

Process intensification and energy transition: A necessary coupling?

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ABSTRACT

The energy transition requires an extensive employment of gas-solid catalytic chemical reactors to support the long-term energy storage. Many renewable resources are decentralised, so that the feedstock for the energy conversion facilities is limited. New reactor technologies will be needed to ensure the efficient conversion of renewable resources in smaller scale than the state-of-the-art processes. Process intensification is a key in this direction, fulfilling the desired conversion efficiency, miniaturization of the process units and integration with the existent facilities. This paper analyses the key aspects of process intensification to be considered and implemented in the development of chemical reactors for the energy transition. The intensification strategies should follow three main directions: miniaturization of the process units, enhanced process efficiency and high reactor flexibility. An effective tackling of these directions is challenging for the standard packed-bed reaction technology, but many alternative and promising options are available. An efficient utilization of reaction engineering principles in the design of the new processes can successfully open the way to the optimal equipment selection for each specific application. Hence, a rationally based, but creative selection of the available technologies will be an essential step in the successful implementation of chemical technology in the energy transition.

1. Introduction

The need for cleaner chemical processes, showing a lower energetic and carbon footprint, is currently calling for an important effort in the development of new chemical synthesis routes [1]. Additionally, as the energy transition towards renewable resources requires energy storage, the need for chemical processes producing synthetic fuels is expected to increase significantly in the next few years [2]. The combined effect of these two trends will require a noteworthy change in the way the chemical processes are designed and operated, because the resources and feedstock will be significantly different. In particular, the use of renewable feedstock and renewable energy will require an important decrease of the size of the equipment, due to the decentral character of the resources. Additionally, the chemical and energy markets may become more volatile, due to the oscillations in the availability of raw materials [3]. Hence, the chemical processes of the future should operate at smaller scale and in a more dynamic way.

Much research is currently addressed at the determination of new process routes to produce common chemicals from renewable resources. In the context of circular economy, CO₂ is regarded as a valuable

feedstock to produce carbon-containing chemicals [4–7]. In order to understand the effect of shifting the chemical production into a CO₂-based economy, Table 1 recollects some dimensions of the possible CO₂ sources. CO₂ can be obtained from post-combustion carbon capture, for example from power plants. In this case, the amount of collected CO₂ is significant (in the order of 400–800 t of CO₂ per MWh produced) [8], but the cost of CO₂ is relatively high, between 40 and 80 \$/t [9]. Many of the current industrial processes are also originating significant amounts of CO₂. Cement and steel plants, as well as process industry (such as oil refining and petrochemical productions) lie in this category and can be seen in the future as CO₂ sources for various applications. The cost of CO₂ from these sources is also relatively high, ranging between 40 and 120 \$/t according to the CO₂ concentration in the flue gas and the capture technology used. If the focus is posed on renewable resources, such as biogas or biomass gasification, the cost of CO₂ is lower, thanks to the opportunity of operating a pre-combustion carbon capture. In this case, the CO₂ cost lies in the range 20–50 \$/t [10]. However, the sources of CO₂ are more limited, and the technologies are not fully commercially mature yet. A last option for the CO₂ supply is the direct air capture (DAC). Despite the interest that this technology arises, thanks to the

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possibility of obtaining CO₂ independently from any other source, the costs of DAC are currently extremely high, being above 500 \$/t [11].

From the analysis above, it is evident that the transition to a CO₂-based chemical industry is possible, at least in the sense of availability of this feedstock. However, the processes from CO₂ require the use of other commodities to activate this molecule. In fact, the carbon contained in a CO₂ molecule has the highest oxidation state possible; hence, this should be reduced to a lower oxidation level. This can be done in several ways, both with thermal and electrochemical processes [5]. Table 2 shows the key parameters characterising some molecules of interest in the CO₂ activation, which are hydrogen, methane and methanol. The main renewable technologies to produce these molecules are electrolysis, gasification and biological fermentation. The resources used are renewable electricity, biomass or waste. The technologies for green commodities production have been demonstrated so far only at small-scale (up to dozens of MW) and their technological readiness is limited (most of the technologies are at demonstration scale). However, the main limitations to the technological scale up are related to process efficiency and land requirements. In fact, the harvesting of renewable electricity, biomass or waste requires large areas, generating important limitations in the supply chain. Therefore, the main limiting element for the green chemical processes will be the reducing agent availability, requiring a significant scale reduction compared to the existing process configurations.

