Syngas Fermentation to Alcohols: Reactor Technology and Application Perspective

I. Katharina Stoll*, Nikolaos Boukis, and Jörg Sauer

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Supporting Information available online

One approach of Power-to-X is the coupling of the energy and chemical sector, using electrolysis for syngas generation and microbial gas conversion for the production of biochemicals. On the verge of commercialization, known challenges of gas fermentation technology are poor mass transfer of syngas, low cell concentration and productivity. These problems can be addressed by an intelligent reactor design. Thus, this article provides an overview on the current state of the art for reactor technology in syngas fermentation and discusses possible concepts with regard to an application at industrial scale.

Keywords: Biotechnological CO\textsubscript{2} fixation, Gas fermentation, Power-to-X, Reactor technology, Syngas conversion

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1 Introduction

The reduction of CO\textsubscript{2} emissions is a major target of the German and the European Union climate policy. This effort catalyzes numerous research activities, as for instance the BMBF Kopernikus P2X project. Power-to-X technologies aim at converting electrical energy into chemical energy in form of energy carriers and energy-intensive chemical products. These concepts have the potential to reduce the use of fossil raw materials in the energy, transport and chemicals sectors.

In addition to H\textsubscript{2} generation via well-known H\textsubscript{2}O electrolysis, a CO\textsubscript{2} electrolyser can convert CO\textsubscript{2} to CO by electrochemical reduction [1]. Using only green electricity, water and CO\textsubscript{2} as chemical feedstock is the first step in this Kopernikus P2X value chain, focusing on the production of green chemicals from synthesis gas. Long-term sources of CO\textsubscript{2} include anaerobic fermentation units, power plants, breweries, cement and steel production plants [2]. In cooperation with the Covestro AG, researchers at Siemens AG discovered the potential of a commercially available gas diffusion electrode applied in industrial chlorine-alkaline electrolysis for CO\textsubscript{2} electrolysis. This technology enables a high electric current density, which is required for a technical application [2]. In the low-temperature electrolyser (30–60 °C), CO\textsubscript{2} is electrochemically reduced to CO \textit{(Eq. (1))} at a silver-based gas diffusion cathode. A competing proton reduction also leads to H\textsubscript{2} production. Oxygen is formed at the anode \textit{(Eq. (2))} [2].

\begin{align*}
2\text{CO}_2 + 2\text{H}_2\text{O} + 4\text{e}^- & \rightarrow 2\text{CO} + 4\text{OH}^- \quad \text{(1)} \\
2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{e}^- + 4\text{H}^+ \quad \text{(2)}
\end{align*}

The generated gas mixture of CO, H\textsubscript{2} and unreacted CO\textsubscript{2} is a suitable feedstock for gas fermentation, a biotechnological approach leading to the sustainable production of valuable chemicals that is investigated by Evonik Creavis [2].

The fermentation of synthesis gas is a promising technology, intensively studied up to industrial scale during the last decade. The volumetric productivity of biotechnological reactions is low, that is why an efficient reactor design as well as an active biocatalyst are necessary to enable economic profitability. This article gives an overview of potential reactor concepts for synthesis gas fermentation and provides a comparison in terms of technical application.

2 Fundamentals of Syngas Fermentation

Synthesis gas fermentation enables the microbial production of basic chemicals and fuels. The gas mixture containing H\textsubscript{2}, CO and/or CO\textsubscript{2} is converted by acetogenic bacteria into acetic acid, ethanol or other organic compounds [3]. Various mesophilic and thermophilic microorganisms are suitable for synthesis gas fermentation processes. Acharya et al. [4], Liew et al. [5], Mohammadi et al. [6] as well as

I. Katharina Stoll, Dr. Nikolaos Boukis, Prof. Dr. Jörg Sauer
ina.stoll@kit.edu
Karlsruhe Institute of Technology (KIT), Institute of Catalysis Research and Technology (IKFT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany.
Munasinghe and Khanal [7], among others, provide a detailed list. Suitable gas sources for syngas fermentation include, next to electrochemical syngas generation [2, 8], gasification of biomass and organic waste and exhaust gases from the steel and oil industries [3, 5].

