Supplementary: Technological and policy options for the defossilisation of chemical manufacturing

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1. Primary chemicals

The chemical industry comprises an intricate network encompassing more than 50,000 compounds. Within this expansive network, seven chemicals are referred to as primary chemicals, i.e. ammonia, methanol and HVCs, from which the vast majority of the remaining ones are synthesised (see **Table S1**). Today, around 65% of the total energy required by the chemical industry is attributed to the production of primary chemicals (8.4 PWh out of 13.2 PWh in 2017), primarily sourced from fossil fuel and supplemented by biomass and waste, heat and electricity[1, 2].

The states of the production volume of the primary chemicals are being reported in the International Energy Agency (IEA), and they also projected the chemical growth of the chemical industry published by IEA in 2013, and in 2018, they served as the basis of the publications included in our analysis.

Table S1. Conventional fossil fuel-based production routes for primary chemicals and their production volume as of 2023.

Primary chemicals			Production volume 2023* (Mt/a)	Carbon in 2023 (MtC/a)	Main applications	Conventional production routes
Ammonia (NH_3)[3]			196	0	Fertilisers, plastics, explosives and synthetic fibres	Steam methane reforming (SMR), coal gasification
Methanol (CH_4O)[4, 5]			117	44	Fuel additives, plastics, plywood, paints, explosives, textiles	Natural gas-based steam reforming, coal gasification
HVCs	Olefins[6]	Ethylene (C_2H_4)	412	360	Plastics, detergent, rubber	Byproducts of refining operations; steam cracking;
		Propylene (C_3H_6)				

	BTX aromatics [7]	Benzene (C_6H_6)			Plastics, nylon, gasoline, resins	fluid catalytic cracking
		Toluene (C_7H_8)				
		Mixed xylenes (C_8H_{10})				

* Production volume of primary chemicals in 2023 as interpolated based on 2017 production volumes and compounded average growth rate (CAGR) reported by IEA[8] (see **Table S2**). HVCs, high-value chemicals.

Ammonia is at the roots of the global food chain and finds its main application as fertiliser being a substantial and limiting nutrient for plant growth (0.03 to 7 wt% N per dry plant material[9]). As plant-based food production is in the order of 1 billion tons dry weight (9.5 billion tons fresh weight in 2021[10]), the amount of nitrogen consumed by humans and livestock is in excess of 70 Mt ammonia equivalents[11]. Due to poor retention in soil and rapid volatilisation[12], it's no surprise that 70% of the 190 Mt of ammonia produced in 2020 are used as mineral fertilisers, while the remainder is used industrially, e.g. for the synthesis of plastics (e.g. polyacrylonitrile and isocyanates for polyurethanes), synthetic fibres (e.g. hexamethylenediamine for nylon 66 and caprolactam for nylon 6), rubber (e.g. nitrile butadiene), or explosives[13]. Owing to its energy density[14], ammonia is also anticipated to in future play a significant role as chemical hydrogen carrier and fuel for the transport sector[15].

Energy and hydrogen required for ammonia synthesis are primarily obtained by natural gas-based gas reforming and coal gasification processes. Approximately 50% to 65% of the energy is used in feedstock, while the remaining is utilised in process energy, mainly for generating heat[13]. Given its irreplaceable role in agriculture, with an anticipated increase in global population by 2050 and in light of cross-sector applications to come, the demand for ammonia is expected to grow dramatically[16].

Methanol is currently predominantly produced by gas-based steam reforming or coal gasification starting from fossil carbon. It serves as a key precursor for the synthesis of HVCs through well-established methanol-to-olefin (MTO)[17] or near-commercial methanol-to-aromatics (MTA) conversion routes[18, 19]. Other than that, methanol finds application in gasoline and diesel blending, as well as in the production of biodiesel. It is also utilised in the manufacture of acetic acid for paints and formaldehyde for plywood production[5]. Furthermore and similar to ammonia, methanol's significance extends to the energy and transport sector, where the production of non-fossil methanol offers means to enhance the value of renewable power and efficiently store hydrogen in a liquid form for later use[5].

