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SUSTAINABILITY OF CARBON MANAGEMENT TECHNOLOGIES

by

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DECLARATION

I herewith declare that this dissertation is the result of my own work and has not been previously submitted for consideration to any other degree or qualification at this or any other university. The work which is not my own has been properly acknowledged.

Amjad Alqahtani

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ABSTRACT

Carbon dioxide (CO_2) is the main contributor to climate change and thereby to global warming. Several technologies have been proposed to reduce atmospheric CO_2 emissions, such as CO_2 capture and storage (CCS), CO_2 capture and utilization (CCU) and hydrogen production. From these proposals, converting the captured CO_2 into valuable products was seen as a promising area to explore. Correspondingly, CCU is achieved when the captured CO_2 is utilised to produce chemicals and fuels that are more environmentally friendly than their fossil-based ones. Yet, the cost of hydrogen and the energy consumption associated are key issues to deal with. This thesis aims to understand and explain the role of hydrogen production, CCS, and CCU in the sustainability context.

The first part of the study focused on the hydrogen production pathways as a crucial component in the decarbonisation of the transport, heating, and chemicals sectors. A linear optimisation model was built to explore carbon-neutral shares of all the investigated production routes in terms of their total cost that included the externalities plus the economic performance. The results supported an approach for establishing strategies for the much-needed energy transition by promoting blue (fossil-based with CCS) hydrogen at present until green hydrogen becomes competitive.

The second part focused on evaluating the best use of wind energy between the CCU route to methanol from CO_2 and hydrogen to be used as a fuel in the transport sector or to decarbonise the electricity mix directly considering the energy systems constraints through scenario-based modelling. It was concluded that, at present, decarbonising the electricity grid using renewable energy sources with CCS would offer greater environmental benefits, without incurring large changes indirect economic costs, compared to producing methanol from the hydrogenation of captured CO_2.

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NOMENCLATURE

Abbreviations

AP	Acidification potential
BAU	Business as usual
CAPEX	Capital expenses
CCU	Carbon capture utilisation
CEPCI	Chemical engineering process cost indexes
DAC	Direct air capture
DALY	Disability-adjusted life years
EQ	Ecosystem quality
GWP	Global warming potential
HEN	Heat exchanger network
HH	Human health
ISO	International Organisation of Standardisation
LCA	Life cycle assessment
LCIA	Life cycle impact assessment
LP	Linear programming
LPG	Liquified petroleum gas
NG	Natural gas
OPEX	Operational expenses
RD	Resource depletion
TRL	Technology readiness levels
WGSR	Water gas shift reaction

Chapter 1 INTRODUCTION

1.1 Carbon dioxide emissions current levels: State of the art

Scientific research has now established that carbon dioxide (CO_2) emissions are one of the main contributors to the global greenhouse effect due to their restricting the amount of energy re-emitted from the earth's surface. This is evident by the relatively rapid increase in CO_2 levels in the atmosphere, represented by 80 ppm increase in the last 200 years with the majority of the increase occurring in the last 50 years, which is much higher rate of increase taking into consideration that it took 10,000 years to increase CO_2 by 80 ppm prior to those 200 years [1]. Fig. 1.1 shows how atmospheric carbon dioxide emissions have drastically increased since 1960 [2]. A large proportion of this growth is due to the use of carbonaceous fuel to generate energy – carbon-based fuels are responsible for 85% of the global energy generated and the manufacture of various chemicals [1]. The increase in carbon dioxide has been sustained by consistent growth in developed economies and exacerbated by rapidly growing economies such as China and India, which means even more energy is needed to meet the demands required to sustain such rapid development [3].

The effects of increasing carbon dioxide emissions – touched on earlier – are driving the increase in global temperature, whether those emissions result from energy production, transport or manufacturing [3]. Changes in climate behaviours have led to frequent extreme weather conditions like increased rainfall in some areas. In addition to the issue of rising global temperatures, the acidity of the oceans is increasing due to surface ocean CO_2. The

effects of climate change will affect crops due to floods, and protecting urban areas and industrial sites will become costlier due to the need for additional flood protections [3].

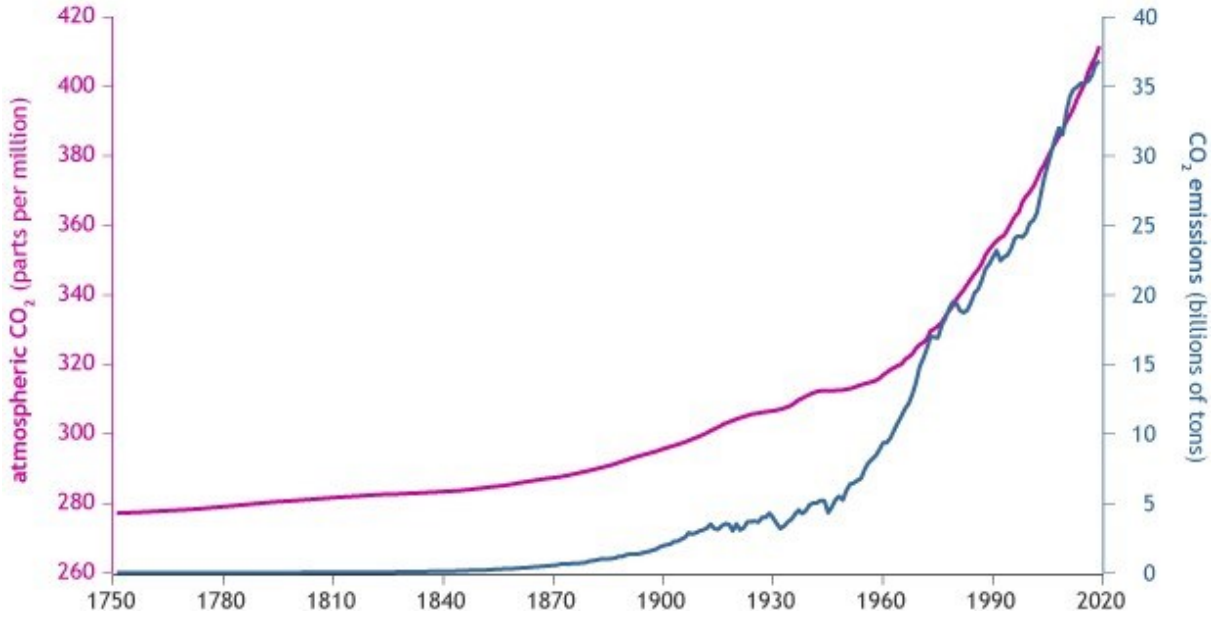


Fig. 1.1 The amount of CO_2 in the atmosphere (pink line) which has increased alongside CO_2 emissions (blue line) since 1750, when the Industrial Revolution began [2].

Given the trends outlined above, there is an increasingly urgent need to reduce carbon dioxide emissions caused by human activities and, ideally, eliminate them. In pursuit of this goal to tackle the issue of global warming, many worldwide initiatives have been carried out, with the Kyoto Protocol (1997) among the best known examples; several countries are now supporting research into methods which will help mitigate or reduce carbon dioxide emissions [4]. Whilst the potential for these technologies is great, they are relatively new and thus can be prohibitive in terms of cost or materials or simply in the very early stages of development. Other technologies that can help mitigate global warming include the development of more efficient processes of producing and consuming energy to reduce their carbon footprints and the development of technologies that reduce or remove CO_2 [3].

Carbon dioxide is classified as a major contributor to climate change and thus global warming. Anthropogenic CO_2 emissions into the atmosphere are sourced primarily from fossil

fuel combustion and flue gases of industrial plants. Mainly, CO_2 emissions come from coal, oil and gas-based sources as shown in Fig. 1.2. Furthermore, these fossil fuels are burned to be used in different sectors, mainly for electricity, heat and transportation as demonstrated in Fig. 1.3.

Accordingly, searching and assessing greener routes for energy sources is crucial and would contribute heavily to reduce greenhouse gas emissions.

There are several approaches to help reduce CO_2 emissions in the atmosphere, including carbon capture and storage (CCS) and carbon capture and utilization (CCU).

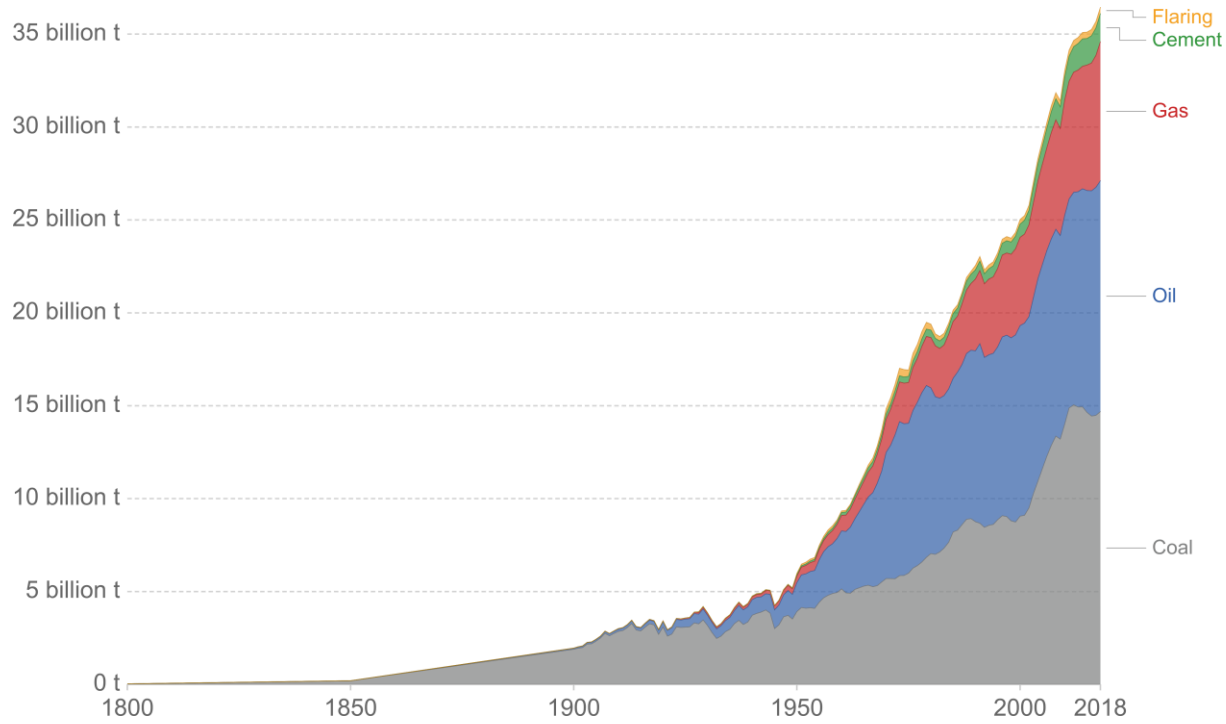


Fig. 1.2 Annual CO_2 emissions from different fuel types quantified in tonnes per year [2].

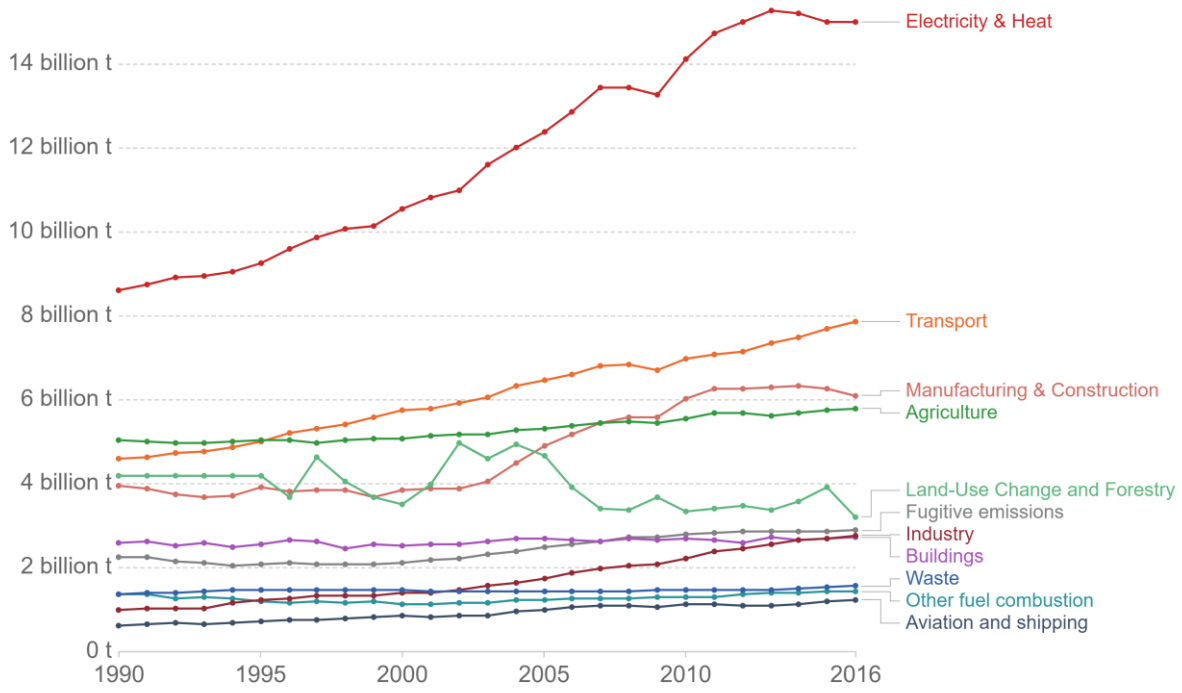


Fig. 1.3 Annual CO_2 emissions from different sectors [2].

1.2 Research objectives and thesis structure

The objective of this thesis is to evaluate the techno-economic and environmental performance of CO_2 reduction technologies, including hydrogen production, CCS and CCU. The evaluation aims to ensure the sustainability of the potential technologies, to address any environmental concerns and to further highlight the phases at which the environmental concern occurs. This is achieved by comparing the performance of CO_2-based technologies against their non-CO_2-based counterparts. An extensive amount of data has been acquired and compiled to offer an in-depth understanding and interpretation of the outputs of the analysis. To that end, the main contributions of this thesis are as follows:

- To investigate hydrogen production technologies as a key factor in deep decarbonisation.
- To address potential and optimal hydrogen production shares in terms of their externalities and economic costs against their greenhouse gas performance.
- To assess the best current use of renewable electricity for hydrogen production or for direct electricity generation from a sustainability perspective.

This thesis is structured based on the following chapters. Chapter 1 aims to introduce and give broad information of the climate change problem, the motivation for the study and the objectives and structure of the thesis. Chapter 2 reviews the related studies in the literature to further understand the current status and then identify the gaps which need to be bridged in this study and future studies. Chapter 3 presents the current existing tools that are used in the literature to evaluate the potential technologies from economic and environmental aspects. Chapters 4-6 address the mentioned literature gaps in Chapter 2 by using sustainability research tools presented in Chapter 3. Finally, Chapter 7 presents the overall conclusions of

all the contributions, the limitations of the study and suggestions for future avenues of research.

Chapter 2 BACKGROUND

This chapter provides an overview of the decarbonisation pathways of CCS, CCU and the role of hydrogen. Some of the CCU products such as urea, formic acid, algae, inorganic carbonates, and methanol are further discussed. Finally, the hydrogen role in the decarbonisation context is provided.

2.1 Carbon capture and storage (CCS)

Though not strictly speaking utilisation, capturing carbon dioxide is a step towards locking carbon dioxide in a form suitable for storage for later utilisation. CCS can be described as the process which captures carbon dioxide at source e.g. an industrial or power plant, transport it through a pipeline or a ship and store it in a geological site that can be depleted oil fields or saline aquifers [5]. Such technology is useful as retrofit for heavy polluters, such as coal power stations, to eliminate the amount of carbon dioxide emitted to the atmosphere [6]. Other CCS examples include the steel and metal manufacturing industry [7].Whilst CCS can be seen as a “sweep it under the rug” solution, it is confidently a significant solution in the roadmap for the climate mitigation solutions. Fig. 2.1 clearly demonstrates the vital role of CCS in heavily emitting sources such as power generation plants and industrial sectors for instance iron and steel [8]. Moreover, excluding CCS from carbon reducing technologies in the mitigation scenarios with 450 ppm can raise the costs of meeting required targets by 70% as reported by the International Energy Agency [8].

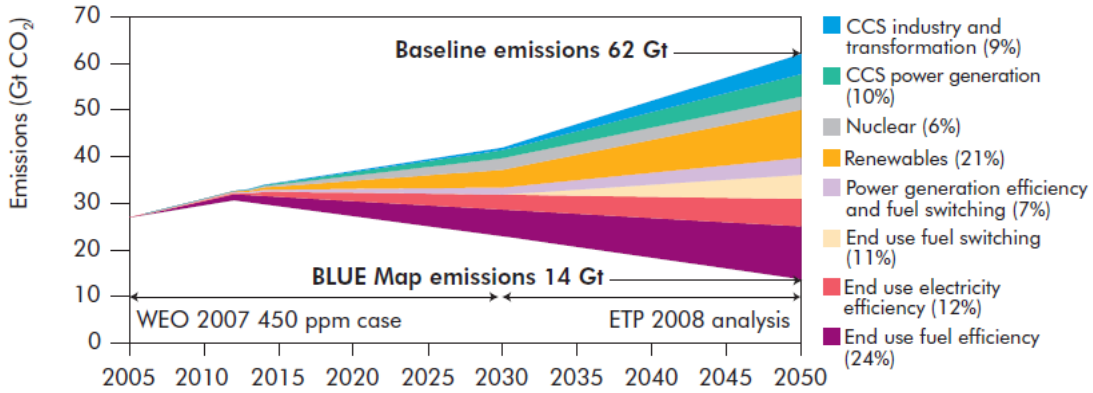


Fig. 2.1 Carbon capture contribution to mitigating carbon dioxide emissions according to the International Energy Agency [8]

Carbon capture and storage process can be broken down into four main steps. The first step is the production of carbon dioxide. This is then followed by capturing it, then transporting and storing it. The sources of carbon dioxide can vary greatly, thus the purity and level of contamination will vary along with it, for instance flue gas emissions from a coal power station will contain substances such as SO_x, particulates and Mercury in addition to the usual combustion products (H_2O and CO_2). Thus they will require more pre-treatment purification steps, hence incurring additional costs. In comparison, high purity sources such as hydrogen, ammonia or gas processing require fewer steps before being able to transport it [9].

Within the combustion plants, there are multiple paths to capturing carbon dioxide, each of which are at different levels of applicability from a development point of view [7]. Post-combustion, where carbon dioxide is captured from flue gases [10]. It can be achieved by absorption, adsorption or membrane technologies where the carbon dioxide is selectively separated from flue gases using solvents (absorbents), solid (adsorbents) or membrane materials [10]. Chemical absorption by amine solvents has been used for decades and thereby is a mature technology with a technology readiness level (TRL) of 9 [6]. Pre-combustion where carbon dioxide is separated from fuel components, leaving hydrogen as a combustion fuel. Moreover, pre-combustion for natural gas processing is mature technology with TRL of

9 as shown in Fig. 2.2. Lastly, oxyfuel, which is essentially the combustion of fuel under oxygen rather than air via using air separation unit (ASU), which simplifies the capture process but intensifies the energy requirement to separate oxygen from air [5]. Further research and development work in the CCS systems are active in the academia and industry - Fig. 2.2.

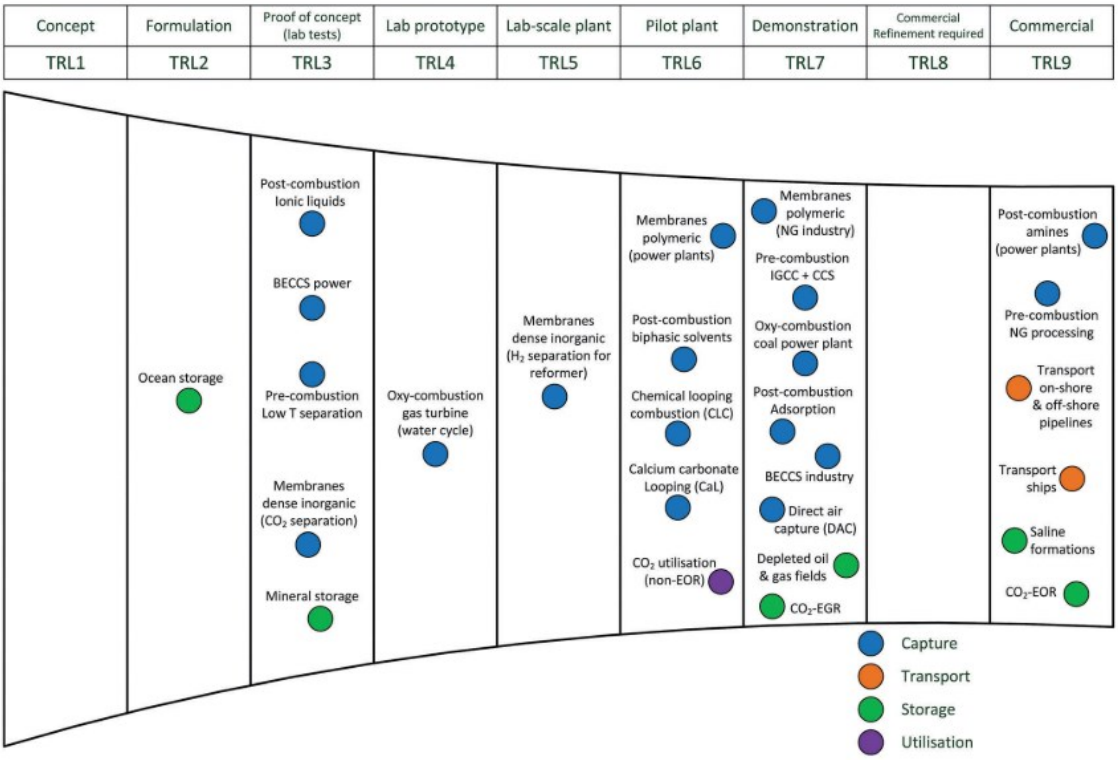


Fig. 2.2 The technology readiness level (TRL) of the current carbon capture, storage and utilization technologies [6]. IGCC = integrated gasification combined cycle, BECCS = bioenergy with CCS, EGR = enhanced gas recovery, EOR = enhanced oil recovery, NG = natural gas.

The next step is transport of carbon dioxide to the storage location. This is done via pipelines for large volumes (where the storage location is relatively close), or ships for smaller amounts and relatively long distances [11]. Carbon dioxide is then stored in locations such as spent hydrocarbon wells or sub-sea geological formations [7]. CO_2 captured can be used in enhanced oil recovery (EOR), which is a mature technique used in the United States, which stores and helps recover more hydrocarbons from oil wells [11]. Many of the

technologies used in transport and storage of carbon dioxide are currently used in the oil and gas industry [11].

The additional energy of CCS for the reboiler duty does increase the total carbon dioxide emissions produced from a plant, however the total carbon dioxide emitted to the atmosphere drops by 80-90% as shown in Fig. 2.3 [11]. It can be deduced from the concept of CCS that there is an increase in both capital and operational costs, as there is no added value to storing carbon dioxide, apart from EOR applications, where it can allow further extraction of oil.

There are a number of barriers that stop CCS from being widely used, some of which are technical and others financial [7]. The technical aspect is mainly represented by the storage location as geological formations require assessment and detailed studies to confirm the capacity and suitability of the storage location [7]. This is further complicated by the physical behaviour of carbon dioxide, which has a relatively great Joule-Thompson effect, which upon injection at high pressures, it depressurises causing a cool down risking freezing hydrates within the formation, which may lead to cement seals failures that compromises the integrity of the storage location and leads to carbon dioxide leakage to atmosphere [12]. Heating the injected carbon dioxide to 75°C is suggested by simulation studies to overcome the potential leakage issue [12]. In addition to these technical problems, earthquakes may well cause catastrophic release of carbon dioxide, which is an issue that will be very difficult to predict and solve [7]. Furthermore, the current efforts currently are directed to offshore storage due to the controversial factor with public acceptance that hinders the utilisation of onshore storage which can be benefitted from the existing infrastructure of transport pipeline to storage sites [13].

The other main issue which is slowing down the implementation of carbon capture and storage is the transport and storage infrastructure, which so far has been fairly underdeveloped in locations outside the United States where EOR is a prevalent practice that led to the

development of a carbon transport network [7]. There is not a single solution which will entirely resolve such issue and gain commercial backing. It has been suggested by Haszeldine that governmental action must take place by supporting such projects by the public sector investment and carbon dioxide taxes [12].

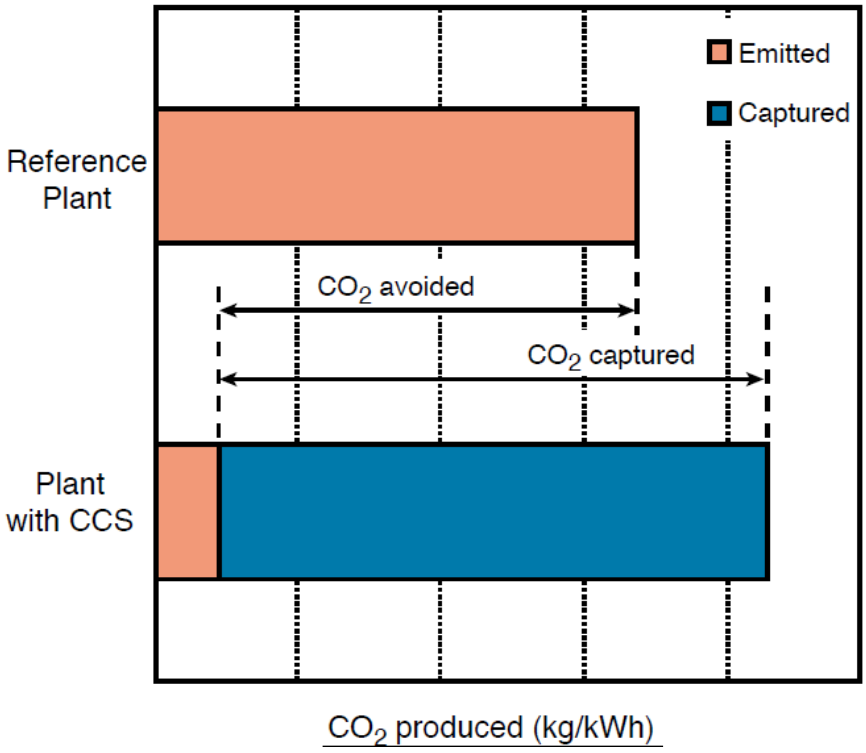


Fig. 2.3 Illustration of the net savings in CO_2 produced when CCS is used in a power plant [11].

2.2 Carbon Capture and Utilisation (CCU)

Based on the previous section, the following can be concluded, that reducing carbon dioxide emissions is essential, and that carbon capture and storage represents a mitigating solution rather than a permanent solution. Utilisation of carbon dioxide is a concept which is partly based on the CCS, but rather than long term storage, CCU aims to fix carbon dioxide into other forms e.g. via chemically reacting it with other substances. As with many technologies, it is not possible to eliminate the emissions of carbon dioxide entirely via CCU, so it must be combined with other methods to have a significant effect [14]. One of the main benefits CCU offers against CCS is the added value made by manufacturing products that can be sold for a tangible commercial value as opposed to storage which can be seen as a "waste disposal" route.

Currently, there is a large number of applications where CO_2 is utilised or has the potential to be utilised, among those applications is enhanced oil recovery (EOR), production of urea, biomass fixation and liquid fuel production [9]. The amount of carbon dioxide that is already being consumed is in the region 80 Mt/year as a non-captive feedstock [9], whilst Aresta *et. al.* stated an annual consumption figure of 200 Mt/year [15]. Both of these figures, however, are dwarfed by the total emissions of CO_2 due to anthropogenic carbon dioxide at 32 Gt/year [16]. This point further reinforces the previous point in that CCU is not the ultimate solution to eliminate or drastically reduce carbon dioxide emissions. However, it is most effective when combined with other methods, for instance due to the highly stable chemical state of CO_2, energy input is required to carry out reactions. Thus, the use of renewable energy can help reduce the energy requirements of CO_2, and therefore the CO_2 emissions associated with the utilisation of CO_2 [5]. This point draws the following requirements that for any CCU to be

implemented as means of reducing CO_2 emissions, then it must be a net consumer of CO_2 rather than a net producer.

In a report prepared by the global CCS institute [9], it is stated that the amount of carbon dioxide that can be captured from a pilot scale CCS plant is approximately 2.5 Mtpa, which exceeds Japan's, South Korea's and Australia's non-captive CO_2 consumption. This again highlights the importance of the scale of production from CCU projects along with the amount of CO_2 used in those plants, as there is a large number of potential candidates for CCU, with varying orders of magnitude of current and future CO_2 utilisation [9]. Based on segmentation of CO_2 utilisation, it can be divided into two main segments: (i) use as a chemical feedstock, for instance in the manufacture of carboxylic acids or methanol, mineral carbonation, biomass capture mainly represented by algal capture; and (ii) technical utilisation such as using it as solvent in the case of supercritical CO_2 (sCO_2) or enhanced oil recovery (EOR) [7], [9]. The various routes described above have various degrees of carbon dioxide capture durability as described in Fig. 2.4 Various CCU technologies, along with their CO2 purity requirement and storage permanency [9]. For instance, urea will be gradually released to the atmosphere once applied to soil. In contrast, mineral carbonation fixes carbon in a solid state as carbonate, which can be used in the construction industry, stored or disposed without the risk of releasing carbon dioxide to atmosphere [7], [9].

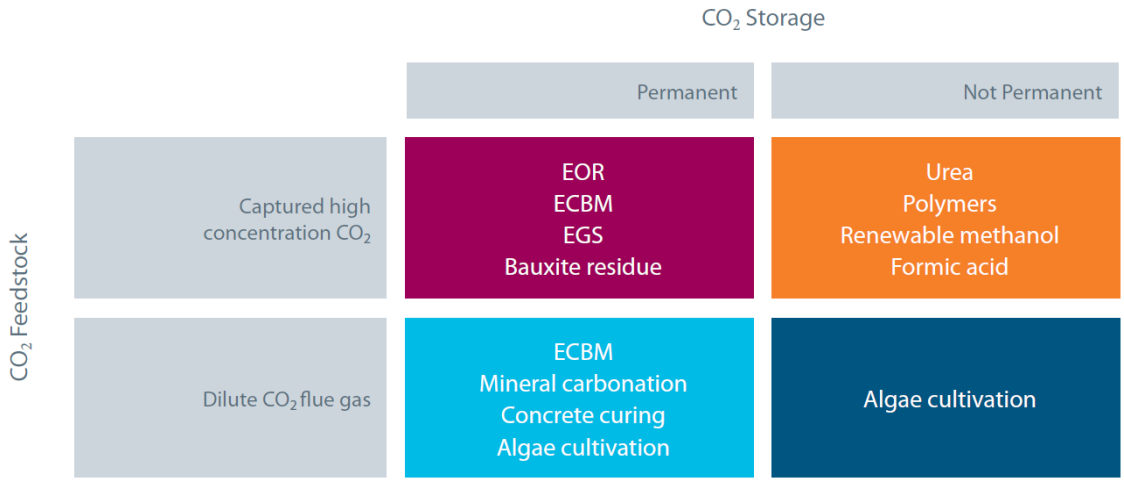


Fig. 2.4 Various CCU technologies, along with their CO_2 purity requirement and storage permanency [9].

2.2.1 Carbon Dioxide as a chemical feedstock:

As was mentioned before, carbon dioxide is very stable in relation to other carbon neutral molecules [7]. Therefore, for a reaction to be viable, sufficient energy has to be supplied via changes in pressure or temperature or catalysing reactions in order to decrease their activation energy [7]. The factors stated must therefore be considered in order to achieve an overall reduction in carbon dioxide emissions. The sustainability of the CO_2 is another factor which must be considered when considering the use of CO_2 as a feedstock. This factor is exacerbated by the great volumes of CO_2 released as a result of power generation and other processes [7]. A key and significant aspect of CCU is the ability to maintain secure and sufficient supply of chemical commodities and fuels as opposed to petrochemical feedstocks. The price of the latter is sensitive to the crude oil prices which are fluctuating leading price instability [7]. Some of the main chemical conversion processes are listed in Fig. 2.5.

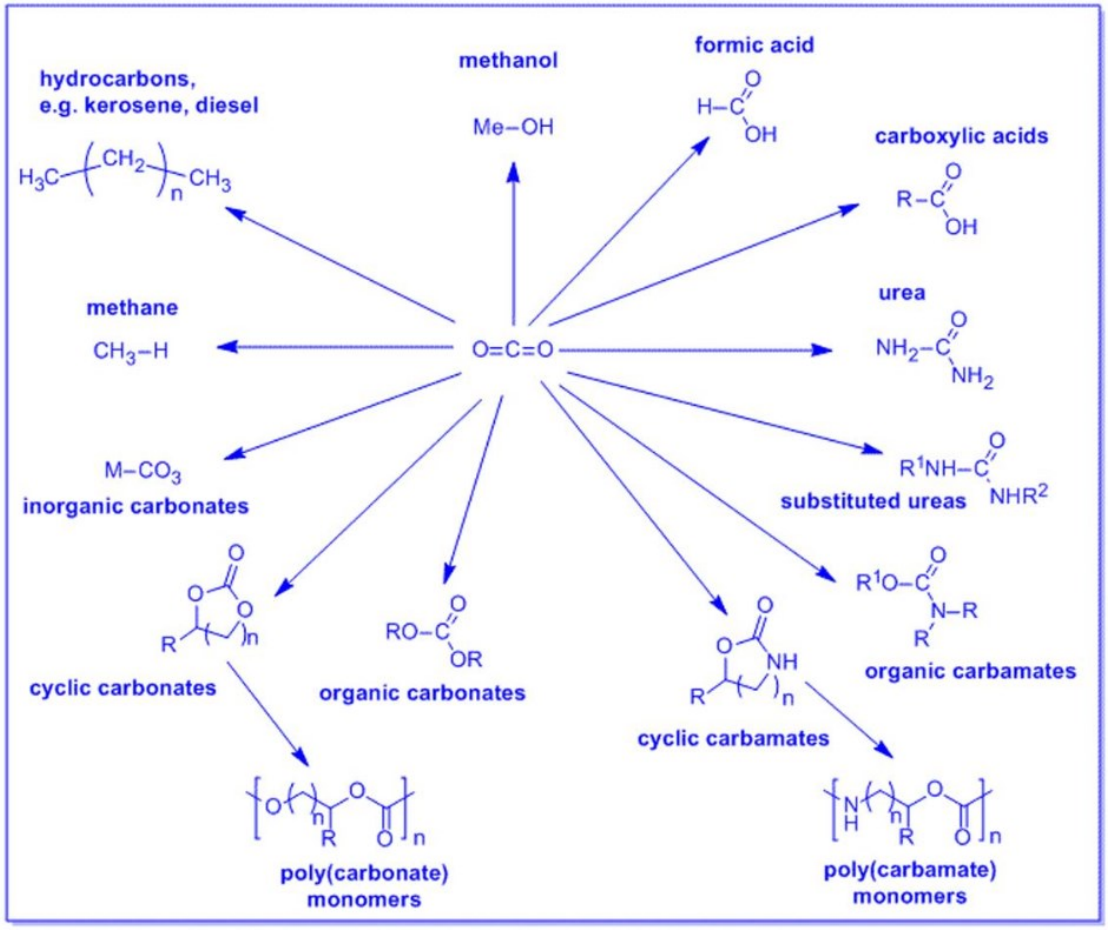


Fig. 2.5 Various chemical products that can be made from carbon dioxide [7].

According to Aresta *et al.* [17], there are five main reaction types which are considered to be the main users of CO_2, the conduction of which will contribute greatest towards the net reduction in carbon dioxide emissions. The reactions are:

1. Direct carboxylation.
2. Use of CO_2 as oxidant.
3. Manufacturing of methanol
4. Gas to liquid (GTL) conversion in the petroleum industry.
5. Supercritical CO_2.

Having defined what is the potential role of CO_2 to produce fuels and chemicals, some the CCU applications are discussed in more detail next. These applications are the production of urea, methanol, formic acid, algae, and inorganic carbonates.

2.2.2 Yield boosting in urea production:

The fixation of carbon dioxide via urea yield boosting is a major if not the biggest chemical produced at 150-176 Mt/year utilising CO_2 [18]. Urea is used primarily in agriculture as a fertiliser, and it can also be utilised in the polymer industry [18]. One of the most popular methods of producing urea is the stamicarbon process, where the process can be broken down into the following steps, as shown in Fig. 2.6

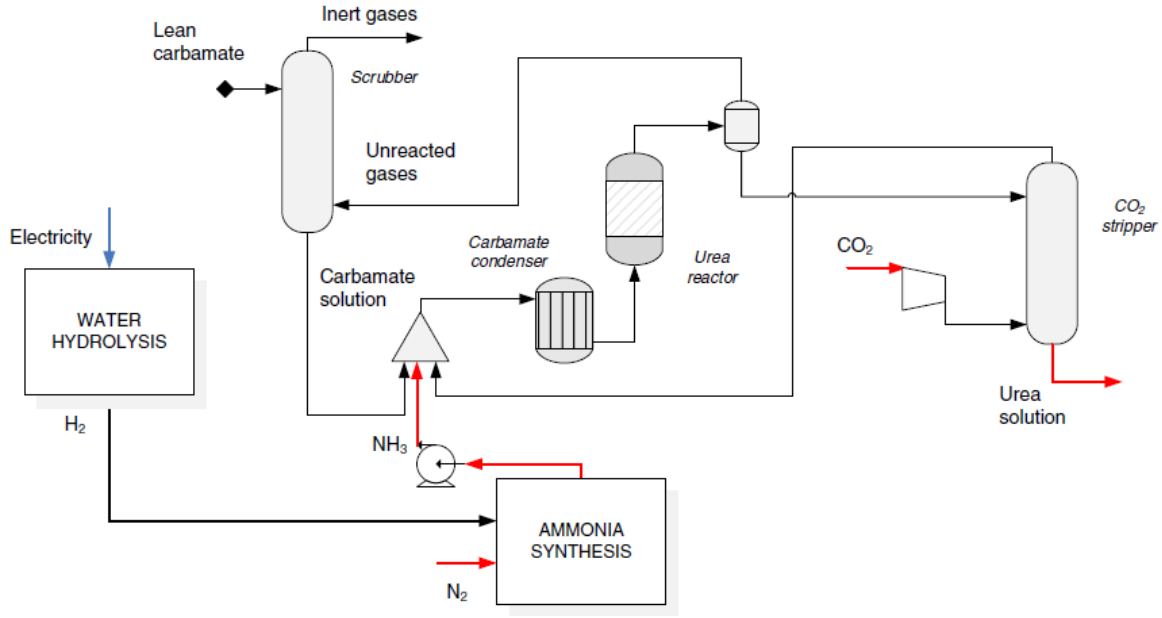


Fig. 2.6 Process flow diagram of urea synthesis from CO_2 [18].

First, ammonia, CO_2 and ammonium carbamate is fed into the system. Then, the following reaction occurs in the carbamate condenser:

$$CO_2 + 2NH_3 \leftrightarrow NH_2CO_2NH_4 \quad (2.1)$$

The heat from the exothermic reaction above is recovered in the urea reactor unit where the unreacted products are recirculated to the scrubber for recovery. Then, reacted products are transferred to the urea reactor where they are dehydrated to produce urea. In the urea reactor, the required heat to decompose the remainder carbamate into urea is provided via the steam on the shell side as per Eq. (2.2): $NH_2CO_2NH_4 \leftrightarrow H_2O + NH_2CONH_2$ (2.2)

Whilst urea as a compound does indeed use carbon dioxide, it will release most of the carbon dioxide it captures when it mixes with soil within eight days [19]. One can thus argue that urea "fixation" is a temporary and short term capture. It does however increase the demand on CO_2 especially when considering that ammonia production produces carbon dioxide as a by-product [19].

Urea can be used in applications other than fertilisation, such as in the pharmaceuticals, petrochemicals and polymer manufacturing [7]. An example of such application is the production of carbonates as described in Fig. 2.7. Conducting such reaction will not only help in reducing carbon dioxide emissions, but also in making production processes inherently safer due to the elimination of phosgene [17].

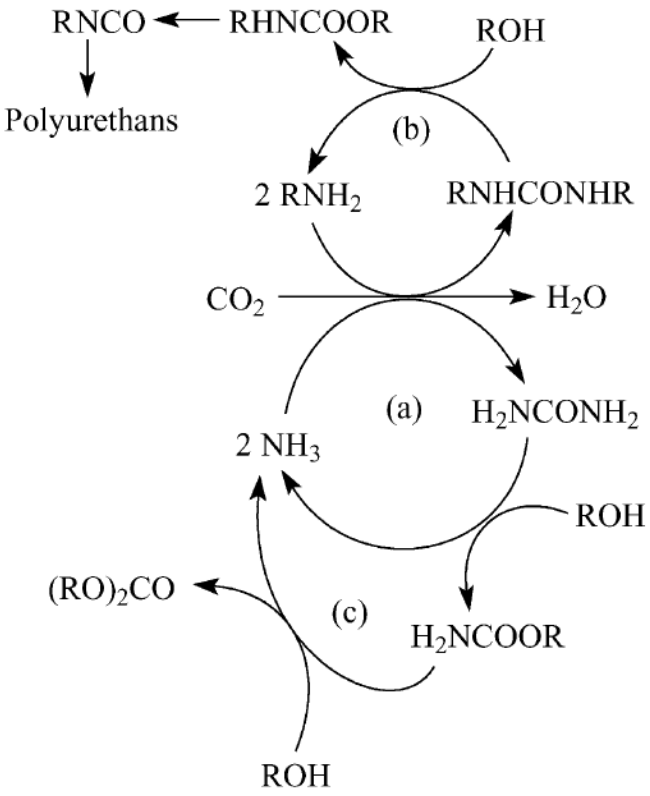


Fig. 2.7 uses of carbon dioxide in the production of various carbonates [17].

Along with using urea and hence CO_2 as an intermediate for other chemicals, ammonia production plants can be made greener via the use of green energy. It is very reasonable to

have urea plants adjacent to ammonia plants to utilise both ammonia and CO_2 produced as a result of ammonia production. Thus making ammonia production greener would have a positive impact on the production of urea from a lifecycle point of view.

2.2.3 Formic acid

Formic acid, also known as methanoic acid, is widely used in a number of industries such as the textiles industry, leather treatment, pharmaceuticals, rubber and livestock feed [20], [21]. 620,000 tonnes of formic acid were produced globally in 2012 and the figure is expected to increase in 2019 to 760,000 tonnes, with a highly localised but securely growing market [22]. In addition to the conventional uses, formic acid can be used as means of "hydrogen storage" as well as a fuel, since it offers the advantage of ease of storage. This makes it in turn a good option for the utilisation of carbon dioxide [22].

In the past, formic acid was usually obtained as a by-product of the production of acetic acid via oxidation of hydrocarbons. However, the development of methanol carbonylation to produce acetic acid shifted formic acid production to other methods such as the hydrolysis of formamide as means to produce formic acid [21]. Due to inefficiencies of the processes described formerly, the hydrolysis of methyl formate was developed, which produces less by-products making it the most popular method of formic acid production [7]. For the purpose of comparison, the standard process to produce formic acid will be described.

Hydrolysis of methyl formate starts by the carbonylation of methanol under a basic catalysts such as sodium methoxide, whereby carbon monoxide is added into methanol to produce methyl ester [21]. A side reaction can occur as well, which will deactivate the catalyst and produce sodium formate. This issue is worsened by the presence of water, which will lead to the precipitation of sodium formate, leading to blockages [21]. The methyl ester is then hydrolysed to produce formic acid and methanol, the methanol is recycled to allow the

production of further formic acid, as per the two equations below. Similarly to the methanol production described earlier, carbon monoxide is produced as a syngas, mainly via steam reforming of methane [20]. Whilst the reaction may seem simple, the issue with the hydrolysis of methyl formate is the re-esterification of formic acid and methanol, which will occur if the unreacted ester is extracted from the mixture. To minimise the esterification, a number of techniques were developed by various producers such as the use of excess water which will produce relatively dilute formic acid that can be purified using liquid-liquid extraction [7]. Alternatively, tertiary amines are made present during the hydrolysis of methyl formate, which helps in generating a salt of the amine and formic acid which shifts the reaction towards making more formic acid. This step is then followed by the extraction of formic acid via distillation with minimum decomposition as explained in Eq. (2.3) and (2.4) [21].

$$CO + CH_3OH \leftrightarrow HCOOCH_3 \tag{2.3}$$

$$H_2O + HCOOCH_3 \leftrightarrow CH_3OH + HCOOH \tag{2.4}$$

Formic acid can also be made via the direct hydrogenation of carbon dioxide using metal catalysts such as palladium or ruthenium and a basic solution such tertiary amines [22]. The basic reaction is described as in Eq. (2.5):

$$CO_2 + H_2 \leftrightarrow HCOOH \tag{2.5}$$

The work by Pérez-Fortes *et. al.* considered the feasibility of industrially producing formic acid via the direct hydrogenation of carbon dioxide [22]. The result of the study shows that the simulated process –based on a patent- is not economically feasible for industrial implementation due to the power requirements and consumables costs. Naturally, the study resulted in similar results as the methanol production, where the costs of electricity to produce hydrogen were prohibitively high and turned the process commercially unviable [20]. In addition to this, the slim likelihood of locating a formic acid plant close to a carbon based

power plant with a capture facility and fed from renewable energy to split water, makes this process difficult to implement in practice, especially where renewable energy is unavailable e.g. in developing countries. It can be argued that there may well be more efficient methods developed that are not available to the public as means of protecting potentially commercially sensitive process routes.