The use of microbiological catalysts for the conversion of synthetic gas offers various advantages over thermochemical conversion such as Fischer-Tropsch synthesis [5, 9]. No high temperatures or pressures are required for the fermentation process, reducing operating and production costs. With regard to the composition of the substrate gas, biocatalysts are significantly more flexible than metal catalysts used in chemical synthesis. On the one hand, microorganisms are less sensitive to impurities contained in the gas mixture and, on the other hand, no specific H2:CO ratio is required for the biological conversion. Therefore, a complex gas composition is not necessary, but a simple gas purification is necessary to achieve an optimal microbial activity. [5, 6, 10]

The microbial conversion of CO, H2 and CO2 to acids and alcohols by acetogenic bacteria is achieved via the reductive acetyl-CoA or Wood-Ljungdahl pathway (WLP) [11]. At first, the intracellular metabolite acetyl-CoA is formed from the gaseous educts via several enzyme-catalyzed reaction steps. Subsequently, metabolic products such as acetic acid and ethanol are formed. A description of the biochemical processes can be found in various review articles, e.g., by Bengelsdorf et al. [12], Phillips et al. [13] or Liew et al. [5]. A detailed report on biochemical details of the autotrophic growth with CO as energy and carbon source was published by Ragsdale [14].

### 2.1 Syngas Fermentation to Medium-Chain Alcohols

Most common products of gas fermentation are acetic acid and ethanol, which can be used as commodity chemicals or fuel. Of economic interest to the chemical industry are higher-value compounds such as butanol and hexanol, which are, therefore, targeted products of Kopernikus P2X. These high-value organic chemicals can be versatilely used, e.g. in coatings, for chemical synthesis as solvents or fuels [2]. Currently, the production of these chemicals is mainly based on oil, which is complex, expensive and not sustainable due to limited resources of fossil energy carriers [2]. Some acetogenic species are able to produce C4 and C6 compounds directly from synthesis gas, e.g., *Clostridium carboxidivorans* [15–17]. Another approach known and pursued in the literature is a two-stage fermentation in which the primary metabolic products, acetate and ethanol, are converted into longer-chain compounds. This chain extension is feasible, for example with *Clostridium kluyveri* [18–20]. In mixed cultures of two or more species, gaseous C1 components can be converted microbially to C4 and C6 chemicals [2, 21–24]. Even the production of C8 compounds (n-caprylate [25] and octanol [24]) was demonstrated. Kopernikus P2X is focusing on butanol and hexanol, using a co-culture of *Clostridium autoethanogenum* and *C. kluyveri*, which converts synthesis gas according to Eqs. (3)–(8) [2]:

#### C. autoethanogenum

\[
2\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_3\text{COO}^- + \text{H}^+ + 2\text{H}_2\text{O} \quad (3)
\]

\[
\text{CH}_3\text{COO}^- + \text{H}^+ + \text{CO} + \text{H}_2 \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{CO}_2 \quad (4)
\]

#### C. kluyveri

\[
\text{CH}_3\text{COO}^- + \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COO}^- + \text{H}_2\text{O} \quad (5)
\]

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{COO}^- + \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COO}^- + \text{H}_2\text{O} \quad (6)
\]

#### C. autoethanogenum

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} + \text{CO} + \text{H}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} + \text{CO}_2 \quad (7)
\]

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH} + \text{CO} + \text{H}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} + \text{CO}_2 \quad (8)
\]

Syngas fermentation presents a very promising platform for biotechnological CO2 fixation in chemicals, but there are still some challenges that need to be addressed. Especially limitations caused by poor gas-liquid mass transfer due to the low solubility of the synthesis gas components, as well as low cell and product concentrations in the fermentation broth [9, 26, 27]. Although globally operating companies such as LanzaTech, INEOS Bio and Coskata Inc. already operate (or operated) various demonstration projects [28], further research and development is essential. The focus lies on the development of a powerful, robust biocatalyst, process parameter optimization, improved reactor design with high gas-liquid mass transfer and efficient downstream processing [29].

The bioreactor as central element is crucial for the successful technical implementation of a biotechnological process. Optimizing the reactor performance is essential in order to reduce process costs and to gain economic viability. The main objective is achieving a high volumetric productivity (kg product per reactor volume and time unit), which is linked to the biocatalyst concentration (cell density) and the flux of CO and H2 into the liquid fermentation broth and the cell itself. Reactor design and operational conditions should, therefore, promote maximum cell functionality. In the following, an overview of possible reactor types for gas fermentation is given and some aspects with regard to a successful technical implementation are discussed.
3 Bioreactor Concepts for Syngas Fermentation

3.1 Basics Types and Configurations

Studies focusing on the comparison of reactor types for synthesis gas fermentation were already performed in the early 1990s [27, 30]. Topics such as reaction-limiting gas-liquid mass transfer (GLMT) and optimization of bioreactor performance are discussed [9, 31]. Generally suitable for synthesis gas fermentation are reactor types such as stirred vessels, bubble columns, gas lift and loop reactors. Reactor concepts with immobilized cells, such as trickle bed or membrane reactors, are also considered as possible alternatives [32]. A schematic description of these reactor types is illustrated in Fig. 1.

