INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 49 (2024) 943–961

Available online at www.sciencedirect.com

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Technology transfer from fuel processing for fuel cells to fuel synthesis from hydrogen and carbon dioxide

Ralf Peters [a,b,*], *Joachim Pasel* [a], *Remzi Can Samsun* [a]

[a] *Institute of Energy and Climate Research - Electrochemical Process Engineering (IEK-14), Forschungszentrum Jülich GmbH, Wilhelm-Johnen-Str., 52428, Jülich, Germany*

[b] *JARA-ENERGY, 52056 Aachen, Germany*

HIGHLIGHTS

- Shift of research topics to synthetic fuels applying existing knowledge in fuel processing.
- Fuel processing reactors are applicable in synthetic fuel systems.
- WGS reactor adapted to product gas inlet values from a pyrolysis reactor with 15–29 vol% CO.
- High performance catalytic burners offers no detectable CO and ultralow NO_x emissions.

ARTICLE INFO

Article history:
Received 10 May 2023
Received in revised form
21 July 2023
Accepted 2 August 2023
Available online 22 August 2023

Keywords:
Fuel processing
water-gas shift reactor
catalytic burner
autothermal reformer
power to fuel
technolgy transfer

ABSTRACT

Improving the energy efficiency of existing technologies such as the on-board power supply of trucks, ships, and aircraft is an important endeavor for reducing primary energy consumption. The approach consists of using fuel cell technology in conjunction with hydrogen production from liquid fuels. However, the energy transition, with the goal of complete climate-neutrality, requires technological changes in the use of hydrogen produced from renewable energy via electrolysis. Synthetic fuels are an important building block for drive systems that will continue to require liquid energy carriers in the future due to their range. This study addresses the question of whether technical devices that were developed for the generation of hydrogen from liquid fuels for fuel cells to generate electricity are now suitable for the reverse process chain or can play an important role in it. The new process chain produces hydrogen from sustainable electricity, combining it with carbon dioxide, to create a synthetic liquid fuel.

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* *Corresponding author*. Institute of Energy and Climate Research - Electrochemical Process Engineering (IEK-14), Forschungszentrum Jülich GmbH, Wilhelm-Johnen-Str., 52428, Jülich, Germany.

E-mail address: ra.peters@fz-juelich.de (R. Peters).

https://doi.org/10.1016/j.ijhydene.2023.08.022

1. Introduction

1.1. Background

Germany's total oil consumption in 2019 was around 87 million tons of crude oil, plus 16.2 million tons of mineral oil products as feedstock [1], adding up to around 103 million tons. Gutte et al. [2] determined that this amount would yield about 90.8 million tons of carbon, assuming a carbon content of 86.5 %mass for crude oil. A refinery produces a broad spectrum of fuels, intermediates, and special chemicals. Fig. 1 A) portrays the inland sales in Germany of refinery products in 2019. About half of the tonnage was made up of gasoline and diesel fuels. In addition, a small proportion (approximately 10%) comprised aviation turbine fuels. The proportion of heating oil was approximately 15%. The remaining 25% belonged to fuel components and naphtha, together adding up to approximately 16%, and finally with bitumen, waxes, coal, lubricants, and other products. Naphtha and gases are highly important intermediates for the chemical industry, especially butene and aromatic compounds.

If the 90.8 million tons of carbon were to be burned, 333 million tons of carbon dioxide would be released. In view of the fact that 75% of the petroleum products are used either as fuels or as a heating medium, the release of more than 250 million tons is realistic and, unfortunately, highly significant. In the course of reducing greenhouse gases, the amount of carbon used must be replaced in the long term by sustainable carbon sources or other technologies must be used in end user applications. Such measures will reduce or replace the need for these refinery products in the long term. Fig. 1 B) lists different measures for the de-fossilization of today's petroleum oil products.

Each sector of the corresponding petroleum oil product must be discussed separately. Gasoline and diesel were utilized in internal combustion engines (ICEs). A remarkable shift to electric transportation (e-transport) deducts a broad share of the carbon dioxide released by ICEs. E-transport can be realized by either battery–electric vehicles (BEVs) or fuel cell–electric vehicles (FCEVs) that use hydrogen as fuel. A higher share of public transport use leads directly to less energy consumption. The role of autonomous driving combined with driverless taxis or car-sharing is difficult to predict, as well as its effects on greenhouse gas emissions. Today, it is already apparent that the share of hybrid vehicles will increase in the future. For heavy-duty transportation, further options must be considered, such as the use of catenary systems hybridized with batteries or diesel-driven ICEs. Electro-fuels or power-to-fuel products will play an important role if high energy densities in fuel for long-distance transport are required.

With respect to the intensive use of heating oil in domestic heating systems, the first measure would be to improve the thermal insulation of buildings in order to reduce their heating requirements. The application of heat pumps and photovoltaic systems reduces the use of combustion processes. Ultimately, it is viable to use natural gas, as the hydrogen-to-carbon ratio is higher than in heating oil. This option is largely only meaningful when biogas is used.

At 10%, the market share of jet fuel is significantly smaller than the shares of gasoline and diesel, but with respect to the use of jet engines, no long-term alternatives are apparent, especially for medium-sized and large aircraft. Therefore, only a switch to liquid fuels of renewable origin such as bio-kerosene and power-to-jet fuel will succeed.

The important market segments of heavy fuel oil, fuel components, and naphtha are also to be provided by the Power-to-X technology. Finally, the latter segments, and that of jet fuel, add up to a 26% share, leading to 28 million tons of refinery products. In addition, a portion of total diesel fuel cannot be substituted due its application, for example, in long-haul heavy-duty trucks.

In the next sections, technologies will be discussed that can contribute to the reduction of carbon dioxide emissions in the area of fuels. It is pointed out that the basic orientation of research and development tasks can change in the overall context of a future energy system, but that special innovative developments of a single orientation can still be made applicable and useable in systems with other orientations.

1.2. Greenhouse gas reduction potential of innovative fuel technologies

In this sub-section, two cases are discussed that result in a reduction in CO_2 emissions, but which are subject to a different focus of research and development work.

a) On-board power supply systems (APUs: auxiliary power units) were developed in order to improve the low efficiency of the main ICEs and/or jet engines operated for electricity generation during idling. These values are approximately 10% for truck applications and 15% for aircraft. The implementation of fuel cell systems based on the transportation fuel, combined with catalytic exhaust gas systems, enables lower CO, NO_x, and particle matter emissions. Moreover, noise is also reduced. This is an especially viable item for maritime applications in harbors. Detailed information is presented in Peters et al. [3,4].
b) A complete switch from fossil fuels to renewable ones reduces greenhouse gas emissions to values near to zero. Such synthetic fuels have lower CO, NO_x, and particle matter emissions. Unfortunately, the process chain from well-to-tank of an electro-fuel is 35–55%, including an efficiency of 70% for polymer electrolyte electrolysis; see Schemme et al. [5,6].

Fig. 2 illustrates both technologies in the case of truck applications. The APU case also opens the possibility of using a variety of fuels, i.e., fossil fuels, bio fuels, and electro-fuels. The question arises as to which technology will lead to more greenhouse gas emissions. Are these technologies truly competing or can they finally be combined?

In order to evaluate the effects, two markets for diesel and jet fuel were considered, namely the U.S. and German fuel markets. Data were taken from Refs. [7–10]. Fig. 3 shows the market share of truck diesel and jet fuel in the United States and Germany. The amount of diesel demand increased slightly from 100 million tons to 130 million tons between 2000 and 2019, with an intermediate decrease to 110 million tons

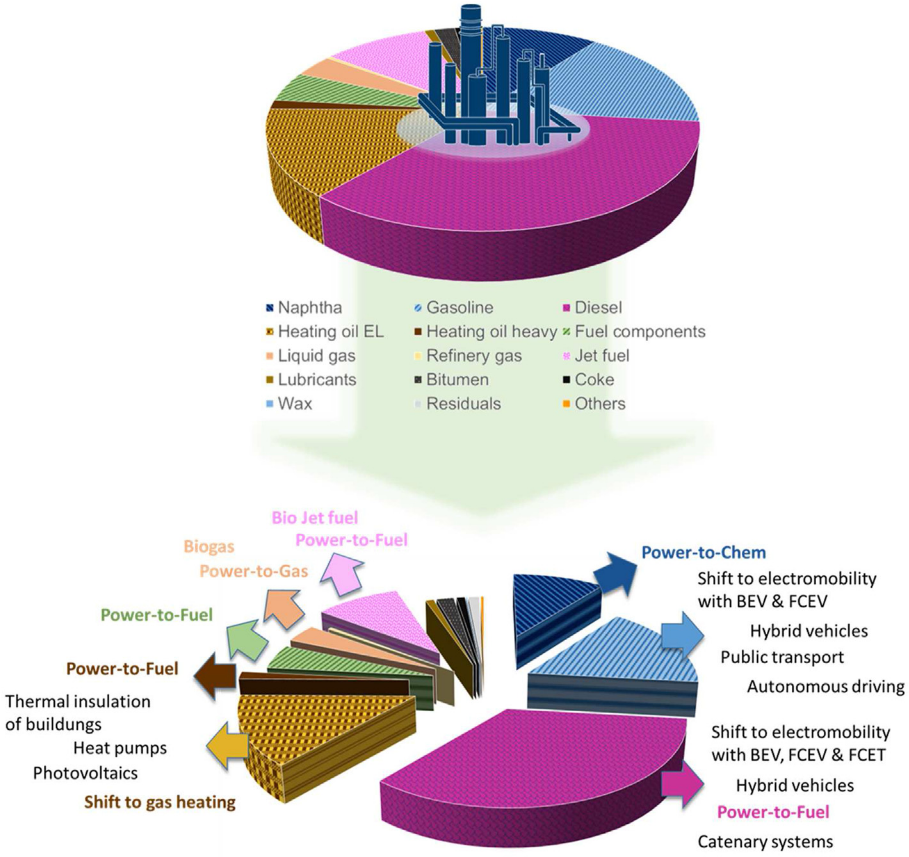

Fig. 1 – Refinery products in Germany. A) Inland sales in 2019 [1]. The volume of products amounts to 109 million tons, corrected due to recycling to 103 million tons in total. B) Measures for the de-fossilization of today's petroleum oil products.

from 2007 to 2009. Jet fuel demand amounted to a minimum of 62 million tons in 2010 and 80 million tons in 2000 and 2020. For the same period, jet fuel consumption increased from 7.5 million to 12 million tons in Germany. In 2020 the consumption dropped suddenly, to 5.5 million, tons due to the COVID-19 pandemic. The diesel demand for trucks was nearly constant at 16 million tons/a in Germany.

