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Alternative sources of carbon for moving towards a sustainable carbon cycle

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This perspective identifies the carbon needs of the chemical and transport industries in the short-to-medium term, categorizes the available renewable alternative carbon sources (biomass, waste-plastics and CO_2) to fossil carbon and discusses their usability and potential for the short-, medium- and long-term use. Given the constraints to the use of biomass (grown on purpose and waste) and the limited overall amount of waste plastics, CO_2 is the most abundant and at-hand source of renewable carbon. The conversion of CO_2 into chemicals, materials and energy products is discussed for meeting the energetic and hydrogen demands. The use of solar energy as a primary energy source and water as a proton and electron source in recycling carbon via CO_2 conversion into energy products is also elucidated. E-fuels and solar-fuels are compared for their commercialization, and the benefits of co-processing CO_2 and water (in electrochemical, photochemical and photoelectrochemical processes) instead of producing green- H_2 for CO_2 reduction are emphasized.

Keywords: Carbon dioxide as source of renewable carbon; Carbon cyclic economy; Photochemistry; Photoelectrochemistry; E-fuels; Solar-fuels

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1 Introduction

Moving away from fossil-C (coal, oil, and natural gas) by implementing a cyclic economy¹ has been urged by the last UN Conferences of Parties (COP26-29) in order to comply with the urgent need of controlling the climate changes. Currently, fossil-C is the source of >81% of the total energy used worldwide (2023 data).2 In particular, oil contributes 31.6% (196 EJ), coal contributes 26.5% (164 EJ) and natural gas contributes 23.1% (144 EJ) to the total amount of energy used globally (620 EJ: it was 607 EJ in 2022). The remaining energy is sourced from nuclear energy (25 EJ, 4.0%) and hydropower (40 EJ, 6.5%), with other perennial energies such as the solar, wind and geothermal energies collectively contributing 8.22% or 51 EJ, surpassing hydropower and showing a continuous growth. Even though non-fossil carbon sources are growing and could possibly fill the gap in the increased energy demand of our society, it does not substitute fossil-C; indeed, the emission of CO2 has reached a new record in 2023,3 equaling to 37.4 Gt_{CO}, (1.1% higher than in 2022). Thus, there are concerns and questions whether the political claim of "defossilization by 2050" is an achievable target. It must be emphasized that, while it is principally conceivable to decarbonize the energy industry, the chemical industry will need carbon as a feedstock forever, and the transport sector will require carbon-based fuels for a while in the aviation and maritime subsectors. Currently, the chemical industry emits 932 Mt_{CO}, (from the use of fossil-C as both fuel and feed) and uses ca. 365 Mt_C y⁻¹ for chemicals

and ca. 360 Mt_C y⁻¹ for plastics. (Table 1). The use in the latter industry is variously classified, according to their properties and applications. 4 Notably, the production of nonfossil carbon must be high enough to stop the extraction of fossil carbon. Alternatively, it will be quite difficult to substitute C-based fuels in the aviation (380 Mt_C as per 2023) and maritime (330 Mt_C as per 2023) transport sectors, demanding an additional 710 Mt_C y⁻¹. Therefore, the raw material-feedstock for chemical industry and avio-maritime transport sectors will collectively require approximately 1.5 Gt_C per year (or 10% of the current total amount of fossil-C used), which must be provided by either the fossil or alternative sources. In my opinion, the defossilization of the entire energy sector will proceed at a lower rate than predicted. Most likely, by 2050 fossil-C extraction will be reduced to 25-35% of the actual amount. In this review, an analysis of the potential non-fossil carbon sources is made, highlighting their limits, bottlenecks and barriers in ensuring that carbon scarcity will not negatively affect the progress of our society in general and that of the developing economies in particular.

In the short term, 700 $Mt_C y^{-1}$ must be added as requested by the aviation and maritime transport sectors which need time to switch from C-based fuels.

2 Discussion

The available sources of non-fossil-carbon can be categorized into biomass (grown on purpose and waste), waste plastics and carbon dioxide. Each category will be discussed to highlight the specific potential of each.