In a continuous stirred-tank reactor (CSTR, Fig. 1A) mixing is achieved by mechanical agitation and defined reaction conditions can be easily adjusted. In large fermenters \((V > 500 \text{ m}^3)\), however, sufficient mixing requires an immense increase of energy input [33]. Bubble columns (Fig. 1B) are attractive for industrial processes due to their simple, cost-effective design and the low energy costs. Large reactor volumes are possible but mixing of the liquid phase in a bubble column is limited. Gas lift reactors are a modified version of a bubble column, where the gas entry occurs at the lower end of a riser and causes an upward flow of the liquid phase along with the gas bubbles. The downflow of the gas-free liquid to the reactor bottom takes place in a separated loop (downcomer), because of density differences (Fig. 1C/D). [33]

Because of this loop, gas lift reactors enable a more defined flow profile and improved mixing [34]. A loop reactor can also be realized with an external liquid pump (bubble column with liquid circulation, Fig. 1E) [35]. In the literature, this reactor type is also described as forced circulation loop reactor [36].

Biofilm reactors such as trickle bed or membrane reactors enable a higher cell concentration by fixation of the biocatalyst, as a wash out of the cells is prevented. High gas-liquid transport rates can also be possible. In a trickle bed reactor (Fig. 1F), the biocatalyst is immobilized as a biofilm on suitable packaging material and is brought into contact with substrate gas and liquid nutrient medium. A hollow fiber membrane bioreactor (HFMBR, Fig. 1G) is a special reactor configuration where microporous hollow fiber membranes

![Figure 1](image-url)
are used as gas distributors. Gas molecules diffuse through the membrane to the side of the liquid phase, where the bio-catalyst adheres to the membrane surface as a biofilm [37]. Thus, an HFM module serves both for gas input and as a carrier material for microorganisms and enables a high GLMT rate [29]. Other, more specialized biofilm reactors include the RPB (rotating packed bed biofilm reactor) [38], see Tab. S1 in the Supporting Information, SI or the MBBR (moving bed biofilm reactor), which was developed for wastewater treatment in the late 1980s [39]. The biocatalyst grows on a carrier material suspended in the liquid phase. Gas is introduced via an injection nozzle, which simultaneously mixes the liquid phase, gas and biofilm carrier (Fig. 1H) [40].

Suitable for gas fermentation are reactor systems that can achieve high mass transfer rates and cell concentrations in an energy-efficient manner [9, 27]. The reactor types presented in Fig. 1 have been investigated in various laboratory studies [30, 38, 43–63]. A detailed overview of these studies describing reactor type, operational conditions and results is given in the Supporting Information (Tab. S1).

In comparison to aerobic heterotrophic bioprocesses, cell growth and biocatalytic activities of acetogens employed in syngas fermentation are restricted, leading to low overall volumetric productivities [64]. Therefore, syngas fermentation at commercial scale can only be economically feasible with a simpler process design and cost-effective control technology [32]. A continuous mode of operation is also advisable, as a higher reactor productivity is achievable than in batch fermentations [43]. Additionally, a two- or multi-stage system could be advantageous in terms of improved process control: Separating growth and productivity stages (acidogenesis and solventogenesis) and optimizing the respective process parameters can increase reactor productivity [32, 52, 65].

In general, a technical reactor concept for syngas fermentation should have a simple structure and generate high gas-liquid mass transfer rates with the lowest possible energy input. Important criteria for the selection of a reactor for are, thus, achievable gas-liquid mass transfer rates, investment and operating costs (energy input) as well as application perspective and scale-up possibilities.

