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The energy transition is pushing the boundaries of technical chemistry because of new requirements in terms of scale and availability of raw materials. The research is actively answering to this demand, by developing new methods for the optimisation of load-flexible reactors and by defining new processes that flexibly adapt to the resource availability.

The challenge of sustainable technical chemistry

The search for cleaner and more sustainable chemical processes is pushing the boundaries of technical chemistry research. The main challenges to be addressed are related to the shift from fossil to renewable resources. Fossil fuels, such as natural gas, coal and crude oil are generally available in large reservoirs, from which they can be retrieved in large quantities and in a continuous way over large periods of time. Renewable resources differ from the fossil fuels in several ways. Primarily, they are available on a stochastic way, which means they can be utilised only when particular conditions are achieved. Additionally, the quantity of energy obtainable varies over the periods of availability. For example, solar energy is available only when daylight is present and with a varying load profile during the day and over the seasons. In addition to this, the renewable resources are usually distributed on the territory, so that large harvesting areas are necessary to obtain a large renewable energy input. This marks another significant difference with the fossil resources, which are normally retrieved from one or few point sources. For this reason, one can imagine that the devices for renewable energy conversion may be of smaller scale than the currently available fossil technologies [1]. If the renewable resources are used to produce basic chemicals, the standard chemical productions chain need to be rethought, to better address the different characteristics of the feedstock. In particular, the chemical reactors need to better adapt to the intrinsic variability in the feedstock availability. As an example, figure 1 reports a typical profile of the wind and photovoltaic load profile over one year in the city of Zürich. One can observe two different trends: a short-term variability (i.e., day/night cycles) and a long-term variability (i.e., difference among seasons). The short-term variability can be at least partially compensated using peak shaving measures, such as using batteries to provisionally store electricity or producing intermediate chemicals like H₂ to be deposited in temporary collection points (e.g., pressurized tanks). In this sense, in most of the practical cases, electricity is first converted in an electrochemical synthesis step, which is relatively flexible and can adapt to the scattered profiles shown in figure 1 [2]. The long-term variability is instead more difficult to handle because it causes significant fluctuations in the availability of the raw materials and requires the chemical processing devices to adapt to the different load profiles over the seasons [3]. This causes significant challenges, because currently the chemical reactors are optimized to operate in a continuous way in steady state [4]. Hence, important research efforts are currently deployed to rethink the chemical reactor design procedures to configure reactors showing an optimal performance with multiple working points. Figure 2 reports

the possible process pathways to produce basic chemicals starting from renewable electricity. The first step is an electrochemical process aimed at the direct conversion of electricity into valuable chemicals. We can here distinguish between two cases: H₂ production and other chemicals synthesis. H₂ production can show different flexibility aspects according to the electrolysis technology used. The most common electrolysis processes, alkaline and proton exchange membrane, are good in handling load changes and can start up in short time (i.e., in few minutes) [5]. H₂ is then at the basis of several possible chemical synthesis routes, leading to the production of basic chemicals. We here recall four main process intermediates: syngas, methane, methanol, and ammonia. All these compounds are essential for the chemical industry and their production from H₂ shows significant challenges that needs to be addressed in view of flexibilization of their synthesis route. Over the last few years, significant research efforts focused on the resolution of these challenges. Syngas is produced from CO₂ and H₂ at high temperature in an endothermic reaction (reverse water-gas-shift), which requires a special attention on the heat transfer mechanism to provide the necessary heat of reaction [6]. Methanol is synthesized from CO₂ and H₂ at high pressure with low conversion, hence requiring recycling of the unreacted reactants [7]. This generates challenges in the load-flexible operation, because of the instauration of different steady-state conditions according to the load case. Methane is produced from CO₂ and H₂ in a highly exothermic reaction, so that the reactor must be designed in a way to efficiently release the excess heat from the reaction, independently from the flow rate [8]. Ammonia is produced from N₂ and H₂ in an exothermic process at high temperature, which requires similar reactor design attention as for the methanol case [9]. The new trends raising in the design of load-flexible reactors will be elucidated looking at the methane synthesis case in the next section.

A possible answer to the need of flexible conversion of electricity comes from the electrochemical synthesis processes. In these processes, electrons are directly used as reagents, to force reactions to progress. These processes were proven for the production of various base chemical, such as H₂, NH₃, CH₄, CH₂O, MeOH and many others [10,11]. The direct use of electricity and CO₂ in the production of chemicals is gaining importance in the research and may become a fundamental solution for the decarbonisation of the energy systems in the near future [12]. In principle, these systems are extremely flexible and can be started up in relatively short time. Additionally, one can imagine adapting the energy intake with an appropriate modularisation and with the adaptation of the voltage used according to the available electricity [13]. Unfortunately, with the notable exception of H₂ production, these technologies are in their infancy and only available at low TRLs. Additionally, the scale up of these electrochemical units is currently challenging. We imagine that future *Trendberichte* will be able to better describe the evolution of this research field. At the moment, the large-scale production of sustainable chemicals is preferentially performed by thermochemical processes using renewable H₂ as feedstock.

To correctly address the load-flexible chemical reactor design, one shall consider the various scales involved in the complex problem. The different aspects included in this multi-scale problem are summarised in figure 3. The chemical reaction occurs at the molecular level, hence appropriate models simulating the chemical reaction and including undesired effects, like side-product synthesis, catalyst deactivation and mass and heat transfer limitations at the particle level are required. Ideally, the reactor design procedures should include appropriate micro kinetic models, which can describe with high accuracy the molecular phenomena [14]. Heat and mass transfer occurs also at higher scale, as it is determined by the flow of reactive fluids, whose properties are determined by

macroscopic phenomena. To control these phenomena, the reactor should be designed with care [15]. However, the reactor design requires the use of heat and mass balances at the macroscale, where the flow patterns can be defined. In the special case of the chemical processes linked to electricity production, it is necessary to add one additional layer of complexity. In fact, the oscillation in the energy availability occurs over a larger time scale than the chemical reaction in the reactor (hours vs. seconds scale). Hence, the complete modelling of a load flexible chemical production from renewable energy should include equations stating the variation in the performance of the reactor over large time scales and evaluate the performance of the system with respect with the load variations [16]. Additionally, the change in the amount of gas to process over time has influence on other units connected to the chemical reactor, such as CO₂ capture upstream or product upgrading units downstream the reactor. This is the case, for example, of the load flexible processes for biogas upgrading through methanation [17]. In this case, the process model must include elements for the flexible coupling of the reactor modelling equations with the balances of other units. This new level of multiscale modelling is subject of intense research work from several research groups since few years. In the following paragraphs, an overview of the latest results in this field is provided.

