

The Role of Carbon Capture and Utilization, Carbon Capture and Storage, and Biomass to Enable a Net-Zero-CO₂ Emissions Chemical Industry

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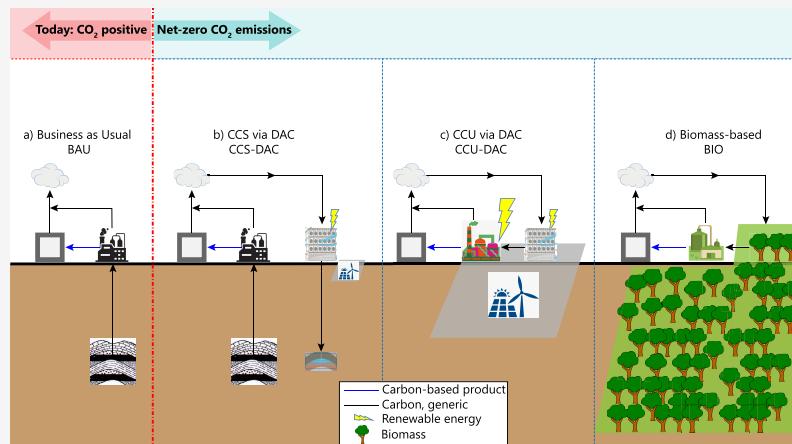


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ABSTRACT: This contribution provides a conceptual analysis and a quantitative comparative assessment of three technology chains that enable a carbon neutral chemical industry in a net-zero-CO₂ world. These are based (i) on the use of fossil fuels and current chemical processes and infrastructure coupled with carbon capture and storage (CCS route), (ii) on the use of captured CO₂ as a feedstock together with “green” hydrogen in new chemical processes (CCU route), (iii) on the use of biomass grown and processed for the specific purpose of making chemicals (BIO route). All routes are feasible and have different pros and cons. Such pros and cons are first discussed through a qualitative comparison of the three routes for a generic chemical product, and are then quantitatively assessed for the specific case of methanol production. In this case, the CCU route results in an electricity consumption 10 to 25 times higher than that of the CCS and BIO routes (excluding the electricity required for heat production), mostly due to the electricity required to produce hydrogen. At the same time, the BIO route requires a land capacity about 40 and 400 times higher than that required by the CCU and CCS routes, respectively. Furthermore, when considering a net-positive-CO₂ emissions world, the CO₂ emissions of the CCU route grow about 8 to 10 times faster than that of the CCS and BIO routes. On the one hand, we identify key hurdles in all cases. These are (i) the availability, accessibility, and acceptance of CO₂ storage sites for the CCS route, together with the continued use of fossil fuels; (ii) the very high electricity and energy demand for the CCU route, with the associated strict requirement of very low carbon-intensity of the electricity mix; (iii) the very high availability of land for biomass growth in the case of the BIO route, with the associated risks of conflict with other uses. On the other hand, we underline that the CCS route offers the possibility of using existing technologies and infrastructures, without the need of a complete reshaping of the chemical industry, and of permanently removing CO₂ from the atmosphere, hence representing a key element not only in the net-zero-CO₂ emissions world studied here, but also in a net-negative-CO₂ emissions world.

1. INTRODUCTION

This contribution addresses the challenge posed by the climate crisis to the chemical industry. The specific question is how the chemical industry can produce carbon-based products and deliver the associated services in all societal sectors in such a way as to not add greenhouse gases (GHG), particularly carbon dioxide (CO₂), to the atmosphere. This

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paper aims at contributing to a very intense and timely debate with both a conceptual analysis and a quantitative comparative assessment of three different technology chains. These three routes are acknowledged to be the only possible approaches toward a net-zero-CO₂ emissions (C-based) chemical industry.

The paper is organized as follows: **Section 2** provides context and background, and states motivation and scope. **Section 3** describes the three technology chains in general terms, and discusses similarities and differences in qualitative terms. **Section 4** analyzes methanol synthesis, use, and postuse fate, and quantifies thoroughly key technical performance indicators for the three routes, thus clearly highlighting pros and cons of the different solutions. Finally, **section 5** draws conclusions.

2. CONTEXT, BACKGROUND, MOTIVATION, AND SCOPE

2.1. The Context: Sustainability Requires Net-Zero-CO₂ Emissions in All Sectors by Midcentury. In a world experiencing a climate crisis due to increasing GHG (particularly CO₂) concentrations in the atmosphere,¹ all sectors of human activity will have to decarbonize, from power generation to mobility, from the industry to the built environment. CO₂ emissions will have to be net-zero sometime between 2040 and 2060, according to the IPCC scenarios, lest the average temperature rise will exceed the 1.5–2 °C maximum stipulated in 2015 by the Paris agreement.²

Climate change is due to the redistribution of carbon among carbon pools: atmosphere (with about 800 Gt carbon), hydrosphere (about 40,000 Gt), biosphere (i.e., vegetation and soil, about 2,500 Gt), lithosphere (i.e., about 65,000,000 Gt, of which about 4,000 Gt consist of high-energy reduced fossil-C in fossil fuels and the rest of low-energy oxidized inorganic carbon fixed in carbonate minerals) and anthroposphere (i.e., carbon stored in manufactured products, such as fuels, fertilizers, polymers, estimated to be 2 to 3 Gt). While natural exchanges between the first three pools are on the order of 100 Gt C/y, GHG anthropogenic emissions are only about 10 Gt C/y, but sufficient to disrupt the preindustrial carbon balance and to change GHG concentrations in the atmosphere.

In a net-zero-CO₂ emissions world at steady state, the anthroposphere will have reached its carbon hold-up capacity compliant with a given global average temperature increase, for example, 1.5 °C. Therefore, any carbon atom extracted from the subsurface (lithosphere) will have to be returned to it, lest it is sooner or later emitted to the atmosphere. And any carbon atom released to the atmosphere as GHG (CO₂ being the most important) will have to be pulled back out of it, thus generating so-called negative emissions, to avoid the rise of GHG concentration in the atmosphere and the global average temperature also. If the 1.5 °C carbon budget is overshoot, the net-zero-CO₂ state has to be followed by a net-negative-CO₂ state.

2.2. Defossilizing the Chemical Industry: Three Alternative Approaches. The chemical industry will have to be decarbonized as well, but faces a special challenge in that an overwhelmingly large fraction of chemical products contains carbon, mostly originating from fossil-C (note that only a few percent of the total fossil-C produced today is used for chemical products other than fuels, while the rest is

burned very soon after extraction). Some of these C-rich products, for example, the windproof and waterproof garments that owe their function to a perfluorinated polymer, deliver an essential service and are based on a sequence of complex, difficult, and possibly dangerous chemical transformations and physical manipulations that are at the heart of organic chemistry and the related chemical engineering processes. After such C-rich products have delivered their service (after a period between a few days to a few years, very rarely after a few decades), they are disposed of and turn sooner or later to gaseous species (CO₂ or CH₄ depending on the disposal conditions, i.e., incinerator or landfill, respectively) that add to the GHG emitted to the atmosphere. Plastics that are disposed in landfill or leaked to the environment (ultimately reaching oceans) hold carbon longer, but, having an equally bad effect on the environment, cannot be regarded as a sustainable carbon storage solution (because of mismanaged waste, 8 Mt/y—3% of global annual plastics waste—leaked to the ocean in 2010,^{3,4} with estimates for 20 Mt/y in 2050⁵).