The remaining five of the primary chemicals are predominantly produced by steam cracking of naphtha derived from fossil reserves yielding ethylene, propylene, benzene, toluene, and mixed xylenes, collectively categorised as HVCs[20]. Noteworthy ethylene is also synthesised from biogenic ethanol produced from plant sugars or from industrial off-gases[21-23]. HVCs primarily serve as raw materials for synthesis of thermoplastics (e.g. in 2019, 110 Mt/a polyethylene [LDPE and HDPE] from ethylene, 73 Mt/a polypropylene from propylene, and 51 Mt/a PVC from benzene[24]). With continuing population growth and a trend towards elevated living standards, the demand for plastics and HVCs is expected to witness substantial increases.

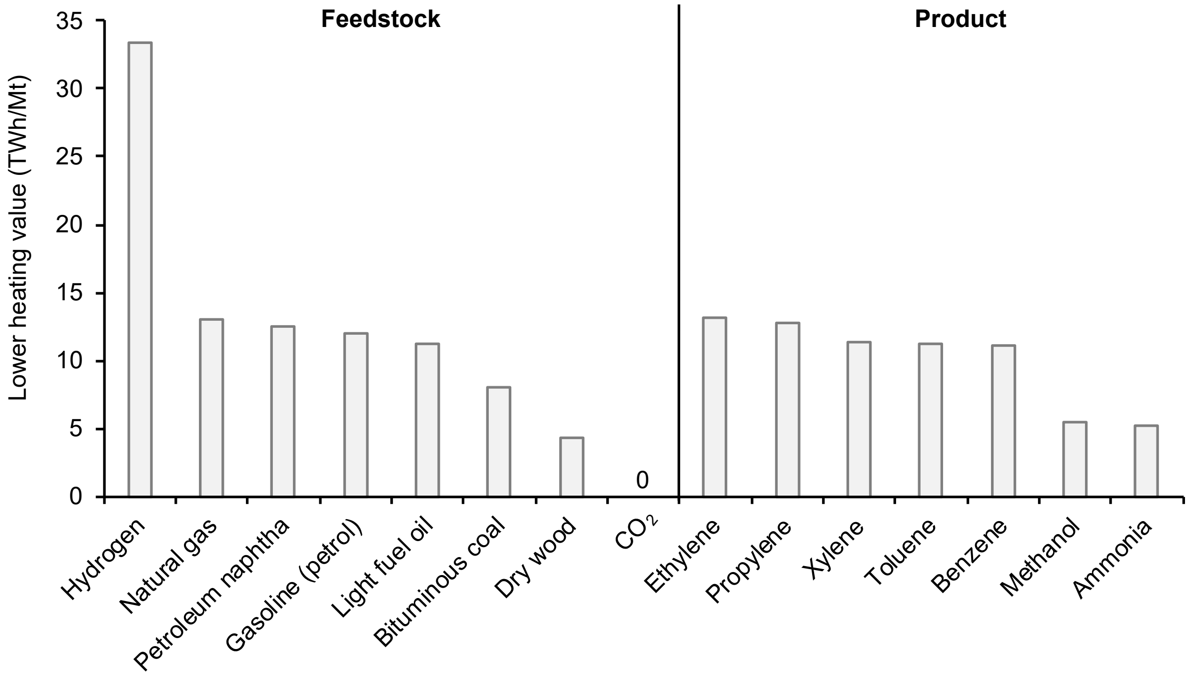

Figure S1. Lower heating value (LHV, net heat of combustion of chemical at standard state) of feedstock and primary chemicals[25-27]. The feedstock category encompasses fossil fuels (natural gas, petroleum naphtha, gasoline, light fuel oil and bituminous coal), biomass (dry wood), and CCU (CO_2 and hydrogen). The products category includes the seven primary chemicals, ammonia, methanol, and the HVCs (ethylene, propylene, benzene, toluene, and xylene).