2.2.4 Algae

Algae was chosen to be reviewed, as it is more promising in comparison to other forms of land based biomass such as wood [23]. Marine based biomass such as algae offers the advantage of high adaptability to grow in various environmental conditions, such as salt water, fresh water (at various levels of pH) and in addition it can sustain itself on wastewater as a form of nutrients carrier [23]. Biomass as energy source represents a viable option to a carbon neutral energy source with minimal investment costs [23]. Though it can be overlooked as a carbon dioxide utilisation option in the presence of "industrial processes", it is in fact a carbon capture route via photosynthesis, which converts carbon dioxide to oxygen and biomass. According to Styring *et al.* [7], algae has the capability of capturing 0.5 tonne of CO_2 per tonne of algae whilst a research paper by Craggs *et. al.* [24] states 1.8 tonnes of CO_2 per tonne algae biomass.

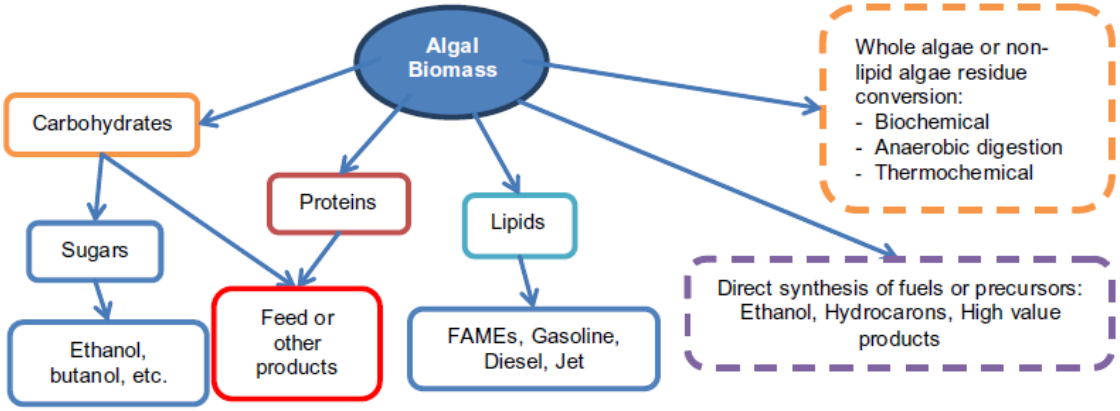


Fig. 2.8 Various options in which algae can be re-used for [25].

Currently some efforts are being directed at utilising algal routes to capture carbon dioxide. High Rate Algal Ponds (HRAP) is an example of such enhancements of the algal CO_2-based route as shown in Fig. 2.9 [26]. In further research by Tsai *et al.* [27], the HRAP method appears to be fairly efficient in capturing carbon dioxide, where ratios of 1.23 CO_2 consumption efficiency are reported (CO_2 weight to algal biomass ratio). As with every

technology, there are drawbacks which include the fairly sensitive contamination parameters of algae that limit the number of species that can be used. Photobioreactors allow higher levels of control over process parameters, thus enabling a larger range of algae species to be cultivated. This, however, comes in at higher costs in addition to issues such as the limitation in the gas/liquid interface and prevention of algae growth on the walls of the reactors (which will reduce the amount of light permitted to the reactor) [7].

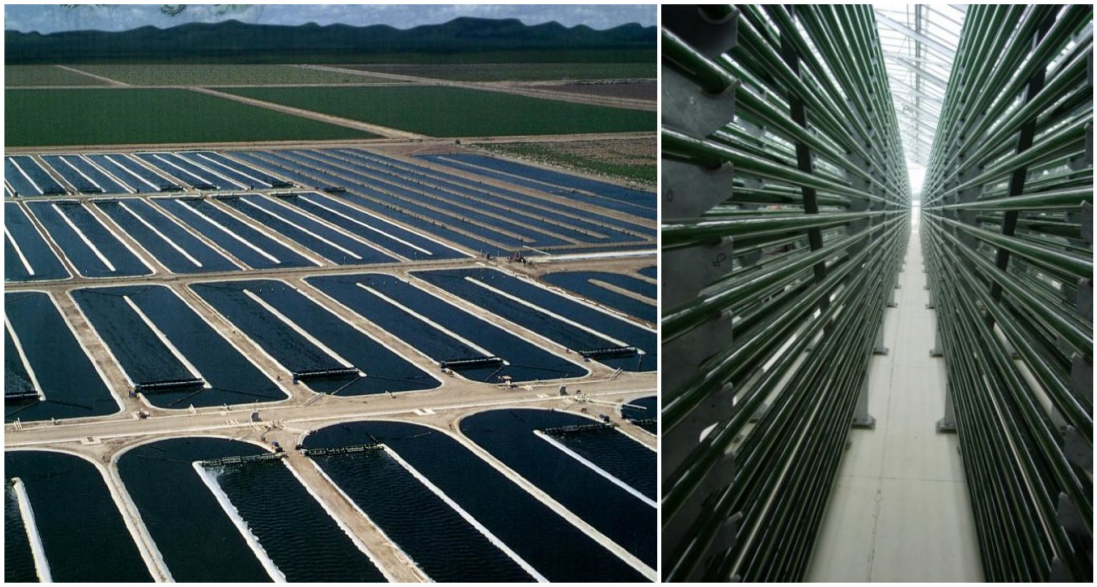


Fig. 2.9 To the left a picture of HRAP and to the right a picture of photobioreactors [7].

2.2.5 Inorganic carbonates

The capture of carbon dioxide in carbonates is another route to capture carbon dioxide [7]. The process has occurred in nature via the weathering reaction illustrated in Eq. (2.6):

$$XO + CO_2 \rightarrow XCO_3 \tag{2.6}$$

Where X is either Calcium (Ca) or Magnesium (Mg)

The reaction, however, is rather slow and occurs over “geological” timescales [28]. Unlike the many CCU technologies and routes where often carbon dioxide is raised in terms of energy state, carbonates are at a lower energy level than CO_2. The carbonation of

calcium/magnesium releases energy, which can be utilised elsewhere [28]. These elements are seldom present in nature in their pure form and are normally found in silicates [29]. This affects the heat of reaction released to approximately half of the pure form [7]. The lower energy state also means higher level of stability, hence representing a longer term carbon capture and utilisation option [30].

There are two general routes to carbonate minerals, direct carbonation and indirect carbonation [7]. By the virtue of its name, direct carbonation is the direct contact between a mineral and carbon dioxide – in its gaseous or aqueous solution form – this route is relatively simple and requires less pre-treatment and generally less complex processing [31]. The drawback of this route is the low speed of reaction, which can be sped up via higher temperatures (>600°C) [32], which drive off any moisture in the mineral, thus increasing the reaction surface area. In addition to this, the mineral can also be crushed to reduce the solids size, which in turn increases the surface area [7]. The route is thus rather slow and is fairly energy intensive, whether carried out at elevated temperatures or crushing the raw minerals. This makes the need to use less energy intensive technique vital in making the process carbon neutral, in addition to sourcing the energy from carbon-neutral or low carbon sources.

Indirect carbonation differs to the direct route in that it involves the conduction of several steps [31], where the mineral used is processed in order to extract the metal, which is then reacted with CO_2 to form the required carbonates [31].

As promising as some of these routes may seem, currently they are hindered by a number of obstacles. The mining for minerals is an intensive process, which defeat the purpose of CCU in this case [33]. Nevertheless, there are other promising routes which may be applicable to increasing the efficiency of the process that are based on carbonation under water containing supercritical carbon dioxide, a process which occurs in subsurface injection of CO_2 such as

EOR [34]. Alternatively it can be used as means to carbonate waste from various industries such as the steel industry or coal fired power stations [35], [36].

2.2.6 Methanol

Methanol is a primary alcohol, which has many uses such as a starting raw material for the production of various hydrocarbons, fuel or means of hydrogen storage [20]. The conversion of CO_2 to methanol has the potential to reduce carbon dioxide emissions due to the reduction in emissions of $0.54 t/t_{methanol}$ in comparison to the conventional method that is from syngas (H_2 and CO) produced from natural gas, and could increase carbon dioxide demand to become $1.46\ t/t_{methanol}$ [20].

Methanol production can be broken into three distinctive stages: 1) the production of syngas, 2) production of methanol and 3) purification of methanol [37]. Syngas formation provides methanol, carbon dioxide/monoxide and hydrogen, which can be made from various feedstocks such as coal, natural gas and biomass [37]. There are various means by which syngas can be produced, typically steam reforming and partial oxidation, depending on the feedstock, a path is chosen [37]. For instance, coal which contains relatively high amount of C atom and low H atoms, undergoes partial oxidation (also known as gasification) where limited supply of oxygen is permitted, thus producing an incomplete combustion resulting in carbon monoxide. To introduce hydrogen, CO is reacted with water [38]. Steam reforming is associated with the natural gas reforming, where methane reacts with water to produce carbon monoxide and hydrogen. Dry reforming can also be used instead, by which methane reacts with carbon dioxide directly to produce carbon monoxide and hydrogen [38].

Following the syngas generation process, the proportions of hydrogen to carbon monoxide is adjusted to two hydrogen molecules to one carbon monoxide to exothermically react under copper or zinc oxide catalysts to produce methanol [38]. Heat of reaction must be removed to

drive the reaction forward and prevent catalysts breakdown [20]. The production method described thus far uses fossil fuels to provide heat (in the form of steam) and uses oxygen if a partial oxidation route is taken. This makes the process net carbon dioxide producer and large consumer of water, which is a finite resource itself [20].

An alternative and greener route can be taken to produce methanol, which utilises carbon dioxide from power plants or other relatively large carbon dioxide producers. This route utilises the captured carbon dioxide to undergo a reaction with hydrogen [39]. The process will also require copper or zinc oxide to catalyse the reaction [39]. In addition to this process, carbon dioxide reduction via photoelectrochemical conversion to produce methanol can be used for utilising carbon dioxide [38], where photoelectrocatalytic cells directly reduce carbon dioxide and splits water to produce methanol [40]. The photoelectrocatalysis method is still under development, as currently the process makes various by-products which will require further treatment in order to purify the methanol needed [38], [40].

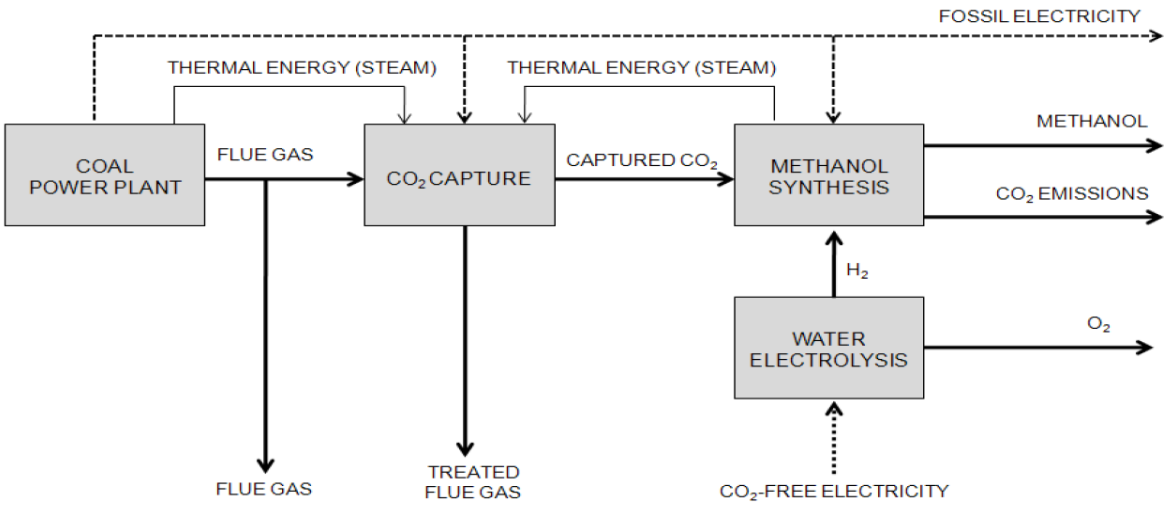


Fig. 2.10 A sketch of the general process of the direct conversion of CO_2 to methanol [39].

The green process described will not only utilise carbon dioxide emissions, but will also reduce methane consumption to produce syngas, which can make the process a carbon dioxide consumer rather than a capturing and re-utilisation facility [20]. This also highlights

another issue, whereby such process is difficult to conduct on an industrial scale due to the difficulty in obtaining carbon free hydrogen [39], [41].

2.2.7 Sustainability of CO_2 reduction processes

As a strong tool to evaluate different projects and processes, sustainability criteria has been considered in this research as it balances between the three pillars of sustainability which are based on economic, social and environmental criteria [42]. Several environmental approaches have been used to assess the sustainability of any process. Life cycle assessment (LCA) tool, which will be explained in further details in Chapter 3, has proved to be the most effective tool since it evaluates the product's life in a systematic way from cradle to grave basis that means that it evaluates the environmental impact of the product throughout its entire life cycle [43].

Several studies have investigated the LCA performance of the CO_2 reduction technologies [16], [44], [45]. It was found from the literature that most of them have only focused on only one or two environmental impacts that are global warming potential (GWP) and fossil depletion potential (FDP) [46]. In essence, this could lead to misleading conclusions about the environmental performance. Most studies overlook the rest of the environmental impacts that could result in improving a set of environmental impacts at the expense of worsening others. For example, biofuels are claimed and proved to emit less GHG emissions than fossil-based fuels such as gasoline and diesel [47]. However, the production of the fertilisers used during the biomass plantation often omitted from the assessment. Furthermore, the land use and water consumption impacts are also often overlooked yet crucial to include to avoid the potential pitfalls of alternatives. Furthermore, it was reported in a recent study that utilising CO_2 in enhanced oil recovery (EOR) reduces the GWP 2.3 times compared to emitting the CO_2 into the atmosphere while the acidification potential (AP) impact was three times higher [48].

Having analysed and identified the risk of assessing CCU processes for one or few selected environmental impacts, the need for a holistic assessment of the sustainability of CCU processes becomes crucial and necessary for sustainable greener fuels or chemicals.

2.3 The role of hydrogen in the CCU context

As most of the CO_2 derived products such as methanol, methane and formic acid require hydrogen to react with the captured CO_2. Most of the CCU studies in the literature have not treated the sustainability of the hydrogen in much detail in the same context with the CCU framework. This is evident by the lack of reliable LCA data to accurately quantify the environmental impacts of hydrogen and the CCU processes. Sustainable hydrogen production pathways will play a significant role in decarbonising many sectors such as transport when used as a fuel in the fuel cell vehicles (FCVs) or to produce CO2-based fuels such as methanol in the current internal combustion engine vehicles (ICEVs). Additionally, it plays crucial role to decarbonise the chemical and heating sectors [49].

The current sources of hydrogen production are from hydrocarbons, biomass and water where 95% of the current production comes from natural gas via steam methane reforming [50]. The literature on the sustainability of hydrogen production has highlighted several economic and environmental aspects. However, much of the literature on hydrogen production lacks clarity regarding a holistic assessment to compare different production pathways from sustainability point of view.

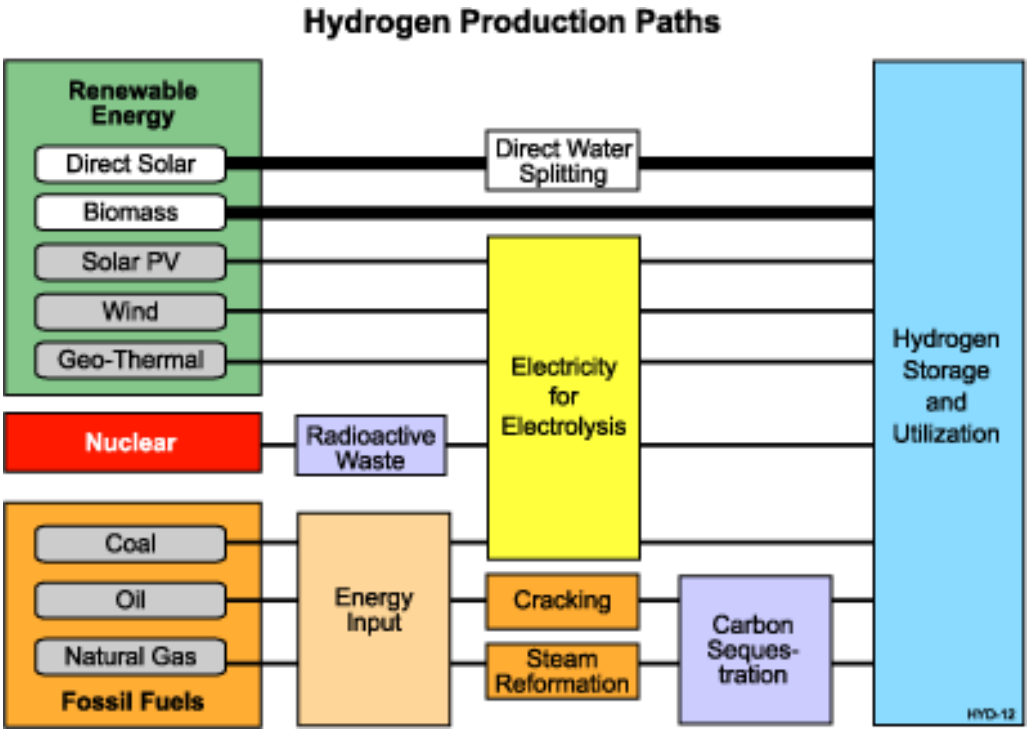


Fig. 2.11 Various pathways for hydrogen production [51].

Hydrogen is classified with different colours based on the production approach and how the CO_2 produced with the process is handled as shown in Fig. 2.12. Mainly, these colours are grey, blue and green hydrogen where grey hydrogen refers to the hydrogen produced from hydrocarbons such as natural gas or oil fractions (LPG or naphtha) and CO_2 is released to the atmosphere, blue hydrogen refers to the production from the same hydrocarbons while CO_2 is captured and sequestered and green hydrogen refers to the hydrogen production from water electrolysis via renewable energy such as wind and solar energies with zero process emissions [50]. The Hydrogen Council and International Energy Agency (IEA) expects significant demand growth from now through 2050, about eight times more than the current demand market. This significant increase is due to the new applications for hydrogen in the transport, power, and industrial sectors. Furthermore, Fig. 2.12 shows how the hydrogen production blend is expected to be from blue and green pathways only by 2050 while grey hydrogen

decreased till phased out. This represents the necessity for a strategic transition plan for the hydrogen production outlook.

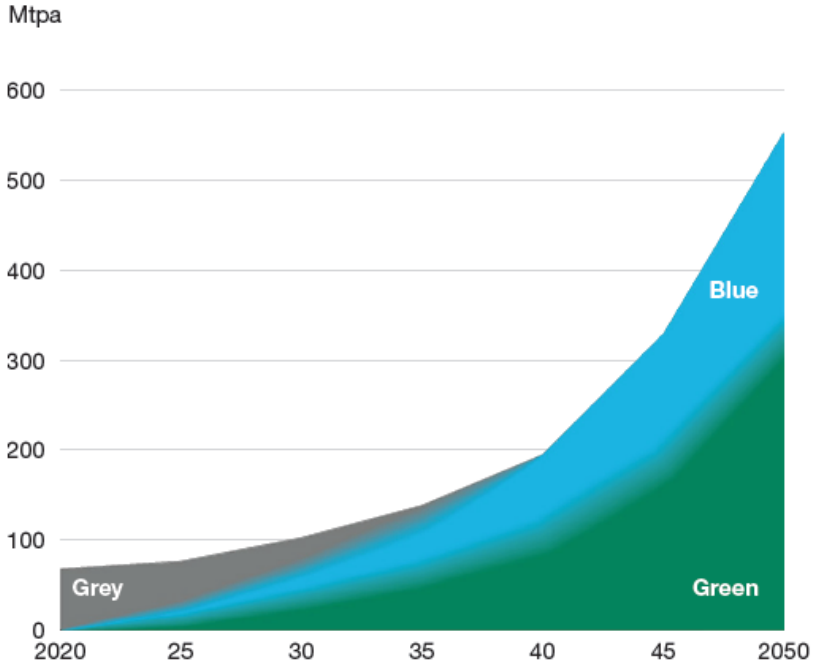


Fig. 2.12: The hydrogen demand from 2020 to 2050 based on the production approach [50]

Hydrogen production pathways and the sustainability of them are discussed in further details in Chapters 4 and 5.

2.4 Literature gaps

The assessment of CCU processes as alternatives to their fossil-based processes presents many challenges from sustainability perspective. At a LCA level, many studies have investigated the environmental and economic performance of potential CO_2-based products. CO_2 conversion processes mostly require hydrogen wheather to go for chemicals or the fuels production. However, how hydrogen production pathways contributes to the CCU products is still not yet fully understood. It is thereby crucial to study in depth the effect of hydrogen production pathways and their interaction to CCU to ensure a sustainable future.

Previous studies in the literature have focused on the economic performance of hydrogen production processes, emissions, and some selected environmental impacts to some stages of production. Depending on the selected economic or environmental impacts, the findings of these studies were drawn and most of the time would result in misleading conclusions by overlooking the whole performance of the investigated hydrogen production system. Furthermore, these studies have highlighted that to ensure a better environmental performance system, the whole life cycle impacts should be taken into consideration as even for renewable-based hydrogen production routes, low emissions are not definite if the whole supply chain is not included in the boundaries of the study. From that end, proper assessment of hydrogen production systems is needed to ensure transition to more sustainable hydrogen and thereby ensure the scope of climate mitigation for CCU. One of the ways to better assess and compare different production systems is through externalities of the environmental impacts. In essence, monetising the whole environmental impacts and add that factor to the economic performance would provide a total cost for a technology. Thus, this would make it clearer to compare and assess for policy makers from sustainability perspectives. To date, there no comprehensive assessment for the hydrogen production systems considering both their economic performance and the externalities of the environmental impacts.

As previously stated, steam methane reforming is currently the main production process for hydrogen. The reforming of other light hydrocarbons such as liquified petroleum gas (LPG) and naphtha which is possible and could be an added value feedstock in the transition of hydrogen production towards green/clean hydrogen. Yet, their sustainability performance has not been extensively studied in the active literature. Also, considering the current shares of hydrogen production from different sources, the transition into full green hydrogen considering externalities with the economic performance has not been studied before and it is

crucial. Integration strategies should be properly assessed and studied to guarantee sustainable development for hydrogen production as it is a key for deep decarbonisation.

As hydrogen production from electrolysis via wind energy has been claimed as the cleanest renewable source for CCU products [52], it received significant interest and studies in the active literature [25], [53]–[55]. The most studied CCU product for both transport and chemical sectors is methanol. Thereby, an extensive work has been done for the best use of the renewable energy as going for fuel application would imply producing massive hydrogen from renewables to satisfy the transport demand with a focus on the GHG emissions and energy consumption [53]. However, assessing the full life-cycle environmental impacts and costs of methanol-based fuel value chains are essential for a study of to be considered comprehensive. Such a study should be handled with caution because the electricity that powers the production of green methanol through water electrolysis could also be utilised to reduce the emissions from the electricity supply.

2.5 Thesis contributions

In this thesis, we address the role/potential of hydrogen production in the transition into sustainable development of decarbonised products and fuels. The main objective of this thesis is to evaluate the sustainability of hydrogen production pathways and the best use of renewable energy into the power and transport sectors through applying the tools of life cycle assessment alongside the economic performance. The sustainability tools used to achieve the objectives of the thesis are discussed in further details in Chapter 3. In this context, these tools are applied to the hydrogen production pathways addressed in Chapters 4 and 5 and to the best potential use of wind energy in the power-transport nexus addressed in Chapter 6.

Chapter 4 presents the monetised values of environmental impacts on human health, ecosystem quality, and resources plus the levelised cost of hydrogen production that gives an

estimation of the "real" total cost of hydrogen. This total cost obtained is then used to transparently rank the alternative technologies considering a holistic approach. The materials of this chapter are based on the following peer-reviewed publication:

A. Al-Qahtani, B. Parkinson, K. Hellgardt, N. Shah, and G. Guillen-Gosalbez, "Uncovering the true cost of hydrogen production routes using life cycle monetisation," *Appl. Energy*, vol. 281, p. 115958, Jan. 2021, doi: 10.1016/j.apenergy.2020.115958.

Chapter 5 presents a techno-economic analysis of reforming of different hydrocarbons including natural gas, LPG and naphtha and compare with other hydrogen production pathways. Also, the environmental performance of these route alongside other routes are investigated providing a roadmap for the transition between the grey (fossil-based), blue (fossil with CCS) till full green (electrolysis via renewable energy) hydrogen, Also, in this chapter, we studied the integration between the blue and green hydrogen via the integration of the co-produced oxygen from electrolysis into the autothermal reforming that requires pure oxygen. Thereby, eliminating the need for an air separation unit (ASU) and reducing the CAPEX associated with it which results in reduced LCOH of hydrogen. This hybrid system was proposed and studied in the road map from today's current shares till becoming full green hydrogen.

Chapter 6 extends the use of wind energy whether we should go for hydrogen production and then methanol production as fuel in the internal combustion engine (ICE) or connect it directly to the energy grid and decarbonise it considering the energy systems constraint. This assessment was taken on a regional level for six countries which differ in their electricity mixes and annual gasoline consumption in order to fully understand the best use of the wind energy. The material of this chapter is based on the contribution published in the following peer-reviewed journal:

A. Al-Qahtani *et al.*, “Electricity grid decarbonisation or green methanol fuel? A life-cycle modelling and analysis of today′s transportation-power nexus,” *Appl. Energy*, vol. 265, May 2020, doi: 10.1016/j.apenergy.2020.114718.

Chapter 7 presents the overall conclusions of the thesis and potential future outlooks.

Chapter 3 SUSTAINABILITY TOOLS

This chapter focuses on the general sustainability methods and tools used to achieve the objectives of this research. It is divided into two main subcategories. The first one emphasizes the economic aspect of the sustainability while the second one focuses on the environmental aspect.

3.1 Life Cycle Costing (LCC)

The initial chemical engineering design is a crucial step to provide an insight about the capital and operating costs. Chemical plants are designed and built to provide a profit that will determine the economic feasibility when the profit is higher than the production cost of a product [56]. There are many proposed economic approaches that are available in the literature in this aspect. When carrying out a techno-economic analysis, the objective of evaluating the associated costs in a process is either to minimise the process costs or to maximize the profit. The main elements to calculate any of the economic indicators are the evaluation of the capital, fixed and variable costs along with the revenues of the products of the process.

To start with, capital costs of any chemical plant concern the costs associated with purchasing the equipment units, including their installation costs [56]. Fixed costs of production (FCOP) are the costs independent of the rate of production, that is, the costs of labour, maintenance, land, insurance, interest payments, overhead, license fees and royalties. On the other hand, variable costs of production (VCOP) are the costs dependent on the rate of production that include the raw materials, utilities, and waste disposal.

Revenue is the profit or the return of selling the products and by-products of the chemical process. The total annualised cost (TAC) is the total of the fixed costs, variable costs, and annualised capital charge (ACC) as shown in Eq. (3.1):

$$TAC = FCOP + VCOP + ACC \tag{3.1}$$

All the calculated costs can be converted to the specified year according to the scope of the study using Chemical Engineering Process Cost Indexes (CEPCI).

To sum up, any of the economic indicators can be applied according to the general objective of the economic assessment of the design. The consistency of selecting the same economic indicator between alternative technologies is the most important factor when performing the economic assessment for multiple processes.

3.2 Life Cycle Assessment (LCA)

As environmental awareness has been increasing nowadays, the issue of people's heath, natural resource depletion and environmental degradation have become a serious concern to the society and therefore exerting pressure on policy makers to justify their decisions. Consequently, the chemical industries and businesses have answered these concerns by evaluating different processes according to environmental criteria and sometimes by providing "greener" products or "greener" processes [43]. The environmental performance of a process is crucial and has prompted industrial companies to explore methods to minimise the impacts of their products. One prevalent tool to achieve this purpose is life cycle assessment (LCA) tools. This technique considers the entire life cycle of a product [43]. Furthermore, it can be used to assess and compare the sustainability of different routes of a product. It considers all the environmental impacts of the process from the initial phase (the extraction of raw materials and construction phases) to the final phase, which is the final disposal of the product. This approach is known as the "cradle-to-grave" analysis. Besides,

the International Organization for Standardization (ISO) have developed systematic methods to evaluate the life cycle assessment of a product or process (ISO 14040) [43].

The main stages of carrying out the LCA are as follows:

1. Goal and scope definition
2. Life Cycle Inventory analysis (LCI)
3. Life Cycle Impact Assessment (LCIA)
4. Life Cycle Interpretation

The procedure and the relation between all these stages is described in Fig. 3.1.Further detailed description of each stage is discussed next.

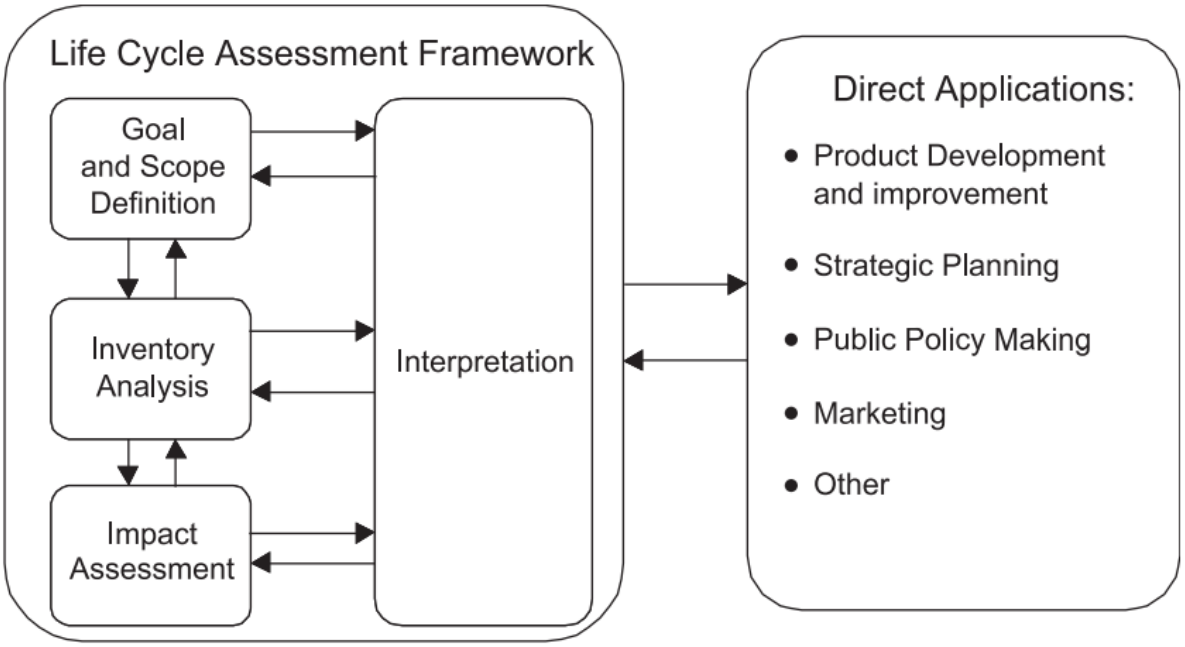


Fig. 3.1 The stages of an LCA as well as its direct applications [57].

3.2.1 Goal and scope definition

The objective of this first step is to identify and state the specific application of the LCA. First, the system boundaries in terms of temporal and spatial dimensions are established. After that, the functional unit is decided, which is a measure of the performance of the system compared to similar systems and a reference for the calculations [43]. This step is carried out by systematically identifying the following:

- The purpose of conducting the LCA study for this specific application or process (the questions that we are seeking answer for).
- A full definition of the product in terms of its uses and life cycle stages.
- Specifying the functional unit.
- Draw the system boundaries to be considered in the LCA study.
- State all the assumptions and limitations related to the study.

3.2.2 Life Cycle Inventory analysis (LCI)

In the inventory step, a simplified flowchart of the process input/output is constructed as shown in Fig. 3.2. After that, the data with all the activities contributing to the production process are collected covering all the inputs and outputs flows.

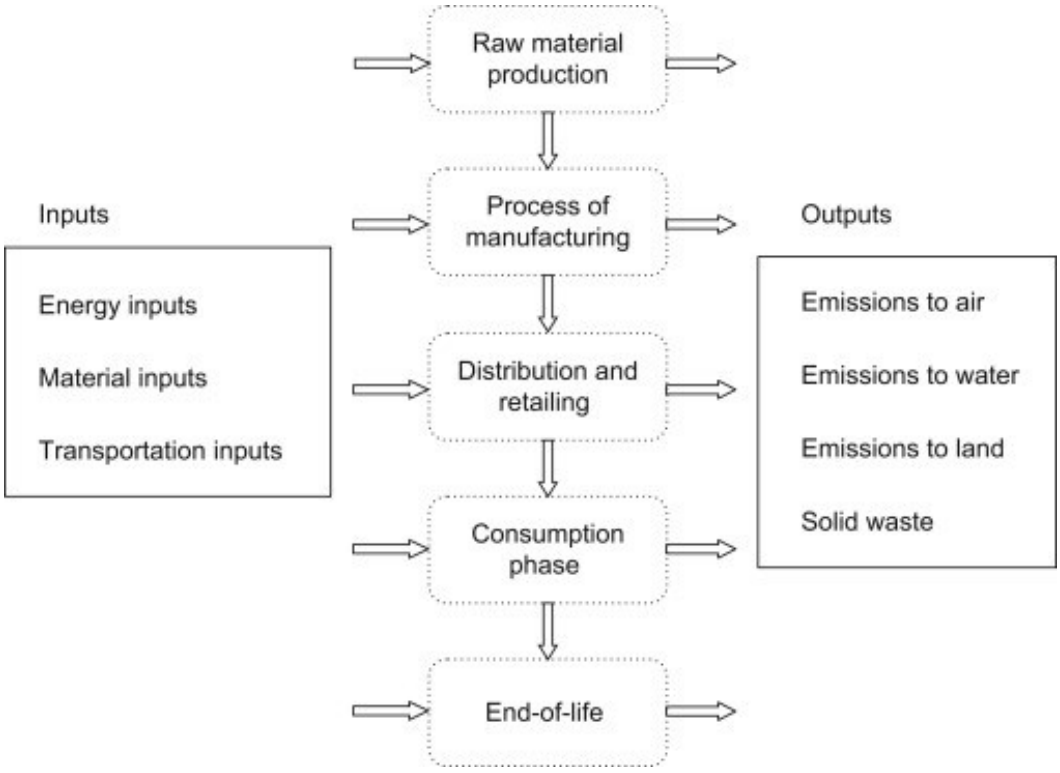


Fig. 3.2 General input/output quantification data that shall be extracted from a process to complete the LCI phase [58].

Many databases are available for the environmental data. Ecoinvent is one of the most popular and reliable databases for the LCIs that was developed by the Swiss Centre for Life Cycle Inventories [59].

3.2.3 Life Cycle Impact Assessment (LCIA)

The main goal of the impact assessment step is to transform all the environmental loads from the inventory step into environmental impacts. This allows further analysis and comparisons of the obtained results as illustrated in Fig. 3.3 and Fig. 3.4 [43], [60].

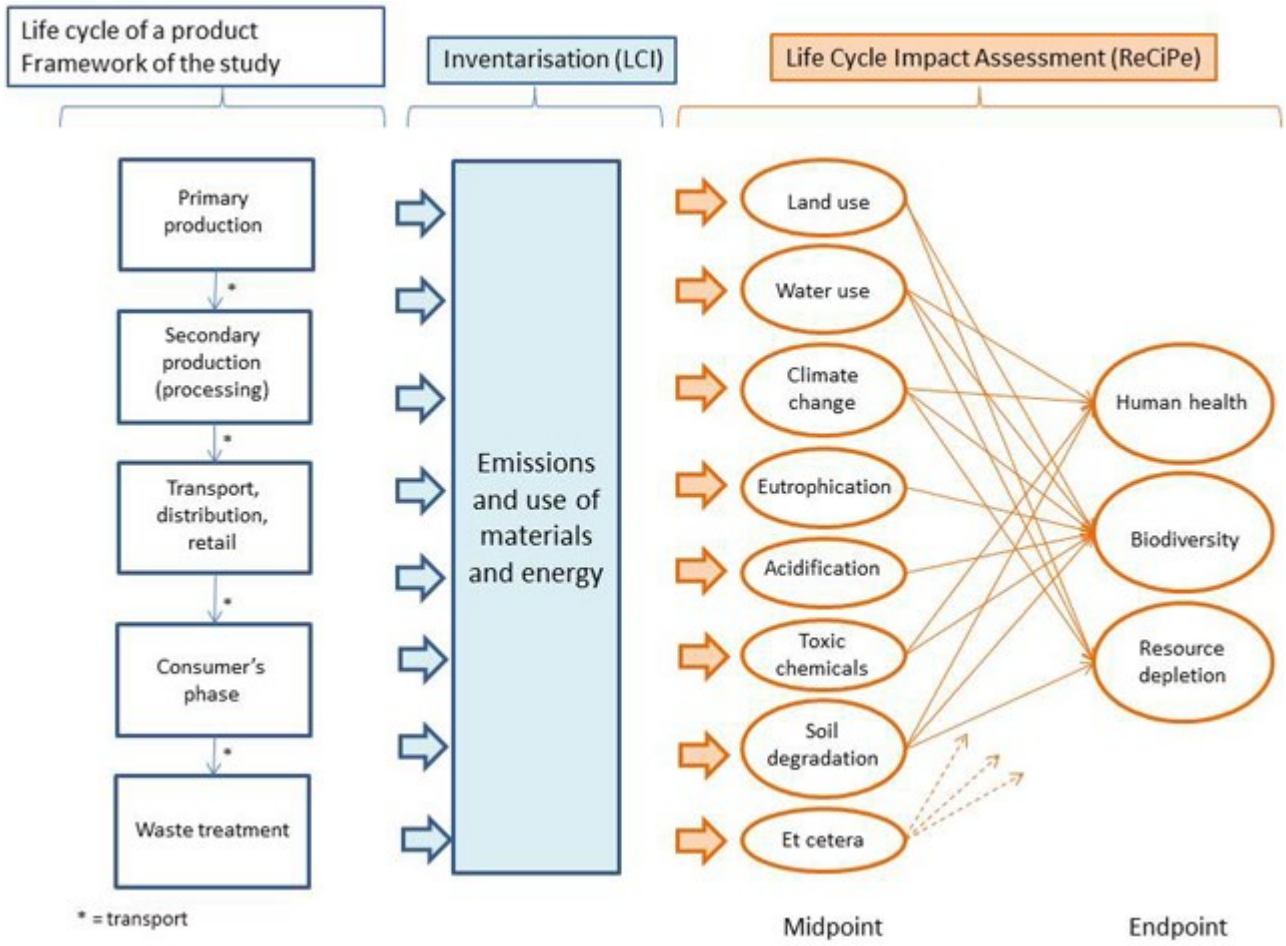


Fig. 3.3 The transition between the inventory and impact assessments steps with the midpoint environmental impacts shown aggregated into their endpoint level in ReCipe 2016 [61].

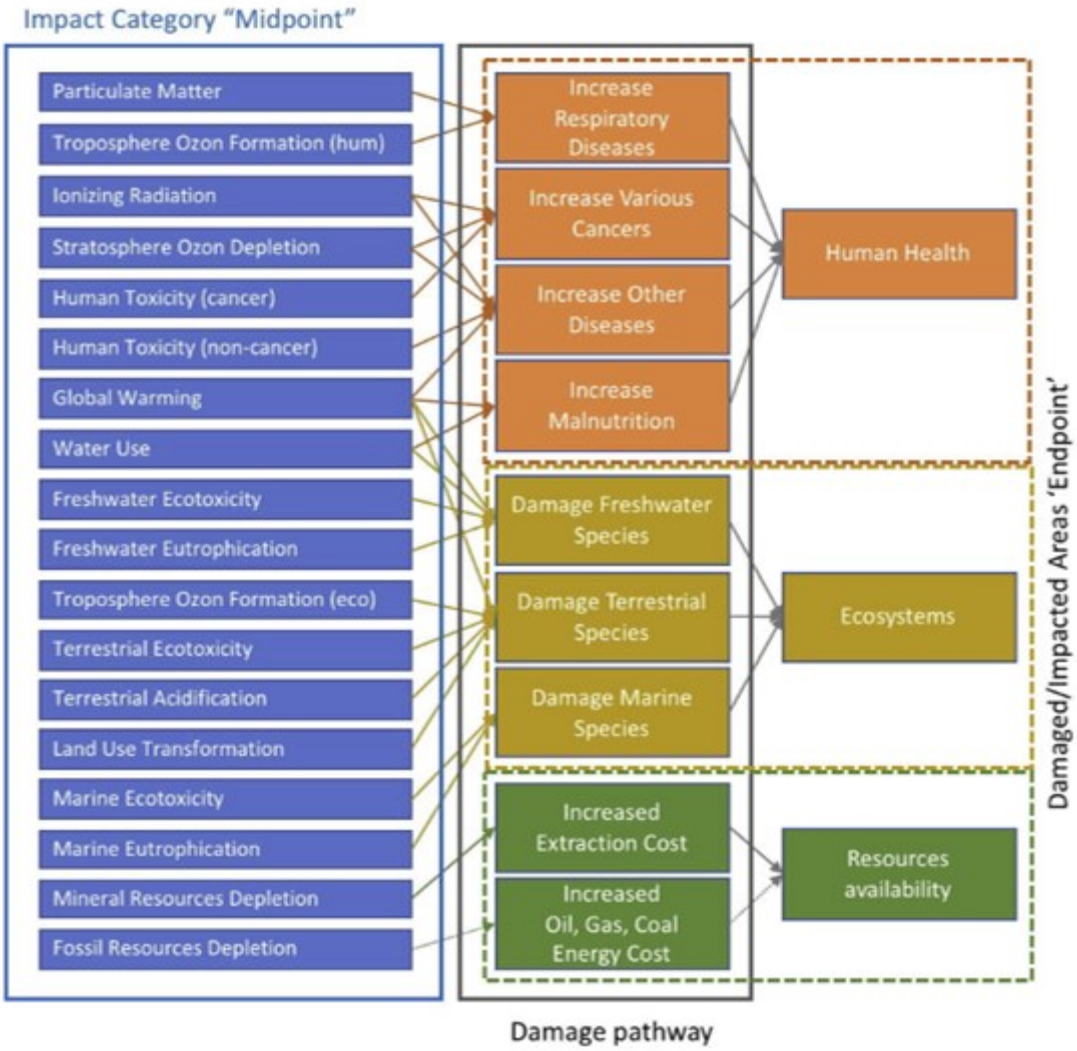


Fig. 3.4 Detailed connections between the midpoint impacts and the endpoint impacts considered in ReCipe 2016 [61].

The impact phase translates the collected inventory data of the LCI step into environmental impacts, for example acidification potential (AP), global warming potential (GWP) and ecotoxicity [62].

According to ISO 14042 and as shown in Fig. 3.5 [63], the LCIA stage consists of the following mandatory and options phases:

- Impact category definition: this is the identification of various groups in which the impacts identified based on the scope of the study can be placed in. Examples of such categories are global warming, toxicity, land use amongst others. This is an

essential step to simplify the assessment of processes, where many impacts can be identified and assessed.

- Classification: this involves placing and assigning the impacts and results of the LCI into the categories defined. This can be done by evaluating the impacts in such a way that they can be compared, e.g. per kg of emitting a substance or per kg of consuming energy.
- Characterisation: this step is calculated based on as explained in Eq. (3.2), which quantifies the amount of the component, and the resulted damage it caused by consuming energy or release of emissions.

$$EI_i = \sum_j e_{i,j} \times B_j \tag{3.2}$$

EI_i is the environmental impact to the ith impact category
$e_{i,j}$ is the characterisation factor of the component j that contributes to the impact i
B_j is the quantity of the jth inventory parameter

The following LCIA stages are optional elements to apply to the environmental impacts:

- Normalisation. The need to compare between the various categories calls the need to standardise the characterisation results. This is done by dividing characterisation result EI_i by a factor assigned to the impact category:

$$N_i = \frac{EI_i}{R_i} \tag{3.3}$$

Where corresponds to the normalised indicator of the i[th] impact category
EI_i is the indicator obtained in the characterisation step
R_i refers to the normalisation reference of the i[th] impact category

- Grouping: this involves placing characterisation results into subgroups to ease the evaluation and interpretation of the environmental results.
- Weighting: the impact is assessed on the basis of its effect on a weighting index, which is based on a number of quantitative and qualitative values e.g. impact on aquatic life and ethical value respectively. This is then summed up into an environmental indicator as per Eq. (3.4):

$$EI = \sum_i w_i EI_i \tag{3.4}$$

Where EI is the weighted impact of the i[th] impact category
w_i is the weighting factor of the i[th] impact category
EI_i is the characterised impact of the i[th] impact category

Data quality analysis: this phase involves the execution of various statistical tools to assess the LCIA results. The assessment includes evaluating the significance of the results as well as carrying out sensitivity analysis to identify the impact of uncertainties. This step is essential to identify the major contributors towards the total impact.