2.1 Biomass

The amount of biomass produced worldwide is estimated to be 146 Gt y^{-1} (or 4500 EJ), of which 50 Gt y^{-1} is land-grown and the balance is aquatic biomass. 16.7 Gt y^{-1} of terrestrial biomass are harvested: 14 Gt y^{-1} are used as food for humans or feed for animals to which 2.7 Gt y^{-1} of wood are added, with 1.3 Gt y^{-1} used for energy production and 1.4 for other

industrial uses. Notably, the "sustainable biomass harvesting" is set at a quite wide range of 8-32 Gt y⁻¹,5 in which the latter figure represents roughly the double of the actual use. Considering that fertile soil is necessary for growing biomass for food-feed, if the use of biomass for energy purposes needs to be extended without further deforestation, three key action-points must be implemented, namely, (i) use of marginal land; (ii) proficient use of aquatic biomass; and (iii) large scale implementation of the integrated biorefinery strategy (IBS), thereby simultaneously fostering forest management and waste valorization.⁶ IBS facilitates a wiser use of the complexity of the biomass, relegating energy-intensive processes based on large entropychanges, such as gasification or even pyrolysis, to the energetic valorization of inert/recalcitrant residues.7 Waste wet-biomass (MSWs, agricultural residues, industrial wastes, farm sewages, and water treatment sludges) should be valorized on a much larger scale than the current level; for instance, the full worldwide biomethane potential is estimated at 730 Mtoe with a large margin of improvement with respect to the current actual potential of ca. 4 Mtoe (1 Mtoe is equal to 11630 GW h or 1.21 Gm³ of gas). The installed power of electricity made from biogas was 18 GW in 2018 (or 47 300 GW h compared with 1 469 133 GW h of total electric energy produced from natural gas in the same year).8 Accordingly, to maximize the use of bio-sourced carbon, aquatic biomass should be better exploited for producing proteins, fine chemicals and energy-products, implementing economically viable technologies for its growing, harvesting and processing, possibly making use of all fractions, such as proteins, carbohydrates, lipids and specialty chemicals.9

The clever deployment of terrestrial and aquatic biomasses and the skilful management of waste can contribute to the long-term availability of renewable carbon for both the chemical and energy industries (several hundreds Mt_C y^{-1}), but solid investments in research and innovation are necessary for its full exploitation. In the shortand medium-terms, its potential is not so high (a few tens Mt_C y^{-1}) with a moderate contribution to the energy sector

 $\textbf{Table 1} \quad \textbf{Use of carbon (Mt}_{\textbf{C}} \ \textbf{y}^{-1} \ \textbf{fossil and} \ \textit{bio}) \ \textbf{in the chemical industry for the production of chemicals, pharmaceuticals and polymers}$

Chemicals	Amount as Mt of carbon per year	Materials (polymers)	Amount as Mt of carbon per year
Benzene, toluene, xylenes	125	Polyethene	135
Ethanol	45	Polypropene	68
Urea	44	Polyurethanes	18
Methanol	42	Polycarbonates	3
Ethene glycol	25	Polyesters	50
Formaldehyde	11	Polystyrene	15
C ₂ + aldehydes	8	ABS (acrylonitrile butadiene styrene)	10
Ketones	7	Polyacrylates (super absorbents)	5
Acetic acid	4	Polyamides	5
Citric acid	3	Others (including bio-polymers)	50
Others (including pharmaceuticals)	50		
Total amount, Mt _C y ⁻¹	364		359

Note: in *italics* the products of *bio-origin*. The Table does not include chemicals such as: ethene (160 Mt y⁻¹), propene (80 Mt y⁻¹), and other olefins that are counted as polymers.

(in the form of biogas-biomethane, biodiesel, bioethanol) and a lower one to the chemical industry (mainly as ethanol for chemicals and polymers) due to the fact that the utilization of biomass as source of fine-chemicals demands time for the development of new processes.

2.2 Waste plastics

Even if the whole amount of waste plastics is recycled as a source of recycled-carbon, it would not meet the energy demand of the sector itself. In fact, as of 2024, *ca.* 360 Mt_C y⁻¹ were used in the sector (Table 1) for the production of approximately 460 Mt of plastics.¹⁰ Up to 220 Mt of plastics entered the compartments of our planet (soil, water, and air), with more than 75% produced by 20 countries alone, while the recycling of plastics was as low as 9%.¹¹ The production of polymeric materials and plastics is expected to grow in future years, and by 2050, it is expected to double or triple the current rate, as reported by E. Amsen, who also recalls a 2024 report by the Lawrence Berkeley National Laboratory.¹² Therefore, an extended recycling of plastics can only partially cover the carbon demand of the same sector.