Throughout the production of primary chemicals, the process essentially involves transferring molecules and chemical energy from the fossil fuel feedstocks (**Figure S1**, values are shown in lower heating value [LHV] of the chemicals, indicating the enthalpy of combustion of chemicals under standard conditions). Carbon molecules are transferred from fossil carbon to the carbon in primary chemicals. Chemical energy, carried by electrons, is transferred to the primary chemicals and also provides the process energy, thus no additional energy is needed. Fossil fuels inherently carry both carbon molecules and hydrogen atoms with electrons, enabling both transformations to occur during combustion. However, defossilised feedstocks typically carry fewer electrons. For example, the lower heating value (LHV) of dry wood is 4.3 TWh/Mt, which is lower than that of primary chemical products, meaning external electrons must be sourced. CO_2 presents an even more extreme case, containing carbon molecules but virtually no electrons, resulting in a LHV of zero. Consequently, electrons must come entirely from external sources, with hydrogen often being favoured due to its high energy content.

2. Assessment of the net-zero transition scenarios

The common goal of all analysed net-zero transition scenarios is the reduction of CO_2 emissions down to near net zero. In an effort to enable direct comparison of the provided data among the net-zero transition scenarios and ensure data transparency, we first harmonised the chemicals and inputs outputs by weight (Mt/a) and then converted them consistently to million metric tons of embedded carbon (MtC/a). For feedstock and energy inputs (fossil fuels, biomass, hydrogen, and electricity), we generally used watt-hours per annum (Wh/a).

In aligning data from diverse sources, not all data were provided in every piece of literature. We only subtracted the corresponding data for primary chemical production, which includes ammonia (urea in EmiH and EmiL), methanol, and HVCs. The production volumes were derived from global chemical flows. Regarding feedstock requirements, chemicals produced from recyclates were excluded, as they represent reductions in virgin chemical demand. The volumes of fossil fuels, biomass, and CCU feedstocks were extracted, and the carbon embedded in these feedstocks was calculated. Energy requirements were divided into two components: the energy embedded in the feedstock, calculated using their LHV, and the energy needed for manufacturing processes. For CCU, this includes the energy in hydrogen along with energy losses during hydrogen generation.

For ZERO1.5, LC-NFAX and HC-NFAX, all relevant information is provided in the main text and the supplementary files. For NZE2050H, the production volume of primary chemicals in 2050 is reported, with the feedstock requirement calculated based on global chemical flows using the LHV of hydrogen, methanol, and biomass to determine corresponding feedstock volumes. The energy requirement is also reported. For EmiH and EmiL, the production volume of primary chemicals in 2050 is calculated from the global CO_2 demand for chemical feedstocks. The feedstock requirement is reported, and the energy requirement is calculated as shown in **Table S3**. For TRLH, all necessary information is included.

Calculations and estimations were performed to further process the data. These calculations may not perfectly align with the original data. However, as our intent is to allow the reader to readily get an overview of the state of the art in the field, we are considering this step as both permissible and inevitable.

Our work may also be understood as an invitation to the community to standardise reporting procedures in order to in future allow direct comparison of results and projections from different sources.