### 3.2 Gas-Liquid Mass Transfer and Energy Input

The gas-liquid mass transfer as a reaction-limiting factor of synthesis gas fermentation receives special attention in the literature [9, 27, 66, 67]. In the fermenter, there is a three-phase system consisting of the gaseous substrate mixture, the liquid nutrient solution and the bacteria cells suspended in the fermentation broth. Various diffusion processes in the gas and liquid phase, as well as the transition at the phase boundary determine the transport resistance and the transfer of gas molecules to the metabolic sites of the microorganisms. The major transport barrier for poorly soluble gases lies in the liquid film at the gas-liquid phase boundary. [27, 68]

The volumetric substrate transfer rate into the fermentation broth can be calculated according to Eq. (9) [27]:

$$\frac{1}{V_L} \frac{dN_G}{dt} = \frac{k_{L,a}(p_G - p_L)}{H}$$

Here, $N_G$ is the mole amount substrate transferred from the gas phase, $V_L$ the liquid volume in the reactor, $k_{L,a}$ describes the volumetric mass transfer coefficient and $H$ the Henry solubility constant. $p_G$ and $p_L$ represent the partial pressure of a substrate component in the bulk gas phase and the partial pressure (dissolved tension) of the substrate in the liquid phase [27]. Eq. (9) also shows the proportional dependence of the transfer rate on the partial pressure of the substrate gas. With increasing partial pressure, the gas transfer into the nutrient solution can be enhanced, as gas solubility is increased according to Henry’s law. A higher process pressure can, therefore, be useful to improve the gas solubility and, thus, the availability of the gaseous substrate for the biocatalyst. So far, the highest ethanol productivity reported (369 g L$^{-1}$d$^{-1}$) was achieved with *Clostridium ljungdahlii* C-01 in a CSTR with an operating pressure of 6 atm [44]. Hurst and Lewis showed that an increase in $p_{CO}$ from 0.35 atm to 2.0 atm increased cell mass of *C. carboxidivorans* by 440 %, also leading to a considerable rise in ethanol concentration [69]. In general, a mildly increased pressure appears to be reasonable in gas fermentation [8, 65, 70] and the increase of total pressure or the partial pressure of a gas component has been investigated in different fermentation systems [27, 69, 71–84]. However, the impact of pressure increase is not fully understood and in order to avoid possible substrate inhibition, a balance between mass transfer and substrate consumption of the bacterial cells has to be found [9].

In addition to pressurization, several strategies to increase GLMT are discussed in literature. An overview is provided by Yasin et al. [85] and Sun et al. [86], examples include impeller configuration, gas supply systems, nanoparticles to increase the dissolved gas concentration by adsorption, electrolytes (or salts) to maintain microbubbles, surface active agents such as polymers, nanoparticles, antifoams and other chemicals to suppress bubble coalescence or vibrational techniques for microbubble generation [85, 86].

The volumetric mass transfer coefficient $k_{L,a}$ is commonly employed for assessing the mass transfer properties of a reaction system. A general range of $k_{L,a}$ values for different reactor configurations was summarized by Bredwell et al. [9] (after Charpentier [87]) and has been extended also for HFMFRs in Tab. 1.

As gas-liquid mass transfer is considered as a reaction-limiting factor of gas fermentation, a high level of research activity with regard to $k_{L,a}$ measurements in different reactor configurations can be observed in this context [66, 67, 88, 90–92]. A description of various studies on $k_{L,a}$
Table 1. $k_\alpha$ range for different reactor types [9, 87].

| Reactor type                  | $k_\alpha$ [h$^{-1}$] |
|-------------------------------|-----------------------|
| Bubble column                 | 18–860                |
| Packed bubble columns         | 18–430                |
| Packed columns – cocurrent    | 1.5–3670              |
| Packed columns – trickle flow | 36–360                |
| Bubble column – microbubble sparged$^a$ | 200–1800            |
| HFMBR$^b$                     | 0.4–1096              |

$^a$[88], $^b$[37, 57, 59, 66, 67, 89]

The specific energy input $P/V$ is linked with the volumetric mass transfer coefficient $k_\alpha$ in various empirically determined correlations. Van’t Riet summarizes several studies on $k_\alpha$ correlations in stirred vessels [101]. Chisti describes $k_\alpha$ correlations for gas lift reactors of various dimensions (8.7 L–5.7 m$^3$) and different fluids (water/salt solution) [34]. An overview of correlations for gas lift reactors and bubble columns can also be found in Bello et al. [102]. For a given system, these correlations allow the prediction of $k_\alpha$ values as a function of energy input and other operating parameters (e.g., gas velocity). However, since many measurements are performed in water, the accuracy when applied to biotechnological systems is usually low. Here, mass transfer is strongly influenced by the components contained in fermentation media (substrates, products, salts, surface-active substances, cells). [33]

In addition, many correlations have a limited range of validity and other different operating variables besides the specific energy input such as gas velocity or gas content often play an important role, making it difficult to compare different reactor types.