2.3 Carbon dioxide

Carbon dioxide is by far the most abundant and at-hand source of renewable carbon. Supposing that the extraction of all fossil carbon forms terminates, the easy-to-deploy sources of CO2 can be categorized as follows: (a) bio-processes (fermentation to produce ethanol and anaerobic wet-biomass digestion to produce biogas) and (b) the atmosphere. The former source can afford approximately 120 Mt_{CO₂} y⁻¹ (or 32.7 Mt_C y⁻¹), with 30 Mt_{CO}, coming from biogas and the balance from ethanol production. The atmosphere contains 880 Gt_{CO}, that could be captured using the advanced technology of direct air capture (DAC) at any point on our planet, making atmospheric CO2 an ubiquitous, freely accessible source of carbon.¹³ Currently, even if DAC is much more expensive (roughly 5-7 times) than CO₂ capture from power plants (that ranges around 80-100 US\$ per t_{CO}, the continuous progress in technology development forecasts an expense of less than 80-100 US\$ per t_{CO2}, which appears as a putative target in the medium-long term. The cost for the recovery of CO2 plays a key role in the implementation of the DAC technology, as it indicates the cost of carbon and goods derived from it. Currently, with a cost of ca. 550 US\$ per t of recovered CO2 using DAC, the cost of derived carbon should be around ca. 2000 US\$ per t_C, which is too high for making any kind of product that might be competitive with the same product derived from fossil-C, eventually making it out of the market. Notably, the cost of carbon sourced from oil is around 400–450 US\$ per $t_{\rm C}$ (at the price of oil of 61–65 US\$ per barrel as per May 2025). Therefore, if the DAC-recovered carbon has to be costeffective, a recovery cost of less than 100 US\$ per $t_{\rm CO_2}$ must be reached. Thus, supposing that efficient processes for converting $\rm CO_2$ into chemicals, materials and fuels will be available in the market, the atmosphere would represent a perennial source of carbon for future generations. It is worth emphasizing that the conversion of $\rm CO_2$ requires a quite different input of energy and materials according to the end product. Table 2 lists the three different classes of $\rm CO_2$ conversion reactions according to the energy required and the eventual need for hydrogen.

Table 3 presents the actual and prospective amount value of the world market of some selected chemicals (actual CAGR is used per product) and almost cover the total amount of CO2 used. Urea has the largest use of CO2. Notably, the CO2 used in the urea industry is generated via the synthesis of ammonia (H2 production). Noticeably, a substantial increase of the amount of used CO2 can be foreseen, as shown in Table 3, in case the new technologies under study (production of methanol and olefins, for example) will reach the manufacture level and will enter the market. As discussed in Table 1, olefins can be used to produce polymeric materials, and thus, the markets of chemicals and materials are cross-linked. The classic production of chemicals from CO2 (Class A reactions) has been studied since the middle 1970s, when the first transition metal bearing CO2 as a ligand was discovered, 14 and a few processes have been developed at the demo scale. Conversely, the use of CO2 as a carbon source for fuels, even if studied since the 1990s, has found application only very recently,15 after cheap PV energy has become available for either energizing the conversion process or producing H2 from water through electrolysis. Notably, if fossil-C sources are used for CO2 conversion into fuels, more CO2 would be released than the fixed amount. Using non-fossil renewable energy for producing hydrogen, it is possible to hydrogenate CO2 to energy products, thereby avoiding CO2 emissions. Either methanol (INOVYN process targeting 8 kt y-1 of CH3OH from CO2 and green-H₂)¹⁶ or methane (Falkenhagen demonstration plant, EU Project 691797)17 can be produced at demo- or even fullscale, while thermocatalytic processes to C_n hydrocarbons, olefins or alcohols are still under development.¹⁸

Table 2 Classes of reactions of CO₂ according to the energy input and hydrogen demand