Supplementary figures

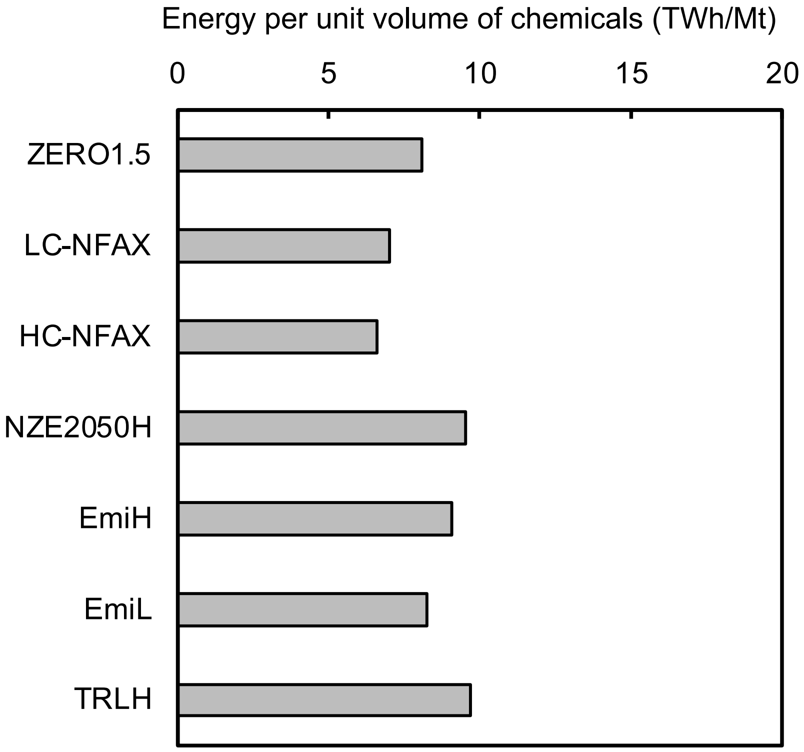

Figure S2. Specific energy content of the *de novo* synthesised chemicals based on actual production volumes (recycling excluded) and lower heating values.

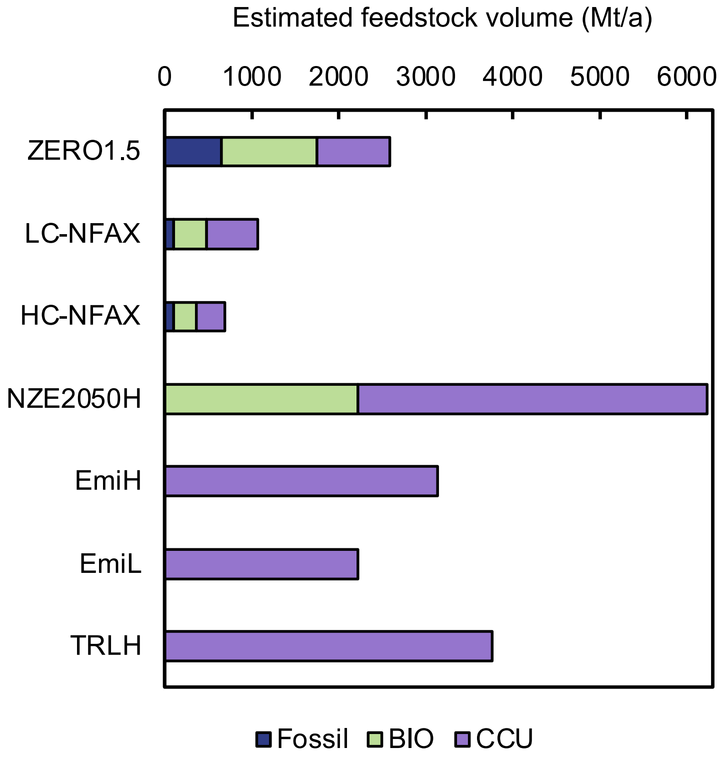

Figure S3. Estimated feedstock volume for the net-zero transition scenarios based on carbon content of natural gas 75%C, dry wood 50%C[28], CO_2 27%C.