As an example, the H₂ production should be performed by water electrolysis or from reforming of biomethane or bio-based waste. These technologies were already proven in various conditions, but the sizes demonstrated so far are small. For example, electrolyzers are currently available only up to 20 MW [19] and the technologies for biomass reforming have been demonstrated up to a similar plant size [22,21]. This is a significantly smaller size than the large-scale steam reforming plants, which can produce up to 200'000 Nm³/h of H₂ [23]. It is foreseeable that these technologies may be importantly scaled up in the future, but the supply of electricity or biomass to the production plant is challenging. In fact, the area required for harvesting is remarkable for both technologies. The electricity demand to operate a large-scale electrolyser can be recovered only with a significant extension of renewable energy generators. For example, when considering solar energy as feedstock (hence with a land footprint between 0.2 and 2 m²/kWh/y), ca. 10⁶ m² are required to produce an amount of H₂ equivalent to the throughput of a steam reformer. A comparable area is required to produce the feedstock for a gasifier or an anaerobic digester aimed at producing ca. 10 MW of H₂. Similar considerations can be formulated for the supply of methane and methanol, resulting in the same supply limitations. Hence, it is evident that the success of the energetic transition is linked to the effective downscaling of the chemical reactors, in order to adapt to the difficulties in producing the raw materials at large-scale.

The downscaling of chemical processes is not trivial. This is mainly due to the loss of performance of chemical reactors during the downscaling. Hence, the development of new applications tailored to the

renewable feedstock should be accompanied by a revitalisation of the chemical reaction engineering principles. In particular, the new chemical reactors should be characterized by a reduction in the equipment size, a higher efficiency and an enhanced flexibility. These three key properties will be discussed in detail in the following.

2. Miniaturization of process units

Currently, most of the catalytic processes for fuel processing are operated in multitubular fixed bed reactors, where the temperature is controlled by means of external cooling or heating. The heat transfer properties are optimized by selection of an appropriate design of the reactors (i.e., optimal geometry and disposition of the reactive section) and by a careful selection of the cooling/heating medium (i.e., by selecting the appropriate temperature and heat transfer properties) [27]. This reactor design routine is employed in a multitude of chemical processes and different reactor types are necessary only for very specific applications (e.g., for extremely exothermal reactions, such as the partial oxidation of complex hydrocarbons) [28]. The reactor design is facilitated by the large dimensions of the equipment and by the relatively constant flow rate. These conditions allow the establishment of good convective heat transfer (high gas velocity), which leads to a precise control of the process and to the reach of high process efficiency [27].

As discussed in the previous section, the boundary conditions for most of the reactions involved in the energy transition are significantly different from the current state-of-the-art. The availability of raw materials (mainly H₂) tends to be limited, hence requiring smaller equipment. This leads to a different reactor design problem, due to the change in the heat transfer properties of the process. In fact, the lower flow rate of reactants causes a decrease in the radial heat transfer coefficient, resulting in a worse reactor performance. This can initially be resolved by a reduction of the reactor diameter (hence keeping the superficial gas velocity constant), but the applicability of this option is limited because too small pipe diameters are impractical due to pressure drop and to the excessive reactor length required. Furthermore, small pipe diameters cause a larger influence of the wall effects, potentially decreasing the reactor performance. The effect of the reduced reactant availability is shown in Fig. 1 for the case of methanol synthesis (details on the simulations shown are reported in the supplementary information). When the H₂ availability is significantly reduced (e.g., the factor 30 present between steam reforming and electrolysis), the lower heat transfer leads to a delayed activation of the reactor, with a consequent low utilization of the initial section of the reactor. Additionally, due to the low heat exchange, the CO₂ conversion increases slowly over the axial coordinate. Hence, the standard packed-bed reactor technology shows a worse performance in the renewable energy conversion processes. For this reason, the energy transition may open the way for the development of new reaction technologies, which ensure a constant heat transfer independently from the flow rate. Fig. 1 summarizes the most promising reactor types that can overcome the down-scaling problems of the

Table 1
Typical dimensions for the CO₂ sources.

