volume flow rate of 10 L h^{-1} (H_2) and 2.5 L h^{-1} (CO_2). The operating temperature was set at 40 °C. The flow rates were adjusted at a high level in order to avoid a complete conversion of the feed gases. This was done to emphasize the differences of the investigated pressure levels.

The examined pressure levels were tested simultaneously in the three reactors. Each pressure level was kept stable for a period of 380–388 h each. During the tests, the pH values, temperature, pressure and redox potential as well as the amount of educt gases were recorded. The product gas quality was measured every 30 min by a gas chromatograph 3000l-GC from Inficon GmbH, Germany.

During the experimental phases, the process liquid was sampled directly at VK 1, VK 2 and VK 3 (Fig. 1) approximately every 80 h in order to measure the content of volatile fatty acids, the chemical oxygen demand, conductivity and salinity as well as the ammonium concentration from the untreated sample.

2.3. Analytical

According to Krümpel et al. (2016) the quality of the product-gases was analyzed by an Inficon 3000l-GC with two columns. H_2, N_2, O_2 and CH_4 were analyzed by Channel A, and the carrier gas was Argon. Channel B, with the carrier gas Helium, was used for the analysis of CO_2 and H_2S. Both channels were connected to an individual TCD-sensor. Injector temperature and sample inlet for both channels were set to 60 °C. To purge the line from the sample point to the GC, the internal pump operated for 45 s at approximately 15–30 ml/min.

To determine the amount of gas produced, a defined amount of Helium tracer gas (quality 5.0) was added by mass flow controllers 8742 from Bürkert GmbH & Co. KG MFC 1.3–MFC 3.3 (Fig. 1) to the gas stream after the reactor and the gas cooler. In the subsequent analysis by gas chromatography, the gas composition was determined. Since the proportions of the gases and the amount of tracer gas are known, the total amount of produced gas can be calculated.

The analysis of the volatile fatty acids including acetic acid, propionic acid, n- and iso-valeric acid, n- and iso-butyric acid and caproic acid of the liquid was carried out in a CP-3800 gas chromatograph from Varian Medical Systems.

The chemical oxygen demand (COD) was measured using the Hach Lange cuvette test (LCK014). Because the test has different measuring ranges (LCK 014: 1000–10,000 mg/L O2), the samples were diluted according to the measuring range. Finally, the COD value is determined after cooling in the photometer from Dr. Lange (DR 3900).

The conductivity and salinity were determined with an EC300 from VWR International GmbH by dipping the conductivity tube into the sample.

2.4. Calculations

According to Götz et al. (2016), important parameters for evaluating the reactor efficiency are the methane formation rate (MFR, Eq. (1)), the gas hourly space velocity (GHSV (Eq. (2)) and the methane content Y_{CH4} in the product gas.

$$MFR = \frac{F_{V,CH4,out} - F_{V,CH4,in}}{V_R}\left(\frac{m^3}{m^3 d}\right) \tag{1}$$

With the MFR, the specific methane yields can be calculated as a function of the reactor volume. $F_{V,\ CH4,\ out}$ and $F_{V,\ CH4,\ in}$ is the volumetric flow rate in and out of the reactor. The reactor volume V_R is the volume of the trickle-bed plus the fixed-bed and amounts to 14.5 L.

The GHSV is a typical value for evaluating the performance of a catalyst or a reactor and refers to the incoming gases.

$$GHSV = \frac{F_{V,G,in}}{V_R}(h^{-1}) \tag{2}$$

$F_{V,G,in}$ of the GHSV is the volumetric flow rate at STP of the feed gas without any inert gases.

Furthermore, the conversion rates of H_2 and CO_2 are calculated. The conversion X_i of an educt gas is defined in Eq. (3). $F_{n,\ i,\ in}$ is the incoming, and $F_{n,i,out}$ the outcoming H_2 or CO_2 in L h^{-1}.

$$X_i = \frac{F_{n,i,in} - F_{n,i,out}}{F_{n,i,in}} * 100(\%) \tag{3}$$

Due to the different pressure stages and the associated increase in the gas concentration, the retention time of the reactant gases in the reactors also changes. The retention time (RT) is calculated as a function of the reactor volume (V_R) and the volumetric flow of the incoming gases $F_{V,\ G,\ in}$.

$$RT = \frac{V_R}{F_{V,G,in}}(h) \tag{4}$$

According to Merkle et al. (2017), who also examined the effects of different operating pressures, the data was statistically analyzed using the Kruskal Wallis Test and subsequently Tukey's Test ($p < 0.05$). The statistical software "R Studio" was used for all calculations.

3. Results and discussion

3.1. Operating parameters

The operating parameters temperature, pressure and pH of the test series are shown in Fig. 2. Aggregating the data of the three independent reactors, the arithmetic average is calculated for each operating pressure. It is apparent, that the target operating parameters regarding pressure and temperature had been achieved with high accuracy and constancy. Only slight temperature differences from Reactor 1 with 40.38 ± 0.15–40.56 ± 0.29 °C to Reactor 3 with 41.02 ± 0.34–41.09 ± 0.15 °C could be observed. The measured pressure did not differ essentially from the target values. At the target level 1.5 bar, pressures from 1.43 ± 0.03 to 1.58 ± 0.02 bar, at pressure level 5 bar, values from 5.09 ± 0.04 to 5.16 ± 0.02 bar and at pressure level 9 bar, values from 9.27 ± 0.01 to 9.29 ± 0.02 bar were recorded.

Deviations of up to 15% from the target value could be detected in the flow rates of H_2− and the CO_2 mass flow controller (Table 1) due to inaccuracies of the instruments. Since the deviations in the CO_2 mass flow controller are significantly larger than in the case of the H_2 mass flow controller, no stoichiometric gas ratios could be set. By that, CO_2 was introduced slightly overstoichiometric in each pressure phase into all reactors, but with a constant ratio over the test phases.

Burkhardt et al. (2015) introduced an overstoichiometric amount of CO_2 into the trickle-bed reactors, too, with a ratio of 1:3.76 of CO_2 to H_2. Similarly, Rachbauer et al., (2016) used different ratios of 1:3.67–1:4.15. The influence of these slight shifts in the feed gas ratios will be subject to further investigations.

The increased operating pressures led to a notable drop of the pH-value in the process liquid from 6.98 ± 0.05 at 1.5 bar to 6.34 ± 0.03 at 9 bar, due to the augmented formation of carbonic acid. The low pH

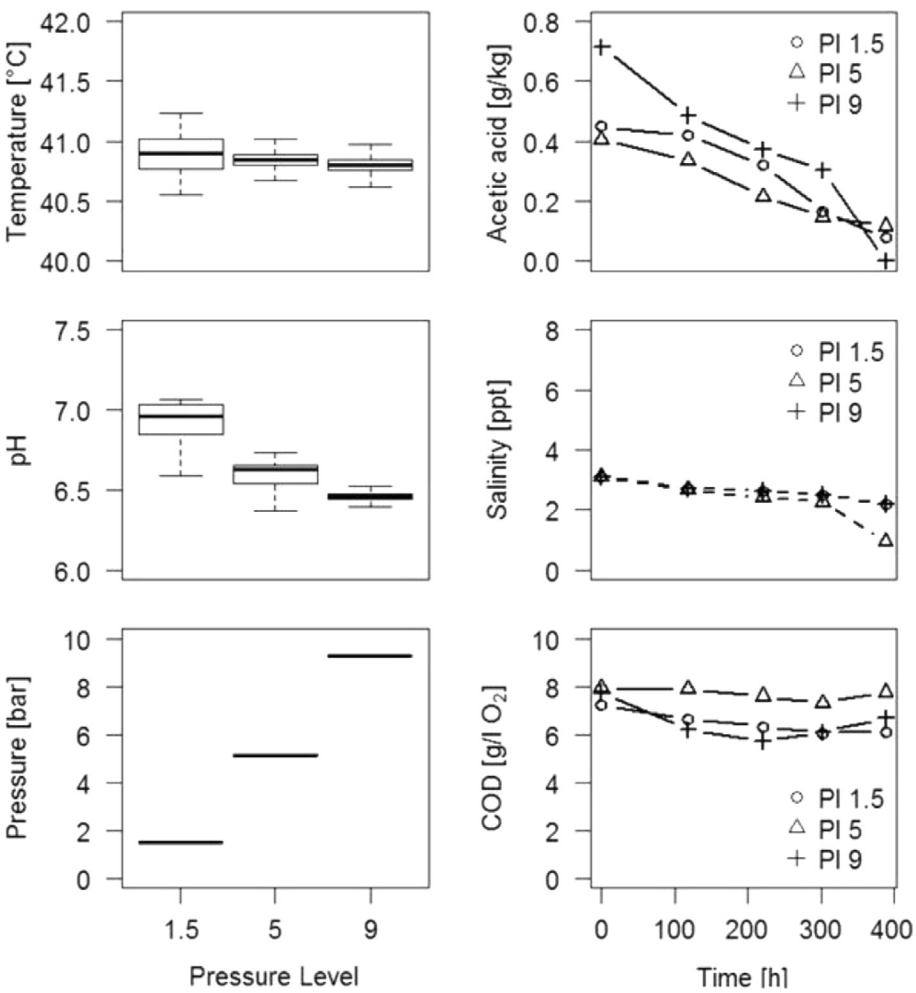

Fig. 2. Operating temperature, pH and pressure parameters as well as the content of the acetic acid, COD and salinity as analysis of the nutrient solution over the experimental period depending on the different pressure levels (Pl 1.5, Pl 5, Pl 9). The results of the three reactors were calculated as an arithmetic average.

Table 1
Overview of the most important operating parameters as well as the set flow rates and gas ratios. The results of the three reactors were calculated as an arithmetic average. The significant differences among the pressure levels are marked with different alphabets ($p < 0.05$, Tukey's test).

Pressure Level	1.5	5	9
Flow H_2 [L h^{-1}]	10.98	10.87	10.92
Flow CO_2 [L h^{-1}]	2.88	2.91	2.82
CO_2:H_2	1:3.81	1:3.74	1:3.87
MFR [m^3 CH_4 m^3 d^{-1}]	4.09 ± 0.10^a	4.28 ± 0.26^a	4.20 ± 0.45^a
GHSV [h^{-1}]	0.86 ± 0.04^a	0.86 ± 0.01^a	0.86 ± 0.01^a
Retention time [h]	1.62	5.40	9.79
Conversion H_2 [%]	93.08 ± 2.64^a	96.97 ± 1.15^{ab}	98.02 ± 1.16^b
Conversion CO_2 [%]	85.95 ± 1.23^a	88.93 ± 0.37^a	90.03 ± 0.42^a

has no observable essential influence on the performance of the methanation process. Merkle et al. (2017) also measured low pH values up to 6.53 in a stable high pressure anaerobic digestion process. In Chen et al. (2014), the pH dropped to 6.4 at a pressure of 10 bar, using a pressurized anaerobic filter. Moreover, an improvement in conversion and gas quality at this pressure and pH level is achieved.

3.2. Analysis of the process liquid

The results of the analysis of the process liquid are also shown in Fig. 2. For the purpose of improved clarity, only the acetic acid is represented, which constituted the largest share (76% and 91% at a pressure level of 9 bar and 5 bar, respectively) of the acids. At the beginning of each experimental phase, the process liquid was partially replaced by the hydrolysate, which contains 0.36 ± 0.05–0.52 ± 0.05 g kg^{-1} organic acids. It is apparent, that these acids were permanently degraded over the experimental periods. Acid accumulation was never observed at any time, thus indicating a high biological process stability. According to the acid degradation, a slight increase in pH was observed during the experiments. There was no observable influence in pressure since the liquid does not compress like the gases in the reactor.

COD and salinity parameters were investigated to study the stability of the process liquid over the experimental period. Nearly stable values were observed for COD and only slight changes in salinity (3.2 ppt at the beginning of the test at 9 bar to 0.7 ppt at the end of the test at 1.5 bar) were recorded. The salinity decreased marginal as a result of water production during BHM, thus diluting the process liquid.

In Chen et al. (2008), optimal ranges of salinity for methanogenic microorganisms of 0.35 ppt are mentioned, slight inhibitions has been detected at 3.5 ppt. The presented investigation indicted that the performance was not affected by an decrease in salinity, so that process inhibitions due to the continuous dilution of the process liquid can be excluded.

3.3. Conversion rates and gas quality

The conversion of carbon dioxide and hydrogen improved with raising the operating pressure in the conducted experiments, as shown in Table 1. The conversion of CO_2 increased from 85.95 ± 1.23 to 90.03 ± 0.42% with an increasing pressure level from 1.5 to 9 bar. However, these differences are not statistically significant. Overall, the conversion rates of CO_2 are lower than H_2. The reason for this could be

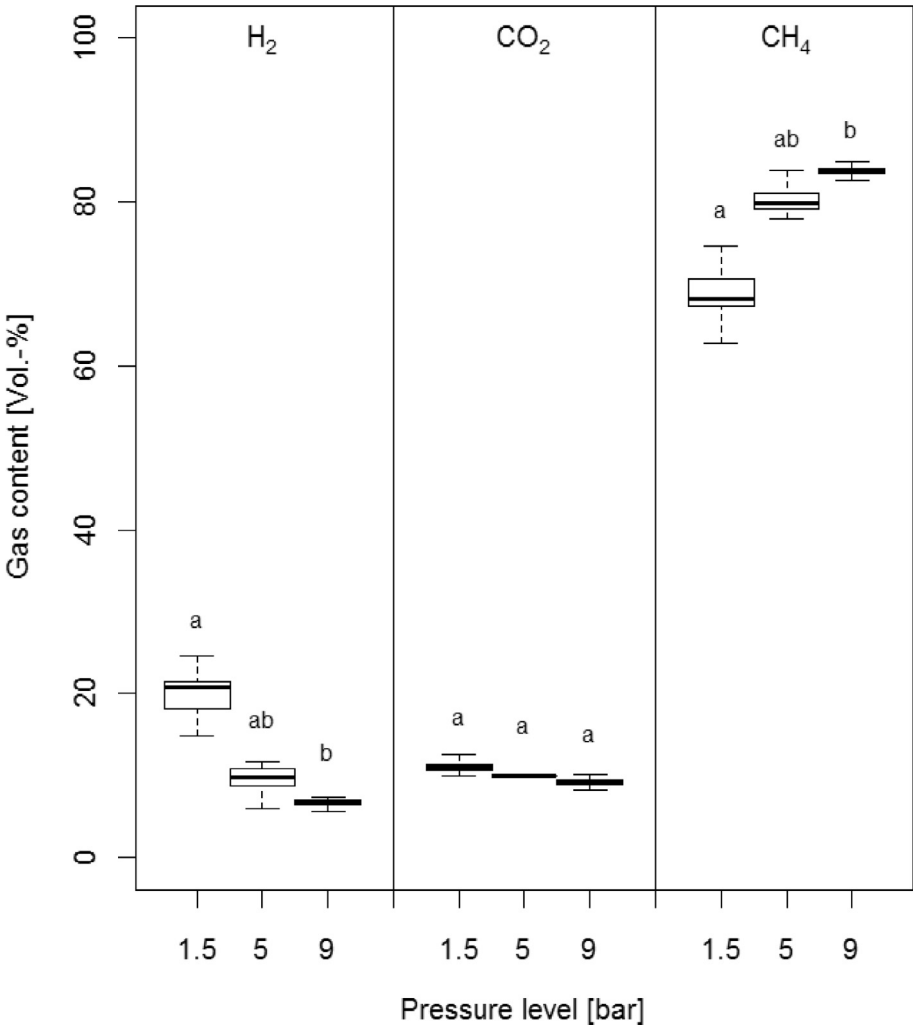

Fig. 3. The gas quality of the product gas depending on the different pressure levels. The significant differences among the pressure levels are marked with different alphabets ($p < 0.05$, Tukey's test).

the overstoichiometric ratio of CO_2. The improvement of the conversion rates of CO_2 with increasing pressure can also be due to the improved availability of H_2.