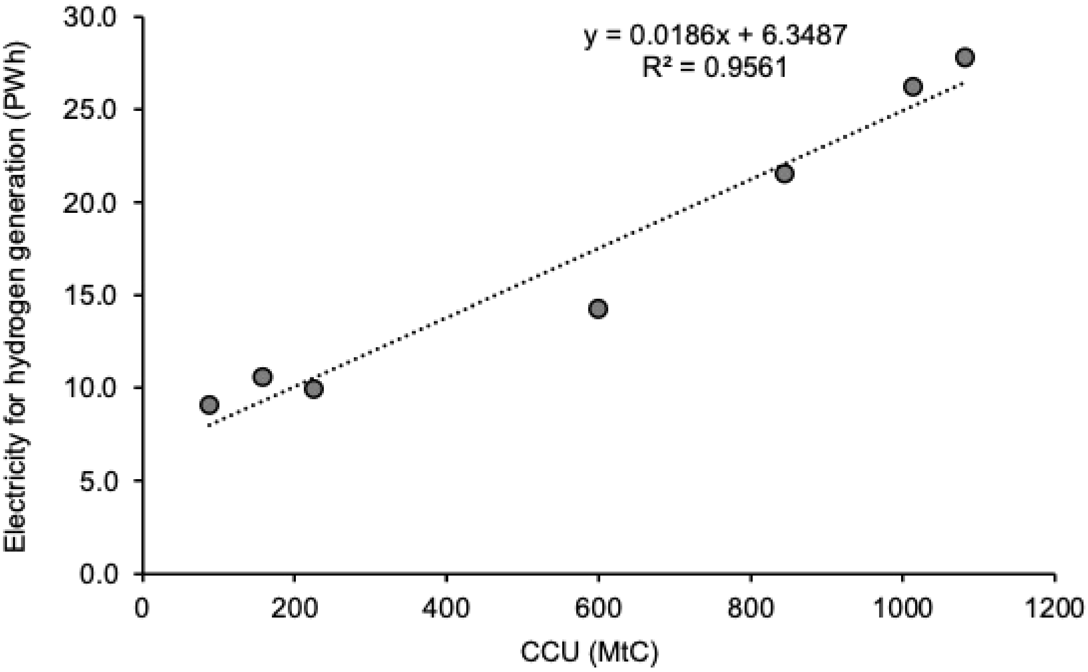

Figure S4. Hydrogen generation-related electricity is positively correlated to the amount of carbon supplied through CCU across all the net-zero transition scenarios.

Supplementary tables

Table S2. Production volumes of primary chemicals.

Production volume (Mt/a)		**2017***	**2023**	**2030***	**2050***
Ammonia		183	196	213	241
Methanol		96	117	147	180
HVCs	Ethylene	175	151	207	255
	Propylene	116	102	135	164
	BTX	121	106	141	160
Total		**639**	**725**	**843**	**1001**

* 2017, 2030, and 2050 data were extracted from IEA (RTS scenario)[8]. The production volumes of 2023 are estimated on the basis of the production volume of 2017 and the CAGR between 2017 and 2030.

Table S3. Process energy assumptions made for **EmiH** and **EmiL**[29].

	Energy requirement (TWh/Mt)	**Notes**
Urea	3.1	1.72 TWh/Mt energy is required for ammonia production, 55% of ammonia will be converted into urea.
Methanol	2.1	
HVC-olefins	7.2	2.83 tons of methanol are required per ton of olefin, which equals 5.82 TWh to provide the methanol and 1.39 TWh for the methanol-to-olefin process energy.
HVC-BTX	10.2	4.3 tons of methanol are required per ton of BTX, which equals 8.84 TWh to provide methanol and 1.39 TWh for the methanol-to-BTX process energy.

Environmental pillar

Table S4. Climate action

Technological option	Rating and rationale
FOS	(–) All the carbon that is extracted as a component of fossil mineral resources is ultimately emitted into the atmosphere as a component of climate-damaging gases.
FOS/CCS	(0) The emission of climate-damaging gases is being sequestered.
BIO	(–/0) The carbon footprint depends heavily on the specific technologies (such as traditional intensive agriculture or algae-derived biomass production) used. Some of the technologies (e.g. sustainable forestry) could even have negative emissions and depending on the end-of-life treatment of the manufactured products, BIO has the potential to cause negative emissions.
CCU	(0) Essentially no emissions of climate-damaging gases. Depending on the end-of-life treatment of the manufactured products, this technology has the potential of negative emissions.

Table S5. Biodiversity conservation

Technological option	Rating and rationale
FOS	(–) Mining of fossil reserves is associated with the utilisation of natural habitats and it's well known from the past that the excavation process poses a high burden that materials can destroy them. Mining is inevitably linked to the deposits, which are often located close to the important habitats.
FOS/CCS	(–) Essentially the same as FOS. In addition, there is a certain land requirement for the installations required for CO_2 sequestration.
BIO	(–/0/+) Impact depends on the specific technology used: expansion of conventional agriculture can destroy habitats while the use of biomass from sustainably reforested areas could certainly have positive effects. Third-generation biotechnological processes have the potential to excel in terms of environmental compatibility.
CCU	(+) Only limited land use for gas conversion if obtained from concentrated point sources. In addition, areas can always be used whose use does not lead to any loss of biodiversity such as existing industrial

	parks. A challenge in terms of biodiversity protection is the significant use of water for the electrolytic production of hydrogen and the rather high requirements for renewable energy. This also applies if electrochemical, electromicrobial or photochemical processes are used, i.e. if the water does not have to be electrolysed beforehand.