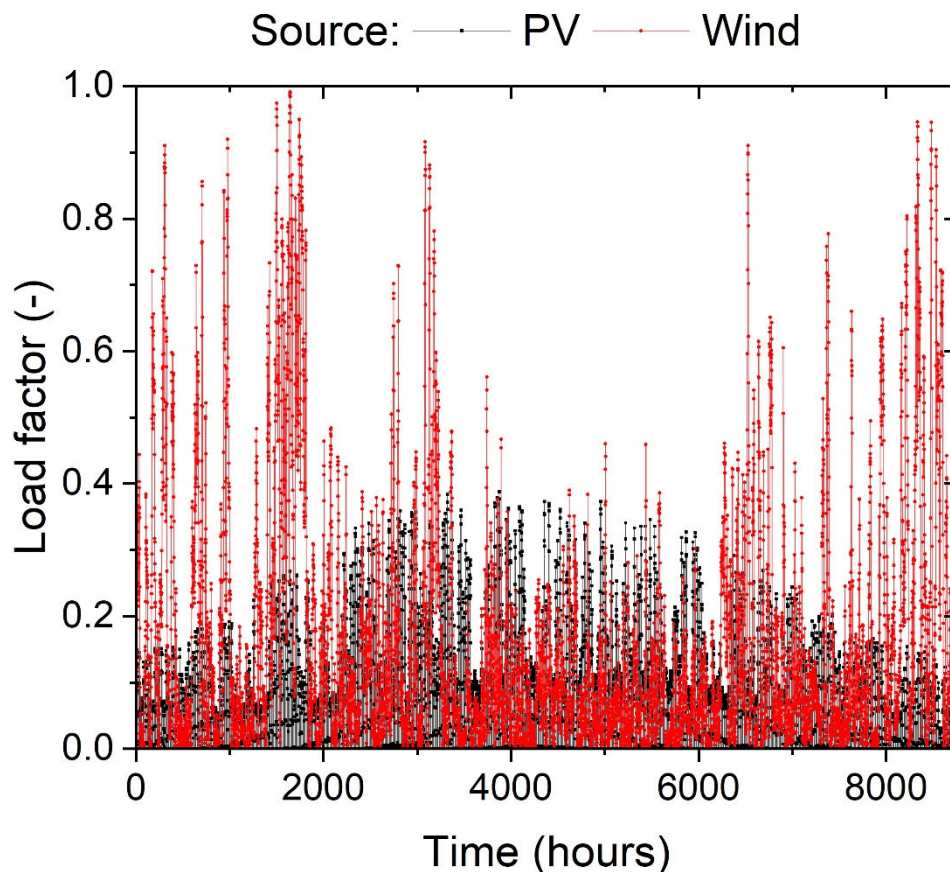


Figure 1 A typical load profile for electricity production over one year in the city of Zürich. Data elaborated based on [18] and averaged over 24 hours periods.

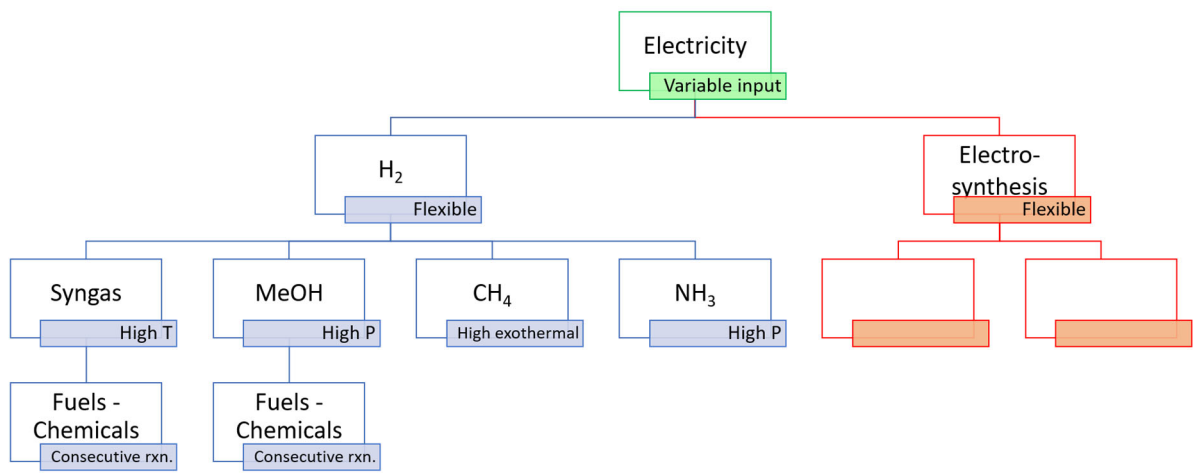


Figure 2 The basic chemicals production routes starting from renewable electricity, including the origin of the main challenges in the synthesis route design.

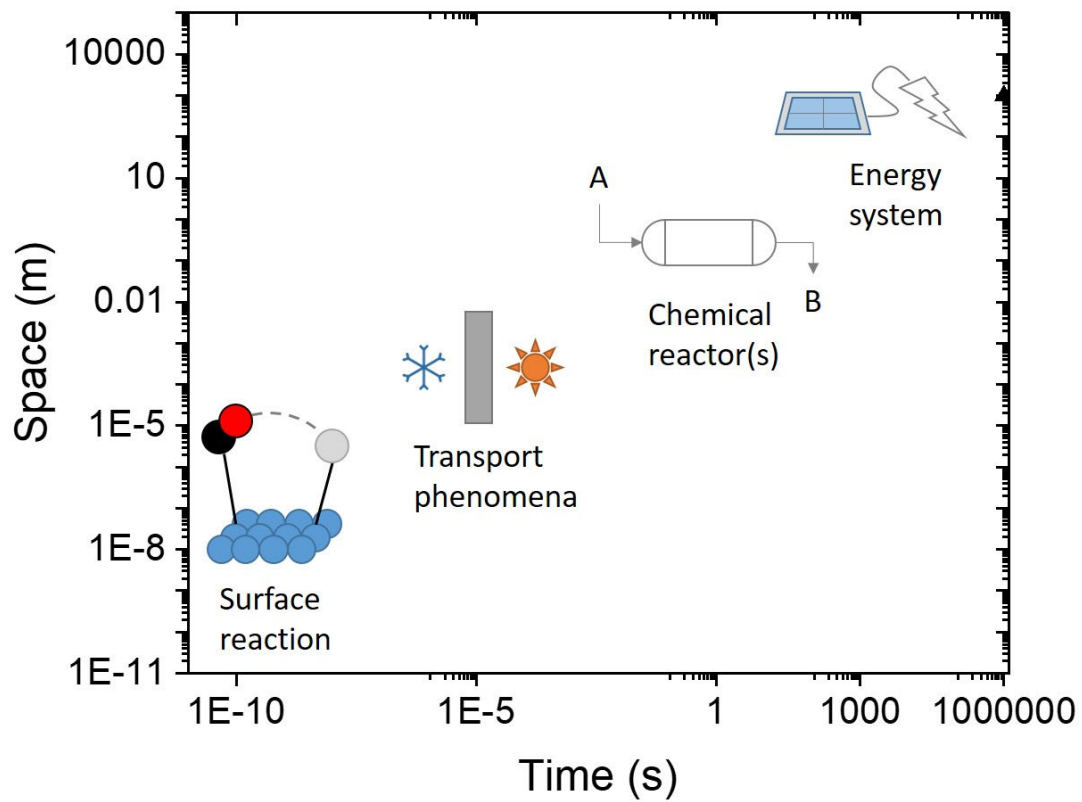


Figure 3 the various scales involved in the design of sustainable basic chemical production.