According to Takors et al., an suitable specific energy input for a gas fermentation process is in the range of $<0.3 \text{ kW m}^{-3}$ [64]. Typical $P/V$ ratios for aerated stirred tanks are in the order of $1 \text{ kW m}^{-3}$ [9], in laboratory studies, even higher values are common (e.g., Kantzow et al.: $11.9 \text{ kW m}^{-3}$ [47]). Bredwell and Worden [88] reported a high efficiency ($0.01 \text{ kW m}^{-3}$) for a bubble column with microbubble dispersion. However, the axial mixing of microbubbles is lower compared to standard bubble columns [88].

$3.3\text{ Commercialization of Syngas Fermentation and Patents}$

In addition to research activities of various universities, three companies are known for their gas fermentation pilot plants: INEOS Bio, Coskata Inc. and LanzaTech [5, 28, 95].
INEOS Bio was established in 2008 [95] with the acquisition of Bioengineering Resources Inc. (BRI) by the INEOS Group [5]. BRI was founded by James L. Gaddy, Professor at the University of Arkansas and pioneer in gas fermentation research. In 2003, BRI started operating a pilot plant, being the first company to realize gas fermentation on an industrial scale [5, 17]. In 2011, a project cooperation with New Planet Energy followed with the construction of a semi-commercial plant near Vero Beach, Florida. The process concept aimed at the production of bioethanol by fermentation of synthesis gas from the gasification of plant and municipal waste. At the end of 2012, the INEOS biorefinery went into operation with an ethanol capacity of approx. 23.7 kt a⁻¹ and an additional electricity production of 6 MW. [103]. After one year, problems with the fermentation process were reported due to HCN content in the biogenic syngas [104, 105]. In December 2014, the HCN scrubbing installation was shut down [106]. Almost two years later, INEOS Bio announced the sale of the plant in Vero Beach [107]. The contract was awarded to Alliance Bio-Products Inc. in mid-2017 [95].

Coskata Inc. was founded in 2006 with close ties to the University of Oklahoma. Originally also focused on the biomass feedstock, the company strategy shifted to synthesis gas from methane reforming [5, 28]. In April 2008, Coskata announced the construction of a demonstration plant [108]. The plant in Pennsylvania with an ethanol capacity of 118 t a⁻¹ was operated from October 2009 to Autumn 2011 [109]. In 2015, Coskata abandoned its gas fermentation technology and was acquired by Synata Bio in early 2016 [28, 110]. Since then, there have been no reports of the company’s activities.

LanzaTech, founded by Sean Simpson and Richard Forster in 2005, is the pioneer in the field of synthesis gas fermentation. The LanzaTech process focuses on the conversion of CO-containing industrial exhaust gases, in particular exhaust gases from steel mills. After a first pilot plant (2008) at a steel mill in Glenbrook, New Zealand, LanzaTech started cooperations with Chinese steel manufacturers. Two demonstration plants with a capacity of 300 Mt a⁻¹ ethanol each went into operation in 2012 and 2013, respectively (BaoSteel, Shanghai and Shougang, Beijing). Now based in the USA, LanzaTech has a strong international network and plans several commercial gas fermentation plants in the coming years. Together with the steel producer ArcelorMittal, the company is building a plant with a capacity of 62 000 Mt a⁻¹ ethanol in Belgium. In China (Shougang) and South Africa (Swayana), plants with capacities of 48 000 and 52 000 Mt a⁻¹, respectively, are to go into operation by 2020. In addition to the steel industry, LanzaTech is also moving towards the mineral oil industry (Indian Oil Corp. Ltd.) and the biomass sector. In California, the first LanzaTech plant with biogenic synthesis gas, produced from agricultural and forestry waste, is being built in cooperation with Aemetis [111, 112]. The development of the company is described in detail by Karlson et al. [111].