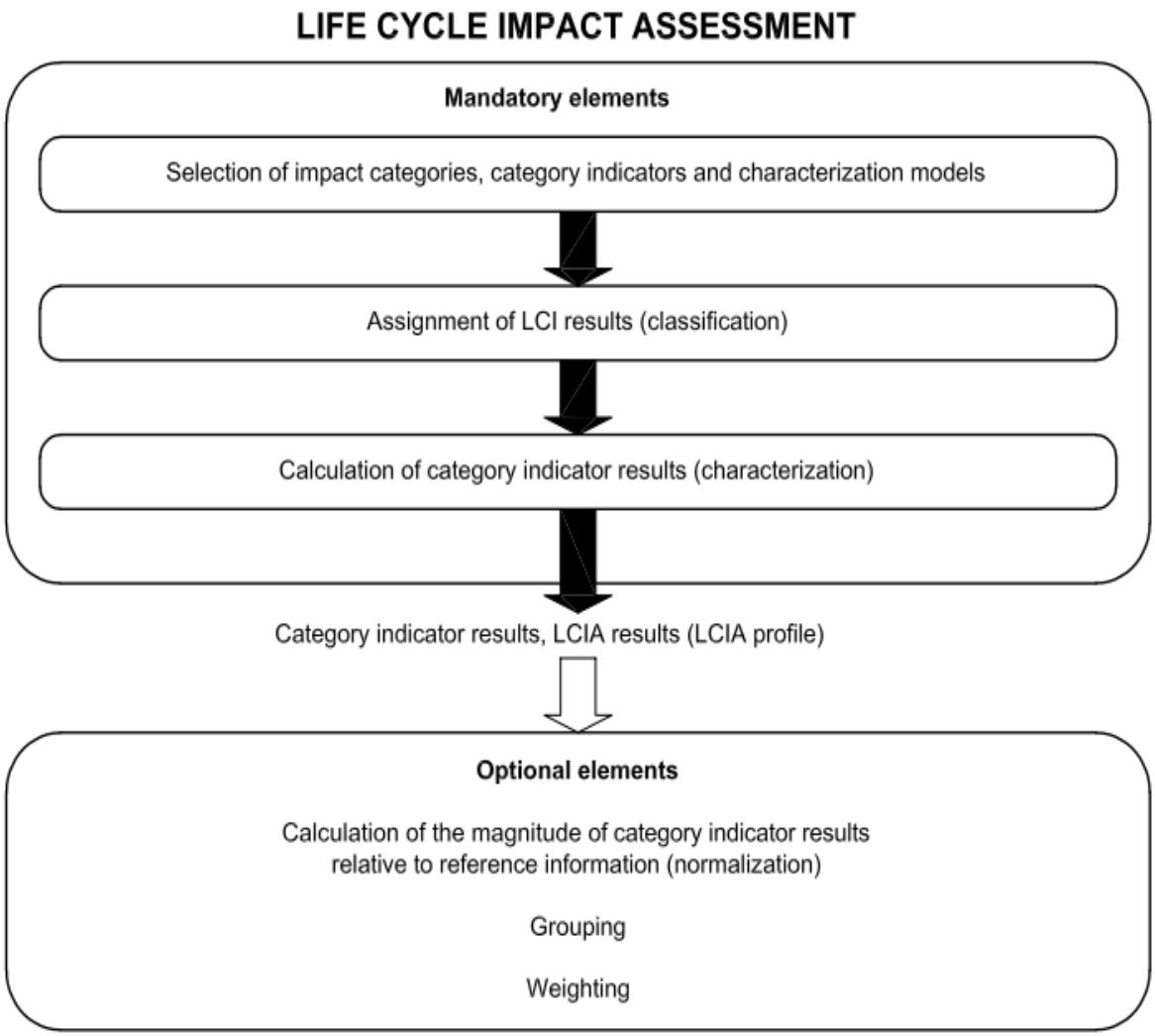


Fig. 3.5 The stages of the LCIA [63].

3.2.4 Life Cycle Interpretation

To complete the LCA, an interpretation of the results is carried out where the results of the inventory analysis and or the impact assessment are evaluated in light of the goal and scope to issue recommendations.

The results are assessed based on quantitative and qualitative methods. Quantitative methods compare the various results at various stages of the LCA. The quantitative method utilises various analysis tools, such as: dominance analysis, which identifies the most polluting step; contribution analysis, which highlights the most energy intense phase; decision maker analysis, which shows direct impacts of the process; and break even analysis, which compares various products on the basis of their lifetime. Uncertainty, sensitivity, and variation analysis can be carried out to assess the strength and weaknesses of the results.

The current practice in the sustainability assessments is to conduct the analysis of the impact following the characterisation and weighting stages, which is aided by sensitivity and uncertainty analysis.

Chapter 4 LIFECYCLE MONETISATION OF HYDROGEN PRODUCTION ROUTES

As hydrogen has been identified as a potential energy vector to decarbonise the transport and chemical sectors to achieve global greenhouse gas reduction targets. In this chapter, a wide range of alternative technologies have been assessed to determine the total cost of hydrogen production by coupling life-cycle assessments with an economic evaluation of the environmental externalities of production. This is done by including monetised values of environmental impacts on human health, ecosystem quality, and resources on top of the levelised cost of hydrogen production, an estimation of the "real" total cost of hydrogen was obtained to transparently rank the alternative technologies. This chapter covers steam methane reforming (SMR), coal and biomass gasification, methane pyrolysis, and electrolysis from renewable and nuclear technologies.

4.1 Background and problem statement

Global decarbonisation of energy services is required to minimise the potentially catastrophic risks of anthropogenic climate change [64]. Given its suitability across a range of energy applications and carbon-neutrality at the point-of-use, hydrogen as a 'green' energy vector offers a unique cross-system opportunity for fundamental change in the energy landscape.

Of the 60 million tonnes of hydrogen currently produced per annum, however, approximately 96% are derived from the reforming of fossil fuel feedstocks (49% natural gas,

29% liquid hydrocarbons, and 18% coal), resulting in high indirect CO_2 emissions [65]. The remaining 4% is produced *via* the electrolysis of water, which is only considered as a low-carbon source if low-carbon electricity with low embodied emissions is used [66], [67]. Furthermore, renewable energy-based processes cannot produce hydrogen at a price or scale that is competitive with fossil fuels [68], [69]. A major hindrance to the economic production of renewable-based hydrogen is the substantial capital expenditure (CAPEX) required [70]. The upfront financial burden combined with the low capacity factors of renewable energy assets makes such processes prohibitively expensive to compete with incumbent technologies [71], [72]. However, as the long-term costs associated with externalities, i.e., indirect costs linked to environmental impacts, of fossil fuels use are typically excluded from such comparisons, the "real" total cost of hydrogen production remains unclear.

Some works studied the merits of alternative hydrogen production pathways considering direct production costs and emissions (CO_2-equivalent). Dincer *et al.* [73] compared 19 different hydrogen production pathways based on renewable and non-renewable sources in terms of environmental impact, cost, energy, and exergy efficiencies. Their study considered the social cost of carbon (\$/t CO_2-equivalent) to evaluate the economic consequences of CO_2-equivalent emissions. Their findings suggested that hybrid nuclear thermochemical cycles are promising candidates for low-cost and low-environmental impact hydrogen. Ewan *et al.* [74] compared 14 different hydrogen production technologies according to CO_2 emissions, power density, land use, and production costs using an overall Figure of Merit. The study found that 'high energy density' technologies using primary energy sources (i.e., nuclear, natural gas, and coal) had an order of magnitude higher 'merit values'. Machhammer *et al.* [75] studied six hydrogen production technologies on cost and carbon footprint, concluding that methane pyrolysis is the most promising technology to produce low-cost and low-carbon footprint hydrogen. Speirs *et al.* [76] investigated the costs and greenhouse gas emissions of nine

hydrogen production routes with a focus on studying the supply chain contributions to the total process emissions. They found that low-carbon hydrogen supply chains had highly variable and non-negligible emissions contributions to the life cycle total. Parkinson *et al.* [68] investigated the cradle-to-gate life cycle emissions and costs of 12 hydrogen production routes, comparing each route to steam methane reforming (SMR) *via* the Levelised Cost of Carbon Mitigation and a set of decarbonisation metrics. The results showed that the most cost-effective methods of decarbonisation still utilised fossil-feedstocks, but only achieved moderate levels of decarbonisation.

Other works have explicitly focussed on quantifying the environmental impacts of hydrogen production technologies through life-cycle assessments (LCA). Valente *et al.* [77] conducted comparative LCAs of 23 hydrogen production routes from non-renewable sources (coal, natural gas, oil, and nuclear) and renewable sources (wind, solar, hydropower, biomass, and geothermal), with a focus on their acidification potential. The authors recommended using harmonised life-cycle impacts covering the global warming potential (GWP), cumulative non-renewable energy demand, and acidification potential indicators in the evaluation of these systems. Moreno *et al.* [78] investigated the LCA of hydrogen production using different biomass feedstocks in Spain, focussing on global warming potential, acidification potential, eutrophication potential, and energy consumption (MJ/kgH_2). The authors identified wastes from forestry as the most promising raw materials for hydrogen from biomass gasification (BG) routes. Utgikar *et al.* [79] also conducted an LCA of hydrogen production *via* high-temperature electrolysis from nuclear energy, compared with SMR, biomass gasification, solar photovoltaics (PV), and wind electrolysis. The LCA comparison focused on two environmental indicators, i.e., global warming potential and acidification potential, identifying hydrogen production from high-temperature electrolysis as a promising route relative to the SMR. Koroneos *et al.* [80] investigated the LCA of six

hydrogen production routes, comparing SMR with water electrolysis with energy supplied via solar PV, wind, biomass gasification, hydropower, and solar thermal. The LCA analysis focused on four environmental categories, namely global warming potential, acidification potential, eutrophication potential, and winter smog effect. The study concluded that, of the technologies assessed, solar PV electrolysis exhibited the worst environmental impacts due to the high acidification potential in the manufacturing phase of the PV panels and the very low efficiency of PV systems [80].

LCA-based approaches have been widely adopted to build strong cases, rooted in quantitative analysis, to replace fossil fuel-based technologies by 'greener' alternatives. However, LCA studies often focus on a reduced subset of technologies and tend to overlook environmental impacts beyond climate change. Notably, the LCA studies previously reported have typically focussed on global warming potential and energy consumption as environmental indicators of interest. Unfortunately, 'burden-shifting,' i.e., improving one impact at the expense of worsening others (or the same impact at a global level when considering the entire life cycle of the product), often arises in science and engineering [81]. Hence, when trade-offs are present between impact metrics, the severity of burden-shifting must be further investigated using tailored approaches applied to the standard LCA results.

Two recent studies by Valente *et al.* [82] and González *et al.* [83] enlarged the scope of conventional LCA's applied to hydrogen generation to include the costs of environmental externalities. The study by Valente *et al.* [82] was the first to monetise the environmental externalities of hydrogen production routes (SMR and biomass gasification). To this end, it applied the 'eco-efficiency' and the monetisation factors for human health (HH) and climate change reported in the CASES project dataset by Porchia and Bigano [84]. They concluded that biomass gasification is a promising alternative to the conventional SMR production pathway [82]. Gonzalez *et al.* [83] assessed the environmental impacts of hydrogen

production from non-fossil routes (wind, solar, biomass, and nuclear) as a feedstock for methanol production using data from Ecoinvent [59] accessed *via* SimaPro [85]. They performed a monetisation analysis based on the ReCiPe 2016 [60] and applied the recently developed concept of planetary boundaries to demonstrate that fossil methanol is globally unsustainable.

Previous studies have focused on the ranges and variations of the levelised cost of hydrogen (LCOH), life cycle emissions, and subsets of other environmental indicators from various stages of production. These works have led to various conclusions of the 'best' hydrogen production route depending on the environmental factors included. The studies have highlighted, however, that 'low-environmental impacts', even for the renewable-based routes, are not guaranteed when the full supply chain is evaluated. In this context, the transition to more sustainable hydrogen generation systems should be underpinned by sound assessments of the available technologies accounting for the additional costs of the environmental impacts over the entire supply chain and point of generation. So far, however, no single work has presented a comprehensive assessment of the most promising hydrogen production technologies considering simultaneously their cost and externalities due to impacts on human health, ecosystem quality (EQ), and resources depletion (RD).

To contribute to filling this gap, herein a detailed assessment of hydrogen production is presented covering ten different technologies (Table 4.1), i.e., methane, coal, and biomass gasification (with and without carbon capture and storage), methane pyrolysis, and electrolysis (from wind, nuclear and solar), and spanning impacts on HH, EQ, and RD. The latter are monetised to uncover the real cost of every technological route, which allows identifying the 'lowest total cost' pathway for at-scale hydrogen production. Hence, no existing studies have performed such an analysis that covers the breadth of technologies considered here for a cradle-to-gate, pressurized hydrogen supply. Notably, the study focuses

on identifying if the ranges of additional costs incurred, when the environmental externalities are accounted for, contribute significantly to the total cost of hydrogen (TCH), thereby addressing the following questions:

i. What are the real costs of a proposed hydrogen production technology compared with SMR (business as usual) considering the future or unaccounted for costs of environmental externalities?
ii. How do the ranges in monetised life cycle emissions values affect the total cost of production of a technology?
iii. What are the barriers to potential technologies in terms of their TCH to compete with SMR?

4.2 Methodology

4.2.1 Selected hydrogen production technologies:

We consider ten representative technologies for H_2 production (Table 4.1, data in Table 4.2). A short description of each route is given next. Note that hydrogen is supplied by all routes at a minimum pressure of 30 bar to be practicable for any downstream uses.

Table 4.1 Production technologies considered in this analysis and their technology readiness level (TRL), as described in reference [86].

No.	Technology name	Short name	TRL
1	Steam methane reforming	SMR	9
2	Steam methane reforming with CCS	SMR+CCS	7-8
3	Coal gasification	CG	9
4	Coal gasification with CCS	CG+CCS	6-7
5	Methane pyrolysis	CH4 pyrolysis	3-5
6	Biomass gasification	BG	5-6
7	Biomass gasification with CCS	BG+CCS	3-5
8	Electrolysis from wind energy	Wind	9
9	Electrolysis from solar PV energy	Solar PV	9
10	Electrolysis from nuclear energy	Nuclear	9

CCS = carbon capture and storage. PV = photovoltaics.

4.2.1.1 Steam methane reforming with and without carbon capture and storage

The SMR process is a two-step process, as shown in Eq. (4.1) and (4.2):

$$\text{Reforming: } CH_4 + H_2O \leftrightarrow \mathrm{CO} + 3H_2 \tag{4.1}$$

$$\text{WGSR: } CO + H_2O \leftrightarrow CO_2 + H_2 \tag{4.2}$$

Natural gas is the main feedstock for SMR, which principally comprises methane, mixed with various hydrocarbons and CO_2. During the reforming, the feedstock reacts with steam at high temperature (Eq. (4.1)). Thereafter, carbon monoxide (CO) and hydrogen are produced together with any unreacted natural gas. Next, additional steam is introduced to react with CO to recover additional hydrogen and convert CO to CO_2 in a water-gas shift reaction (WGSR –

Eq. (4.2)). The overall process efficiency is approximately 76% (CH_4 to H_2 on a higher heating basis) [87]. The SMR process emits large amounts of CO_2, which can be reduced by deploying a carbon capture and storage system, where the flue gases are removed and separated from the products stream. Thereafter, CO_2 is absorbed with amine solvent (monoethanolamine - MEA) to capture up to 90%. The treated flue gas stream is vented into the atmosphere. CO_2 is thereafter thermally desorbed and compressed at 110 bar for storage [88]. The energy efficiency for SMR+CCS is 68% (CH_4 to H_2 on a higher heating basis), mainly due to the energy required to regenerate the MEA and the electricity required for compression. Thus, relative to the base case without CCS, the additional energy consumption expressed in heat provided by methane (assuming methane was used as a heat source for the stripper of the CCS plant and to produce the electricity for compression) amounts to 3.79 MJ CH_4/kg CO_2 captured. This figure fits within the range stated in the literature which are in the range from 3.6 to 4 MJ CH_4/kg CO_2 captured [89]–[91]. Furthermore, the CO_2 emissions from the capture process amount to 0.21 kg CO_2/kg CO_2 captured, based on the work by Farajzadeh *et al.* [92]. Further details on the calculations are available in Appendix A.

In both cases (with and without CCS), hydrogen is further purified to 99.99% after the WGSR in a pressure swing adsorption unit, which is also used in the coal gasification (CG) and BG technologies [87].

4.2.1.2 Methane pyrolysis

Pyrolysis processes decompose hydrocarbons into solid carbon and hydrogen - Eq. (4.3) - at high temperatures (thermally or catalytically) [93]. As no oxygen is present, no carbon oxides are formed, potentially eliminating the need for secondary processing steps such as the WGSR and, therefore, reduces the CAPEX and operational expenditures (OPEX) compared to SMR [94]. The higher H_2 concentration of the product gas stream also has considerable

potential for minimising downstream clean-up processes [68]. The cost of methane pyrolysis is strongly dependent on the processing route, the price of natural gas, and the by-product solid carbon [68]. Several pyrolysis processes including plasma-based, high-temperature thermal (thermal black), solid catalytic, and molten metal catalytic systems have been proposed and developed, a detailed discussion can be found in [95]. Here we assume a catalytic molten metal process (TRL 3-5, Table 4.1). From a carbon-storage perspective, pyrolysis processes offer a distinct advantage in storing a solid C-product as opposed to gaseous CO_2 - Eq. (4.3).

$$CH_4 \leftrightarrow C + 2H_2 \tag{4.3}$$

4.2.1.3 Coal gasification with and without carbon capture and storage

In this route, coal is partially oxidised in the presence of oxygen or air to produce a syngas mixture (CO, H_2, CO_2, and unreacted CH_4) at high temperatures (800-1300 °C) and pressures of 30-70 bar [96]. The syngas is further enriched by the WGSR to recover more hydrogen. Coal gasification is less efficient than SMR (55%) but offers higher single-train capacities [97]. The overall reaction is presented in Eq. (4.4). The lower carbon to hydrogen ratio in coal relative to natural gas results in significantly higher direct CO_2 emissions from the process. The inventory data for both coal gasification routes (without and with CCS) are taken from the works by Ruthowski and Vickers, respectively [98], [99].

$$\mathrm{C} + 2H_2O \leftrightarrow CO_2 + 2H_2 \tag{4.4}$$

4.2.1.4 Biomass gasification with and without carbon capture and storage

Biomass resources can be used for hydrogen production [100]. Similar to coal, gasification is the optimum pathway for biomass feedstocks as biomass gasification provides the highest

yield taking place at high temperatures, typically at 500-1400 °C [101]. The overall reaction is shown in Eq. (4.5) [68].

$$Biomass + H_2O \leftrightarrow CO + H_2 + CO_2 + CH_4 + Tar + Char \quad (4.5)$$

There is a wealth of interdependent research related to LCAs that investigate biomass-to-hydrogen processes differing in the biomass feedstock and system configurations [101]. This study considers poplar and covers the plantation phase of the biomass, fertilisers requirements, and water consumption following the work done by Peters *et. al.* [102]. Biomass gasification can be also integrated with CCS to yield a negative carbon balance. The inventory data for both biomass gasification systems without and with CCS are taken from Susmozas *et al.* [103], [104], respectively. Further details on the inventory data of the poplar can be found in Table A3 in Appendix A.

4.2.1.5 Electrolysis-based routes

High purity hydrogen (≈100% hydrogen) can be produced from water electrolysis as described by Eq. (4.6) *via* electrical energy. Alkaline and proton exchange membrane (PEM) electrolysers operate at low temperatures (70-90 °C), while solid oxide electrolysis cells can work at high temperatures (650-850 °C) [105]. In this study, a PEM electrolyser is considered as it provides a faster start, higher flexibility and can work with intermittent power technologies such as solar and wind, attaining an efficiency as high as 85% [106]. Furthermore, the PEM electrolyser produces hydrogen at 30 bar, which enables a consistent comparison between the investigated production routes [107]. Our study compares electricity from nuclear, wind, and solar to cover the electrolyser's energy needs. The inventory data for the electrolysis process is taken from Colella *et al.* [107].

$$2H_2O \rightarrow 2H_2 + O_2 \quad (4.6)$$

4.2.2 Environmental assessment

The study herein comprises six steps consistent with the general LCA methodology. The first three steps correspond to the goal and scope definition, inventory analysis, and impact assessment phases, with the remaining steps connected to the interpretation phase using externalities and considering as well the main uncertainties affecting the calculations. The six steps are described below.

First (I), an LCA of the selected technologies using the ISO14040 standards was performed [63]. The goal of this work is to assess the environmental impacts of hydrogen production routes from several different feedstocks, including fossil, biomass, and carbon-free based sources. Hydrogen end-use applications are excluded from this study; however, such applications may warrant further investigation to match supply-demand profiles accurately. Accordingly, the functional unit corresponds to one kilogram of hydrogen product pressurised to a minimum of 30 bar to ensure a consistent comparison between the fossil and carbon-free processes as well as to satisfy hydrogen end uses. For electrolytic routes where O_2 is generated, no value or burden allocation was assigned to the O_2 by-product. The motivation for this assumption is twofold. First, O_2 would have to be compressed before being sold, which would increase the energy needs and, consequently, the environmental impact of the process. Second, the market would be very likely unable to absorb the amount of O_2 produced at a large scale, assuming a high H_2 demand. A cradle-to-gate scope that encompasses all the embodied input burdens (upstream), production, and additional pressurization (if required) has been adopted (Table 4.2). The system boundaries are illustrated in Fig.4.1. The location of this study was based on the United States (US).

The main limitations of the LCA analysis presented in this study are summarised below:

- The environmental impacts of the electrolyser in the electrolysis routes were omitted from the analysis. This assumption is motivated by the fact that the electricity input

needed to produce 1 kg of hydrogen (54.2 kWh) has been shown to be the main contributor to the total environmental impacts of these hydrogen production pathways [108].

- The emissions embodied in the equipment units of the plants were excluded from the analysis. This is a common assumption in LCA studies, where the main contributors to the total environmental impacts tend to be the raw materials and energy consumption and infrastructure is neglected [83].
- Further assumptions and limitations for the background processes are available in the documentation available in [59].

Second (II), the life cycle inventory (LCI) of each technological route was quantified from the raw materials (feedstock) requirements, energy consumption or generation, waste, and emissions to air, soil, and water. The life cycle inventory data for all the investigated technologies and their respective sources are shown in Table 4.2. For the embodied burdens, inventories were taken from Ecoinvent v3.4 accessed *via* SimaPro v9. Further details on the inventory flows can be found in Table A2 in Appendix A. In the US, wind power was assumed to be 100% from onshore, according to IRENA [109].

Third (III), the LCI's were used in a life-cycle impact assessment (LCIA) following the ReCipe 2016 method [60], which translates all the LCI data into 18 environmental impacts at the midpoint level; these are further aggregated into damage to human health, ecosystem quality and resources depletion at the endpoint level. All the calculations were implemented in SimaPro v9. The three environmental impacts in the endpoints areas of protection were monetised using the values reported by Fantke *et al.* [110], which enables consistent comparisons of process alternatives [111]. The monetary values for the human health and ecosystem quality impacts are 74,000 €/DALY and 9.5 x 10^6 €/Species.yr, respectively. All the monetised values were adjusted to USD2019 by inflation. Further details on the monetisation conversion calculations are available in Table A1 in Appendix A. Note that the endpoint environmental impacts are the primary focus of this work, while additional

information regarding the impacts at the midpoint level are presented in Figures A1a, A1b, and A1c in Appendix A.

Fourth (IV), the monetised cost of environmental externalities was combined with the levelised cost of hydrogen (Eq. (4.7)) to generate estimates of the TCH. Variations in direct hydrogen production costs are often large, heavily dependent on the process variables, and the financial modelling assumptions used. These have been studied in exhaustive detail elsewhere and are not the main-focus here [38], [54], [112], [113]. The average production costs for each technological pathway reported by Parkinson *et al.* have been used here [68]. Thus, the TCH from any production route can be represented by Eq. (4.7):

$$TCH = Monetised\ Indicators\ x\ LCIA\ Impact + LCOH \quad (4.7)$$

Fifth (V), the combined results of the monetised LCIA and levelised cost of hydrogen (TCH) were used to identify stages in the life-cycle of each process contributing the most to the environmental impact. This analysis allows us to draw meaningful insights and recommendations for the systems studied.

Six (VI), the main uncertainties affecting the LCA calculations, mainly in the life cycle inventory entries, were assessed and quantified. To this end, 1,000 scenarios were generated using the Monte Carlo sampling method implemented in SimaPro v9, each entailing different values of the endpoint indicators sampled from the associated multi-variate probability distribution. The reported monetisation values were applied to each such scenario to obtain a range of monetised impacts for the range of life cycle inventory entries. Further details on the uncertainty analysis can be found in Appendix A.

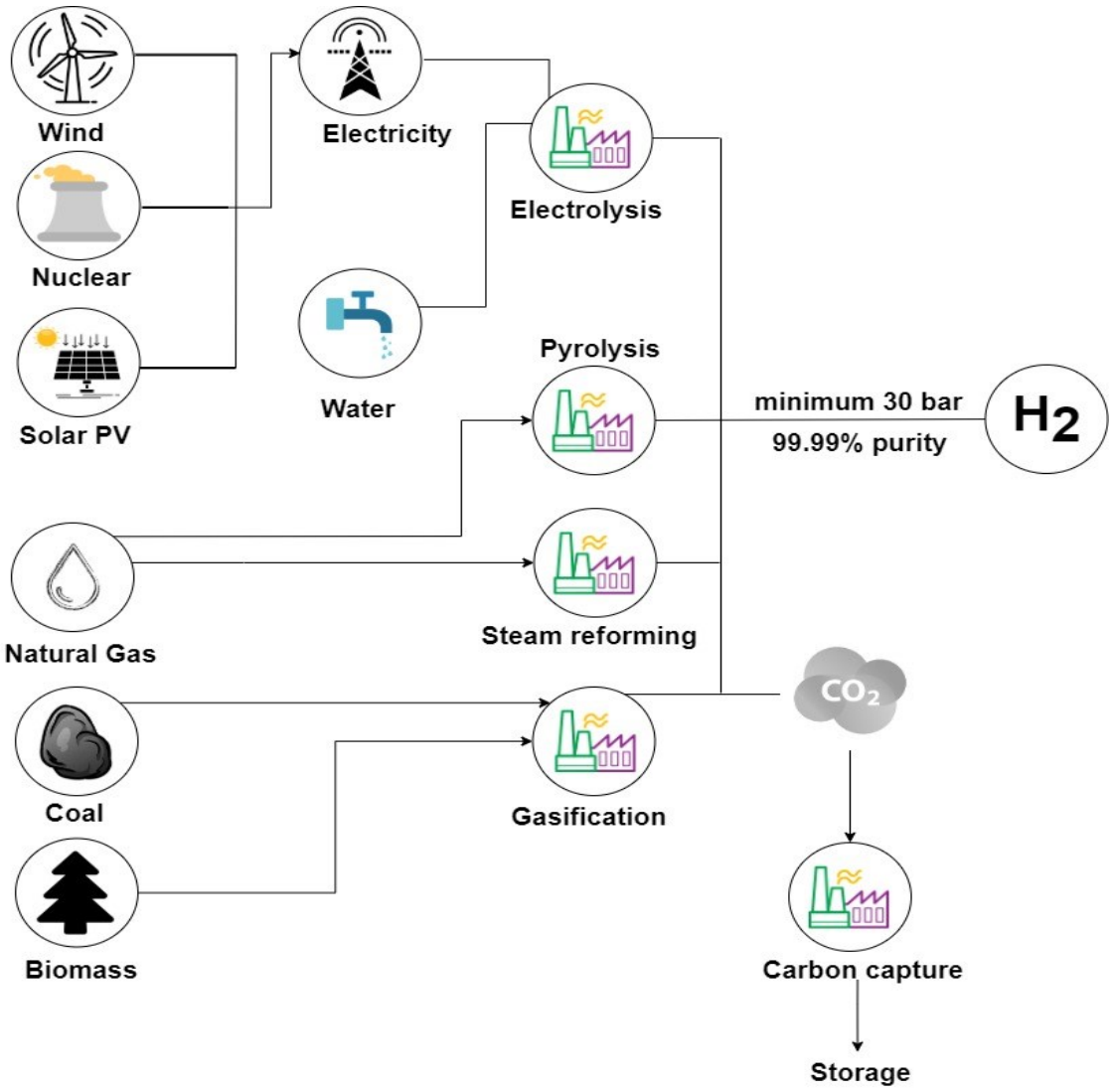


Fig.4.1 Production processes considered in this analysis to produce 1 kg of hydrogen at a minimum of 30 bar and 99.99% purity.

Table 4.2 Life cycle inventories (LCI) of the investigated technologies to produce 1 kg of hydrogen at a minimum of 30 bar. Further information on the embodied inputs can be found in Table A2 in Appendix A.

Embodied Inputs	**Unit**	**SMR**	**SMR+CCS**	**CH_4 Pyrolysis**	**CG**	**CG+CCS**	**BG**	**BG+CCS**	**Nuclear**	**Solar PV**	**Wind**
Natural Gas	kg	3.36	3.76	4.86	-	-	-	-	-	-	-
Electricity	kWh	0.31	1.11	-	-	1.36	-	3.58	54.2	54.2	54.2
Water	kg	21.90	23.70	8.08	11.28	38.08	47.48	47.96	10.00	10.00	10.00
Coal	kg	-	-	-	8.51	9.70	-	-	-	-	-
Biomass Feedstock	kg	-	-	-	-	-	36.28	36.34	-	-	-
Biomass transport	t.km	-	-	-	-	-	2.90	2.93	-	-	-
Direct Emissions											
CO_2	kg	9.26	1.03	2.50	22.00	4.13	32.84	16.77	-	-	-
CH_4	kg	-	-	-	$2.66x10^{-02}$	$3.22x10^{-02}$	-	-	-	-	-
N_2O	kg	-	-	-	$6.97x10^{-06}$	$1.87x10^{-05}$	-	-	-	-	-
NO_2	kg	-	-	-	-	-	0.01	$7.74x10^{-3}$	-	-	-
Co-product											
Solid Carbon	kg	-	-	3.00	-	-	-	-	-	-	-
Electricity	kWh	-	-	-	3.18	-	2.07	-	-	-	-
Reference			[88], [114]		[98]	[99]	[103]	[104]	[79]	[115]	[52]
LCOH	USD2019[b]	1.35	2.01	1.87	1.48	2.32	2.40	3.71[a]	4.95	9.49	5.61
Reference					[68]			[68], [116]		[68]	
Product											
Hydrogen	kg					1.00					

[a] An average value of \$4.67 and \$2.27/kg H_2 from [68], [116]; [b] LCOH was converted from 2016 to 2019 using 1.07 inflation conversion factor

4.3 Results and discussions

The results of the study are presented in three main sections. First, the LCA endpoint indicators and individual breakdowns for each technology are presented. Second, global warming potential results are presented. Third, the total cost of hydrogen for each production route is assessed by combining the levelised cost of hydrogen and monetised environmental impacts.

4.3.1 Environmental impacts in endpoint area of protection

The endpoint environmental impacts on human health, ecosystem quality, and resources depletion for each hydrogen production route are shown in Fig.4.2. Further breakdowns for each endpoint (damage-oriented) indicators in terms of their midpoint-level (problem-oriented) indicators are available in Figure A1 in Appendix A.

Unabated coal gasification demonstrates the highest impact on human health, generally followed by coal gasification with carbon capture and storage and unabated biomass gasification, then SMR, solar PV, biomass gasification with carbon capture and storage, SMR with carbon capture and storage and methane pyrolysis, and finally wind and nuclear technologies. For ecosystem quality, biomass gasification shows the highest impact, followed closely by, biomass gasification with carbon capture and storage and coal gasification, coal gasification with carbon capture, and storage, SMR, and solar PV. Then, methane pyrolysis, SMR with carbon capture and storage, nuclear and wind. Finally, fossil-utilising technologies, especially natural gas, exhibit the highest levels of resources depletion while wind and nuclear electrolysis have the lowest resources depletion impacts.

A deeper analysis of the midpoint-level indicators (Figures A1a, A1b, and A1c in Appendix A) reveals that the high human health and ecosystem quality impacts are driven mainly by the

high global warming potential, the formation of fine particulate matter (FPMF), land-use and water consumption.

For SMR, the integration of carbon capture and storage reduces direct CO_2 emissions and thereby reduce human health by 48% and ecosystem quality by 63%. The same applies to coal gasification with carbon capture and storage which improved by 20% in human health and 44% in ecosystem quality compared to the unabated coal gasification. Notably, methane pyrolysis shows very close human health and ecosystem quality results to SMR with carbon capture and storage due to low direct CO_2 emissions in both cases. Furthermore, the impacts on resources depletion associated with the SMR with carbon capture and storage and methane pyrolysis routes are higher than SMR without carbon capture and mainly driven by the nature of the feedstock consumed (natural gas).

For biomass routes, although biomass gasification with carbon capture and storage shows lower human health compared to SMR, this technology route didn't show negative human health compared to the negative global warming potential (Fig.4.3). The negative CO_2 emissions are accredited to carbon fixation during the biomass growth phase and storage with carbon capture and storage. The same credit is not observed for unabated biomass gasification, as the fixated carbon source is re-released to the atmosphere. The high impact on human health in biomass gasification and biomass gasification with carbon capture and storage routes relates to water consumption at the midpoint level (Figure A1a in Appendix A). Similarly, the high impact on ecosystem quality in these routes is driven by the high land-use change and water consumption linked to the biomass plantation phase (Figure A1c in Appendix A), often neglected when assessing only the global warming potential.

For electrolysis routes, the high human health and ecosystem quality of solar PV electrolysis are predominately driven by the manufacturing phase and the crystalline silicon requirements for the production of the photovoltaic panels [117]. For nuclear and wind

electrolysis, the human health and ecosystem quality impacts embodied in electricity are the main dominant factor. This impact is strongly connected to the manufacturing phase of the electricity generation facilities that power water electrolysis. For wind electrolysis, the impact is mainly due to the materials for construction for the wind turbine, of which steel and iron materials are the major contributors to the environmental impacts [52]. For nuclear electrolysis, the mining of uranium and the production of nuclear fuel are the main contributors to the environmental impacts [118].

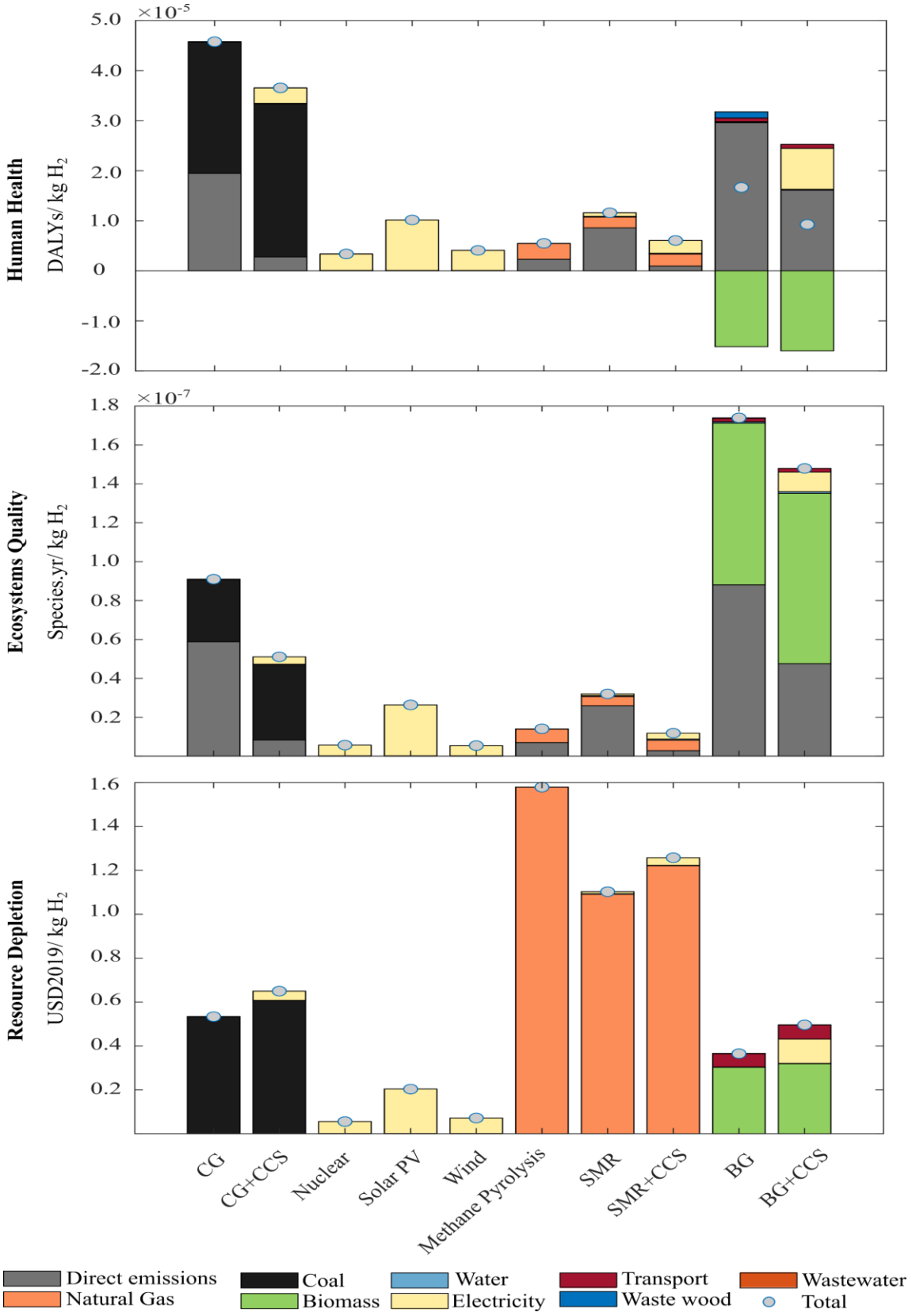


Fig.4.2 Breakdown of the endpoint environmental impacts for the assessed hydrogen production processes considered in the analysis. The electricity contribution in the renewables refers to electricity generated from the specified form of energy, i.e., power technology.

4.3.2 Global warming potential of the evaluated hydrogen production technologies

Fig.4.3 provides the total greenhouse gas emissions per 1 kg of hydrogen produced. Biomass gasification with carbon capture and storage shows the lowest global warming potential value (−13.11 kg CO_2-eq/kg H_2, as carbon capture and storage, leads to a net-negative carbon balance). This global warming potential value is in good agreement with the only LCA study reported for biomass gasification with carbon capture and storage, i.e., −14.63 kg CO_2-eq/kg H_2 [104]. This technology is followed by the unabated biomass gasification process (0.65 kg CO_2-eq/kg H_2), where both global warming potential values (biomass gasification and biomass gasification with carbon capture and storage) fit well within the range previously reported [68]. The biomass routes are then followed by water electrolysis by nuclear and wind energies, i.e., 0.67 and 0.86 kg CO_2-eq/kg H_2, respectively, and then solar PV (3.1 kg CO_2-eq/kg H_2). In all of the cases, the electricity source supplied to the electrolyser is the main contributor to the total global warming potential. These technologies are followed by SMR with carbon capture and storage, methane pyrolysis and coal gasification with carbon capture and storage, and, finally, coal gasification and SMR, which show the highest global warming potential values (25.24 and 11.24 kg CO_2-eq/kg H_2, respectively). Note that all the global warming potential values obtained herein are consistent with the values reported elsewhere [68].

Our results, therefore, show that assessing global warming potential only could potentially lead to misleading conclusions. For example, when omitting land use and water consumption for the biomass cases, they emerge as superior; however, the same biomass technologies display the worst ecosystem quality impact values. Therefore, covering the endpoint metrics is crucial to ensure a meaningful assessment relative to the fossil pathway.

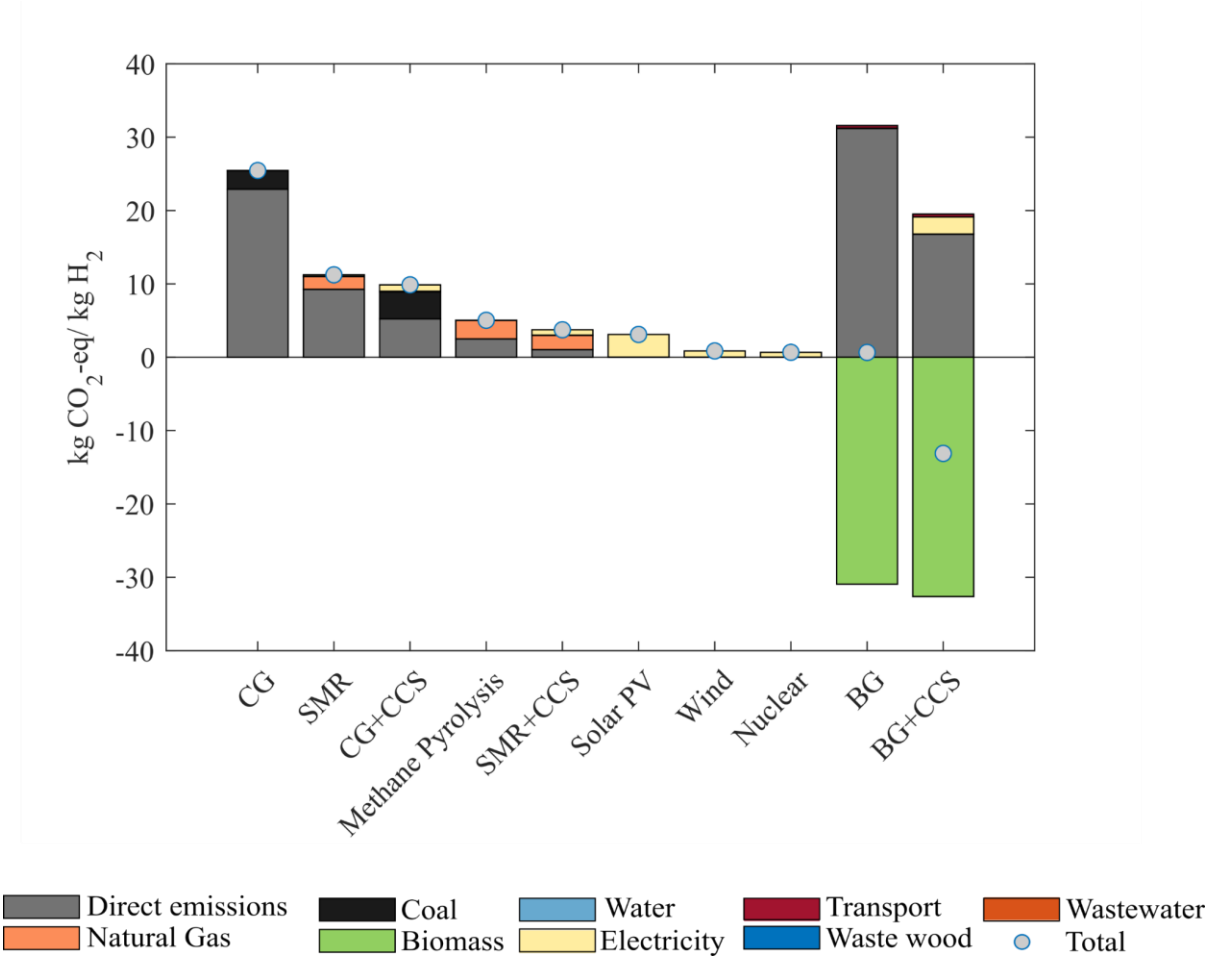


Fig.4.3 Breakdown of the global warming potential (GWP) for the evaluated processes. The technologies are ranked from highest to lowest with respect to their GWP values.

4.3.3 Total cost of hydrogen production

The TCH production (Fig.4.4) was calculated from Eq. (4.7) by combining the monetised environmental impacts with the average LCOH for each production route from Parkinson *et al.* [68]. The average monetised environmental impacts account for significant fractions of the TCH for fossil-based routes (76% SMR, 57% SMR with carbon capture and storage, 62% methane pyrolysis, 88% coal gasification, 78% coal gasification with carbon capture and storage). Meanwhile, the direct production costs (LCOH) dominate the TCH in the electrolytic routes (86%, 77%, 86% for nuclear, solar, and wind electrolysis, respectively). Furthermore, the externalities account for 68% and 81% of the TCH for the BG with and without carbon capture and storage, respectively. Hence, our results show that externalities

can represent a significant fraction of the TCH and should be accounted for in the economic assessment.

The uncertainty ranges of the TCH shown by the superimposed box plots in Fig.4.4 were generated by Monte-Carlo analysis of 1,000 scenarios (see details in section 4.2.2 – sixth step). The endpoint indicators were subsequently obtained for each such scenario and monetised accordingly to evaluate the robustness of the findings. The box bars in Fig.4.4, follow a lognormal distribution. It is characterised by a standard deviation that encompasses the 95% confidence interval. Further information on the uncertainty analysis is provided in Appendix A. Note that the LCOH variables were not varied in Fig.4.4.