It is interesting to compare the CO_2 emissions related to the applications that are illustrated in Fig. 2. APU use in long-haul heavy-duty trucks saw its original academic attention in the U.S.A. Detailed information about such APUs were presented by Peters [3] for light-duty vehicles and trucks and for ships and aircraft by Peters and Westenberger [4]. Assumptions were drawn regarding total CO_2 emissions using data from Lim [11] for trucks in 2002 and Srinivisan et al. [11,12] for aircraft in 2006. Finally, trucks emitted approximately 10.8 million tons of CO_2 and aircraft about 6.8 million tons CO_2 in APU applications alone. In comparison to those numbers, the complete CO_2 emissions for operating trucks and aircraft in Germany amount to 35 million and 50 million tons of CO_2, respectively. If the efficiency targets of 40% for a fuel cell-based APU system can be achieved and if an average

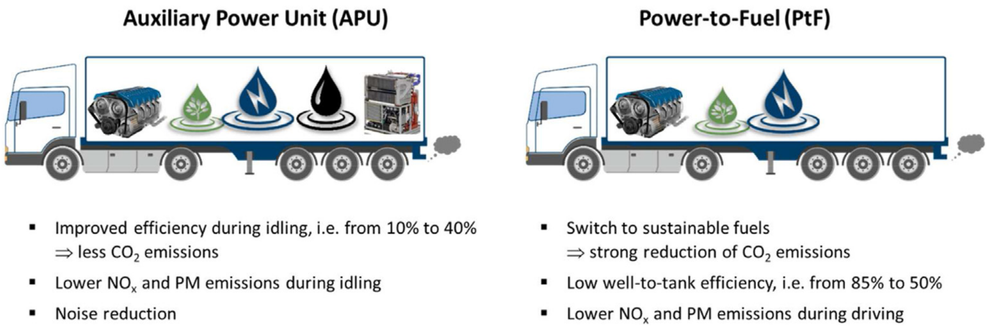

Fig. 2 – Innovative fuel technologies for truck applications.

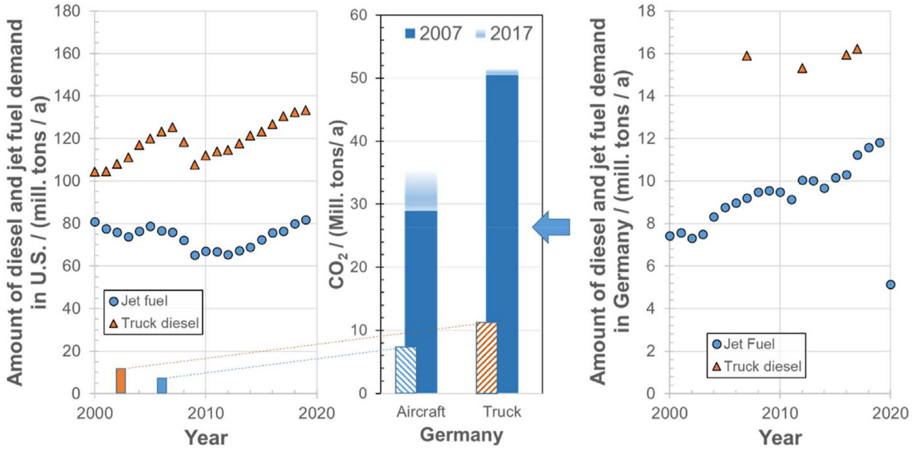

Fig. 3 – Market share of truck diesel and jet fuel in the United States and Germany. Impact of APU usage for trucks and aircraft in the US on total CO_2 emission in comparison to German fuel usage for the corresponding drivetrains. Data taken from Refs. [7–10].

efficiency of 10% for trucks and 15% for aircraft during idling is assumed, CO_2 savings of 70% can be gained in the U.S.A., i.e., a reduction from 17.6 million tons to 5.3 million. The CO_2 savings of 12.3 million tons for US APU systems in trucks and aircraft can be compared with the total fuel requirements for propulsion in the same categories in Germany, which total 85 million tons, i.e., a factor of nearly seven.

In general, it is difficult to evaluate both applications on a common basis, as they are utilized at different points in the energy system. In the case of the APU application, the energy efficiency is improved and so four million tons of middle distillate can be saved. With a production efficiency of the fossil chain of approximately 86–91% [13,14], this corresponds to a reduced primary energy demand of 55 TWh/a. A switch to biofuels results in lower cradle-to-tank efficiencies. The CONCAWE data, which were published by Edwards et al. [13] in a corresponding report, offers an efficiency of about 50% for syndiesel from Fischer-Tropsch synthesis and for FAME and HVO. Higher values of 60% can be reached by bio-DME-based on black liquor. The primary energy demand increased to 93.6 TWh/a, assuming an efficiency of 50% for the production chain.

However, these values also indicate the limits if a complete conversion of diesel and jet fuel for trucks and aircraft to power-to-fuel and biofuels is to be made. A demand of 28 million tons of truck diesel and jet fuel in Germany cannot be fulfilled by biofuels alone. In parallel, electro-fuels provided by power-to-fuel processes contribute to liquid fuel demand. Efficiencies for such process chains are mostly based on process analysis calculations. A fair comparison is difficult because the various groups applied a different set of parameters, as reported by Haarlemmer et al. [15], Brynolf et al. [16], and Schemme et al. [17]. Efficiencies for the production of methane, methanol, DME, FT liquids, and MTG were calculated by Brynolf et al. [16] and Schemme et al. [17]. Additionally in Ref. [17], process chains are reported for methanol, ethanol, butanol, octanol, OME1, and OME3-5 representing the basis of the own R&D work. Important process conditions include efficiencies for electrolysis and the energy demand for CO2 separation, for example 70% for PEM electrolysis and 1.2 MJ/t CO2 for separation from the flue gas of a cement plant according to Ref. [17]. Important results in the context of this paper are the PTF efficiencies (ηPTF) for diesel substitutes such as DME, FT diesel, octanol, and OME3-5, as well as FT-kerosene as a jet fuel substitute. Schemme et al. [17] reported efficiencies (ηPTF) of 60% (DME), 51% (FT diesel, FT-kerosene), 42% octanol, and 27–30% for OME3-5 depending on the synthesis process route. Similar values result from the calculations according to Brynolf et al. [16], with totals of 56% and 51% (ηPTF) for DME and FT products, respectively. Only König et al. [18] reported much lower values of 43.3% (ηPTF) for FT products. A process chain efficiency of 50% leads to a demand for primary energy in Germany for these applications of 672 TWh; in this case renewable electricity. It must be taken into account that the total electricity generation in Germany in 2019 was 512 TWh [19], with a maximum of 540 TWh reached in 2007 and 2010. An increase in efficiency of 55% reduces the demand on renewable electricity to 611 TWh, i.e., a decrease of 61 TWh/a. This is again on the same order of magnitude as the savings in primary energy through the use of more efficient systems for the on-board power supply of trucks and aircraft in the U.S.A.

The results show that the enormous amounts of energy in the transport sector can only be achieved with an intelligent substitution strategy consisting of a technology change in the drivetrains and variable sources of primary energy for several fuel chains. Peters et al. [20] analyzed the various options for light and heavy commercial vehicles in a review article. Finally, redirecting the transportation sector remains a much greater challenge than improving the energy efficiency of on-board power supply units. It is therefore understandable if a change in research focus takes place. On the other hand, it is also desirable if technical developments from one research area can be transferred to another. This article looks into this matter.

2. Methodology

The research question of this article must be formulated very clearly. How can broad expertise on fuel processing be re-used for a new research field such as the sustainable fuel synthesis? Nevertheless, it is challenging to find an unequivocal answer based on scientific and technical methods. This is certainly the reason why the results of the investigations described below are more complex compared to a catalyst benchmark or a reactor test. Based on many years of experience in the field of reforming, a specialist book entitled Fuel Cell Science and Engineering was published in 2012, in which the methods developed for research and development of fuel cells, in particular APU systems, were described. In connection with the question formulated here, the following aspects are very important, which are described in the book sections "Principles of system engineering" by Blum et al. [21], "Computional fluid dynamics simulation using supercomputer calculation capacity" by Peters and Scharf [22] and "Methologies for fuel cell process engineering" by Peters and Samsun [23]. The methods detailed therein were applied to identify research gaps and open meaningful technology transfer gates.

2.1. *Literature review*

The next section analyzes the perception of the topics of APUs and power-to-fuel in the research community on the basis of the number of publications that feature these keywords. The keywords have been slightly modified. Instead of APU, the keywords "reforming" and "autothermal reforming" were checked because the main goal of this exercise is to transfer knowledge from fuel processing to fuel synthesis. The core process of fuel processing is the reforming process to generate hydrogen or syngas. In order to cover a broader spectra in fuel synthesis, the search was extended to the keywords "power-to-fuel," "power-to-liquid," and "electrofuels."

With respect to the topic of autothermal reforming, the interested reader can approach the matter using several approaches: a) browsing the most-cited publications on the topic; b) seeking out the latest review articles; or c) analyzing the publications of the most active research groups. For this term, the eight most-cited publications and three most recent review articles are briefly summarized. A detailed processing of the approach under c) leads to the keyword "autothermal reforming" reaching 1942 hits, with more than 40 papers from our own group.

2.2. *Process design*

Process design plays an important role in system development. System development includes basic engineering, detailed engineering with piping and instrumentation, FMEA, component selection and drawings, procurement and assembly, see also Blum et al. [21]. In this article, only the first drafts of the process design are presented in block diagrams. Process simulations usually were performed by using thermodynamic and reaction kinetic data. This is supplemented by techno-economic analyses, see Schemme et al. [5]. In this early stage detailed engineering studies were not necessary. This task must worked-out as a next step to evaluate different competing systems. Results will be presented in future contributions.