Class A	Use of the entire CO_2 molecule (carbon $n_{ox} = +4$)	DH < 0, DG = ><0	M ₂ CO ₃ , RO-C(O)OR, HR'N-CO ₂ R"	Polycarbonates, polyurethanes, and fine chemicals
Class B	Formation of C–C bonds (carbon $n_{ox} = +3$)	DG > 0	<i>R</i> -CO ₂ H, HO ₂ C-CO ₂ H	Acids, esters, lactones, pyrones, and other carboxylates
Class C	Formation of reduced forms of carbon (carbon $n_{ox} \rightarrow \text{down to } -4$)	$DG \gg 0$ and H_2	CO, CH ₂ O, CH ₃ OH, CH ₄ , HCs	Energy products and bulk chemicals

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Compound	Formula…Coxidation state	World capacity 2023 (Mt y ⁻¹)	CO_2 used $(Mt y^{-1})$	Expected market capacity by 2040 (Mt y^{-1})	Expected CO ₂ use by 2040 (Mt y ⁻¹)
Urea	$(H_2N)_2CO\cdots+4$	186	136	366	266
Carbonates linear	OC(OR) ₂ ···+4	>2	< 0.1	10	5
Carbonates cyclic	Used as basic unit for polycarbonates (see below)···+4		<0.1		
Polycarbonates	-[OC(O)OOCH ₂ CHR]-n···+4	5	< 0.1	9–10	2-3
Polyurethanes	$-[R(H)N-CO_2]-\cdots+4$	ca. 50	<1	>70	ca. 20
Poly-acrylates	CH ₂ =CHCOOH···+3	66	<1	>80	40
Formic acid	$HCO_2H\cdots+2$	1	0.9	>10	>9
Inorganic carbonates	$M_2CO_3\cdots+4$	CaCO ₃			
	$M'CO_3$ (Na ₂ CO ₃ , K ₂ CO ₃)	250	70	500	125
Methanol	CH ₃ OH···-2	113	<10	150-200	200-260
Total	-		219		667-728
Ethene	$CH_2 = CH_2 \cdots -2$	160	0	270 (ca. 3.5% per y CAGR)	ca. 170
Propene	$CH_3CH = CH_2 \cdots -2$	80	0	150 (ca.3.5% per y growth)	ca. 90
Ethene glycol	HOCH ₂ CH ₂ OH···-1	30	0	50 (ca. 5% per y growth)	ca. 70
Grand total			207	, , , , , , , , , , , , , , , , , , , ,	997-1058

The use of hydrogen for the hydrogenation of CO₂ to fuels is often questioned because the direct use of H₂ as an energy vector would save approximately 20% of the energy lost during the chemical process of hydrogenation of CO₂. Therefore, finding an alternative route to CO2-reduction that would not demand molecular-H2 and save the necessary resources for its production, storage, transport and utilisation is very appealing. Co-processing CO2 and water under solar energy using either photochemical or photo(electro)chemical processes is a very attractive option, which is currently under deep study. 19 Major issues that prevent the large-scale exploitation of such innovative options include the unavailability of materials for building photoelectrodes, instability of photomaterials over long-term applications (months to year), and upscale of the entire apparatus. The use of rare, expensive and critical materials must be avoided. Interestingly, solar CO2 reduction processes could be integrated with solar water treatment to use waste water20 as a source of protons and electrons. However, a serious and continued investment program in the research and development is necessary to deploy such a nature-inspired approach to carbon-cycling. Thus far, C₁ species (methanol, methane, CO, and formic acid) or C2-Cn species (ethanol, hydrocarbons, acetone, and multicarbon-alcohols) can be produced by coprocessing CO₂ and water, ²¹ opening a way to a potential market-utilization of such energy products.

Integrating photocatalytic processes, photoelectroprocesses and hybrid catalysis, which include the use of enzymes or microorganisms coupled with electrocatalysis, 22 represent a strategy to overcome the bottlenecks and barriers for boosting the technologies and upscaling the results to industrial application. Stable and reproducible photomaterials must be produced that may afford usable amounts of fuels made from recycled carbon. Notably, water and CO2 are ubiquitous, and the technology discussed above may sustain the carbon economy of developing countries or countries that do not have large reserves of fossil-C. Innovative technologies may, thus, reduce the dependence on third parties of a number of economies, making energy and chemicals for the development of our society internally accessible while stopping the atmospheric accumulation of CO₂, mitigating climate changes, and implementing a man-made carbon cycle that might be integrated with the natural cycle.