The gas composition and the conversion rates of Reactor 1 are worth being emphasized separately. Here, the highest methane concentrations and the highest conversion were achieved throughout all pressure levels. This overperformance is the main reason for the quite high standard deviation of the aggregated results, leading to statistically significant differences only between pressure level 1 and 9 for the content of H_2 and CH_4 in the product gas (Fig. 3). In addition, the differences in CO_2 conversion would be statistically significant without reactor 1. Reactor 1 has a performance up to 18% higher than Reactor 2 and 3 regarding the gas quality over all three pressure levels in the test period. However, the improvement of the gas quality as a result of the increased operating pressure was observed in all three reactors and pressure levels. Although it was not possible to obtain quantitative evidence, the overperformance of the first reactor may have resulted from an improved growth of the microorganisms on the packing material of Reactor 1, thus leading to higher concentrations of microorganisms. For a more detailed investigation, the reactors will be opened at the end of all experiments.

The influence of the operating pressure is reflected in the product gas composition, too, as shown in Fig. 3. At a pressure of 1.5 bar, the average hydrogen content was 20.05 ± 6.78 vol-%, compared to a minimum of 6.71 ± 2.29 vol-% at the highest pressure 9.28 bar. Since CO_2 was sub-stoichiometrically injected into the reactors, high conversion rates were achieved, so that the content of CO_2 in the product gas did not vary significantly between the different experimental phases.

According to the decreased content of H_2 and CO_2 and the higher conversion rates with increased pressure, the content of methane in the product gas rises with increasing operating pressure. While the methane content at the pressure level 1.5 bar only amounted to 64.13 ± 3.81 vol-%, the mean values reached 86.51 ± 0.49 vol-% at the pressure level of 9 bar.

As shown in Burkhardt et al. (2015) and Rachbauer et al. (2016), even higher methane contents in the product gas of up to 98% can be reached with trickle-bed reactors. These values were confirmed in preliminary tests with the described reactors of this study. In order to emphasize the influence of the operating pressure, the experiments were conducted at high flow rates to ensure incomplete conversion processes throughout all experimental phases, thus leading to maximum methane contents of up to 86.51 ± 0.49 vol-% in the product gas.

In general, higher methane concentrations are reported for trickle-bed reactors compared to other reactor configurations. Alitalo et al. (2015) could reach in a fixed-bed system methane contents in the product gas of > 90 vol-%. In CSTR reactors, maximum CH_4 concentrations of 85 vol-% were achieved (Seifert et al., 2014).

3.4. Performance parameters and retention time

According to the constant input flow rates, the average methane formation rates (MFR) only varied between 4.09 ± 0.10 and

4.29 ± 0.26 m^3 CH_4 m^{-3} d^{-1}, depending on the process phase, although significant differences in the conversion rates were detected (Table 1). From pressure levels of 1.5–5, the MFR changes from 4.09 ± 0.10 to 4.28 ± 0.26 m^3 CH_4 m^{-3} d^{-1}. But in pressure level 9, the MFR changes to 4.20 ± 0.45 m^3 CH_4 m^{-3} d^{-1}, thus indicating that the improved conversion rates did not lead to a significant change of the MFR. A reason for this could be the reduction in the volume by a factor of 5 at the process of biological methanation, resulting in very similar product gas amounts throughout the experiment. Burkhardt et al. (2015) achieved MFRs of 1.49 m^3 CH_4 m^{-3} d^{-1} with a similar experimental setup. However, in a pressureless state and with a much higher methane content of up to 98 vol-%.

Compared to other studies, the investigated set-up was run at quite low MFRs. Alitalo et al. (2015) described MFRs of up to 6.35 m^3 CH_4 m^{-3} d^{-1} in fixed bed reactors, but with retention times of 144 h. In biological methanation, the highest MFRs are recorded for CSTR-systems. Seifert et al. (2014) reached 137 m^3 CH_4 m^{-3} d^{-1} with a methane content of 85 vol-% at a process temperature of 65 °C and stirrer speeds of 1500 rounds per minute.

In contrast to the MFR, the GHSV is related to the amount of gases, injected into the reactor. Since the flow rates were almost identical over the different pressure levels, the GHSV was nearly identical for all pressure levels with 0.86 h^{-1} showing no statistical differences.

During the microbial conversion of CO_2 and H_2 to CH_4 and H_2O, the volume of the feed-gases is nearly five times higher than the volume of the product gases. However, calculating the retention time of the gaseous substrates in the digesters according to Eq. (4), where the reduced volume was neglected, results in an underestimation of the real retention time of the gases in the reactor. In contrast to the GHSV, the retention time of the gases in the reactor increased.

As shown in Table 1, the retention time increased proportionately with the operating pressure from 1.62 h (1.5 bar) to 9.79 h (9 bar). With regards to the increase in gas quality, the question arises whether the improved conversion rate is caused by the enlarged retention time of the gases in the reactor or by the augmented mass transfer due to the higher operating pressure. This interesting topic will be subject to further investigations.

Overall, the experiments of this study show, that the biological power-to-gas technology is a stable and reliable process, using the proofed reactor concept. These findings are in line with the reports of other studies (Burkhardt et al., 2015; Rachbauer et al., 2016). Based on the results presented and the necessity for feeding the compressed gas into the gas grid, process efficiency can be improved by elevating operating pressures.

4. Conclusion and outlook

The present study shows that by raising operating pressures, higher CO_2 and H_2 conversion rates and higher methane contents in the biological methanation by means of trickle-bed reactors can be achieved. The tests of three different pressure stages 1.5, 5 and 9 bar showed an improvement in the gas quality. The methane content of at least 64.13 ± 3.81 vol-% at a pressure level of 1.5 bar could be increased by up to 86.51 ± 0.49 vol-% at 9 bar with MFR in the range of 4.09 ± 0.10–4.28 ± 0.26 m^3 CH_4 m^{-3} d^{-1}. However, it should be considered that with increasing pressure, higher safety precautions are required, especially regarding full scale applications. Additionally it should be clarified, whether a pressure increase for gas quality enhancement justifies the necessary technical and economical effort.

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3. Publikation 2: Performance enhancement of biological methanation with trickle bed reactors by liquid flow modulation

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Performance enhancement of biological methanation with trickle bed reactors by liquid flow modulation

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Abstract

Experiments were carried out to investigate the influence of liquid flow modulation of trickle bed reactors (TBR) on biological hydrogen methanation (BHM). The modulation promises to improve the gas-liquid mass transfer and has already been demonstrated in trickle bed reactors of other fields of application. Therefore, the influence of four different circulation intervals with pauses from two to 1,440 min was investigated in TBR for BHM. The results showed that as pause intervals without sprinkling became longer, the methane content increased from 88.61 ± 1.58 vol-% at a circulation interval of 2 min to up to 97.19 ± 0.46 vol-% at a circulation interval of 1,440 min. The analysis of the process liquid indicated a stable biological process at any trial phase. This study demonstrated that the performance of TBR on BHM can be significantly improved by liquid flow modulation, thus significantly reducing operating costs.

KEYWORDS

biological methanation, hydrogen, liquid flow modulation, power-to-gas, renewable energy, trickle-bed-reactor

1 | INTRODUCTION

The volumetric productivity of biological hydrogen methanation (BHM) can be improved by enhancing the gas-liquid mass transfer (Seifert, Rittmann, & Herwig, 2014). Thus, over the past few years, trickle bed reactors (TBRs) have been investigated in order to improve BHM performance (Burkhardt, Koschack, & Busch, 2015; Strübing, Huber, Lebuhn, Drewes, & Koch, 2017; Ullrich et al., 2018).

Trickle bed reactor is one of the classical multiphase packed bed reactor configurations with extensive applications in petroleum industries including hydrocracking, hydrotreating and alkylation. TBRs are also commercially utilized in chemical industries for hydrogenation of aldehydes and reactive animation (Atta, Roy, Larachi, Deo, & Nigam, 2014). In biotechnology, these reactor systems are often used for enabling biological conversion of gaseous substrates under defined conditions, which are performed for multiple purposes. They are characterized by an efficient control of pH, temperature, moisture content and pressure (Ullrich et al., 2018). In biotechnological TBR, also known as biotrickling filters, the source gases pass through a biofilm immobilized on a packed bed, which is normally continuously irrigated with a nutrient solution (Quijano, Miguel-Romera, Bonilla-Morte, & Figueroa-Gonzalez, 2017). The reaction gases are initially absorbed in the trickling aqueous solution and subsequently converted in the fixed biofilm. The packed bed provides a large specific surface area and thus a large phase contact area, which enables high mass transfer rates (Burkhardt et al., 2015). Therefore, improved mass transport is achieved which increases the final productivity of the entire system. In contrast to several other reactor systems such as continuous stirred tank reactors (CSTR), fixed bed or bubble column reactors, the gaseous phase surrounds the packing

material and the microbial community colonizing them completely. This allows for independent control of the superficial gas velocity (Strübing et al., 2017). However, the presence of a continuous water layer over the biofilm often entails a limited abatement performance for hydrophobic gases as a result of their poor gas-liquid mass transport (Quijano et al., 2017).

Another possibility to enhance the mass transfer from the gaseous to the liquid phase in such systems is to increase the operating pressure of the reactor (Klasson et al., 1990; Vega, Clausen, & Gaddy, 1990). According to Henry`s law, the amount of a dissolved gas in the liquid phase is proportional to its partial pressure in the gas phase. Pressurised TBRs were investigated in Ullrich et al. (2018), where the methane content of the TBR was increased by 34 vol-% with an increase in pressure from one to nine bar absolute.

Many studies have investigated the operating pressure of TBRs in order to increase the gas-liquid mass transfer, thus achieving higher performance. As with the BHM, high operating pressures are commonly used for this purpose (Wongkia, Suriye, Nonkhamwong, & Praserthdam, 2013).

However, recent studies are focusing on the periodic operation of TBRs (Liu & Mi, 2005). In general, TBRs operate under steady-state mode with constant feeding rates under a constant and often a low liquid flow rate (5–10 L $m^{-3}_{reactor\ volume}$ min^{-1}) (Quijano et al., 2017). Urseanu, Boelhouwer, Bosman, and Schroijen (2004) conclude that there is a poor interaction between the gas and the liquid. Many studies have successfully demonstrated that periodic operation improves TBR catalytic performance for many reactions (Banchero, Manna, Sicardi, & Ferri, 2004; Stradiotto, Hudgins, & Silveston, 1999; Turco et al., 2001; Urseanu et al., 2004).

A common approach is a periodic liquid feed modulation with a continuous gas phase (Wongkia et al., 2013). In this case, a distinction is made between two different periodic operation types, commonly known as flow modulation strategies. In the mode of operation *base-pulse*, the liquid flow rate switches between a low level (*base*) and a high level (*pulse*). When the base liquid flow rate is set to zero, it is called an *on-off* mode. Using such an *on-off* mode, Liu and Mi (2005) were able to improve conversion and selectivity of hydrogenation of 2-ethylanthraquinone significantly compared with those under steady-state. Wongkia et al. (2013) investigated styrene hydrogenation in a TBR. Using periodic operation of the liquid, a maximum improvement of styrene conversion of 18% was observed.

Ayude, Cassanello, Martínez, and Haure (2005) also described the potential to enhance performance through better supply of reactants to the catalyst and improved fluid dynamics and catalyst wetting. Atta et al. (2014) assumed that periodic operation in a TBR would considerably enhance the mass transfer rate of the gaseous reactant, thus resulting in a higher solubility of the gaseous phase within the liquid. He also states that periodic liquid flow modulation can minimize liquid maldistribution in the TBR, which strongly affects reactor performance. Liu et al. (2009) demonstrated this fact while analysing the transient behaviours of the liquid holdup of an air kerosene system in a periodically operated TBR. Modulation of the liquid flow minimizes the possibilities of hot spot formation. An improved liquid distribution over the catalyst surface using periodic operation was mentioned by Liu and Mi (2005). Catalyst wettings are significantly higher for the periodic operation. In some operating states, a further advantage mentioned is a decrease in liquid film thickness due to drainage in the OFF phase of the on-off mode (Liu & Mi, 2005).

It is widely accepted that unsteady-state operation is becoming a promising intensified technological process and will be implemented on industrial TBRs in the future (Liu, Zhang, Wang, Zhang, & Mi, 2008).

However, the advantages of improved gas–liquid mass transfer by periodic circulation have not yet been investigated for biological TBR. In addition, to improve the conversion, the periodic operation can also reduce the energy consumption of the process. In this biological system, however, it is important to note that the process fluid carries not only the reaction gases, but also the nutrients for the microorganisms. Therefore, a liquid flow modulation should not affect the nutrient supply.

In order to specify this more precisely, various liquid flow modulation strategies were investigated in this study. The aim was to increase the conversion and improve the overall performance of BHM in trickle bed reactors, while maintaining a stable biological process by adequate nutrient supply. For this purpose, a continuous and automated experimental plant was developed and constructed at the University of Hohenheim. The evaluation of the system performance is based on important parameters like gas quality and methane formation rate.