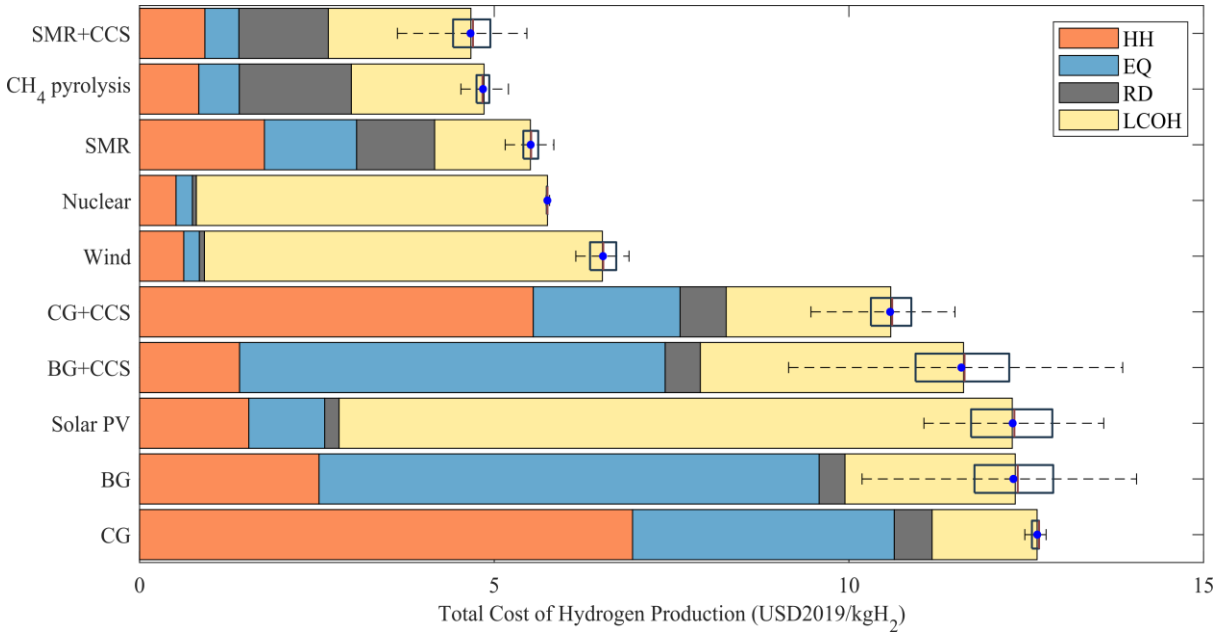


Fig.4.4 Total cost of the assessed H_2 production routes (TCH) in terms of externalities (HH, EQ, and RD) and LCOH. For the uncertainty analysis of externalities, the boxplot bars represent the 95% confidence interval assuming a lognormal distribution. The dot represents the mean TCH and the red line represents the median. HH refers to the monetised human health indicator, EQ refers to the monetised ecosystem quality indicator, RD refers to the monetised resources depletion and LCOH refers to the levelised cost of hydrogen. All indicators are expressed in USD2019 per kg H_2.

The lowest TCH value corresponds to the natural-gas blue hydrogen fossil routes (SMR with carbon capture and storage and methane pyrolysis), despite their higher CO_2 emissions compared with electrolytic routes. Notably, SMR with carbon capture and storage is the most

cost-effective production route (considering externalities) despite its larger LCOH compared with the unabated SMR [\$1.88 /kgH_2 and 1.26 /kgH_2 for SMR with carbon capture and storage and SMR, respectively]. More precisely, the TCH value for unabated SMR is \$5.51 /kgH_2 compared with SMR+CCS at \$4.67 /kgH_2, highlighting the influence of the monetised environmental externalities on the TCH. The large externality costs are mainly driven by the higher global warming potential (Figure A1 in Appendix A) in the former route. The question of how to improve the TCH of the hydrogen routes, which was addressed elsewhere [119]–[121], falls beyond the scope of this work. In contrast, opportunities for improving environmental performance are discussed next.

4.3.3.1 Steam methane reforming with carbon capture and storage

SMR and SMR with carbon capture and storage show very similar supply chains but differ in their fuel usage and direct emissions. In the SMR with carbon capture and storage, improving the capture rate above 90% would decrease the impact on the human health and ecosystem quality categories due to the associated reduction in direct CO_2 emissions, which is the major contributor to those categories. The OPEX and CAPEX are also linked to the capture rates, with higher capture rates requiring greater fuel duty and additional equipment [122]. As demonstrated, removal rates are often around 80%, while the costs of deep decarbonisation (>90%) remain unclear [88], [123]. Replacing the MEA solvent used in the post-combustion absorption of the flue gas by other means of capture, such as adsorption, could improve the capture rate and the environmental impacts while offering potential cost reductions [124]. Metal-organic frameworks (MOF) are a promising family of porous crystalline adsorbents, which are still at pilot/ research stages. MOFs can act as capture and storage materials for CO_2 due to their high surface area and pore volumes [125]. MOF

materials could, therefore, help to address the limitations of the conventional storage currently used [6].

The resources depletion category is the other major contributor to the total cost of environmental externalities. Approximately 70% of the resources depletion impact arises from the natural gas feedstock, with the remaining 30% given by the process fuel requirements [126], [127]. The latter contribution could be reduced by using waste energy streams through process integration, though this will likely have additional integration costs [128]. Hence, whilst SMR with carbon capture and storage currently offers the lowest total cost solution, the opportunities for reduced environmental impacts are limited over the medium-long term. Despite this, it is the best technology in terms of TCH, with a marginal LCOH increase compared to SMR.

4.3.3.2 Methane pyrolysis

Methane pyrolysis is the second cheapest total cost route. It emits less direct CO_2 emissions and less FPMF (Figure A1a in Appendix A) than SMR, which leads to lower human health and ecosystem quality impacts. However, methane pyrolysis consumes more natural gas per unit of H_2 than SMR, which increases the resources depletion costs. In this route, human health and ecosystem quality account for 17% and 12%, respectively, of the TCH. These impacts are mainly driven by the natural gas supply chain emissions and the required heat for the process, which is assumed to be sourced from natural gas. Notably, the sweetening of natural gas and the fugitive methane emissions are the main contributors to the natural gas supply chain emissions. The higher supply chain impacts due to larger natural gas consumption are offset by the lower direct emissions of methane pyrolysis. Other means of heat sources could further reduce the environmental impacts. For the resources depletion category, about 18% of the natural gas is used for heating in the process with an overall

efficiency of 53% [119]. Finding alternative heat sources could help reduce the impacts in this category, although this would likely increase the process costs.

Cost reduction opportunities for methane pyrolysis are direct production cost-related (38% of the TCH - Fig.4.4). Similarly, as with SMR and SMR with carbon capture and storage, there might be limited opportunities for additional reductions in externalities. The levelised cost of hydrogen of this route is highly sensitive to the natural gas prices and the opportunities for selling the solid carbon produced. For the current analysis, no value was assigned to the solid carbon; hence, finding potential carbon markets and applications would bring the levelised cost of hydrogen down [119]. Currently, solid carbon produced by high-temperature methane pyrolysis is commercially used in tires and electrical equipment; however, the physical and electrical properties determine its suitability for higher-value market applications [119]. Another important aspect to highlight is that this technology still exhibits a relatively low TRL [3-5], with only early-stage pilot plants in operation [119]. Thus, additional technological developments and learning curves may further reduce its TCH.

4.3.3.3 Coal gasification with and without carbon capture and storage

Despite the low costs of the coal feedstock, coal gasification has the highest TCH [\$12.65 /kgH_2] because of the high environmental externalities (88% of the overall TCH). When coupled with carbon capture and storage, the TCH for coal gasification with carbon capture and storage [\$10.59 /kgH_2] is improved by 16%, primarily driven by the decrease in the human health and ecosystem quality impacts linked to lower direct CO_2 emissions (81% reduction with capture rates of 86.85% [99]). Carbon capture and storage, however, cannot reduce the environmental impacts associated with the coal feed; these are mainly linked to the methane emissions in the mining and pre-treatment stages (~ 70%, 36 kg CO_2-eq/kg CO_2

[60]). Hence, the potential improvements in carbon capture and storage are mainly focused on the direct emissions of the gasification plant.

4.3.3.4 Biomass gasification with and without carbon capture and storage

Both the LCOH and externality impacts are high contributors toward the TCH for biomass gasification and biomass gasification with carbon capture and storage technologies. Carbon capture and storage reduces the impact on human health substantially, as it is strongly linked to CO_2 emissions. In contrast, the impact on ecosystem quality is not significantly reduced when deploying carbon capture and storage because it is mainly connected to the biomass feedstock (due to the high contributions of the water consumption and land use impacts) (Figure A1c in Appendix A).

For biomass gasification with carbon capture and storage, the available LCOH estimates in the literature are scarce; only two LCOH values were found [\$2.27 /kgH_2 and 4.6 /kgH_2] [68], [116]. The average of those two values used in the nominal case represents 32% of the TCH of this route. Since the TRL of this route is still at the research phase [3-5], there is significant uncertainty in the cost estimations in the medium to long terms. Hence, this topic should be the subject of further investigation.

Notably, our analysis is quite sensitive to the biomass feedstock type as land use impacts, water consumption, fertilisers for feedstock plantation, and the transport of the biomass to the point-of-conversion vary spatially. The former information should be taken into consideration when performing further studies in biomass-based hydrogen production pathways.

The obtained results are aligned with previous studies concerning the midpoint impacts, i.e., biomass gasification emits approximately 0.39 $kgCO_2/kgH_2$ [103] and -14.63 $kgCO_2/kgH_2$ when equipped with carbon capture and storage [104]. For the ecosystem quality impact, the biomass feedstock is the main contributor to the total impact due to the land utilisation and

water consumption in the biomass plantations (Figure A1c in Appendix A). Despite the potentially low environmental impacts of biomass gasification with carbon capture and storage, one of the main limitations of biomass routes is the relatively low hydrogen yields from biomass [6–12 wt.% H_2/kg biomass] [129]. For example, a hydrogen yield of 7.97 wt.%/kg biomass would require ~48% of the US agricultural crop area to satisfy the current global H_2 demand of 60 million tonnes per annum [87]. Thus, despite the relatively low global warming potential of this route (Fig.4.3), there is significant uncertainty in the future potential of such conversion routes at scale.

4.3.3.5 Electrolysis-based routes

Electrolysis-based hydrogen may benefit substantially from future cost reductions (the levelised cost of hydrogen represents at present between 77 to 86% of the TCH for solar PV, wind, and nuclear electrolysis routes, respectively). Bearing this in mind, wind and nuclear electrolysis would emerge as potentially attractive options because their TCH is 4-18% higher than the TCH of SMR (and 39-23% higher than the TCH of SMR with carbon capture and storage). Consequently, a decline in electricity costs and/or the capital investment of the electrolyser may make them economically competitive [65], [71].

Environmental costs are mainly driven by the electricity source – wind, nuclear and solar PV. Although the electrolysis process has zero direct emissions, the supply chain emissions of each electricity source are not negligible [118]. Opportunities for reducing the environmental impacts further might be very limited for the case of wind and nuclear, where externalities represent, in turn, a small percentage of the TCH [~ 14%]. For solar PV, the environmental impacts are dominated by the manufacturing phase of the panels, currently made of crystalline silicon. Thereby, reducing the required materials of a panel or finding alternative materials with lower embodied emissions would improve the environmental performance of this route.

The LCOH is highly dependent on the electricity cost, electrolyser's capital cost, and the capacity factor of the power technology [65]. The capital cost of nuclear power plants, as well as the cost of uranium fuel, are the main dominant factors in the nuclear route to hydrogen [130]. This is reflected in a range of levelised cost of electricity of [0.08-0.12 $/kWh] with an average value of [0.1 $/kWh] [68]. Furthermore, this route benefits from the clean nature of the uranium source and its higher capacity factor compared to wind and solar PV (95% vs. 33% and 20%, respectively). Additionally, the electrolyser's capital cost, currently in the range of [400-1000 $/kW] with an average of 800 $/kW, is another major contributor to the total cost [68]. Thus, a reduction in the electrolyser's CAPEX would significantly improve the cost competitiveness of the electrolytic hydrogen. It is worth highlighting in Fig.4.4 that SMR with carbon capture and storage shows a higher uncertainty range compared to SMR. This can be attributed to the uncertainties stemming from the additional electricity needs of carbon capture and storage. The severity of this effect varies with the grid infrastructure across countries. This applies as well to coal gasification with carbon capture and storage and biomass gasification with carbon capture and storage. The large variation in TCH for the biomass gasification and biomass gasification with carbon capture and storage, depicted by the superimposed box plots, is driven by the variation in biomass source and type, plantation requirements for different crops, and water consumption during the growth phase.

On the other hand, methane pyrolysis shows tighter uncertainty ranges compared to SMR, as its impact is mainly driven by the natural gas feedstock (no electricity input is required). Hence, this technology might be appealing to underpin a transition phase until greener, electrolytic hydrogen becomes more economically competitive. Nuclear-based hydrogen shows good performance and a narrow uncertainty range. However, its cost, together with public acceptability issues, are the main barriers at this stage.

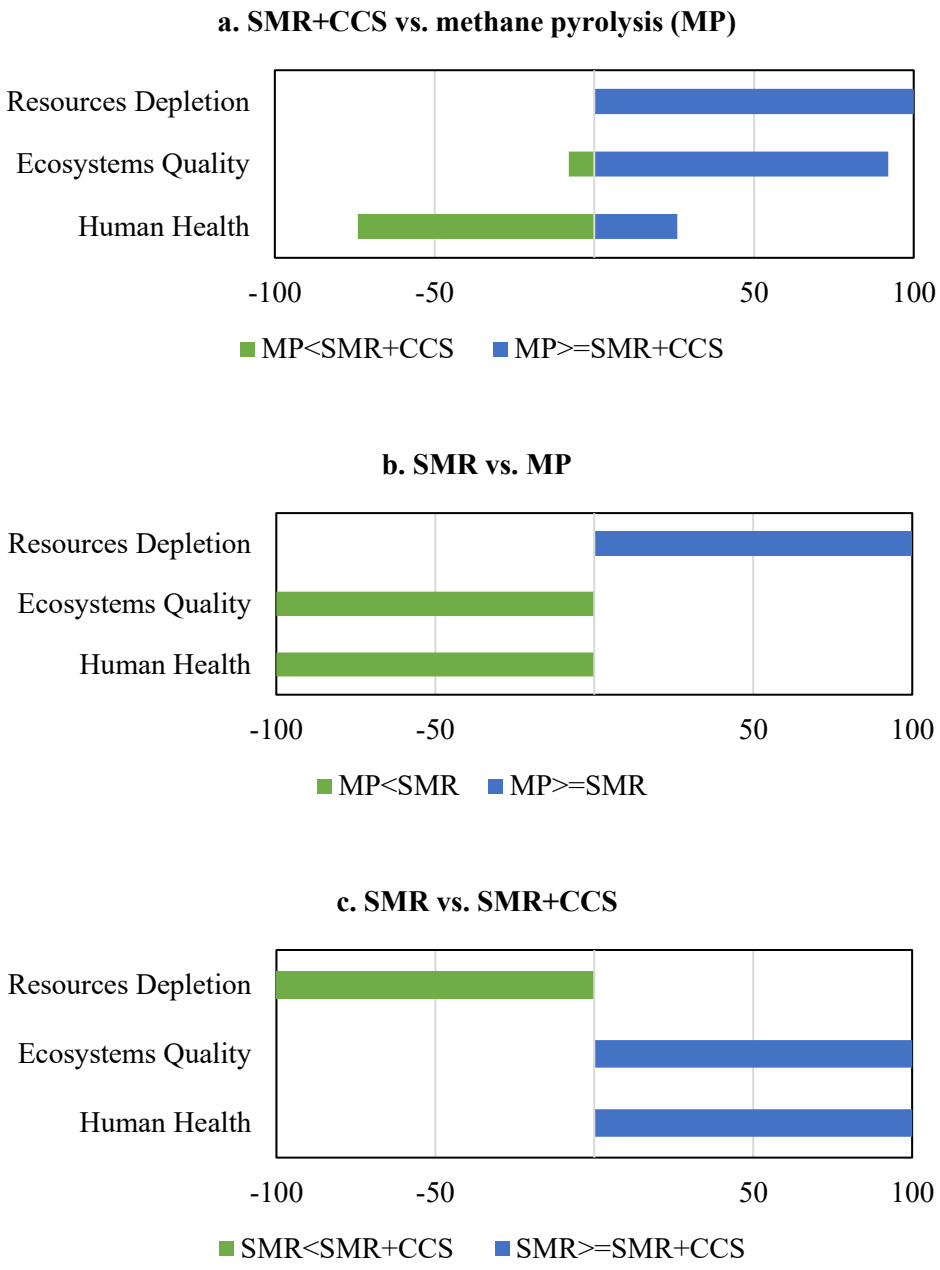


Fig.4.5 Pair-wise comparisons between the three cheapest technologies in terms of their TCH (i.e., probability of the impact of technology A being higher than that of B in a given category):(a) SMR+CCS versus methane pyrolysis, (b) SMR versus methane pyrolysis, and (c) SMR versus SMR+CCS. Comparisons are shown per impact category at the endpoint areas of protection.

Finally, Fig.4.5 shows the results of a set of pair-wise comparisons of those technologies displaying the lowest TCH (SMR with carbon capture and storage and methane pyrolysis). This analysis is carried out to shed further light on their performance, as they show similar

mean costs accompanied by uncertainty ranges that overlap in Fig.4.4. Notably, to further address the significance of the uncertainty differences between the two technologies, a Monte Carlo analysis for each of the two pathways was performed. The results were generated by repeating the comparison between the two pathways for 1,000 scenarios which follow a lognormal distribution that its standard deviation encompasses the 95% confidence interval (Fig.4.5). In Fig.4.5a, the blue bars represent the number of times that technology A is worse than B (i.e., A has a larger impact in that category), while the green bars show the probability of the converse. Thus, there is a 100% probability that methane pyrolysis is worse than SMR with carbon capture and storage in the resources depletion category, 26% in human health, and 92% in ecosystem quality. Furthermore, Fig.4.5b and Fig.4.5c show that methane pyrolysis outperforms SMR in human health and ecosystem quality (100% probability) and is worse in resources depletion (100% probability too). Finally, SMR with carbon capture and storage outperforms SMR in all the categories (100% probability) except for resources depletion, mainly due to its lower CO_2 emissions but larger energy requirements.

4.4 Conclusions

This work presented a detailed economic and environmental analysis of hydrogen production processes based on grey (fossil, including coal and natural gas), blue (fossil with carbon capture and storage), and green (renewable and from green sources) hydrogen. LCA principles were applied to assess the environmental performance, while the TCH, defined as the LCOH plus the monetised environmental impacts, was selected to quantify the economic performance.

The results demonstrated that environmental externalities could represent a large percentage of the total hydrogen cost (in the range 14-88%), which highlights the importance of including them in the assessment. SMR with carbon capture and storage emerged as the

lowest-total cost hydrogen production method, mainly due to its low production cost and lower direct greenhouse gas emissions (relative to SMR without carbon capture and storage), followed closely by methane pyrolysis. The latter route shows similar total costs compared to SMR with carbon capture and storage, yet its future LCOH is unclear due to the relatively low TRL and uncertain market opportunities for the solid carbon produced as a by-product. These fossil routes are followed by wind and nuclear electrolysis, which could become competitive if the electrolyser's CAPEX and electricity generation costs decrease significantly. Solar PV electrolysis is more expensive than wind and nuclear and shows also larger externalities due to the crystalline silicon panel manufacturing, thereby resulting in worse total economic performance. Finally, coal and biomass can be perceived as relatively cheap feedstocks, yet, in practice, their "real" cost is significantly higher due to their large externalities. Carbon capture and storage can decrease their direct CO_2 emissions substantially (which, in turn, reduces their externalities). However, carbon capture and storage cannot make them economically competitive compared to SMR, methane pyrolysis, or water electrolysis from nuclear and wind. We note that the results for the case of biomass, emerging as superior when impacts beyond climate change are omitted, strongly depend on the biomass feedstock and its location.

While the economic weights employed to monetise the environmental impacts might be controversial, the LCA results highlight that alternative hydrogen technologies may outperform the standard SMR technology when the full life cycle costs are included. Furthermore, while carbon capture and storage improves the environmental performance of the SMR technology substantially, in a broad sense, carbon capture and storage might not be regarded as sustainable technology. The reason is that SMR coupled with carbon capture and storage transforms fossil carbon into CO_2, which would then be stored in reservoirs with

limited capacity that would be exhausted at some point. The same applies to coal gasification that is based also on fossil carbon.

Future work should complement the analysis of externalities with other methods, with emphasis on absolute sustainability assessments based on planetary boundaries. Furthermore, more precise monetisation values should be established, which should be the focus of future research together with a better characterization of the uncertainties in the emissions and cost data.

Overall, the analysis undertaken herein widens the scope of the evaluation of hydrogen production systems to ultimately provide a more transparent assessment of alternative technologies based on sound criteria.

Chapter 5 THE TRUE COST OF HYDROGEN PRODUCTION FROM LIGHT HYDROCARBONS

In this chapter, we extended the investigated systems considered for hydrogen production and assessed their TCH as illustrated in Chapter 4. Steam reforming of natural gas (BAU), LPG, naphtha (both with carbon capture and storage (CCS) and without), autothermal reforming (ATR) with and without CCS, and methane pyrolysis were analysed for fossil-based hydrogen production, while electrolysis via wind energy was considered and analysed for renewable (green) hydrogen production. A new integrated system was proposed and analysed that combines the best features of ATR+CCS and the oxygen generated from the wind electrolysis as a by-product. Additionally, all the investigated production systems in Chapters 4 and 5 were fed into a linear programming (LP) model that aimed to explore carbon-neutral shares of production technologies with optimal TCH and GWP.

5.1 Background and problem statement

Reduction of the potentially catastrophic risks caused by climate change requires deep decarbonisation of all energy sectors. However, these changes require massive investment in technological, economic and social levels. Hydrogen has received increasing interest in recent years as a green energy carrier. Given its suitability across a range of energy applications and carbon-neutrality at the point-of-use [66], [131], hydrogen offers both a platform to store

electricity from renewable energy and the potential to be used in the transport, heating, or industrial sectors.

Hydrogen production technologies currently available rely on feedstock from either fossil fuels or renewable energy [49], [131]. The production of hydrogen from fossil-based options is referred to as grey hydrogen and involves thermal conversion processes mainly represented by a form of reforming and pyrolysis [132]. These processes claim to be the best in terms of production capacity and they are the most utilised technologies for hydrogen production in terms of maturity and efficiency [133], [134]. Among them, the reforming of hydrocarbons is the most applied technology and it can be classified into three classes: steam reforming, partial oxidation and autothermal reforming [75], [135]–[137]. The only technology currently used to produce hydrogen with low emissions is water electrolysis powered by renewable energy (green hydrogen), such as wind, solar or nuclear. Today, about 60 million tonnes of hydrogen are produced per year, of which 96% are produced from reforming of fossil fuel feedstocks (49% from natural gas, 29% from liquid hydrocarbons and 18% from coal) leading to high CO_2 emissions ranging from 10 to 25 kg CO_2-eq/ kg H_2 [65]. The remaining 4% is produced via water electrolysis.

Steam reforming (SR) involves the reaction between a hydrocarbon and steam in a reformer where a synthesis gas (mainly H_2 and CO) is generated. This syngas is then fed into two stages of high temperature and low-temperature water gas shift reactors (WGSR) to recover more H_2 and convert all the CO into CO_2. The hydrogen stream is further purified via pressure swing adsorption (PSA) to reach about 100% purity. The separated exhaust gas streams are either vented to the atmosphere or fed into a CO_2 capture system to be further purified to reduce the CO_2 emissions released to the atmosphere. The captured CO_2 can be then injected in depleted reservoirs or utilised via carbon capture and utilisation (CCU) processes [138]–[141]. Light hydrocarbons are usually preferred in reforming reactions

ranging from natural gas (NG), ethane, propane, butane, liquefied petroleum gas (LPG) which is a mixture of C3 and C4, light or heavy naphtha. Before introducing these raw materials into the reformer, a desulphurisation step is necessary to avoid the poisoning of the catalyst in the reformer. Steam methane reforming is the most common and developed process for large-scale hydrogen production with 74-85% energy efficiency [142].

Partial oxidation (PO) methods are mainly the reaction of hydrocarbons and oxygen to produce syngas, which is then fed into the same WGS reactors as in SR. Heavy hydrocarbon feedstocks such as coal and heavy oil residues are suitable raw materials for PO methods. Pure oxygen is required to partially oxidize the hydrocarbon raw material. An air separation unit (ASU), which is an energy-intensive and expensive process, is used to provide pure oxygen. Requirements for desulphurised feedstock and pure oxygen make this route less attractive compared to SR methods.

Autothermal reforming (ATR) methods are a combination of SR and PO methods. In this process, a hydrocarbon reacts with oxygen and steam in the same reformer. This combines the best features of both methods, as the heat generated from the exothermic PO and is used in the endothermic SR to increase hydrogen production [143]. As in the PO method, it requires pure oxygen, provided from an air separation unit (ASU), which makes it less attractive than the SR method. However, the process has the added benefit of producing a high-pressure CO_2 stream, which is suitable for sequestration.

An emerging technology for hydrogen production is hydrocarbon pyrolysis. This is a route where the hydrocarbon is pyrolysed into hydrogen and solid carbon. As it does not produce any CO_2, the WGSR and gas purification steps are not required in this pathway. The main hydrocarbon evaluated in this pathway is methane as it has the highest hydrogen to carbon ratio. The technology readiness level (TRL) is 3-5 as it is still under research and development[68]. The main barrier for this pathway is the limited market and demand for the

solid carbon produced with hydrogen. From an environmental point of view, methane pyrolysis could represent a more attractive alternative to SMR given the avoidance of CO_2 emissions during the production process. The main environmental emissions for this pathway are the supply chain emissions of natural gas. Therefore, assessing its performance against other technologies could provide major insights to take this approach into higher TRLs.

Green hydrogen, along with oxygen, is produced by splitting water applying renewable energy. The main technologies available include alkaline electrolysis cells, proton exchange membranes, and solid-oxide electrolysis cells. These technologies present different levels of commercial maturity, with alkaline electrolysers operating at a commercial scale, followed by PEM, and SOEC electrolysers still at the demonstration level. Despite the low emissions associated with these technologies, water electrolysis is still economically unattractive compared to production from fossil fuels [68], [69]. One of the main cost barriers is the capital costs of the electrolyser [70], whose cost contribution can vary significantly depending on the electrolyser type and working load (capacity factor), which is affected by the intermittent nature of renewable energy. Besides, the current cost of renewable electricity (wind and solar), still makes it hard to compete with fossil-based technologies [71].

An alternative to reduce direct CO_2 emissions from fossil-based technologies up to 99%, is to couple them with carbon capture and storage (CCS) [144]. Given the current portfolio for hydrogen production and the benefits of CCS, this option has been highlighted as the most sustainable way to deploy the hydrogen economy until green hydrogen becomes financially competitive [145]. Due to limited storage capacity and leakage potential issues of the captured CO_2, this strategy does not represent a permanent solution for the CO_2 emissions. However, it will provide a great way for a smooth transition to CO_2-free chemical products or fuels. As previously described, methane reforming is the predominant process to produce hydrogen. The reforming of different oil fractions is also possible and could provide an additional

valuable feedstock in the transition toward green hydrogen. However, their performance has not been yet addressed in the literature. Similarly, as we think about the transition, integration strategies among technologies are crucial to guarantee sustainable development.

The aim of this chapter is therefore to assess the economic and environmental performance of grey, blue, and green hydrogen according to current technologies available. On this basis, we propose to evaluate the reforming of different feedstocks with and without CCS. Also, we propose an integrated system combining an ATR system coupled with carbon capture and storage (CCS) that benefits from the oxygen co-produced in the water electrolysis via wind energy. The main motivation for the integration is to provide the high purity oxygen required for the ATR without having the ASU resulting in less CAPEX and energy consumption. Based on the monetary valuation of environmental impacts (i.e. externalities), we seek to provide total technology's costs that help to identify the best deployment strategies for a carbon-neutral hydrogen technology superstructure.

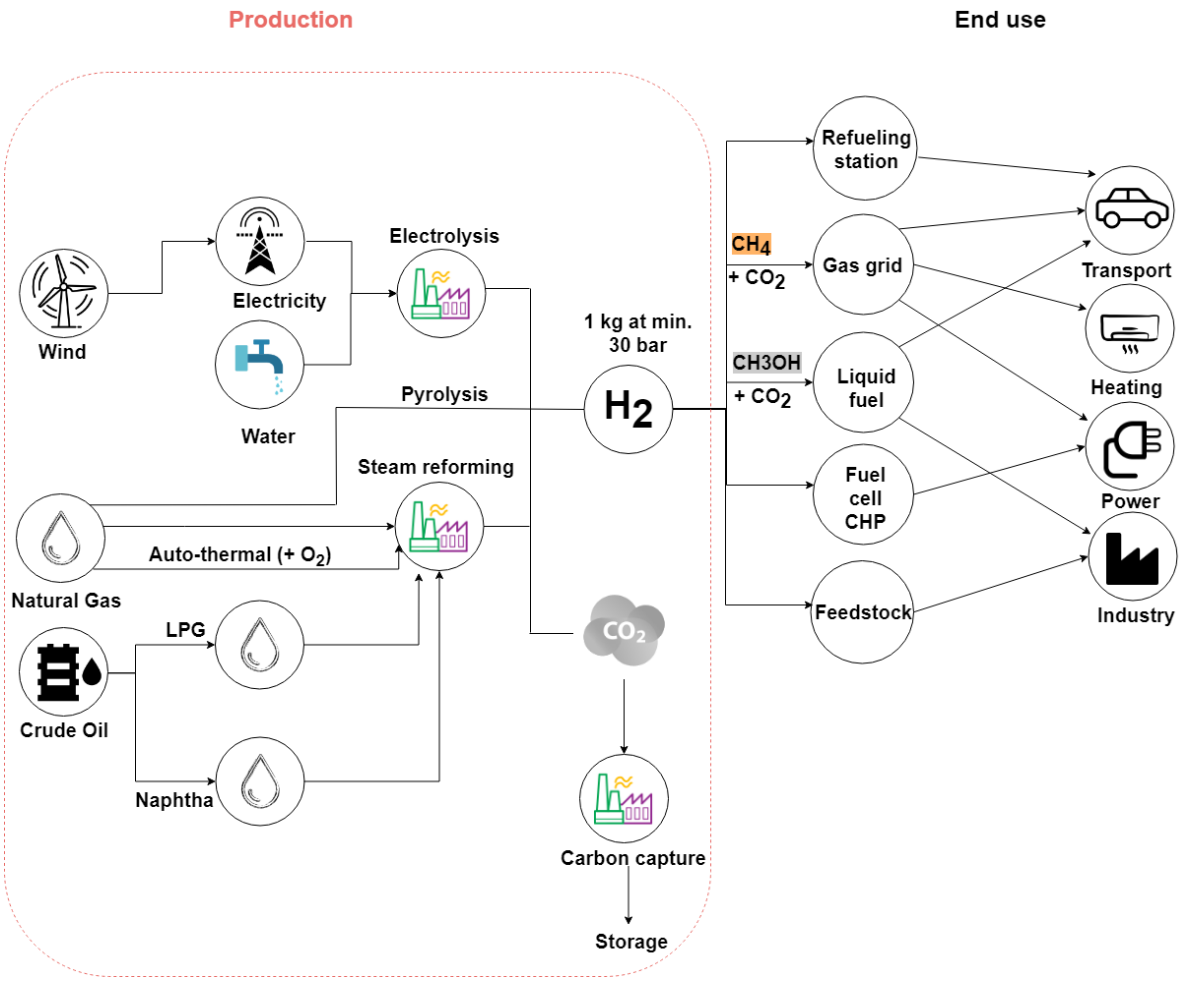


Fig. 5.1 The production pathways considered in the analysis to produce hydrogen at a minimum of 30 bar for any potential downstream use. The red dashed line represents the production phase of the hydrogen outlook.

5.2 Methodology

Fig. 5.2 illustrates the methodology followed to evaluate the different hydrogen production processes listed in Table 5.1. We combine process modelling for the steam reforming routes, economic analysis, LCA principles, and monetisation of the environmental impacts at endpoint levels leading to the carbon-neutral superstructure for hydrogen production. A detailed description of each step is now described.

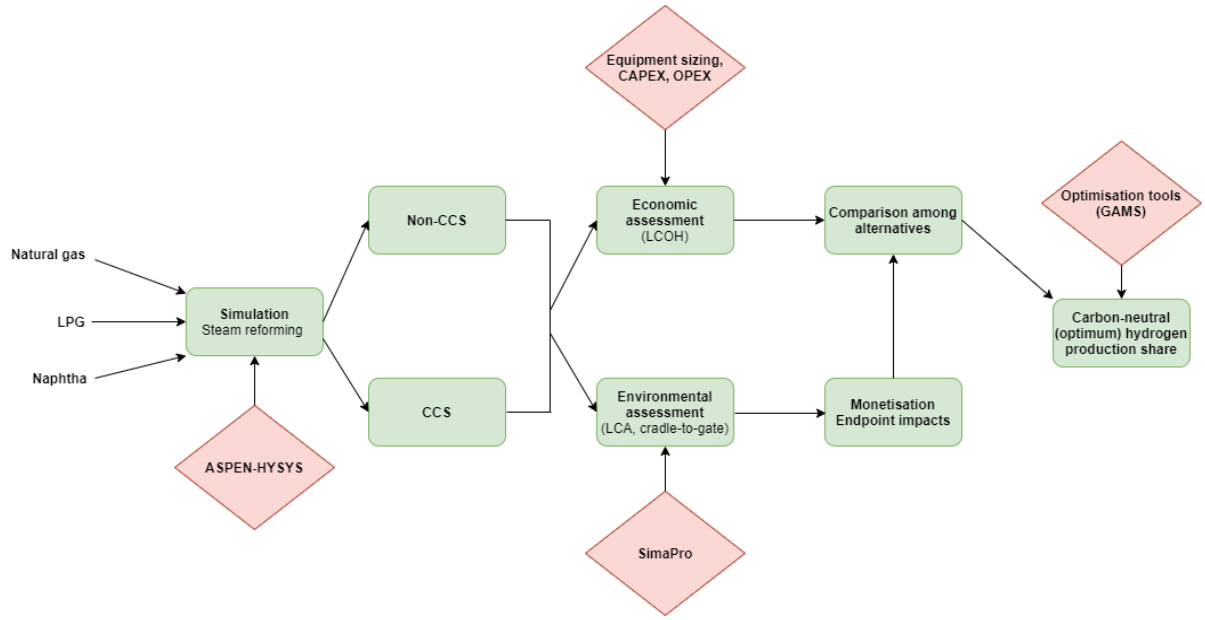


Fig. 5.2 Illustrative scheme of the methodology followed in the analysis that combines the techno-economic and environmental assessment with monetisation to generate a carbon-neutral superstructure of hydrogen production.

5.2.1 Selected hydrogen production routes

In Table 5.1, we present the 11 technologies considered in this analysis for H_2 production, which are described next.

Table 5.1 Investigated production pathways to produce hydrogen at 99.99% purity and 30 bar alongside their technology readiness levels (TRLs). TRLs data adopted from [146].

No.	Technology name	Short name	TRL
1	Steam methane reforming	SMR	9
2	Steam methane reforming with CCS	SMR+CCS	7-8
3	Autothermal reforming	ATR	9
4	Autothermal reforming with CCS	ATR+CCS	9
5	Methane pyrolysis	MP	3-5
6	Steam LPG reforming	SLR	9
7	Steam LPG reforming with CCS	SLR+CCS	7-8
8	Steam naphtha reforming	SNR	9
9	Steam naphtha reforming with CCS	SNR+CCS	7-8
10	Electrolysis via wind energy	Wind	9
11	ATR+CCS with O_2 integrated from wind	ATR+CCS*	9

5.2.1.1 Steam reforming with and without CCS

The process flow diagram (PFD) for the steam reforming (SR) route is shown in Fig. 5.3. This process is based on the one reported by Soltani *et al.*[128], where natural gas was used as feedstock (SMR). In this analysis, feedstocks are expanded to LPG (SLR) and naphtha (SNR). In essence, hydrocarbons (in these cases: natural gas, LPG and naphtha) react with steam to produce hydrogen and CO in a reformer at 815 ℃ and 19 bar (Eq. 5.1), followed by a water-gas shift reaction (WGSR) (Eq. 5.2) at high and low temperature to recover more hydrogen and convert the CO into CO_2:

$$\mathrm{C_nH_m} + \mathrm{nH_2O} \leftrightarrow \left(\frac{\mathrm{m}}{2} + n\right)\mathrm{H_2} + \mathrm{nCO} \tag{5.1}$$

$$\mathrm{CO} + \mathrm{H_2O} \leftrightarrow \mathrm{CO_2} + \mathrm{H_2} \tag{5.2}$$

The hydrogen produced and exhaust/tail gas are separated using a pressure swing adsorption (PSA) unit where hydrogen is further purified to 100% purity. The exhaust gases are combusted and recycled back to the reformer as heat. The hydrogen stream is further compressed to 35 bar to be suitable for any downstream uses.

Each of the previous feedstocks (SMR, SLR, and SNR) is also analysed under a scenario considering CO_2 capture (SxR+CCS) where x represents the feedstock type. The process considered in this section is shown in Fig. 5.3b, where the absorption of CO_2 is achieved using monoethanolamine (MEA) as a solvent. The treated (sweet) gas is further purified in a PSA unit, where hydrogen is recovered (Fig. 5.3c). The rich amine stream (MEA+CO_2) enters a distillation column to separate the solvent and send it back to the absorber while the CO_2 is purified to 99% and compressed to 110 bar to be injected into the storage site [30], [147], [148].

The process modelling data were simulated using Aspen HYSYS V9 and the obtained results presented in the mass and energy balances for each pathway were compiled in Table 5.2 and further used in the techno-economic and LCA assessments. Further details on the assumptions considered in this part of the analysis are available in Appendix B.

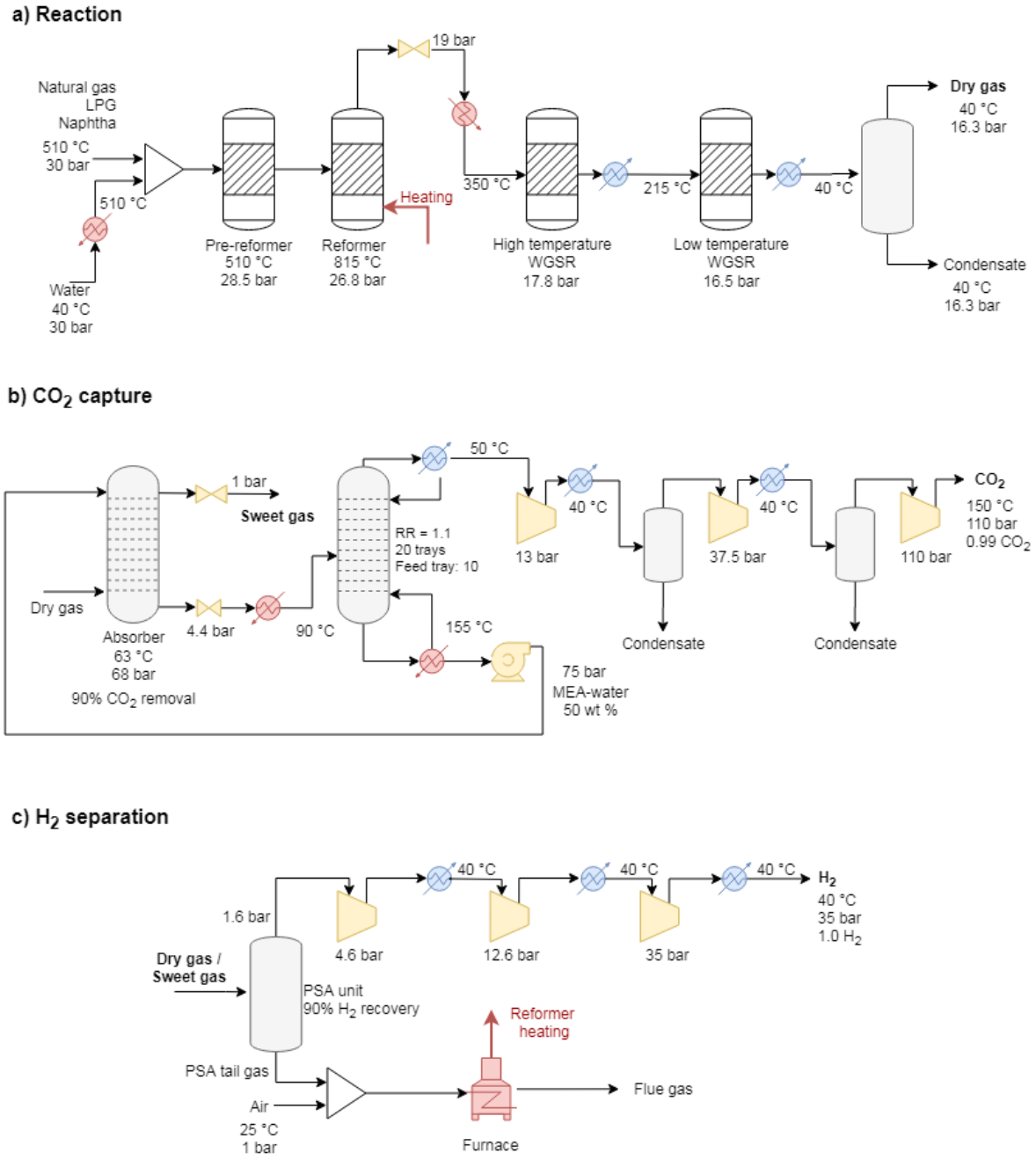


Fig. 5.3 Process flow diagram of the steam reforming process from hydrocarbons to produce hydrogen at 35 bars and 100% purity. The process was simulated in Aspen HYSYS based on data provided in Soltani *et al.*[128]

5.2.1.2 Autothermal reforming with and without CCS

This process combines the endothermic nature of the steam reforming of high hydrogen production with the exothermicity of the partial oxidation reaction. As a result, the heat required by the process is supplied by the partial oxidation reaction, avoiding the need for an external furnace, as the case with the steam reforming process [144]. In this process, both steam and oxygen are fed into the process and react simultaneously with methane according to (Eq. 5.3) [142].

$$CH_4 + \frac{1}{2}\mathrm{H_2O} + \frac{1}{4}O_2 \leftrightarrow \frac{5}{2}\mathrm{H_2} + \mathrm{CO} \tag{5.3}$$

After leaving the reactor, the syngas goes through the same WGS as in the steam reforming routes (Eq. 5.2). While air could be considered as the oxygen source in this route, the presence of nitrogen reduces the purity of the hydrogen. To avoid that, pure oxygen is required, which is obtained via an air separation unit. Mass and energy balances for this route were taken from Antonini *et al.*[144].

In addition to the scenarios ATR and ATR+CCS, we propose an integrated scenario ATR+CCS*, as shown in Fig. 5.4. This scenario refers to the case when the oxygen source comes from the co-produced oxygen in the electrolysis process via wind energy. The motivation behind this scenario is to give use to the oxygen generated as a by-product of the water electrolysis while reducing (or avoiding) the need for an ASU in the ATR process. Replacing this crucial yet energy-intensive and expensive component in the ATR could improve the environmental and economic part of the process and create synergies between technologies during the transition toward a full green hydrogen economy.