Hence in the case of the chemical industry, one should talk about defossilization rather than about decarbonization, as it is not possible to imagine a future without C-rich chemical products, i.e. where humankind is still present. In this work, we interpret defossilization quantitatively as a scenario equivalent to net-zero-CO₂ emissions, in full agreement with the IPCC scenario.

Many argue that the chemical industry can be defossilized only by substituting the carbon provenience, that is, from the high-energy reduced fossil-C to the oxidized low-energy carbon in the CO₂, that had been captured somehow from CO₂ emitters or from the atmosphere. This is the so-called CCU route (carbon capture and utilization). Accordingly, it is argued that a brand-new chemical industry, organic chemistry, and catalysis science must be developed that use CO₂ as the source of carbon. At the same time, the question where under the CCU scenario the missing energy and the missing hydrogen atoms will be coming from is kept in the background.^{6–18}

Others maintain that those C-rich chemicals should be produced using biomass,^{19–24} that is, within the scope of the biorefinery concept. Note that biomass contains both carbon and hydrogen atoms, as well as energy, namely solar energy chemically stored thanks to photosynthesis, that is, the process that uptakes CO₂ from the atmosphere and converts it into biochemicals, from which in principle all chemicals currently used can be derived.

There is also a third alternative though, where chemicals are synthesized from fossil-C using the current organic chemistry; the CO₂ generated at the end of life is captured back, returned to the lithosphere where the fossil-C originally had come from, and safely stored in suitable underground geological structures. This is the so-called CCS route (carbon capture and storage).

While the capture component of CCS is a “conditio sine qua non” of CCU as well, the CO₂ storage element is unique to CCS among the three options described here. Two remarks are worth making though. First, CO₂ storage in aquifers and in oil and gas reservoirs has been practiced at the commercial scale with undisputable technical and operational success for decades in the North Sea, North America, Australia, and elsewhere.^{25,26} To overcome public and political acceptance issues especially in continental Europe and as part of its 2050 climate action, the European Union (and Norway as well) is

planning to establish CO₂ storage hubs in the North Sea that will enable European emitters to capture CO₂ and to exploit centralized storage volumes to sequester it.²⁷ Second, CO₂ storage is an essential component of negative emissions technologies (NETs) based on BECCS (bio-energy with carbon capture and storage) and DACCS (direct air capture with carbon storage); humankind might need NETs in the second half of the century to compensate for an overshoot in global temperatures and to cope with unavoidable positive emissions, for example, from aviation and shipping and from agriculture.²⁸ The IPCC projects a cumulative need from 100 to 1000 Gt CO₂ between now and 2100 (today's CO₂ emissions are of 35–40 Gt CO₂/y).² In the case of BECCS, biomass can also be used to generate heat and power, followed by CO₂ capture and storage, whereas in the case of DACCS only the environmental service of removing CO₂ from the atmosphere is fulfilled, to a net extent that depends on the carbon intensity of the energy utilized as input. Thus, concluding, if one believes that climate change is an issue and that negative emissions technologies will have to be implemented, one must support as an obvious consequence a timely and widespread deployment of CO₂ storage.

2.3. A Thorough Comparative Assessment of the Three Alternative Routes Is Missing. For all the three alternatives, identified for simplicity with the acronyms CCU, BIO, and CCS, how to enable net-zero-CO₂ emissions production of chemicals and delivery of the corresponding societal service has already been described elsewhere in the literature.^{18,29–32} Nevertheless, and strangely enough, to the best of our knowledge, there has been no thorough attempt to compare them in a quantitative manner.

A SAPEA report from 2018 compares them qualitatively,³⁰ and highlights an important difference. If in the CCU approach the CO₂ used as feedstock for the production of chemicals is captured from a point source where it originates from fossil-C, then there is at maximum a single reuse of the fossil carbon atom, thus potentially reducing emissions by 50%. Although this is undoubtedly a major improvement with respect to the BAU (business as usual) situation, it is by no means a solution compatible with a net-zero-CO₂ emissions constraint.

The same point is made with reference to the synthesis of methanol (MeOH) by others.²⁹ Here, the authors highlight also how the environmental performance of CCU is critically linked to the carbon intensity of the electricity grid, because of the large amount of electricity needed to make the hydrogen that reacts then with CO₂ to synthesize MeOH.²⁹ They compare CCS and CCU with BAU in terms of the carbon footprint (CO₂ emissions per unit MeOH produced), but do not include the direct capture of CO₂ from the atmosphere after MeOH use, that is, they do not operate in the net-zero-CO₂ emissions framework.

Bardow and co-workers perform a cradle-to-grave analysis of CCU for the production of the 20 chemicals that yield 75% of the carbon emissions of the chemical industry.³¹ They conclude that CCU has the potential to drastically reduce the chemical industry's GHG emissions, but with an ensuing massive increase in the material flows and in the electricity requirements (under the condition that the carbon intensity of power generation be indeed very low, i.e. a condition that only a handful of countries fulfill at the moment). Importantly, they underline that a net-zero-CO₂ emissions chemical industry will require that all three approaches contribute, with the

preferred solution being most likely case- (and country-) specific.

Finally, with reference again to the synthesis of MeOH, a recent paper compares the CCU approach with the BAU solution based on fossil-C, in terms both of planetary boundaries, that is, environmental performance, and of costs.³² The authors draw conclusions about how much "green" hydrogen costs have to drop to make the CCU solution commercially attractive. They acknowledge that there is an alternative CCS route, but for whatever reason they declare it is beyond their paper's scope.

2.4. Scope of the Work and Structure of the Paper.

This work aims at filling the gap by providing a general qualitative comparison among the CCS, CCU, and BIO routes for a generic chemical product (see section 3), as well as a specific quantitative comparison for the case of MeOH (see section 4). We have chosen MeOH because of (i) the plethora of reliable data about the different synthesis routes, (ii) its important role as commodity chemical and fuel (global demand is of the order of 100 million metric tons per year), and (iii) its potential role as a platform molecule, on which a "methanol economy" could be based.^{33,34}

The comparison will be based on technical performance, not on costs, because of the higher level of robustness of the technical key performance indicators with respect to the economic ones. All qualitative and quantitative considerations will be based on the net-zero-CO₂ emissions framework, advocated in the seminal paper by Davis et al.³⁵ on net-zero emissions energy systems. Such framework has also been used recently to study the technical performance of C-free and C-rich synthetic fuels (namely hydrogen and ammonia, and methane and methanol) in power–fuel–power and power–fuel–propulsion applications, for which the input power is assumed to be coming from carbon-free renewables.³⁶ We argue that implementing the net-zero-CO₂ emissions framework avoids considering solutions that might reduce emissions in today's world, but will never be part of the net-zero emissions world of the second part of the century.