2 | MATERIALS AND METHODS

2.1 | Experimental setup

As described in detail in Ullrich et al. (2018), the experimental plant was designed with three identical TBRs. The nutrient solution for the microorganisms was sprinkled over the trickle bed in countercurrent with the source gases carbon dioxide (CO_2) and hydrogen (H_2). The structure of the plant is shown as a piping and instrumentation diagram in Figure 1.

The reaction volume for the immobilization of the microorganisms amounts to a total of 14.5 L and consists

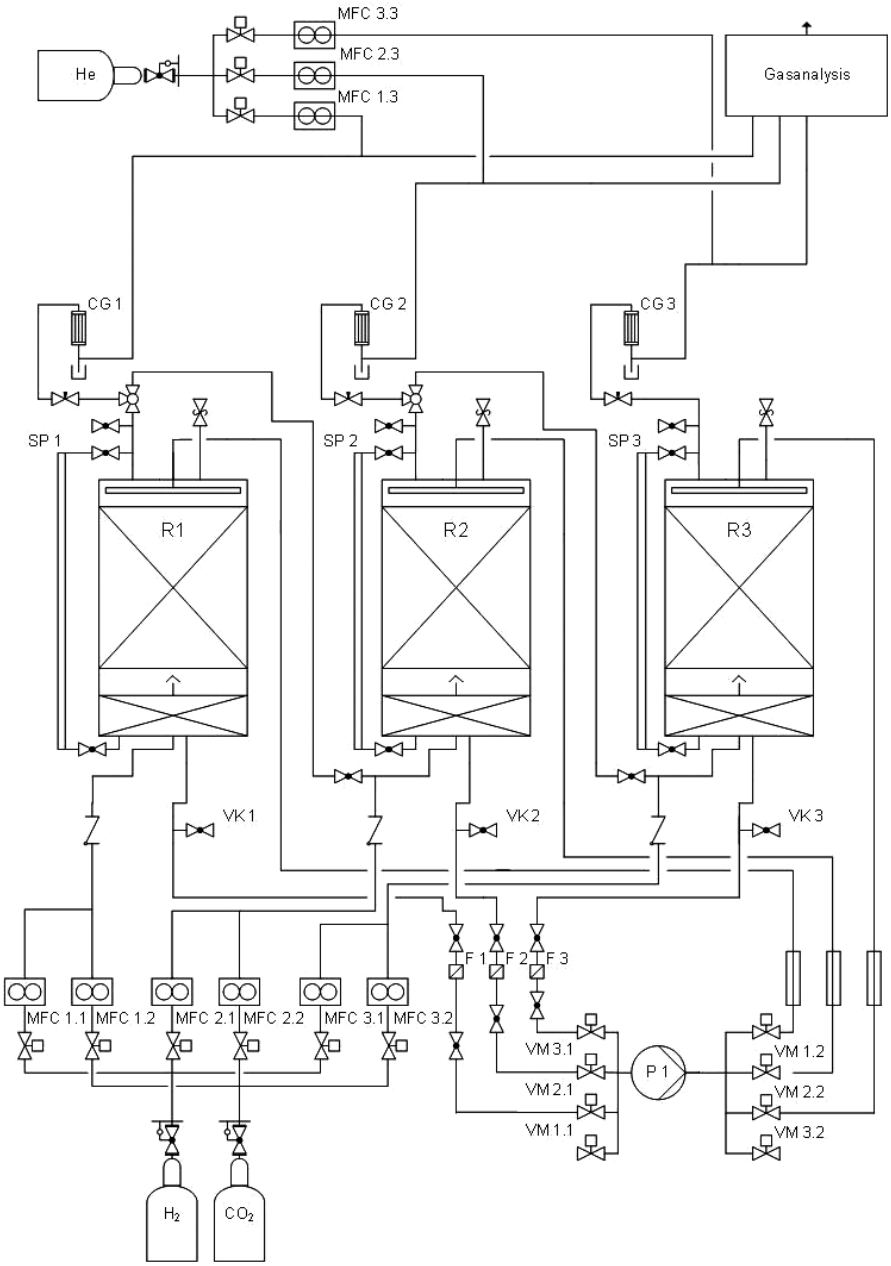

FIGURE 1 Piping and instrument diagram of the test facility with the three trickle-bed reactors (R1–R3), the injection of the educt gases CO_2 and H_2 (MFC 1.1–MFC 3.2), the circulation unit of the nutrient solution (P 1, VM 1.1–VM 3.2), the gas analysis and the gas quantity measurement (MFC 1.3–MFC 3.3) with He as the tracer gas. The figure also shows the gas coolers (CG 1-3), the sighting pipes (SP 1-3) and the sampling valves (VK 1-3)

of a 13 L trickle bed in the gas phase, as well as a 1.5 L fixed bed in the liquid phase in the sump of the reactors. The remaining volume within the reactors was required for sprinkler and gas entry, which was placed between the fixed bed and the trickle bed.

The trickle bed had a height of 0.74 m with a total surface area of 11.193 m². The packing bed was made of filling elements HX09 from Christian Stöhr GmbH & Co. KG, Germany. The elements are made of high density polyethylene with a diameter of 9 mm and a length of 7 mm. They offer a specific area of 861 m²/m³. Together with the fixed bed in the sump, a surface area of 12.489 m² was available for colonization by microorganisms.

The pressure sensors 261AS from ABB Ltd., Switzerland were mounted on the top blind flange of the reactors. They have a measuring range between 0 and 10 bar absolute with a basic accuracy of 0.1% and are equipped with a gold-coated membrane for protection against aggressive media. The temperature sensor Easytemp TMR31 from Endress + Hauser Messtechnik GmbH + Co.KG., Germany, was attached to the bottom blind flange. This measured the temperature between the sump and the trickle bed of the reactors. The combined pH/redox electrodes Memosens CPS16D from the same manufacturer were installed in the reactor periphery.

The nutrients were supplied with the circulated process liquid. For this purpose, the product liquid of a continuous

two-stage anaerobic digestion experimental plant from Merkle et al. (2017) was used. According to Vintiloiu, Lemmer, Oechsner, and Jungbluth (2012) and Vintiloiu et al. (2013), this predigested process liquid is advantageous because it contains all essential nutrients for the methanogenic microorganisms and nearly no energy rich substances, such as acids and alcohols, that could affect the methane production of the reactors (Table 1).

A by-product of the methanation of hydrogen and carbon dioxide is water, which dilutes the nutrient solution over time. Thus, half of the process liquid needed to be replaced before starting a new modulation. For this purpose, the liquid of the filter was drained during the OFF time, which was half of the total liquid. The shut-off valves upstream and downstream of the filter allowed the liquid to be changed without pressure loss.

2.2 | Experimental procedure

The pilot plant had already been used for investigating different operating pressures prior to this study (Ullrich et al., 2018). Thus, the trickle bed was already covered with a biofilm at the beginning of the experiments, so that no separate start-up period was required.

To investigate the influence of the trickling interval on the gas–liquid mass transfer and thus the conversion of H_2 and CO_2 to CH_4, a method involving liquid flow modulation, commonly performed for trickle bed reactors in petrochemical applications, should be used (Banchero et al., 2004; Stradiotto et al., 1999; Turco et al., 2001; Urseanu et al., 2004). Various modulation strategies were examined for this purpose. Within a modulation, the amount and duration (ON) of the circulating liquid can be varied, as well as the intervals (OFF) between them. For the tests carried out in this study, the ON time (1 min) of the circulation and liquid flow rate (4.1 L hr^{-1} $L_{reaction\ volume}{}^{-1}$) were kept constant for all modulations. Only the OFF times were varied.

At the beginning of the trial phase, steady-state liquid flow modulation with an ON time of 1 min and an OFF time of 2 min was used. As only one common pump is available for the circulation of the three reactors, this modulation represents the shortest possible interval. Furthermore, modulations with longer OFF times of 240, 480 and 1,440 min were investigated. The tests were carried out in the order 2—480—1440—240 min. This results in an effective "trickling time" of 8 hr/day and reactor in the first trial period which is reduced to 1 min/day and reactor in the last phase. Table 2 gives an overview of the implemented modulations and their specifications.

The modulations were carried out simultaneously in the three reactors for a duration between 130 and 144 hr each. For a clear representation, the results of the reactors were calculated as an arithmetic average.

The flowrates of the mass flow controllers were adjusted to 12 L/hr for H_2 and 3 L/hr for CO_2 for each reactor to achieve a stochiometric ratio. That means that according to the reaction equation (Equation 5), there must be a ratio of H_2 to CO_2 of 4:1 to form one molecule of methane and two molecules of liquid water. Due to the low inaccuracies of the H_2- and CO_2- mass flow controllers, the real quantities fed in were calculated using the results of the gas analysis and the He - tracer gas. Over the entire duration of the experiment, the operating temperature was set to 40°C and the pressure to 5 bar absolute.

The process liquid was sampled at the start and the end of each modulation. The content of volatile fatty acids and total alkalinity, the chemical oxygen demand, conductivity and salinity, as well as the ammonium concentration were measured from the untreated sample.

2.3 | Analytical

As described in Ullrich et al. (2018), the quality of the product-gases was analysed by a 3,000 L-Gaschromatograph from Inficon GmbH, Germany. The product gas amount was determined by injecting a defined quantity of tracer gas (Helium) to the gas stream. By analysing the gas proportions by gas chromatography, the amount of the product gas was calculated.

The volatile fatty acids in the liquid were analysed by a 2010plus gas chromatograph with AOC-20i Autoinjector from Shimadzu, Japan. The chemical oxygen demand (COD) was measured using the Hach Lange cuvette test

TABLE 1 Nutrient composition of the process liquid

Cu	Ni	Zn	Fe	B	Co	Mn	Mo	Se	Al	W	As
mg/kg DM											
4.8	13.0	156.0	1,768.4	29.7	2.5	303.5	3.9	1.2	147.9	0.9	1.1
Cd	**Pb**	**Sn**	**V**	**Cr**	**Sb**	**P**	**K**	**Mg**	**Na**	**Ca**	**S**
mg/kg DM						% of DM					
0.1	0.9	0.3	0.5	1.8	0.3	1.3	12.7	0.7	0.5	1.5	0.5

TABLE 2 The different modulation strategies with the set parameters examined in this study

Modulation strategy	2	240	480	1,440
Liquid flow [L hr^{-1} $L_{reaction\ volume}{}^{-1}$]	4.1	4.1	4.1	4.1
Circulation time: ON [min]	1	1	1	1
No circulation: OFF [min]	2	240	480	1,440

(LCK014). By inserting the conductivity tube from an EC300 from VWR International GmbH into the liquid sample, taken from the filter of the reactor during the OFF time at the beginning and end of a test phase, the conductivity and salinity were determined. The ratio of volatile fatty acids and total inorganic carbon (VFA/TIC) was analysed using an automatic titrator 785 DMP Titrino from Metrohm AG, Switzerland.

2.4 | Calculations

A parameter for evaluating the reactor efficiency is the methane formation rate (MFR, Equation 1). It describes the methane yield as a function of the produced methane and the reactor volume. $F_{V,CH4,out}$ and $F_{V,CH4,in}$ is the volumetric flow rate in and out of the reactor (Götz et al., 2016). In this study, the reaction volume V_R consists of the trickle-bed plus the fixed-bed zone and amounts to 14.5 L.

$$\mathrm{MFR} = \frac{F_{\mathrm{V,CH4,out}} - F_{\mathrm{V,CH4,in}}}{V_R}\left(\frac{m^3}{m^3 d}\right) \tag{1}$$

The gas hourly space velocity (GHSV) is another important parameter. It is a value for evaluating the incoming gases of a catalyst or a reactor. $F_{V,G,in}$ of the GHSV is the volumetric flow rate at STP of the source gas without taking any inert gases into account (Götz et al., 2016).

$$\mathrm{GHSV} = \frac{F_{\mathrm{V,G,in}}}{V_R}\left(\mathrm{hr}^{-1}\right) \tag{2}$$

Furthermore, the conversion X_i of both feed gases is defined in Equation 3. $F_{n,i,in}$ is the incoming, and $F_{n,i,out}$ is the outcoming H_2 or CO_2 in L/hr.

$$X_i = \frac{F_{\mathrm{n,i,in}} - F_{\mathrm{n,i,out}}}{F_{\mathrm{n,i,in}}} \times 100\,(\%) \tag{3}$$

The retention time (RT) describes the time the gases remain in the reactor. It was calculated as a function of the reaction volume (V_R) and the volumetric flow of the incoming gases $F_{V,G,in}$.

$$\mathrm{RT} = \frac{V_R}{F_{\mathrm{V,G,in}}}\,(\mathrm{hr}) \tag{4}$$

The statistical software "R Studio" was used for all calculations, as well as for the statistical analysis with the Kruskal–Wallis test and subsequently Tukey's test ($p < 0.05$).

3 | RESULTS AND DISCUSSION

3.1 | Operating parameters

The adjusted pressure was achieved with high constancy over the four modulations in all three reactors. After aggregating the data of the three reactors, the arithmetic average was calculated for each modulation. An overview of the results is presented in Table 3.

The operating pressure of the modulation experiments was set at 5 bar absolute to avoid a possible impairment of the results by low pH values. As shown in Ullrich et al. (2018), the pH value dropped to 6.34 ± 0.03 when the pressure was increased to 9 bar due to the improved solubility of the injected CO_2.

However, the concern about low pH levels was unfounded. As indicated in Table 2, the pH values varied between 7.31 ± 0.22 at modulation 2 and 7.44 ± 0.21 at modulation 480. A slight decrease in pH was observed with proceeding test duration, which can be explained by the dilution of the process liquid and thus a decrease of the buffer capacity. A similar behaviour was also observed in Strübing et al. (2017), especially with high gas feed rates and associated high metabolic water production. Overall, the pH value was demonstrated to be very stable in this study and varied only slightly within the optimal range of 6.5 and 8.5 for methanogenic microorganisms (Bassani, Kougias, Treu, & Angelidaki, 2015).

The aimed mesophilic process temperature of 40°C was achieved with a high accuracy and was kept very constant —both between the experiments and the different reactors. A slight increase in temperature can be seen with progressive OFF times. For example, the average temperature for modulation 2 was 40.97 ± 0.18°C, which rose to 41.57 ± 0.10°C for modulation 1,440. Methanation follows the exothermic Sabatier reaction (Equation 5).