	Size demonstrated (MW, input)	CO ₂ footprint (t _{CO2} / MWh)	CO ₂ cost (\$/t _{CO2})	CCS Technology readiness level (TRL)	Refs.
Fossil CO ₂ sources					
Coal-fired power plant	100 to 5000	820	47	7-9	[12,13]
Natural gas-fired power plant	100 to 1000	490	76	7-9	[8,9]
Industrial CO ₂ sources					
Cement plants	Up to 50 kt _{CO2} /y	0.6-0.8 (t _{CO2} /t _{concrete})	40-85	7-9	[14,15]
Steel production	Up to 4 kt _{CO2} /y	1.4-2 (t _{CO2} /t _{steel})	20-90	5-9	[14,16]
Process industry	Up to 4000 kt-CO ₂ /y	2.7-99.2 (kg _{CO2} /bbl)	50-120	7-9	[14,17]
Renewable CO ₂ sources					
Biogas	up to 20	Ca. 100	20	5-9	[10]
Gasification	up to 20	Ca. 200	20-50	5-8	[10,18]
Direct air capture	up to 4000 t _{CO2} /y	-	>500	4-6	[11]

Table 2

Typical sizes of the renewable inputs for the chemical industry (AE=Alkaline Electrolyser, PEM=Proton Exchange Membrane Electrolyser, SOEC=Solid Oxide Electrolyser, PV=Photovoltaic).

Process	Size demonstrated (MW, thermal input)	Process efficiency (MW _{product} /MW _{feedstock})	Land required (m ² /kW _{product})	Technology readiness level (TRL)	Refs.
Green H ₂ supply					
Electrolysis (e ⁻ → H ₂)	Up to 20	0.5-0.75 (AE/PEM) Up to 0.9 (SOEC)	0.2 to 2 (with PV electricity)	6-9	[19, 20]
Dry biomass (gasification + steam reforming)	Up to 15	0.2-0.6	1-2	3-6	[21]
Wet biomass (anaerobic digestion + steam reforming)	Up to 70	0.2-0.6	0.5-1	4-6	[22]
Methane steam reforming (reference)	Up to 600-1000	Ca. 0.7	-	9	[23]
Green CH ₄ supply					
Dry biomass	Up to 20	Up to 0.6	1.3-2.5	6-8	[24]
Wet biomass	Up to 100	Up to 0.6	0.75	6-9	[25]
Green MeOH supply					
Dry biomass	Up to 5	0.1-0.5	1-2	3-6	[26]