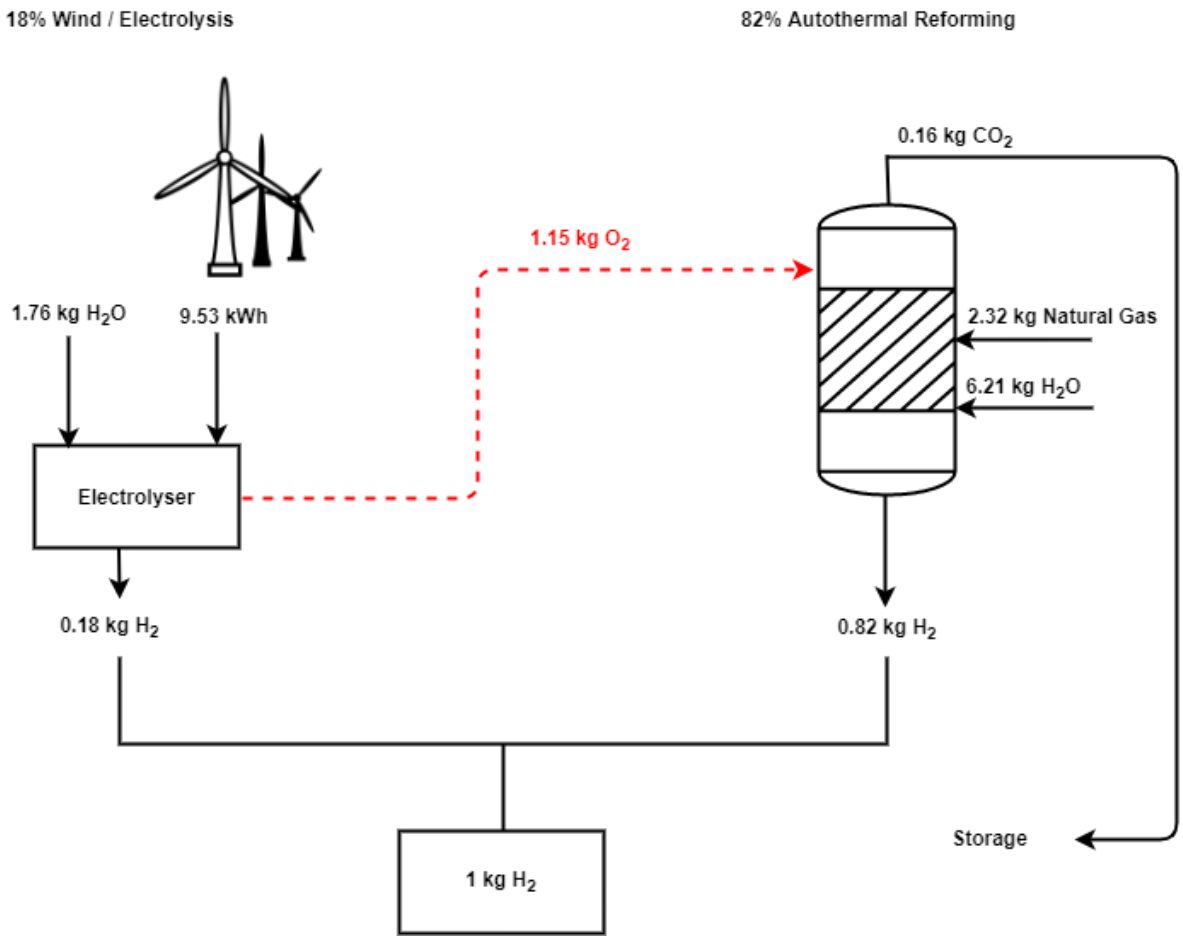


Fig. 5.4 The integrated system evaluated in this analysis which considers the production of hydrogen from ATR+CCS and electrolysis via wind energy. The motivation behind this approach is providing oxygen which is a by-product of the electrolyser as an input for the ATR+CCS system.

5.2.1.3 Methane pyrolysis

In this route, methane is decomposed into solid carbon and hydrogen (Eq. 5.4) at high temperatures (thermally or catalytically) [93]. This approach benefits from eliminating the WGS reaction step in SMR as no oxygen is present in the reactants and thereby reducing the CAPEX and OPEX compared to SMR [94]. The economics of methane pyrolysis is strongly dependant on the price of natural gas and the co-produced solid carbon [68]. Pyrolysis takes place in several forms such as high-temperature thermal, plasma-based, solid catalytic and molten metal catalytic systems [95]. In this context, a catalytic molten process is assumed

with a TRL of 3-5 (Table 5.1) [145]. Additional details on the process are further discussed in the literature [68], [113].

$$CH_4 \leftrightarrow C + 2H_2 \quad (5.4)$$

5.2.1.4 Electrolysis via wind energy

Water electrolysis takes place in an electrolyser, where the water molecules split into hydrogen and oxygen when an electric current is applied, as described in Eq. (5.5). Electricity sources can be from the grid or green sources (e.g. nuclear, solar or wind energies) [142]. Three electrolyser types are currently considered for hydrogen production: alkaline, proton exchange membrane (PEM) and solid oxide electrolysis cells (SOEC). Alkaline and PEM are commercially available and benefit from operating at low temperatures (70-90 °C). SOEC are still at demonstration scale and operate at high temperatures (650-850 °C) [105]. In this analysis, the PEM electrolyser is considered as it fits well with the study's scope of producing hydrogen at a minimum of 30 bar and high purity (≈100%) achieving high efficiency of 85% [106], [149]. We also consider wind energy as an energy source due to it is renewable nature and low global warming potential compared to other renewable energies (e.g. solar photovoltaics) [52]. Moreover, there is no economic/environmental allocation has been assigned to the co-produced oxygen in this route. The life cycle inventory data for this route was taken from a work by Colella *et. al.*[107] where further details can be found about this route.

$$2H_2O \leftrightarrow O_2 + 2H_2 \quad (5.5)$$

5.2.2 Economic analysis

Variations in direct hydrogen production costs are large, heavily dependent on the process variables and financial modelling assumptions used. Production costs were assessed on a levelised cost of hydrogen (LCOH - \$ kg^{-1} H_2) basis. Table 5.2 shows the LCOH values of the considered routes alongside their references. For the simulated processes (steam reforming routes), the LCOH was calculated following the formula:

$$LCOH = \frac{\sum_{t=1}^{T} \frac{(CAPEX + OPEX + Feed)}{(1+r)^T}}{\sum_{t=1}^{T} \frac{Production}{(1+r)^T}} \quad (5.6)$$

Where r is the discount rate and T is the plant life. The discount rate of 2.75% [150] and 20 years of operation was assumed [56]. Moreover, the LCOH was found in the literature for the rest of the investigated routes. Further economic data and assumptions are available in Appendix B.

5.2.3 Environmental assessment

Life cycle assessment (LCA) principles were applied to the systems under study following the ISO14040 standards [62], the main LCA steps followed are described in detail next.

5.2.3.1 Goal and scope

The goal of this work is to evaluate different hydrogen routes using a variety of feedstocks including fossil-based (natural gas and oil) or carbon-free (water electrolysis) sources. The functional unit is the production of 1 kg of H_2 pressurised to a minimum of 30 bar to ensure the consistent comparison between the fossil and carbon-free processes, as well as to satisfy hydrogen end uses. Power supplied for pressurization is assumed to have been supplied by an electricity source of the same carbon intensity as the production technology (i.e. wind in the electrolysis route and the electricity grid for the fossil routes). A cradle-to-gate scope has been

applied, which encompasses all the upstream processes (supply chain), point of production and additional pressurisation if needed. The system boundaries are illustrated in Fig. 5.1. Hydrogen end-use applications are excluded from this study but may require further detailed analysis to accurately match supply-demand markets. The location of the study was based in the United States (US).

5.2.3.2 Life Cycle Inventory (LCI)

The inventory analysis phase quantifies the LCI entries from the raw materials (feedstocks) requirements, energy consumption or generation, waste and emissions to air, soil and water considering the functional unit defined in the previous step. The LCI data for all the investigated technologies were retrieved from different sources, as presented in Table 5.2. Background processes were taken from Ecoinvent v3.4 accessed via SimaPro v9 [59], [151]. Mass and energy inputs and outputs of the foreground system, i.e., the hydrogen production processes, were retrieved from the literature [68], [108], [152]. For steam reforming-based routes, where natural gas, LPG and naphtha were used as feedstocks, mass and energy inputs were obtained from the simulation carried out in this study.

Furthermore, wind electricity was assumed to be 100% from onshore in the US, according to a study by IRENA [109].

The LCI data in terms of resources consumption and direct emissions released by the production plant for the considered technologies are presented in Table 5.2.

5.2.3.3 Life cycle impact assessment (LCIA)

The environmental impacts are quantified according to the Recipe 2016 methodology[60]. The focus is on the GWP (midpoint) and three impact categories at the end-point level: human health, ecosystems quality and resource scarcity. These end-point indicators result

from the aggregation of 18 midpoint impact categories: Global warming, ozone depletion, terrestrial acidification, freshwater eutrophication, marine eutrophication, human toxicity, photochemical oxidant formation, particulate matter formation, terrestrial ecotoxicity, freshwater ecotoxicity, marine ecotoxicity, ionising radiation, agricultural land occupation urban land occupation, natural land transformation, water use, mineral resource depletion and fossil fuel depletion.

5.2.3.4 Interpretation

In this step, we evaluate the outcomes of the LCI and LCIA phases to draw meaningful conclusions and report the total potential of each technology. In our case, the interpretation phase is underpinned by the use of a monetisation method, which converts the endpoint impacts into monetary values using appropriate conversion factors available in the literature[110].

Table 5.2 Life cycle inventory (LCI) of the investigated technologies to produce 1 kg of hydrogen at a minimum of 30 bar

Resources	**Unit**	**SMR**	**SMR+CCS**	**MP**	**ATR**	**ATR+CCS**	**ATR+CCS***	**Wind**	**SLR**	**SLR+CCS**	**SNR**	**SNR+CCS**
Natural gas	kg	3.31	3.32	4.86	2.80	2.82	2.82	-	-	-	-	-
Electricity	kWh	0.63	0.82	-	0.62	1.62	1.00	54.20	0.66	0.86	0.69	0.93
Water	kg	10.87	10.63	8.08	7.54	7.54	7.54	10.00	4.48	4.55	4.66	4.70
Naphtha	kg	-	-	-	-	-	-	-	-	-	6.47	8.64
LPG	kg	-	-	-	-	-	-	-	4.24	5.51	-	-
Direct Emissions												
CO_2	kg	8.06	1.57	2.50	8.99	0.19	0.19	-	11.56	1.73	13.26	2.06
Co-product												
Solid Carbon	kg	-	-	3.00	-	-	-	-	-	-	-	-
Oxygen	kg	-	-	-	-	-	-	8.00	-	-	-	-
Reference		[128]		[113]		[144]				[128]		
LCOH	USD2019	1.61	1.70	1.87	1.89	2.05	1.64	5.61	2.46	3.08	5.06	6.31
Reference		Calculated from [88]		[68]	[153]		[143]	[68]		Calculated from [56], [59]		
Product												
Hydrogen	kg	1										

5.2.4 Monetisation

In this analysis, the monetisation tools were applied based on the following approach: the three endpoint metrics (human health, ecosystem quality and resource depletion) were translated into monetary values using the values reported in Fankte *et al.* [110]. For the human health indicator, the monetary value was reported as 74000 €/ DALY. For the ecosystem quality indicator, the monetary value was taken as 9.5 x 10^6 €/Species.yr while the impact of resources depletion is already expressed in USD2013. All the monetised values were adjusted to USD2019 using the CEPCI. Note that monetisation enables a direct comparison of technologies, thereby providing valuable insight to policymakers. This approach has been used and applied in the literature previously to assess the production of hydrogen, methanol and propylene [83], [111], [145].

5.2.5 Total cost of the hydrogen production route

The total cost of any hydrogen production route refers to the summation of the monetised cost of the environmental impacts and the LCOH as described earlier by Eq. (4.7), presenting both the environmental and economic performances of the process.

The total cost indicator used in this analysis allows comparing different production pathway on the same monetary basis. Thereby, it helps in highlighting the major contributors to the total value in terms of lifecycle stages or direct LCOH, drawing meaningful conclusions and recommendations for the investigated production systems of hydrogen.

5.2.6 Nomenclature

The indices and parameters associated with the proposed model are listed below:

Indices

i	Technologies
d	Damage categories
J	Epsilon constraint solutions
N	Curve generation index

Parameters

c(i)	Cost of technology i
m(d)	Monetisation values
w(i,d)	Damage category of technology i

Variables

TC	Total cost
x(i)	Share of technology i
EI(d)	Environmental impact of damage category d

5.2.7 Carbon-neutral hybridisation model

As burden-shifting, improving one environmental impact at the cost of worsening another environmental impact, is a common pitfall in the LCA and sustainability assessments, a proper evaluation of the proposed alternative technologies and the optimum way for introducing them into the current hydrogen production system is crucial. In essence, we are interested in evaluating the hydrogen production technologies and find the production technology shares that reduce both the total cost (TC) and the global warming potential

simultaneously. The current shares of hydrogen production technologies are used as the basis for the analysis and referred to as the business-as-usual (BAU) [65]. To enlarge the set of evaluated technologies and further explore the full potential of them, we have included coal and biomass gasification with and without CCS (CG, CG+CCS, BG, BG+CCS) as well as electrolysis via nuclear and solar photovoltaics (nuclear, solar PV). Levelized cost and environmental impacts were taken from Al-Qahtani *et al.* [145], and are reported in Table B2 of Appendix B.

The optimal level of shares is quantified using a linear programming (LP) model. The objective of the model is to minimise the differences calculated of the new point that has new shares with the shares of BAU.

The total cost (TC) that was described earlier in Eq. 4.7 is first computed via Eq. 5.8, where each environmental impact (EI) category at endpoint levels (d=HH, EQ, RD) is multiplied by its monetisation value (m(d)) and combined with the LCOH.

$$TC = LCOH + \sum_{d} m(d) \times EI(d) \tag{5.8}$$

$$EI(d) = \sum_{i} w(i,d) \times x(i) \quad \forall d \neq GWP \tag{5.9}$$

$$LCOH = \sum_{i} c(i) \times x(i) \tag{5.10}$$

In mathematical terms, the new shares of technologies i are calculated using equations (5.9 and 5.10) where each technology i has different environmental impact categories d and levelised cost of hydrogen c. Therefore, the environmental impact is calculated by multiplying the environmental impact at endpoint level w(i, d) by the share of the technology x(i). Then, the levelised cost of hydrogen (LCOH) is calculated by multiplying the cost of each technology I by its share.

As the shares should always be 100%, we impose a constraint to the fractions of the new shares of technologies x(i) to be equal to 1 as shown in Eq. (5.11):

$$\sum_{i} x(i) = 1 \tag{5.11}$$

The difference between the BAU and new shares of technology i is referred to as SD(i) and is computed as in Eq. (5.12), where the share of technology x(i) is equal to the share of the same technology in BAU plus the SD(i). The absolute difference ASD(i) should always be greater than or equal to +/-SD(i) as computed in Eq. (5.13 and 5.14).

$$x(i) = x(i)_{BAU} + SD(i) \tag{5.12}$$

$$ASD(i) \geq SD(i) \tag{5.13}$$

$$ASD(i) \geq -SD(i) \tag{5.14}$$

After calculating the difference of new and BAU shares of all the technologies, a term referred to as a total distance (TD) is calculated. It is defined as the sum of ASD(i) for all the technologies and is computed in the model as shown in Eq. (5.15). This term can be interpreted as the indicator to identify the maximum and minimum objective function values.

$$TD = \sum_{i} ASD(i) \tag{5.15}$$

Multiple curves N are generated based on TD between BAU and the new points J on each curve. Furthermore, GWP and total cost for each point J are calculated and new shares are generated. Thus, the overall objective function seeks to minimise the total cost can be expressed in compact form as follows:

$$\min TC$$

$$s.t. eqs\ 5.8 - 5.15$$

We apply and solve this LP model in the General Algebraic Modelling System (GAMS) [154] software version 24.9.2 using the CPLEX solver.

5.3 Results and discussions

The results of the study are presented following three main sections. First, the LCA results for both the endpoint indicators with the GWP are presented and discussed. Second, the total cost of each technology is assessed by combining the LCOH and monetized environmental costs of the end-point indicators as explained earlier in Eq. (4.7). Finally, the results of the hybridisation model are presented and discussed.

5.3.1 LCA of hydrogen technologies

Fig. 5.5 presents the environmental impact values of the investigated technologies. In terms of GWP, larger CO_2 emissions are observed in all the fossil-based options without CCS. The values range from 10.49 kg CO_2-eq/ kg H_2 for SMR to 17.83 kg CO_2-eq/ kg H_2 for SNR. This is due to the increasing number of carbons from methane (C1) to naphtha (C7). Thereby, the direct CO_2 emissions from the reforming process are dominating the GWP performance if CCS is not integrated. The CCS versions of these technologies capture 90% of the direct emissions, releasing, therefore, a lower amount of CO_2 emissions compared to their unabated ones. However, higher contributions of their feedstocks and electricity consumptions are observed to meet the requirements for the CCS system retrofitted to the existing plant. This is a common trade-off of the CCS systems where CO_2 reduction comes at the cost of higher raw materials and utility requirements.

This is the case as the heating requirement increases to meet the stripper duty of the CCS plant and the electricity for the compression of the captured CO_2[89]. From this end, the interest in evaluating the production process over its life-cycle from endpoint perspectives has gained greater value and insight for a proper understanding of the effects of these different CCS approaches.

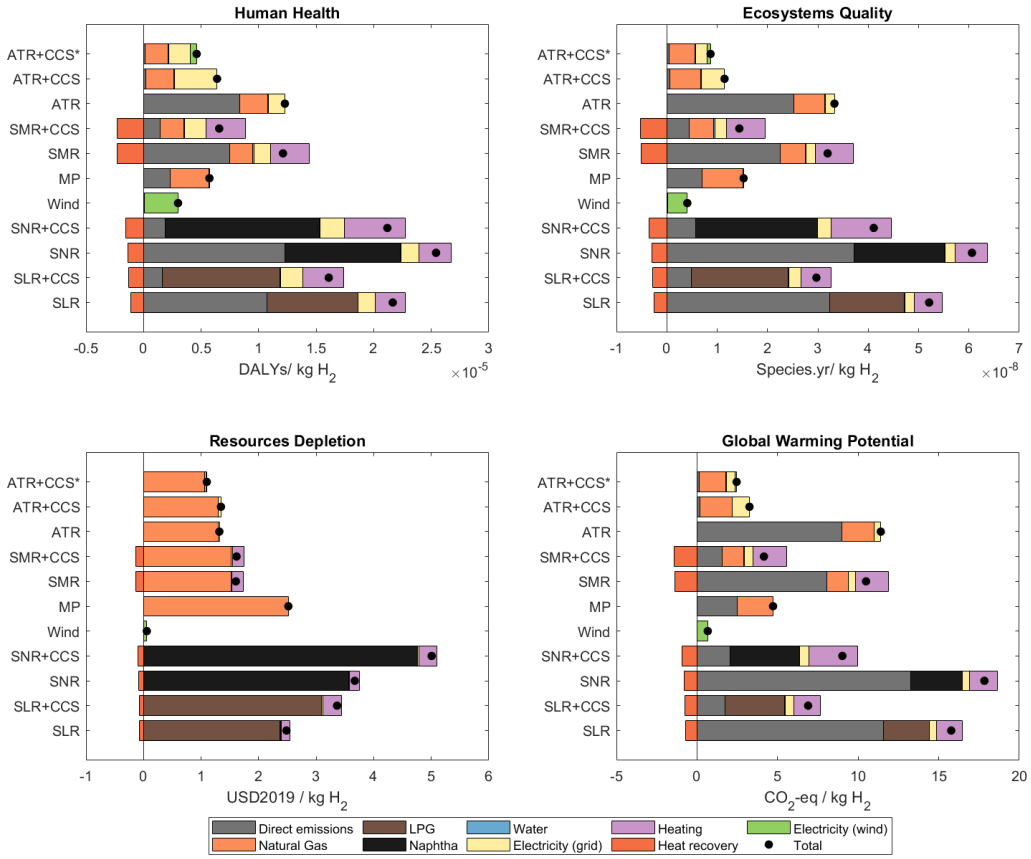


Fig. 5.5 The breakdown of the GWP and the end-point environmental impacts at endpoint levels of the investigated pathways from cradle to gate for the production of 1 kg of hydrogen at a minimum of 30 bar.

Methane pyrolysis releases lower CO_2 emissions amongst fossil-based production systems (4.72 kg CO_2-eq/kg H_2). Although methane pyrolysis emits almost no emissions during the process itself, CO_2 is released as a result of the combustion of natural gas used in the pyrolysis reactor. More natural gas feedstocks are needed for methane pyrolysis compared to SMR to generate the same amount of hydrogen [68].

For electrolysis-based hydrogen from wind energy, CO_2 emissions are the lowest compared to the rest of the technologies with a GWP value of 0.67 kg CO_2-eq/kg H_2. As the electrolysis process emits zero emissions, the emissions come mainly from the manufacturing phase of the wind turbines. These results are aligned with previous studies in literature [52], [55], [115], [118], [145].

The integrated ATR+CCS* system is the second-lowest CO_2 emitting technology after water electrolysis with a GWP value of 2.46 kg CO_2-eq/kg H_2. The use of the pure oxygen generated from the electrolyser resulted in lower energy requirements for the ASU by 25%, and thereby lower CO_2 emissions for the ATR+CCS* technology as shown in Fig. 5.4.

Fig. 5.5 also shows the endpoint results for the studied technologies. In the three categories, fossil-based technologies show the worst performance compared to water electrolysis powered by wind energy. Similarly, fossil-based routes with CCS (e.g. SMR+CCS and ATR+CCS) and methane pyrolysis are lower than their non-CCS ones confirming that implementing fossil-hydrogen with CCS (blue hydrogen) could lead to significant environmental savings for the short to medium term [155]. A deeper analysis of the environmental performance at the midpoint level (see Figure B1 in Appendix B) reveals that GWP has a significant impact on HH and EQ. As a result, high values in direct CO_2 emissions from the production phase would result in high values over HH and EQ [156]. After GWP, fine particulate matter formation (FPMF) indicator at midpoint levels is the second main contributor to the total HH as a result of the human intake of the particulate matter mainly

comes from the hydrocarbons leading to increased toxicity and thereby causing damage to the human health [60].

For the grey hydrogen routes (SMR, SNR and SLR), the environmental impacts are mainly driven by the nature of the feedstocks (natural gas and oil fractions) used during their production processes. SNR has the highest HH among the technologies due to high global warming performance as seen in Figure B1a in Appendix B. Although naphtha and LPG use relatively easy to produce feedstock, it requires multiple pre-treatment stages before the reforming stage due to feedstock impurities [136]. Pre-treatment stages aim mainly to remove sulphur alongside other impurities to avoid catalyst poisoning and coke formation [157]. SNR and SLR routes have higher HH and EQ than SMR making them less attractive technologies. The use of CCS increases the electricity consumed but lowers the overall impact in HH, EQ and GWP except for the resource depletion category as it requires higher feedstocks to meet the heating requirements for the desorption process. Methane pyrolysis shows lower HH and EQ compared to the SMR route by 53% and 52% respectively. Also, it does not require any electricity input, which further improves its performance as it avoids the impact embodied in the electricity production phase [75], [158].

For the clean energy sources (electrolysis from wind), it can be seen in Fig. 5.5 that the impact embodied in electricity is the main dominant factor. This impact is strongly connected to the manufacturing phase of the electricity generation facilities that power water electrolysis [54], [118], [159].

5.3.2 Total cost of hydrogen

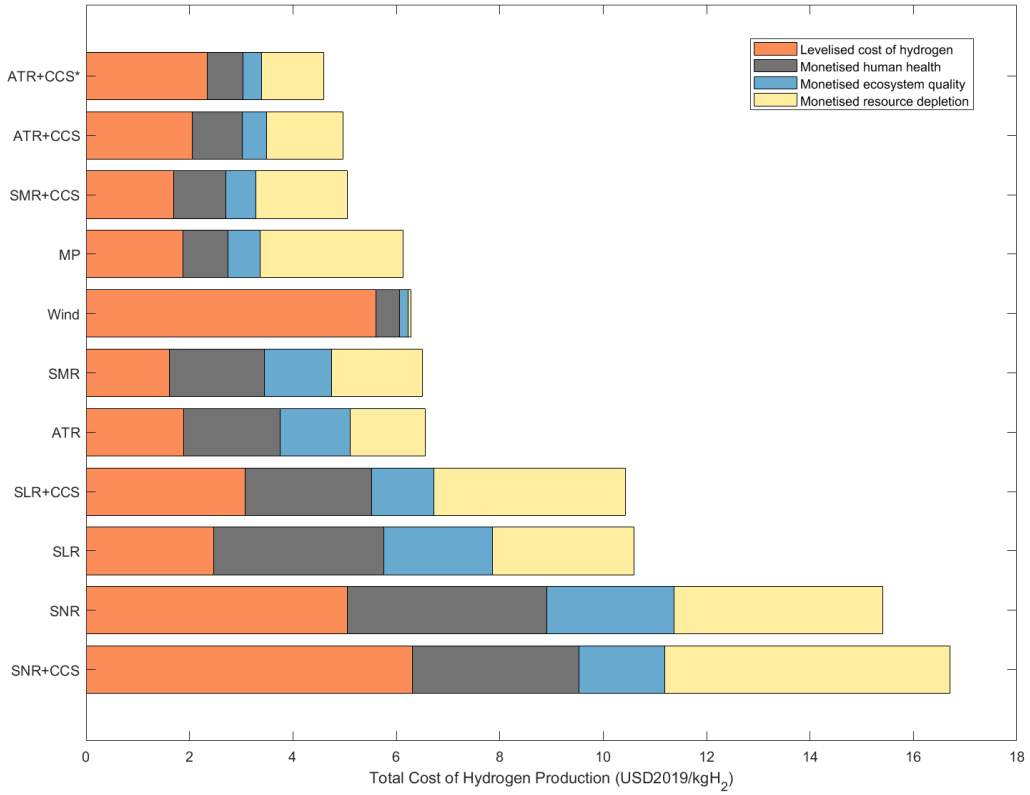


Fig. 5.6 The breakdown of the total cost of hydrogen production pathways by applying monetisation values to the endpoint environmental impacts combined with the levelised cost of hydrogen.

The total cost of hydrogen production after monetizing the environmental impacts and combining them with the levelised cost of hydrogen as explained earlier in Eq. (4.7) is shown in Fig. 5.6. The monetized environmental impacts account for significant fractions of the total cost for fossil-based routes (75% SMR, 66% SMR+CCS, 69% methane pyrolysis , 67% SNR, 62% SNR+CCS, 77% SLR, 70% SLR+CCS, 71% ATR+CCS) while direct production costs dominate the total cost for renewable routes (89% wind electrolysis). The monetised environmental impacts for the integrated scenario ATR+CCS* are reduced by 22% compared to the non-integrated case, showing the benefits of the proposed integration strategy described in Fig. 5.4.

Despite higher CO_2 emissions than electrolytic routes, the total cost is still the cheapest for natural-gas fossil routes, with the proposed integrated ATR+CCS technology being the most cost-effective despite showing higher LCOH compared to the standard SMR route without CCS (\$2.34/kg H_2 vs. 1.61/kg H_2 for SMR)[68]. More precisely, for SMR, the total cost is \$6.51 that is higher than its CCS counterpart (\$5.06/kg H_2 with an LCOH of \$1.70/kg H_2). This is due to the higher GWP in the former route, which results in larger impacts and, therefore, higher externalities (Fig. 5.5). The total cost of methane pyrolysis (\$6.13/kg H_2) is cheaper than that of SMR, emitting less CO_2 emissions and thus showing lower HH and EQ than SMR. However, this process consumes more natural gas than SMR and thus shows higher RD than the latter. SMR+CCS, ATR+CCS and the integrated ATR+CCS* represent the cheapest amongst other routes benefiting from both the improved environmental performance and relatively cheap production cost compared to green hydrogen from renewables. This highlights the importance of a smooth transition deploying CCS and benefitting from the existing hydrogen infrastructure until green hydrogen becomes cost-competitive [45], [53], [160]. Despite the low production costs for the oil feedstock (\$0.44/kg LPG and \$0.52/kg naphtha) [59], SNR and SLR still show high total cost values (\$15.41/kg H_2 and \$10.60/kg H_2, respectively). This is caused by the associated high environmental impacts, resulting in very large externalities. Indeed, naphtha and LPG routes are more expensive than SMR. Thus, oil-based technologies should be discarded from the pool of potential hydrogen production technologies.

5.3.3 Carbon-neutral hybridisation model

The results of the optimisation model M1defined earlier are presented in Fig. 5.7. Taking BAU as the reference point, the lowest total distance TD point to it is ATR+CCS* while the highest TD is achieved in BG+CCS. Thus, N5 represents the optimum curve and the *J* solutions in between represent the possible blends between those two optimum technologies. The results generated from the model suggest that a hybrid hydrogen production share can be further gradually improved by moving from BAU towards the carbon-neutral shares and negative GWP shares considering the externalities embodied in the total cost. For example, taking the closest generated solution J20 on the N1 curve (the closest point to SMR in Fig. 5.7), the GWP is 7.34 kg CO_2-eq/kg H_2, achieving a 45% reduction compared to the GWP of BAU (13.38 kg CO_2-eq/kg H_2). Furthermore, the total cost is \$6.02/kg H_2 that is 33% lower than the total cost of BAU \$8.92/kg H_2. The new shares of this solution are very similar to BAU which suggests the use of 49% SMR, 42% ATR+CCS*, 7% SLR and 2% wind electrolysis. These insights show the great potential of ATR+CCS* to reduce the GWP of the current shares of hydrogen production (BAU) with improved fossil-based processes while gradually increasing the shares of green technologies as their production costs decline in the short to medium terms. The optimal hybrid shares will strongly depend on the cost of the electricity of green sources (specifically wind and nuclear energies - Fig. 5.7). As costs of green hydrogen decrease, new technologies will appear on the potential shares.

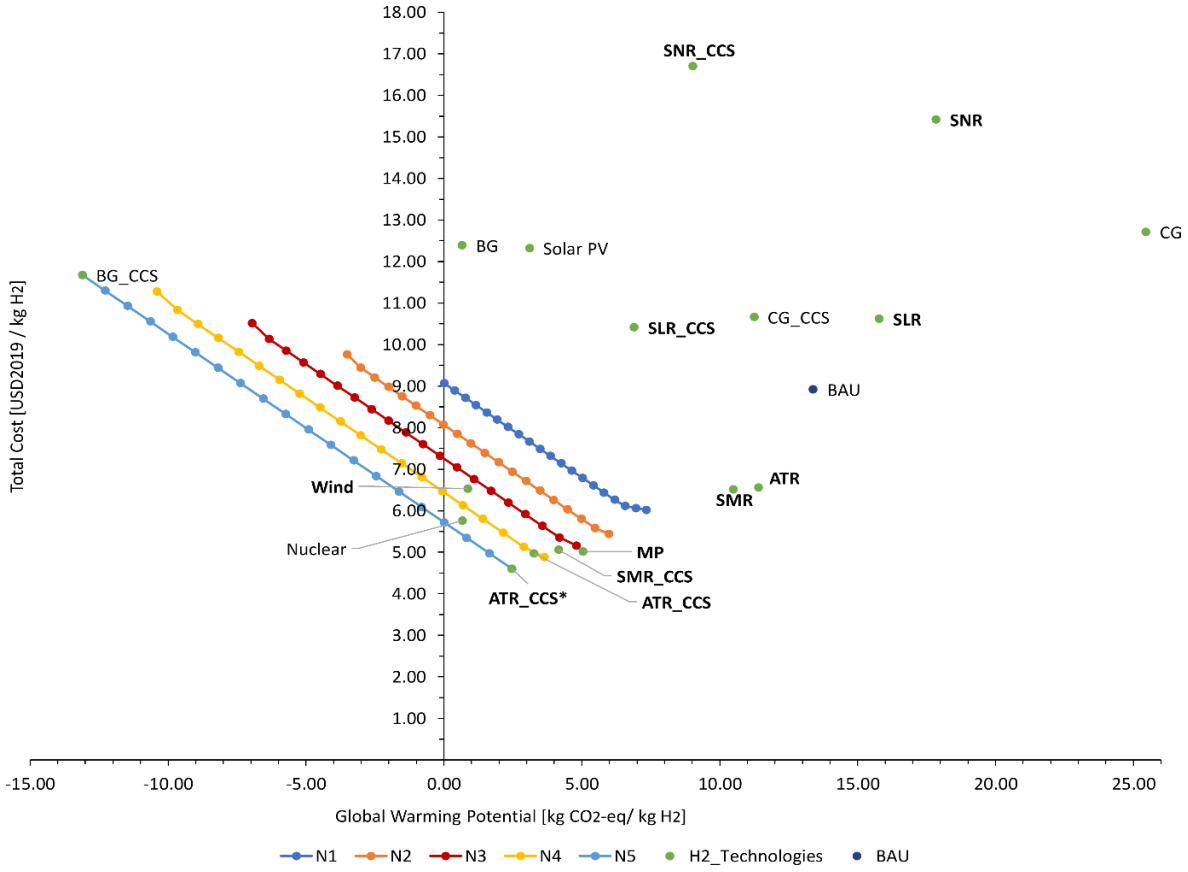


Fig. 5.7 The GWP vs. total cost for the considered hydrogen production routes in the analysis. The natural gas and oil-based production processes are shown in bold that was studied extensively in this study while the rest of the technologies were adopted from the previous work [145]. The generated curves *(N)* were obtained from the model with 20 solutions (*J)* on each curve. The new shares, total cost and GWP for each J on each N are presented in table B3 and B4 and figures B2-B6 in Appendix B. BG refers to biomass gasification, CG refers to coal gasification, nuclear and solar PV refer to the hydrogen produced from electrolysis via nuclear and solar energies respectively.

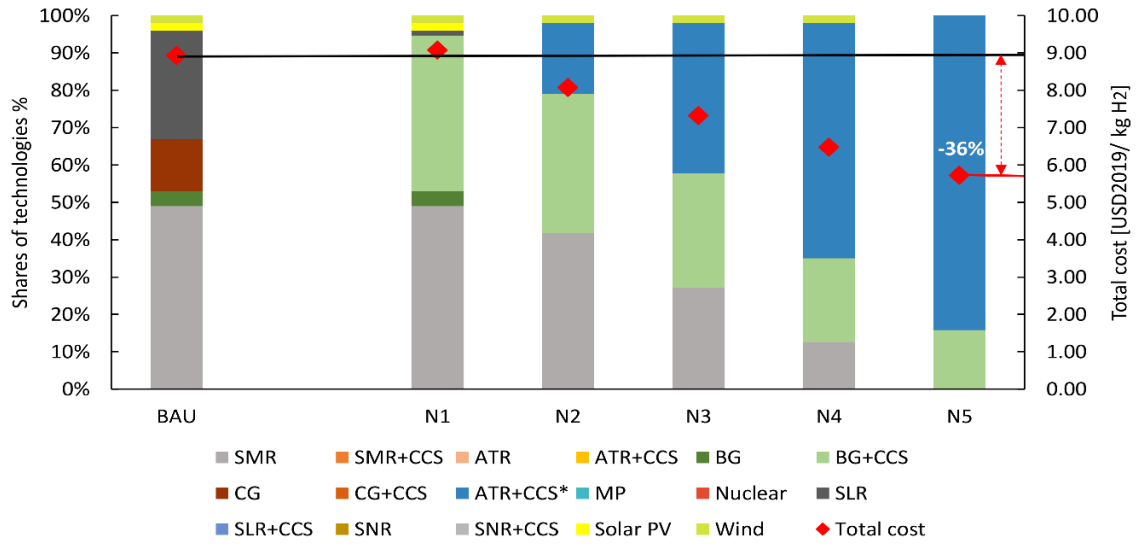


Fig. 5.8 Total cost of the BAU against the carbon-neutral (100% reduction of GWP relative to the GWP of BAU) point J on each generated curve N. The new shares of the optimum point on each curve alongside the shares of BAU. The black line represents the total cost of BAU and the red line shows the total cost of the cheapest total cost compared to BAU.

Fig. 5.8 shows selected carbon-neutral solutions on each curve from N1 to N5. The total cost of each solution is always lower than the total cost of BAU, except for N1 that is slightly higher due to the high externalities of BG+CCS which represents a high contribution in the mix of 42%. Further details on the high externalities of the biomass routes can be found in [145]. Interestingly, it can be seen that the generated solution (J17) for N5 would lead to a 36% reduction in terms of the total cost compared to BAU. This optimal hybrid solution would combine 84% of ATR+CCS* and 16% of BG+CCS.

Finally, these results will be affected by the scale-up of some potential technologies (e.g. methane pyrolysis, BG+CCS and ATR+CCS*). Under the current scenario, the obtained results highlight the importance of blue hydrogen in the transition towards green production pathways and encourage investing further in the research of the blue hydrogen with low TRL such as methane pyrolysis and ATR+CCS, along with the synergy strategies, such as the one presented here (ATR+CCS*).

5.4 Conclusions

Techno-economic and life cycle (LCA) assessments were carried out and applied to grey (fossil), blue (fossil with CCS) and green (sourced from green energy) hydrogen. Steam reforming for methane, LPG, and naphtha with and without CCS were simulated and evaluated from techno-economic perspectives. LCA approaches were used to evaluate environmental performance while the LCOH was chosen and considered as the economic indicator of the processes. The monetisation approach was applied to the environmental impacts at endpoint levels and combined with the LCOH leading to the total cost of technology. The total cost indicator allows a comparison between technologies on a monetary basis and thus would help to avoid burden-shifting, a common pitfall in LCA assessments.

Our results show that monetising the endpoint environmental impacts can present a large percentage of the total costs when added to the LCOH (from 11% to 77%) and emphasises the crucial role that such an analysis approach can play in policymaking. Also, assessing the technologies at endpoint levels provided a more holistic analysis by considering all the midpoint (problem-oriented) and endpoint (damage-oriented) environmental impacts in contrary to focusing on one category such as GWP.

The total cost analysis supported the conclusion that blue hydrogen plays a key role in the energy transition and thus deep decarbonisation as hydrogen is linked to all the CO_2 emitting sectors (e.g. transport and chemicals sectors). From fossil-based processes, ATR+CCS*, ATR+CCS, SMR+CCS and methane pyrolysis showed the lowest total cost technology compared to SMR. Such insight highlights the potential of CCS based technologies in the current need to lower fossil-based hydrogen. Moreover, it encourages investing in a low TRL technology as in the methane pyrolysis and finding new potential markets for the co-produced solid carbon that will further improve economic performance.

Furthermore, electrolysis-based hydrogen may be competitive in the future when the electricity and electrolyser's capital costs decline as the LCOH showed a high percentage of the total cost (e.g. ≈ 90% for wind/electrolysis). In the absence of economically feasible solutions for renewable energy storage, the intermittent nature of renewable energy would present a barrier for full green hydrogen adoption at present.

The proposed integrated system – ATR+CCS*– showed great environmental and economic performance, as it lies between blue and green hydrogen. Therefore, conducting further studies of this approach is recommended for further improvements.

The hybridisation model was formulated based on the current shares of hydrogen production (BAU) and solved to find the potential curves alongside their different solutions that differ in the new shares, GWP and total cost. The hybridisation model would help to find the lower total cost and GWP and thus drawing the transition to carbon-neutral shares and would even lead to negative GWP when the shares of green hydrogen increases. In this context, ATR+CCS* emerges as an appealing technology to operate, given its existing infrastructure of ATR, more environmentally friendly with a marginal increase of economic cost as opposed to SMR.

Overall, the analysis presented here is intended to expand upon the current evaluation process for assessing sustainable hydrogen production to provide a more robust assessment of alternative hydrogen production pathways based on a detailed set of evaluation criteria which includes all impacts from economic, environmental, and social aspects.

Chapter 6 SUSTAINABILITY ANALYSIS OF TODAY'S TRANSPORTATION-POWER NEXUS

Methanol from captured CO_2 provides a more sustainable alternative to gasoline due to its low carbon footprint, yet it requires a large amount of renewable energy that is used for hydrogen production and could be used instead to decarbonise the electricity mix. Hydrogen produced from electrolysis powered by wind energy has shown to be the greenest hydrogen sources as studied in Chapters 4 and 5 and will be investigated in this chapter. A techno-economic and environmental analysis of methanol produced from captured CO_2 and renewable energy are conducted to shed light on the transportation-power nexus. The investigated scenarios differ in how the carbon-free energy source – electricity from wind – is used to either decarbonise the electricity mix or produce green methanol to displace conventional fossil fuels. The assessment is carried out for six countries that differ in the composition of their electricity mix and gasoline consumption.

6.1 Background and problem statement

Carbon capture and utilization (CCU) has recently gained a lot of interest in the chemical industry. Carbon dioxide (CO_2) captured from point sources (e.g. coal-fired power plants) or directly from the atmosphere (e.g. direct air capture) can be used as feedstock for the production of a wide range of added-value chemicals, such as methanol, formic acid and

ethylene [161]. This contrasts with conventional carbon capture and storage (CCS), which brings about no tangible economic benefits. However, the full potential of CCU for CO_2 reduction remains unclear on a global scale. To start with, most CCU routes are based on products with low demand, unable to chemically store the amount of emissions needed to keep global warming well below the 2 °C limit – from the current 35 Gtons-CO_2-eq/year down to 6 Gtons-CO_2-eq/year – given the current estimated CCU potential of around 3.5 Gtons-CO_2-eq/year [41], [162], [163]. Most existing CCU routes are furthermore uneconomical or show low technology-readiness levels (TRL), which raises the question of whether it would be better to deploy first alternative mitigation strategies. Considering all this, it has recently been suggested that CCU should not be regarded as an effective large-scale mitigation strategy, but rather as a complement to other mitigation options that might only be deployed when deemed profitable [41].

Of the available CCU technologies, CO_2 conversion into fuels using renewable energy has gained significant interest. The most prominent option is methanol production by reacting CO_2 captured from point sources (e.g. power plants) with hydrogen (H_2) generated via water electrolysis powered by renewable energy (e.g. wind or solar). This CO_2 hydrogenation route to fuels is an attractive strategy to overcome the dependence on fossil-based fuels and could lead to a feasible “methanol economy” [164]. Methanol could be used in standard spark-ignition vehicles in a blend with gasoline and thus play an important role in the transition towards electric vehicle fleets. At the same time, it could find broad applications in the chemical sector as a platform chemical with high TRL technologies for methanol conversion into olefins and aromatics [165].

The use of alcohol-based molecules such as methanol and ethanol has been tested and used for years. Methanol has been used as a fuel for car and drag racing particularly in the United States and China. Trials to use methanol as a fuel also took place in the 1980s and 1990s over

large fleets until the focus shifted to ethanol production in "fuel farms" [166]–[168]. Oxygenates, namely fuel additives that have alcohol or ether, can optimise an engine's performance and efficiency by increasing the air-to-fuel ratio and thereby reduce exhaust emissions [169]. Methanol and ethanol have been proven to decrease net emissions in comparison to diesel and gasoline with minimal impact on engine performance [170], [171]; the exception being an increase in nitrogen oxide, although this can be tackled by modifying the combustion system to limit the peak pressure rise rate [172].

In contrast to ethanol production, methanol production does not impact the use of farmlands, i.e. the food-energy nexus, and can also be used as a feedstock for certain polymers and polyesters [173]. Of course, the use of methanol or ethanol does not come without challenges. Alcohols can degrade thermoplastics, thermosets and metals, and so car construction materials need to be modified, including the fuel delivery hoses and components in contact with the fuel [173]. This extends to construction material used in a gas station as well.

A proper assessment of methanol-based fuel production requires the consideration of life-cycle environmental impacts and costs across the broader chemical supply chain. This assessment is particularly challenging since the electricity used to power water electrolysis in green methanol synthesis may as well be used to decarbonise the electricity mix. Understanding such a complex *transportation-power nexus* is nonetheless key to sustainable development [53].

These cross-sectoral interactions are often overlooked in the literature, where the focus has been on analysing the GWP while paying little attention to other important environmental categories such as human health, ecosystems quality and resource depletion [174]. A thorough life-cycle assessment (LCA) across the transportation-electricity nexus and covering a wide range of impact categories is, therefore, still lacking.

To fill in this knowledge gap, we conducted a full life-cycle assessment of methanol production from CO_2 in several representative countries. The focus is on understanding the links between the transportation and power sectors and their potential competition for renewable energy sources. The proposed methodology combines, for the first time, detailed process simulation with life-cycle environmental impact and economic assessment with expanded systems boundaries, while accounting for the main operational constraints of the electricity grid. In this chapter, we evaluated the behaviour of both sectors simultaneously and the implementation of cleaner technologies based on CCU and water electrolysis. This regional assessment on the best use of wind energy was not studied before. The implications of the findings would provide useful insights for policymakers from sustainability perspectives.

6.2 Materials and methods

We carry out an environmental and economic assessment of alternative uses of renewable energy and carbon capture to shed light on the transportation-power sector as it stands today. The main steps and assumptions adopted in this assessment are described next, including the scenarios definitions (Fig. 6.1 and Table 6.1). A comparison is conducted for six countries, which differ in their electricity mix and total annual gasoline consumption: The USA and Germany are representative of a medium coal-based electricity mix (25-50%); Poland and China of a heavy-coal mix (>50%); and the UK and France of a light-coal mix (<25%) [175], [176].

6.2.1 Goal and scope definition

A standard attributional LCA is considered. We conduct a cradle-to-gate analysis of electricity production and a well-to-wheel analysis of transportation. We account for all of the impacts in the life cycle of electricity production, while transportation accounts for fossil fuels/raw materials extraction, fuels production and distribution, and direct emissions from fuel combustion in engines.

A key point in the LCA concerns the definition of a functional unit that is consistent with the analysis of the transportation-power nexus and enables a fair comparison across alternatives offered by CCS, direct air capture (DAC) and renewable electricity. Our functional unit considers both the amount of electricity delivered and the total amount of kilometres travelled by gasoline vehicles, as shown in Table 6.2. This dual functional unit enables a fair assessment for the use of renewable wind energy to either decarbonise the current mix or to produce hydrogen via water electrolysis for the synthesis of methanol to power vehicles. Electric vehicles (EVs) are excluded from the analysis, as this would require replacing the current vehicles fleet, which is seen as a longer-term decarbonisation strategy.

Considering all the above, we defined several scenarios that differ in how the demands in electricity and fuel are satisfied (Fig. 6.1, Table 6.1):

- Scenario BAU: All electricity is covered by the current electricity mix, which is analysed for every country on an annual basis, and all vehicles remain powered by gasoline – business-as-usual (BAU).
- Scenarios M90: All gasoline for vehicles is replaced by an M90 blend consisting of 90% methanol and 10% gasoline on a volume basis. The following three electricity and methanol production routes are furthermore considered:
- Scenario M90-NG: All methanol is produced from syngas derived from natural gas and all electricity is covered by the current energy mix.