We will also apply a simplified system analysis of the different technology chains, very much in the spirit of recent papers.^{30,36} We fully agree with the methodology behind this approach, that considers the simplified analysis as a complementary tool with respect to a comprehensive life cycle analysis (LCA). Such a simplified system analysis is very useful in the scope of a conceptual evaluation of systems, particularly of systems involving new technologies, on which the large amounts of detailed data needed by LCA is not readily available. After the sanity check provided by this analysis, a full-blown LCA can be performed on specific, promising solutions and systems.

In the case of MeOH, we are able to calculate power and heat requirements of the different technology chains, as well as land use and CO₂ storage space required (in the case of CCS). The former set of indicators allows for a straightforward comparison among the three technology chains, whereas the latter set of indicators does not. Within this context, we also present a quantitative comparison of the different technology chains within a net-positive-CO₂ emissions world, by computing the CO₂ emissions resulting from the three routes as a function of the carbon intensity of the available electricity. Although a straightforward ranking of the CCS, CCU, and BIO routes is thus not possible, our analysis underlines clearly their pros and cons.

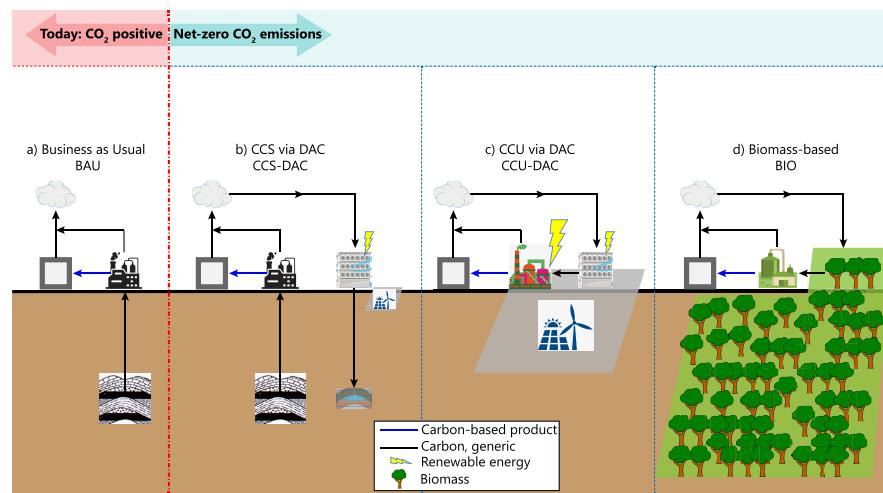


Figure 1. Simplified representation of the main possible routes for synthesis of a carbon-based product via (a) business-as-usual (BAU), (b) CCS with CO₂ recovery from air (CCS-DAC), (c) CCU with CO₂ recovery from air (CCU-DAC), and (d) biomass-based synthesis (BIO). While case (a) is CO₂ positive, cases (b), (c), and (d) are all compliant with the net-zero-CO₂ framework identified above. Moreover, it should be noted that (i) cases where CO₂ is recovered from flue gases are not shown here but reported in the MeOH case study below (see Figure 2), (ii) the gray squared box receiving the carbon product represents the end-user service, (iii) the size of renewable energy input (gray area in this figure) is proportional to the real needs, while the size of land use for biomass is not (exact data are though reported in Table 1 for MeOH), and (iv) the biomass type is not strictly identified by wood.

3. DESCRIPTION AND ASSESSMENT OF THE ROUTES FOR PRODUCTION OF C-RICH PRODUCTS

Four routes for the production of a carbon-based product that delivers the societal service under consideration are illustrated in Figure 1.

The first route (from the left-hand side of the figure) represents the current route, BAU, for which a fossil fuel provides the carbon atoms, (part of) the hydrogen atoms, and the vast majority of the energy required for the product synthesis (electricity might be imported from the grid or cogenerated locally). This route yields net-positive-CO₂ emissions into the atmosphere over the product lifetime, which is typically significantly shorter than any climate-relevant time-scale. In such a chain, the bulk CO₂ emissions are due to the product synthesis, and to the end-of-life disposal of the carbon content in the product as gaseous CO₂ or other GHG (e.g., via combustion or decomposition). Additional emissions, yet in most cases minor when compared to the product synthesis and disposal, are due to the fossil fuel extraction and preparation (as indication, the global volume-weighted carbon intensity of crude oil upstream is 10.3 gCO₂eq/MJ³⁷).

All the other technology chains illustrated in Figure 1 are compatible with the net-zero-CO₂ emissions framework.

The second route shown (CCS-DAC) still relies on utilization of fossil fuels, but in this case all CO₂ emissions produced along the chain (i.e., product synthesis, end-of-life disposal, and any other CO₂ positive processes) are compensated by recapturing the corresponding carbon amount from air (DAC, direct air capture) and permanently storing it underground. The energy requirement in the chain is provided by renewable energy sources for the product synthesis and DAC. Notably, the latter can be geographically decoupled from the product plant, and placed where adequate renewable sources and CO₂ underground storage volumes are best available. As an alternative, which for the sake of simplicity is not shown in Figure 1, CO₂ emissions can be

captured from point sources (PSC, point source capture) available along the technological chain. This will depend on the characteristics of the product synthesis and of the end-of-life processes. Finally, any optimal combination of capture from point sources and air is possible. Whenever point source capture is employed, and given that 100% CO₂ removal is hardly feasible, additional, yet limited, DAC capacity would be required to comply with the net-zero-CO₂ emission scenario (see Figure 2 below illustrating the methanol case for a clear illustration of these two alternatives). As for the energy requirement for the CO₂ capture from concentrated source, this could be met by additional fossil fuel consumption, reuse of waste heat if available from the synthesis, and renewable energy sources (with the latter being considered here). It is important to note that such routes are viable today in the form of commercial technologies, with costs that range from few tens of \$/t_{CO₂} for capture from concentrated sources to few hundreds for capture from air.³⁸

In the third route shown in Figure 1, labeled CCU-DAC, CO₂ is extracted from the atmosphere via DAC and converted into the targeted carbon-based product. This requires parallel production of H₂, which provides the hydrogen atoms found in the final molecule as well as the energy for the product synthesis and CO₂ activation. As for CCS-DAC, point source CO₂ capture and any combination with DAC is possible depending on the product end-of-life type of disposal, and on the product synthesis process. In order for CCU-DAC to be compliant with the net-zero-CO₂ framework, all energy needs along the chain must be provided by carbon-free renewable sources, which includes electricity supply as well as additional hydrogen supply for all medium/high temperature processes, for example, CO₂ activation.

The last route shown, labeled BIO, relies on the use of sustainable managed biomass as carbon and feedstock to the product synthesis. Indeed, such chain captures CO₂ from air via photosynthesis during the biomass growth, thus resulting in a net-zero-CO₂ emissions chain. Here, the energy need of

the process is met via additional biomass input, and via renewable electricity.

3.1. Qualitative Assessment of the Different Routes. First, the four different routes can be qualitatively compared from a few key perspectives.

Global CO₂ Footprint. With the exclusion of BAU, all other routes illustrated in Figure 1 are CO₂ neutral. However, it can be noted that the CO₂ balance varies when considering a cradle-to-gate or a cradle-to-grave analysis: Clearly, in order to correctly keep track of carbon emissions, the product disposal must be included in the analysis.