3 Conclusion

Alternatives to fossil-C (biomass, waste plastics, and CO2 of either biogenic or atmospheric origin) have a different cost and potential and can afford a variety of products using a number of innovative single or hybrid technologies. Fig. 1 shows the integration of products and technologies. CO2 is by far the most abundant and at-hand source of renewablecarbon, and CCU is a strategic technology for the sustaining the future of humans. Different technologies may produce tangible results in a short-term (5-7 years), medium-term (8-14 years), or long term (15-20 years). Cost-effective capture of CO₂ from various sources is a key issue. In fact, the price of the "captured-carbon" must be such that the goods derived from it have a price comparable (or as much as close) to those of the same goods derived from "fossil-C" for being competitive. Today, the Fischer-Tropsch process is largely used for the synthesis of C_n hydrocarbons and their O-containing derivatives from syngas (the mixture of CO + 2H₂ produced via the steam reforming of LNG or low hydrocarbons or coal). Therefore, in the most favourable cases, one can think of converting the captured CO2 into CO (using the known reverse water gas shift technology, i.e. by converting CO2 into CO by reacting with green-H2 according to $CO_2 + H_2 = CO + H_2O$) and use the existing facilities for syngas conversion. Within such a framework, it is possible to calculate the suited price of the captured CO2 to assess its competitiveness with fossil-C. If LNG is used for producing syngas via the methane steam reforming process according to $CH_4 + H_2O = CO + 3H_2$, 1 t of methane priced at 0.5 US\$ per scm (average world price as per May 2025) will produce

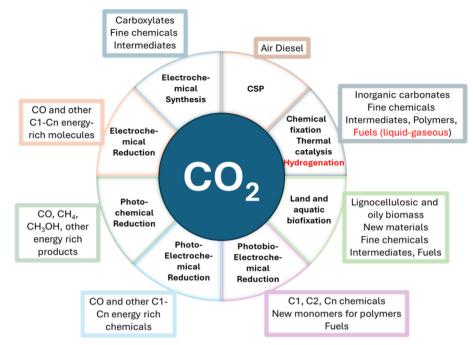


Fig. 1 Integration of innovative technologies and renewable C-sources for substituting the use of fossil-C.

carbon priced at 755 US\$ per t. If one wishes to use captured- CO_2 as a source of carbon and keep the cost of carbon at the same level, it must be considered that for converting 1 t of CO_2 into CO (636 kg) 45.4 kg of H_2 (priced at 3.8–12 US\$ per kg, depending on the location where it is produced) has to be used at a cost of 173 US\$ per $\mathrm{t}_{\mathrm{CO}_2}$ converted (assuming the lowest cost for green- H_2).

The production of 1 t of recycled-active-carbon would cost 519 US\$ in terms of the hydrogen demand. Therefore, the cost of production of captured CO_2 should be around 240 US\$ per t_C (or 65 US\$ per t_{CO_2}) to keep the overall cost comparable with that of fossil-C and to be competitive on the market. Table 4 shows the cost of CO_2 recovered from

various sources and their size. CO₂ produced in the ammonia industry (mainly in H₂ production) is since long time recovered and used in the production of urea; this an interesting case of carbon recycling at a significant scale. Ethene oxide does not have a great potential for the same. Bioethanol produces quite pure CO₂, which is easy to recover and can be immediately used in several applications, including the food industry. Even if NG is the fossil-carbon with the lowest emission of CO₂ per kWh in the production of electric energy, it should follow the fossil-C reduction trend: therefore, an expansion of its use seems to be ruled out. H₂ refinery will be slowly substituted by PV-H₂. The growth of cement and steel production will be

Table 4 Cost of capture of CO₂ from different point-sources. Decreasing the size of the plant increases the cost of capture (data adapted from ref. 22, except the last two listed cases)