LanzaTech is highly active in research and holds numerous patents. The company uses a specially developed microorganism and is involved in metabolic engineering [113–116]. There is great interest in alternative products in addition to ethanol [117–120]. Sun et al. provide a description of patents in the field of synthesis gas fermentation with focus on microorganisms and gene manipulation, process development and control as well as reactor design [86]. Selected examples for reactor design and process development are [32, 40–42, 44, 72, 93, 121–128]. Reports on synthesis gas fermentation with a reactor scale > 5 L can be found almost exclusively in patent examples (Tab. 2), with the exception of the 75-L STR of Oklahoma State University [51]. To our knowledge, process details for existing pilot plants have not been published to date.

3.4 Reactor Concept for Commercial Syngas Fermentation – A Summary

Many reaction-engineering investigations on synthesis gas fermentation are performed in a stirred tank reactor, continuously operated or in batch mode. However, these studies are often focusing on basic research, e.g., on the influence of various process parameters, but not on the development of an optimized reactor configuration. In literature, a CSTR is, thus, often named the most common reactor type for synthesis gas fermentation [4, 7], even though it is excluded for industrial-scale due to the high power demand [4, 5, 29] (usually citing Bredwell et al. [9]). A high specific energy input is difficult with regard to an economic scale-up, especially for low value-added products such as C2 alcohols or acids [64]. Accordingly, reactor types with a lower specific energy input, without moving internals, have a higher application potential.

The simplest alternatives are bubble columns or gas lift reactors. According to current knowledge, only a few studies have been published on gas fermentation with these reactor types (see Tab. 2 and Tab. S1). The flow conditions are complex and axial gradients with respect to the partial pressures of the gas components as well as the concentrations of biomass, products and pH in the liquid phase along the height of the reactor are very likely. Additionally, in GLRs, the gas void fraction in the downcomer area is low, which could eventually lead to substrate limitation. Improved mixing of the liquid phase and higher k_La values are possible by circulating the fermentation broth with an external pump (bubble column with circulation or loop reactor), which is why this configuration is more frequently found in literature (see SI, Tabs. S1 and S2).

A downside of continuously operated bioreactors with suspended cells is a wash out of the biocatalyst, so that high cell densities can only be achieved with additional retention methods. This is one reason for the increased research activity regarding biofilm reactors with immobilized cells [95]. Due to the high mass transfer rates at low operating
The use of HFMBRs due to their high mass transfer rates is available. Additionally, hardly any research data existations, such as the rotating bed biofilm reactor or the moving bed biofilm reactor. Another point is the long-term stability of the membrane module under real fermentation conditions. Biofouling and other process-related problems can reduce reactor productivity. In their patent, Datta et al. report a decrease in productivity after 361 h due to pore wetting in the porous membrane layer. The energy-efficient gas input via the membrane module is considered a major advantage, but the structure of this reactor configuration is relatively complex. The mass transfer in an HFMBR is improved if the membrane module is located outside the vessel. This results in the need for an additional reservoir and a pump to circulate the liquid phase, which increases operating costs. If liquid circulation is waived, inhomogeneities and reduced reactor productivity may be the consequence.

Detailed data on the reactor design and performance of pilot plants for synthesis gas fermentation are not available in literature. Patent specifications and information articles indicate the use of CSTR (BRI/Ineos Bio) and loop reactor (LanzaTech). Coskata presumably operated a reactor with HFMB module, but no reports on reactors with a volume >10 L are published. The pilot plants of Ineos Bio and Coskata are no longer in operation, solely LanzaTech is still successful at larger scale. Takors et al. name a “continuously operated bubble column/gas lift loop reactor” as reactor