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O\ \Delta H^0 = -165\,\mathrm{kJ/mol} \tag{5}$$

Higher conversion rates at long OFF times may have led to a higher release of reaction energy, thus resulting in higher digester temperatures. Furthermore, the heat can no longer be dissipated as efficiently due to the long OFF time.

The gas flows were adjusted to an overstoichiometric ratio of CO_2. In other studies on biological methanation in TBR, the advantages of overstoichiometric ratios were mentioned. In Burkhardt et al. (2015), a complete conversion was achieved with a CO_2: H_2 ratio of 1:3.76 and in Strübing et al. (2017), ratios of 1:3.75–1:4 were used. Due

TABLE 3 Overview of the operating parameters, flow rates and conversion. The results of the three reactors were calculated as an arithmetic average. The significant differences among the modulation strategies are marked with different alphabets ($p < 0.05$, Tukey's test)

Modulation [min]	2	240	480	1,440
Temperature [°C]	40.97 ± 0.28[a]	41.46 ± 0.14[ab]	41.53 ± 0.14[ab]	41.57 ± 0.10[b]
Pressure [bar]	5.17 ± 0.03[a]	5.18 ± 0.03[a]	5.18 ± 0.02[a]	5.17 ± 0.03[a]
pH	7.31 ± 0.22[a]	7.44 ± 0.21[a]	7.40 ± 0.16[a]	7.38 ± 0.16[a]
Flow H_2 [L/hr]	13.33	13.52	13.59	13.64
Flow CO_2 [L/hr]	3.42	3.45	3.46	3.47
CO_2:H_2	1:3.89	1:3.92	1:3.93	1:3.93
MFR [m^3 m^3 day^{-1}]	5.36 ± 0.12[a]	5.61 ± 0.09[b]	5.61 ± 0.10[b]	5.62 ± 0.10[b]
GHSV [hr^{-1}]	1.16 ± 0.02[a]	1.16 ± 0.02[a]	1.15 ± 0.02[a]	1.15 ± 0.02[a]
Retention time [hr]	4.48	4.47	4.47	4.48
Conversion H_2 [%]	98.33 ± 0.01[a]	99.41 ± 0.00[b]	99.59 ± 0.00[b]	99.67 ± 0.00[b]
Conversion CO_2 [%]	94.47 ± 0.00[a]	98.01 ± 0.00[b]	98.49 ± 0.00[b]	98.62 ± 0.00[b]

to deviations of the mass flow controllers, the ratios were not completely identical between the experiments. There were fluctuations in the range from 1:3.89 to 1:3.93 between modulation 1,440 and 240. By that, the source gas ratio was kept quite stable compared to recently published experimental set-ups (Strübing et al., 2017).

3.2 | Analysis of the process liquid

The process liquid was sampled at the beginning and the end of an experiment. The VFA/TIC fluctuated in a range of 0.19 ± 0.04 for modulation 480 and 0.27 ± 0.03 for modulation 240. The values were in a small range, and overall the VFA/TIC indicates a continuous stable methanation process (Merkle et al., 2017).

As already suspected during the discussion of the moderately declining pH values, a slightly decreasing TIC was measured, which indicates a dilution of the process liquid by metabolic water production. The largest reduction was observed in modulation 240. Here, the TIC decreased from 2,084 ± 85 mg $CaCO_3$ L^{-1} at the beginning of the trial period to 1,795 ± 119 mg $CaCO_3$ L^{-1} at the end of the same period.

At the beginning of modulation 480, a low acid concentration was measured in a single reactor. An acetic acid concentration of 0.12 ± 0.07 g/kg and a propionic acid concentration of 0.03 ± 0.002 g/kg was determined. These small acid concentrations were metabolized till the end of the trial period. An influence on the conversion or the product gas quality was not determined in this case. Further acid concentrations could not be measured in any trial period.

The salinity of the process liquid can also be regarded as stable, but at a high level. The lowest values were observed at 2.57 ± 0.06 ppt for modulation 2, and the highest at modulation 240 with 3.03 ± 0.15 ppt. Optimal areas for methanogenic microorganisms are in the range of 0.35–3.5 ppt (Chen, Cheng, & Creamer, 2008). Slightly larger fluctuations were observed in the COD. At modulation 240, the COD was 3.86 ± 0.23 g L^{-1} O_2^{-1}, in modulation 480, values of 5.23 ± 0.35 g L^{-1} O_2^{-1} were detected. Overall, the data indicate high biological process stability throughout all experimental phases.

3.3 | Performance parameters

The conversion rates of H_2 and CO_2 significantly increased with the modulations and longer OFF times. The conversion of H_2 was raised from 98.33 ± 0.01 to 99.67 ± 0.00% by extending the OFF time from 2 to 1,440 min. The conversion of CO_2 was also significantly improved and increased in the same modulation to 98.62 ± 0.00%. Although there was a slight increase between the modulations 240, 480 and 1,440, they are not statistically significant.

The increasing conversion of H_2 and CO_2 with an increase in OFF times is also reflected in the gas qualities. The highest gas quality was achieved in modulation 1,440. Compared to modulation 2, the content of H_2 in the product gas was reduced from 5.97 ± 1.69 vol-% to 1.29 ± 1.23 vol-% (Figure 2). The values of CO_2 were also significantly reduced from 5.18 ± 0.29 to 1.36 ± 0.32 vol-%.

During the entire duration of the experiment, the product gas contained a noticeably high amount of CO_2, reaching a level close to that of H_2. For a complete conversion of CO_2, however, a four times higher amount of H_2 is required according to Equation 5. Due to these so-called overstoichiometric injection of CO_2, higher conversion rates of hydrogen compared to the carbon source were

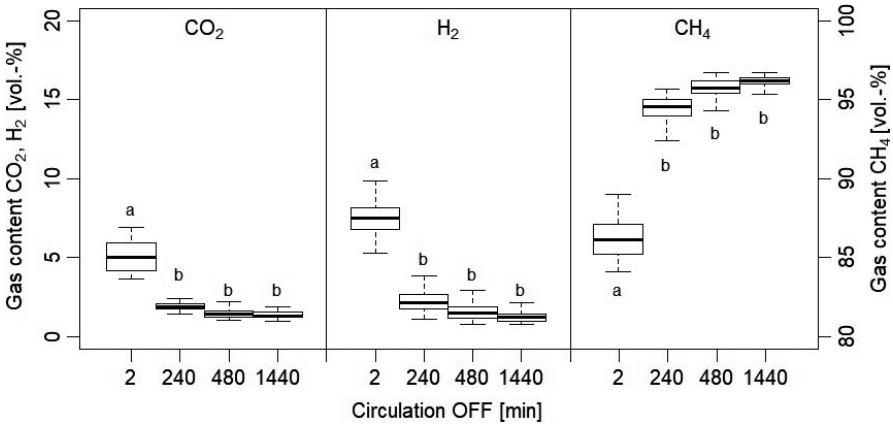

FIGURE 2 Gas quality of the product gas depending on the different modulation strategies. The significant differences among the modulation strategies are marked with different alphabets ($p < 0.05$, Tukey's test)

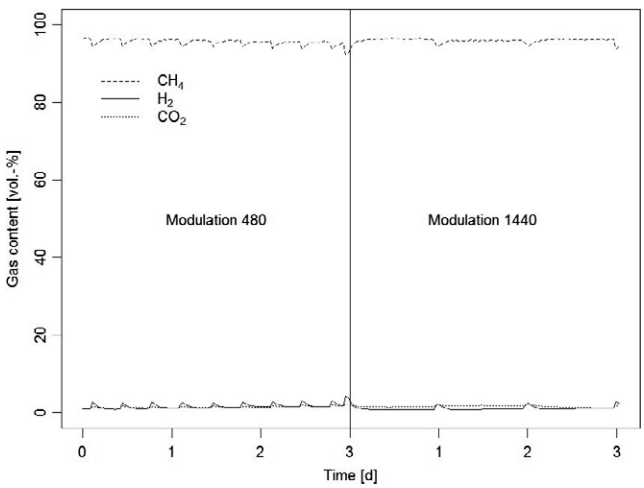

FIGURE 3 The influence of different modulation strategies on product gas quality. Modulation 480 and modulation 1,440 over a three-day period

achieved, thus indicating that an exact gas ratio of 4:1 leads to higher overall conversion rates and methane contents. A recommended ratio of 1:3.76, as described in Burkhardt et al. (2015), cannot be confirmed in these experiments.

Similar to the decreasing contents of H_2 and CO_2 and the improved conversion rates, the share of CH_4 in the product gas increases in the course of the modulations. There were significant differences only between modulation 2 and modulations 240, 480 and 1,440. Modulations 240, 480 and 1,440 were not significantly different. The largest differences were observed between modulation 2 and 1,440, where the content of CH_4 increased from 88.61 ± 1.58 to 97.19 ± 0.46 vol-%. Thus, the periodic circulation in modulation 1,440 significantly increased the content of CH_4 by 10%.

With regard to the significance, it must be mentioned that the conversion rates of modulations 240, 480 and 1,440 are at a very high level. It is more difficult to achieve significant differences at these high levels than with low conversion rates.

In Figure 3, the direct influence of the process liquid sprinkling on the product gas quality is shown. The CH_4 content decreased and the H_2 and CO_2 content rose immediately after each circulation. After about 2 hr, the gas qualities returned to the previous level.

In modulations with longer OFF times, less gas peaks were found and thus smaller standard deviations were observed. The standard deviations for modulation 2 and modulation 1,440 were 1.58 and 0.46, respectively. By that, longer OFF times contribute to stable high methane contents in the product gas. The slightly larger peak between modulations 480 and 1,440 on day 3 was caused by the fluid change before each new modulation.

Due to the immediate change in circulation, an increased concentration of microorganisms can be excluded as a reason for the rapidly changing gas composition. This would require a longer acclimatization period of the microorganisms.

During the whole trial period, the performance of the three different laboratory scale reactors was very similar, which is indicated by the small standard deviations presented in Figure 2 and Table 3. The largest differences were observed in modulation 2 with small fluctuation ranges of a maximum of 1.3% between reactor 2 and 3. This demonstrates the high reliability and reproducibility of the gained data.

Numerous studies have already proven that high gas qualities are possible with TBR (Burkhardt et al., 2015; Rachbauer, Voitl, Bochmann, & Fuchs, 2016; Strübing et al., 2017). In these studies, methane contents of up to 98 vol-% were achieved. For alternative reactor concepts, methane contents higher than 90 vol-% (fixed-bed systems) (Alitalo, Niskanen, & Aura, 2015) and 85 vol-% (CSTR

systems) (Seifert et al., 2014) are reported. Compared to these results, the chosen set-up of this study led to very high conversion rates of the injected source gases.

In this study, the MFR increased from 5.36 ± 0.12 m^3 m^{-3} day^{-1} for modulation 2 to 5.62 ± 0.10 m^3 m^{-3} day^{-1} for modulation 1,440. The differences between modulations 240, 480 and 1,440 were not significant. The MFR in this study had a maximum value of 5.62 ± 0.10 m^3 m^{-3} day^{-1} which is at a high level compared with similar studies. Burkhardt et al. (2015) reached 1.49 m^3 m^{-3} day^{-1} and Rachbauer et al. (2016) 1.9 m^3 m^{-3} day^{-1} with methane contents of 98 and 96 vol-%, respectively. Pressures up to 9 bar absolute, an MFR of 4.28 ± 0.26 m^3 m^{-3} day^{-1}, and a methane content of 86.51 ± 0.49 vol. % were achieved by Ullrich et al. (2018). Only Strübing et al. (2017) achieved a significantly higher result with a maximum of 15.4 m^3 m^{-3} day^{-1} and 98 vol-% CH_4 in the product gas.

No significant differences were found in the GHSV and the associated gas flow in the reactors, nor in retention time. Differences in MFR and conversion rates are therefore due to the liquid flow modulation.

The tests have shown that by modulating the process liquid flow, the performance of TBR for the biological methanation of hydrogen can be significantly increased. The results are consistent with investigations regarding TBRs in other fields of application (Banchero et al., 2004; Stradiotto et al., 1999; Turco et al., 2001; Urseanu et al., 2004). In addition, this application offers a very simple way to save electrical energy in practice by reducing pumping activity which can help to make the biological methanation process with TBR more cost-efficient.

4 | CONCLUSION AND OUTLOOK

Liquid flow modulation in TBR has been shown to increase BHM performance in various experiments. For this purpose, the trickling was suspended for OFF times of 2, 240, 480 and 1,440 min. The analysis of the process liquid revealed that the biological process, which was kept stable during the experimental phase, was not negatively influenced by the modulation. The methane content of at least 88.61 ± 1.58 vol-% at modulation 2 was significantly increased by up to 97.19 ± 0.46 vol-% at modulation 1,440.

It should be mentioned, that the OFF times cannot be extended indefinitely. The microorganisms depend on a sufficient supply of nutrients, which are provided with the liquid. The maximum OFF time could not be identified in this study, but further research investigating this is encouraged. This OFF time is expected to depend on the amount of injected educt gas. In the context of ensuring nutrient supply, the influence of the dilution of the process liquid on the reactor performance is another important topic that is worthy of attention.

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4. Publikation 3: Effect of different operating temperatures on the biological hydrogen methanation in trickle bed reactors

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Effect of Different Operating Temperatures on the Biological Hydrogen Methanation in Trickle Bed Reactors

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Abstract: To improve the reactor efficiency, this study investigated the influence of temperature on the biological hydrogen methanation (BHM) in trickle-bed reactors (TBR). Rising temperatures increase the metabolic activity of methanogenic microorganisms, thus leading to higher reactor specific methane formation rates (MFR). In order to quantify the potential for improved performance, experiments with four different operating temperatures ranging from 40 to 55 °C were carried out. Methane content increased from 88.29 ± 2.12 vol % at 40 °C to 94.99 ± 0.81 vol % at 55 °C with a stable biological process. Furthermore, a reactor specific methane formation rate (MFR) of up to 8.85 ± 0.45 m^3 m^{-3} d^{-1} was achieved. It could be shown that the microorganisms were able to adapt to higher temperatures within hours. The tests showed that TBR performance with regard to BHM can be significantly increased by increasing the operating temperature.

Keywords: biological hydrogen methanation; Trickle-Bed-Reactor; operating temperature; Power-to-Gas; hydrogen; renewable energy

1. Introduction

A promising technology for the conversion of hydrogen and carbon dioxide to methane for the purpose of energy storage and biogas upgrading is biological hydrogen methanation (BHM) by using methanogenic archaea [1].