Source of CO ₂	Cost of capture US\$ per $t_{\rm C}$	Plant capacity Mt y ⁻¹ product (CO ₂)	Current world market Mt y ⁻¹ _{product}	Prospective (2030) Market-CAGR% per y	Notes
Ammonia production ²³	51.4-102.8	2.1-0.5	192	210	All CO ₂ recovered and used
Ethene oxide ²³	85-173	0.77-0.10	31	36	
Bio-ethanol ²²	66–140	0.16-0.012	110	140	Pure CO ₂ used in the food industry
NG processing ²³	45-106	6500-1500	400 MNm3	440 MNm3	·
H2 refinery ²³	176-246	135-78	90 Mt	90 Mt	Green-H ₂ produced
Cement ²³	217-272	1.35-0.58	4100	8000?	50% in China
Steel ²³	198-338	6.3-1	1950	2150	
Biogas ²⁴	100-200		4.64 GNm ³	100 GNm ³ (800 GNm ³ max)	Cost of purification, no cost for separation
Power plant	183.5-239	1.8-0.18(CO ₂)			Various combustion technologies
540 MW^{25}		14 Gt _{CO2} produced worldwide			are used. They will decrease over the years
Direct air capture-DAC ²⁶	844-1982	Small units so far: $ca. 14 t_C y^{-1}$	$840~{ m Gt_C}$ in the atmosphere	n.a.	Air is the largest source of CO ₂

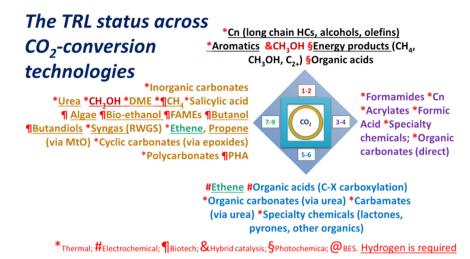


Fig. 2 TRL (Technology Readiness Level) of various technologies that convert CO_2 into chemicals, materials and fuels as main substitutes of fossil-C. Symbols "*, #, § etc." indicate the technology listed at the bottom of the figure. The underlined products demand hydrogen in addition to energy. The same product can appear at different TRLs depending on the manufacturing technology considered.

driven by the growth of the living standard of the world population and will grow mainly in China, India, Africa and South America. A particular case is the upgrading of biogas to biomethane, in which the capture cost of CO_2 is zero as it is a by-product that needs to undergo purification for use. Such a source has a great potential for growth and is rich in CO_2 (40% v/v as average). It is foreseeable that in next decades, power plants will be decommissioned. Anyway they are not a preferred source of CO_2 as such CO_2 is considered fossil- CO_2 and its use will not be encouraged. The atmosphere is the largest source of CO_2 , but currently, the cost of capture puts this carbon source out of the market. However, despite great expectations, cost reductions have been limited.

In conclusion, the new sources of carbon-alternative to fossil-C that are worth to be exploited include biogenic sources of CO₂ and the atmosphere. An integrated investment effort must be done in order to promote the R&D&I in DAC; if the cost of capture of DAC technology decrease to one tenth of the actual cost, the conversion of CO2 into fuels (either by using green-H2 or better by direct coprocessing with water in photo- or photoelectro-chemical processes) on a large scale will become a reality. The EU (and other large key world economies) is elaborating complex directives for accelerating CO2-reduction emission strategies to benefit from the use of such carbon as an alternative to virgin fossil-C. Special supporting actions have been funded (gathering academic and industrial partners and ROs), which have been continuously developing roadmaps and strategic plans for years to assess the potential of CO₂ utilization as source of carbon alternative to fossil-C. Such studies will deliver their evaluations in the coming two years, and most likely, will shed light on the real potential of CCU as a strategic technology for our future. In the next five years, a much more defined reference framework will likely be available for setting new operative frameworks for the use of captured CO₂.

Fig. 2 represents the current TRL status of the state-of-theart innovative synthetic technologies based on the costeffectiveness of captured-CO₂ and their potential.

Thus, it is quite clear that the use of biogenic and atmospheric CO_2 has great potential as substitutes for fossil-C. However, to fully exploit their potential and to take a substantial step from the linear- to cyclic-economy of carbon, clear policies (international and national) are necessary to boost investment in research, development and innovation (R&D&I). Special attention must be paid by funding Agencies to organize a continuous financial support (Special Calls with defined targets and adequate Funding Programmes) that may integrate the effort of Academia (Universities and Research Organizations) and Industry (Start-ups, SMEs and Large Industries) on common key-objectives that may fill the gap between TRL 4-5 and 7-8, a most critical phase, and scale-up from laboratory-scale to demo-scale the innovations.

Data availability

Reported data are available in the cited papers in the list of References.

Conflicts of interest

The author declares no conflict of interest.

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