2.3. *CFD analysis*

The detailed modelling methodology for the CFD simulations were published by Scharf [24]. Therefore, only the main highlights of the modelling approach will be explained here. The ceramic monoliths housing the catalytic burner catalysts exhibit an ordered channel structure. A complete resolution of the small-scale porous structures would be extremely computationally and time consuming, so these structures are modeled as porous bodies. A porous structure is not modeled in Fluent as a solid body traversed by a fluid, but only via its flow interactions, considering a heat balance averaged over the control volume. In the conservation equations, the porosity and, in the case of multiphase flow, additionally the volume fraction of the conservation variable is taken into account. In the momentum balance, an additional vector term describes the influence of the porous body on the flow. It is not resolved in the finite volume between flow and solid body. The flow and conduction effects between two neighboring control volumes are calculated based on the values determined in this way, which leads to a homogenization of the modeled temperature gradient. The heat conduction through the solid porous matrix is attenuated. To accurately model the chemical reactions via the reaction rate, knowledge of the catalytically active surface area is required. Scharf [24] relates the model reactions derived for modeling of the catalytic burner to the surface-to-volume ratio of the uncoated catalyst support and fits them to experimental results. As a result, higher reaction rates are assumed in the model to compensate for the lower active area. Reaction modeling based on a known real active catalyst surface area thus requires adjustment of the model parameters, especially the pre-exponential factors. The flow behavior in the monoliths is determined by the porosity and the flow resistance. Both factors have a direct influence on the reaction process. The flow velocity in the monolith is calculated from the quotient of the incident flow velocity in the free cross-section and the porosity. To correctly represent the residence time behavior in the monolith, the CFD model calculates with the physical velocity. The Fluent model library provides correlations for the oxidation reactions of hydrogen, carbon monoxide and methane. The model parameters assume of a volumetric reaction and must be adjusted to model the surface reactions in the monolith with the active surface.

The process simulations for the development of the water-gas-shift reactor concept were based on the approach of minimizing the free enthalpy of the reactions, in other words the Gibbs energy. Based on previous findings from experimental work, the methane was considered as an inert species. The modelling methodology for process simulations can be found in Samsun et al. [25].

2.4. *Experimental set-up*

The experimental work on water-gas shift reactors and details about the test rigs at Forschungszentrum Jülich was published by Pasel et al., in 2005 [26,27] in 2018.

The reactor and catalyst used were designed for the composition of a product gas (reformate) from the autothermal reforming of liquid hydrocarbons (diesel and kerosene), which typically contains between 9 and 11 vol% of CO after the excess water has been condensed out. For this purpose, a Pt-based catalyst from Johnson Matthey was used, which was coated on a ceramic monolith. The other main components of the reformate were H_2, CO_2, and CH_4. Under unfavorable reaction conditions, short-chain and aromatic hydrocarbons, such as ethene, ethane, propene, or benzene can be produced.

In order to determine the composition of the product streams of the water-gas shift reactor two different analytical methods were combined. A mass spectrometry (Cirrus 2mass spectrometer, MKS Instruments Deutschland GmbH) and a Fourier transform infrared spectrometry (Multigas 2030 FT-IR Analysator, MKS Instruments Deutschland GmbH) were used to determine the gas concentrations in the outlet of the water-gas shift reactor.

For the experimental validation of the process simulation results presented in combination with the experimental results, a series of experiments was carried out, for which Jülich's autothermal reformer (ATR) was used to produce simulated pyrolysis gases with widely varying CO outlet concentrations. More information on Jülich's ATR technology and experiments can be found in Refs. [28–34].

3. Results and discussion

In this section, the results of the literature research are first evaluated in order to find ways to integrate existing reactor developments into a new research field. First general considerations of integration within the framework of the process design are made. Based on three main components of APU technology, options for reactor implementation in fuel synthesis systems are presented using CFD design, experimental methods and basic engineering.

3.1. *Reflections from the literature on APUs and PTF*

In this section the results from the literature review were discussed. Fig. 4 shows the number of yearly hits in Scopus for searches of these keywords. As is apparent, the keyword “reforming” is something of a generic term and the number of hits increase form 500 per annum (p.a.) in 2000–2600 p.a. in 2020. The main contributions to this derived form authors from the U.S.A., China, the U.K., Japan, Germany, Italy, and South Korea. Under the keyword, “autothermal reforming,” only a maximum of 120 papers p.a. could be found, mainly from authors from the U.S., China, the U.K., South Korea, Germany, and Italy. The field of “power-to-fuel” technologies is fairly new, but achieved over 400 hits in 2020. The main contributions to this were from authors in Germany, the U.S.A., Italy, and China.

In addition, Table 1 presents the number of yearly hits in Scopus for the keyword “autothermal reforming” with respect to countries. As can be seen, the research topic was at highest interest in the U.S.A. between 2003 and 2014, and in Germany between 2001 and 2019. In this period, half of all published papers had authors from these three countries.

Contributions from Italy and Spain can be interpreted as early followers, with maximum intensities reached between 2009 and 2019, depending on the country. In the next section, the results of the literature search in steps a)-c) are discussed. The analysis starts with the most-cited publications on the topic.

Peña et al. published a review of new catalytic routes for syngas and hydrogen production [35]. They presented an overview of autothermal reforming, catalytic partial oxidation, and steam and CO_2 reforming. They opened their report with methane reforming and continued with methanol reforming and the reforming of residues. Peña et al. offered a good starting point by collecting operational conditions and catalyst formulations.

In 2001, Krumpelt and Ahmed [36] reported on the activities of Argonne National Laboratory on the fuel processing of

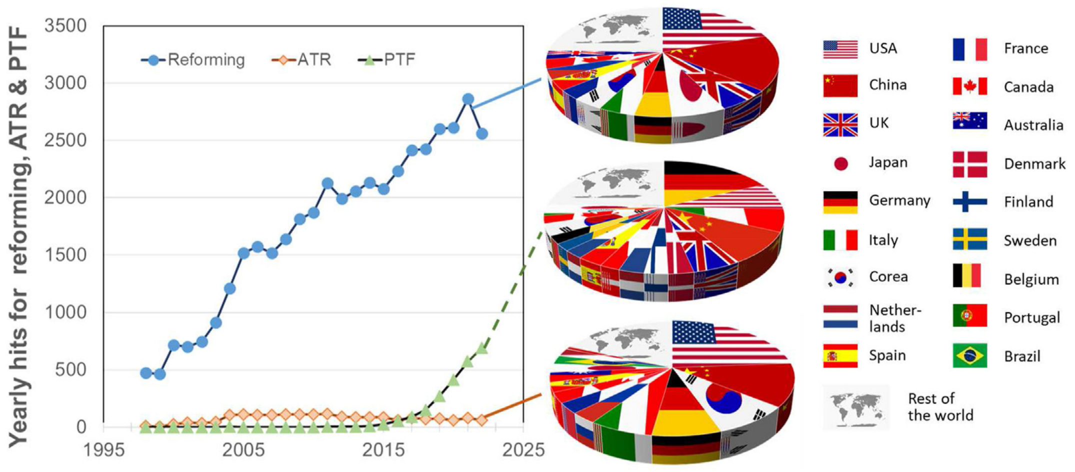

Fig. 4 – Number of yearly hits in Scopus for the keywords “reforming,” “autothermal reforming,” and “power to fuel.” Under the label *power-to-fuel*, the keywords “power-to-fuel,” “power-to-liquid,” and “electrofuels” are summarized. The pie charts depict the share of different countries of all contributing authors.

Table 1 – Number of yearly hits in Scopus for the keyword “autothermal reforming” by country.

	USA	China	Germany	Italy	South Corea	Canada	Spain	Russia	Japan	Netherlands
Sum	440	220	156	136	143	73	69	58	57	54
2022	7	17	0	1	7	7	6	5	3	1
2021	8	12	4	4	7	4	5	10	1	3
2020	10	11	1	2	5	2	1	3	1	1
2019	8	11	7	6	9	6	6	8	2	1
2018	11	15	5	10	3	3	4	4	0	4
2017	13	6	14	11	6	6	3	7	1	3
2016	10	7	9	10	3	1	5	2	0	4
2015	12	7	9	8	5	0	5	3	0	6
2014	21	12	10	8	4	0	3	3	0	2
2013	14	7	4	10	7	0	8	1	0	2
2012	15	13	8	8	4	2	4	0	0	4
2011	20	16	5	7	13	5	8	1	0	3
2010	28	17	4	10	12	3	2	2	1	4
2009	33	14	4	8	10	7	1	2	9	5
2008	31	13	8	4	23	4	3	1	5	4
2007	34	9	11	7	11	3	2	2	3	2
2006	37	16	8	5	8	4	1	1	8	2
2005	36	4	8	5	3	10	0	1	1	2
2004	46	6	14	1	0	1	0	1	10	0
2003	17	0	7	2	1	0	0	1	5	1
2002	9	1	6	2	1	1	0	0	3	0
2001	8	2	6	0	1	1	0	0	1	0
2000	1	4	2	0	0	0	1	0	2	0
1999	1	0	2	0	0	1	0	0	0	0
1998	1	0	0	6	0	1	0	0	1	0
1997	9			1		1	1			

hydrocarbons, mainly gasoline substitutes, for automotive propulsion systems utilizing fuel cells combined with reforming devices. The article is an artefact of a research period that focused on on-board reforming in mobile systems. This development was halted by the Department of Energy (DoE) with its Go/noGo decision [37]. On-board fuel processing systems were seen to be too complex and bulky. From then on, the research groups dealt with the on-board power supply based on fuel cells and liquid fuels.

In 2002, Ghenciu [38] published a further review on fuel processing catalysts for hydrogen production in PEM fuel cell systems. The paper focused on catalyst selection from a manufacturer's perspective, namely that of Johnson Matthey Ltd. Ghenciu described catalytically-active materials for methane and hydrocarbon steam reforming and partial oxidation for the autothermal reforming of gasoline (hydrocarbons) and methanol reforming. In addition, the water–gas shift reaction with both precious and non-precious metal catalysts and CO fine cleaning with preferential CO oxidation were considered.