Optimisation methods for the load flexible reactors

The optimization of a load flexible reactors is significantly different than the optimization of standard steady-state reactors. The origin of the higher problem complexity lies in the instauration of multiple working points, which may result in significantly different properties of the reaction. The optimisation problem is constrained by safety limits (e.g., maximal temperature) and productivity restrictions (e.g., acceptable product gas composition), which may become challenging in certain operation points. In the case of CO₂ methanation, the main challenge is linked to the efficient removal of the reaction heat. The problems linked to the operation in different conditions are summarised in figure 4. Normally, the reaction is operated in cooled-wall fixed-bed reactors, where the appropriate heat exchange is achieved with high surface area-to-volume ratio [19]. The load variation causes the change in the axial velocity of the fluid, with evident consequences on the heat transfer properties. This change in the heat transfer has several consequences [20]. Primarily, the extent of the hotspot may vary, increasing the stress on the catalyst due to higher temperature. In the worst cases, this may even lead to reaction runaway. Secondly, the temperature profile may shift over the axial reactor coordinate, due to an earlier or later activation of the chemical reaction. This is detrimental for the reactor performance, as the required productivity may not be achieved because part of the reactor would not perform the reaction as expected. Thirdly, the further variation of the reactor load may originate wrong-way behaviour, which means that the reactor would stabilise at a different steady-state point than expected. The most obvious parameter to use to avoid undesired effects while changing the reactant flow rates is the coolant temperature. In the past, the effect of changing this parameter was analysed in various studies [21,22]. The main limitation of this approach is the restricted flexibility of the cooling system, which has a certain dynamic behaviour set by the design. Hence, the research effort is currently evolving towards new directions, exploring innovative process intensification strategies. The main alternatives in this sense are summarised in figure 5. With respect to fixed-bed reactors, it is possible to: (i) use a staged feed of the reactants, or dilution of the feed gas, where needed, (ii) dilute the catalyst in the reactor, (iii) use novel materials and formulations of the catalyst (e.g., using support materials), (iv) use different catalysts to control the reaction rate. In addition, it is possible to envisage the use of different reactor types, such as the fluidised-bed reactor, which show a lower dependence of the heat transfer properties from the feed flow.

In the past, it was shown that the use of a staged feed of the reactants does not improve the performance of the CO₂ methanation reactor in steady state conditions. A positive effect on the reactor performance can be achieved by progressively removing a product (e.g., water) from the gas stream [23]. However, staging of a single reactant (preferentially CO₂ to avoid coking due to high C/H ratio), may be beneficial in dynamic conditions, as it limits the variation in the reaction hotspot [24]. Recently, it was observed that the use of multi-stage reactors has a positive effect on the overall performance of the load-flexible methanation reactor. However, a larger optimization potential is achieved when the composition of the catalyst is modified over the stages, with an increasing fraction of active particles over the axial coordinate of the reactor [25]. This means that the solutions (i) and (ii) can be successfully combined to improve the reactor performance, together with the degree of utilisation of the reactor. The dilution of the catalyst can be performed in various ways. One can imagine forming a mechanical mixture of an active and an inert layer, which would be beneficial if the fraction of inert progressively decreases, to reduce the reaction rate at the reactor inlet and enhance it towards the outlet [4]. The inert layer can also be tailored by using an

inert/support with large heat capacity [26]. Alternatively, inert and catalyst can be mixed using egg shell/core shell configurations, to take advantage of the different diffusion properties of the two layers. For the CO₂ methanation reaction, the use of core shell pellets can be beneficial, thanks to the formation of diffusion limited layer that limits the reaction rate at high temperature [8]. This layer allows the formation of diffusional limitations that would otherwise would not be present in homogeneous or egg-shell catalysts [27]. It was shown that such catalysts could be synthesised by fluidized-bed coating [28], realising reactors more resistant to the instauration of excessive reaction hotspots [29]. In this way, it is possible to better control the reactor performance at varying reactor conditions.

The use of structured catalysts for the CO₂ methanation reaction is the object of several research works over the last few years. Recently, the process intensification potential of such systems was shown with various model catalysts. For example open-cell foam systems [30,31], monolithic structures [32], mini-monoliths [33], nanofibrous veils [34] and ceramic fibrous structured catalysts [35] were proven as solutions to enhance the performance of methanation reactors. The enhancing effect of these solutions in the dynamic CO₂ methanation reaction lies in the decrease of the influence of the gas velocity on the heat transfer mechanism. In fact, the contribution of conduction in the overall heat transfer coefficient is larger than in standard packed-bed reactors, so that the heat transfer is not strongly modified by a change in the gas velocity (differently than in the case of essentially convective heat transfer) [36].

A further option to tailor the reaction rate in the reactor, making the process more robust with respect to load variations is the use of different catalysts. As various catalysts show different reaction rates, these can be selected according to the temperature expected in the reactor [37]. Similarly to the case of catalyst dilution, it is beneficial to progressively increase the activity of the catalyst over the reaction coordinate [38]. This can be achieved using successive catalyst layers, with different active phases [39], or with different formulations of the same catalyst [40]. A specific advantage of this solution is the robustness towards the formation of undesired carbon-forming species in the hotspot (e.g., CO), which can be selectively converted in a coke-resistant successive step [39,41].

For highly exothermic reactions such as the methanation reaction, it can be worth to consider different reactive systems than the standard fixed-bed reactors. In fact, the heat transfer can be significantly improved by exploring different heat transfer options, such as the circulation of the catalyst. In this sense, the fluidized-bed reactor appears as an interesting solution to increase the heat transfer and hence increasing the flexibility of the system. Recently, several experimental reports showed the feasibility of this reaction mode [42–44]. A similar performance was also achieved in slurry bubble methanation reactors [45]. The fluidization regime allows eliminating a pronounced hotspot, hence improving the performance of the system. Consequently, in specific conditions, the fluidized bed reactor can become a more promising solution than the fixed-bed reactor from an economic point of view [46]. The response of this system to load changes can be adjusted by changing the pressure of the system, so that the fluidization regime is maintained, keeping a good heat transfer in the reactor [17]. However, the main advantages of this technology appear when processing more challenging feedstock than pure H₂ and CO₂ mixtures, such as CO/CO₂ mixtures, as the circulation of the catalyst helps avoiding deactivation phenomena [15,47].