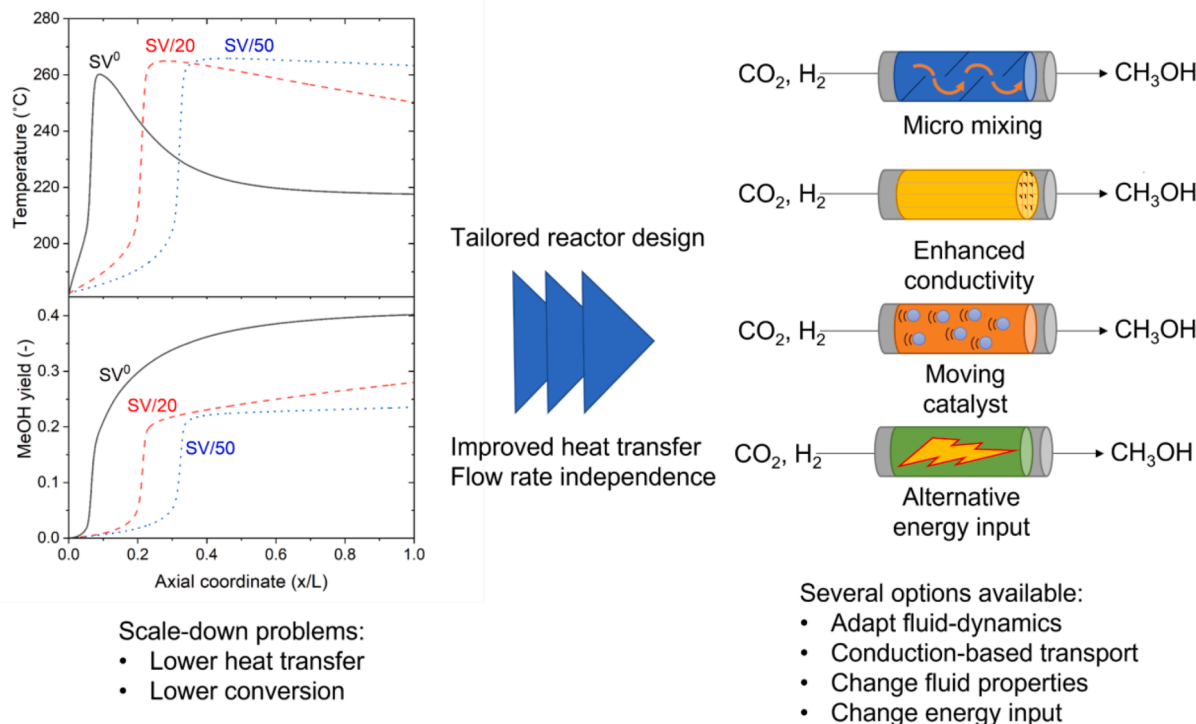


Fig. 1. The reactor design strategy to tackle the process downscaling problem (based on the example of the CO₂ to methanol reaction). Due to lower input flow rate, the heat transfer in packed-bed reactors is lower, causing a decrease in the conversion. This problem can be limited by increasing the heat transfer via micro-mixing (i.e., increasing the heat transfer parameter), by using special conductive structures (i.e., changing the dominant heat transfer mechanism) or by moving the catalyst (i.e., introducing an additional heat transfer mechanism). (SV=Space Velocity (s⁻¹), details on the model used are provided in supplementary materials).

packed-bed reactors. A first option is the use of specific devices to increase the fluid mixing at the microscale. In this case, the convective heat transfer mechanism is modified, to enhance the heat exchange in the reactor [29]. This can be achieved with several microstructured devices, such as static mixers [29], sieve plates with different pore diameters [30], wire meshes to increase the effective interfacial area [31] or spinning disks to create a high liquid velocity [32]. The second option concerns the utilization of specific reactor fillings to increase the heat transfer and to shift the transport mechanism from a mainly convective to a mainly conductive condition [33]. In this way, it is possible to limit the dependency of the heat transport from the gas flow rate. Among these specific reactor fillings, one can enumerate monolithic

honeycombs [34], random shape foams [35] and periodic open cellular structures (POCS) [36]. The third option is the use of a reactor with moving particles, which importantly increase the heat transfer, thanks to the back mixing operated by the particles [37]. In this category are fluidized and entrained flow reactors, as well as rotating bed reactors for gas-liquid applications [38]. All the three solutions show pros and cons, but the complementarity of the proposed technologies makes it possible to forecast their applicability in a wide range of processes. In addition to the above-mentioned process intensification options, recent developments are focusing in changing the way energy is delivered to the chemical processes. New processes may rely on new strategies to activate the molecules, instead of heat. Examples in this field are resistive

heating [39], induction heating [40] and microwave heating [41].