In 2004, Deluga et al. [39] reported in a Science publication on their research on ethanol reforming with rhodium-ceria catalysts. The conversion of this catalytic partial conversion was greater than 95% and they claimed that more than 50% of the energy from photosynthesis could be captured as electricity.

In 2007, Navarro et al. [40] published a paper dealing with hydrogen production from carbon feedstocks from fossil fuels and biomass. Besides the well-known processes of steam reforming, catalytic partial oxidation, and the autothermal reforming of the liquid hydrocarbons of methanol and methane, they give room for coal gasification and CO_2-free reactions such as methane decomposition and aromatization. Several biomass conversion technologies were presented as alternative hydrogen production pathway. All chemical reactions were discussed in the context of applied catalysts and operating conditions.

Also in 2007, Nia et al. [41] published a study focused primarily on catalyst development for ethanol steam reforming. They achieved the best performance with Rh- and Ni-based catalysts. Supports such as MgO, ZnO, CeO_2, and La_2O_3 can inhibit carbon deposition to some extent.

In 2009, Holladay et al. [42] presented a further overview of hydrogen production technologies. They built a bridge from fuel processing, including reforming processes, desulfurization, pyrolysis and on, to biomass conversion with different technologies such as gasification and fermentation and, finally, to the different water electrolyzer technologies, namely alkaline, proton exchange membranes, and solid oxide cells. As a special item, ammonia reforming was introduced.

Over a long period, research papers from Rostrup-Nielsen [43,44] offered a huge amount of detailed information on reforming catalysts and their properties.

Recently-published review papers are far more specialized, as the small selection described in the next section will show. Skabelund and Milcarek [45] focused their work on a review of thermal partial oxidation reforming with an integrated solid oxide fuel cell. Finally, they proposed a direct flame fuel cell (DFFC) that inserted the SOFC from the anode side into the flame. The technology as tested was for 300 h only. Amiri et al. [46] published a review on membrane reactors for sustainable hydrogen production via the steam reforming of hydrocarbons. More broadly, Avargani et al. [47] discussed a variety of hydrogen production technologies, i.e., from hydrocarbon reforming and coal gasification as fossil routes and water electrolysis and biomass processing as renewable pathways. Additionally, hydrogen usage was included, for example, in fuel cell-driven passenger cars. Finally, the papers took into account approach b), which will not lead to a technology transfer strategy.

In addition to the most cited publications on the production of hydrogen from hydrocarbons, a number of other important scientific contributions reflect the developments in the field of reforming in a temporal context very well. This brief inset should be used for explanation with aid of reviews from literature between 2002 and 2014 [48–54]. Gosselink [49] reported about the pathways to a more sustainable production of energy: sustainable hydrogen from the perspective of an energy and fuel provider such as SHELL, already in 2002–20 years ago. Gosselink described a trend away from traditional centralized sites for electricity generation based on largely fossil-powered plants towards distributed generation. is reshaping the size and function of electricity. There was the vision of novel methods of linking different components – today sector coupling, the existence of small-to mid-scale units, which can produce heat, electricity and hydrogen and the usage of compact hydrogen storage for automotive applications.

In 2005, Bowers et al. [48] described the development of onboard fuel processor for PEM fuel cell vehicles. For the time being, they believe that onboard hydrogen storage and infrastructure will remain challenges in future and that onboard fuel processors offer a promising solution to produce hydrogen for the fuel cell on the vehicle using conventional fuels such as gasoline or bio fuels such as ethanol. Qi et al. [52] stated that fuel processing is a complex system and it demands technologies of process intensification and optimization to make the whole system integrated, more efficient and compact. Microchannel technologies should, particularly fulfill this role. A number of activities were reflected by the most important papers on this field, see Refs. [50,51,53]. Due to the complexity of the technology and the missing target numbers, the DOE Go/No-go decision from 2004 [37,55], finally stopped these activities and led to a strong focus on APU development.

O'Connell et al. [51] reported about the mass production of microstructured fuel processors for application in future distributed energy generation systems in 2012 while Kolb [50] described currently developed microstructured reactors for distributed and renewable production of fuels and electrical energy in 2013.

In 2014, Specchia [54] summarized all fuel processing activities at European level. A main message was that a secure and competitive energy supply will be a key challenge to meet our future energy requirements. Most important are measures to slow-down the rate of energy-related CO_2 emissions. Specchia [54] demanded on a decoupling of CO_2 emissions from economic growth. More innovative technological development are required for mobility and industries. Keywords were: sustainable, distributed production of energy, usage of renewable fuels and improved utilization of fossil fuel resources. It is important to note that for the time being research and development on several reforming systems for fuel processor (FP) units has gained an important role for auxiliary power units (APUs) and for compact systems in stationary applications, i.e. combined heat and power units (CHPs).

Considering the idea of approach c), a description of own research and development work as one of the main active groups in the field of reforming technologies is still missing. A deeper insight into technical development in the case of diesel reforming should identify options for technology transfer to the field of fuel synthesis. This task is difficult to realize by only studying review papers. It is remarkable that the task of diesel reforming only began in 2002 with a paper by Palm et al. [56] on small-scale testing. Based on a series of publications, the development history of a very specialized area of research could be read and understood. Several generations of autothermal reformers were described by Pasel et al. [28–33], including different fuels and long-term stability experiments during the research period 2007–2020. Special measurement recipes were developed to analyze important by-products in the sub-ppm range; see Meissner et al. [57]. Mixture formation and nozzle development was always a very specialized issue with respect to complete conversion, as analyzed by computational fluid dynamics (CFD) and experimentally; see Porš et al. [58] and Peters et al. [59]. A complex heat exchanger integration was developed to incorporate compact devices [60]. In addition to ATR development, catalytic burners and water–gas shift reactors were developed and tested by Meissner et al. [61–63] and Pasel et al. [27,64], respectively. The different types of reactors were applied in compact on-board power supply systems, i.e., APUs; see papers by Samsun et al. [25,65–69]. Based on the initial dynamic simulations by Wiethege et al. [70] who analyzed different start-up strategies in 2014, special start-up devices were implemented over the subsequent years; see Refs. [66,67].

The expertise that is described fairly briefly above should be transferred to reactor design of fuel synthesis. Regarding the central question of the paper about the transfer of expertise in the field of fuel processing to fuel synthesis, the literature gives first hints. Here, a look must be taken at microreactor technology, which has already been discussed on the basis of references [50,51,53]. At the Institute for Micro Process Engineering, Karlsruhe Institute of Technology, the transfer from a membrane reactor for methane steam reforming to Fischer-Tropsch synthesis was carried out with similar reactors [71–73]. Essentially, other catalyst systems had to be coated and the heat balance has to be adapted. The next section outlines some options for applying this knowledge and the application range of the developed component technology.

3.2. *Process set-up of fuel processing for APUs*

Fig. 5 shows the process chain for the production of a hydrogen-rich gas from diesel or jet fuel, including after gas treatment for a state-of-the-art fuel cell APU [49]. The core technology for fuel processing in this system is autothermal reforming. The selected fuel cell technology is a high-temperature polymer electrolyte fuel cell. A two-stage

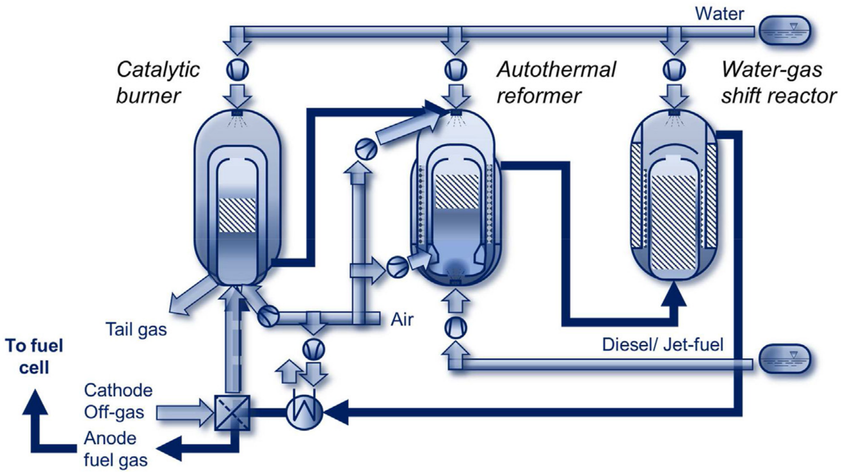

Fig. 5 – **Process chain from diesel or jet fuel to anode fuel gas via autothermal reforming and the water–gas shift reaction, coupled with thermic integration to a catalytic burner.**

water–gas shift reactor reduces the carbon monoxide content of the reforming product to a level that can be tolerated by the selected fuel cell type. The electrochemical conversion of the hydrogen-rich gas in the fuel cell leads to the production of electricity and heat. The anode fuel gas is converted into steam and carbon dioxide in the catalytic burner.

In order to achieve the U.S. DOE targets for power density and start-up, multifunctional fuel processing reactors were developed and utilized for the above system. For this purpose, the start-up and heat exchange functions are integrated into the components. For example, the newly-designed water–gas shift reactor includes a heat exchanger to reduce the temperature of the product gas to the inlet temperature of the anode section of the fuel cell stack. This is achieved via a parallel heating of the air to operate the fuel cell stack. The newly-developed catalytic burner is designed to combust the total amount of reformate produced during the start-up stage to provide heat to the fuel cell stack. The stack and catalytic burner were therefore thermally-coupled through the heat exchange fluid, whose main function is to cool the stack during normal operation. Excess heat from catalytic combustion is made available for providing superheated steam and heated air for reformer operation. The start-up of the fuel processor is performed by integrated electrical heating wires in the reformer and water–gas shift reactor and a glow plug placed at the catalytic burner inlet [67]. Further highlights from system development include the selection of compact and highly efficient balance of plant components, such as turbo compressors and the combination of two fuel cell stacks and the fuel processor system with the help of manifolds optimized by CFD simulations and produced via laser-additive manufacturing.