Use of Resources. The four chains make use of several resources as input, yet they differ significantly both in type and amount when considering the different routes. Especially, we can recognize four critical categories:

- Land use: the land use is primarily proportional to the efficiency of the processes providing the energy and carbon feedstock. As fossil fuels are almost unbeatable in terms of specific energy and carbon content (i.e., as MJ/kg and MJ/m³), the land use in the BAU route is limited to the production plant premises (this might change for land-intensive extraction processes, as for tar sands and, to a certain extent, fracking). When considering the CCS-DAC route, the land use requirement is increased by the need of providing renewable energy to the DAC process and by the large amount of air to be processed by the DAC. Moreover, this route would imply the use of subsurface for CO₂ storage, which anyhow would (i) benefit of a large storage potential, estimated in 10,000 Gt_{CO₂} worldwide,^{2,39} (ii) not require a large volume with comparison to the accessible subsurface, thanks to the high density (600–700 kg/m³) at which CO₂ is stored, and (iii) not compete with other useful uses of the pore volume. Compared to the first two routes, the land use increases significantly for the DAC-CCU, and dramatically for the BIO route. In the former, significant land must be provided to artificially exploit wind and/or sun-based energy for green H₂ production (as a rule of thumb, the area is 20 times the area for renewable energy-based DAC separation). In the latter, land is used to harvest biomass; this must cope with the low photosynthesis efficiency and with the fact that the global carbon budget stored in biomass must stay constant over time (or possibly increase via reforestation).
- Scarce materials and minerals: here, two different classes can be recognized. On the one hand are those materials that can be considered scarce because of the lack of production capacity (e.g., new CO₂ capture solvents, electrodes for PEM electrolyzers), and on the other are those that are *a-priori* scarce or difficult to mine on Earth (e.g., platinum, rare metals). While the first category can be tackled via capacity expansion, the second might result in price peaks and in geopolitical tensions. Therefore, care must be taken in designing the right combination of renewable carbon-free energy sources (e.g., PV vs wind) and in limiting the requirement of precious metals and rare materials in, for example, catalysts. From this perspective the CCU-DAC route is the most exposed to consumption of scarce materials and minerals.

• Fossil carbon: while there is currently broad consensus that fossil fuels are not scarce on earth, the continuous use of fossil fuels, even in a net-zero-CO₂ mode, poses questions regarding the environmental impact of such extraction activity, for example, with regards to non-CO₂ greenhouse gases and to change in local ecosystems, and the societal acceptability of such a chain. Therefore, while CCS-DAC is the only route capable of timely making the chemical industry as is CO₂ neutral (especially when pursuing a global average temperature increase of 1.5 °C), it also entails the continuous use of a controversial resource. Moreover, there exists a systemic financial risk associated with the continuous use of fossil fuels within a society on track to limit global warming to 1.5 °C: decrease in consumption and sell-out of shares are likely to make coal, oil, and gas reserves nonviable, that is, “stranded assets”.^{40,41} On the other hand, and especially for countries with inefficient state-owned fossil fuel industries, the continued use of fossil resources in a carbon-neutral mode could limit the disruption arising from the possible or needed reconversion of jobs in the oil and gas and coal sectors.

• Water: undoubtedly, water scarcity will become more and more severe as climate change progresses. In all four chains described above water is of key importance for different process units: from cooling fluid and H₂ provision via steam reforming and water gas shift (fossil fuel-based routes), to feedstock for electrolysis (CCU), and to feedstock for biomass growth (BIO). Therefore, though beyond the scope of this work, a detailed water balance must be drawn when comparing the different routes for a specific geographical location.

Competition with Other CO₂ Reduction Measures. To reach a net-zero-CO₂ emissions world a combination of different measures in all sectors of the society will be required.⁴² Within this framework there will be competition for the sustainable use of resources, such as low-carbon energy and materials for PV panels and DAC plants, across several sectors. From this perspective, all routes producing a carbon-rich product using DAC will prevent the use of DAC as negative emission pathway (i.e., DACCS), especially in a scenario where the value of such service is clearly recognized and monetized. Moreover, the CCU-DAC pathway requires a substantial amount of carbon-free renewable energy, especially to power water electrolysis for the production of H₂: It is of paramount importance that such a route does not compete with or hamper the decarbonization of the electricity grid. In fact, as quantified below for methanol, for the CCU-DAC route to be net-zero-CO₂ emissions the carbon footprint of the electricity grid must be zero. As for the BIO route, several sectors regard biomass as the holy grail for an easy switch to a sustainable system, including, for example, fuel production for aviation and chemicals.^{43,44} Moreover, the deployment at scale of negative emission technologies largely rely on bioenergy coupled with CCS (BECCS). However, all these will have to come to grips with a limited availability of sustainable biomass.

Need of a Common CO₂ Network. In a net-zero-CO₂ emissions world where multiple chains based on the CCU, CCS, or BIO approaches are deployed at large scale, a CO₂ network will be needed. In fact, CO₂ will be collected from