Independent of the reactor concept used, BHM offers the advantage of being very tolerant of impurities in the product gas [2]. Additionally, BHM is very flexible in terms of load changes [3] and can be switched from stand-still to full load within hours, although it is based on a biological conversion by living organisms. BHM is also characterized by its high conversion efficiency [1].

However, biological reactor concepts are not very high performing [3]. The gas hourly space velocity (GHSV), which refers to the gases entering a reactor, can be used as a performance parameter [4]. In catalytic concepts, it is up to 5000 h^{-1} [3]. Only maximum values of 300 h^{-1} are given for the BHM [5], which are very optimistic and have not yet been reached. More realistic values are significantly less than 100 h^{-1} [3].

Due to their advantageous design, trickle bed reactors (TBR) are increasingly gaining attention today and recent studies intend to improve reactor performance [4,6–8]. TBRs have the advantage of very high phase contact surfaces, which increases the gas-liquid mass transfer and thus the productivity of the entire system [7].

To further improve the gas-liquid mass transfer and thus the performance, test series in TBRs with different pressures have already been investigated [4]. In this case, the output could be increased

significantly by more than 30%. However, the technical effort required to operate the process at high pressures is comparatively high and the question arises as to whether the effort is economically justified [4].

BHM is a process involving biological metabolism, which means that performance can be enhanced through the process temperature. Methanogens span a huge temperature range [9,10]. A distinction is made between mesophilic (30–40 °C) and thermophilic (50–60 °C) temperature ranges [11]. In anaerobic digestion, the growth rate of methanogenic archaea is higher at thermophilic temperatures, thus making the process faster and enabling higher organic loading rates [12]. Therefore, in [13] optimal conditions for anaerobic digestion at thermophilic temperatures could be determined. Many studies confirm the increasing efficiency and degradation rate of the process with rising temperatures [14–16].

Recent studies on the BHM also indicate, that temperature has a substantial impact on the reaction velocity and the response time, which allows higher loading rates to be achieved [17]. It is reported that the operation of a BHM system is significantly more efficient at 65 °C than at 55 °C [18]. Reference [19] are slightly more specific and describe an increase in the conversion of H_2 and CO_2 by 60%, with an increase in the process temperature from mesophilic (37 °C) to thermophilic (55 °C). In [20], there is even a quadrupling of the conversion speed reported.

Higher performance at higher temperatures may be due to increased growth rates. Thermophilic methanogens have a growth rate that is 2 to 3 times higher than mesophilic methanogens [11,21,22]. Beside these biological aspects, the increased metabolic activity has an accelerating impact on the physical mass transfer from the gaseous phase into the liquid biofilm. High metabolic processes keep the concentration of the diluted source gases low, thus resulting in larger concentration differences between the gas and the liquid phase which enhances the mass transfer rate and methane production [23]. Although the solubility of gas decreases with rising temperatures, it is compensated by the increased growth rate and improved mass transfer [17].

There are investigations of BHM at mesophilic and thermophilic temperatures, but the temperatures have not been varied within one study, especially with regard to different types of reactors.

Continuous stirred tank reactors (CSTR) are a main design for BHM. The investigations do not consider the influence of different temperatures. The investigated temperatures range from 37 °C [24,25] to 65 °C [1,5,26,27] without being varied within one examination. The use of different enriched cultures makes it more difficult to estimate the influence of temperature on the performance parameters. The majority of TBRs, another main design, operate at a temperature of 37 °C [7,8,28]. The methane formation rate (MFR), a major reactor performance parameter representing the specific methane yield as a function of time [4], reaches a maximum of 2.5 $m^3\ m^{-3}\ d^{-1}$ at this temperature level. In contrast, another study investigating TBRs achieved a MFR of 15.4 $m^3\ m^{-3}\ d^{-1}$ at a thermophilic temperature of 55 °C [6]. The influence of the process temperature on important performance parameters, such as the MFR, is not sufficiently detailed in these studies.

A direct influence of the temperature on the conversion efficiency and MFR cannot be deduced from previous investigations of BHM, since temperature has not been studied in this context; especially if innovative TBR systems are used. However, studies have shown that the reaction speed of biological systems can be increased with rising temperatures, and thus should be considered in more detail. This would therefore represent a promising possibility to significantly increase the performance of BHM. In order to specify this more precisely, the aim of the study was the investigation of different temperatures on performance parameters such as GHSV, MFR, conversion and product gas quality of the BHM under consistent conditions using TBRs. A high practical demand of this investigation was to ensure a product gas with a high methane content. For this purpose, a continuously operated and automated test facility was developed and built up at the University of Hohenheim.

2. Methods

2.1. Experimental Setup

The experimental plant was realized with three identical TBRs. The structure of the plant is shown as a piping and instrumentation diagram in Figure 1.

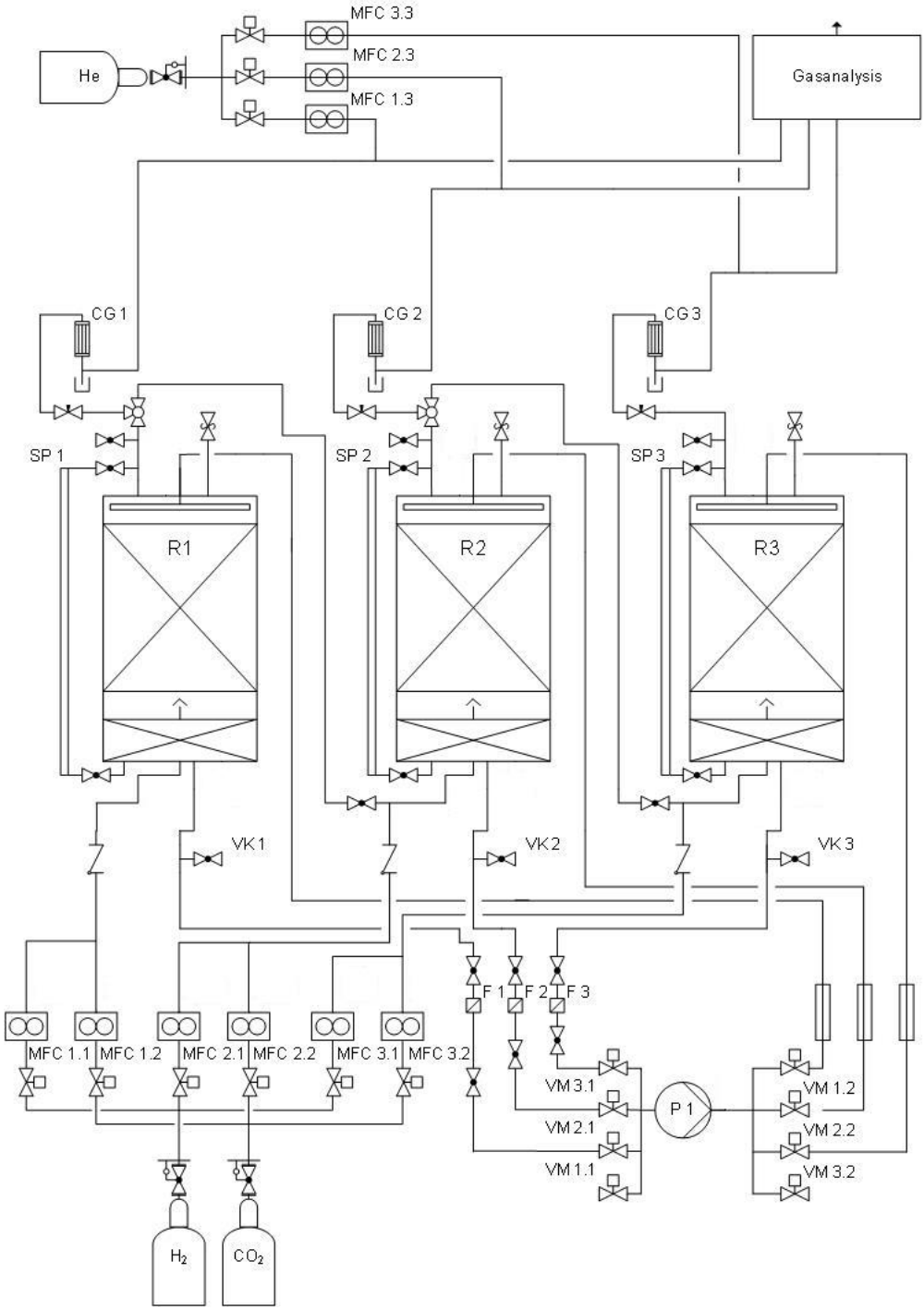

Figure 1. Piping and instrument diagram of the test facility with the three trickle-bed reactors (R1–R3), the injection of the educt gases CO_2 and H_2 (MFC 1.1–MFC 3.2), the circulation unit of the nutrient solution (P 1, VM 1.1–VM 3.2), the gas analysis and the gas quantity measurement (MFC 1.3–MFC 3.3) with He as the tracer-gas.

The reaction space of each reactor was equipped with a fixed and a trickle bed. The trickle bed in the gas phase had a volume of 13 L. It was filled with the HX09 packing elements from Christian Stöhr GmbH & Co. KG (Marktrodach, Germany), and had a total surface of 11.2 m^2. The sump in the liquid phase at the bottom of the reactors were equipped with a 1.5 L fixed bed of the same packing elements, resulting in a total surface of 1.3 m^2. This sums up to a total active volume of 14.5 L per reactor and a surface area of 12.5 m^2 for immobilization of the microorganisms.

The effluent of an anaerobic filter [29] was used as the process liquid to provide the necessary nutrients and was sprinkled over the fixed bed in counter current with the gases. This anaerobic filter was part of a two-stage lab-scale biogas system and was run at a pressure of up to 50 bars. When collecting the effluent, this methane reactor was operated at a continuous and stable mode. The liquid used did not contain significant amounts of acids or alcohols, which could affect the conversion of H_2 and CO_2. Due to the extremely low process liquid-based gas production, a correction of the results according to [4] was not considered necessary.

As the process liquid passed through the trickle bed, it was accumulated in the sump of the fixed bed. With the magnetic valves VM 1.1–VM 3.2, it was possible to switch between various closed circuits, because a central pump (P 1) was used for circulation of the process liquid in all three reactors. The liquid filters (F 1, F 2, F 3) were used to protect the central gear pump P 1 against particles. SP 1, SP 2 and SP 3 were sighting tubes outside the reactor to control the filling level inside the reaction space. Half of the process liquid (1.4 L per reactor) was replaced before starting a new test procedure, because the water produced during the methanation process diluted the process liquid permanently

With mass flow controllers (MFC) MFC 1.1–MFC 3.2, the gases were injected into the reactors.

Using a mechanical pressure control valve at the top of the reactors, the product gases were released from the reaction chamber. For condensate removal, the product gases flowed through the gas coolers CG 1, CG 2 and CG 3.

The pressure sensors used were 261AS from ABB Ltd. (Zürich, Switzerland), and have a measuring range of 0–10 bar absolute with a basic accuracy of 0.1%. They have an operating temperature range from −40 °C to 85 °C and were equipped with a gold-coated membrane to prevent hydrogen corrosion. The temperature was measured between the sump and the trickle bed with the temperature sensor Easytemp TMR31 from Endress + Hauser Messtechnik GmbH + Co. KG (Reinach, Germany). For regular maintenance and calibration, the pH/Redox electrodes Memosens CPS16D of the same manufacturer were installed in the piping outside of the reactors.

2.2. Experimental Procedure

The test facility was in a condition ready for operation including a well-established biofilm of microorganisms [4]. Therefore, a start-up period or preliminary testing phase was not necessary.

To investigate the influence of temperature on the methanation process, tests were done with this plant with four temperature levels: 40, 45, 50 and 55 °C. These levels were carried out in ascending order to enable the microorganisms to adapt to rising temperatures.

The trickle bed was sprinkled with the process liquid every 12 h for one minute with a circulation quantity of 60 L h^{-1}. As studies of TBRs have shown, especially from the petrochemical industry [30–33], such a trickling strategy has positive effects on the conversion of the source substances. Own tests confirmed an improved conversion of CO_2 and H_2 and sufficient nutrient supply for a stable operation.

The flowrates of the mass flow controllers were adjusted to 5 L h^{-1} CO_2 and 20 L h^{-1} H_2 to achieve a stoichiometric ratio of CO_2 to H_2 of 1:4. Due to the low inaccuracies of the mass flow controllers, the real quantities of the educt gases were additionally calculated using the results of the gas analysis.

The investigation of the temperature levels was carried out simultaneously in the three reactors for a duration of 148–161 h each at a constant operating pressure of 5 bar absolute. Previous studies

and reports have shown that this elevated process pressure has a positive impact on MFR compared to lower pressure levels [4].

2.3. Analytical

The quality of the product-gases was analysed every 30 min by a 3000 L gas chromatograph from Inficon GmbH, Cologne, Germany.

In order to determine the gas quantity, a specific and constant amount of helium (0.5 L h^{-1}) was added to the product gas of each reactor. With this tracer gas and the analysis of the gas proportions by gas chromatography, the amount of the product gas and the individual components were calculated.

The process liquid was sampled at the beginning and end of each temperature level. It was analysed for the content of volatile fatty acids, the chemical oxygen demand as well as the conductivity and salinity. Volatile fatty acids were analysed with a CP-3800 gas chromatograph from Varian Medical Systems. With the Hach Lange cuvette test (LCK014), the chemical oxygen demand (COD) was measured. The conductivity and salinity were determined by dipping the conductivity tube of an EC300 from VWR International GmbH (Darmstadt, Germany), into the untreated sample.