- Scenario M90-DAC: All methanol is produced from CO_2 and H_2, where the former is obtained from DAC and the latter generated by water electrolysis powered by wind energy. In the DAC system assessed, only heat in the form of natural gas is considered as the process energy requirement [177]. Hence, all electricity is covered by the current energy mix without the need for capacity expansion to support DAC.
- Scenario M90-CAP: All methanol is produced from CO_2 and H_2, where the former is captured from point sources and the latter generated by water electrolysis using wind energy. To cover the CO_2 demand for methanol production, the electricity mix is modified by first deploying CCS in coal power plants, then CCS in natural gas power plants as necessary.
- Scenario DEC: All electricity is covered by a decarbonized mix achieved by deploying the maximum amount of wind, subject to certain operability constraints (see below). This is complemented by the deployment of CCS in coal and natural gas power plants. All vehicles remain powered by gasoline as in the BAU.

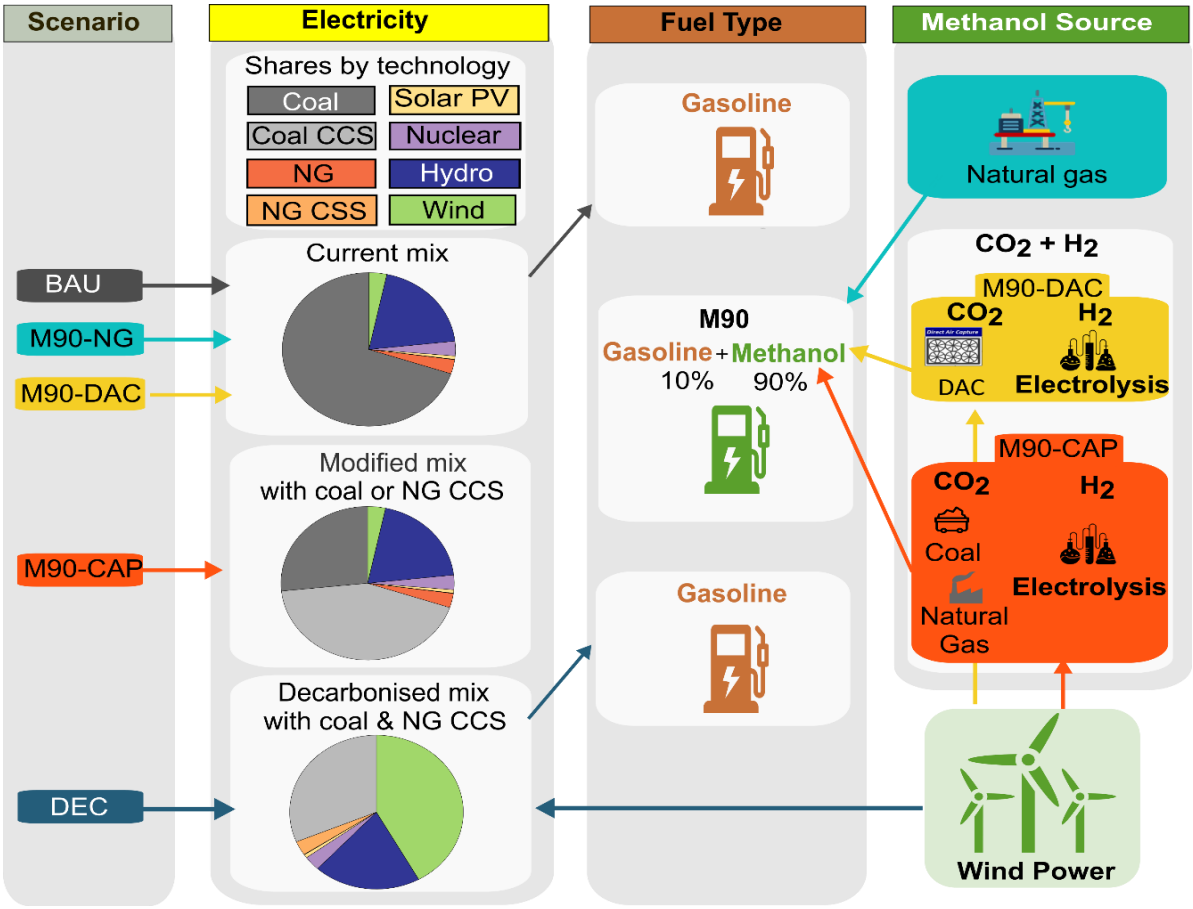


Fig. 6.1 Production pathways of electricity and transportation fuels in each investigated scenario. Further details on the scenarios are in Table 6.1.

Table 6.1 Transportation and power pathways in each investigated scenario.

	Transportation				Power
Scenario	Fuel Type	Methanol Source	CO_2 Source	H_2 Source	Electricity grid
BAU	Gasoline (BAU)	-	-	-	Current (BAU)
M90-NG	M90 (90% MeOH and 10% gasoline by vol.)	NG (Fossil-based)	-	-	Current (BAU)
M90-DAC		CO_2+H_2 (CO_2-based)	DAC	Water electrolysis from wind energy	Current (BAU); since the DAC system assessed consumes only heat from natural gas with no electricity input [177]
M90-CAP			Coal/NG - CCS		Modified mix where CCS is installed [first] in coal and [then in] natural gas [power plants] until capturing enough CO_2 to cover the demand for methanol synthesis used in the transportation sector
DEC	Gasoline (BAU)	-	-	-	Decarbonised grid with the wind+ CCS for coal and NG power plants

Abbreviations; BAU – Business as usual, NG – Natural gas, CCS-Carbon capture and storage, DAC – Direct Air Capture

Table 6.2 Dual functional unit using 2015 data for gasoline consumption and electricity generation in the investigated countries.

Country	Total travelled distance by gasoline vehicles [km/year] [178]	Total electricity generation [TWh/year] [175]
USA	5.60×10^{12}	3.97×10^{3}
UK	2.06×10^{11}	3.36×10^{2}
France	1.16×10^{11}	5.65×10^{2}
Germany	2.75×10^{11}	6.38×10^{2}
Poland	5.67×10^{11}	1.65×10^{2}
China	1.23×10^{12}	5.58×10^{3}

The calculations of scenario DEC considers three constraints associated with the electricity mix operation. The first constraint enforces a minimum 1:1 ratio between dispatchable and

non-dispatchable technologies to ensure a reliable grid operation [179]. Here, dispatchable energy refers to technology that can be used for on-demand power generation such as energy sources such as fossil fuels, bioenergy and hydro energy; whereas non-dispatchable energy includes solar and wind power [180], [181]. A 1:1 ratio ensures that for every 1 W of renewable energy capacity there is 1 W of on-demand back up energy during periods of adverse weather [179]. The second constraint is to keep the country's electricity demand satisfied. The third constraint is to avoid exceeding the maximum generation potential for each power technology. The maximum amount of wind introduced for decarbonising the transport and power sectors is within the wind potential of each country. Here, the wind potential refers to the total wind generation capacity that can be installed in a country, given limiting factors such as land utilisation (Table C11 in Appendix C) [182], [183]. The LCA calculations are therefore repeated for all six countries to reflect their current electricity mixes and electricity and fuel demands.

6.2.2 Life cycle inventory (LCI) analysis

The LCI covers the life-cycle emissions to air, soil and water, feedstock procurement and waste production in reference to the functional unit (step 1). Data from several sources are combined as follows. Mass and energy flows associated with methanol production are based on a published Aspen-HYSYS simulation model [83], [184]. Those associated with hydrogen production from wind and CO_2 from CCS and DAC are modelled using literature data combined with background system data from environmental databases [52], [59], [147], [177]. LCI entries for the conventional (fossil-based) methanol production are retrieved from Ecoinvent v3.4 [59]. All the calculations are implemented in the LCA software SimaPro v9 interfaced with Ecoinvent v3.4 and using emissions data from GREET to estimate the direct emissions from combustion engines – see below for details [151], [185].

6.2.2.1 Transportation

The conventional route of methanol production uses syngas as feedstock, whereas the CCU route relies on catalytic CO_2 hydrogenation [186], [187]. CO_2 can be either captured from relatively large point-source emitters (e.g. power plants) or removed directly from the atmosphere (direct air capture) [16]. Hydrogen can be produced via steam reforming of natural gas (SRNG), biomass, or water electrolysis [74], [188]. Herein, the focus is on H_2 generated via water electrolysis, a technology that has been shown to provide the best environmental performance in terms of GHG emissions if the electricity is obtained from clean energy sources such as nuclear, wind or solar [131], [149]. Since the CCU route consumes CO_2, it can potentially make methanol a CO_2 sink on a well-to-tank basis [20], [160], that is, without considering the emissions released during the combustion in the vehicles' engines. When used in the transport sector, green methanol reduces the demand for oil extraction and processing, while contributing also to mitigating the CO_2 emissions from power stations [53], [164].

6.2.2.2 Methanol production from syngas (well-to-tank)

The conventional process for methanol production from syngas (scenario M90-NG) relies on a $Cu/ZnO/Al_2O_3$ catalyst, which allows the reactors to operate under conditions in the range of 210-270 °C and 50-100 bar. Carbon monoxide and hydrogen are fed to the reactor and then catalytically converted into methanol according to the following reaction:

$$CO_{(g)} + 2H_{2(g)} \leftrightarrow CH_3OH_{(l)} \quad (6.1)$$

The necessary data to calculate the LCI entries of this process are from Ecoinvent v3.4 accessed via SimaPro v9 (Table C6 in Appendix C).

6.2.2.3 Methanol production from CO_2 (well-to-tank)

The process flow diagram (PFD) for this route (scenarios M90-DAC and M90-CAP) is shown in Fig.6.2. Further details on the process flowsheet and operating conditions can be found in reference [83]. In essence, CO_2 reacts with hydrogen to produce methanol, while competing with the reverse water-gas shift (RWGS) reaction:

$$CO_{2(g)} + 2H_{2(g)} \leftrightarrow CH_3OH_{(l)} + H_2O_{(l)} \quad (6.2)$$

$$CO_{2(g)} + H_{2(g)} \leftrightarrow CO_{(g)} + H_2O_{(l)} \quad (6.3)$$

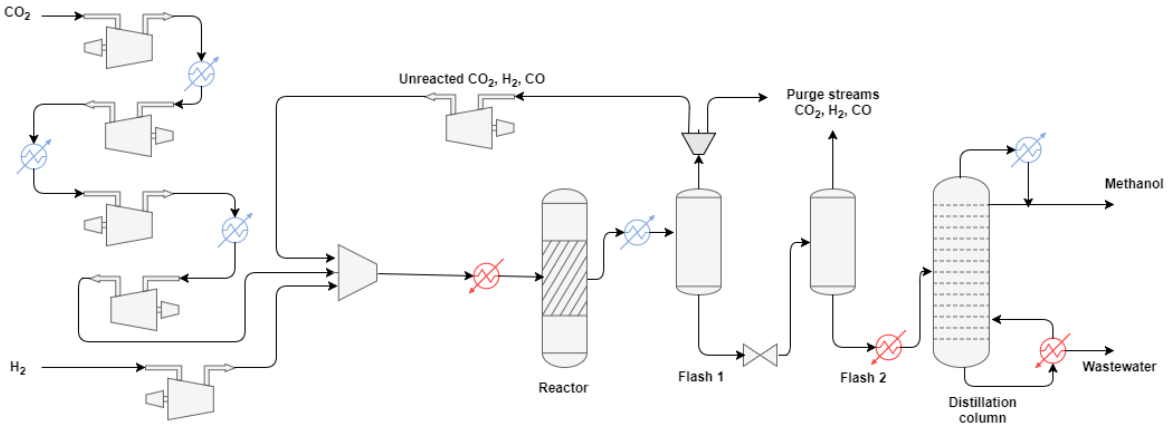


Fig.6.2 Process flow diagram of methanol production using CO_2 with hydrogen produced from water electrolysis via wind energy.

The produced methanol and water are separated from the unreacted gases in a first flash vessel. The unreacted gases are recycled back to the reactor inlet after purging around 1 wt% of the stream to prevent inerts from accumulating [83]. The mixture of methanol and water is further purified in a second flash vessel. The liquid outlet from the flash is heated to 80°C and then fed to a distillation column. Methanol is recovered from the top of that column, with a purity of >99.9 vol%, while the water recovered from the bottom is sent to treatment.

Several alternative methanol production routes are derived from this general process that differs in the source of CO_2 and H_2 used as feedstock:

- Hydrogen from water electrolysis powered by wind energy: This technology is modelled using data from [52].
- CO_2 capture from power plants: The modelling of CO_2 capture in coal power plants follows the work by Iribarren [147] which considers absorption with monoethanolamine (MEA), the most mature and studied CCS process. CO_2 capture in natural gas power plant considers a pre-combustion process as modelled by Iribarren [189]. Note that allocation between the electricity and captured CO_2 in the same power plant is not necessary here since both the power and transport sectors are assessed simultaneously.
- CO_2 capture from the atmosphere using DAC: The considered DAC technology adsorbs CO_2 selectively from the air using potassium hydroxide as the sorbent. The process removes about 50% of CO_2 and the treated air is returned to the atmosphere. The adsorbed CO_2 is released by heating the adsorbent. The CO_2 is finally compressed to reach the operating conditions in the plant. The LCI is sourced from [177].

The collected LCI data for hydrogen, CO_2 from a point source and DAC are provided in Tables C2, C3 and C4 of Appendix C.

6.2.2.4 Methanol (tank-to-wheel)

The tank-to-wheel (TTW) emissions (Table 6.3 and C8 in Appendix C) are estimated using the GREET software [185]. The focus is on the vehicle operation phase only, omitting the production, manufacturing, maintenance, and end-of-life phases. The reason for this is that internal combustion engines (ICE) can use indifferently blends of methanol and gasoline or only gasoline, so accounting for the vehicle impact would not add any discriminatory power to the analysis. The M90 fuel containing a mixture of 90% methanol and 10% gasoline on a

volume basis. It was reported to be the most efficient methanol/gasoline fuel blend with a 7% higher efficiency compared to conventional gasoline fuel [190]. Methanol also has a higher octane number and heat of vaporisation compared to gasoline that leads to higher thermal efficiency and power output [191]. The main emissions per km during the operation phase (tank-to-wheel) are shown in Table 6.3, using the recommended engine efficiency value from GREET [185] as a measure of kilometres travelled per unit of fuel used. Gasoline (well-to-tank): The well-to-tank (WTT) LCI entries for gasoline (Table C7) are retrieved from Ecoinvent v3.4 [59]. The gasoline consumption per total km travelled in each country is taken from [178].

6.2.2.5 Gasoline (tank-to-wheel)

Similar to the M90 fuel, the TTW emissions of gasoline (Table C8 in Appendix C) are estimated from GREET [185] for internal combustion engine vehicles, as shown in Table 6.3.

Table 6.3 Tank-to-wheel emissions for the fuels (Assuming an ICE efficiency of 22.5%) [185].

Fuel	Fuel consumption	GHG-100	PM10	NO_x	CO	VOC
	MJ/km	g/km	g/km	g/km	g/km	g/km
Gasoline	2.81	192.3	3.3×10^{-3}	6.87×10^{-2}	1.6	7.28×10^{-2}
M90	2.63	183.0	3.3×10^{-3}	6.87×10^{-2}	1.6	7.28×10^{-2}

6.2.2.6 Electricity:

The technology shares in the current electricity mix of each country are taken from [175] (Figure C1 in Appendix C). The changes in the electricity mix applied in Scenarios M90-CAP and DEC have been described earlier as part of the goal and scope definition (Fig. 6.1). Inventory data for all the power technologies are taken from Ecoinvent v3.4 [59].

6.2.3 Life cycle impact assessment (LCIA)

The environmental impacts are quantified according to the Recipe 2016 methodology [60]. The focus is on three impact categories at the end-point level. Human health, ecosystems quality and resource scarcity. These end-point indicators result from the aggregation of 18 mid-point impact categories at the midpoint level: Global warming, ozone depletion, terrestrial acidification, freshwater eutrophication, marine eutrophication, human toxicity, photochemical oxidant formation, particulate matter formation, terrestrial ecotoxicity, freshwater ecotoxicity, marine ecotoxicity, ionising radiation, agricultural land occupation urban land occupation, natural land transformation, water use, mineral resource depletion and fossil fuel depletion.

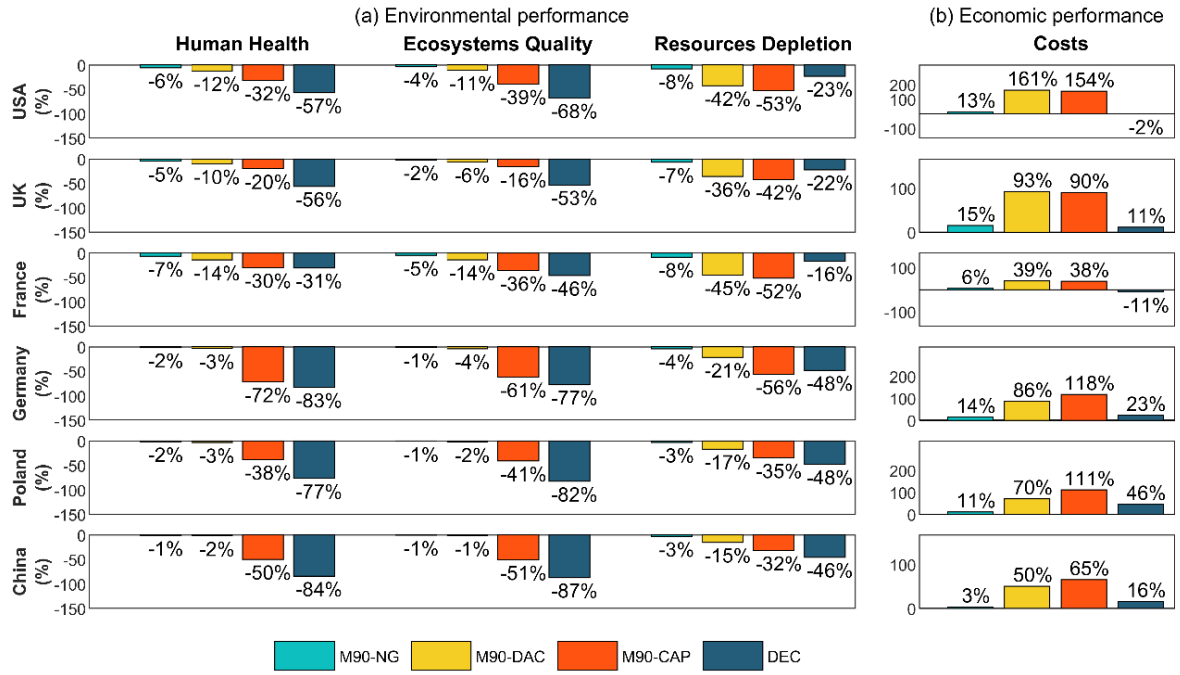
6.2.4 Economic assessment

Concerning the transportation sector, the cost analysis considers the production costs of methanol (Table C1 in Appendix C) and gasoline considering the total travelled distance in a year for each country using appropriate efficiency conversion factors (Table 6.2) [177], [192], [193]. Notice that the cost of introducing methanol tanks in the fuel stations is excluded from the analysis. Apart from the current lack of data, the infrastructure will need to be modified regardless of the fuel chosen, and it represents a small cost of the CCU deployment scenario. For the electricity sector, the levelised costs of electricity (LCOE) is considered as the main economic indicator based on the data reported in [194] (Table C10 in Appendix C).

6.3 Results and discussion

Fig.6.3 shows the overall economic and environmental performance attained in each scenario for every country, where the base case (scenario BAU) is taken as the reference for comparison. Full details of the corresponding electricity mixes are reported in Figure C1 in Appendix C.

Fig.6.3 Environmental and economic performance attained in all the scenarios relative to the base case scenario



(BAU) for all the six countries considered in the analysis.

It is noticeable that the largest improvements in environmental performance in the human health and ecosystem categories are attained in scenario DEC for all of the countries. This scenario is followed by scenario M90-CAP, then scenario M90-DAC, and ultimately scenario M90-NG. Regarding resources, the largest predicted improvement is in scenario M90-CAPfor the USA, the UK, France, and Germany. By contrast, the electricity mix in China and Poland is heavily reliant on coal and the highest improvement is in scenario DEC which introduce about 40% of wind in the mix. Electricity is found to be the largest contributor to the total

environmental impact in all of the countries (between 50–97%, depending on the category and country, (Figures C7–C12 in Appendix C). This relative contribution is highly dependent on the electricity mix, the vehicles fleet, and the electricity and transportation demands.

In terms of economic performance, scenarios M90-DAC and M90-CAP ($ 0.24-0.26/km) are clearly worse than scenarios BAU, M90-NG and DEC ($ 0.05-0.07/km). This is mainly due to the higher cost of methanol production from CO_2, which is itself the result of the high cost of hydrogen from water electrolysis ($7/kg H_2 including the compression cost to 30 bar) [192]. Notice that scenario M90-CAP is cheaper than scenario M90-DAC in the USA, the UK and France, and vice versa in Germany, Poland, and China. This is because the electricity mix of the latter countries would require more coal coupled with CCS (40-43%) compared to the former countries (2-26%), thus incurring in higher costs (Table C10 in Appendix C). Instead, scenario M90-DAC relies on the current electricity mix since the DAC technology only uses heat from natural gas without further electricity input [177].

Focusing on the USA case study now, it can be seen from Fig.6.3 that scenario M90-CAP outperforms the fossil-based scenarios in all of the environmental categories (HH: -32%; EQ: -39%; RD: -53%). Recall that the electricity mix in scenario M90-CAP deploys CCS in coal plants (Fig.6.4 – top plot) leading to significant reductions in environmental impacts, (Fig.6.4 – bottom plot). The environmental impacts worsen when replacing the CO_2 from coal power plants in Scenario M90-CAP with CO_2 from DAC in scenario M90-DAC. This is attributed to the large heat requirements of 8 MJ for each kg of CO_2 captured using the DAC technology, which is sourced from natural gas. These results are also consistent with published studies of DAC [45], [195]. The use of renewables or even low-grade heat to power this technology could lower its environmental footprint, albeit making it potentially more costly. Scenario M90-NG performs slightly better than scenario BAU in all of the environmental impacts as well (HH: -6%; EQ: -4%; RD: -8%), but it raises the cost due to the higher production cost of

M90 from syngas ($0.07/km) compared to that of pure gasoline ($0.05/km). Similarly, the cost is predicted to increase in scenario M90-CAP, since the M90 blend with methanol from CO_2 hydrogenation ($0.24/ km) is not yet economically viable; and even less in scenario M90-DAC due to the low efficiency of the DAC technology ($0.26/km).

Moving on to scenario DEC finally, all of the environmental impacts are also reduced compared to scenario BAU (HH: -57%; EQ: -68%; RD: -23%) in addition to reducing the cost by 2%. We reiterate that CO_2 is captured and stored in scenario DEC, while the captured CO_2 is used to produce methanol in scenarios M90-DAC and M90-CAP, which is then released back into the environment after combusting the M90 fuel.

Analysing the electricity mix in the USA (Fig.6.4 – top plot), the wind share in scenario DEC increased from 4% to 50% after introducing the maximum amount of wind energy into the current electricity mix (scenario BAU) while meeting the energy systems constraints on the final mix. The coal share is phased out and the natural gas share (22%) is coupled with CCS. These changes also explain why scenario DEC is cheaper than scenario BAU in the USA, where wind energy ($73.6/MWh) is cheaper than coal ($95.2/MWh) and natural gas ($75.1/MWh) [194]. Consequently, the savings resulting from this substitution offset the extra costs of CCS installation on the remaining natural gas power plants. The breakdown of the total environmental impacts of electricity generation (Fig.6.4 – bottom plot) reveals that coal and natural gas in the USA represent the largest contributors to the total impact (scenario BAU). Introducing as much wind as possible in the mix, phasing out coal and deploying CCS coupled with natural gas all together, enables substantial improvements in scenario DEC.

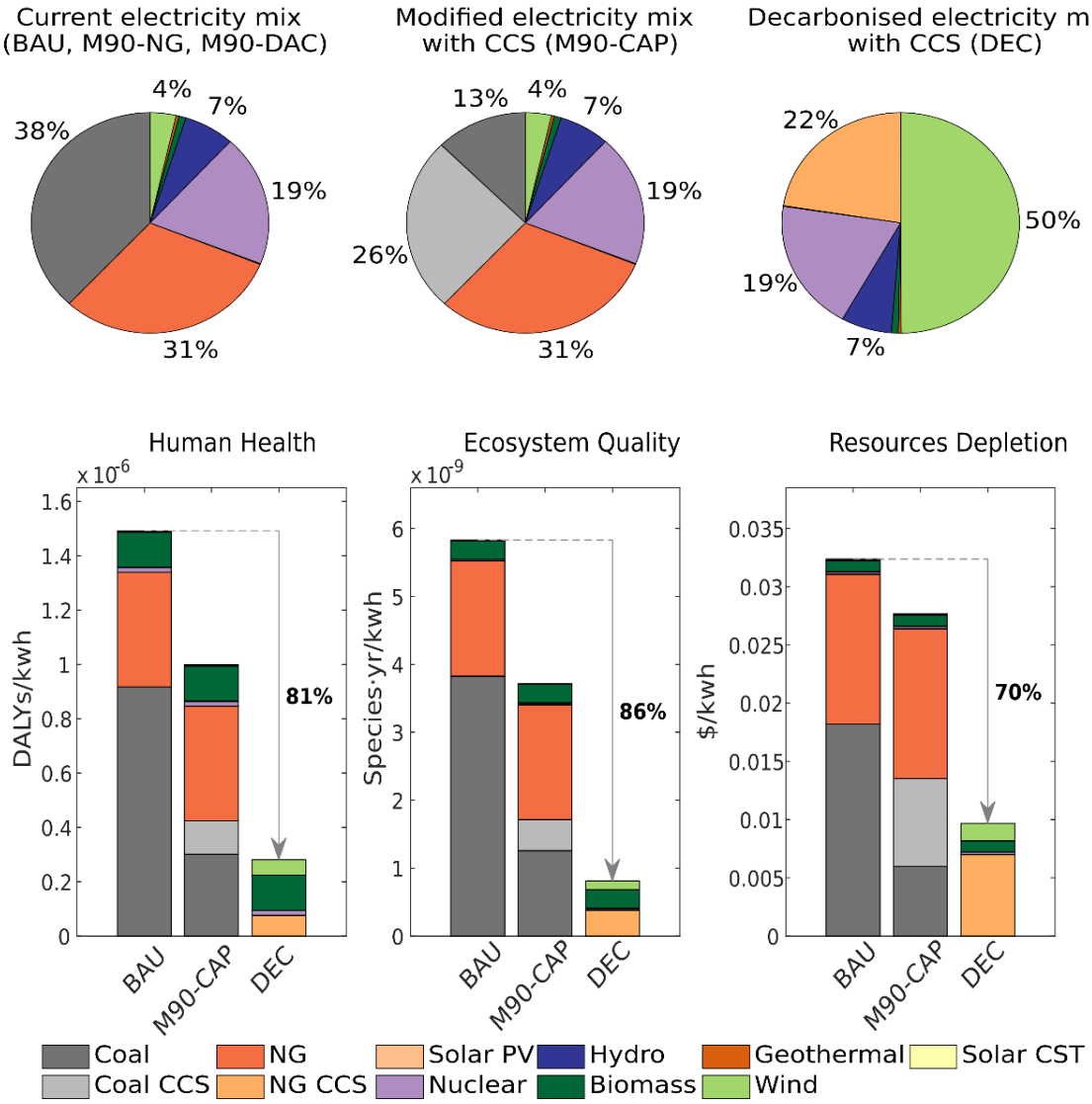


Fig.6.4 The technology shares (top plots) and contributions to the end-point environmental impacts (bottom plots) in the USA case study for each scenario – current mix (which is the basis for scenarios BAU, M90-NG and M90-DAC), modified mix (scenario M90-CAP) and decarbonised mix (scenario DEC)

A similar analysis of the other five countries (Figures C2--C6 in Appendix C) shows that scenarios M90-NG, M90-DAC, and M90-CAP – which differ in their methanol type – all generate lower environmental impacts than scenario BAU, yet by increasing the total cost. In all of the countries but France the total CO_2 needed to produce the M90 blend (scenario M90-CAP) can be met by CCS on coal power plants only; while in the French scenario, 71% of the

required CO_2 is obtained from coal power plants and the remaining 29% is captured from natural gas power plants.

Decarbonizing the mix by introducing as much wind as possible while adding CCS capacity to the remaining coal and natural gas shares under scenario DEC provides large reductions in the environmental impacts compared to scenarios BAU and M90-fuels from different methanol sources. In Poland and China, where the electricity mix is heavily reliant on coal (Figure C1 in Appendix C), these reductions are seen across all three end-point impacts. In the USA, the UK, France, and Germany, where the coal share is lower, scenario DEC also provides the largest reductions in terms of human health (HH) and ecosystem quality (EQ) indicators but is inferior to scenario M90-CAP in terms of resources depletion (RD) indicator.

Additional benefits from using wind energy and CCS to decarbonise a country's electricity mix rather than producing methanol emerge when comparing the cost indicators among countries (Fig.6.3 and Figures C7–C12 in Appendix C). The reason behind scenario DEC being more expensive than scenario BAU in the UK, Germany, Poland and China is two-fold: (i) wind is more expensive than fossil-based technologies in these countries (Table C10 in Appendix C); and (ii) the CCS versions of coal and natural gas technologies are more expensive than their unabated counterparts, which are not totally phased out in these countries. By contrast, scenario DEC is cheaper than scenario BAU in the USA (as explained earlier) and France. In France, wind is more expensive than coal but cheaper than natural gas. Thus, given the LCOEs of these technologies and noting that the share of natural gas in the original mix is larger than the coal share, the complete phasing out of these two technologies lowers the overall cost of the electricity mix.

Turning our attention to transportation, the end-point impacts of gasoline and M90 per km travelled are reported in Fig.6.5. M90 scenarios are environmentally superior to gasoline (scenarios BAU and DEC) across all three impact categories except for M90-NG in the

resource depletion indicator due to the extraction of natural gas. Furthermore, M90 produced with CO_2 captured from power plants or using DAC and electrolytic hydrogen (scenarios M90-CAP and M90-DAC) are superior to M90 with methanol from syngas (scenario M90-NG). These results are in line with previous studies [47]. However, even though replacing gasoline with M90 blends can provide large environmental benefits, at present, it is not competitive with directly utilizing renewable energy – herein wind energy – to decarbonise the electricity mix. Although replacing gasoline with M90 is currently uneconomical, applying the total amount of electricity from wind energy to decarbonize the mix is predicted to reduce the costs in the USA and France or incur a marginal cost increase in the UK, Germany, Poland and China (Fig.6.3).

At present both a small contribution of the transport sector and a larger share of coal and natural gas in the electricity mix make it more profitable for a country to decarbonise its energy mix (scenario DEC) against increasing the penetration of green methanol as a transportation fuel. This conclusion is in line with previous studies assessing the viability of CO_2-based products against their fossil-derived counterparts [53]. It is unlikely, therefore, that CCU products using renewable energy will become both environmentally and economically attractive until a large share of the grid has been decarbonised.

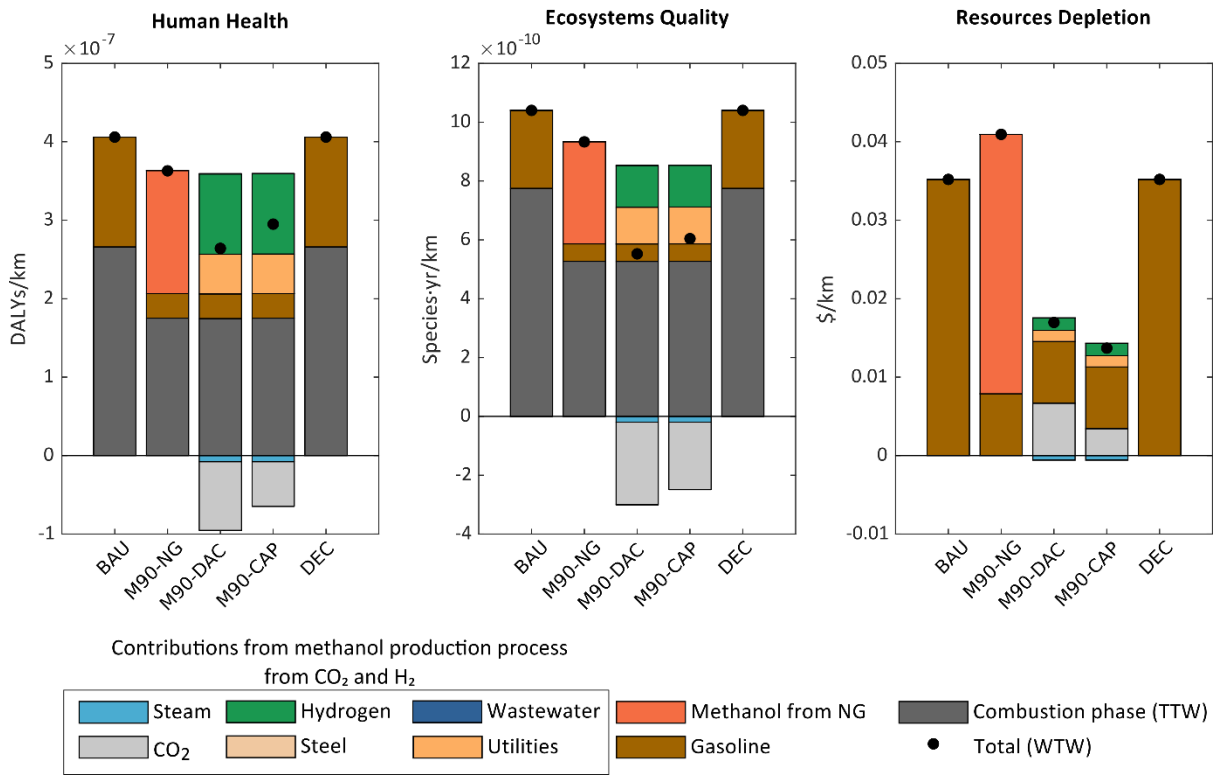


Fig.6.5 The process contributions of the total environmental impacts of the studied fuels [gasoline (the fuel considered in scenarios BAU and DEC) and M90 (The fuel considered in scenarios M90-NG, M90-DAC, M90-CAP)].

6.4 Conclusions

Methanol from captured CO_2 is being promoted as a "greener" fuel compared to gasoline as it can help to reduce CO2 emissions. In this chapter, we analysed the potential of using wind energy to either produce methanol from electrolytic hydrogen or use it to decarbonise the energy grid mix, from both the economic and environmental perspective. The results compared the potential of both scenarios with the status quo for the transport and power sectors in six selected countries. Hence, the conclusions of this work will well vary in the future as the electricity mixes reach lower carbon intensity levels and the production of electrolytic hydrogen becomes cheaper.

Our results show that, at present, using renewable energy to decarbonise the electricity mix outperforms producing electrolytic hydrogen for methanol production. The application of a holistic approach based on a life-cycle assessment analysis has revealed that producing methanol via hydrogenation of captured CO_2 using renewable energy to cut greenhouse gas emissions is inferior to redirecting the renewable energy towards decarbonizing the electricity mix. This is in line with recent results presented by Abanades [53].

Despite the environmental benefits of methanol as a fuel for the transport sector alone, its production cost remains too high to be economically competitive with the introduction of more wind into the electricity mix. The latter could even lead to cost reductions in certain countries (the USA and France), while marginally increasing the cost in other countries (the UK, Germany, Poland, and China). This regional assessment demonstrates the potential of a holistic approach to determining the best use of renewables across the two major greenhouse gases emitting sectors of transportation and power, considering the specific status quo of a region.

We expect, however, that as the mix is becoming more decarbonized, it will become more environmentally and economically effective to use renewable energy for water electrolysis and methanol production. Green methanol could replace fossil-based methanol in the mid or long term, given its superior environmental performance and the likely reduction in electrolytic hydrogen cost [83]. Regardless of whether methanol is consumed massively for transportation, its role as a platform chemical is called upon to increase, for instance with the methanol-to-olefins and ethanol-to-aromatic processes that could help decarbonise the whole chemical sector [163]. These technologies already show high technology-readiness levels and would enable full decarbonisation of the chemical industry by replacing the fossil-based commodity chemicals with methanol-based ones, where the latter will be synthesized from a renewable H_2 source and CO_2 captured from power plants or directly from the atmosphere.

Chapter 7 CONCLUSIONS AND FUTURE WORK

7.1 Conclusions

This thesis set out to better understand the interaction between hydrogen, CCS and CCU and thereby the optimal integration between them given the current absence of carbon price and available infrastructure. The study has examined the full potential of hydrogen production pathways and CCU products represented by methanol from a sustainability point of view. The overall objectives of the thesis were achieved by using a holistic and robust sustainability assessment. The key strengths of the study are the inclusion of the environmental assessment using LCA tools, monetisation of the environmental impacts at endpoint level as well as the economic performance of the studied technologies. Prior to this investigation, the influence of hydrogen production on CCU had not been thoroughly investigated. Furthermore, the environmental concerns and the phases where they occur were addressed and further explored.

As hydrogen was identified as a key factor to achieve deep decarbonisation in many sectors including heating, transport, and chemical industries. Chapter 4 presented a detailed sustainability assessment of some selected grey (fossil-based), blue (fossil + CCS) and green hydrogen. The technologies were quantified in terms of their total cost that include the economic performance represented by the levelised cost of hydrogen plus the monetised environmental impacts at endpoint levels. The uncertainty associated with the environmental

impacts were also examined for the total cost of technology. The analysis provided a wider breadth of technologies for a cradle-to-gate for pressurised hydrogen supply to be applicable for any downstream use.

The second objective of this thesis was to explore hydrogen production from steam reforming of light hydrocarbons. Chapter 5 investigated the potential of hydrogen production from oil fractions (LPG and naphtha) as grey and blue pathways. Detailed techno-economic and life cycle assessment were conducted. Furthermore, autothermal reforming of natural gas was explored and compared to the rest of the technologies in terms of their total cost. An integrated system between autothermal reforming with CCS and electrolysis via wind energy was studied in depth combining the best features of both systems. This synergised system provided a blend between blue and green hydrogen that is useful for the transition to sustainable hydrogen. All the studied hydrogen production pathways in Chapters 4 and 5 were compiled based on their total cost against their global warming potential aiming to provide hybridisation shares of the technologies starting from the current shares of hydrogen production. The hybridisation model addressed and highlighted different shares that could lead to a carbon-neutral hydrogen production system. It is capable to provide a roadmap to policymakers for decarbonised and sustainable hydrogen and thereby will contribute significantly to the climate mitigation goals.

Hydrogen production from electrolysis via wind energy was claimed to be the greenest renewable route. In the CCU context in Chapter 6, this route was further investigated in the CO_2 hydrogenation process to produce methanol as a fuel. The main objective was to assess the best use of the massive amount of renewable energy from the wind turbines that are required to satisfy the transport demand when methanol is to replace gasoline whether it better be used for the transport sector or to be directly connected to decarbonise the electricity grid. Different scenarios were investigated for different CO_2 sources (captured from a main

concentrated source or directly from the atmosphere). A dual functional unit of both sectors was considered for six countries that differ in their gasoline consumption and electricity mix. The main findings for all the countries confirmed the priority to decarbonise the power sector as this will lead to better environmental benefits with marginal cost increase.

7.2 Future work

The present studies carried out herein lays the groundwork for future research into the sustainability assessments for hydrogen, CCS and CCU and their interaction to achieve the climate benefits. As we focused on the economic and environmental performances of the investigated technologies which are two pillars of sustainability, the inclusion of the social aspect as the third pillar of sustainability would bring clearer and holistic insight into the proposed solutions.

To evaluate the full potential of a technology, a reliable and robust set of data can be collected and stored in a database to ensure high quality of data and thereby better understating and interpretation of the findings. Furthermore, more studies should be dedicated to identifying a reliable range of externalities for the environmental impacts given its current controversial status in the active literature.

Finally, future work in the decarbonisation scenarios shall also include absolute sustainability assessments on a planet level represented by the concept of planetary boundaries.

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APPENDIX A

Energy calculations of the CCS system in SMR+CCS case

The natural gas consumption, in this case, increases compared to the base case (SMR) as a result of the heat that is used for the solvent regeneration step and the electricity consumed by the compression step. The calculations for heat and electricity consider 1 kg of CO_2 captured. The additional heat is calculated based on the higher heating value of methane, as follows:

$$Heat\left(\frac{MJ_{CH_4}}{kgCO_{2,capt.}}\right) = \frac{(3.76-3.36)kg_{CH_4}}{kg\ H_2} \times \frac{55.5MJ_{CH_4}}{kg_{CH_4}} \times \frac{kg\ H_2}{(9.26-1.03)kgCO_{2,capt.}}$$

$$= 2.70\frac{MJ_{CH_4}}{kgCO_{2,capt.}}$$

The compression process was deemed to have inefficiency factors, one is the efficiency of the compressor, and the second efficiency factor stems from the efficiency of turning natural gas into electrical power which powers the compressor. The compressor was assumed to have an efficiency of 80% and the power generation process an efficiency of 40%, those two factors were used to calculate the amount of methane required to produce the electricity required by the compressor. The electricity needed for the compression step is calculated as follows:

$$Electricity\left(\frac{MJ_{CH_4}}{kgCO_{2,capt.}}\right)$$

$$= \frac{(1.11-0.31)kWh_{CH_4}}{kg\ H_2} \times \frac{3.6\ MJ}{kWh} \times \frac{kg\ H_2}{(9.26-1.03)kgCO_2} \times \frac{1}{0.4\ \times 0.8}$$

$$= 1.09\frac{MJ_{CH_4}}{kgCO_{2,capt.}}$$

Accordingly, the additional total energy requirement of both heat and electricity for the CCS process is 3.79 MJ CH_4/kg of CO_2 captured. Furthermore, burning methane emits specific CO_2 emissions in the CCS process, as reported by Farajzadeh *et al.*, of 0.055 kg CO_2/MJ CH_4 [1]. Thus, the additional CO_2 emissions accounted for the CCS step is:

$$3.79 \frac{MJ_{CH_4}}{kgCO_{2,capt.}} \times 0.055 \frac{kgCO_2}{MJ_{CH_4}} = 0.21 \frac{kgCO_2}{kgCO_{2,capt.}}$$

Monetary valuation

Monetisation was applied to express the end-point indicators on a common monetary basis [2]. The values reported by Dong [3] were chosen here, which apply to the ReCipe 2016 end-point metrics. All the monetised values were expressed in USD2019 to match the economic indicator considered in the analysis, as shown in table A1.

Table A1 Monetisation values factors of the three environmental impacts at end-point levels.

Endpoint indicator	Environmental unit	Equivalent monetary value (USD2019)
Human health	DALY	1.52×10^5
Ecosystem quality	Species.yr	4.06×10^7
Resources depletion	USD2013	1.10

Life-cycle inventory data

Table A2 provides the LCI data of the foreground systems.

Table A2 Inventory flows of the foreground system retrieved from Ecoinvent v3.4. [4].

Flow	Technology	Description in Ecoinvent v3.4.
Coal	CG, CG+CCS	Lignite coal, combusted in industrial boiler/US
Electricity consumed from the grid	SMR, SMR+CCS, MP, CG+CCS, BG, BG+CCS	Electricity, high voltage {US}| production mix | Cut-off, U
Electricity produced from nuclear energy	Nuclear	Electricity, high voltage {WECC, US only}| electricity production, nuclear, pressure water reactor | Cut-off, U
Electricity produced from solar energy	Solar PV	Electricity, low voltage {WECC, US only}| electricity production, photovoltaic, 570kWp open ground installation, multi-Si | Cut-off, U
Electricity produced from wind energy	Wind	Electricity, high voltage {WECC, US only}| electricity production, wind, >3MW turbine, onshore | Cut-off, U
Natural gas	SMR, SMR+CCS, MP	Natural gas, high pressure {GLO}| market group for | Cut-off, U
Water consumed by the gasification processes	BG, BG+CCS, CG, CG+CCS	Tap water {GLO}| market group for | Cut-off, U
Water consumed in the electrolysis routes from renewables energies and natural gas sources	Nuclear, Solar PV, Wind, SMR, SMR+CCS, MP	Water, deionised, from tap water, at user {GLO}| market for | Cut-off, U

CG: Coal Gasification; CG+CCS: Coal Gasification with carbon capture and storage; SMR: Steam Methane Reforming; SMR+CCS: Steam methane reforming with carbon capture and storage; MP: Methane pyrolysis; BG: Biomass Gasification; BG+CCS: Biomass Gasification with carbon capture and storage; Nuclear: water electrolysis using electricity from nuclear energy; Solar PV: water electrolysis using electricity from solar energy; Wind: water electrolysis using electricity from wind energy.

The poplar biomass considered in the current study was modelled according to Peters et al. [5], as shown in Table A3.