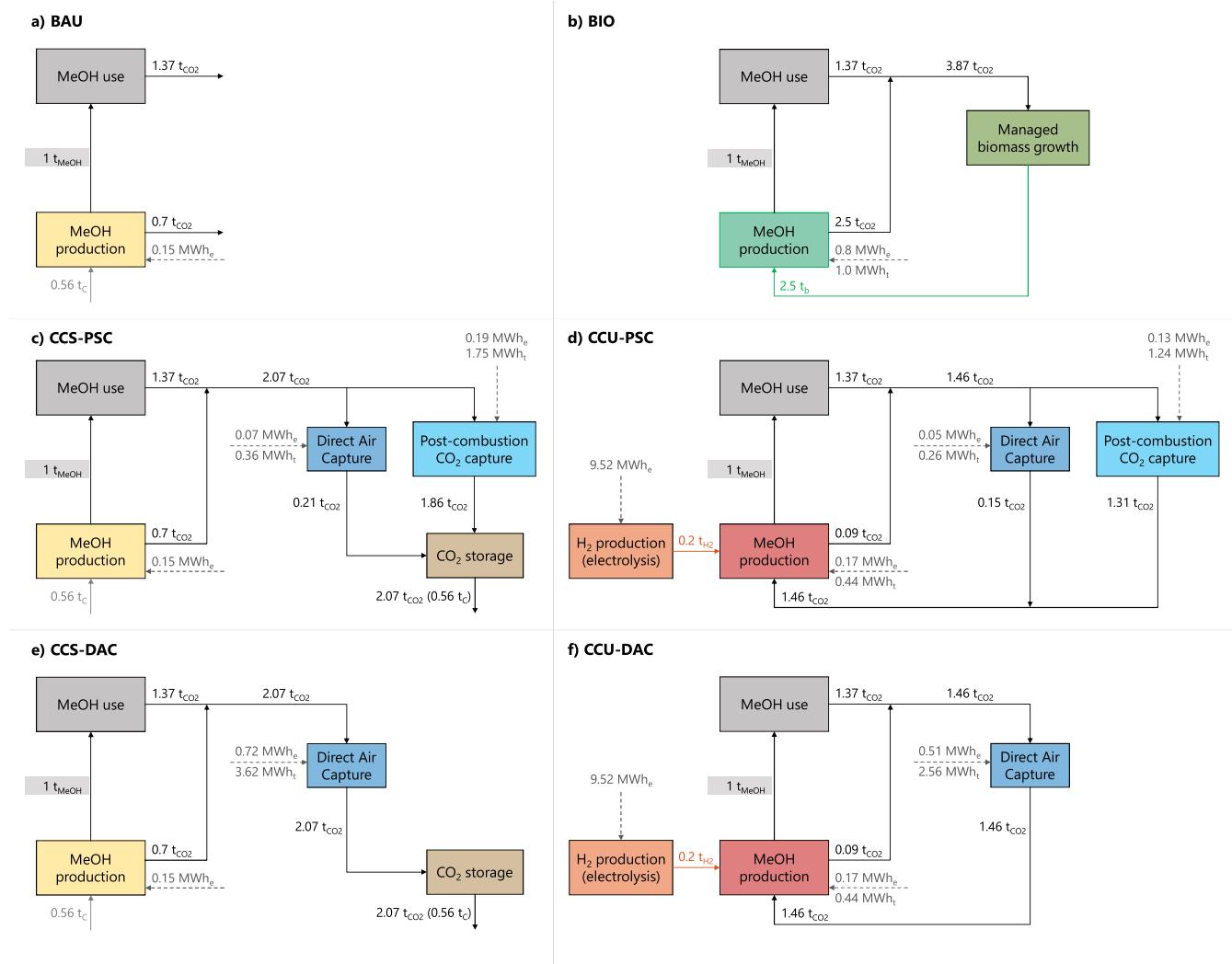


Figure 2. Schemes illustrating the six considered technology chains for the production of one ton of MeOH starting from fossil carbon for the BAU and CCS routes,⁴⁵ CO₂ and H₂ for the CCU route,⁴⁸ and biomass for the BIO route.^{51,52} All routes, except the business-as-usual one (a), are compliant with the net-zero-CO₂ emissions framework identified above thanks to CO₂ capture and to the use of carbon-free renewable electricity.

large scale point sources or absorbed from the atmosphere at multiple locations. It will be transported over short and long distances using trucks, trains, barges, ships, pipelines. It will thus be conveyed to diverse CO₂ sinks, namely either permanent sinks in CO₂ underground storage hubs (such as the Northern Lights CCS project²⁷), or temporary sinks in locations where CO₂ is used to manufacture C-rich products and materials. It is therefore obvious that such a CO₂ network infrastructure, which is not existing today, will be shared by the three technology chains discussed in this paper. In thinking of such a network, two challenges coexist, namely on the one hand the optimal configuration of the relevant infrastructure when at full scale, and on the other hand the most efficient way to develop such an infrastructure during the transition period.

4. THE CASE OF METHANOL PRODUCTION

Let us apply the qualitative framework presented above to the case of methanol (MeOH), which is one of the major target products in studies of CO₂ conversion or CO₂ capture and utilization.^{32,36} Detailed process simulations of MeOH

synthesis from CO₂ and H₂ have been previously published;^{45–50} hence, the wealth of data available allows for a meaningful comparative assessment of the chains illustrated in general in Figure 1 and for the specific case of MeOH in Figure 2. While a detailed assessment of the proposed systems requires a comprehensive life cycle analysis, we adopt the simplified framework introduced above to provide useful insights for the general comparison of CCS, CCU, and BIO routes for methanol production. Note that this implies neglecting the energy consumption and the CO₂ emissions associated with the transport of CO₂ and with the building process of the technologies of interest.

4.1. Quantitative assessment of net-zero CO₂ emissions routes for MeOH production. In Figure 2 we illustrate the six technology chains considered, all delivering the specific societal service provided by one unit of MeOH (one ton of MeOH is used here as functional unit for our analysis). They consist of several building blocks, which are described in the following and whose characteristics are summarized in Tables 1 and 2.

Table 1. Summary Evaluation of the Six Considered Routes for the Production of One Ton of MeOH Starting from Fossil Carbon (C) for the BAU and CCS Routes,⁴⁵ CO₂ and H₂ for the CCU Route,⁴⁵ and Biomass for the BIO Route^{51,52a}

		BAU ^{29,45}	CCS-PSC ^{29,45}	CCS-DAC ^{29,45}	CCU-PSC ^{29,45}	CCU-DAC ^{29,45}	BIO ^{51,52}
feedstock		C	C	C	CO ₂ , H ₂	CO ₂ , H ₂	biomass
input material [t/t _{MeOH}]	C	0.56	0.56	0.56			
	CO ₂				1.46	1.46	
	H ₂				0.20	0.20	
	biomass						2.5
input electricity [MWh _e /t _{MeOH}]	total	0.15	0.94	1.78	10.4	10.9	1.05
	MeOH production	0.15	0.15	0.15	0.17	0.17	0.8
	DAC		0.07	0.72	0.05	0.51	
	PSC	0	0.19	0	0.13	0	0
	H ₂ production				9.52	9.52	
	heat production		0.53	0.91	0.48	0.75	0.25
input heat [MWh _t /t _{MeOH}]	total	0	2.11	3.62	1.93	3.00	1
	MeOH production	0	0	0	0.44	0.44	1
	DAC		0.36	3.62	0.26	2.56	
	PSC		1.75		1.24		
CO ₂ emissions [t _{CO₂} /t _{MeOH}]	total	2.07	0	0	0	0	0
	MeOH production	0.7	0.7	0.7	0.09	0.09	2.5
	MeOH use	1.37	1.37	1.37	1.37	1.37	1.37
	DAC		-0.21	-2.07	-0.15	-1.46	
	PSC		-1.86		-1.31	0	
	biomass						-3.87
land use [m ² /(t _{MeOH} /a)]	total	0.92	4.60	10.9	62.7	67.2	2505
	RES-MeOH production	0.92	0.92	0.92	1.71	1.71	4.91
	RES-DAC		1.00	9.97	0.70	7.03	
	RES-PSC		2.69		1.89		
	RES-H ₂ production				58.4	58.4	
	DAC		0.01	0.10	0.01	0.07	
	biomass						2500
volume of CO ₂ storage [m ³ /(t _{MeOH} /a)]		73.9		73.9			

^aAll routes, except the business-as-usual one, lead to net-zero CO₂ emissions thanks to CO₂ capture and to the use of carbon-free renewable electricity.

Table 2. Summary of Assumptions Required to Calculate the Energy Consumption and the Land Use of the Six Considered Technology Chains

quantity	unit	technology chain	value
carbon intensity of electricity	t _{CO₂} /MWh _e	all	0 ^a
conversion efficiency electricity-to-heat (heat pump)		CCS/CCU, PSC/DAC	4 ⁶¹
conversion efficiency electricity-to-H ₂ (PEM electrolyzer)	MWh _e /t _{H₂}	CCU, PSC/DAC	47.6 ³⁶
DAC electricity consumption	MWh _e /t _{CO₂}	CCS/CCU, PSC/DAC	0.35 ³⁶
DAC heat consumption	MWh _t /t _{CO₂}	CCS/CCU, PSC/DAC	1.75 ³⁶
PSC electricity consumption	MWh _e /t _{CO₂}	CCS/CCU, PSC	0.1
PSC heat consumption	MWh _t /t _{CO₂}	CCS/CCU, PSC	0.94 ⁵⁵
land use factor for RES (solar)	m ² /(MWh _e /a)	all	6.14 ⁶²
land use factor for DAC	m ² /(t _{CO₂} /a)	CCS/CCU, PSC/DAC	0.049 ³⁶
land use factor for biomass	m ² /(t _b /a)	BIO	1000 ^{36,59,60}
underground volume factor for CO ₂ storage	m ³ /t _{CO₂}	CCS, PSC/DAC	35.7
solar efficiency		all	0.17 ⁶¹
biomass uptake	t _{CO₂} /t _b	BIO	1.55

^aA carbon intensity of the electricity mix equal to zero applies to the net-zero emissions framework only, while a parametric analysis on this parameter is presented and discussed in section 4.2.