3.3. *Processes for power-to-fuel and power-to-gas technologies*

Fig. 6 A) shows a power-to-fuel system for a direct DME synthesis from carbon dioxide and hydrogen integrated with a catalytic burner for purge gas treatment. The purpose of using a catalytic burner in this set-up arises from the requirement of having adequate removal of off-gases from the synthesis unit, which originate from the recycling of purge gas-containing flammable gases. In typical industrial units, flare stacks are used to burn off-gases. This technique would, however, require a constructional change at an installation site and necessitate a new certification procedure for the completed site. As an alternative technique, the catalytic burner technology, which was originally developed for fuel cell APUs, was implemented. Catalytic burners enable flameless combustion, thus releasing no harmful pollutants into the environment.

Fig. 6 B) depicts a methanation system, including a high-temperature pyrolysis unit, a water-gas shift reactor, and a biological methanation reactor based on the set-up from the BiRG Project, funded by the Federal Ministry for Economic Affairs and Climate Action. The project aims for the production of bio-methane from biogenic residues. The residues are converted into a gas containing hydrogen, carbon monoxide, carbon dioxide, and methane in a high-temperature pyrolysis process. The pyrolysis unit produces only bio-coal as a by-product, which is a valuable feedstock for agricultural applications. As the microorganisms in the biogenic methanation reactor are sensitive to carbon monoxide, the latter's content at the inlet of this reactor will ideally be limited by 1 vol%. For this purpose, an adapted version of water–gas shift reactors originally developed for fuel cell-based APUs can be utilized.

Fig. 7 shows a simplified sketch of a conventional Fischer-Tropsch synthesis system. According to this set-up, the light hydrocarbons that are separated from the Fischer-Tropsch product stream are partially fed back to the reverse water–gas shift reactor and partially released from the system as a purge gas. The system can be optimized using an autothermal reformer, which can utilize the light hydrocarbon fractions that do not fit into the desired product fractions for naphtha, kerosene, diesel, and wax according to Fig. 7. The produced synthesis gas can then be fed into the reverse water–gas shift reactor, which in turn reduces the heat

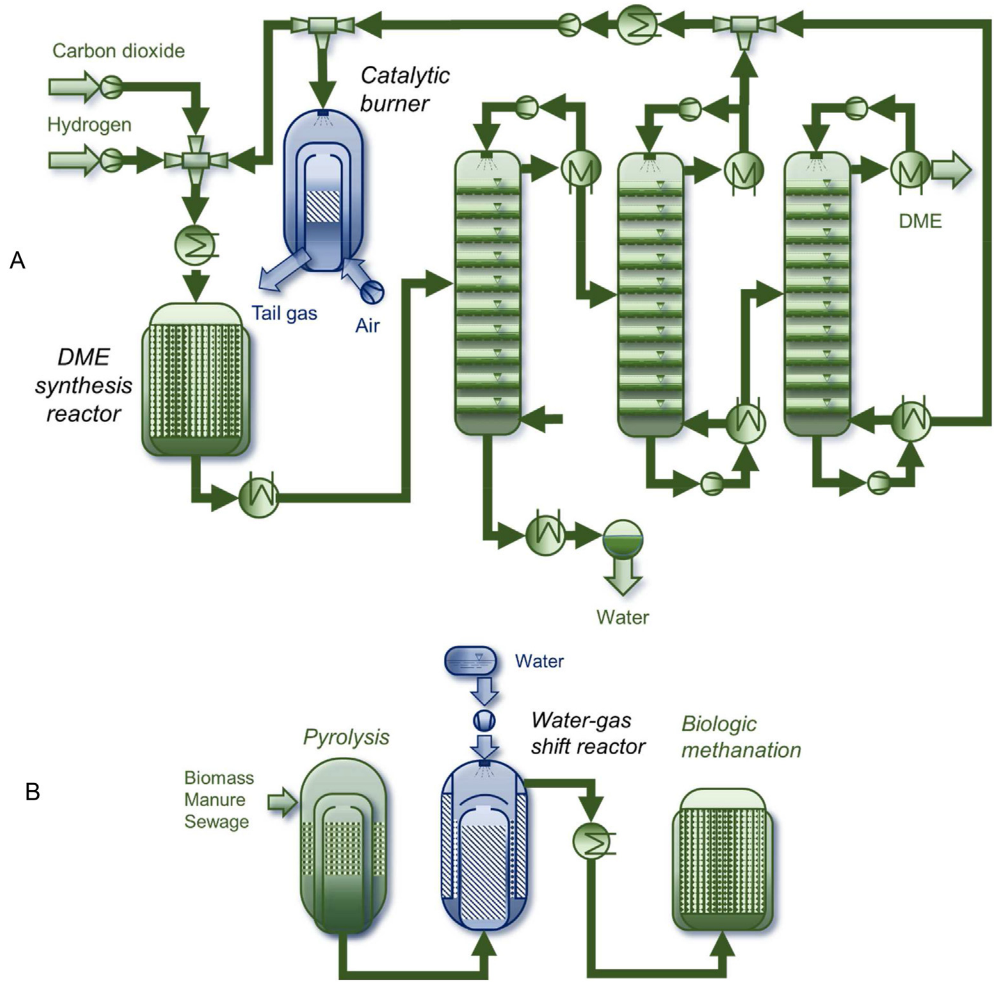

Fig. 6 – Examples for the use of reactors from fuel processing systems for renewable fuel production. A) Power-to-fuel system for the direct DME synthesis from carbon dioxide and hydrogen integration of a catalytic burner for purge gas treatment. B) Sketch of a methanation system, including a pyrolysis unit, water–gas shift reactor, and biological methanation reactor.

demand of the shift reactor and enables an energetic use of the by-products of the synthesis, further increasing the overall efficiency. The application of an autothermal reformer can also enhance the efficiency of the production of additional power-to-fuel products, including ethanol, hydrocarbons through the methanol-to-gasoline route, as well as higher alcohols such as octanol and butanol [5].

3.4. *CFD supported reactor design for catalytic combustion in fuel synthesis systems*

The first transfer was achieved for the catalytic burner according to the flow sheet shown in Fig. 6. The adaptation of the catalytic burner technology from fuel processing to fuel synthesis was achieved with the help of CFD simulations for concept development and proof of concept. For a simulation-based case study, various purge gas compositions and volumetric flow rates were defined. Case 1 shows the lowest volumetric flow rate of 820 l_N h^{-1}, the composition of which was 13% CO_2, 4.9% CO, 1.2% DME, and 80.9% H_2, all in (vol)%. In cases 2 and 3, the purge gas consists of less hydrogen and DME, with 72% and 0.3%, respectively, and more CO_2 (17.1%) and CO (10.5%). The volumetric flow rate increases to 11,500 l_N h^{-1} in case 2 and 15,750 l_N h^{-1} in case 3. The highest H_2 concentration presented in cases 4 and 5, with 82.2%. The CO_2 (10.9%) and CO (6.7%) concentrations showed medium values, with the DME concentration being the lowest at 0.2%. The volumetric flow rate further increased for these cases, namely to 18,100 l_N h^{-1} in case 4 and 22,650 l_N h^{-1} in case 5. The cases primarily differ based on the strongly varying volumetric flow rates, whereas the concentrations vary only within a small window. Case 2 is defined as the reference case and the remaining cases can be considered extreme. In all cases, the catalytic combustion was simulated assuming a huge amount of excess air ($\lambda = 3.2$) in order to control the adiabatic reaction temperature within the allowed limits.

Fig. 8 shows the simulation results for the operation of the catalytic burner for the five cases. On the left-hand side, the

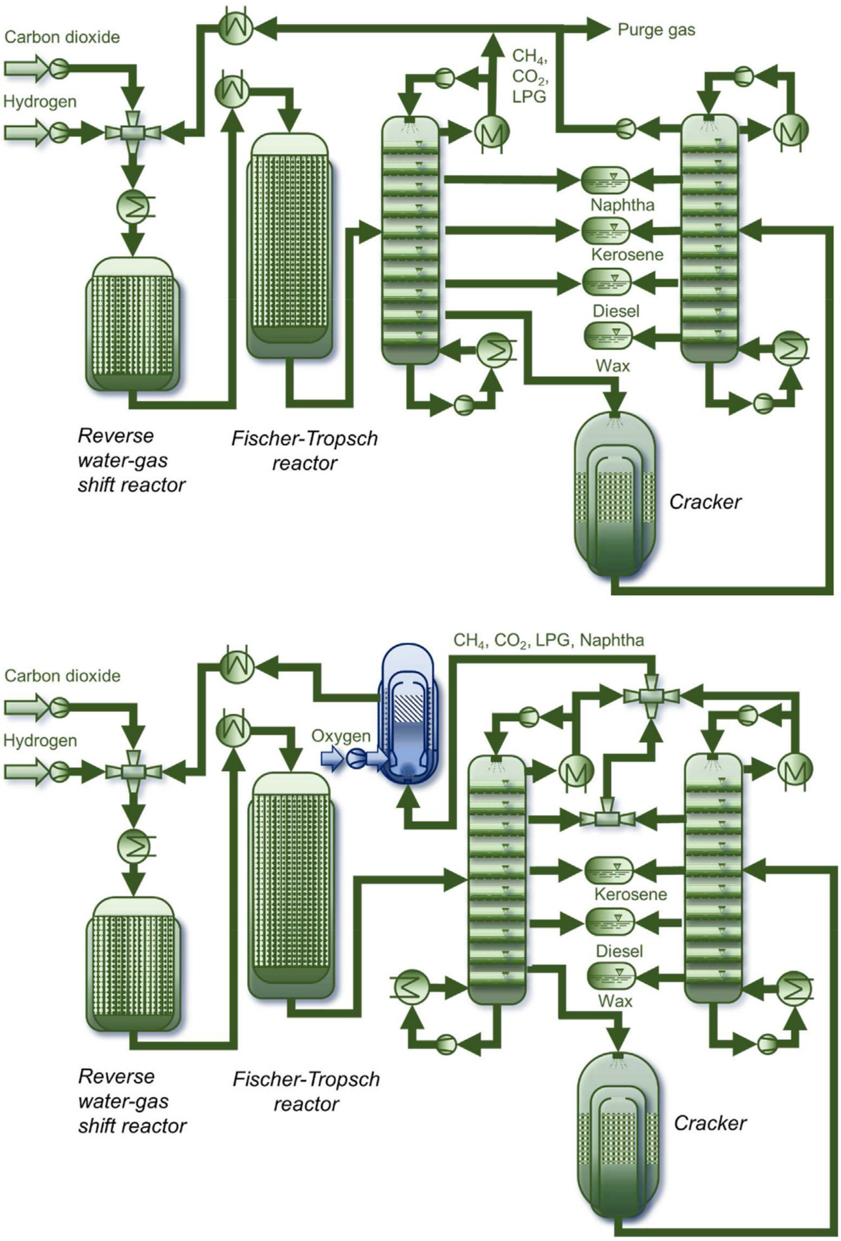

Fig. 7 – Simplified sketch of a Fischer-Tropsch synthesis system with and without an autothermal reformer.

complete temperature profile of a cross-section of the catalytic burner is presented for case 1, with selected critical positions for the case study shown on the right-hand side. 950 °C is defined as the maximum temperature at the end of the catalyst bed. For the baffle 850 °C is defined as the limit to avoid it facing mechanical stress. 700 °C is defined for the torispherical head and for the off-gas outlet as the maximum allowable temperature based on the material properties. For the steam outlet segment, as the cooling loop is not operated under pressure, the temperature limit is defined as 600 °C. The first analysis shows that the defined temperature limits can be sustained in every case, and so the operation of the selected catalytic burner generation under the defined conditions is feasible.