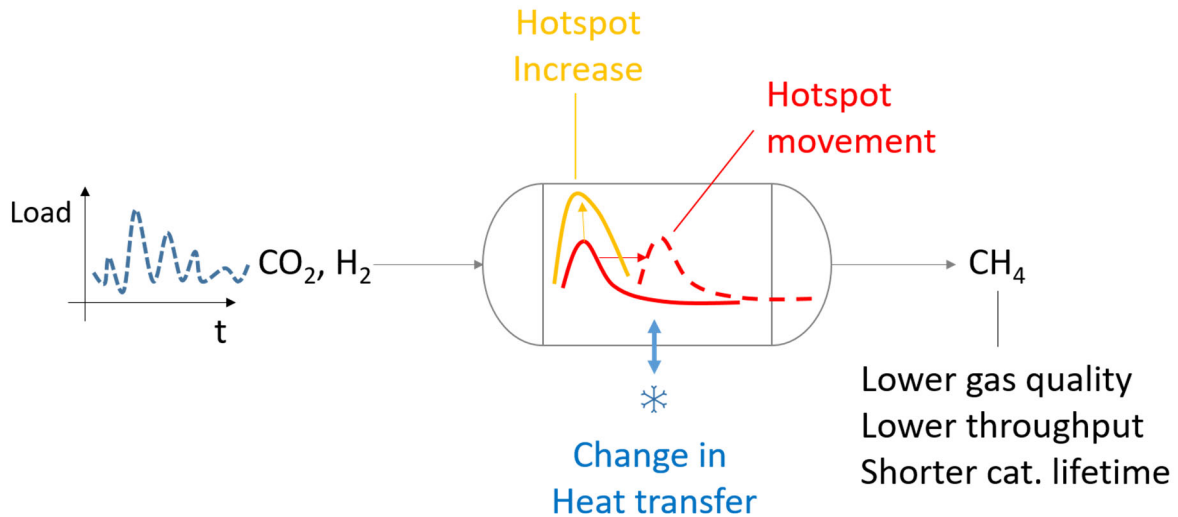


Figure 4 The challenges related to the load flexible operation of a CO₂ methanation reactor

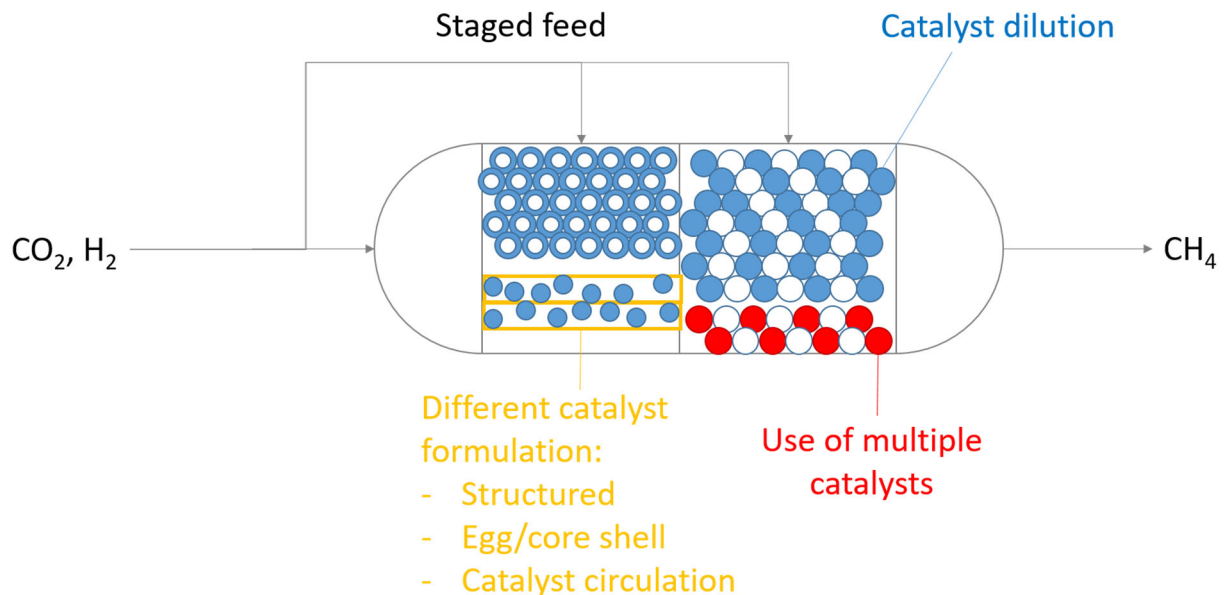


Figure 5 Some of the possible solutions to improve the robustness of the reactor in load flexible operation

Flexible use of bioenergy to enhance the productivity of energy storage reactors

Bioenergy provides a significant potential in terms of flexibility of the energy system. In fact, most of the products from energetic handling of biomass contain fractions of CO₂, which can be considered as climate neutral due to their biogenic nature. This CO₂ can be used either as a base for the production of carbon-neutral synthetic fuels with renewable H₂ or it can be captured and permanently stored resulting in negative CO₂ emissions. In the former case, we refer the system as carbon capture and utilisation (CCU) [48]. In the latter case, one can name the process as bioenergy with carbon capture and storage (BECCS). The BECCS strategies are currently regarded as one of the most promising pathway to reach carbon neutrality in a short term perspective [49]. An important unlocked potential lies in the combination of the two strategies, which can foster the role of bioenergy in the development of the carbon neutral energy system. In this sense, the biomass

production systems can be seen as a platform to absorb the excess energy, when available, or to provide negative emissions in standard operation [50]. Here we highlight the possibility to develop such a system for two specific cases: biogas upgrading and biomass gasification. Nevertheless, the principle can be applied to several other bioenergy production systems.