3. Enhanced reactor efficiency

Another important challenge that the chemical reactor technology must face with the energy transition is the need for more efficient processes. Energy efficiency is essential in a context where electricity may be expensive (especially in seasons where renewable resources are scarce). However, the required reactor downscaling results in additional challenges to increase the process efficiency. The use of special thermal fluids or the installation of several heat exchangers are difficult due to the small spaces available and to the need of limiting the capital investment in small projects. Hence, the design of special reactors aimed at the direct recovery of the waste heat will play a special role in process intensification. The synthetic natural gas (SNG) production from renewable electricity-based water electrolysis and CO₂ is an important example of this tendency. The efficiency problem for this process relevant for energy storage is summarized in Fig. 2. The efficiency (HHV-based) of the power-to-methane process with AE/PEM electrolysis lies in the range 50–60% [42]. The remaining energy is converted into waste heat, available at different temperature according to the conversion technologies employed. For example, the use of catalytic reactors produces waste heat at 200–300 °C [43], while the biological methanation process offers waste heat at low temperature [44]. This causes a significant difference in the possible utilization of the waste heat, limiting or extending the options for process coupling and for the realization of more efficient integrated processes. An interesting example for the process coupling in the SNG production is the utilization of the waste heat from the methanation reaction for the production of pressurized steam to use in a high-temperature electrolyzer (i.e., a solid oxide electrolyzer) [45]. This process coupling is highly desirable in terms of process efficiency but it generates important challenges in the design and operation of this integrated system. An important task for process intensification engineers is the design of new units that can guarantee the required heat transfer while producing the waste heat in the specific conditions required by process coupling. This can be done, for example, by tailoring the heat exchange properties of cooling/heating fluids [46], by designing reactors with several separated cooling/heating zones [47] or by introducing intermediate utilization of the waste heat [48]. In this sense, new unconventional process units can have a space in the coupled

processes, such as devices for the compression of gases with waste heat (e.g., metal hydride compressors [49]) or systems for the production of electricity from low-grade waste heat (e.g., organic Rankine cycles [48]).

4. High reactor flexibility

In addition to lower dimension and increased process efficiency, the chemical processes for the energy transition need to adapt to the challenge of intermittent or variable availability of the raw materials. A schematic representation of this challenge is depicted in Fig. 3. When the supply of H₂ is linked to renewable energy, the reactor load varies significantly between times of large availability of the raw material and intervals with scarce or absent supply. This phenomenon can be mitigated by installation of intermediate storage devices, but the cost of these devices tends to grow rapidly with capacity (especially for H₂ storage) [50]. Hence, the design of flexible reactors that can handle different reactant load is of great interest, because it would simplify the management of the entire process.

Most of the CO₂-involving energy storage reactions are strongly exothermic. This causes significant difficulties in the operation of the reactors in highly dynamic conditions because of the presence of reactor hotspots and to the so-called parametric sensitivity. The parametric sensitivity refers to a sudden radical change of the reactor behavior after a limited modification of the process parameters. For the case of SNG production, the parametric sensitivity results in the reactor light off according to many parameters, mainly gas inlet temperature, space velocity and pressure [51]. When the feed flow rate to the reactor is decreased (i.e., the space velocity decreases), the temperature profile in the reactor changes, causing a modification in the location of the reaction light off. Generally, the temperature hotspot would move towards the end of the reactor [52]. If the flow rate reduction overcomes a critical value, the reactor progressively switches off thermally, due to the decrease of the reaction rate. Hence, the standard technologies for the CO₂ methanation reaction (multistage adiabatic and packed-bed reactors) can only partially adapt to the oscillations in the reactant availability [53]. In order to achieve a better stability of the reactor in dynamic conditions, several process intensification actions are required. Primarily, the heat transfer properties of the reactor should be optimized, to control better the parametric sensitivity. This can be done with