In a second step, the emissions of the catalytic burner were analyzed. The TA Luft (Technical Instructions on Air Quality Control) regulation defines a maximum concentration of 100 mg m^{-3} for CO. According to the simulation results, this limit can only be realized in case 1 with a fairly low volumetric flow rate of the feed gas. For the reference case, namely case 2, the CO concentration corresponds to 146.9 mg m^{-3} and exceeds the limit by approximately 50%. Amongst the remaining cases, the CO emissions are the highest in case 5, with 934.3 mg m^{-3}. This is also the case with the lowest residence time and an average CO concentration in the feed. The second highest CO emission was observed in case 3, at 843.6 mg m^{-3}, which combines the highest CO concentration with an average residence time. Case 4 features the second-lowest residence time

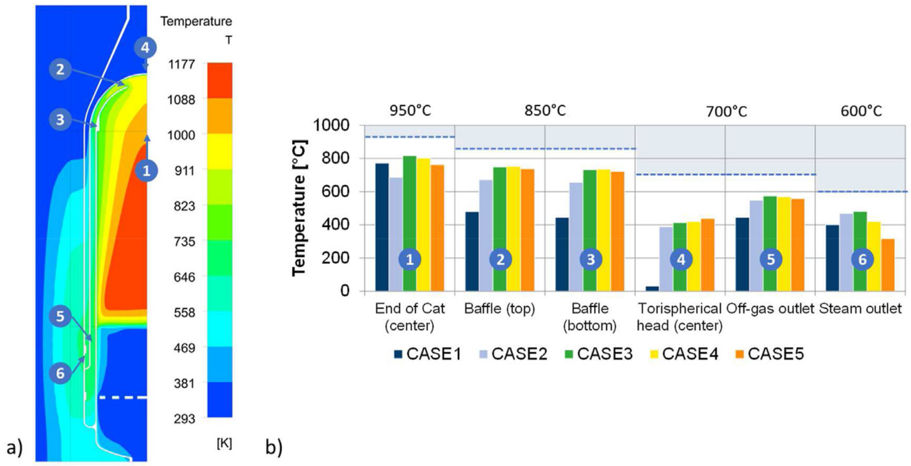

Fig. 8 – Analysis of critical temperatures in the catalytic burner: a) Cross-sectional view of the catalytic burner simulation for case 1. b) Analysis of the critical temperatures for selected locations in the catalytic burner.

and an average CO concentration of 686.3 mg m^{-3}. All three cases (3–5) exceed the CO emissions limit by a factor of 6.9–9.3.

In order to reduce the CO emissions to values below the TA Luft limits, a new operating strategy was developed in which three reactors are utilized in parallel instead of one. According to the simulation results, case 2 emits only 9.6 mg m^{-3} CO, which is factor 10 lower than the emission limits. However, the emissions for cases 3–5 are still higher than the allowable limit. In further simulations, it was shown that the purge gas flow rate must be reduced by up to 55% in order to keep the CO concentrations below the TA Luft limits, if the system is operated according to cases 3–5. For reference case (2), three catalytic burners were operated in parallel, which can reduce the system emissions to values well below the TA Luft limits without the necessity of reducing the volumetric flow rate.

Three catalytic burners (details by Meissner et al. [62]) were implemented, as in the reference case (2), in the demo plant. Preliminary emission measurements showed the high performance of the applied burner configuration with no detectable carbon monoxide emissions and nitrogen oxide emissions of 2.1–6.6 ppm [74]. In Germany, the technical instructions for keeping the air clean (*TA Luft*) specify limit values for various technologies such as gas engines, gas turbines, and diesel engines. The strictest values for gas turbines are 75 ppm of NO and 100 ppm of CO. Further investigations will be necessary in the future.

Following this approach, the simulation-based adaptation procedure enables the utilization of the catalytic burner technology, which was originally developed for utilization in mobile fuel cell systems, in a new application area.

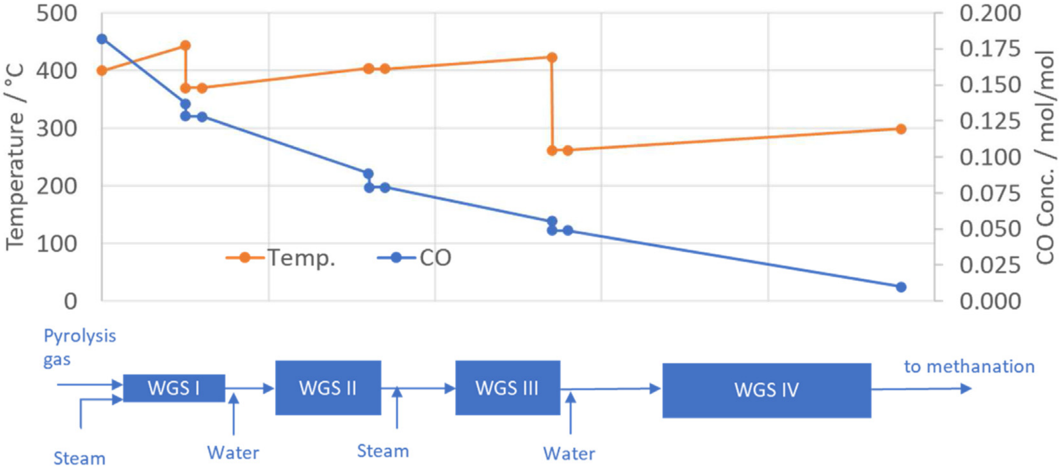

Fig. 9 – The course of temperatures (left axis) and carbon monoxide concentrations along the four shift stages (upper diagram). The reactor configuration is displayed in the lower diagram, with the size of each box representing the size of each catalyst bed relative to each other.

3.5. *Experimental adaption of water–gas shift reactors for biological methanation*

For many years, the Forschungszentrum Jülich has been developing reactors for the water–gas shift (WGS) reaction, which is described by reaction equation (1), below. In the context of Jülich's R&D work on fuel cell systems, this reaction serves to reduce the concentration of CO in the educt gas for the anode side of a fuel cell and to increase the concentration of H_2. Low concentrations of CO (<1 vol%) are required to protect the anode catalysts from poisoning and so a loss of activity via irreversible CO adsorption. The second transfer has been realized for the WGS according to the flow sheet in Fig. 6. Higher H_2 concentrations are advantageous for the operation of a fuel cell. Jülich's WGS reactor features high-temperature (HTS) and low-temperature (LTS) shift stages. The HTS stage works at approximately 400 °C and profits from fast kinetics at thermodynamically-limited CO conversion. In contrast, the LTS stage working around 300 °C allows for higher CO conversion from a thermodynamic point of view, but exhibits slower reaction kinetics.

$$CO + H_2O \rightarrow CO_2 + H_2 \text{ exothermic} \quad (1)$$

The task of Forschungszentrum Jülich in the BiRG project was to adapt the existing reactor for the water–gas shift reaction to the CO content of a product gas from the pyrolysis of biogenic residues, which can contain more than 20 vol% CO. The aim in BiRG was not to exceed a CO concentration of 1.0 vol % in the moist pyrolysis gas after the water–gas shift reaction, while simultaneously complying with the upper temperature limit of the catalyst of 450–470 °C. Higher temperatures might lead to the formation of agglomerates of the catalyst particles, resulting in irreversible catalyst deactivation.

As the water–gas shift reaction is exothermic, the amount of heat released and so the adiabatic reaction temperature increases with each mole of CO being converted in this reaction. Process simulation results, which were validated by experiments that are presented in detail below, showed that the higher CO content in the pyrolysis gas could lead to temperatures exceeding the allowable limit of 450–470 °C for the precious metal catalyst used in the water–gas shift reaction. For a feed temperature of 400 °C, which makes use of a high reaction rate, which is typically the case in a high-temperature shift stage, the adiabatic reaction temperature can increase to values of between 460 °C and 535 °C for 20 (vol.)% CO in the pyrolysis gas. The higher value of the temperature is reached for pyrolysis gas compositions that have less CO_2 in the feed.

In order to control the temperature and at the same time profit from high reaction rates at higher temperatures, a four-stage reactor concept was developed for pyrolysis gas with high CO concentrations in the feed, instead of a two-stage reactor in a fuel cell system. In this concept, the temperature is controlled by the amount of water/steam addition to the different reactor stages. In the reference water–gas shift reactor, the cooling between the high- and low-temperature shift stages is realized via water quench. The evaporation cooling between stages not only provides additional steam for the shift reaction, but thanks to the flow of the steam/product gas mixture in the hollow space separating the first and second stages, an integrated cooling mechanism is realized within the reactor. Based on the new concept, only a limited amount of steam is provided to the first stage of the reactor. Beyond this stage, the fresh water feed reduces the temperature to a slightly lower value than the starting level of 400 °C, providing additional water for further shift reactions. Before the third stage, steam is added to the product gas, enabling a further course of the reaction, which still an approximate 400 °C starting temperature. With this approach, the reactions for the high-temperature shift with quick reaction kinetics are distributed to three reactor stages, without bringing the temperatures to the critical ranges. Prior to the fourth stage, the water feed again cools the product gas and provides additional water for the water–gas shift reaction, this time in the region of the low-temperature shift stage at around 300 °C. Due to the slower reaction kinetics at this temperature level, the catalyst bed has a four times higher volume than the first stage and twice as high of a volume as the second and third stages. Fig. 9 presents process simulation results for this concept based on thermodynamic equilibrium calculations.