Biogas is a mixture of CH_4 and CO_2 , resulting from several waste recovering processes [51]. The separation of CO_2 can be performed with several alternative technologies, such as physical or chemical scrubbing or by membrane separation [50]. The resulting highly concentrated CH_4 stream can be directly injected in the natural gas grid and substitute fossil methane. The CO_2 stream generally contains high amount of this compound, so that it can be further utilised with relatively low additional effort (i.e. according to the final use CO_2 requires compression or liquefaction). The development of integrated BECCS/CCU units can show significant synergies between the two operation modes, reducing the CAPEX and extending the operation hours for the energy storage mode. A clear example in this direction is the biogas upgrading via membrane separation. Commercial membranes for the CO_2/CH_4 separation are effective also in the H_2/CH_4 separation. Hence, they can be successfully employed both downstream a biogas production plant and after a CO_2 methanation reactor (to eliminate the H_2 in excess to the grid injection requirements) [52]. In this way, the same equipment can be used in both operation modes, delivering the same product all over the year, but in different quantities according to the boundary conditions. Additionally, this flexible operation of the biogas upgrading plant allows a significant extension of the operation of the methanation reactor, which can be kept in hot standby when renewable energy is temporarily not available. Thanks to the coupling with the biogas upgrading, all the ancillary units (e.g. compression) work in a continuous way, so that the switch between the two operation modes is simple and can be performed in short time [53]. In this way, it is also possible to profitably operate the process in part-load [17]. The main research challenge related to this utilisation of power-to-X strategy is connected to the distributed nature of the feedstock, which is generally available in plants of limited dimensions. This requires a rethinking of the production chains, as the process integration commonly used in large scale may not be feasible [54].

Another possible flexible use of bioenergy involves the integration of gasification and energy storage. The syngas produced in biomass gasification contains carbon in excess with respect to H_2 , with a ratio depending on the properties of the feedstock [55]. Hence, either CO_2 must be removed or H_2 must be added to adjust the C/H ratio. In this case, a synthetic fuel production unit is operating continuously, and its operation range can be extended by addition of H_2 from renewable energy. With a limited increase in CAPEX, the operation of the system can be switch from a steady-state case to a highly dynamic case, where the system can advantageously import electricity when cheap. The load change in this case is easier to achieve, as this simply involves an increase from the base load and not a start-up phase. The operation of such a dynamic system is more profitable than the steady state gasification in most of the practical cases [56]. Additionally, this reaction scheme can be applied to several products, such as SNG [57], methanol [58] or Fischer-Tropsch fuels [59].

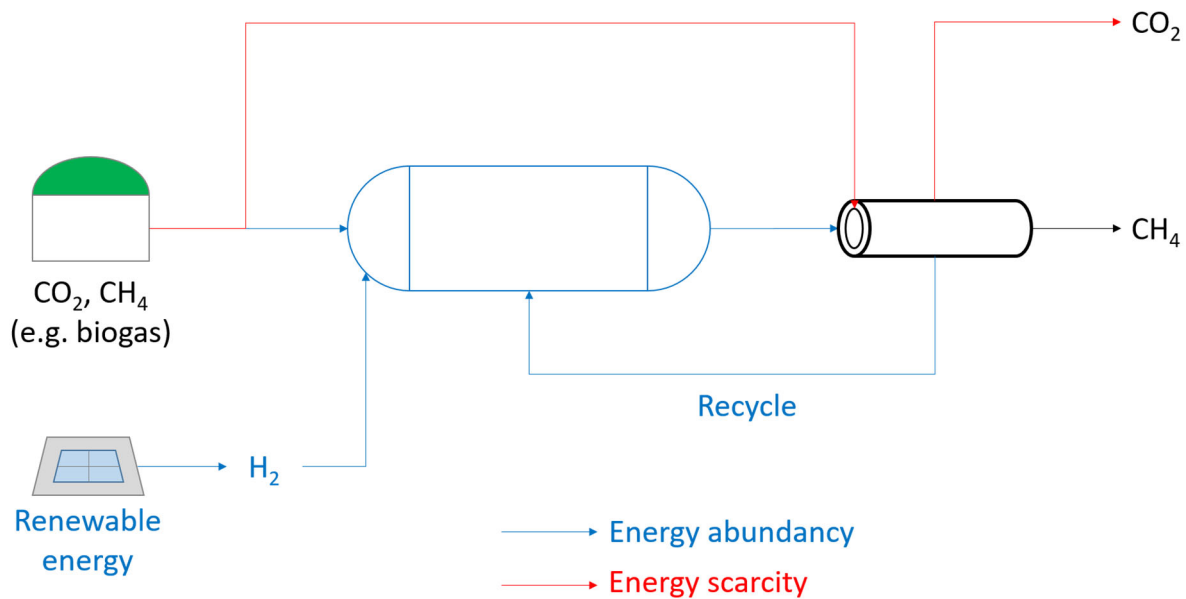


Figure 6 The flexible operation of biogas upgrading: when energy is scarce, biogas is upgraded by membranes (red lines); when energy is abundant, H₂ is produced and biogas is performed by methanation (blue lines). The membranes are used to upgrade the produced SNG.

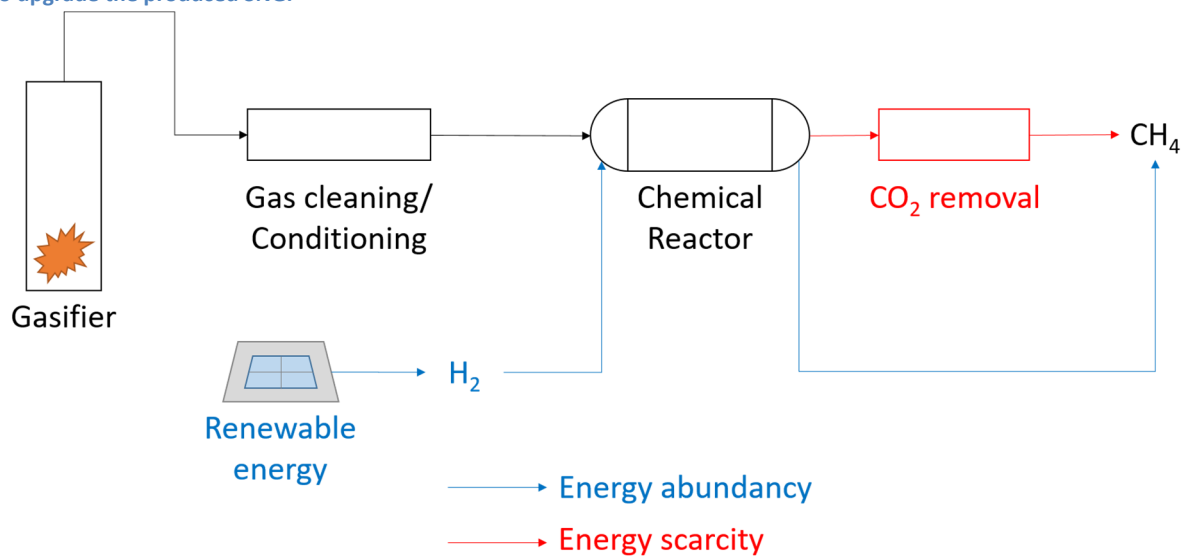


Figure 7 The flexible operation of gasification units: when energy is scarce, syngas is used to produce synthetic fuels and the excess carbon is eliminated in a CO₂ removal unit (red lines); when energy is abundant, the load of the chemical reactor is increased by using H₂ from renewable energy (blue lines).