Table A3 The inventory data used to model 1 kg of the biomass feedstock (poplar) from [5]

Products		
Wood chips, poplar, at plantation	1	kg
Resources		
Occupation, agriculture	3.70×10^{-01}	m^2a
Carbon, organic, in soil or biomass stock	9.13×10^{-02}	kg
Carbon dioxide, in air	9.22×10^{-01}	kg
Materials/fuels		
Transport, tractor, and trailer, agricultural {GLO}| market for | Cut-off, U	4.70×10^{-02}	tkm
Ammonium nitrate, as N {GLO}| market for | Cut-off, U	2.00×10^{-03}	kg
Phosphate fertiliser, as P2O5 {RoW}| triple superphosphate production | Cut-off, U	3.33×10^{-04}	kg
Potassium chloride, as K2O {GLO}| market for | Cut-off, U	1.20×10^{-03}	kg
Glyphosate {GLO}| market for | Cut-off, U	9.88×10^{-06}	kg
Pyrethroid-compound {GLO}| market for | Cut-off, U	2.47×10^{-06}	kg
Dithiocarbamate-compound {GLO}| market for | Cut-off, U	1.23×10^{-06}	kg
Tree seedling {GLO}| market for | Cut-off, U	2.47×10^{-06}	p
Tillage, ploughing {GLO}| market for | Cut-off, U	2.47×10^{-06}	ha
Mowing, by rotary mower {GLO}| market for | Cut-off, U	2.47×10^{-06}	ha
Hoeing {GLO}| market for | Cut-off, U	2.47×10^{-06}	ha
Harvesting, by complete harvester, beets {GLO}| market for | Cut-off, U	2.47×10^{-06}	ha
Tillage, rotary cultivator {GLO}| market for | Cut-off, U	2.47×10^{-06}	ha
Planting {GLO}| market for | Cut-off, U	2.47×10^{-06}	ha
Application of plant protection product, by field sprayer {GLO}| market for | Cut-off, U	9.88×10^{-06}	ha
Fertilising, by broadcaster {GLO}| market for | Cut-off, U	$1.48 \times 10^{-0.5}$	ha
Combine harvesting {GLO}| market for | Cut-off, U	$1.23 \times 10^{-0.5}$	ha
Irrigation {GLO}| market group for | Cut-off, U	1.47×10^{-01}	m^3
Tillage, currying, by weeder {GLO}| market for | Cut-off, U	2.47×10^{-06}	ha
Emissions to air		
Ammonia	4.86×10^{-05}	kg
Dinitrogen monoxide	4.78×10^{-05}	kg
Nitrogen oxides	1.00×10^{-05}	kg
Carbon dioxide	-9.22×10^{-01}	kg
Carbon dioxide, land transformation	-9.13×10^{-02}	kg
Emissions to water		

Nitrate	groundwater	9.72×10^{-04}	kg
Phosphorus	river	6.48×10^{-06}	kg
Phosphate	groundwater	7.95×10^{-06}	kg
Cadmium	river	7.30×10^{-10}	kg
Chromium	river	7.32×10^{-8}	kg
Copper	river	5.39×10^{-8}	kg
Lead	river	6.53×10^{-09}	kg
Nickel	river	5.06×10^{-8}	kg
Zinc	river	7.24×10^{-8}	kg
Cadmium	groundwater	1.85×10^{-09}	kg
Chromium	groundwater	7.85×10^{-07}	kg
Copper	groundwater	1.33×10^{-07}	kg
Lead	groundwater	2.22×10^{-8}	kg
Zinc	groundwater	1.22×10^{-06}	kg
Emissions to soil			
Cadmium		-2.39×10^{-07}	kg
Chromium		-5.01×10^{-07}	kg
Copper		$-1.30 \times 10^{-0.5}$	kg
Lead		-7.09×10^{-07}	kg
Nickel		2.83×10^{-07}	kg
Zinc		$-3.33 \times 10^{-0.5}$	kg
Glyphosate		9.88×10^{-06}	kg
Pyridine		2.47×10^{-06}	kg
Potassium bis(2-hydroxyethyl)dithiocarbamate		1.23×10^{-06}	kg

Uncertainty

The uncertainty of the life cycle inventory (LCI) was evaluated for the production pathways. For the background data, Ecoinvent v3.4 assumes that the inventory entries follow lognormal distributions, which are characterised using a squared geometric standard deviation (σ^2) that encompasses the 95% confidence interval. The standard deviations are estimated using the Pedigree matrix (Equation A1), as recommended by Weidma [6], based on the uncertainty factors shown in Table A4. The factors U_1 – U_6 refer to the reliability, completeness, temporal correlation, geographical correlation, and sample size, respectively. Furthermore, U_b refers to the uncertainty factor that is assessed based on the expert's judgement.

$$\sigma^2 = \exp \sqrt{\sum_{i=1}^{6} \ln(U_i)^2 + \ln(U_b)^2} \quad \text{(A1)}$$

Table A3 Uncertainty factors for the pedigree matrix associated with the modelled hydrogen production processes in Table A2.

	Inputs						
	Natural Gas	Electricity (US mix)	Tap water	Deionised water	Coal	Biomass feedstock (poplar)	Biomass transport
Reliability	1.00	1.20	1.20	1.20	1.00	1.20	1.20
Completeness	1.02	1.00	1.02	1.02	1.00	1.10	1.10
Temporal correlation	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Geographical correlation	1.01	1.00	1.01	1.01	1.00	1.02	1.02
Technological correlation	1.50	1.00	1.00	1.00	1.00	1.50	1.50
Sample size	1.20	1.20	1.20	1.20	1.20	1.20	1.20
Basic factor	1.05	1.05	1.00	1.00	1.05	1.05	2.00

LCIA results using ReCipe 2016 method at midpoint levels (22 indicators) expressed in terms of endpoint per 1 kg of hydrogen

In this section, we provide additional results. Figure A1a shows the LCIA results of the human health indicator at its disaggregated midpoint levels, including their breakdown into reactants, utilities, and direct emissions. Figures A1b and A1c show the LCIA results of the ecosystems quality and resources depletion indicators, including their breakdown. Further details on the ReCipe methodology and their characterisation factors can be found in [7].

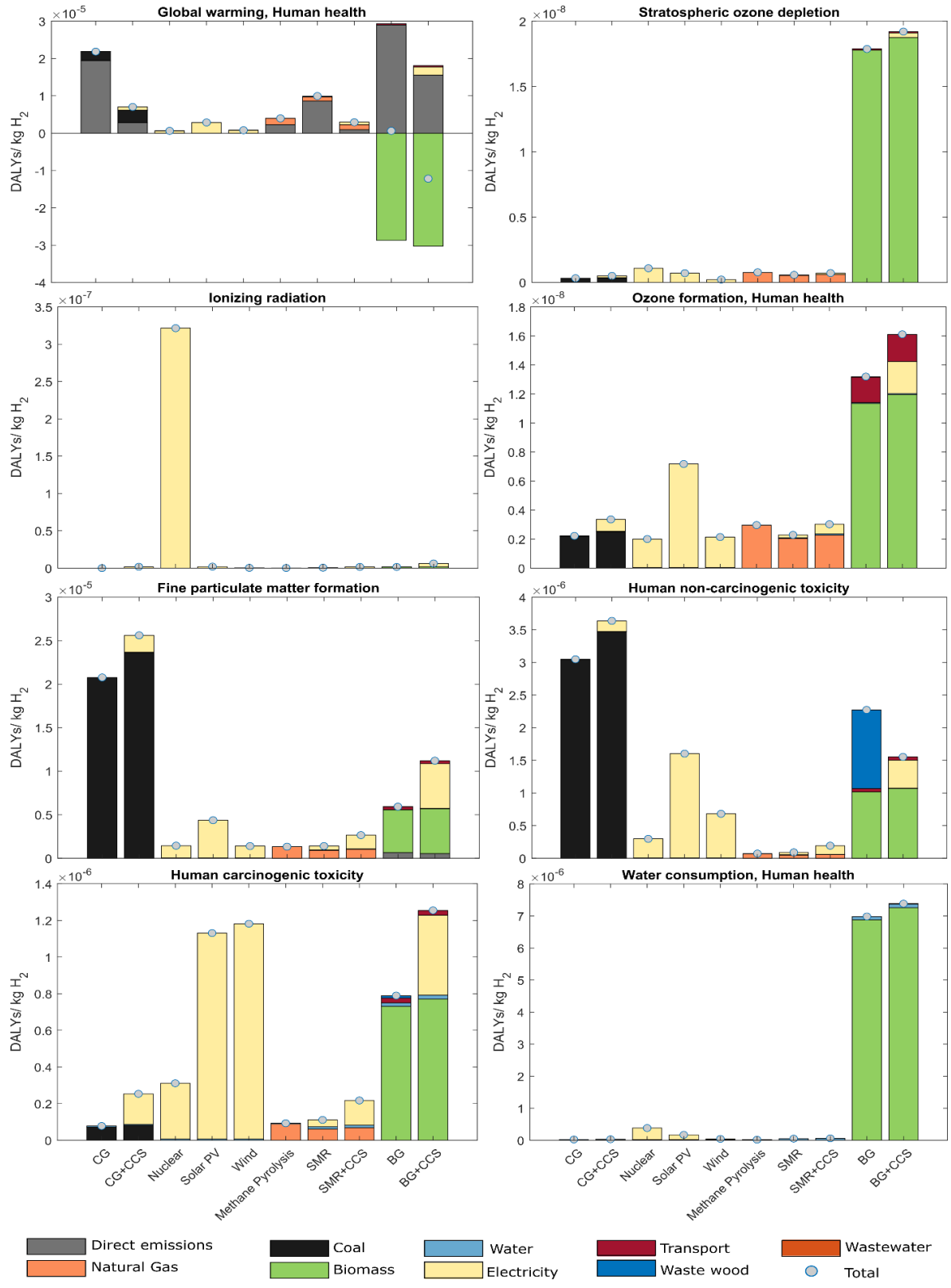


Figure A1a. ReCipe 2016 LCIA results at the midpoint level of all the hydrogen production routes analysed, contributions to human health endpoint indicator expressed in DALYs per 1 kg of H_2.

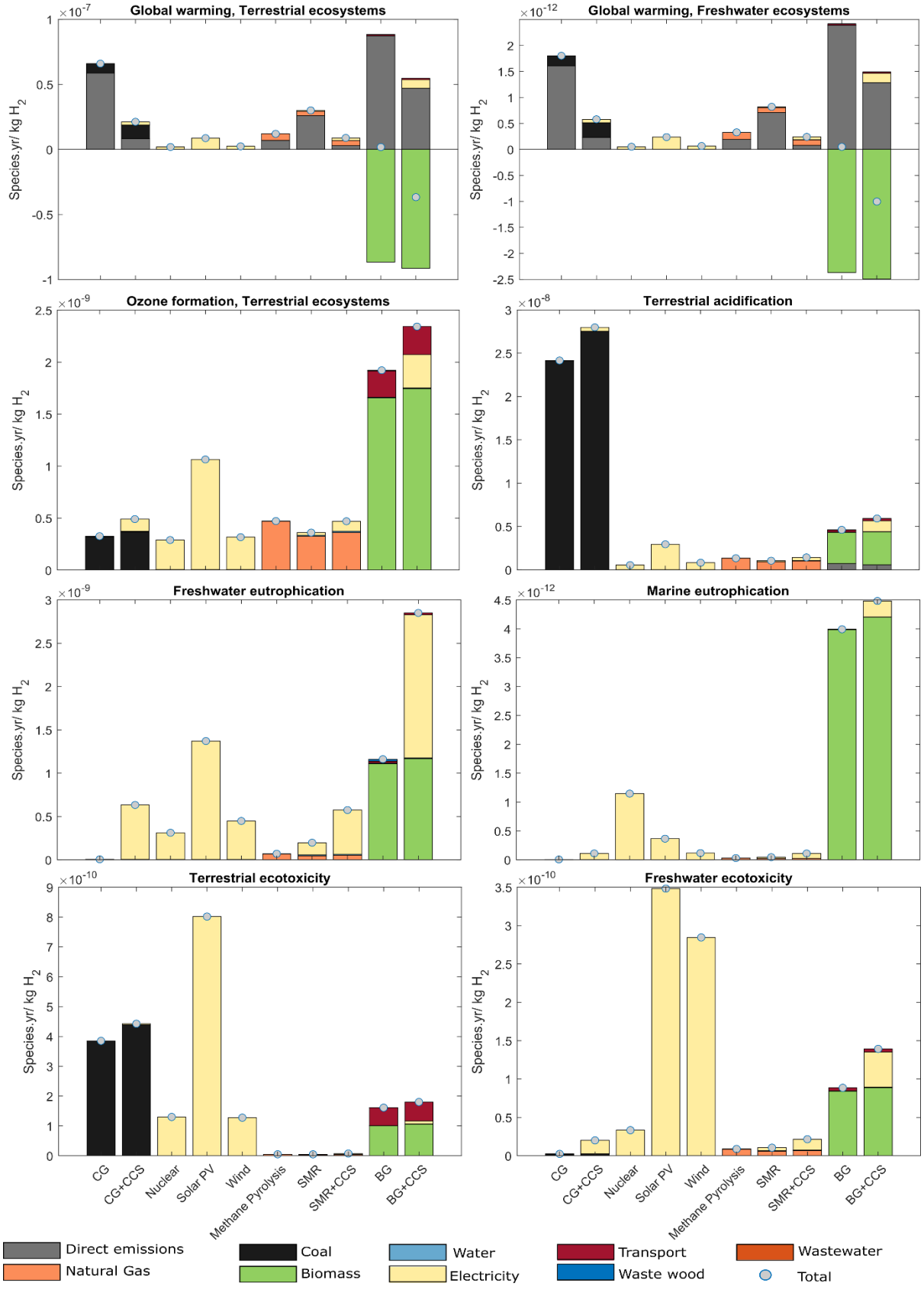


Figure A1b. ReCipe 2016 LCIA results at midpoint level of all hydrogen production routes analysed, contributions to ecosystem quality endpoint indicator expressed in Species.yr per 1 kg of H_2.

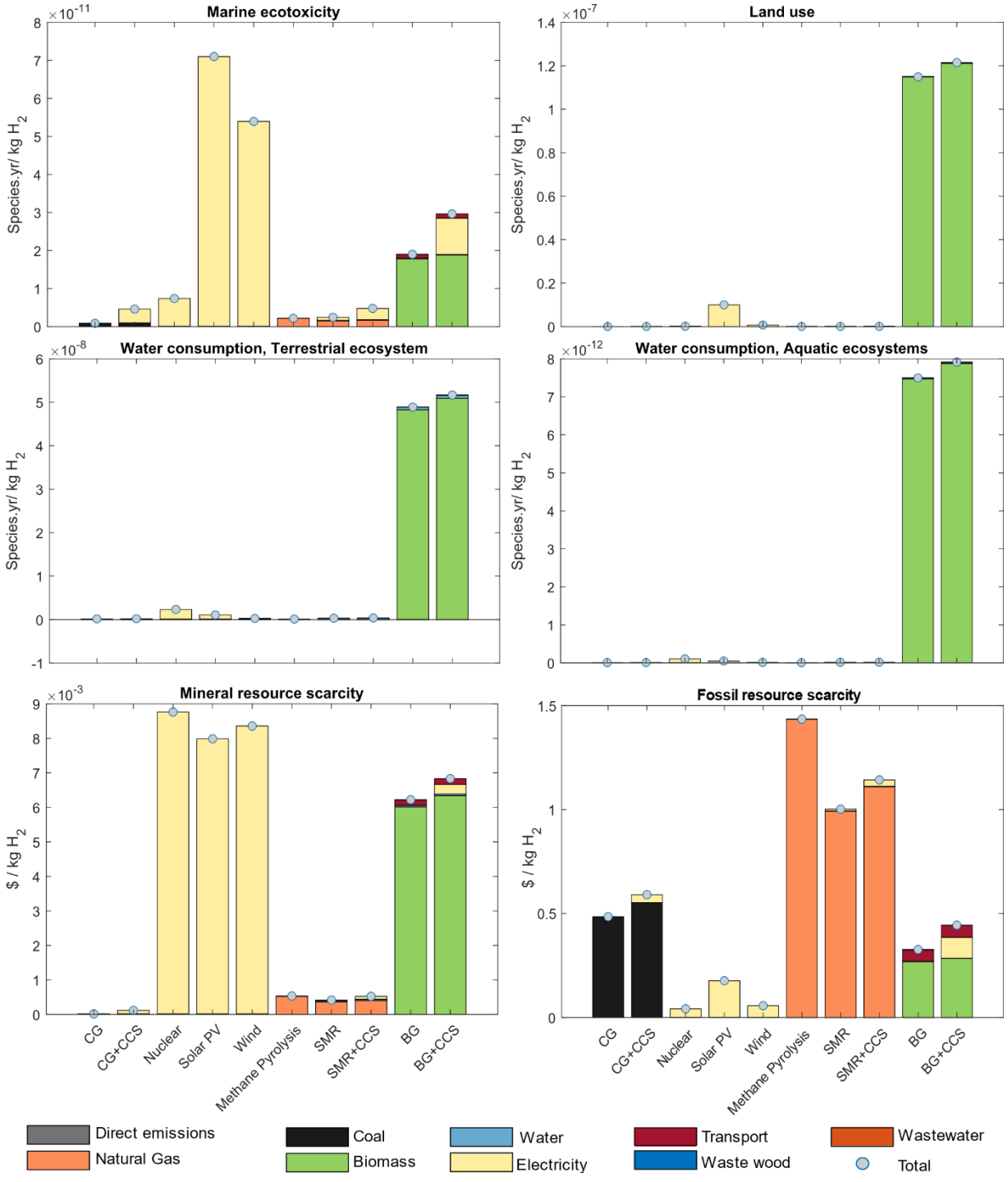


Figure A1c. ReCipe 2016 LCIA results at midpoint level of all hydrogen production routes analysed, contributions to ecosystem quality, and resource depletion endpoint indicators expressed in Species.yr and USD2019 per 1 kg of H_2.

APPENDIX B

Key assumptions used in the steam reforming process modelling

1. The hydrogen produced by the steam reforming plant has a purity of 100% and has a pressure of a minimum of 30 bar to be applicable for any downstream use.
2. LPG feedstock was assumed to be 50% of propane and 50% butane.
3. Naphtha feedstock was assumed to be 100% C_7H_{16}.
4. Steam to carbon ratio was set to 3.

Economic assessment

The levelised cost of hydrogen (LCOH) for the simulated steam reforming routes was calculated following Eq. (4.7) and using the data in Table B1.

Table B1 The economic data used in the OPEX calculations

Item	Unit	Cost	Reference
Natural gas	$/kg	0.31	[8]
LPG	$/kg	0.44	[4]
Naphtha	$/kg	0.52	[4]
Water	$/t	14.30	[9]
Electricity	$/MWh	104.61	[10]

Life cycle environmental impacts in terms of midpoints levels

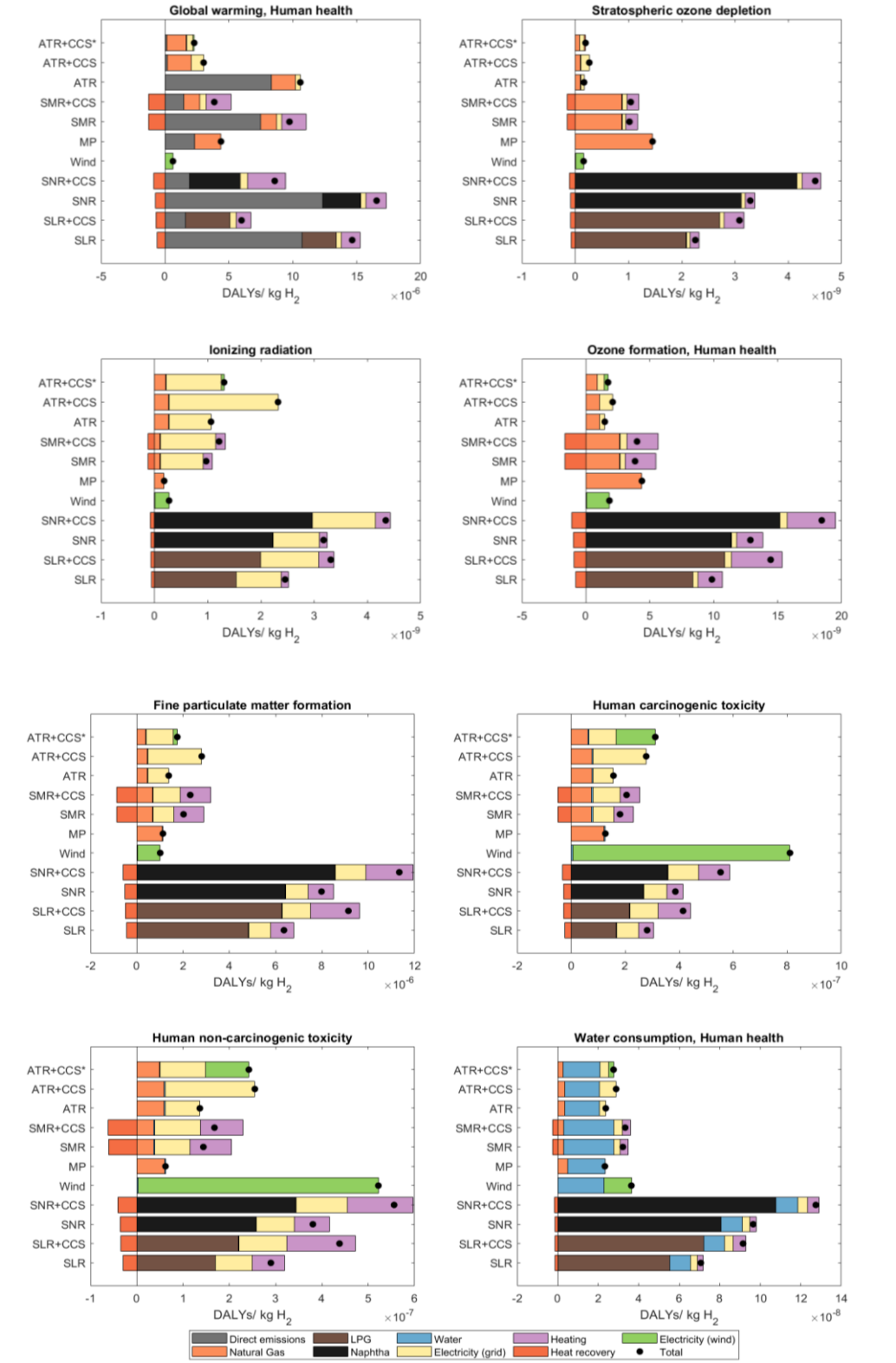


Figure B1a. The human health environmental impact expressed in terms of midpoint categories

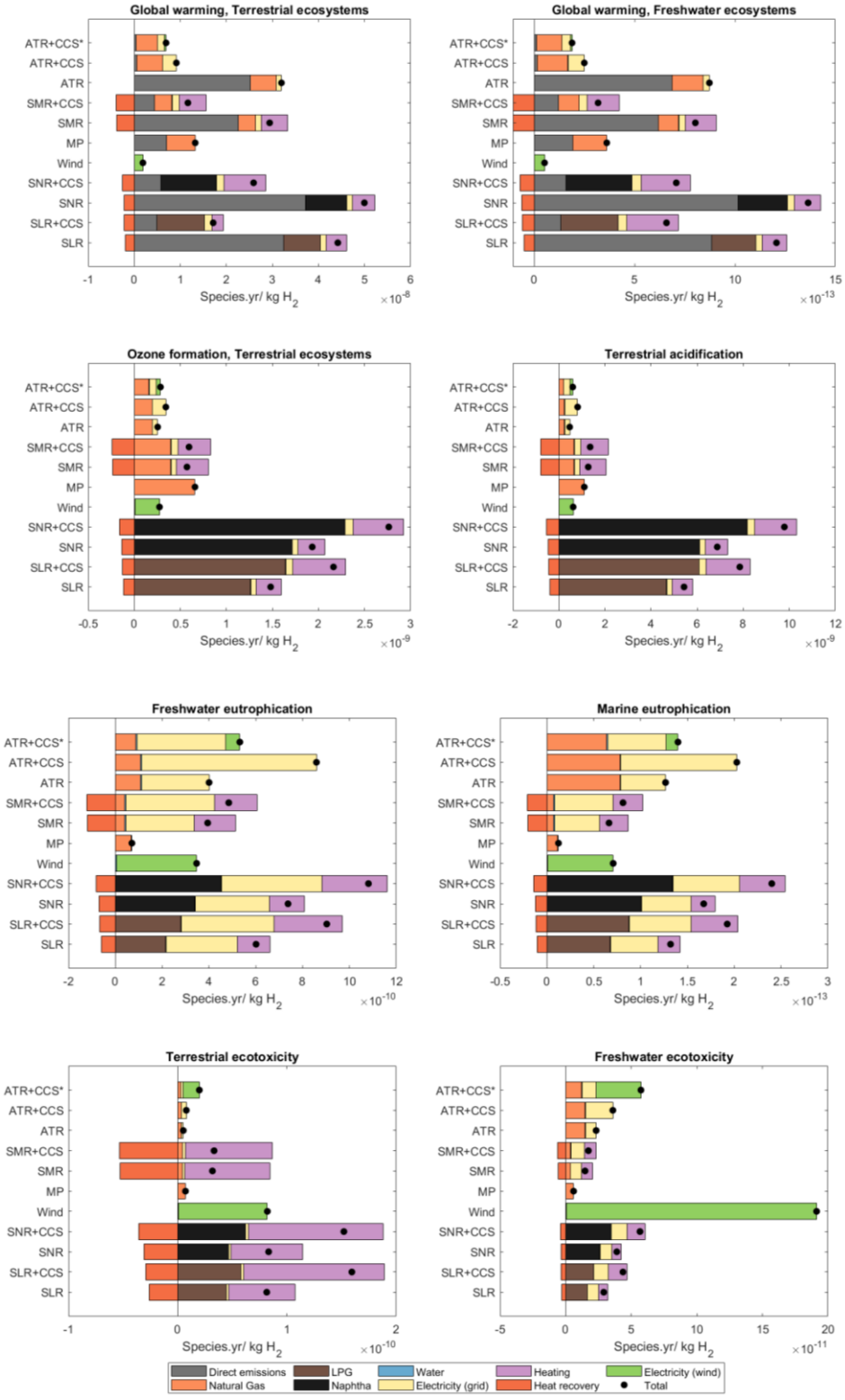


Figure B1b. The ecosystem quality environmental impact expressed in terms of midpoint categories

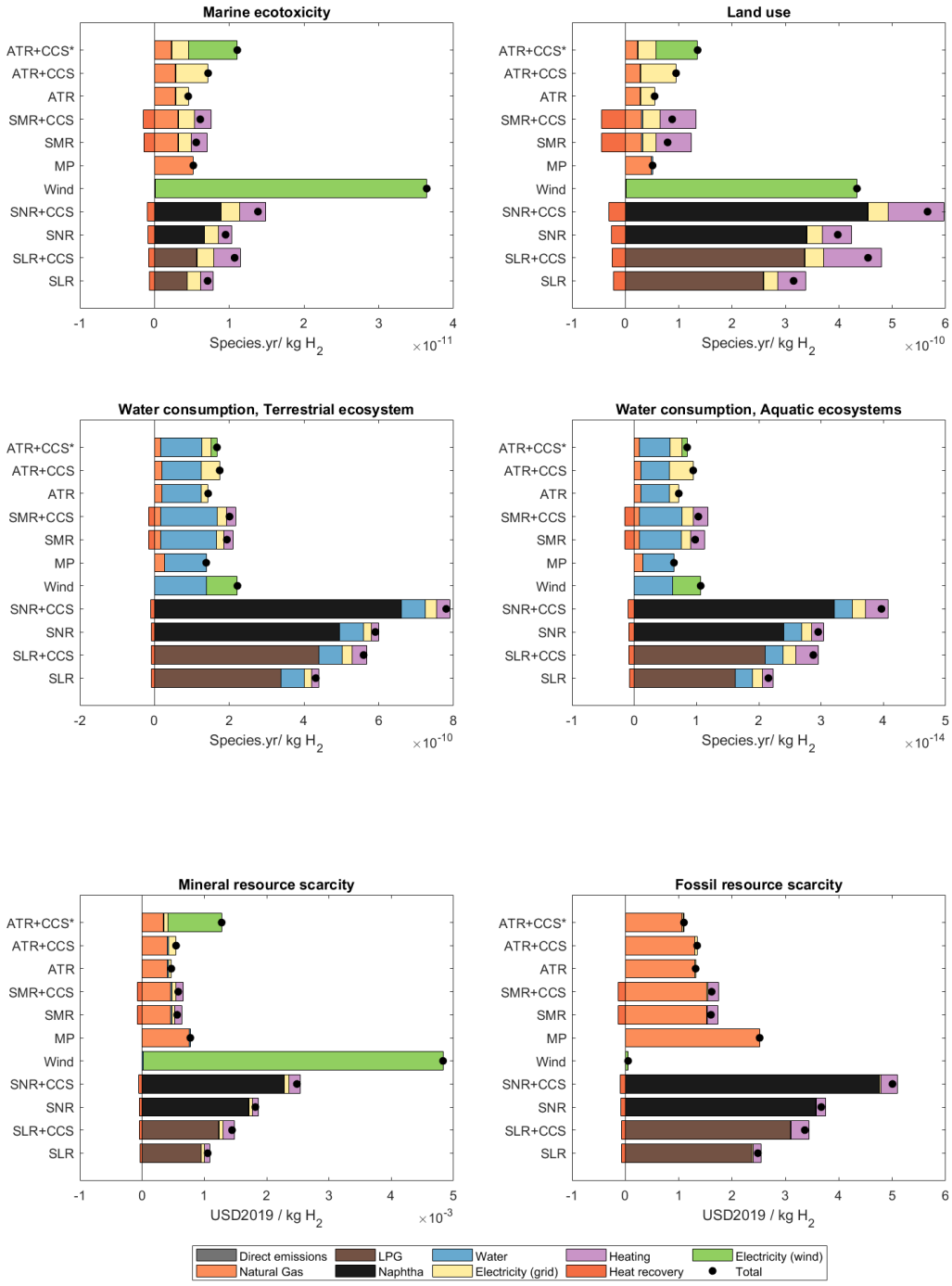


Figure B1c. The ecosystem quality (top four) and resources depletion (two in the bottom) environmental impacts expressed in terms of midpoint categories

Carbon-neutral hybridisation model

Table B2 The model data for the evaluated hydrogen technologies

		Human health	**Ecosystem quality**	**Resources depletion**	**GWP**	**LCOH**
	(unit/ kgH_2)	DALY	species.yr	USD2019	kg CO_2-eq	USD2019
SMR	i1	$1.21x10^{-5}$	$3.19x10^{-8}$	1.60	10.49	1.61
SMR+CCS	i2	$6.57x10^{-6}$	$1.44x10^{-8}$	1.62	4.15	1.70
ATR	i3	$1.23x10^{-5}$	$3.33x10^{-8}$	1.32	11.41	1.89
ATR+CCS	i4	$6.39x10^{-6}$	$1.15x10^{-8}$	1.35	3.26	2.05
BG	i5	$1.67x10^{-5}$	$1.74\ x10^{-7}$	0.36	0.65	2.40
BG+CCS	i6	$9.27x10^{-6}$	$1.48x10^{-7}$	0.50	-13.11	3.71
CG	i7	$4.58\ x10^{-5}$	$9.10x10^{-8}$	0.53	25.45	1.48
CG+CCS	i8	$3.66\ x10^{-5}$	$5.11x10^{-8}$	0.65	11.24	2.32
ATR+CCS*	i9	$4.62x10^{-6}$	$8.70x10^{-9}$	1.10	2.46	2.34
MP	i10	$5.50x10^{-6}$	$1.41x10^{-8}$	1.58	5.04	1.87
Nuclear	i11	$3.38x10^{-6}$	$5.69x10^{-9}$	0.06	0.67	4.95
SLR	i12	$2.17x10^{-5}$	$5.25x10^{-8}$	2.48	15.77	2.46
SLR+CCS	i13	$1.61x10^{-5}$	$2.93x10^{-8}$	3.36	6.89	3.08
SNR	i14	$2.54x10^{-5}$	$6.06x10^{-8}$	3.67	17.83	5.06
SNR+CCS	i15	$2.12x10^{-5}$	$4.11x10^{-8}$	5.01	9.02	6.31
Solar PV	i16	$1.02x10^{-5}$	$2.64x10^{-8}$	0.20	3.10	9.49
Wind	i17	$4.10x10^{-6}$	$5.44x10^{-9}$	0.07	0.86	5.61

Table B3 The generated total cost (TC) for each point j in the obtained curves N

TC	N1	N2	N3	N4	N5
j1	9.07	9.77	10.52	11.27	11.67
j2	8.90	9.44	10.13	10.83	11.30
j3	8.72	9.21	9.85	10.50	10.93
j4	8.54	8.98	9.57	10.16	10.56
j5	8.37	8.76	9.29	9.83	10.19
j6	8.19	8.53	9.01	9.49	9.81
j7	8.02	8.30	8.73	9.16	9.44
j8	7.84	8.07	8.45	8.82	9.07
j9	7.67	7.85	8.17	8.49	8.70
j10	7.49	7.62	7.89	8.15	8.33
j11	7.32	7.39	7.60	7.81	7.95
j12	7.14	7.17	7.32	7.48	7.58
j13	6.96	6.94	7.04	7.14	7.21
j14	6.79	6.71	6.76	6.81	6.84
j15	6.61	6.49	6.48	6.47	6.46
j16	6.44	6.26	6.20	6.14	6.09
j17	6.26	6.03	5.92	5.80	5.72
j18	6.11	5.81	5.64	5.47	5.35
j19	6.07	5.58	5.36	5.13	4.98
j20	6.02	5.44	5.16	4.88	4.60

Table B4 The global warming potential (GWP) values for each point j in the obtained curves N

GWP	N1	N2	N3	N4	N5
j1	0.00	-3.51	-6.96	-10.40	-13.11
j2	0.39	-3.02	-6.34	-9.66	-12.29
j3	0.77	-2.52	-5.72	-8.92	-11.47
j4	1.16	-2.02	-5.10	-8.19	-10.65
j5	1.55	-1.52	-4.48	-7.45	-9.83
j6	1.93	-1.02	-3.86	-6.71	-9.01
j7	2.32	-0.52	-3.24	-5.97	-8.19
j8	2.70	-0.02	-2.63	-5.23	-7.37
j9	3.09	0.48	-2.01	-4.49	-6.55
j10	3.48	0.98	-1.39	-3.75	-5.74
j11	3.86	1.48	-0.77	-3.02	-4.92
j12	4.25	1.98	-0.15	-2.28	-4.10
j13	4.64	2.48	0.47	-1.54	-3.28
j14	5.02	2.98	1.09	-0.80	-2.46
j15	5.41	3.48	1.71	-0.06	-1.64
j16	5.80	3.98	2.33	0.68	-0.82
j17	6.18	4.48	2.95	1.41	0.00
j18	6.57	4.97	3.56	2.15	0.82
j19	6.96	5.47	4.18	2.89	1.64
j20	7.34	5.97	4.80	3.63	2.46

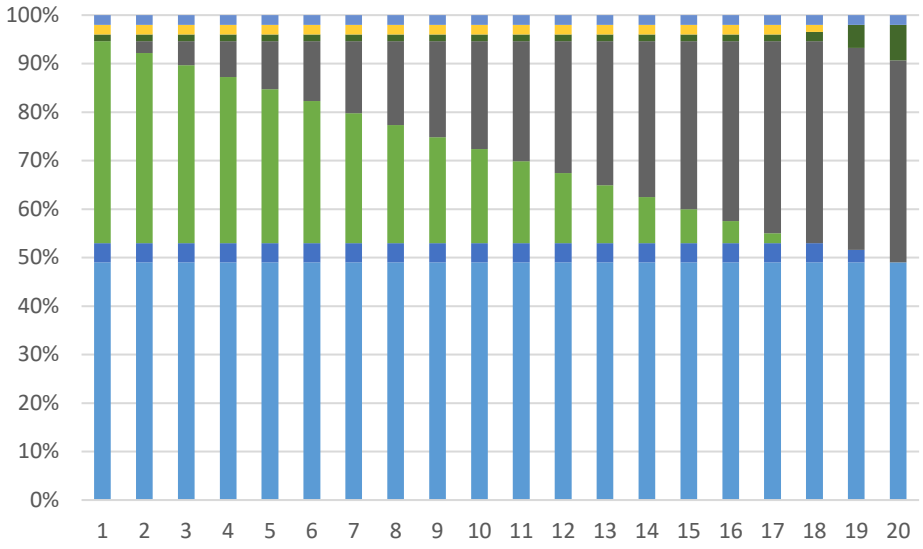


Figure B2. The new shares of the 20 solutions (j) in N1 curve

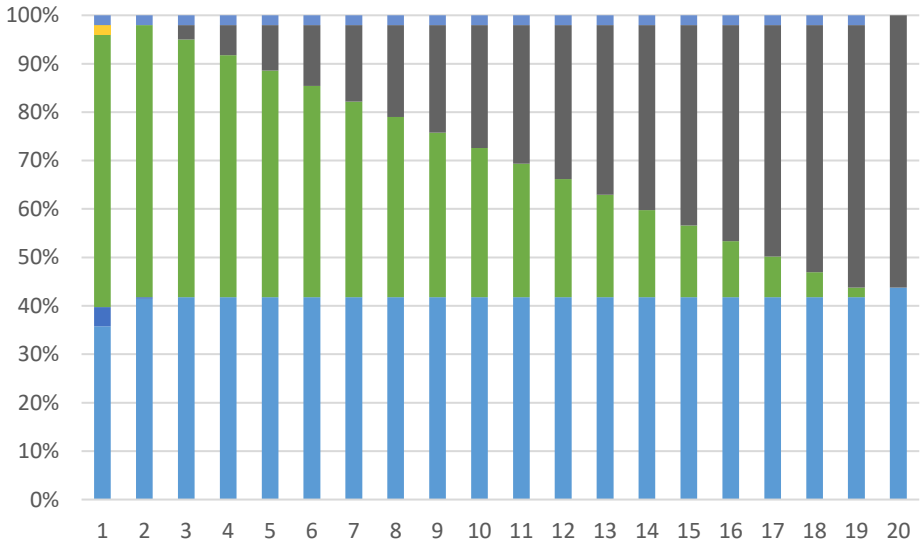


Figure B3. The new shares of the 20 solutions (j) in N2 curve

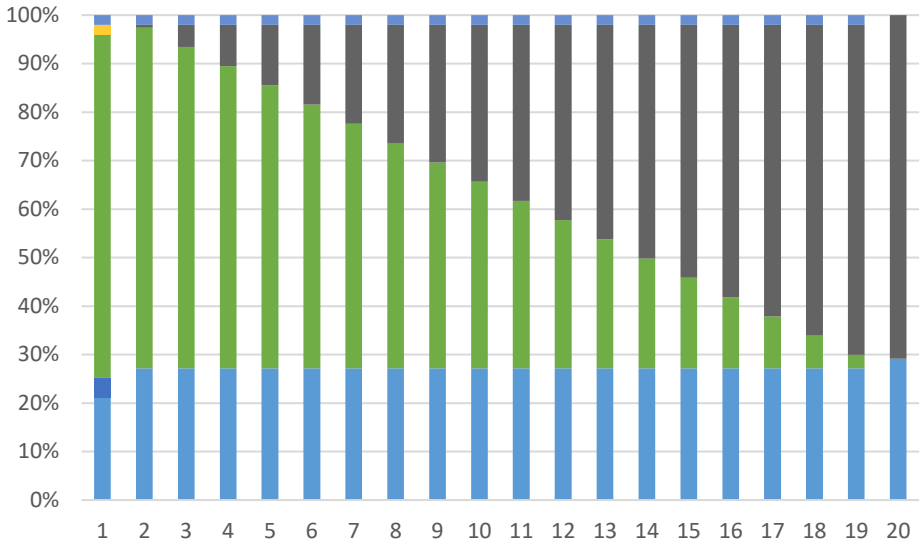


Figure B4. The new shares of the 20 solutions (j) in N3 curve

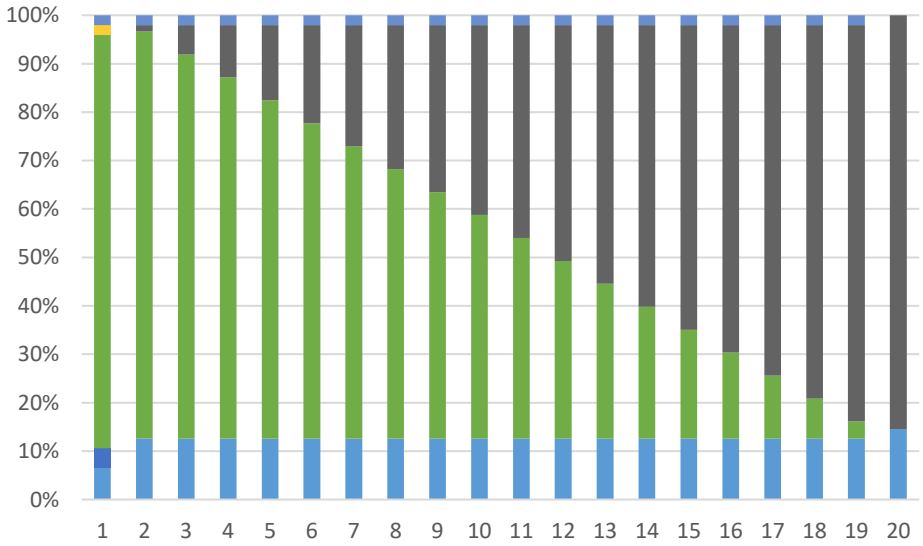


Figure B5. The new shares of the 20 solutions (j) in N4 curve

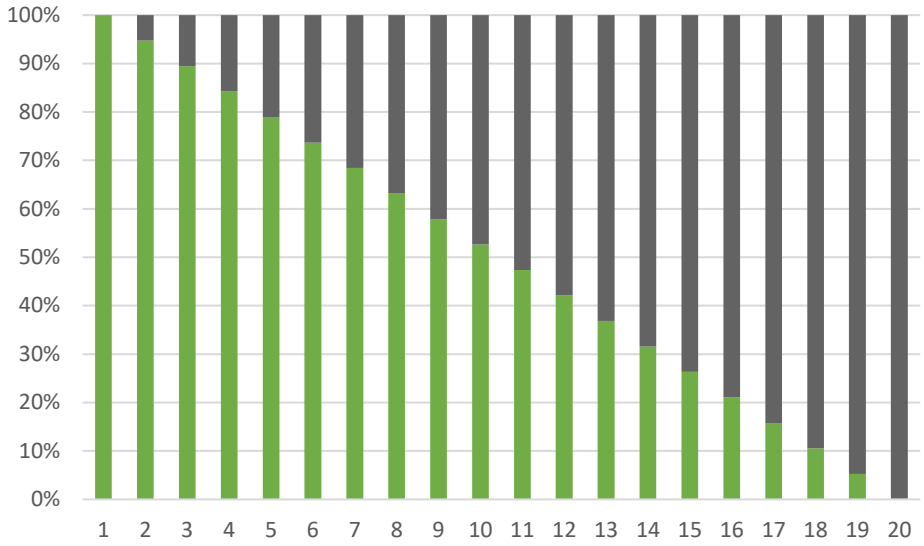


Figure B6. The new shares of the 20 solutions (j) in N5 curve

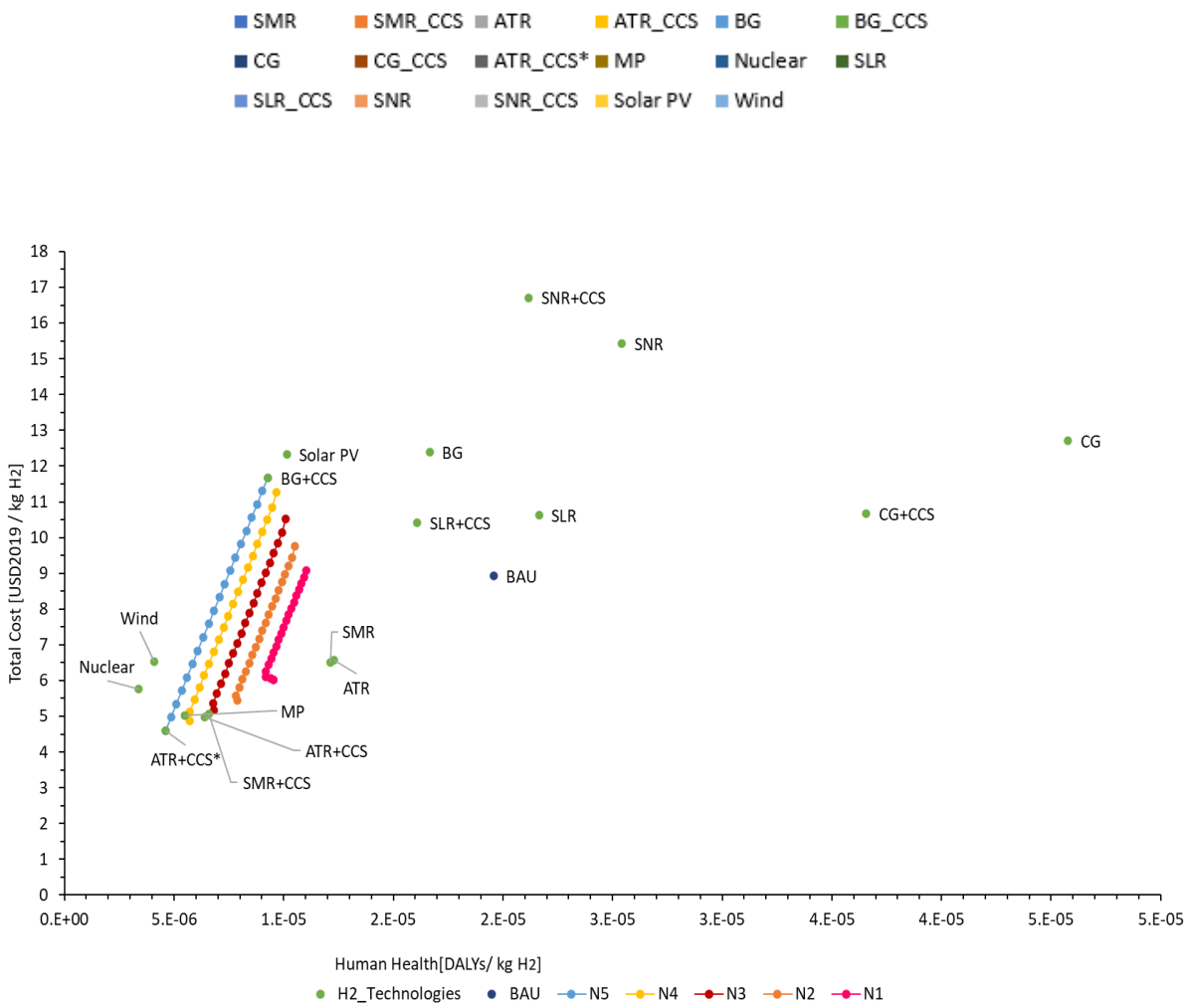


Figure B7. Human health versus total cost for the considered hydrogen production systems in the analysis.