First, the autothermal reformer was put into operation without a combination with the water–gas shift reaction. In this case, the CO concentration was 10.5 vol%. When the autothermal reformer was connected to the two-stage WGS reactor (with the internal abbreviation WGS 6B), the CO concentration could be reduced to 0.6 vol%, while in parallel all temperatures were below the above-mentioned limit for the catalyst of 450–470 °C recommended by the manufacturer, Johnson Matthey. Table 2 presents the results of experiments for which the CO concentration in the educt gas of the WGS reactor was increased continuously in several steps from

Table 2 – Reaction conditions and dry gas concentrations in the product gas of the water–gas shift reaction at different additions of CO and steam.

	2. Test point	3. Test point	4. Test point	5. Test point	6. Test point
Additional steam [g/h]	400.0	808.6	1197.6	1600.6	1999.1
Additional CO [l/h]	531.6	905.0	1488.9	1991.8	2483.3
Molar ratio CO/steam [–]	1.07	0.90	1.00	1.00	1.00
CO_{in} [vol%]	15.3	18.4	22.8	26.2	29.2
H_2O to LTS [g/h]	1700	2000	2250	2500	2700
$N_{2,out}$ [vol%]	31.7	28.8	26.4	24.4	22.7
$CO_{2,out}$ [vol%]	22.2	24.5	26.3	27.7	29.0
CO_{out} [vol%]	0.7	0.9	1.1	1.3	1.5
$H_{2,out}$ [vol%]	44.8	45.3	45.8	46.2	46.4

15.3 vol% to 29.2 vol% (second test point to the sixth one). Higher CO concentrations could be achieved by adding CO via an additional CO line. To keep the molar ratios between CO and steam constant at a value of around 1.0, additional steam was also injected.

It becomes clear that the CO concentrations in the simulated dry pyrolysis gas after the WGS reactor increased from 0.7 vol%, with an inlet concentration of CO of 15.3 vol%, to 1.5 vol% with a CO input concentration of 29.2 vol%. At this point, it is difficult to compare these dry concentrations precisely with the above-defined target of 1.0 vol% in the moist pyrolysis gas after the WGS reactor, as the water content in the pyrolysis gas is not always constant. However, it can be concluded that the existing WGS reactor of the FZJ comes very close to this target, especially with lower input concentrations of CO.

Fig. 10 (a) shows the course of the temperatures in the high-temperature stage of the WGS 6B as a function of time during test points 2–6 at different positions in the axial direction of the monolith. It is clear that all temperatures increased as the molar flow of CO into the reactor was increased because of the exothermicity of the WGS reaction and the high CO conversions at all test points. It can be seen that the temperatures after 62 mm and 87 mm were beyond the above-mentioned maximum temperature range for the WGS catalyst of 450–470 °C throughout the test period. Here, the conclusion can be drawn that a new concept for operating the WGS reactor with pyrolysis gas is required. The temperatures in the low-temperature stage of the WGS reactor, the curves of which are depicted in Fig. 10 (b), showed comparably increasing tendencies with higher input concentrations of CO. However, they remained well below the target of 450 °C throughout the course of the test.

As a consequence of the excessively high temperatures in the high-temperature stage of the WGS 6B, concept IIb, shown in Fig. 11, was investigated experimentally. In this concept, an additional Jülich WGS reactor was connected between the ATR and WGS 6B, which carries the internal designation WGS 6. In this concept, the WGS reaction now has four reaction stages available to reduce the CO concentration. WGS 6 differs from WGS 6B, in that the catalyst volumes in both shift stages are only half as large as in WGS 6B. In concept IIb, the product gas from pyrolysis and purification is first mixed with steam and then flows into the HTS stage of WGS 6 (HTS1 in Table 2). Cold water was added before the LTS stage of the WGS 6 (LTS2). The product gas was again mixed with steam before the HTS stage of the WGS 6B (HTS3). Before the product gas flows into the LTS stage of the WGS 6B (LTS4), cold water was mixed for a second time. However, as the product gas of the ATR (used to produce simulated pyrolysis gas, as mentioned above) already contains significant amounts of water vapor before it enters the HTS1 of WGS 6, it was possible to dispense with the addition of water vapor at this point in the experiments. Higher CO concentrations could again be achieved by adding CO via an additional CO line. Table 3 shows the reaction conditions and the measured dry concentrations in the product gas of the water gas shift reaction with different additions of CO (in the HTS1) and water vapor (in the HTS3). The table makes it clear that the CO concentrations in the dry pyrolysis gas following the series of WGS stages increased from 0.1 vol%, with an inlet concentration of CO of 10.6 vol%, to 0.8 vol% with a CO input concentration of 29.3 vol%. Fortunately, all of the CO concentrations in the dry simulated pyrolysis gas in Table 3 were well below the target of 1.0 vol% (moist) mentioned above. The continuous increase in the CO concentration in the product gas of the WGS reaction, which can be seen in Table 3, can be explained by the steadily decreasing hydrodynamic residence time of the molecules on the catalyst surface. The molecules have less and less time to adsorb and then react.

In Fig. 11, in addition to the course of the CO concentration already described, the course of the values for CO_2 and H_2 in the product gas of the WGS reactor can be seen. Due to the stoichiometry of the water–gas shift reaction and because of the steadily increasing input concentration of CO, both concentrations continuously increase. It is noticeable that in the case of the concentration of CO at the beginning of each test point, there was a sharp, short-term rise above the stationary mean. This is because the temperatures in the individual shift stages only became constant a few minutes after a new test point with the associated volume and mass flows had been set. However, as a pyrolysis reactor usually operates at a stationary operating point, this observation is not of great importance.

Fig. 12 (a) displays the course of the temperatures in the high-temperature stage of WGS 6 (HTS1) as a function of time during the six test points in Table 3 at different positions in the axial direction of the monolith. It can be seen that the temperatures at all positions were below the above-mentioned maximum temperature range for the WGS catalyst of

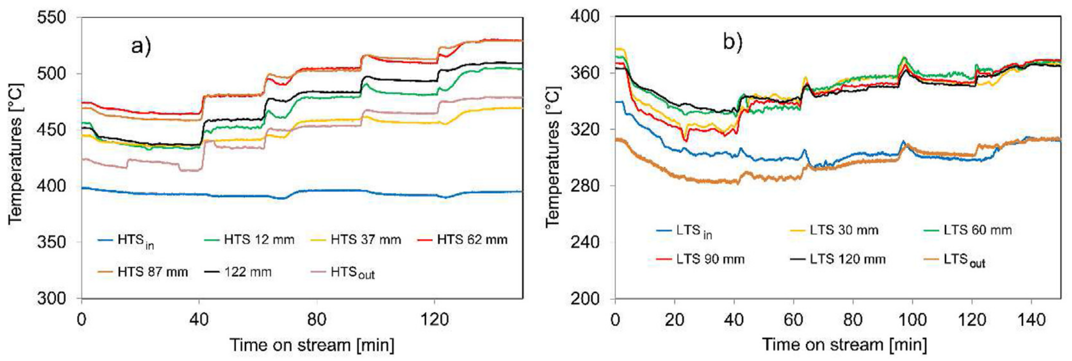

Fig. 10 – Temperatures in the high-temperature (a) and low-temperature (b) stage of the WGS 6B at test points 2–6.

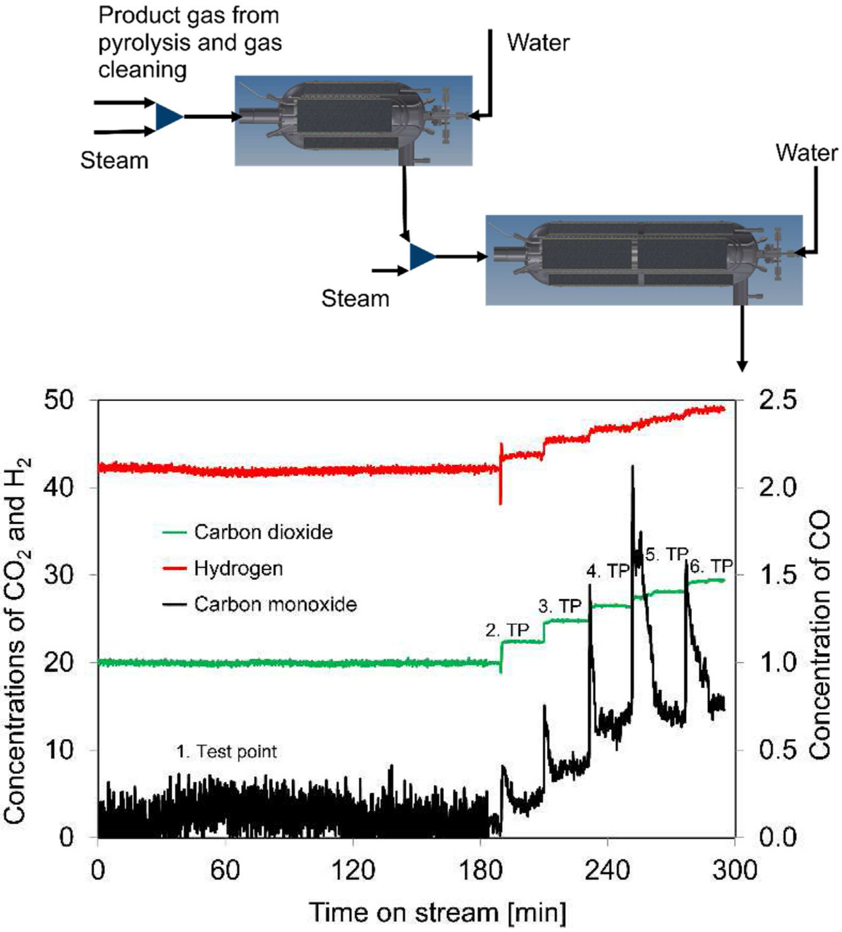

Fig. 11 – Concept IIb: four-stage WGS reactor with steam addition before stage 3; left: scheme; right: concentrations of CO, CO_2, and H_2 in the product gases of the WGS reactors during test points 1–6 with the new concept IIb.