Perspectives for technical chemistry

In conclusion, we observed that the chemical processes are evolving towards new directions dictated by the requirement of avoiding carbon emission and better using the distributed feedstock. Generally, the chemical processes will need to adapt to smaller scale and to a generalized more challenging supply chain of the raw materials and energy for the production of chemicals. This results in the need to design more robust reactors with respect to load variable operation. Additionally, the synthesis of process schemes needs to include these flexibilization aspects from the initial steps of the design, selecting process units that better integrate together in the determination

of a globally more flexible process. In the first steps towards a decarbonized energy system, the generation of negative emissions by capturing readily available biogenic CO₂ (e.g. from bioenergy upgrading units) can be an easy solution to demonstrate the technology readiness of carbon capture technologies. Hence, it is essential to develop new solutions dynamically integrating bioenergy production with CCS and CCU to advance the technological availability of all the single conversion units required in the decarbonized chemical and energy systems. In this paper, it was shown that the main tools for the experimental and theoretical investigation of such systems are already available and can serve the paradigm shift for technical chemistry, involving the rethinking of process design, from highly optimized steady state systems to load-flexible and dynamic systems. The main challenges for technical chemistry will hence involve a modification of the tools used, with a larger focus on unconventional aspect of process design, which will gain importance over the next few years.

References

- [1] E. Moiola, Process intensification and energy transition : A necessary coupling ?, *Chem. Eng. Process. - Process Intensif.* 179 (2022) 109097. <https://doi.org/10.1016/j.cep.2022.109097>.
- [2] M. Reuß, T. Grube, M. Robinius, D. Stolten, A hydrogen supply chain with spatial resolution: Comparative analysis of infrastructure technologies in Germany, *Appl. Energy.* 247 (2019) 438–453. <https://doi.org/10.1016/j.apenergy.2019.04.064>.
- [3] N. Vulic, M. Rüdüsüli, K. Orehounig, Evaluating energy flexibility requirements for high shares of variable renewable energy: A heuristic approach, *Energy.* 270 (2023) 126885. <https://doi.org/10.1016/j.energy.2023.126885>.
- [4] K.L. Fischer, H. Freund, Intensification of load flexible fixed bed reactors by optimal design of staged reactor setups, *Chem. Eng. Process. - Process Intensif.* 159 (2021). <https://doi.org/10.1016/j.cep.2020.108183>.
- [5] A. Buttler, H. Spliethoff, Current status of water electrolysis for energy storage, grid balancing and sector coupling via power-to-gas and power-to-liquids: A review, *Renew. Sustain. Energy Rev.* 82 (2018) 2440–2454. <https://doi.org/10.1016/j.rser.2017.09.003>.
- [6] J.A. Hernandez Lalinde, P. Roongruangsree, J. Ilsemann, M. Bäumer, J. Kopyscinski, CO₂ methanation and reverse water gas shift reaction. Kinetic study based on in situ spatially-resolved measurements, *Chem. Eng. J.* 390 (2020) 124629. <https://doi.org/10.1016/j.cej.2020.124629>.
- [7] E. Moiola, T. Schildhauer, Eco-Techno-Economic Analysis of Methanol Production from Biogas and Power-to-X, *Ind. Eng. Chem. Res.* 61 (2022) 7335–7348. <https://doi.org/10.1021/acs.iecr.1c04682>.
- [8] R.T. Zimmermann, J. Bremer, K. Sundmacher, Load-flexible fixed-bed reactors by multi-period design optimization, *Chem. Eng. J.* 428 (2022). <https://doi.org/10.1016/j.cej.2021.130771>.
- [9] T. Cholewa, M. Semmel, F. Mantei, R. Güttel, O. Salem, Process Intensification Strategies for Power-to-X Technologies, *ChemEngineering.* 6 (2022). <https://doi.org/10.3390/chemengineering6010013>.
- [10] W.L. Becker, R.J. Braun, M. Penev, M. Melaina, Production of Fischer-Tropsch liquid fuels from high temperature solid oxide co-electrolysis units, *Energy.* 47 (2012) 99–115.

- <https://doi.org/10.1016/j.energy.2012.08.047>.
- [11] C. Graves, S.D. Ebbesen, M. Mogensen, K.S. Lackner, Sustainable hydrocarbon fuels by recycling CO₂ and H₂O with renewable or nuclear energy, *Renew. Sustain. Energy Rev.* 15 (2011) 1–23. <https://doi.org/10.1016/j.rser.2010.07.014>.
- [12] E. Klemm, C.M.S. Lobo, A. Löwe, V. Schallhart, S. Renninger, L. Waltersmann, R. Costa, A. Schulz, R.U. Dietrich, L. Möltner, V. Meynen, A. Sauer, K.A. Friedrich, CHEMampere: Technologies for sustainable chemical production with renewable electricity and CO₂, N₂, O₂, and H₂O, *Can. J. Chem. Eng.* 100 (2022) 2736–2761. <https://doi.org/10.1002/cjce.24397>.
- [13] K. Roh, L.C. Brée, P. Schäfer, D. Strohmeier, A. Mitsos, Flexible operation of modular electrochemical CO₂ reduction processes, *IFAC-PapersOnLine*. 55 (2022) 298–303. <https://doi.org/10.1016/j.ifacol.2022.07.460>.
- [14] E.B. Sterk, A.E. Nieuwelink, M. Monai, J.N. Louwen, E.T.C. Vogt, I.A.W. Filot, B.M. Weckhuysen, Structure Sensitivity of CO₂ Conversion over Nickel Metal Nanoparticles Explained by Micro-Kinetics Simulations, *J. Am. Chem. Soc.* 2 (2022) 2714–2730. <https://doi.org/10.1021/jacsau.2c00430>.
- [15] Y. Du, J. Liang, S. Yang, J. Hu, G. Bao, H. Wang, Numerical investigation of the Ni-based catalytic methanation process in a bubbling fluidized bed reactor, *Energy*. 257 (2022) 124708. <https://doi.org/10.1016/j.energy.2022.124708>.
- [16] E. Moioli, Linking heat and electricity supply for domestic users: an example of power-to-gas integration in a building, *RSC Adv.* 12 (2022) 10355–10365. <https://doi.org/10.1039/d2ra00951j>.
- [17] A. Gantenbein, T.J. Schildhauer, Challenges in part load operation of biogas-based power-to-gas processes (part I), *Front. Energy Res.* 10 (2022). <https://doi.org/10.3389/fenrg.2022.1049687>.
- [18] S. Pfenninger, I. Staffell, Long-term patterns of European PV output using 30 years of validated hourly reanalysis and satellite data, *Energy*. 114 (2016) 1251–1265. <https://doi.org/10.1016/j.energy.2016.08.060>.
- [19] R. Schlautmann, H. Bo, A. Zauner, F. Mo, R. Tichler, F. Graf, T. Kolb, Renewable Power-to-Gas : A Technical and Economic Evaluation of Three Demo Sites Within the STORE & GO Project, (2021) 568–579. <https://doi.org/10.1002/cite.202000187>.
- [20] K.L. Fischer, H. Freund, On the optimal design of load flexible fixed bed reactors: Integration of dynamics into the design problem, *Chem. Eng. J.* 393 (2020) 124722. <https://doi.org/10.1016/j.cej.2020.124722>.
- [21] K.L. Fischer, M.R. Langer, H. Freund, Dynamic Carbon Dioxide Methanation in a Wall-Cooled Fixed Bed Reactor: Comparative Evaluation of Reactor Models, *Ind. Eng. Chem. Res.* 58 (2019) 19406–19420. <https://doi.org/10.1021/acs.iecr.9b02863>.
- [22] J. Bremer, K. Sundmacher, Operation Range Extension via Hot-Spot Control for Catalytic CO₂ Methanation Reactors, *React. Chem. Eng.* 4 (2019) 1019–1037. <https://doi.org/10.1039/c9re00147f>.
- [23] A. El Sibai, L.K. Rihko Struckmann, K. Sundmacher, Model-based Optimal Sabatier Reactor Design for Power-to-Gas Applications, *Energy Technol.* 5 (2017) 911–921. <https://doi.org/10.1002/ente.201600600>.