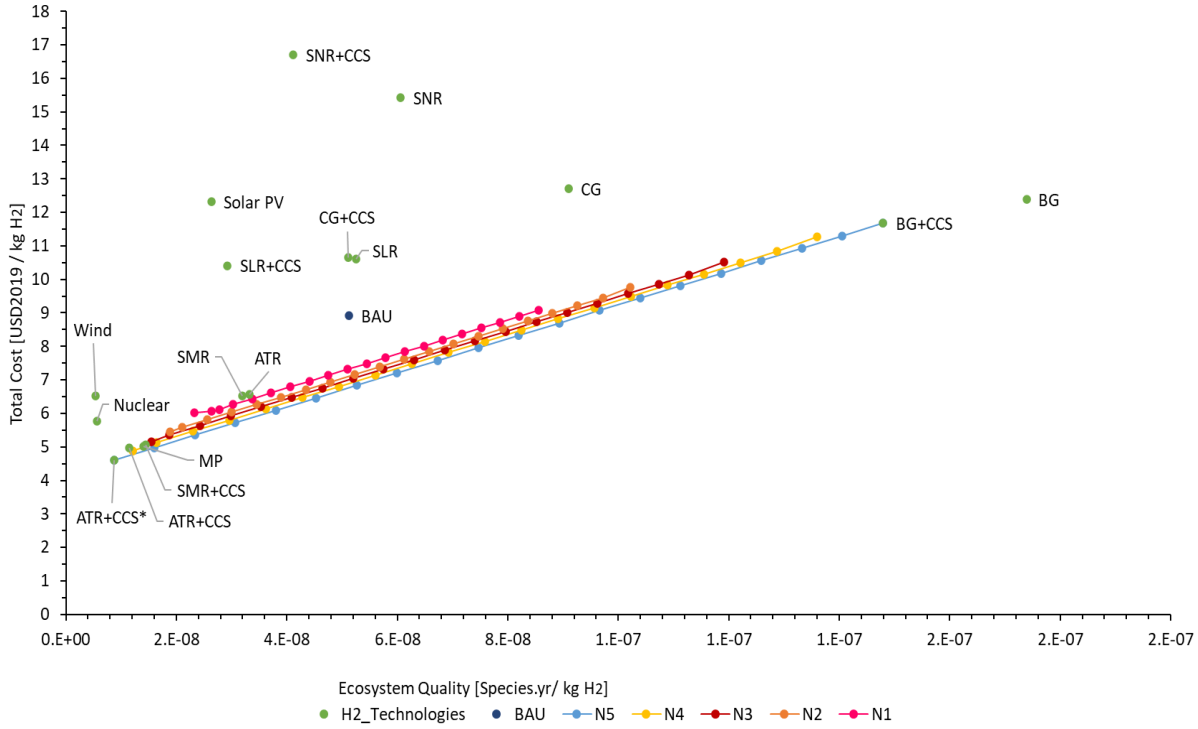


Figure B8. Ecosystem quality versus total cost for the considered hydrogen production systems in the analysis.

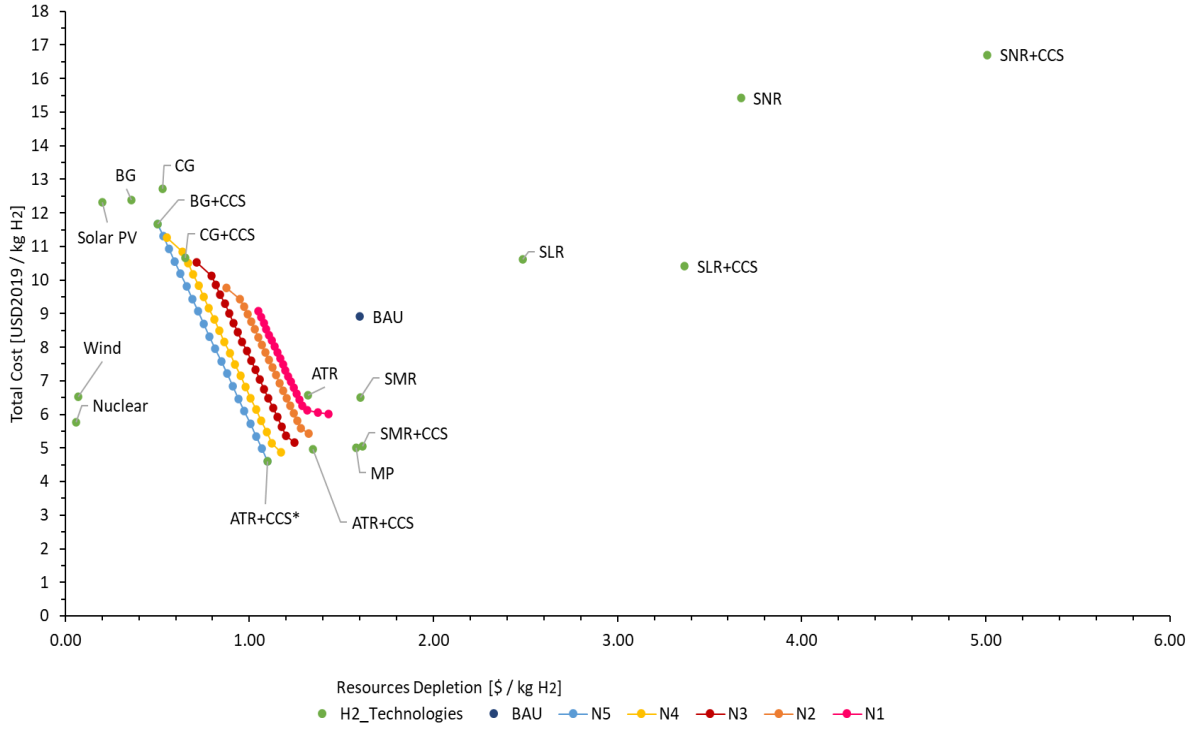


Figure B9. Resources depletion versus total cost for the considered hydrogen production systems in the analysis.

APPENDIX C

Economic assessment

Table C1 Costs of the commodities considered in the OPEX calculations

Flow	Cost (USD unit^{-1})	Reference
CO_2 from coal power plants (kg)	$6.5x10^{-2}$	[11]
CO_2 from direct air capture (DAC) (kg)	0.148	[12]
H_2 from wind/electrolysis (kg)	7.00	[13]
Electricity (kWh)	0.07	[10]
Water (t)	0.50	
Cu/ZnO/Al_2O_3 catalyst (kg)	95.24	[14]
Wastewater to be treated[8] (m^3)	1.50	[10]

LCA of methanol production

Table C2 Inventory flows required to capture 1 kg of hydrogen from wind energy via water electrolysis considering a PEM electrolyser [15].

Technology	Hydrogen from wind/electrolysis
Water (kg)	18.04
Wind electricity (kWh)	53.00

Table C3 Inventory flows required to capture 1 kg of CO_2 from coal and natural gas power plants

Technology	CO_2 from coal power plant [16]	CO_2 from natural gas power plant [17]
Product	Electricity (0.775 kWh)	Electricity (3.23 kWh)
Materials (inputs)		
Air (kg)	-	20.19
Water (kg)	-	1.5161
Natural gas (m^3)	0.00078	0.8636
Limestone (kg)	0.04263	-
Light fuel oil (kg)	0.00620	-
Hard coal (kg)	0.52093	-
Monoethanolamine (kg)	0.00155	0.0088
NaOH (kg)	0.00012	-
NH_3 (kg)	0.00115	-
Waste (undesired outputs)		
Municipal solid waste, to sanitary landfill	0.00406	-
Wastewater	-	1.6452
Direct emissions (undesired outputs)		
CO_2 (kg)	0.05240	0.3286
SO_2 (kg)	0.00007	-
NO (kg)	0.00106	0.0016
Particulates, unspecified (kg)	0.00011	-
NH_3 (kg)	0.00027	-
Monoethanolamine (kg)	0.00009	0.0035

Table C4 Inventory flows required to capture 1 kg of CO_2 from direct air capture (DAC) [12].

Technology	CO_2 from direct air capture
Materials (inputs)	
Air (kg)	1467.84
Heat from natural gas (MJ)	8.81

Table C5 Inventory flows required to produce 1 kg of methanol from the natural gas (BAU) [4].

Materials	Methanol
Aluminium oxide (kg)	2.40×10^{-4}
Copper oxide (kg)	9.00×10^{-5}
Electricity (kWh)	7.40×10^{-2}
Molybdenum (kg)	1.00×10^{-5}
Heat (MJ)	6.93
Natural gas (m^3)	6.52×10^{-1}
Nickel (kg)	2.00×10^{-5}
Water (kg)	8.50×10^{-1}
Zinc (kg)	3.00×10^{-5}
Emission and waste	
Methane (kg)	9.80×10^{-4}
Methanol (kg)	5.30×10^{-4}
Nitrogen oxides (kg)	1.50×10^{-4}
Wastewater, average (m^3)	3.34×10^{-3}

Table C6 Inventory flows required to produce 1 kg of methanol from the hydrogenation of CO_2 [18].

Materials	Methanol
CO_2 (kg)	1.51
H_2 from wind/electrolysis (kg)	0.21
Electricity (kWh)	0.27
Steel (kg)	1.53×10^{-4}
Steam “credit” (MJ)	0.44
Emission and waste	
CO_2 (kg)	0.08
Methanol (kg)	0.01
NO_2 (kg)	1.78×10^{-6}
Wastewater, average (m^3)	5.71×10^{-4}

Table C7 Inventory flows of the foreground processes sourced from Ecoinvent v3.4. [4]

Flow	Technology involved	Description in Ecoinvent
Petrol	Gasoline	Petrol, low-sulfur {RoW}| market for | Cut-off, S
Methanol from syngas produced from natural gas	Methanol	Methanol {GLO}| market for | Cut-off, U
Light fuel oil	CO_2 capture from coal power plant	Light fuel oil, at regional storage
Ammonia	CO_2 capture from coal power plant	Ammonia, as 100% NH3 (NPK 82-0-0), at plant/RER Mass
MEA	CO_2 capture from coal power plant	Monoethanolamine {GLO}| market for | Cut-off, U
Electricity produced by wind energy for water electrolysis	Hydrogen from wind/electrolysis	Electricity, high voltage {RoW}| electricity production, wind, <1MW turbine, onshore | Cut-off, U
Electricity consumed during the methanol production process from CO_2 and H_2	Methanol	Electricity, high voltage {US, GB, FR, DE, PL, CN}| production mix | Cut-off, U
Steel production	Methanol	Steel, chromium steel 18/8 {RoW}| steel production, electric, chromium steel 18/8 | Cut-off, U
Wastewater production with the methanol	Methanol	Wastewater, average {RoW}| market for wastewater, average | Cut-off, U
Water	CO_2 capture from direct air capture (DAC)	Tap water {GLO}| market group for | Cut-off, U
Calcium carbonates	CO_2 capture from direct air capture (DAC)	Calcium carbonate, precipitated {RoW}| calcium carbonate production, precipitated | Cut-off, U
Heat	CO_2 capture from direct air capture (DAC)	Heat, district or industrial, natural gas heat and power co-generation, natural gas, conventional power plant, 100MW electrical | Cut-off, U

Well to Wheel (WTW) analysis: Assumptions and further details

We consider the total impact of transportation and electricity generation. For transportation, the impact is given by the burdens embodied in the fuel, plus the direct emissions of fuel combustion. Our analysis omits the impact related to the manufacturing of the vehicle, as it would add no discriminatory power to the assessment. Hence, the impact is determined as shown in equation C1:

$$WTW = WTT + TTW \quad (C1)$$

Where the Well-to-Tank (WTT) part evaluates the energy consumed and GHG emissions released in the production and distribution processes that deliver the fuel into the on-board tank of a vehicle. On the other hand, the Tank-to-Wheel (TTW) part accounts for the emissions from the fuel combustion.

The following assumptions and LCA details apply to our work:

1. The functional unit was set to 1 km travelled.
2. System boundaries: The system boundaries have been expanded to include the combustion of the methanol (fossil- and CO_2-based) and compare it to other fuels. This expansion in the transportation sector is known as well-to-wheel (WTW) approach, which is equivalent to cradle-to-grave in LCA. All the fuels are assumed to operate in internal combustion engines (ICEs). Thus, the life cycle stages of the vehicle, including manufacturing, maintenance and disposal were not considered in this assessment.
3. All the engines were assumed to be spark ignition engines.
4. An engine efficiency of 22.5% was considered. [19]
5. The fuel consumption per 1 km was retrieved from [20].

6. The LCA of the TTW phase focuses only on GHG-100, PM10, SO_x, NO_x, CO and VOC emissions. (Adopted from GREET [20]).

The LCI calculations of the WTT and TTW phases were modelled in SimaPro v9 [21].

Table C8 Fuels considered in this study and their WTT pathways (energy consumption and GHG emissions adopted from [22]).

Investigated fuel	Code	Description of the process
Conventional gasoline	Gasoline	Petrol, low-sulfur {RoW}| market for | Cut-off, S
Methanol derived from natural gas	MeOH_BAU	Methanol derived from syngas from natural gas
Methanol derived from CO_2 capture	MeOH_CO_2	The alternative pathways for methanol production which are explained earlier.

The LCI data for the TTW stage were taken from GREET software for the fossil-based fuels and the M90 blend.

The gasoline results are therefore considered as the starting reference for comparison.

The two inputs considered here were mainly:

1. Fuel energy (MJ/km) necessary to perform the new European driving cycle (NEDC)
2. Combustion emissions during the cycle (g /km)

Table C9 LCI inputs for the TTW analysis [20].

	TTW (ICEV – Assume engine efficiency 22.5%)								Reference
	Fuel consumption		GHG-100	PM10	SO_x	NO_x	CO	VOC	
Indicator / Fuel Type	MJ/ 100 km	MJ/ km	g /km	g /km	g /km	g /km	g /km	g /km	
Gasoline	281	2.81	192.30	$3.3x10^{-3}$	0.00	$6.87x10^{-2}$	1.60	$7.28 x10^{-2}$	[20]
M90, BAU	263	2.63	183.0	$3.3x10^{-3}$	0.00	$6.87x10^{-2}$	1.60	$7.28 x10^{-2}$	
M90, Wind-CCU									
M90, Wind-DAC									

LCOE data

Table C10 Data for the levelised cost of electricity (LCOE) for each technology in the electricity mixes for the countries considered in this analysis [23].

	UK	FR	PL	DE	US	CN
LCOE	$/MWh					
Coal	85.76	85.76	85.76	75.53	95.20	81.57
Oil	350.48	350.48	350.48	350.48	350.48	350.48
Natural Gas	103.59	97.22	101.65	102.56	75.10	95.13
Nuclear	100.75	82.64	86.52	86.52	95.20	64.40
Hydro	174.91	126.93	126.93	123.17	83.60	28.39
Wind	123.97	91.29	99.61	93.53	73.60	82.27
Biomass	272.57	167.01	167.01	112.17	100.40	179.69
Solar	167.76	134.51	140.00	127.15	125.30	87.98
Geothermal	116.98	98.93	98.93	98.93	47.80	103.44
Coal CCS	185.00	185.00	190.00	180.00	125.00	120.00
NG CCS	130.00	130.00	130.00	130.00	100.2	130.00

Wind potential versus introduced wind in the CCU and decarbonised grid scenarios

Table C11 The amount of wind introduced in the transport and power sectors in the CCU and decarbonised grid scenarios compared to the wind potential in each of the assessed countries

	Wind needed for hydrogen production in scenarios [M90-CAP,-DAC], MWh	Wind introduced in the decarbonised grid [DEC], MWh	Wind potential, MWh	Reference
US	4.71×10^{9}	1.98×10^{9}	7.40×10^{10}	[24]
UK	1.74×10^{8}	1.39×10^{8}	2.15×10^{9}	[25]
France	9.76×10^{7}	5.32×10^{7}	7.10×10^{8}	
Germany	2.32×10^{8}	2.56×10^{8}	1.49×10^{9}	
Poland	4.77×10^{7}	8.60×10^{7}	1.07×10^{9}	
China	1.03×10^{9}	2.34×10^{9}	3.90×10^{10}	[24]

Electricity shares by technology

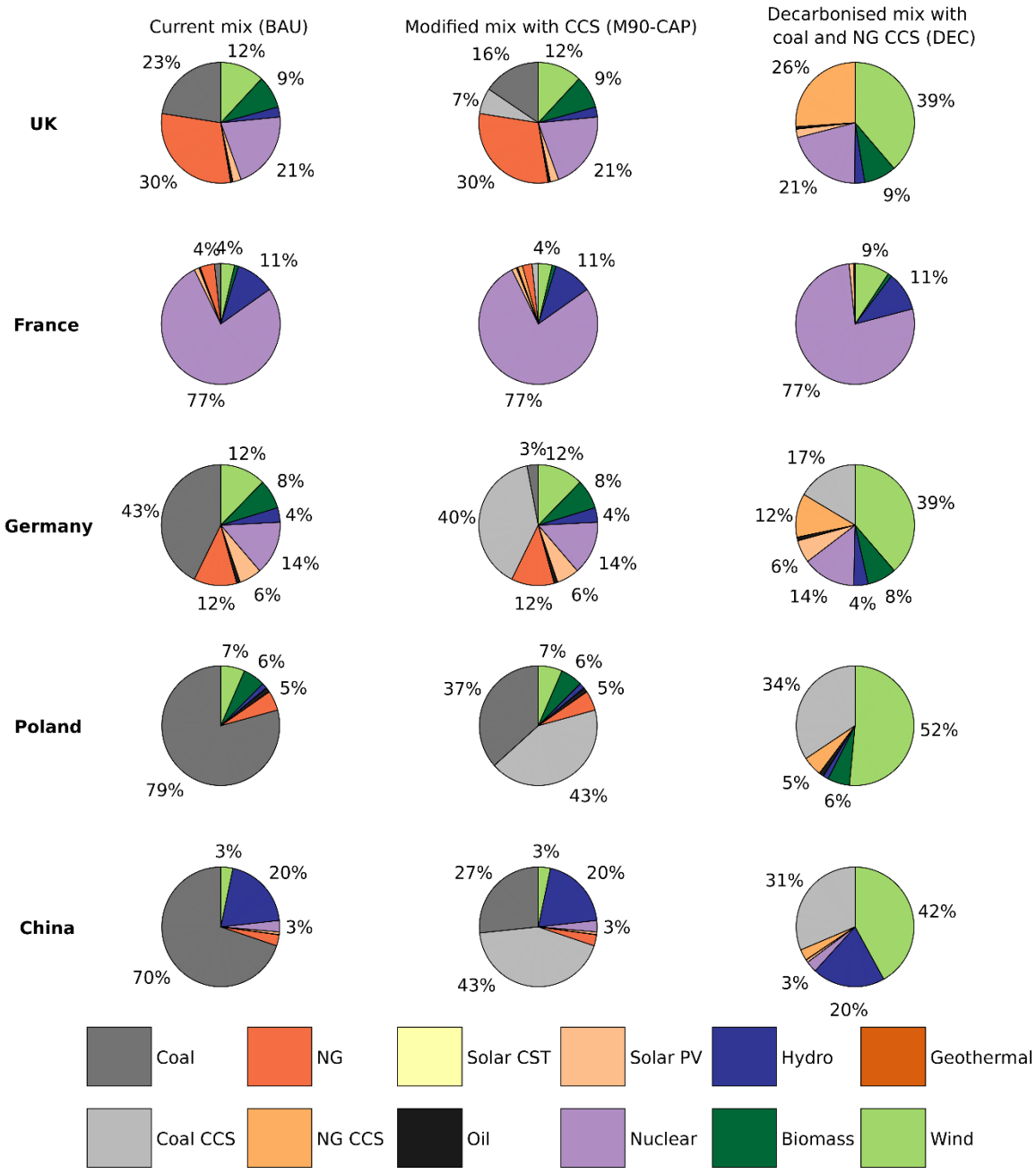


Figure C1 Technologies shares in the studied countries' electricity mixes in 2015 for all the scenarios BAU (which is the same as M90-NG & M9-DAC), M90-CAP and DEC (Data for European countries were adopted from[26] while for China from [27].

Contributions to environmental impacts

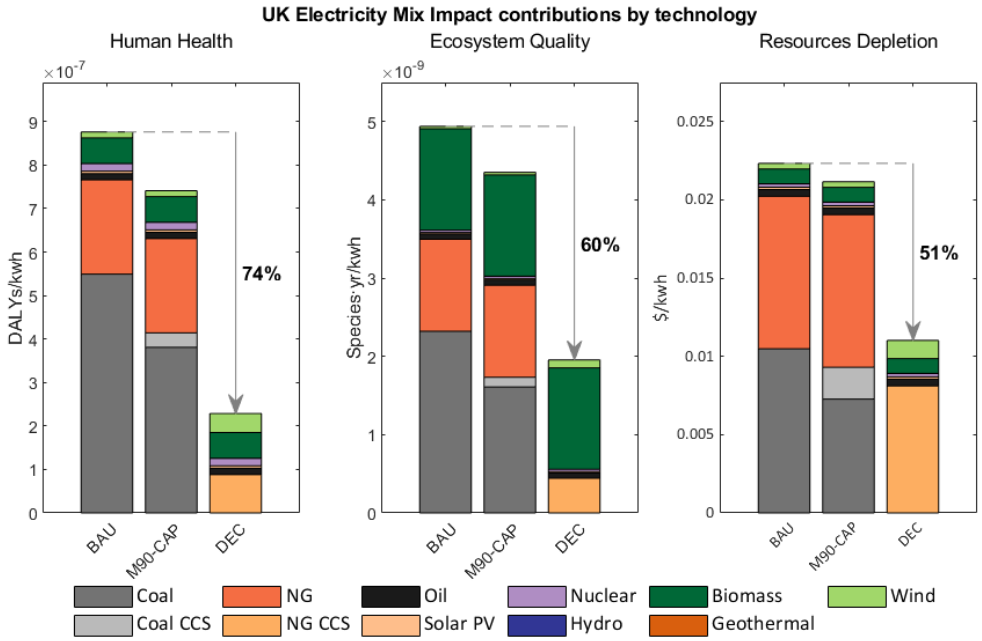


Figure C2 Process contributions to the total environmental indicators in the UK per (1kWh).

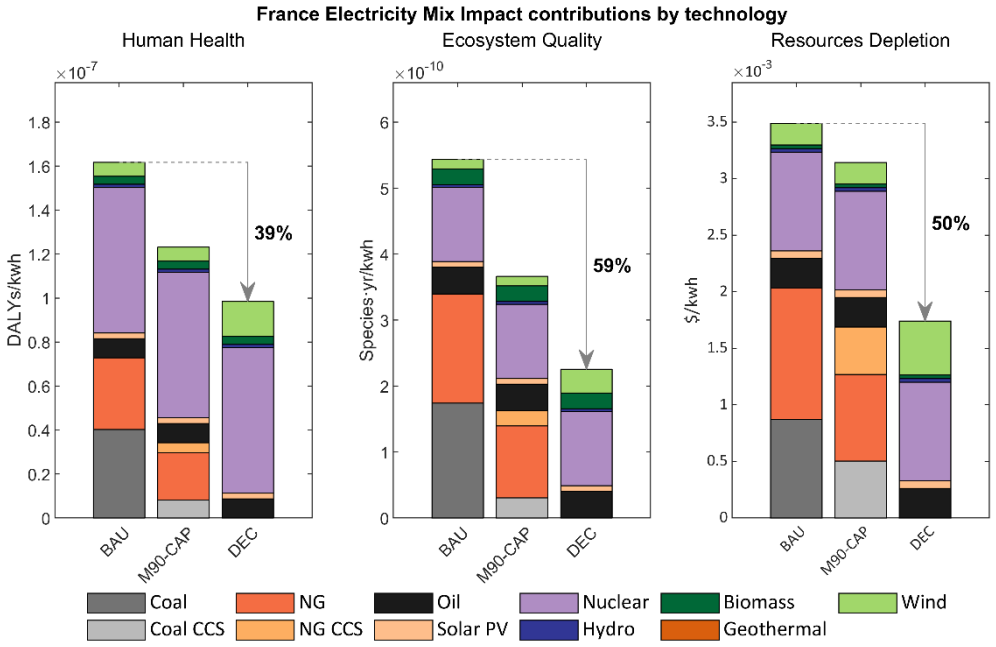


Figure C3 Process contributions to the total environmental indicators in France per (1kWh).

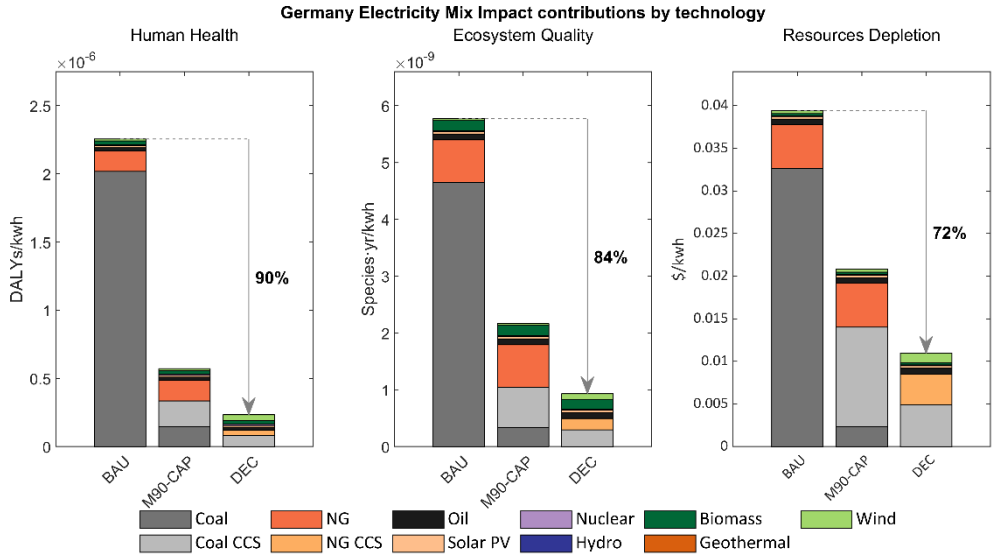


Figure C4 Process contributions to the total environmental indicators in Germany per (1kWh).

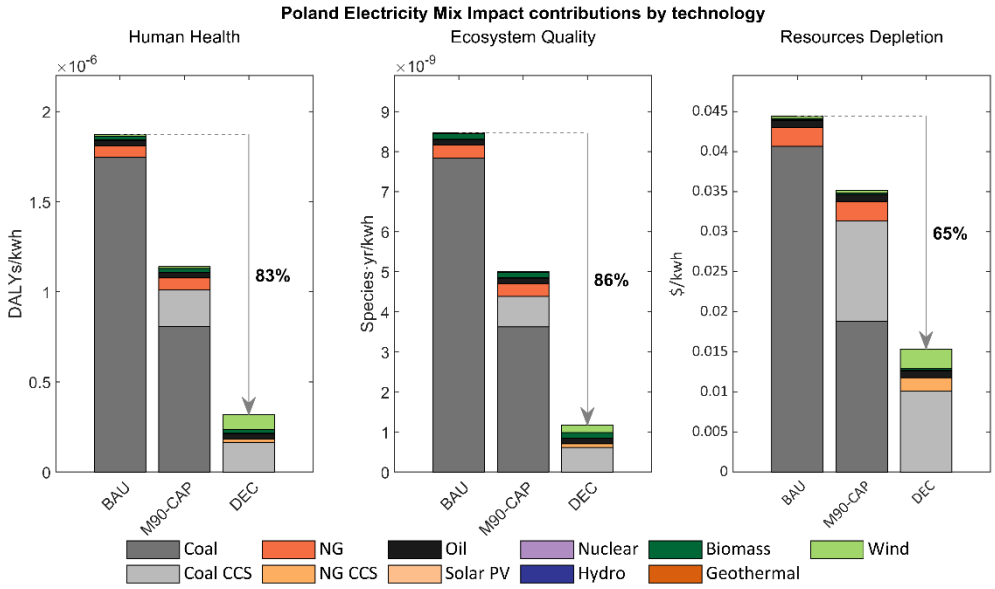


Figure C5 Process contributions to the total environmental indicators in Poland per (1kWh).

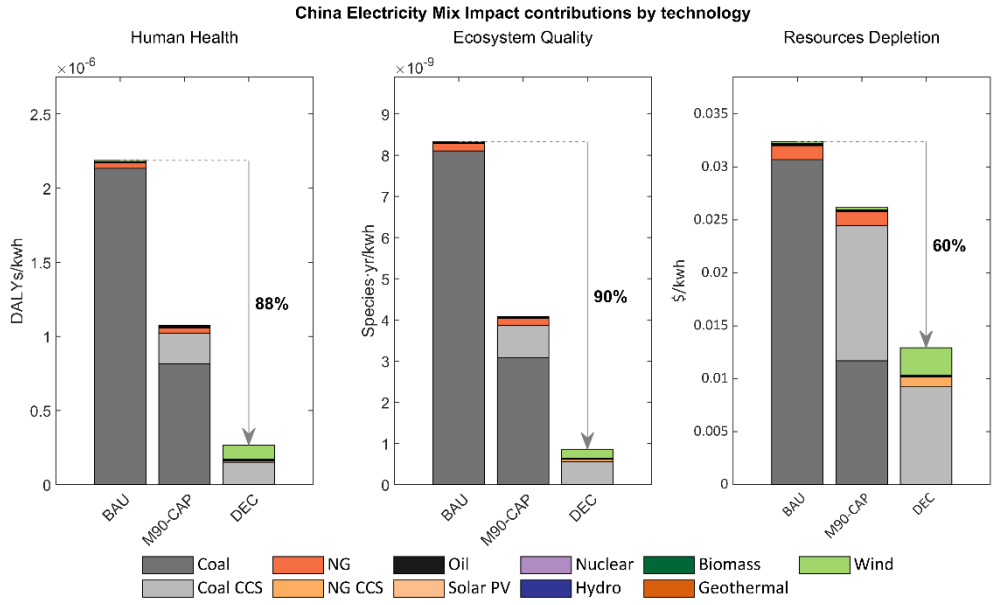


Figure C6 Process contributions to the total environmental indicators in China per (1kWh).

Countributions of transportation and electricity to the total environmental impacts

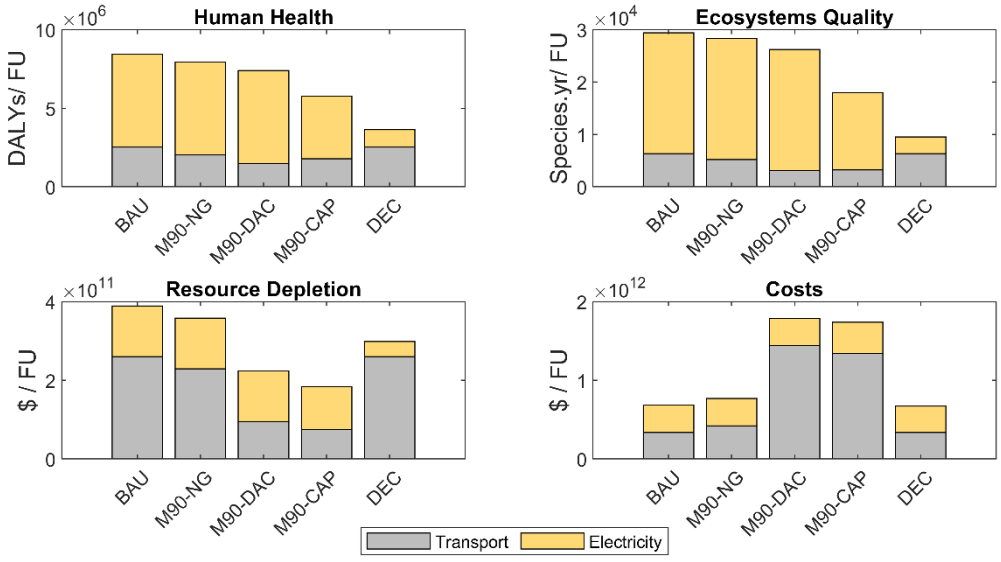


Figure C7 Contributions of the total environmental impacts of both electricity and transport sectors in the US.

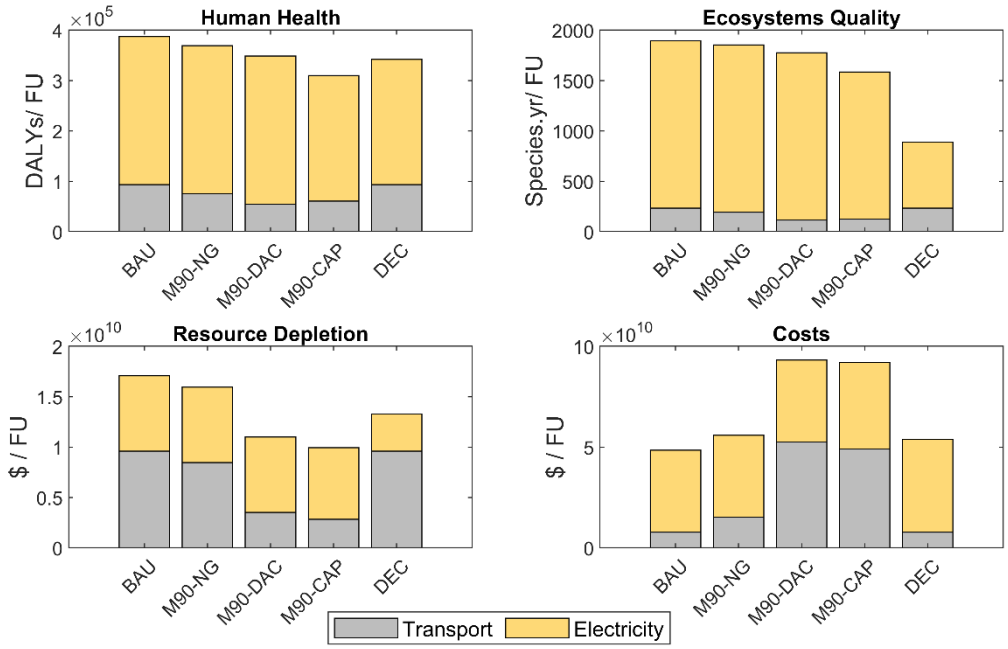


Figure C8 Contributions of the total environmental impacts of both electricity and transport sectors in the UK.

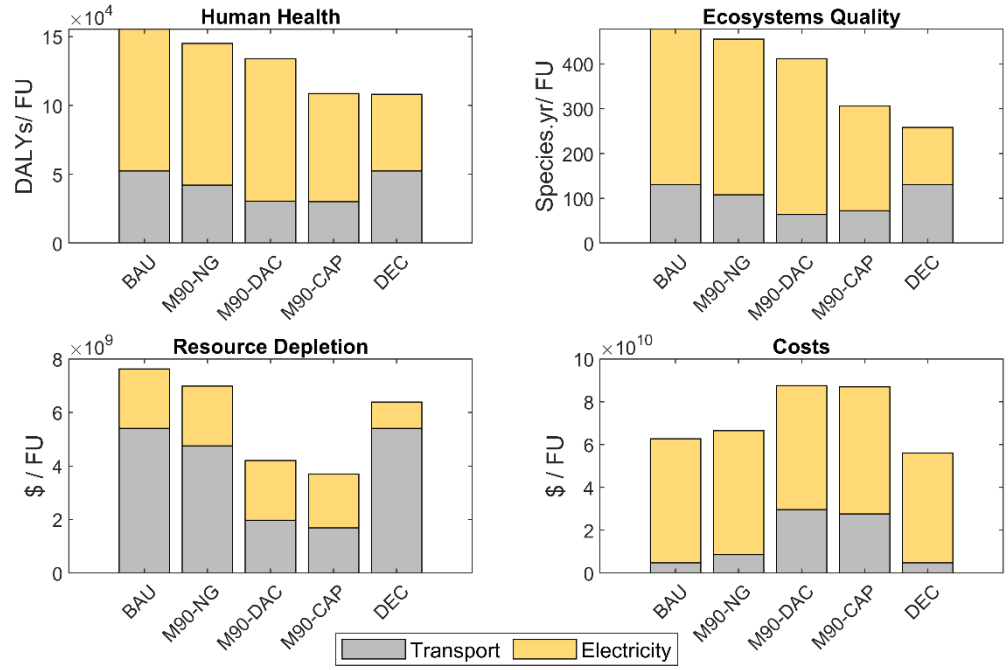


Figure C9 Contributions of the total environmental impacts of both electricity and transport sectors in France.

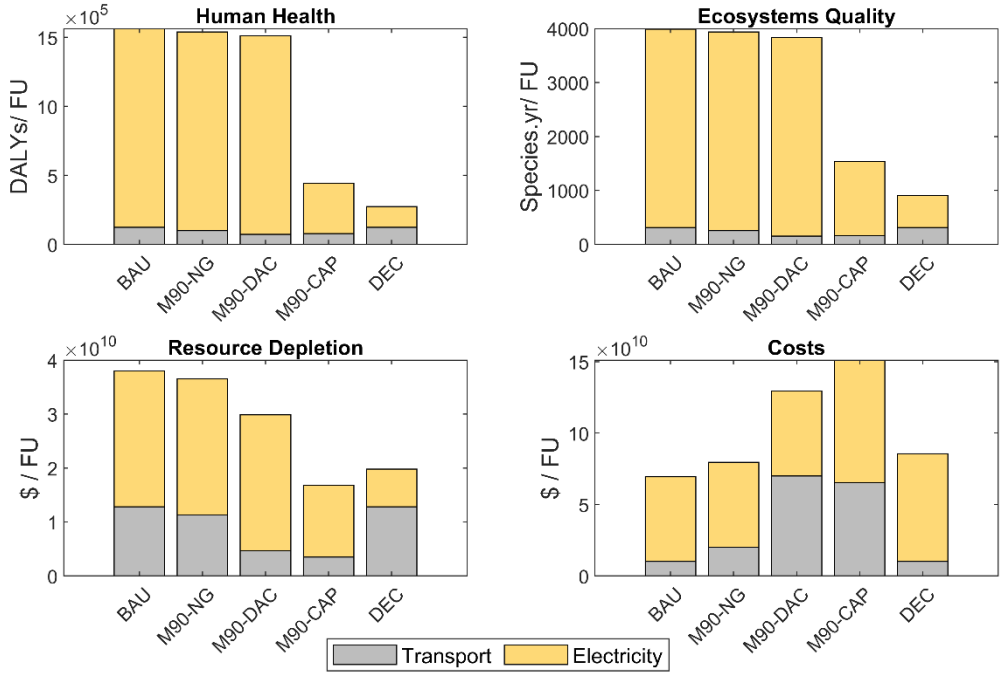


Figure C10 Contributions of the total environmental impacts of both electricity and transport sectors in Germany.

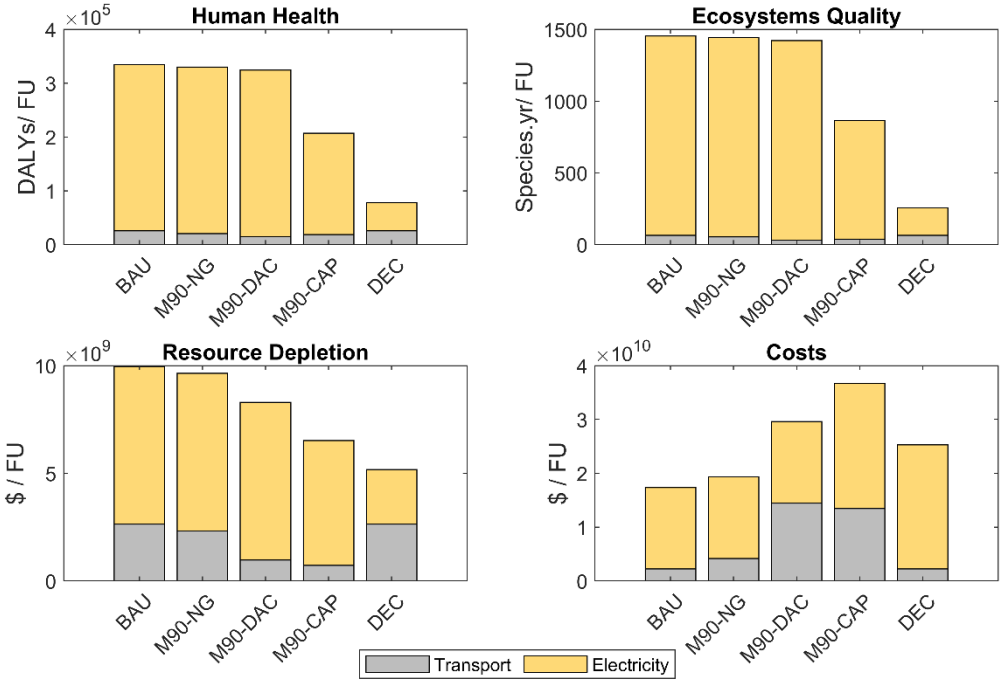


Figure C11 Contributions of the total environmental impacts of both electricity and transport sectors in Poland.

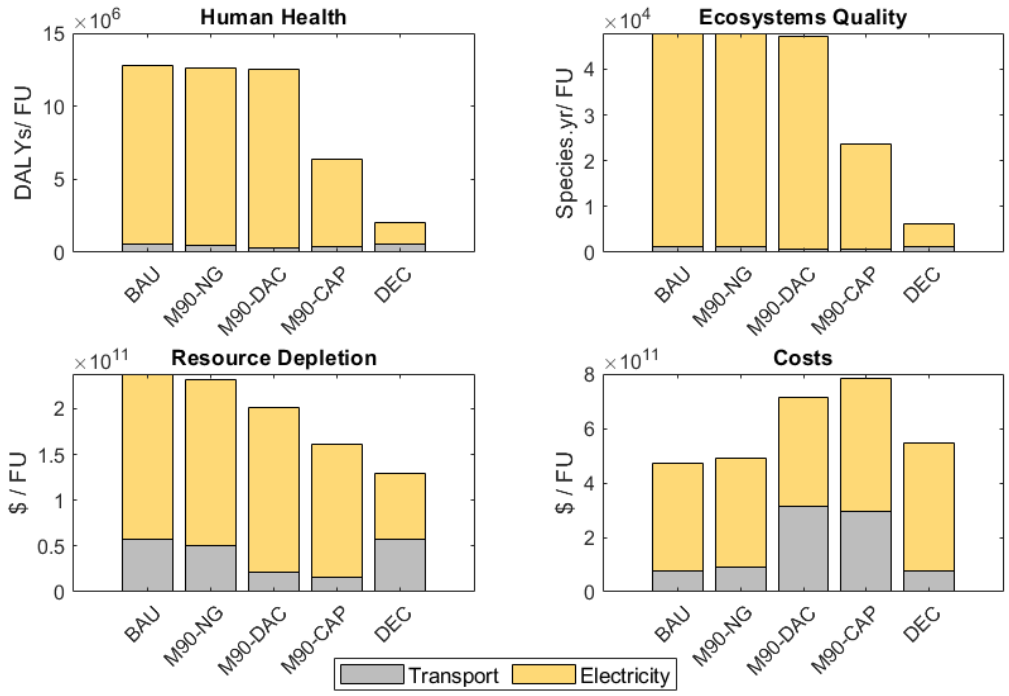


Figure C12 Contributions of the total environmental impacts of both electricity and transport sectors in China.

APPENDIX REFERENCES

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