Some of these blocks are common to all chains, for example, the use of MeOH, while others are peculiar of specific chains, for example, the carbon capture processes.

- **MeOH use.** This block (gray block in Figure 2) is common to all technology chains. It is modeled through a simple carbon balance to avoid considering specific uses of MeOH (e.g., fuel for power or propulsion purposes), hence resulting in 1.37 ton of CO₂ emitted per ton of MeOH used.²⁹ Note that this approach allows avoidance of the calculation of the efficiency characterizing specific uses of MeOH, which would not improve the scope of the present analysis.
- **MeOH production.** Different production processes are considered for the different configurations.

More specifically, the BAU and CCS routes adopt a conventional production plant (yellow block in Figure 2a,c,e), which uses 0.56 ton of fossil carbon and 0.15 MWh of electricity (MWh_e) to produce one ton of MeOH.⁴⁵

The production plant adopted by the CCU routes (red block in Figure 2d,f) is modeled as presented by Perez-Fortes et al.,⁴⁵ and uses 1.46 ton of CO₂, 0.2 ton of H₂, 0.17 MWh of electricity, and 0.44 MWh of heat (MWh_t) to produce one ton of MeOH.

Finally, the methanol production plant of the BIO route (dark green block in Figure 2) is modeled based on the work of Hannula and Kurkela⁵¹ and on discussion with industry experts,⁵² and uses 2.5 ton of biomass (wood chips, with a lower heating value of 17 MJ/kg), 0.8 MWh_e, and 1 MWh_t to produce one ton of MeOH.

The required thermal energy is provided via heat pumps that use carbon-free electricity for the CCS and CCU chains, whereas it is provided by biomass for the biomass route (already accounted for in the amount of biomass entering the production block). For all processes, the required electrical energy is provided by carbon-free electricity. This results in no indirect emissions, while 0.7, 0.09, and 2.5 ton of CO₂ are directly released per unit MeOH by BAU and CCS, CCU, and BIO technology chains, respectively.

- **Point-source carbon capture (PSC).** The same PSC unit (light blue block in Figure 2c,d), is considered for the CCS-PSC and CCU-PSC technology chains, in which the CO₂ emissions due to the MeOH production and use blocks are captured via a combination of PSC and DAC processes.

The PSC unit is modeled as an amine-based CO₂ capture process with 90% removal efficiency, which captures CO₂ from a concentrated source (i.e., from a fluegas with a CO₂ concentration of 5–15%). It requires 0.94 MWh_t/t_{CO₂} for the capture process and 0.1 MWh_e/t_{CO₂}^{53–55} for CO₂ compression (from 1 to 110 bar), which results in the energy consumption per unit MeOH reported in Figure 2. Both electricity and heat are provided by carbon-free electricity, with the former being supplied directly and the latter through heat pumps. This results in no additional CO₂ emissions for the capture process and allows for a net-zero-CO₂ emissions framework.

- **Direct air capture (DAC).** The same DAC unit (dark blue block in Figure 2c,d,e,f) is needed in all CCS and

CCU technology chains. DAC can be deployed either in combination with PSC or alone. In the former case, that is, CCS- and CCU-PSC, the DAC unit is used to capture the 10% of CO₂ that is not captured via PSC. In the latter case, that is, CCS- and CCU-DAC, the entire CO₂ emissions are captured via DAC. Here, the entire amount of CO₂ generated is assumed to be emitted to the atmosphere in a distributed fashion and has to be captured back from there (i.e., at a concentration of about 400 ppm).^{56,57} The DAC unit is modeled as presented by Sutter et al.³⁶ and requires 0.35 MWh_e and 1.75 MWh_t to capture one ton of CO₂. The electricity consumption is due to the capture process (0.25 MWh_e/t_{CO₂}) and to CO₂ compression (0.1 MWh_e/t_{CO₂}).⁵⁸ Similar to PSC, both electricity and heat are provided by carbon-free electricity. A land use factor of 0.049 m²/(t_{CO₂}/a) is considered for the installation of the DAC facilities.³⁶

- The captured CO₂ is sent to the storage facility and stored underground in the CCS route, whereas it is conveyed back to the MeOH production plant in the CCU route.
- **H₂ production.** This is only present in the CCU route to provide the H₂ necessary for the synthesis of MeOH. Here, H₂ is supplied via an electrolyzer (orange block in Figure 2d,f), which uses carbon-free renewable electricity. A conversion efficiency of 70% is considered (hydrogen LHV), thus resulting in 47.6 MWh_e/t_{H₂}.²⁹
- **Managed biomass growth.** This block (light green block in Figure 2b) is present in the BIO route only, where the CO₂ produced by the production and use blocks is uptaken and removed from the atmosphere during the biomass growth. The value of biomass uptake is that required to meet the carbon balance, namely 1.55 t_{CO₂}/t_b. A land use factor of 1000 m²/(t_b/a)^{36,59,60} is considered for the managed biomass growth installation.
- **CO₂storage.** This block (brown block in Figure 2c,e) is present in the CCS route only, in which the captured CO₂ is sent to a storage site. We consider underground CO₂ storage with an available storage factor of 4%,^{25,26} for which CO₂ has a density of 700 kg/m³.
- **Carbon-free electricity from renewable energy sources (RES).** For the time being, we assume that the energy required by the MeOH synthesis and by the capture processes is supplied by carbon-free solar electricity, which allows achieving net-zero-CO₂ emissions for the CCS and CCU routes (we neglect the energy required for the managed biomass growth). The solar facilities produce electricity with a conversion efficiency of 17%.⁶¹ This electricity is used to supply the heat required by the capture processes via heat pumps, which are characterized by a coefficient of performance of 4.⁶¹ A land use factor of 6.14 m²/(MWh_e/a) is considered for the installation of the solar facilities, resulting by considering a solar productivity of 1000 MWh_e per peak MW per year.⁶²

The input material and energy flows, as well as the land use associated with the different routes are reported in Table 1. All assumptions made to perform such calculations are summarized in Table 2. The electricity and heat consumption are further plotted in Figure 3 for the sake of illustration (the