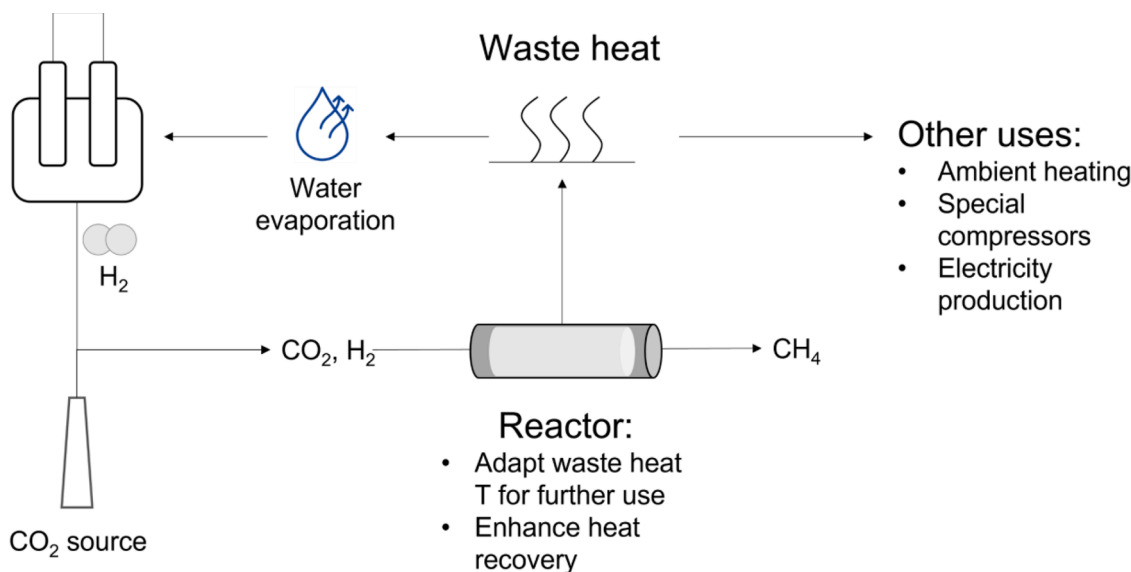


Fig. 2. The need of enhanced reactor efficiency in the case of SNG production. Since the scope of the process is energy storage, SNG is not the only product, but the waste heat must be valorised at within short time. Hence, the reactor design must consider also an optimal heat management, allowing the efficient utilization of waste heat.