Table S6. Pollution prevention

Technological option	Rating and rationale
FOS	(–) Hard to control emissions (e.g. methane) during extraction and processing plus accidental spills. Only limited numbers of suitable sites which could be frequently vulnerable habitats. Massive use of chemicals during mining and processing.
FOS/CCS	(–) Essentially the same as FOS.
BIO	(–/0) The pollution depends very much on the specific technology used. Conventional intensive agriculture for instance is accompanied with significant emissions of chemical substances, such as fertilisers, NO_x and pesticides. Contained systems for solar-powered algae/microbial cultivation (third-generation BIO) would need to be evaluated based on wastewater handling.
CCU	(0) This technology has an intrinsically low potential of pollution. However, if seawater is used for preparation of demineralised water for electro- or photochemical reactions, it must first be desalinated according to the current state of technology. This produces vast streams of desalination brine which may either have to carefully given back to the oceans or sequestered.

Table S7. Conservation of resources

Technological option	Rating and rationale
FOS	(–) This technology area is based on the continued consumption of limited fossil carbon sources.
FOS/CCS	(–) This technology area is based on the continued consumption of limited fossil carbon sources.
BIO	(–/0/+) The outcome depends very much on how the biomass is being generated, i.e. type of agriculture or forestry or fermentation, etc. This

	technology could have certain advantages over CCU when it comes to producing more complex molecules which are not so easily obtained with chemical synthesis.
CCU	(+) CO_2 is an unlimited resource. The use of water and vast amounts of energy for electrolysis or electrochemical or photochemical reactors will, however, require resource-saving management[30].

Social pillar

Table S8. Health and well-being of the workers

Technological option	Rating and rationale
FOS	(–/0/+) Depends on the specific practised working conditions and the impact on the communities in contact with the mining and processing sites. Intrinsic toxicological properties of the substances present in the mined materials and in the chemicals used for extraction are to be taken care of. Sites of mining cannot be freely chosen but depend on the location of the deposits, and therefore this parameter depends on the occupational health and safety conditions at these specific sites.
FOS/CCS	(–/0/+) The same as FOS. Depends on the specific practised working conditions and the impact on the communities in contact with the mining and processing sites of the fossil resource as well as with the sites where sequestration takes place.
BIO	(–/0/+) Depends on the specific working conditions practised and the impact on the communities near which the biomass is produced and processed. As locations are spread all over the world, the health and safety conditions in these different locations can vary greatly.
CCU	(0/+) Depends also on the local and national regulatory requirements for the protection of workers and communities; however, novel technologies offer in most cases better working conditions than conventional ones as they are usually developed taking into considerations the state of the art in the respective areas[31].

Table S9. Social equity and justice

Technological option	Rating and rationale
FOS	(–/0/+) Depends on the specific practised conditions in the country where mining and processing takes place.
FOS/CCS	(–/0/+) Depends on the specific practised conditions in the country where mining and processing takes place. In addition, with this option, appropriate worker protection not only has to be enforced at the sites where fossil raw materials are mined but also at the sites where the sequestration takes place.
BIO	(–/0/+) Depends on the specific practised conditions in the country

	where the generation of the biomass and its processing takes place.
CCU	(–/0/+) Depends on the specific practised conditions in the country where the carbon capture and the processing of the obtained basic chemicals take place.

Table S10. Community engagement and empowerment

Technological option	Rating and rationale
FOS	(–/0/+) Depends on the specific practised conditions in the country where mining and processing takes place. However, due to the specific geographical location of the fossil deposits, the freedom to choose the fossil resources which are generated with high social standards might be limited.
FOS/CCS	(–/0/+) Depends on the specific practised conditions in the country where mining and processing takes place. However, due to the specific geographical location of the fossil deposits, the freedom to choose materials which are generated with high social standards might be limited. In addition, with this option, high social standards not only have to be enforced at the places where fossil raw materials are mined, but also at the places where the sequestration takes place.
BIO	(–/0/+) Depends on the specific practised conditions in the country where generation of the biomass and its processing takes place. An advantage could be that BIO by its nature is less centralised and can support more communities including those outside metropolitan areas.
CCU	(–/0/+) Depends on the specific practised conditions in the country where capture and processing of the produced basic chemicals takes place. An advantage could be that CCU by its nature is decentralised and can support more communities.