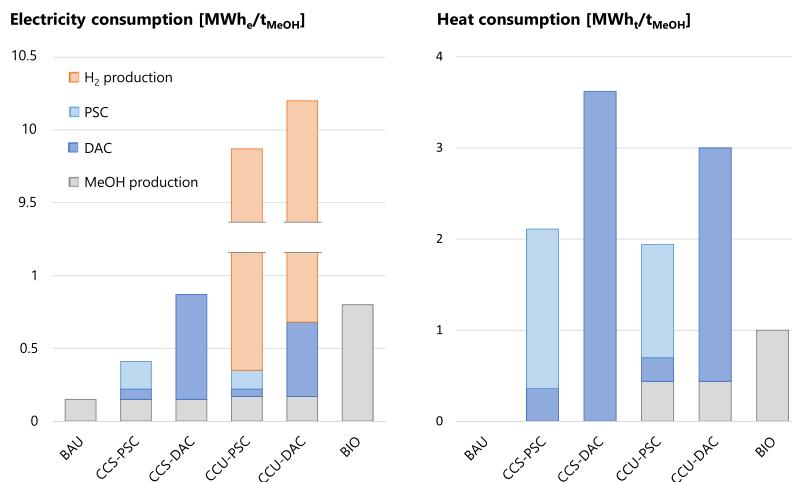


Figure 3. Electricity consumption (left) and heat consumption (right) of the six considered routes. All routes, except the business-as-usual one (BAU), lead to net-zero-CO₂ emissions thanks to CO₂ capture and to the use of carbon-free renewable electricity to satisfy both electricity and heat consumption.

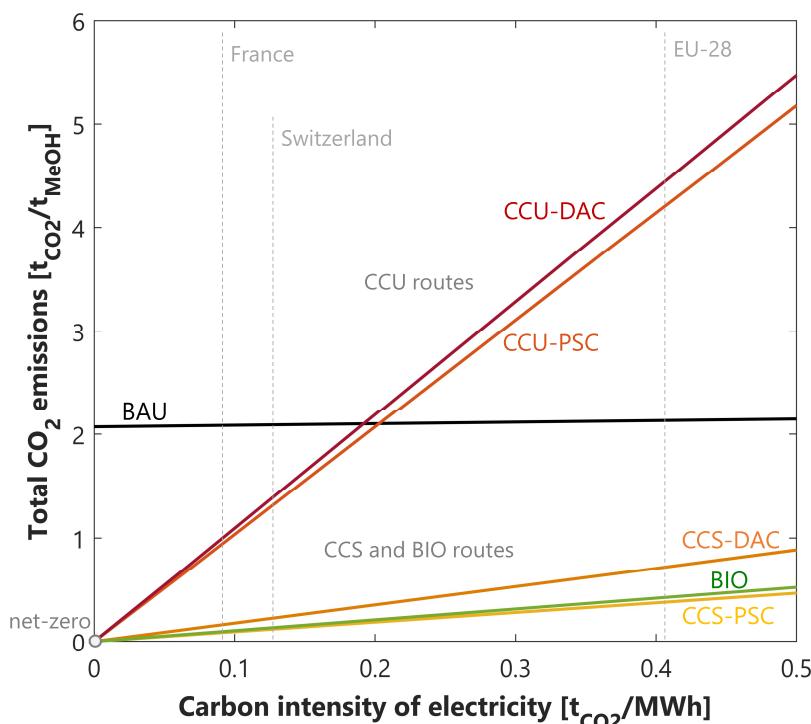


Figure 4. CO₂ emissions for the six considered MeOH production routes as a function of the carbon intensity of the available electricity.

land use is not included in the figure because of the very different values for the three routes).

Concerning electricity consumption (left-hand side of Figure 3), the CCU route is characterized by a value around 10 MWh_e/t_{MeOH}, which is about 25 times higher than the CCS route when adopting PSC, and about 10 times higher when adopting DAC only. This is mostly due to the contribution of hydrogen production, which accounts for about 95% of the total electricity consumption.

Concerning heat consumption (right-hand side of Figure 3), similar values around 3 MWh_t/t_{MeOH} are obtained for both routes, with CCS consuming more heat than the CCU routes because of the greater amount of CO₂ emitted by the MeOH production process, that is, 0.7 versus 0.09 t_{CO₂}/t_{MeOH}.

The BIO route is characterized by an electricity consumption of about 0.8 MWh_e/t_{MeOH}, which is similar to the case of CCS-DAC, and by a heat consumption of about 1 MWh_t/t_{MeOH}, which is about one-third of that needed for the CCS and CCU routes.

Such energy consumption translates into a higher land use of the CCU route with respect to the CCS route (see Table 1). More specifically, the CCU land use is about 15 times higher than that of CCS when adopting PSC, and about 6 times higher when adopting DAC only. Concerning the BIO route, the land use is due almost entirely to the contribution of the managed biomass growth, which requires 2500 m²/ (t_{MeOH}/a). This is about 40 times higher than CCU and 400 times higher than CCS.

Table 3. Values of the Most Relevant Assumptions of the Quantitative Model across the Considered References and Corresponding Overall Electricity Consumption

input quantity	unit	this study	Gonzalez-Garay et al. ³²	Sutter et al. ³⁶
heat supply		heat pumps	heat pumps/hydrogen ^a	hydrogen
DAC electricity consumption	MWh _e /t _{CO₂}	0.35	0.46	0.35
DAC heat consumption	MWh/t _{CO₂}	1.75	1.71	1.75
conversion efficiency PEM electrolyzer (electricity-to-H ₂)	MWh _e /t _{H₂}	47.6	52.3	47.6
total electricity consumption	MWh _e /t _{MeOH}			
CCS-PSC		0.94	1.29	3.96
CCS-DAC		1.78	5.40	6.96
CCU-PSC		10.4	11.2	13.2
CCU-DAC		10.9	15.3	15.2

^aIn the work of Gonzalez-Garay et al.,³² which is not framed within a net-zero-CO₂ emissions world, heat is supplied via conventional fossil fuels. Owing to our net-zero-CO₂ emissions constraint, we consider such fossil fuels to be replaced by H₂ in the case of DAC (heat required at high temperature⁶⁴) and by heat pumps in the case of PSC (heat required at low temperature).

It is worth noting that such values cannot be compared to the underground volume required to store CO₂ in the CCS route, which is about 75 m³/(t_{MeOH}/a).

It is also worth noting that the land quality needed for renewable energy installations and for managed biomass growth are going to be very different. We believe that the quantitative comparison makes sense, but the difference of the type of land should also be kept in mind.

4.2. CO₂ Emissions of the Considered Routes for Electricity with Carbon Emissions. So far, we have considered carbon-free solar electricity to supply the energy required by the MeOH production processes and by the CO₂ capture technologies. However, operating the investigated technology chains with currently available electricity, which is characterized by a different carbon intensity depending on the geographic location, would result in positive values of the CO₂ emissions. This is shown in Figure 4, which reports the amount of CO₂ emitted per unit MeOH as a function of the carbon intensity of the available electricity.

The BAU route results in about 2 t_{CO₂}/t_{MeOH} and is essentially independent of the electricity mix. In this case, the largest share of CO₂ emissions is due to the use of fossil carbon to produce and use methanol, while the electricity required for the production process, which is responsible for the increase of CO₂ emissions, plays a minor role. In contrast, the CO₂ emissions of the other routes increase with the electricity carbon intensity, with those of CCU growing about 8 to 10 times faster than those of CCS and BIO. This is proportional to the larger total electricity consumption (including both electricity and heat requirements) of the CCU route, which is mostly due to the electricity required to produce hydrogen. As an example, consider the electricity mixes of France (92 t_{CO₂}/MWh), Switzerland (127 t_{CO₂}/MWh), and EU-28 (407 t_{CO₂}/MWh).⁶³ The CCU route emits about 0.9, 1.2, and 3.8 ton of CO₂ more than the CCS route per ton of produced MeOH (average of -PSC and -DAC technology chains). Similar trends are observed for the CCS-PSC and the BIO chains, since the greater heat demand of the former is balanced by the greater electricity demand of the latter.