| Reactor type                      | Volume | Description                                                                                                           | Ref. |
|----------------------------------|--------|-----------------------------------------------------------------------------------------------------------------------|------|
| CSTR                             | 160 L  | Fermentation of flue gas with Clostridium ljungdahlii ERI2 ATCC 55380, stirring tank with operating pressure up to 6 bar, 322 rpm, 13.2 g L⁻¹ acetate (diffusion rate D = 1.05 h⁻¹). Membrane module for cell retention. | [72] |
| Trickle bed reactor              | 144 L  | Fermentation of flue gas with C. ljungdahlii ERI2 ATCC 55380, direct current operation with liquid phase circulation, operating pressure 1.58 bar, 6.4 g L⁻¹ acetate at D = 0.57 h⁻¹. Membrane module for cell retention. | [72] |
| HFMBR                            | 10 L   | Fermentation of an H₂/CO/CO₂ mixture with Clostridium ragdalei ATCC BAA-622. Hollow fiber membrane module: thin, liquid impermeable layer between two porous layers. Stirred tank (100 rpm) as liquid reservoir for circulation. After t > 360 h, pore wetting leads to a reduction in gas consumption and ethanol productivity. | [41] |
| HFMBR                            | 7.5 L  | Fermentation of an H₂/CO/CO₂ mixture with C. ragdalei ATCC BAA-622. Membrane module with hydrophilic hollow fibers. Stirred tank (100 rpm) as liquid reservoir for circulation. Biofilm layer: 30–40 μm. Decrease in productivity after t > 400 h. | [124] |
| Loop reactor                     | 71 L   | Fermentation of steel mill exhaust gas with C. autoethanogenum DSMZ 19630. Loop reactor with external pump for the circulation of the liquid phase. Gas-liquid contact zone to improve mass transport (various packing materials, static mixers or other internals). Ethanol productivity up to 23.9 g L⁻¹ d⁻¹. | [93] |
| Gas lift reactor                 | 50 L   | Fermentation of steel mill exhaust gas with C. autoethanogenum DSMZ 10061 or DSMZ 19630. Mixing in the reactor by recirculation of the gas phase (15 L min⁻¹). Fresh gas supply 0.5–1 L min⁻¹. | [126] |
| Forced-circulation loop reactor  | 390 L  | Fermentation of a mixture of H₂, CO and CO₂ with C. autoethanogenum DSMZ 19630. The reactor consists of a riser (80 % of the total reactor volume) and a downcomer area with external pump. An additional recirculation loop leads to an improved gas conversion. | [42] |
| Moving bed biofilm reactor       | 9800 L | Fermentation of a mixture of H₂, CO and CO₂ with C. ragdalei ATCC BAA-622. Gas flow: 15 L min⁻¹, liquid recycle flow rate: 400 L min⁻¹. Biomass carrier: polymer (AnoxKaldnes K1). Ethanol productivity up to 26.6 g L⁻¹ d⁻¹ after 30 days of continuous operation. | [40] |

Table 2. Patent examples: reactor types for synthesis gas fermentation.
type for the planned industrial plant in Ghent, Belgium [64]. A loop reactor or a bubble column with circulation of the fermentation broth is expected to be an advantageous concept for the commercial realization of syngas fermentation. A standard column with circulation pump requires a relatively low investment and the forced circulation enables adequate mixing of the liquid phase and GLMT rates. The required power input is determined by the flow rate of the pump and the substrate gas volume flow. In order to avoid high energy costs, GLMT should be optimized not by the conventional increase of gas or liquid flow rates but, e.g., by installing internal packings [93], improved gas delivery systems [85, 127] or using other supporting technologies [85]. An increased mass transfer driving force by moderate pressurization is additionally advisable [64, 85], as the enhanced solubility at higher pressure improves substrate gas availability for the biocatalyst.

4 Conclusion and Outlook

This study provides an overview on reactor technology and considerations with regard to a commercial realization of syngas fermentation. Promising are loop reactors or similar bubble column, optimized for adequate, energy-efficient gas-liquid mass transfer. With this target in mind, future investigations should focus on appropriate strategies, for example an increased process pressure. Here, additional research is essential to fill existing knowledge gaps and to allow a solid process design. Existing challenges include productivity, reactor scalability and particularly the economic implementation at industrial scale. Therefore, a detailed look into scale-up considerations for syngas fermentation is recommendable for future studies.

P2X technologies are part of a sustainable future where fossil resources will no longer be the major source of energy. The coupling of electrolysis using green electricity and biotechnological CO₂ fixation via fermentation is one sustainable alternative with great potential. A next step in this direction is a satellite of Kopernikus P2X, Rheticus. This 2.8-million Euro project is a joint research project launched in January 2018 by Evonik and Siemens to produce valuable specialty chemicals from carbon dioxide and green electricity. In the Rheticus project, both steps – electrolysis and fermentation – are brought together on a laboratory scale in a technical pilot plant. [130, 131].

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I. Katharina Stoll began her studies of Chemical Engineering at the Karlsruhe Institute of Technology (KIT) in 2010 and received her Master’s degree in 2016. Afterwards, she started as a PhD student at the Institute for Catalysis Research and Technology (IKFT), where she is working on process development in the field of synthesis gas fermentation, with focus on the influence of increased pressure. This research is done in cooperation with Evonik Creavis and is embedded in the national BMBF project Kopernikus P2X.