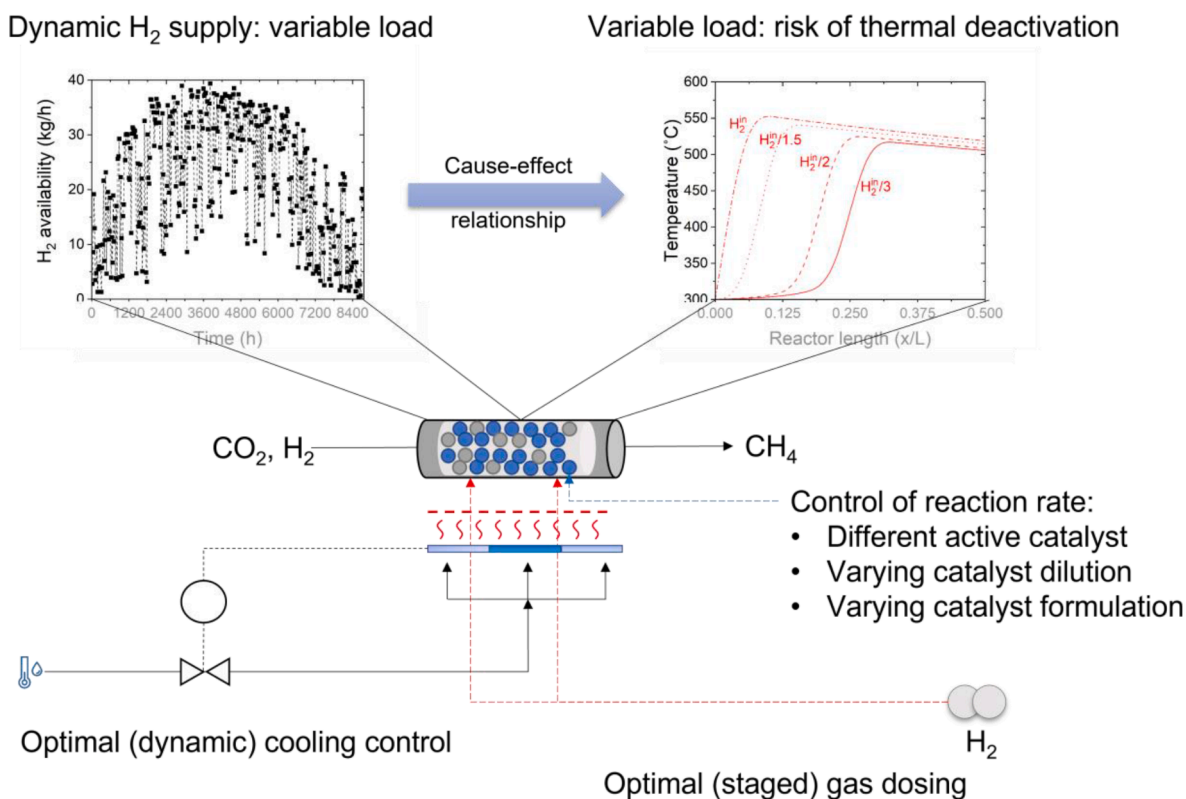


Fig. 3. The strategies to enhance the reactor flexibility for the SNG production process. The reactor needs to be robust with respect to the variation in the reactant flow rate. The main challenges are related to the risk of reactor thermal deactivation when decreasing the flow rate and to the risk of exceeding the maximal temperature when increasing the flow rate. Typical solutions to this problem involve the use of an advanced control of the cooling, the staged gas dosing adaptable to the reactant availability and the use of a tailored catalyst distribution to control the reaction rate. (H_2^{in} = inlet H_2 flow rate, details on the model used are provided in the supplementary materials).

the same strategies elucidated in the process miniaturization section (micro-mixing, use of high conductive structures or catalyst movement). Secondly, an appropriate process control should be envisaged. This is necessary to adapt the reaction conditions, including cooling, with the aim of extending the operation window of the reactor. An effective control can be operated by tailoring the coolant flow rate [54] or by modifying the staged feed of reactants according to the feed rate [55]. An additional control option concerns the adaptation of the properties of the catalyst over the axial coordinate, to tailor the heat production and better adjust the reaction rate to the possible oscillations of the feed flow. This can be operated by providing different catalysts over the axial coordinate of the reactor, by utilizing different formulations of the same catalyst or by changing the catalyst dilution [43].

5. Conclusions

The energy transition significantly pushes the boundaries of the chemical technology, due to the different scale of the feedstock capacity and to the varied time availability of the raw materials. This will force the realization of a larger amount of smaller and more flexible units, that can deliver the chemical products in a more sustainable way. Due to the different nature of these chemical plants, a significant effort towards process intensification will be needed, in order to define new reactor design routines aimed at the synthesis of smaller, but more efficient and flexible process units. To achieve these goals, new technologies allowing more efficient heat exchange will be needed. It is forecastable that several reactor types, now only used in niche applications, will find a wider application in the chemical industry. For example, structured and fluidized bed reactors, now employed only in very specific cases (i.e., when low pressure drops are required or with very exothermic reactions, respectively) may find a wider field of applications, thanks to their

larger flexibility and operability in different flow rates. Structured reactors may open the way for catalytic applications at smaller scales, thanks to the intrinsic higher heat transfer achievable also with low mass flows. Fluidized bed reactors may also extend the operability window of selected chemical reactions, thanks to their flexibility in terms of radial and axial heat transfer in an extended range of flow rates (thanks to the possibility of adapting the fluidization regime by modifying the process pressure [56]. Additionally, new reactor concepts, including staged, microchannel and 3D printed reactors [57–59] can find an applicability in specific cases, where their advantages become important. Process intensification offers a significant range of options to provide efficient units for the energy transition and the main challenge for the scientists in the field will be the determination of the optimal solution for each specific application. Due to the intrinsic larger need of chemical processing units in the renewable energy landscape, the energy transition will only be possible through a significant intensification of the chemical processes, to enable efficient processing at small-scale. Hence, the coupling of process intensification and energy transition is an essential step for the development of more sustainable energy and chemical loops. In this sense, the role of process intensification experts is expected to become of growing importance, as the number of non-standard chemical applications will increase significantly.

Declaration of Competing Interest

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

Data availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:[10.1016/j.cep.2022.109097](https://doi.org/10.1016/j.cep.2022.109097).

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