2.4. Calculations

The MFR and GHSV were calculated to evaluate the performance of the reactors regarding quantitative parameters. The MFR (Equation (1)) describes the methane yield per day independent of the reactor volume. $F_{V,CH4,out}$ and $F_{V,CH4,in}$ is the volumetric flow rate in and out of the reactor (Götz et al., 2016). V_R describes the volume of the reaction space of the reactor which amounts to 14.5 L in case of our lab-scale system.

$$MFR = \frac{F_{V,CH4,out} - F_{V,CH4,in}}{V_R} \quad (\frac{\mathrm{m}^3}{\mathrm{m}^3\mathrm{d}}) \tag{1}$$

The *GHSV* describes the volumetric flow rate ($F_{V,G,in}$) at standard temperature and pressure (STP) (1013 mbar, 273 K) of the feed gas without any inert gases as a function of the reaction space of a reactor [3].

$$GHSV = \frac{F_{V,G,in}}{V_R} \qquad (\mathrm{h}^{-1}) \tag{2}$$

In addition to the methane content in the product gas, the conversion of both feed gases was calculated. It is defined in Equation (3), where $F_{n,i,in}$ describes the incoming and $F_{n,i,out}$ the outcoming H_2 or CO_2 in L·h^{-1}.

$$X_i = \frac{F_{n,i,in} - F_{n,i,out}}{F_{n,i,in}} \qquad (\%) \tag{3}$$

The retention time (*RT*) was calculated as a function of V_R and the volumetric flow of the incoming gases $F_{V,G,in}$. The volume reduction during the conversion of CO_2 and H_2 to CH_4 was not taken into account for this calculation.

$$RT = \frac{V_R}{F_{V,G,in}} \qquad (\mathrm{h}) \tag{4}$$

The statistical software "R Studio" (V0.99.903, RStudio, Inc., Boston, MA, USA) was used for all calculations, as well as for the statistical analysis with the Kruskal Wallis Test and subsequently Tukey's Test with a *p*-value of $p < 0.05$ [34,35]. The *p*-value indicates the probability of error and was chosen with <5%, since it is a level of significance common in statistics.

3. Results and Discussion

3.1. Operating Parameters

In the experiments, four temperature levels between 40 and 55 °C were investigated, which were adjusted in parallel in all three reactors. The respective results were summarized as an arithmetic

average. As shown in Table 1, the different temperature levels could be set with high stability and accuracy. The largest deviation was observed at 40.41 ± 0.12 °C with a target value of 40 °C.

Table 1. Overview of the operating parameters, flow rates and conversion. The results of the three reactors were calculated as an arithmetic average. The significant differences among the temperature levels are marked with different letters ($p < 0.05$, Tukey's test).

Aimed Temperature Level	40	45	50	55
Temperature [°C]	40.41 ± 0.12 [a]	44.99 ± 0.12 [b]	50.12 ± 0.14 [c]	55.08 ± 0.17 [d]
Pressure [bar]	5.21 ± 0.03 [a]	5.22 ± 0.02 [a]	5.21 ± 0.03 [a]	5.20 ± 0.04 [a]
pH	7.44 ± 0.09 [a]	7.45 ± 0.11 [a]	7.57 ± 0.08 [a]	7.54 ± 0.05 [a]
Flow H_2 [L h^{-1}]	21.67	22.01	20.83	21.04
Flow CO_2 [L h^{-1}]	5.46	5.59	5.27	5.29
CO_2:H_2	1:3.96	1:3.94	1:3.95	1:3.97
MFR [m^3 m^3 d^{-1}]	8.48 ± 0.45 [a]	8.85 ± 0.43 [a]	8.46 ± 0.40 [a]	8.59 ± 0.38 [a]
GHSV [h^{-1}]	1.86 ± 0.09 [a]	1.90 ± 0.09 [a]	1.80 ± 0.07 [a]	1.82 ± 0.06 [a]
Retention time [h]	2.79	2.75	2.89	2.85
Conversion H_2 [%]	97.68 ± 0.01 [a]	98.52 ± 0.00 [b]	99.12 ± 0.00 [c]	99.24 ± 0.00 [d]
Conversion CO_2 [%]	96.42 ± 0.00 [a]	97.51 ± 0.00 [b]	97.88 ± 0.00[c]	98.10 ± 0.00 [d]

[a, b, c, d] Significant differences are given with different letters.

The operating pressure was set at 5 bar for all temperature levels. Due to the improved solubility of the CO_2 at rising pressures, this comparatively low pressure should prevent low pH values. The pH values finally reached a range of 7.44 ± 0.09 at 40 °C to 7.57 ± 0.08 at 50 °C and was thus in a optimal range for methanogenesis [36]. Although the process fluid is continuously diluted by the formed water during methanation reaction within the different experimental phases, no significant drop in pH was observed. These small fluctuations indicate a high buffering capacity of the process liquid used.

The amount of hydrogen introduced ranged from 20.83 L h^{-1} at temperature level 50 to 22.01 L h^{-1} at temperature level 45, so slightly more hydrogen was introduced into the reactors as set. However, since too much CO_2 was also introduced, an almost stoichiometric ratio of CO_2:H_2 in the range 1:3.94 to 1:3.97 was achieved. Due to small fluctuations in the flow rates and constant pressures, the retention times of 2.75 to 2.89 h were also constant to guarantee consistent reaction conditions.

3.2. Analysis of the Process Liquid

The tests were sampled at the beginning and end of each temperature level. With regard to the analysis of the acids, acetic acid enrichment of 0.11 ± 0.02 g kg^{-1} was observed at the end of temperature level 45. Furthermore, a propionic acid concentration of 0.06 ± 0.01 g kg^{-1} was measured at the end of temperature level 55. In the remaining experiments, no acid concentrations were observed in the process liquid. Due to stable methane formation rates across all experiments, no negative influence of this low acid formation is assumed. With regard to further investigations with this methanation concept, attention should be paid to the aspect of acid production, respectively acid accumulation.

The salinity of the process liquid was measured in particular to monitor its dilution. Some experiments observed a decrease in salinity as is the case when the process liquid becomes more diluted. At temperature level 55, the salinity decreased from 2.43 ± 0.06 ppt to 2.17 ± 0.06 ppt, which was the largest difference during the experiments. Furthermore, a maximum of 2.63 ± 0.05 ppt and a minimum of 2.17 ± 0.06 ppt were achieved, which is in the optimum range for methanogenic microorganisms [37].

The COD can also be considered stable. It ranged between 2568 ± 427 g L^{-1} ${O_2}^{-1}$ at temperature level 40 and 3745 ± 140 g L^{-1} ${O_2}^{-1}$ at temperature level 45. In contrast to salinity, there was no sign of a decline in the COD due to increasing dilution.

Overall, the analyses of the process liquid indicate a stable biological process over the duration of the experiments.

3.3. Performance Parameters

Rising temperatures increase the reaction speed and the growth rate and thus the performance of biological systems [11,17,21,22]. This was confirmed by the conversion rates of the experiments, which increased with increasing temperature. In the case of hydrogen, the conversion rate could be continuously increased from 97.68 ± 0.01% at 40 °C to 99.24 ± 0.00% at 55 °C. Since CO_2 was introduced into the reactors slightly over stoichiometrically, its conversion rates were at a lower level, but could also be increased significantly from 96.42 ± 0.00% to 98.10 ± 0.01%.

In regard to BHM in the TBR, the literature describes an ideal ratio of CO_2 to H_2 of 1:3.76, in which a complete conversion of the gases should be possible [7]. In the experiments carried out, the ratio was 1:3.94 to 1:3.97. Nevertheless, the conversion rates still suggest a CO_2 proportion that was slightly too high, which means that the published optimum ratio cannot be confirmed in these experiments. A complete conversion seems more likely with a stoichiometric ratio.

With increasing conversion rates of H_2 and CO_2, the quality of the product gas also increased. Thus, the methane content could be increased from 88.29 ± 2.12 vol % at 40 °C to 94.99 ± 0.81 vol % at 55 °C. However, no significant differences could be detected between the temperature levels of 50 and 55 °C.

As the methane content increased, the proportion of CO_2 and H_2 in the product gas was continuously reduced. Therefore, the average H_2 content was reduced from 8.34 ± 1.54 vol % at 40 °C to 3.17 ± 0.79 vol % at 55 °C. Due to the stoichiometric reaction ratio, the proportion of CO_2 was reduced only from 3.26 ± 0.51 vol % to 1.83 ± 0.34 vol % (Figure 2). This confirms the assumption that a stoichiometric ratio should be targeted for a complete conversion of the educt gases.

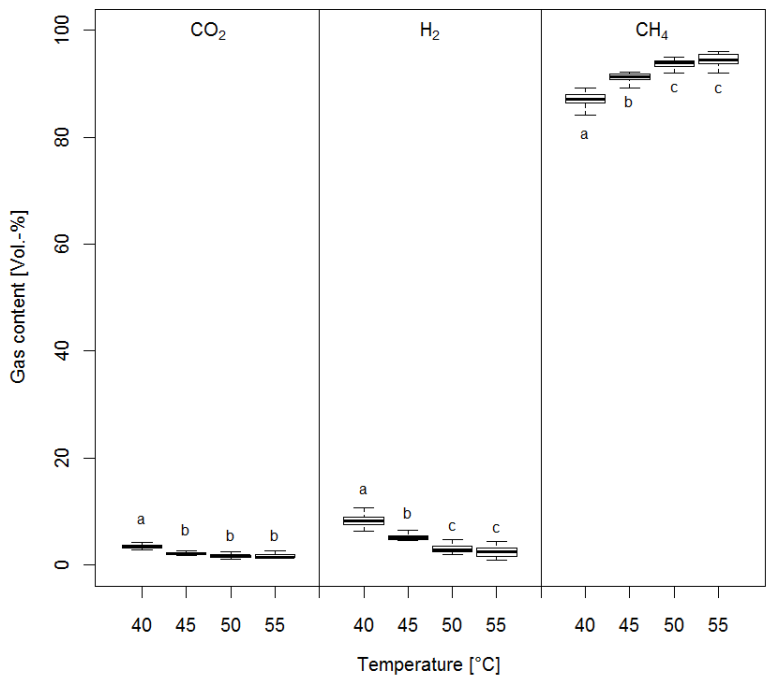

Figure 2. Gas quality of the product gas depending on the different temperatures. The significant differences among the temperature levels are marked with different letters ($p < 0.05$, Tukey's test).

The GHSV in these tests ranged from 1.80 ± 0.07 h^{-1} to 1.90 ± 0.09 h^{-1}. Although the values differ between the temperature levels, the differences were not statistically significant. The same was

for the MFR, which was achieved in the range 8.46 ± 0.45–8.85 ± 0.45 m^3 m^{-3} d^{-1}. The temperature increase therefore only increased the gas quality. Differences in the amount of gas produced could not be determined and can be traced back to slightly different amounts of injected gas between the experiments. Another reason for this could be the reduction in the volume by a factor of 5 during the biological methanation process, which was also observed and described in [4].

In addition to increasing conversions with rising temperatures, the tests also showed that the adaptation of microorganisms to higher temperatures occurred very quickly. Figure 3 shows a section of the experiments, incorporating the transition from 40 to 45 °C. It is apparent that the proportion of CH_4 increased immediately after the temperature rose and the conversion of CO_2 and H_2 was improved. The adaptation of microorganisms to changing temperatures is carried out directly in this reactor concept and demonstrates high flexibility and stability of the process. Also, the direct influence of the process liquid sprinkling on the product gas quality is shown. The CH_4 content decreased and the H_2 and CO_2 content rose immediately after each circulation. After about 2 h, the gas qualities returned to the previous level.

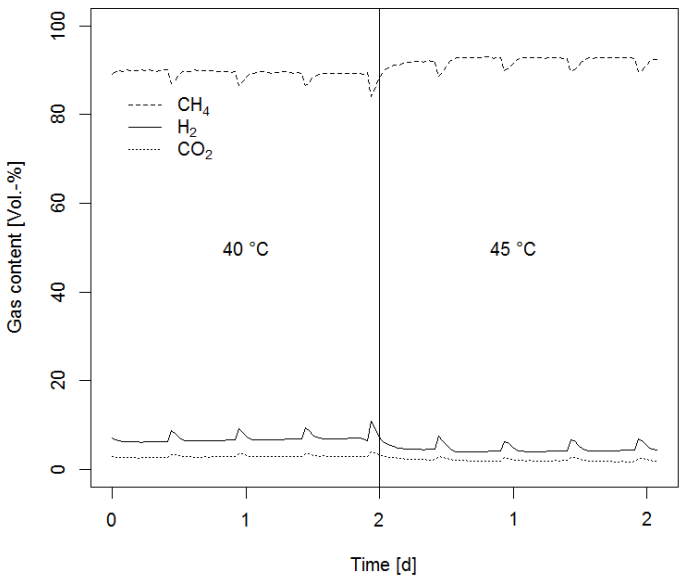

Figure 3. The influence of different temperatures (40 °C and 45 °C) on product gas quality over a period of two days.

The experiments confirm further studies on TBR that high methane contents can be achieved with this reactor concept [4,6–8]. For long-term tests, [7] achieved an almost complete conversion of CO_2 and H_2 with a methane content of 98 vol % with an MFR of 1.49 m^3 m^{-3} d^{-1}; with a slightly higher MFR of 1.9 m^3 m^{-3} d^{-1}, a methane content of 96 vol % was achieved [8]. The best results by far were achieved with an MFR of 15.4 m^3 m^{-3} d^{-1} and methane contents >98 vol % [6] which show the high potential of this concept.

The results confirm studies of other biological systems with regard to temperature increases in BHM [18–20]. However, the increases were lower than described there. In [19], an increase in conversion of 60% was observed with a rise in temperature from mesophilic (37 °C) to thermophilic (55 °C) and [20] reported a quadrupling of the conversion. These dramatic increases seem not to be plausible in the view of the reported results here. There were no increases of this magnitude detected. However, the conversion and methane content were already at a high level of 88.29 ± 2.12 vol %, at the beginning of the experiments. This was because a product gas with a high methane content relevant to practice was to be produced at the end of the experiments. Further increases from this high starting level are more difficult to achieve.

Overall, the experiments showed that the conversion of BHM is significantly improved with rising temperatures and contributes to a further increase of the gas-liquid-mass transfer in TBR.

4. Conclusions and Outlook

The investigations showed that the conversion of H_2 and CO_2 significantly increased with rising temperatures within the context of BHM in TBR, thus improving the gas quality. In experiments with four different temperature levels from 40 to 55 °C, the methane content continuously increased from 88.29 ± 2.12 vol % to 94.99 ± 0.81 vol %. Furthermore, a MFR of up to 8.85 ± 0.45 $m^3\ m^{-3}\ d^{-1}$ was achieved. The analysis of the process liquid indicated a stable biological process and a rapid adaptation of the microorganisms to the changing temperatures was observed.

In the literature, BHM is also carried out at temperatures of up to 65 °C, but not in TBR. Investigations with further temperature increases are recommended. Furthermore, studies on the optimum ratio of CO_2 to H_2 are also of great interest, since the indications discussed in recent studies could not be confirmed. The dependence of optimum gas ratios on the process temperature and pressure should also be investigated in this context.