- [24] E. Moioli, N. Gallandat, A. Züttel, Parametric sensitivity in the Sabatier reaction over Ru/Al₂O₃ – theoretical determination of the minimal requirements for reactor activation, *React. Chem. Eng.* (2018). <https://doi.org/10.1039/C8RE00133B>.
- [25] K.L. Fischer, H. Freund, Intensification of load flexible fixed bed reactors by optimal design of staged reactor setups, *Chem. Eng. Process. - Process Intensif.* 159 (2021). <https://doi.org/10.1016/j.cep.2020.108183>.
- [26] L. Truong-Phuoc, J.M. Nhut, S. Sall, G. Tuci, A. Rossin, V. Papaefthimiou, C. Duong-Viet, C. Petit, M. Arab, A. Jourdan, L. Vidal, G. Giambastiani, C. Pham-Huu, Not Just Another Methanation Catalyst: Depleted Uranium Meets Nickel for a High-Performing Process Under Autothermal Regime, *ChemSusChem.* (2022). <https://doi.org/10.1002/cssc.202201859>.
- [27] A. Porta, L. Falbo, C. Giorgio, L. Lietti, C. Bassano, P. Deiana, Synthesis of Ru-based catalysts for CO₂ methanation and experimental assessment of intraporous transport limitations, *Catal. Today.* 343 (2020) 38–47. <https://doi.org/10.1016/j.cattod.2019.01.042>.
- [28] M. Capece, R. Dave, Application of fluidized bed film coating for membrane encapsulation of catalysts, *Powder Technol.* 211 (2011) 199–206. <https://doi.org/10.1016/j.powtec.2011.04.015>.
- [29] R.T. Zimmermann, S. Weber, J. Bremer, V. Idakiev, R. Pashminehazar, T.L. Sheppard, L. Mörl, K. Sundmacher, Core–shell catalyst pellets for effective reaction heat management, *Chem. Eng. J.* 457 (2023). <https://doi.org/10.1016/j.cej.2022.140921>.
- [30] R. Balzarotti, G. Drago Ferrante, C. Italiano, M. Laganà, L.F. Francis, A. Vita, C. Cristiani, L. Pino, RhNi/CeO₂ catalytic activation of alumina open cell foams by dip-spin coating for the CO₂ methanation of biogas, *Surf. Coatings Technol.* 441 (2022). <https://doi.org/10.1016/j.surfcoat.2022.128563>.
- [31] C. Italiano, G. Drago Ferrante, L. Pino, M. Laganà, M. Ferraro, V. Antonucci, A. Vita, Silicon carbide and alumina open-cell foams activated by Ni/CeO₂-ZrO₂ catalyst for CO₂ methanation in a heat-exchanger reactor, *Chem. Eng. J.* 434 (2022). <https://doi.org/10.1016/j.cej.2022.134685>.
- [32] Y. Chen, X. Wu, Q. Liu, M. He, H. Bai, Ni-Foam Structured Ni-Phyllosilicate Ensemble as an Efficient Monolithic Catalyst for CO₂ Methanation, *Catal. Letters.* 152 (2022) 2738–2744. <https://doi.org/10.1007/s10562-021-03850-y>.
- [33] N. García-Moncada, J.C. Navarro, J.A. Odriozola, L. Lefferts, J.A. Faria, Enhanced catalytic activity and stability of nanoshaped Ni/CeO₂ for CO₂ methanation in micro-monoliths, *Catal. Today.* 383 (2022) 205–215. <https://doi.org/10.1016/j.cattod.2021.02.014>.
- [34] E. Loccufier, G. Watson, Y. Zhao, M. Meledina, R. Denis, P.G. Derakhshandeh, P. Van Der Voort, K. Leus, D. P. Debecker, K. De Buysser, K. De Clerck, CO₂ methanation with Ru@MIL-101 nanoparticles fixated on silica nanofibrous veils as stand-alone structured catalytic carrier, *Appl. Catal. B Environ.* 320 (2023) 121972. <https://doi.org/10.1016/j.apcatb.2022.121972>.
- [35] A. Sánchez, V.G. Milt, E.E. Miró, R. Güttel, Simulation Study of Ceramic Fibrous Structured Catalysts for CO₂ Methanation—Enhancement of the Performance and Comparison to Pellet Catalysts, *Top. Catal.* 65 (2022) 1317–1330. <https://doi.org/10.1007/s11244-022-01675-6>.
- [36] S. Razza, T. Heidig, E. Bianchi, G. Groppi, W. Schwieger, E. Tronconi, H. Freund, Heat transfer performance of structured catalytic reactors packed with metal foam supports: Influence of