450–470 °C throughout the entire test period. A similar picture emerged for the temperature profiles of the other three shift stages LTS2 (cf. Fig. 12 (b)), HTS3, and LTS4. HTS3 and LTS4 can be seen in Fig. 12 (c) and Fig. 12 (d), respectively. From the experimental results shown in relation to concept IIb, it can be concluded that this concept is very well suited to reducing the CO concentration in the moist product gas of a pyrolysis reactor below the target mark of 1 vol% without exceeding the maximum temperatures in the catalyst.

3.6. *General considerations on oxy-ATR*

The literature survey of Schemme [75] showed that autothermal reformers are already a part of commercial facilities

Table 3 – Reaction conditions and measured dry concentrations in the product gas of the water–gas shift reaction at different additions of CO and steam during the evaluation of concept IIb.

	1. Test point	2. Test point	3. Test point	4. Test point	5. Test point	6. Test point
Additional steam HTS3 [g/h]	397.6	397.6	797.1	1206.4	1593.6	2002.1
Additional CO HTS1 [l/h]	0	490.6	1054.4	1499.6	1973.5	2497.2
Molar ratio CO/Dampf [–]	n.a.	0.99	1.06	1.00	0.99	1.00
CO_{in} [vol%]	10.6	15.0	19.5	22.8	26.1	29.3
H_2O to LTS2 [g/h]	782	989	1088	1198	1202	1202
H_2O to LTS4 [g/h]	600	899	900	1000	1100	1200
$N_{2,out}$ [vol%]	37.4	33.1	28.8	25.6	22.7	20.4
$CO_{2,out}$ [vol%]	19.9	22.4	24.8	26.5	28.1	29.4
$CO_{ou}t$ [vol%]	0.1	0.2	0.4	0.7	0.7	0.8
$H_{2,out}$ [vol%]	41.9	43.7	45.5	46.7	48.0	49.0
$Ar_{out}t$ [vol-%]	0.5	0.5	0.5	0.4	0.4	0.4

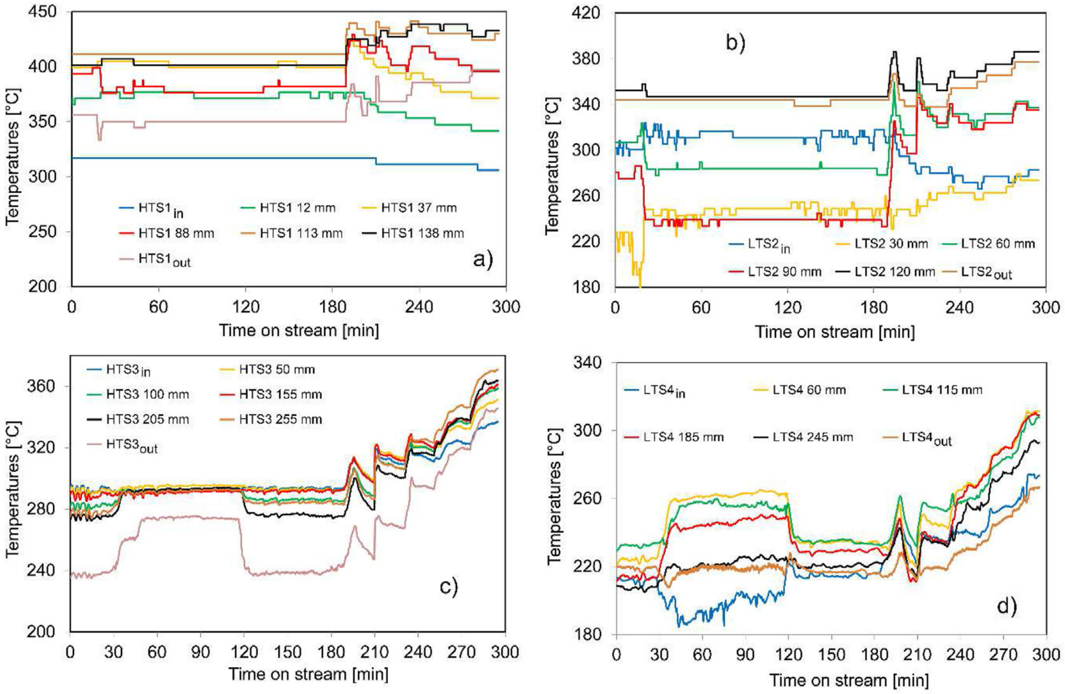

Fig. 12 – **Temperatures in WGS reactor 6B with the new concept IIb: high-temperature stage HTS1 (a); low-temperature stage LTS2 (b); high-temperature stage HTS3 (c); and *low-temperature stage LTS4* (d).**

for producing synthetic fuels and chemicals from natural gas on a large scale. Oxygen-based ATR operation with low steam-to-carbon ratios are preferred for synthesis gas production in gas-to-liquid units [76]. Soot-free operation with a steam-to-carbon ratio of 0.6 is reported in industrial applications, e.g., by Haldor Topsoe [77]. Ni-based catalysts such as SiO_2/α-Al_2O_3/Ni or Ni/Mg–Al_2O_3, in combination with high reactor outlet temperatures (950–1050 °C) and 40 bar operating pressures are reported in the literature and offer a high thermal stability [78,79]. Such ATR reactors are composed of, first, a non-catalytic zone for the exothermal partial oxidation step and, second, a catalytic zone for endothermic steam reforming [80]. If we assume a reactor outlet temperature of 950 °C, it becomes clear that the first zone of the reactor faces a much higher temperature, which must also be tolerated, at least at the beginning of the second zone.

In process simulations for FT synthesis that are enhanced by a reformer, the exit temperature of the reformer was defined as 950 °C, which is in agreement with the literature [81]. The pressure was set to 30 bar, which is in good agreement with the overall process. The steam-to-carbon ratio was defined as 0.6 based on industrial practices [77,82]. In accordance with the process conditions, the inlet temperature was defined as 925 °C. Finally, the temperature control was realized by the oxygen feed rate, which has the aim of keeping the exit temperature at 950 °C. Assuming a complete partial oxidation in the first reactor zone until the fed oxygen amount is consumed, the adiabatic combustion temperature was calculated as 1085 °C.

The simulated concept cannot be realized without radical modifications in the ATR technology, which was originally developed for diesel-based fuel cell systems. The main differences can be listed as different temperature levels, catalyst types, and educt states. Autothermal reformers developed for diesel reforming are fed by liquid diesel fuel at room temperature, superheated steam/air mixture at around 460 °C, and pre-heated air at approximately 180 °C. Upon mixing and evaporation, the diesel/steam/air mixture enters the catalyst bed at around 320 °C if no pre-reactions occur in the mixing chamber. The temperature in the catalyst bed increases rapidly to about 850–950 °C due to oxidation reactions. At the outlet of the reforming catalyst, the temperature drops to about 700 °C due to endothermic steam reforming. In comparison, the temperature increase in the ATR concept developed for the FT synthesis by Schemme [75] is less moderate, but results in a higher temperature due to the higher starting temperature of 925 °C. In addition, the lower steam-to-carbon ratio results in an outlet temperature that is only slightly higher than the inlet temperature. The selected inlet and outlet temperatures are defined based on the upstream and downstream processes in the synthesis route. However, the resulting adiabatic reaction temperature can be critical for the catalytic process if the ATR reactor utilizing precious metal catalysts from diesel reforming is adapted for the synthesis process, which typically uses nickel-based catalysts. Therefore, dedicated research activities are required to optimize the ATR process further, so that the ATR reactors from diesel reforming can be adapted for synthesis processes based on the findings. A switch to other catalyst formulations might be necessary if the temperature level cannot be reduced through process modifications. This would bring the advantage of using non precious metal catalysts in the reformer. On the other hand, if a proper process concept is identified that further utilizes the precious metal catalysts in the reformer, the advantage would be operation at lower temperatures, which enables the selection of lower cost materials. As a conclusion, it is obvious that a more radical adaptation of the reformer technology is required in comparison to the transfer of WGS reactors and catalytic burners from diesel reforming to fuel synthesis.

4. Conclusions

In the course of the energy transition in Germany, a thematic reorientation of research topics has taken place. It has long been the goal to make energy processes more efficient. The fuel cell is an important component of increasing efficiency. In order to achieve a wide range of applications – especially in transportation – it was necessary to reformate hydrogen from liquid fuels such as kerosene and diesel. The origin of the liquid input materials for this was initially fossil-based; later, biomass in the form of biofuels came into play. However, the implementation of the energy transition will entail massive upheavals in the energy infrastructure. Hydrogen generation processes via electrolysis will play a decisive role here. This hydrogen can be used directly in various applications: for hydrogen-powered fuel cell vehicles or for steel production. Carbon is sequestered in various ways via CO_2 in synthetic fuels and platform chemicals for the chemical industry. The question now arises as to whether all of the components that were developed for the provision of hydrogen are no longer required. This study demonstrates that such reactors can also be used in systems for the production of synthetic fuels. Examples from projects show that this has already occurred in practice.

Preliminary emission measurements prove the high performance of catalytic burners [62] from fuel cell technology with no detectable carbon monoxide and nitrogen oxide between 2.1 and 6.6 ppm [74].

In the BiRG project, an existing reactor for the water–gas shift reaction was adapted to the CO content of a product gas from the pyrolysis of biogenic residues, which can contain 15–29 vol% CO. The experimental results of the adapted design achieve outlet concentrations of 0.1–0.8 vol% CO. These low concentrations fulfil the requirements of a subsequent biological methanation that tolerates carbon monoxide concentrations at a maximum of 1 vol% CO.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors would like to thank all members of the Institute for Electrochemical Process Engineering (IEK-14) for fruitful discussions on all of the technologies of the energy transition and their role in the future energy system. We convey a special thanks to the research groups in the process engineering of fuel synthesis and chemistry of fuel synthesis. The results from the water–gas shift reactor were achieved within the scope of the BiRG project, which is funded by the German Federal Ministry of Economics, Energy and Climate, number: 03EI5415B.

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