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5. Gesamtdiskussion

Die biologische Methanisierung ist ein vielversprechender Ansatz, regenerativ erzeugten Wasserstoff in Methan umzuwandeln, um somit überschüssige elektrische Energie über einen chemischen Energieträger zu speichern. In der Literatur werden verschiedene Reaktorkonzepte beschrieben, ohne jedoch den Einfluss verschiedener Betriebsparameter innerhalb eines Konzeptes zu analysieren beziehungsweise diese zu quantifizieren. Mit der im Rahmen dieser Arbeit entwickelten kontinuierlichen Versuchsanlage wurden erstmals gezielt einzelne Betriebsparameter variiert, um den optimalen Betriebspunkt bestimmen zu können. Ziel der Arbeit ist die Entwicklung und Erprobung eines neuartigen Hochdruck-Rieselbett-Reaktor-Konzeptes für die biologische Wasserstoffmethanisierung. Im folgenden Abschnitt werden nun die Ergebnisse der durchgeführten Versuchsreihen und deren Auswirkungen auf die Leistungsfähigkeit des Reaktorkonzeptes in einem Gesamtkontext diskutiert.

5.1. Prozessstabilität

Die Nutzung des entwickelten Reaktorkonzeptes in zukünftigen technischen Applikationen setzt voraus, dass eine hohe Konstanz der Erzeugung bei einer gleichzeitig hohen reaktorspezifischen Methanproduktionsrate erreicht wird. Diese gleichbleibende, stabile Konversion von Wasserstoff und Kohlenstoffdioxid zu Methan setzt ein komplexes Zusammenspiel von biologischen Stoffwechselprozessen mit der Steuer- und Regelungstechnik der Reaktoren voraus. Um diese komplexen Interaktionen erfassen zu können, wurden umfangreiche Messungen und Analysen an den drei Reaktoren der Versuchsanlage durchgeführt.

Die Messungen betreffen einerseits die Betriebsparameter wie etwa Druck, Temperatur oder Gasstrom eines jeden einzelnen Reaktors. Durch den Einsatz von online-Messtechnik und einem hohen Grad an Automatisierung der entwickelten Versuchsanlage sollte diesbezüglich eine hohe zeitliche Auflösung der Messwerte erreicht werden. Ergänzend dazu wurden Analysen der Prozessflüssigkeit durchgeführt. Es galt, einen biologischen Prozess hinsichtlich stabiler Methanbildungsraten einzustellen und aufrecht zu erhalten. Eine ausreichende Nährstoffversorgung über die Prozessflüssigkeit sollte dies garantieren und etwa die Bildung anaerober Gärprodukte unterbinden. Weiterhin sollte eine zu starke Verwässerung der Prozessflüssigkeit durch das Reaktionsnebenprodukt Wasser frühzeitig erkannt werden.

5.1.1. Betriebsparameter

Die geringen Standardabweichungen bei den Betriebsparametern Druck und Temperatur lassen erkennen, dass die diesbezüglich eingestellten Ziel-Werte in allen Experimenten stabil und konstant eingehalten wurden. Damit erwies sich die entwickelte automatische Steuer- und Regelungstechnik als sehr zuverlässig und zur Durchführung der Untersuchungen gut geeignet. Auch das Temperierungskonzept über Wasserbäder in Kombination mit Heiz-Thermostaten war der Aufgabenstellung angemessen. Zwischen den drei Reaktoren konnten lediglich geringe Temperaturunterschiede beobachtet werden, was auf unterschiedlich hohe Wärmeverluste in den Zuleitungen des Heiz-Thermostats zurückzuführen ist. So wurde in Publikation 1 die größten Differenzen mit 40.38 ± 0.15 °C in Reaktor 1 und 41.09 ± 0.15 °C in Reaktor 3 beobachtet. Die geringe Standardabweichung zeigt die hohe Konstanz der Werte über die Versuchsabläufe hinweg, so dass unbeabsichtigte Einflüsse ausgeschlossen werden können.

Bei der Untersuchung unterschiedlicher Betriebsdrücke in Publikation 1 konnten unterschiedliche pH-Werte festgestellt werden. Dieser sank von 6.98 ± 0.05 bei einem Betriebsdruck von 1.5 bar auf 6.34 ± 0.03 bei 9 bar. Hervorgerufen wird dieser Effekt durch den mit dem Betriebsdruck steigenden CO_2-Partialdruck in der Gasphase. Entsprechend dem Henry-Gesetz erhöht sich proportional dazu auch die Konzentration von CO_2 in der Prozessflüssigkeit und führt über die Bildung von Hydrogencarbonaten zu sinkenden pH-Werten bei steigendem Betriebsdruck. Die weiteren Versuche in Publikation 2 und 3 bestätigen diese Annahme. Da der Druck hier nicht variiert wurde, konnte der pH-Wert stabil und konstant zwischen 7.31 ± 0.22 und 7.44 ± 0.21 in Publikation 2 sowie zwischen 7.44 ± 0.09 und 7.57 ± 0.08 in Publikation 3 eingehalten werden. Der Betriebsdruck in diesen Versuchen wurde jedoch auf 5 bar festgelegt, um trotz der gesteigerten Gasflüsse und dem damit gestiegenen CO_2-Volumenströmen ein weiteres Absinken des pH-Wertes zu verhindern. Denn auch wenn kein negativer Einfluss des geringen pH-Wertes von 6.34 ± 0.03 bei 9 bar auf die Leistungsparameter festgestellt werden konnte, ist ab einem pH-Wert < 6 mit einer Hemmung der methanogenen Mikroorganismen zu rechnen (Capri and Marais, 1975).

Die Gasflüsse konnten durch die Massflowcontroller als einziger Betriebsparameter nicht exakt auf die Ziel-Werte eingestellt werden. Hier wurden in Publikation 1 Abweichungen bis zu 15 % gemessen. Mit den gesteigerten Durchflussraten in Publikation 2 und 3 konnten die Abweichungen jedoch deutlich verringert werden. Eine hohe Konstanz der eingespeisten

Gasmengen war aber trotz dieser Abweichungen gegeben und wurde von einer stets stabilen und konstanten Gasqualität bestätigt.

Die Ungenauigkeiten der Massflowcontroller führten in Publikation 1 zu einem überstöchiometrischen Verhältnis an CO_2. Die anteilig größte Menge CO_2 wurde mit einem Verhältnis von 1 : 3,74 beim Betriebsdruck von 5 bar erreicht. Diese Überstöchiometrie von CO_2 und der damit verbundene erhöhte Partialdruck ist auch ein Grund für die resultierenden niedrigen pH-Werte. Zwar wurden mit überstöchiometrischen Verhältnissen von 1 : 3,76 bereits Methangehalte > 98 % erreicht (Burkhardt et al., 2015), bestätigt hat sich diese Vorteilhaftigkeit jedoch nicht. Daher wurde das Verhältnis im Lauf der Versuche bis zu 1 : 3,97 in Publikation 3 angepasst, was auch die pH-Werte ansteigen ließ.

Die eingestellten Betriebsparameter konnten mit der Versuchsanlage somit stabil und mit hoher Konstanz eingestellt werden und haben stabile Betriebsbedingungen während der Versuchsdurchführung gewährleistet. Diese konstanten Prozessparamenter in den Versuchsanlagen sind die Voraussetzung, um gezielt den Einfluss einzelner Faktoren zu untersuchen.

5.1.2. Prozessflüssigkeit

Die übergreifende Betrachtung aller durchgeführten Untersuchungen über die drei Publikationen hinweg zeigt, dass bereits von der gewählten Prozessflüssigkeit ein erheblicher Einfluss auf die Leistungsfähigkeit der Rieselbettreaktoren ausgeht. Sämtliche verwendeten Prozessflüssigkeiten wurden mit einer Spurenelementmischung, die speziell für methanogene Mikroorganismen in Biogasanlagen vertrieben wird, angereichert. Ein Einfluss unterschiedlicher Nährstoffkonzentrationen kann daher ausgeschlossen werden.
Betrachtet man die verwendeten Prozessflüssigkeiten im Detail so zeigt sich, dass in den Untersuchungen, die der Publikation 1 zugrunde liegen, ein Hydrolysat mit einem geringen Anteil von maximal 0.52 ± 0.05 g kg^{-1} an organischen Säuren verwendet wurde. Dieses Hydrolysat wurde aus der ersten Stufe einer zweistufigen Labor-Biogasanlage gewonnen. Die enthaltenen Säuren wurden im Versuchsverlauf kontinuierlich abgebaut, eine Säureanreicherung fand nicht statt. Neben einem erhöhten CO_2-Partialdruck war auch durch die Verwendung dieser säurehaltigen Flüssigkeit der pH-Wert auf einem niedrigeren Niveau als in Publikation 2 und 3. Aufgrund des niedrigen pH-Wertes in Publikation 1 von minimal 6.34 ± 0.03 wurden für die weiteren Untersuchungen in Publikation 2 und 3 eine Prozess-

Flüssigkeit ohne organische Säuren eingesetzt, was in einem höheren pH-Wert resultierte. Das für die Untersuchungen der Publikationen 2 und 3 verwendete Effluent entstammt der zweiten Reaktorstufe (Festbettreaktor) der gleichen zweistufigen Biogasanlage wie das zuvor verwendete Hydrolysat. Eine Säurekonzentration konnte in diesem Effluent nur vereinzelt in geringem Umfang bis maximal 0.12 ± 0.02 g kg^{-1} in Publikation 2 festgestellt werden.

Bei der Verwendung unterschiedlicher Prozessflüssigkeiten konnte beobachtet werden, dass allein der Einsatz des Effluents die Leistung der Reaktoren bereits verbesserte. Denn trotz gesteigerter Gasdurchsätze um 20 %, bei sonst identischen Betriebsbedingungen der Versuche in Publikation 2, wurde die Gasqualität im Vergleich zu den Versuchen in Publikation 1 deutlich gesteigert.

Hinsichtlich der weiteren bestimmten Parameter der Prozessflüssigkeit, wie CSB, Salinität oder FOS/TAC, wurde im Verlauf der Versuche eine mit den steigenden Durchflussraten auftretende geringfügige Verwässerung sichtbar. Waren sinkende Werte insbesondere der Salinität als Indikator für eine Verwässerung in Publikation 1 trotz längerer Versuchsdauer nicht erkennbar, sank diese im Verlauf der Versuche in Publikation 3 in maximaler Ausprägung von 2.43 ± 0.06 ppt auf 2.17 ± 0.06 ppt. Der Grund wird in den verdoppelten Durchflussraten der Gase und deren deutlich gesteigerten Umsätzen vermutet, welche auch in einer gesteigerten Wasserproduktion resultiert. Ähnliche Untersuchungen bestätigen eine zunehmende Verwässerung der Prozessflüssigkeit bei hohen Durchflussraten (Strübing et al., 2017). Der beobachtete Effekt kann jedoch als unbedenklich erachtet werden, da sich die gemessenen Parameter trotz der geringfügigen Verwässerung in einem für Mikroorganismen optimalen Bereich befanden (Chen et al., 2008). Die Analysen der Prozessflüssigkeit deuteten somit auf einen stabilen biologischen Prozess während der Versuchsdurchführungen.

Für die technische Umsetzung des Reaktorkonzepts sind die Bereitstellung einer geeigneten Prozessflüssigkeit und deren periodischer Austausch essentielle Voraussetzungen für einen stabilen Betrieb. Hierzu sollten ergänzende Untersuchungen durchgeführt werden, so dass eine technische Flüssigkeit gleichbleibender und bekannter Qualität den Betreibern zur Verfügung gestellt werden kann.

5.2. Reaktoreffizienz

5.2.1. Gasqualität

Zur qualitativen Bewertung der Reaktoreffizienz wurden die Konversionsraten von H_2 und CO_2 sowie der Methangehalt bestimmt. Über alle durchgeführten Untersuchungen hinweg kann auch der Einfluss der Relation der Eduktgase auf die Gasqualität und die Konversionseffizienz beurteilt werden – obwohl dieser Betriebsparameter nicht gezielt Gegenstand der Untersuchungen war. Stöchiometrisch betrachtet ist zur vollständigen Umsetzung der Edukt-Gase Kohlenstoffdioxid und Wasserstoff ein Verhältnis von 1:4 erforderlich. Aufgrund technischer Ungenauigkeiten der verwendeten Massendurchflussmesser wichen die real in die Reaktoren eingebrachten Gasverhältnisse geringfügig vom stöchiometrischen Optimum ab, was auch die Konversionsraten der Eduktgase beeinflusste. So wurde in den Untersuchungen der ersten Publikation Kohlenstoffdioxid deutlich überdosiert. Dies führte zu Konversionsraten bei CO_2 von maximal 90.03 ± 0.42% und bei H_2 von maximal 98.02 ± 1.16 %, bei einem Verhältnis von 1 : 3,87 (CO_2 zu H_2.) Mit der Anpassung des Gasverhältnisses in den weiteren Untersuchungen glichen sich auch die Konversionsraten an. So konnten die Konversionsraten von CO_2 und H_2 in Publikation 3 auf 98,10 ± 0,00 % und 99,24 ± 0,00 % gesteigert werden bei einem Verhältnis von 1 : 3,97. Dass für eine vollständige Konversion ein überstöchiometrischen Verhältnis von H_2 zu CO_2 von 1 : 3,76 benötigt wird (Burkhardt et al., 2015), konnte in keiner der drei Publikationen bestätigt werden.

Der Methangehalt des Produktgases ist eng mit den Konversionsraten von Wasserstoff und Kohlenstoffdioxid korreliert. Wurden in Publikation 1 maximal 86,41 Vol.-% CH_4 erreicht, lag dieser Wert in Publikation 2 trotz 20 % gesteigerter Durchflussraten im Maximum bei 97,21 Vol.-%. Bemerkenswert sind die Ergebnisse von Publikation 2 in der Hinsicht, dass mit reduziertem Energieinput infolge reduzierter Pumpaktivität eine deutliche Steigerung der Gasqualität erreicht werden konnte. Insgesamt wurden die Durchflussraten im Verlauf der Versuche nahezu verdoppelt, dennoch wurde in Publikation 3 ein Methangehalt von 94,99 Vol.-% erreicht. Auffällig war außerdem die schnelle Reaktion des Systems auf die sich ändernden Betriebsparameter. In Publikation 1 stiegen die Methangehalte unmittelbar nach den jeweils 24-stündigen Druckaufbauphasen auf ein konstantes Niveau. Ein ähnliches Verhalten wurde auch in Publikation 3 beobachtet. Nach einer 3-stündigen Temperatursteigerung wurden hier die finalen Methangehalte nach weiteren 8 - 10 Stunden erreicht. Ohne auf das Erreichen eines neuen Betriebszustandes warten zu müssen, konnten signifikante Steigerungen des

Methangehaltes in Publikation 2 bereits 1 – 2 Stunden nach dem Aussetzen der Zirkulation beobachtet werden. Die schnellen Reaktionszeiten vor allem in Publikation 2 schließen etwa eine veränderte Mikroorganismenkonzentration oder -selektion als Grund für verbesserte Umsetzungsraten aus und bestätigen die durch die Optimierungsmaßnahme hervorgerufene Steigerung der Gas-Flüssig-Stoffaustauschrate.