Nikolaos Boukis studied Chemistry at the University of Athens (NKUA). He completed his doctorate in 1985 at the Ruprecht-Karls-Universität Heidelberg and the Nuclear Research Centre Karlsruhe, Institute for Hot Chemistry (IHCh, today KIT – IKFT). After his doctorate, he was called up for military service and did research at the Greek National Defense Research Center. Subsequently, he has worked in the field of spent nuclear fuel reprocessing at the former IHCh. Since 1992, he has been in charge of application-oriented work in the field of supercritical water (reactor material corrosion and biomass gasification) and since 2016 also in the field of microbial fermentation of synthesis gas at high pressure.
Jörg Sauer studied Chemical Engineering at the Friedrich-Alexander University of Erlangen-Nürnberg and earned his PhD at the University of Karlsruhe, now KIT, in 1994. He had different managerial positions in industry, at Degussa, later Evonik Industries AG, in the areas of research & development, production and process technology & engineering. As his last position, he served as head of the department Chemical Reaction Technology in Marl before he was appointed as full professor of Process Technology and Catalysis and head of IKFT in 2012. His research includes chemical reaction engineering, scale-up, catalyst manufacturing, applied catalysis in the field of renewable derived fuels and technologies for circular carbon economy.

### Symbols used

| Symbol | Unit | Description |
|--------|------|-------------|
| \(d\) | [m] | diameter |
| \(D\) | [h\(^{-1}\)] | dilution rate |
| \(g\) | [m s\(^{-2}\)] | acceleration due to gravity |
| \(h\) | [m] | height |
| \(h_L\) | [m] | height of the liquid phase |
| \(H\) | [M bar\(^{-1}\)] | Henry solubility constant |
| \(k_L a\) | [h\(^{-1}\)] | volumetric mass transfer coefficient |
| \(n\) | [s\(^{-1}\)] | stirrer speed |
| \(N_G\) | [mol] | amount of transferred substrate |
| \(N_G\) | [mol s\(^{-1}\)] | molar gas flow rate |
| \(N_e\) | [-] | Newton number |
| \(p_G\) | [bar] | partial pressure of a substrate gas component in the bulk gas phase |
| \(p_{G,in}\) | [bar] | inlet gas pressure |
| \(p_{h}\) | [bar] | reactor headspace pressure |
| \(p_L\) | [bar] | partial pressure (dissolved tension) of a substrate gas component in the liquid phase |
| \(P\) | [W] | power |
| \(P/V^*\) | [W m\(^{-3}\)] | volumetric power input |
| \(R\) | [J mol\(^{-1}\)K\(^{-1}\)] | universal gas constant |
| \(Re\) | [-] | Reynolds number |
| \(R_p\) | [g L\(^{-1}\)h\(^{-1}\)] | volumetric productivity |
| \(T\) | [K] | temperature |
| \(t\) | [h] | (run)time |
| \(V\) | [L] | volume |
| \(V_G\) | [m\(^3\) s\(^{-1}\)] | gas volume flow |

### Greek letters

| Symbol | Description |
|--------|-------------|
| \(\beta\) | [g L\(^{-1}\)] | mass concentration |
| \(\rho_L\) | [kg m\(^{-3}\)] | density of the liquid phase |
| \(\eta\) | [-] | efficiency |

### Sub- and Superscripts

| Symbol | Description |
|--------|-------------|
| \(G\) | gas |
| \(G_{in}\) | gas inlet |
| \(h\) | headspace |
| \(max\) | maximum |
| \(L\) | liquid |
| \(P\) | productivity |
| \(R\) | reactor |

### Abbreviations

- acetyl-CoA: acetyl coenzyme A
- BC: bubble column
- BRI: Bioengineering Resources Inc.
- CSTR: continuous stirred-tank reactor
- GLMT: gas-liquid mass transfer
- GLR: gas lift reactor
- HF: hollow fiber
- HFM: hollow fiber membrane
- HFMBR: hollow fiber membrane bioreactor
- MBR: monolithic biofilm reactor
- MBBR: moving bed biofilm reactor
- n/a: not available
- P2X: Power-to-X
- RPB: rotating bed biofilm reactor
- STR: stirred-tank reactor
- TBR: trickle bed reactor
- WLP: Wood-Ljungahl pathway

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