- wall coupling, *Catal. Today*. 273 (2016) 187–195.
<https://doi.org/10.1016/j.cattod.2016.02.058>.
- [37] R. Mutschler, E. Moioli, A. Züttel, Modelling the CO₂ hydrogenation reaction over Co, Ni and Ru/Al₂O₃, *J. Catal.* 375 (2019) 193–201. <https://doi.org/10.1016/j.jcat.2019.05.023>.
- [38] Y. Jeong, J. Park, M. Han, Design and Control of a Fixed-Bed Recycle Reactor with Multicatalyst Layers: Methanation of Carbon Dioxide, *Ind. Eng. Chem. Res.* 60 (2021) 4650–4667. <https://doi.org/10.1021/acs.iecr.0c05784>.
- [39] E. Moioli, R. Mutschler, A. Borsay, M. Calizzi, A. Züttel, Synthesis of grid compliant substitute natural gas from a representative biogas mixture in a hybrid Ni / Ru catalysed reactor, *Chem. Eng. Sci. X*. 8 (2020) 100078. <https://doi.org/10.1016/j.cesx.2020.100078>.
- [40] E. Moioli, Enhancement of Power-to-Gas via Multicatalyst Reactors Tailoring Reaction Rate and Heat Exchange, *Chimia (Aarau)*. 76 (2022) 288–293.
<https://doi.org/10.2533/chimia.2022.288>.
- [41] D. Meyer, J. Friedland, J. Schumacher, M.G. Gäßler, R. Güttel, Hydrogenation of CO/CO₂ mixtures under unsteady-state conditions: Effect of the carbon oxides on the dynamic methanation process, *Chem. Eng. Sci.* 250 (2022) 117405.
<https://doi.org/10.1016/j.ces.2021.117405>.
- [42] J. Witte, A. Calbry-Muzyka, T. Wieseler, P. Hottinger, S.M.A. Biollaz, T.J. Schildhauer, Demonstrating direct methanation of real biogas in a fluidised bed reactor, *Appl. Energy*. 240 (2019) 359–371. <https://doi.org/10.1016/j.apenergy.2019.01.230>.
- [43] M. Hervy, J. Maistrello, L. Brito, M. Rizand, E. Basset, Y. Kara, M. Maheut, Power-to-gas: CO₂ methanation in a catalytic fluidized bed reactor at demonstration scale, experimental results and simulation, *J. CO₂ Util.* 50 (2021) 101610. <https://doi.org/10.1016/j.jcou.2021.101610>.
- [44] B. Hwang, S.I. Ngo, Y. Il Lim, M.W. Seo, S.J. Park, H.J. Ryu, H. Nam, D. Lee, Reaction Characteristics of Ni-Based Catalyst Supported by Al₂O₃ in a Fluidized Bed for CO₂ Methanation, *Catalysts*. 12 (2022) 9–11. <https://doi.org/10.3390/catal12111346>.
- [45] S. Sauerschell, S. Bajohr, T. Kolb, Methanation Pilot Plant with a Slurry Bubble Column Reactor: Setup and First Experimental Results, 2022 (2022).
<https://doi.org/10.1021/acs.energyfuels.2c00655>.
- [46] J. Witte, A. Kunz, S.M.A. Biollaz, T.J. Schildhauer, Direct catalytic methanation of biogas – Part II: Techno-economic process assessment and feasibility reflections, *Energy Convers. Manag.* 178 (2018) 26–43. <https://doi.org/10.1016/j.enconman.2018.09.079>.
- [47] J. Kopyscinski, T.J. Schildhauer, S.M.A. Biollaz, Methanation in a fluidized bed reactor with high initial CO partial pressure: Part II- Modeling and sensitivity study, *Chem. Eng. Sci.* 66 (2011) 1612–1621. <https://doi.org/10.1016/j.ces.2010.12.029>.
- [48] P. Gabrielli, M. Gazzani, M. Mazzotti, The Role of Carbon Capture and Utilization, Carbon Capture and Storage, and Biomass to Enable a Net-Zero-CO₂ Emissions Chemical Industry, *Ind. Eng. Chem. Res.* (2020). <https://doi.org/10.1021/acs.iecr.9b06579>.
- [49] L. Rosa, D.L. Sanchez, M. Mazzotti, Assessment of carbon dioxide removal potential: Via BECCS in a carbon-neutral Europe, *Energy Environ. Sci.* 14 (2021) 3086–3097.
<https://doi.org/10.1039/d1ee00642h>.

- [50] E. Moioli, T. Schildhauer, Negative CO₂ emissions from flexible biofuel synthesis: Concepts, potentials, technologies, *Renew. Sustain. Energy Rev.* 158 (2022) 112120. <https://doi.org/10.1016/j.rser.2022.112120>.
- [51] A. Anca-Couce, C. Hochenauer, R. Scharler, Bioenergy technologies, uses, market and future trends with Austria as a case study, *Renew. Sustain. Energy Rev.* 135 (2021) 110237. <https://doi.org/10.1016/j.rser.2020.110237>.
- [52] A. Gantenbein, J. Witte, S.M.A. Biollaz, O. Kröcher, T.J. Schildhauer, Flexible application of biogas upgrading membranes for hydrogen recycle in power-to-methane processes, *Chem. Eng. Sci.* 229 (2021) 116012. <https://doi.org/10.1016/j.ces.2020.116012>.
- [53] P. Colbertaldo, G. Guandalini, Techno-economic assessment of enhanced Biogas&Power-to-SNG processes with high-temperature electrolysis integration, *J. Phys. Conf. Ser.* 2385 (2022). <https://doi.org/10.1088/1742-6596/2385/1/012045>.
- [54] E. Moioli, A. Wötzel, T. Schildhauer, Feasibility assessment of small-scale methanol production via power-to-X, *J. Clean. Prod.* 359 (2022) 132071. <https://doi.org/10.1016/j.jclepro.2022.132071>.
- [55] S. Heyne, M. Seemann, T.J. Schildhauer, Coal and biomass gasification for SNG production, in: S. Biollaz, T.J. Schildhauer (Eds.), *Synth. Nat. Gas from Coal, Dry Biomass, Power-to-Gas Appl.*, John Wiley & Sons, Inc, 2016.
- [56] A. Poluzzi, G. Guandalini, S. Guffanti, M. Martinelli, S. Moioli, P. Huttenhuis, G. Rexwinkel, J. Palonen, E. Martelli, G. Groppi, M.C. Romano, Flexible Power and Biomass-To-Methanol Plants With Different Gasification Technologies, *Front. Energy Res.* 9 (2022) 1–23. <https://doi.org/10.3389/fenrg.2021.795673>.
- [57] C. Antonini, K. Treyer, E. Moioli, C. Bauer, T. Schildhauer, M. Mazzotti, Hydrogen from wood gasification with CCS - a techno-environmental analysis of production and use as transport fuel, *Sustain. Energy Fuels.* 5 (2021) 2602–2621. <https://doi.org/10.1039/d0se01637c>.
- [58] A. Poluzzi, G. Guandalini, M.C. Romano, Flexible methanol and hydrogen production from biomass gasification with negative emissions, *Sustain. Energy Fuels.* 6 (2022) 3830–3851. <https://doi.org/10.1039/d2se00661h>.
- [59] H. Gruber, P. Groß, R. Rauch, A. Reichhold, R. Zweiler, C. Aichernig, S. Müller, N. Ataimisch, H. Hofbauer, Fischer-Tropsch products from biomass-derived syngas and renewable hydrogen, *Biomass Convers. Biorefinery.* 11 (2021) 2281–2292. <https://doi.org/10.1007/s13399-019-00459-5>.