Economic pillar

Table S11. Job creation

Technological option	Rating and rationale
FOS	(–/0) Little potential of creating additional jobs. Anyway, because conventional fossil fuel mining is coming under increasing pressure due to its negative environmental impact, the highly specialised jobs there are certainly at risk in the long term. In locations where fossil raw materials are mined, mining poses a major risk to long-term labour market stability.
FOS/CCS	(0/+) Little potential of creating additional jobs in the area of mining. Anyway, because conventional fossil fuel mining is coming under increasing pressure due to its negative environmental impact, the highly specialised jobs there are certainly at risk in the long term. In locations where fossil raw materials are mined, mining poses a major risk to long-term labour market stability. There is, however, quite some potential for job creation in the area of carbon capture and sequestration.
BIO	(0/+) Little potential of creating new jobs in conventional agriculture and forestry. However, in innovative areas of generation of biomass and of its processing (third-generation biomass), there is potential of creating high-qualified jobs. It is inherently more decentralised than FOS and FOS/CSS and has the potential to create jobs in disadvantaged regions and/or outside metropolitan areas.
CCU	(+) This new technology area has the potential of creating jobs. It is inherently more decentralised than FOS and FOS/CSS and has the potential to create jobs in disadvantaged regions.

Table S12. Long-term success of sector-specific investments

Technological option	Rating and rationale
FOS	(–) The extraction and use of fossil raw materials cannot be regarded as a promising investment in the period up to 2050. It harbours a cluster risk due to the high concentration among a small number of players. It is demonstrably susceptible to market fluctuations and economic cycles. It is not flexible in its choice of location and is therefore intrinsically susceptible to political crises, sanctions, coercion, and expropriation. It is also expected that there will be greater fiscal pressure as some countries

	strive to make this industry less financially attractive (e.g. by EU taxonomy[32]).
FOS/CCS	(0) Essentially very similar to FOS. The fiscal pressure might, however, be less intense as in the case of FOS. Carbon capture and sequestration activities are receiving some support from government actors.
BIO	(–/0/+) Depends very much on the specific way the biomass is generated and processed, such as conventional agriculture or third-generation biomass processing[33]. In particular the latter option offers opportunities for robust long-term returns.
CCU	(–/0/+) In the long term (with a time horizon of 2050), the opportunities are positive. With increased capacities for renewable energy and hydrogen, the field will gain additional momentum[34].

Table S13. Diversity (redundancy) of supply

Technological option	**Rating and rationale**
FOS	(–) In the area of fossil fuels and basic chemicals, there is a very high concentration of relatively few players. In addition, the massive distribution infrastructure required (ports and pipelines) leads to oligopolies that limit the opportunities for supply chain diversification.
FOS/CCS	(–) In terms of fossil raw materials essentially the same as FOS. As sequestration will also be bound to a relatively limited number of sites, this could also lead to a limited choice of sequesterers.
BIO	(0/+) Depends on the specific source of biomass. Some agricultural products are produced in few dominating countries.
CCU	(0/+) Due to the large geographic distribution of CO_2 capture, we assume that the corresponding supply chains to be developed will be relatively diverse. However, CCU fed with CO_2 isolated by direct air capture could be geographically tied to areas where huge capacities for sustainable power production is available.

Table S14. Promoting technological innovation

Technological option	**Rating and rationale**
FOS	(–/0) The technologies for extracting fossil fuels still have little room for

	technical improvement and are about to approaching the limits of what is economically and technically feasible.
FOS/CCS	(0/+) Although mining and processing of fossil raw materials is probably close to its economically achievable optimal performance, the carbon capture and sequestration technology has still a large potential for further development.
BIO	(–/0/+) Depends on how the biomass is being generated. Some of the technological options, in particular the biotechnological ones, have a large innovation potential.
CCU	(+) The technology is relatively young and has significant development potential.

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