Für die technische Umsetzung des Reaktorkonzeptes erscheint es auf Basis der Versuchsergebnisse empfehlenswert, die Steuer- und Regelungstechnik der Reaktoren zu erweitern. In den durchgeführten Untersuchungen wurden H_2 und CO_2 in fest eingestellten Verhältnissen den Reaktoren zugeführt. Aufgrund technischer Limitationen der Massendurchflussmesser wurden die optimalen Gasverhältnisse nicht immer erreicht. Gleichzeitig reagierten die TBR sehr schnell auf veränderte Betriebsparameter. Es erscheint für eine praktische Umsetzung des Konzeptes daher sinnvoll, lediglich eines der Eduktgase (z.B. Kohlenstoffdioxid) mit einem fest eingestellten Volumenstrom zu dosieren und das zweite Gas anhand dessen Konzentration im Produktgasstrom automatisch geregelt zu dosieren. So können unvorteilhafte Eduktgasrelationen vermieden werden.

5.2.2. Leistungsparameter GHSV und MFR

Zur Beschreibung der quantitativen Reaktorleistung wird neben der reaktorspezifischen Methanproduktionsrate (methane formation rate (MFR)), mit welcher die Produktgasmenge beschrieben wird, auch die Gas Hourly Space Velocity (GHSV) hinzugezogen (Götz et al., 2016). Sie beschreibt die Summe der eingespeisten Eduktgase am Reaktoreingang in Relation zum Reaktorvolumen.

Da die Eduktgasmenge im Laufe der Untersuchungen kontinuierlich gesteigert wurde, stieg auch die GHSV. In Publikation 1 wurde mit durchschnittlichen Volumenströmen von 10,92 L h^{-1} und 2,87 L h^{-1} (H_2 und CO_2) eine GHSV von 0,95 ± 0,02 h^{-1} erreicht. In Publikation 3 wurden die Gasmengen auf insgesamt durchschnittlich 21,39 L h^{-1} H_2 und 5,40 L h^{-1} CO_2 erhöht. Somit wurde die Menge an H_2 während der Versuche um insgesamt 95,88 % gesteigert; aufgrund der Anpassung des Gasverhältnisses in stöchiometrischer Richtung wurde die Menge an CO_2 um einen etwas geringeren Anteil von 88,24 % erhöht, womit maximal eine GHSV von 1,85 h^{-1} in Publikation 3 erreicht wurde.

Mit dem Anstieg der Volumenströme der Edukt-Gase konnte durch die Optimierung der Betriebsparameter neben der Produktgasqualität auch die Produktgasquantität deutlich

gesteigert werden. In Publikation 1 wurde eine MFR von 4,28 ± 0,26 m^3 m^{-3} d^{-1} erzielt. Entsprechend dem gesteigerten Gasfluss und einem deutlich höheren Methananteil konnte die MFR in Publikation 3 um mehr als das doppelte auf 8,85 ± 0,43 m^3 m^{-3} d^{-1} gesteigert werden.

Obwohl in allen drei Publikationen die Produktgasqualität durch die Variation der jeweils untersuchten Betriebsparameter signifikant verbessert wurde, konnte eine signifikante Verbesserung der MFR innerhalb der Versuche nicht beobachtet werden. Der Grund wird in der Volumenreduktion um den Faktor 5 bei der Reaktion von H_2 und CO_2 zu CH_4 vermutet. Ein Anstieg der Gasqualität, gekennzeichnet durch hohe Methangehalte, hat somit nur eine geringe Auswirkung auf das Volumen, welches durch die MFR beschrieben wird.

5.3. Schlussfolgerung und Ausblick

Bei der Untersuchung der Betriebsparameter Druck, Zirkulation und Temperatur zur biologischen Wasserstoffmethanisierung in Rieselbettreaktoren offenbarte diese Arbeit ein großes Optimierungspotential. Es konnte nachgewiesen werden, dass die in der Literatur genannten Maßnahmen zur Steigerung der Gas-Flüssig-Stoffaustauschrate auch auf TBR als Reaktorkonzept erfolgreich angewendet werden können.

Die Leistungsfähigkeit bezogen auf die MFR konnte in allen drei Versuchen signifikant gesteigert werden; dabei war es möglich, die Maßnahmen aufeinander aufbauend zu kombinieren um schließlich die Leistungsfähigkeit des Reaktorkonzeptes um mehr als das Doppelte zu steigern.

Die Ergebnisse mit stabilen, kontinuierlichen Methanbildungsraten und einem hohen Methangehalt zeigen, dass TBRs ein vielversprechendes Konzept zur BHM darstellen. Das mit reduzierter Pumpaktivität der Energieinput noch weiter gesenkt und eine deutliche Steigerung der Gasqualität erreicht werden konnte, kann bei einer wirtschaftlichen Umsetzung des Anlagenkonzeptes von hoher Relevanz sein. Somit stellen sie zunehmend eine interessante Alternative für die bisher etablierten CSTR dar.

Die Fortführung der Untersuchungen mit einem auf 9 bar gesteigertem Druck aufbauend auf den Betriebsparametern von Publikation 3 konnte die MFR nochmals auf 12,72 ± 0,23 m^3 m^{-3} d^{-1} steigern bei einem Methangehalt > 95 Vol.-%. Somit wird weiteres Potential zur Leistungssteigerung im Druckbereich > 10 bar erwartet, was in weiteren Untersuchungen quantifiziert werden sollte. Ebenso sollte der Einfluss der eingesetzten

Flüssigkeit auf den Methanisierungsprozess Gegenstand nachfolgender Untersuchungen sein. Als Schwerpunkte sind hier zum einen der Einfluss des pH-Wertes auf die Konversionsraten zu nennen. Ebenso ist vor dem Hintergrund der kontinuierlichen „Verwässerung“ der Prozessflüssigkeit die Entwicklung der Nährstoffzusammensetzung und -konzentration bei hohen Umsetzungsraten von großer Bedeutung. Da sich die Angaben in der Literatur bezüglich des optimalen Gasverhältnisses von H_2 und CO_2 nicht bestätigt haben, sollten auch hier weitere Untersuchungen Klarheit verschaffen.

6. Zusammenfassung

Um die Klimaschutzziele zu erreichen, werden zukünftig vor allem die intermittierenden und dezentralen Energiequellen Windkraft und Photovoltaik ausgebaut. Dies stellt große Herausforderungen an die Stabilität der bestehenden Stromnetze und erfordert eine zunehmende Ausweitung der Energiespeicherung.

Hierzu kann die Power-to-Gas Technologie, ein Verfahren zur Umwandlung elektrischer in chemische Energie, eine zentrale Rolle einnehmen. In einem zweistufigen Prozess wird zunächst Wasserstoff mittels Elektrolyse aus „Überschussstrom“ erzeugt, welcher schließlich mit Kohlenstoffdioxid zu Methan umgewandelt wird. Dieses ist nahezu unbegrenzt im Erdgasnetz speicher- sowie transportierbar und kann flexibel in den unterschiedlichsten Anwendungen genutzt werden.

Neben der chemisch-katalytischen Konversion kann Methan auch durch Mikroorganismen aus Wasserstoff und Kohlenstoffdioxid gebildet werden. Diese biologische Wasserstoff-methanisierung (Biological Hydrogen Methanation (BHM)) zeichnet sich durch ein flexibles Lastwechselverhalten sowie eine ausgeprägte Robustheit hinsichtlich der Eduktgasbeschaffenheit aus. Im Vergleich zur chemisch-katalytischen Methanisierung werden jedoch nur deutlich geringere Gasdurchsätze erreicht, was zur relativ großen Reaktoren führt und als eine der größten Herausforderung dieses Verfahrens gilt.

Aus diesem Grund war es das Ziel dieser Arbeit, Hochdruck-Rieselbettreaktoren zur biologischen Wasserstoffmethanisierung hinsichtlich ihrer Leistungsfähigkeit zu optimieren. Der Fokus lag dazu auf Maßnahmen zur Verbesserung des Gas-Flüssig-Stofftransports, wie sie in der Literatur zwar beschrieben sind, im Zusammenhang mit diesem Konzept jedoch noch nicht untersucht wurden.

Zur Durchführung der experimentellen Untersuchungen wurde eine vollständig automatisierte und kontinuierlich betriebene Versuchsanlage im Labormaßstab neu konzipiert und aufgebaut. In den Untersuchungen der ersten Publikation wurde zunächst der Betriebsdruck in den Stufen 1,5, 5 und 9 bar variiert. Dabei konnten mit steigendem Druck die Konversionsraten erhöht und die relative Gasqualität um 34 % gesteigert werden. Weiterhin wurde in einer weiteren Publikation die Zirkulation der Prozessflüssigkeit auf das Rieselbett der Reaktoren für die Dauer von bis zu 1440 min pausiert. Es zeigte sich eine deutliche Steigerung aller Leistungsparameter bei maximalen Methangehalten > 97 Vol.-% mit steigender Zirkulationspause. Schließlich wurden auch unterschiedliche Temperaturstufen von 40 – 55 °C untersucht. Trotz der kontinuierlichen Steigerung der Gasdurchsätze im Zuge der Publikation konnten auch hier die Leistungsparameter nochmals gesteigert werden. Insgesamt konnte mit der Kombination der Optimierungsmaßnahmen die Leistung bezogen auf die reaktorspezifische Methanproduktionsrate (Methane Formation Rate (MFR)) von 4,28 ± 0,26 m^3 m^{-3} d^{-1} auf 8,85 ± 0,43 m^3 m^{-3} d^{-1} mehr als verdoppelt werden, bei einer gleichzeitigen Steigerung des Methananteils im Produktgas.

Regelmäßige Analysen der Prozessflüssigkeit, insbesondere der Säurekonzentrationen, sowie die konstanten Konversionsraten deuteten in allen Versuchen auf einen stabilen biologischen Prozess hin. Die Durchführung der Versuche mit drei baugleichen Reaktoren unterstreicht zudem eine hohe Reproduzierbarkeit der Ergebnisse. Auffällig war eine schnelle Adaption der Mikroorganismen an die sich ändernden Betriebsparameter innerhalb von maximal 24 Stunden. Die Leistungssteigerungen konnten somit auf die erfolgreiche Steigerung der Gas-Flüssig-Stoffaustauschrate bezogen werden und nicht etwa auf eine veränderte Mikroorganismenkonzentration oder -selektion.

Insgesamt wurde in der vorliegenden Studie das Ziel der Leistungssteigerung des untersuchten Reaktorkonzeptes durch die Optimierung der Prozessparameter erfolgreich nachgewiesen. Die Untersuchungen belegen zudem, dass Hochdruck-Rieselbettreaktoren sehr gut für die biologische Wasserstoffmethanisierung geeignet sind. Dieses Reaktorkonzept zeichnete sich in den vorliegenden Untersuchungen durch einen äußerst stabilen und unkomplizierten Betrieb über mehrere Monate hinweg aus. Damit ist das Verfahren der biologischen Methanisierung von Wasserstoff und Kohlenstoffdioxid in Hochdruck-Rieselbettreaktoren ein zuverlässiges, flexibles und somit vielversprechendes Konzept für Power-to-Gas Anwendungen im technischen Maßstab.

7. Summary

In order to achieve climate protection targets, intermittent and decentralised energy sources such as wind power and photovoltaics will be expanded in the future. However, the power grids are not designed for the large-scale expansion and connection of different decentralised and fluctuating generation plants. This represents a major challenge for grid stability and requires an increasing expansion of energy storage.

Power-to-Gas technology, a process for converting electrical energy into chemical energy, will play a central role in this process. In this two-stage process, hydrogen is first produced by electrolysis, which then reacts with carbon dioxide to form methane. It can be stored and transported in the natural gas grid almost indefinitely and can be used flexibly in a wide variety of applications.

In addition to the chemical-catalytic methanation of hydrogen, there is also the biological methanation process. Characteristic features are a flexible load change behaviour and a marked robustness regarding the educt gas composition. Compared to chemical-catalytic methanation, however, the gas flow rates are significantly lower, which is the greatest challenge of this process.

For this reason, the aim of this work was to optimize the performance of trickle-bed reactors for biological hydrogen methanation. The focus was on improving the gas-liquid-mass-transfer as described in the literature, but not yet which has not yet been investigated in the context of this promising concept.

In an automated and continuous test plant, the operating pressure was initially varied in stages of 1.5, 5 and 9 bar in the first publication. With increasing pressure, conversion rates were improved and gas quality increased by 34%. Furthermore, the circulation of the process liquid to the trickling bed of the reactors was paused for periods up to 1440 min in the second publication. As the circulation pause rose, there was a noticeable increase in all performance parameters with maximum methane contents > 97 Vol.-%. Finally, different temperature levels of 40 - 55 °C were also examined. In spite of the continuous increase in gas volumes in the three publications, the performance parameters increased again. Overall, the combined optimization measures more than doubled the output with an MFR of 4.28 ± 0.26 m^3 m^{-3} d^{-1} to 8.85 ± 0.43 m^3 m^{-3} d^{-1}, while simultaneously increasing the methane content in the product gas.

Periodical analyses of the process liquid, especially the acid concentrations, as well as the stable conversion rates indicated a stable biological process in all experiments. The tests were done with three identical reactors, underlining the high degree of reproducibility. It was noticeable that the microorganisms quickly adapted to the changing operating parameters within a maximum of 24 hours. The performance increases could thus be related to the successful increase in the gas-liquid-substance exchange rate and not to a changed microorganism concentration or selection.

The studies have also revealed further optimisation potential. In particular, the properties of the process liquid with regard to pH and nutrient composition should be the subject of further investigations. Thus, the present study not only successfully demonstrated the goal of increasing performance; with stable and uncomplicated operation over several months and a wide range of operating parameters, it also demonstrated that trickle bed reactors for the biological methanation of hydrogen are a reliable, flexible and thus promising concept in the context of power-to-gas applications.

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