For both CCS and CCU, the CO₂ emissions are higher when adopting DAC only. More specifically, they grow about 1.9 (CCS) and 1.1 (CCU) times faster than those obtained by deploying a combination of PSC and DAC (i.e., -PSC chains).

This is because of the higher efficiency of capturing CO₂ from concentrated sources versus capturing CO₂ from air.

This implies that the CCS route performs better than the CCU one in terms of energy consumption and CO₂ emissions, with the maximum benefit being achieved by deploying a combination of PSC and DAC.

4.3. Discussion. Finally, let us discuss the most relevant assumptions for the quantitative assessment, and compare them with existing literature, namely, (i) the heat supply technology, (ii) the energy penalties (electricity and heat) of DAC, and (iii) the energy consumption of water electrolysis. This implies focusing on the CCU and CCS routes, since the BIO route is not affected by such assumptions and its specific critical hurdle is the sustainable availability of land. The values of the parameters of interest, as well as the resulting total electricity consumption for the CCS and CCU routes, are reported in Table 3.

- (i) *Heat supply.* While in this work heat is supplied via heat pumps using carbon-free electricity, different choices are made in different studies. More specifically, Sutter et al.³⁶ developed a net-zero-CO₂ emissions framework through which heat is supplied via H₂ boilers. In their case, H₂ is first produced starting from carbon-free electricity via water electrolysis and is then burnt in boilers to supply heat. This results in a significantly lower efficiency of the electricity-to-heat conversion process, which is 4 in our work and around 0.6 in theirs.³⁶ On the other hand, Gonzalez-Garay et al.³² consider a different DAC technology, that is, that presented by Keith et al.⁶⁴ In such a process, the CO₂ regeneration is carried out via a natural gas-based oxyfuel combustion, while in the DAC technology considered here and in Sutter et al.³⁶ low temperature heat is used. Note that while in the original references^{32,64} natural gas is used as fuel, for comparison purposes within the boundaries of our net-zero-CO₂ emissions framework, we replace natural gas with H₂ in calculating the values reported in Table 3; using H₂ boilers instead of heat pumps to satisfy the heat demand results in higher values of the total electricity consumption. This applies to all chains when this choice is made for all technologies,³⁶ whereas it is limited to the chains based on the DAC when this assumption concerns the DAC technology only.³²

- (ii) *Energy penalties of DAC.* Values of electricity and heat consumption different than those used in this work are used in the paper by Gonzalez-Garay et al.³² Again, this is because they consider the technology presented by Keith et al.,⁶⁴ which features (i) a higher electricity consumption and (ii) a lower heat consumption, with heat required at higher temperature. Since the numbers in Table 3 are calculated for a heat supply via H₂ combustion, overall this results in higher values of the total electricity consumption for the chains based on DAC.
- (iii) *Energy penalty of water electrolysis.* Values of efficiency different than those used in this work are found in the paper by Gonzalez-Garay et al.³² More specifically, they use a more conservative value of 52.3 MWh_e/t_{H₂} (64% LHV efficiency), while we use a more optimistic value of 47.6 MWh_e/t_{H₂} (70% LHV efficiency). This explains their higher value of total electricity consumption for the CCU routes. It is worth noting that when considering values of the electrolysis efficiency close to thermodynamic limit (around 80% LHV), a reduction of total electricity consumption of about 10% only is obtained for the CCU routes; hence, the considerations presented in this work remain valid.

Table 3. Overall, our assumptions lead to more optimistic values of the total electricity consumption for all technologies and chains, especially concerning the DAC technology and the CCU route.

5. CONCLUSIONS

This paper provides a conceptual analysis of the three technology chains that enable a carbon neutral chemical industry in a net-zero-CO₂ emissions world, that is, in the world that all future scenarios indicate that we need to reach by mid of the century (see section 3). Such routes are based (i) on the use of fossil fuels and current chemical processes and infrastructure together with CO₂ capture and storage (CCS route), (ii) on the use of captured CO₂ used as feedstock together with “green” hydrogen in new chemical processes (CCU route), and (iii) on the use of biomass grown and processed specifically for the purpose of making chemicals (BIO route). This paper also provides a quantitative comparative assessment of the three routes for the production of methanol (see section 4). Though parts of this comparison had already been carried out and reported earlier, we are convinced that our thorough and comprehensive technical comparison is novel, timely, interesting, and useful. The analysis of methanol production in section 4 allows quantification of, in the specific case, the qualitative comments made in section 3, without losing general relevance. In other words, we are persuaded that similar results would be obtained if other chemicals were considered instead of methanol.

From the analysis reported here we can draw a few important take-home messages.

- (1) The chemical industry can indeed be defossilized, while continuing to deliver the chemical products and the services that are so essential to our life and activities. Defossilization, as defined in the second paragraph of section 2.2, can be accomplished in three different ways, that is, following the CCU, CCS, or BIO approaches discussed and comparatively assessed in this work. All

three are feasible and viable, because under specific conditions they can be realized in such a way that CO₂ emissions to the atmosphere are net-zero.

- (2) A thorough assessment of the pros and cons of different technology chains requires a systemic analysis, which can be carried out in a simplified manner first, to be followed by a full-blown life cycle analysis (and cost evaluation). When looking at the whole system, one also realizes how many common elements the three technology chains have.
- (3) Among the CCS, CCU, and BIO routes there is no clear winner, because each has its pros and cons, and because some of the key performance indicators, for example, land use, cannot be directly compared. We interpret this observation in a positive manner, by drawing the conclusion that under different technical, economical, and geographical circumstances one or the other of the technology chains might be preferred. Of course, all three routes perform worse than the business as usual (BAU) route in terms of energy (heat and power) and land penalties. However, this is the price to pay to enable a net-zero-CO₂ emissions chemical industry.
- (4) Key hurdles have been identified for each of the three net-zero-CO₂ routes. In a nutshell, these are (a) the availability, accessibility, and acceptance of CO₂ storage sites for the CCS route, but not their safety, which has been extensively proven;^{25,26} (b) the very high electricity and energy demand (due to the need to synthesize hydrogen via electrolysis and to energize CO₂) for the CCU route, with the associated strict requirement of very low carbon-intensity of the electricity mix; (c) the availability of land for biomass growth in the case of the BIO route, with the associated risks of conflict with other uses. On the other hand, it would be wrong not to underline two big advantages of the CCS route: (i) it can exploit the existing technology and the infrastructure in place of the current petrochemical and chemical industry, without the need of a complete reshaping of it; (ii) CO₂ capture from point sources and/or from air plus permanent CO₂ storage in geological formations constitute the key elements of the negative emissions technologies, on which future scenarios targeting a global warming below 1.5 or 2 °C rely.

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