CARBON NEUTRAL FUELS AND CHEMICALS:

Techno-economic and environmental assessment of novel technologies and processes' integration

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Abstract

This work addresses the issue of the transition of the petrochemical industry to a net zero scenario. The chemical industry is responsible for 10% of greenhouse gas (GHG) emissions when both direct and indirect emissions are considered. This industry plays a key role in mitigating global warming due to its sheer size, and its links to many other sectors. Because of the need for carbon atoms as feedstock, all solutions aim to achieve a net-zero carbon footprint rather than full decarbonization. A comprehensive literature review of Life Cycle Sustainability Assessment (LCSA) is used to identify the status and challenges of this industry, followed by a discussion of the applicability and performance of various practical solutions. As a general result obtained by different studies, Demand Side Measures (DSM) and Supply Chain Management (SCM) are the most effective and efficient mitigation strategies. Thanks to high circularity, the consumption of fossil fuels for short-lived plastics could decrease towards zero, thereby reducing the generated impact. E-fuels and e-chemicals are only a viable option if they employ 100% renewable energy and Direct Air Capture (DAC). Power-to-X is an important application area for these technologies, likely be dominated by chemicals with simple molecules (H_2, NH_3, CH_4). Biofuels and bio-chemicals should be used to promote Waste-to-X, and bioenergy carbon capture and storage concepts to achieve the highest gains without burden shifting. Drop-in alternatives should be prioritized in hard-to-abate sectors and are an effective tool in the short and medium term. The second part of the work focuses on the analysis of four different sustainable aviation fuels production systems by applying a simplified LCSA. The results are consistent with the literature; e-jet fuel is four times more expensive than fossil jet fuel with 93% lower GHG emissions on a Cradle to Grave (CtG) basis. These technologies are capital expenditure (CAPEX) intensive, with the cost of electricity accounting for more than two-thirds of the final production cost. Solid Oxide Electrolysis (SOE) remains the most promising technology, enabling a reduction in production cost of nearly 2.4 c€/MJ. Finally, the price has been identified as the main obstacle to these technologies, necessitating strong and smart policy (Research and development). Nonetheless, if alternative technologies are not well-designed and deployed in the right place at the right time, they could lead to higher impacts than traditional ones.

Keywords

e-fuels; sustainable aviation fuel; net-zero carbon; petrochemical industry; life cycle assessment; Fischer-Tropsch process.

Abstract

Il presente lavoro di tesi è incentrato sulla transizione dell'industria petrolchimica, responsabile del 10% delle emissioni globali di gas serra. In particolare, vengono discusse una serie di tecnologie alternative che mirano a raggiungere la carbo-neutralità di questo settore data l'inevitabile necessità di carbonio come input dell'industria. La prima parte di questa tesi si focalizza sulla disamina di molteplici articoli scientifici riguardo Life Cycle Sustainability Assessments di alternative praticabili nel breve e medio periodo. Il modo più efficace per ridurre l'impatto generato da questo settore è la diminuzione della domanda tramite Demand Side Measures e Supply Chain Management come il riciclo di plastiche definite a breve termine. Per quanto riguarda gli e-fuels, essi necessitano energia rinnovabile e DAC per essere considerati sostenibili. Power-to-X è una famiglia di tecnologie che si svilupperanno attorno a e-chemicals semplici (H_2, NH_3, CH_4). Biofuels nascondono una serie di problemi legati all'uso del suolo e al consumo di acqua, e per questo le applicazioni di queste tecnologie che generano l'impatto minore sono Waste-to-X e BioEnergy Carbon Capture and Storage. Infine, grazie a drop-in tecnologies e process integration è possibile abbattere costi ed emissioni. La seconda parte della tesi riguarda un LCSA eseguito su 4 sistemi di produzione di SAF (Sustainable Aviation Fuels). I risultati ottenuti sono in linea con I valori riscontrati durante la prima fase del lavoro. Il costo di produzione del e-jet fuel si è rilevato quattro volte maggiore del costo del carburante da fonti fossili. E-fuels sono tecnologie ad alta intensità di capitale, derivante per più di due terzi dal costo dell'energia rinnovabile. Le emissioni generate sono all'incirca il 93% inferiori su base CtG (Cradle to Grave). SOE (Solid Oxide Electrolysis) è una tecnologia innovativa col potenziale di ridurre i costi di produzione fino a 2.4 c€/MJ. Un altro risultato importante è il ruolo del costo di produzione come principale ostacolo verso la distribuzione su larga scala; perciò, sono richieste politiche mirate e ben designate per garantire una transizione efficace ed equilibrata.

Parole chiave

e-fuels; combustibili sostenibili per l'aviazione; carbo-neutralità; industria petrolchimica; life cycle assessment; processo di sintesi Fischer-Tropsch;

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1. Introduction

The goal of keeping the temperature increase under 1.5 °C requires tremendous amount of effort in all sectors to perform a transition to a more sustainable paradigm. The petrochemical industry comprises both the petroleum industry and the chemical industry. The petroleum industry, commonly known as the oil industry, encompasses all processes aimed at obtaining refined products starting from crude oil extraction. Among these products, gasoline and diesel cover the largest share of this industry's economic output, primarily destined for the transportation sector. On the other hand, the term chemical industry denotes the field of chemical product manufacturing. The number of goods produced by this industry is significantly higher than that of the petroleum industry, leading to a wider distribution of small manufacturing facilities. Each facility is focused on producing a specific product or a family of goods.

The reason for selecting the petrochemical industry as the focal point of this study lies in the unique requirement for a carbon input to produce its goods, placing the industry in the category of hard-to-abate sectors. Addressing this issue on a global scale can be overwhelming and, to some extent, ineffectual. Therefore, this work concentrates on some of the main steps and products of this industry with the goal of obtaining tangible results, while also allowing room for further analysis, particularly of the downstream processes. Moreover, in the contemporary interconnectedness of all sectors, achieving a net-zero future for any sector necessitates the sustainability and transition of all sectors connected to the supply chain. Some ancillary sectors, such as shipping and aviation, present additional challenges as some of the traditional solutions are deemed unfeasible. These considerations elucidate the choice of focusing on the products at the center of this research: primary chemicals, diesel, and jet-fuel.

Regarding the novel technologies described in this work, they have been selected not only because of their performance, both current and projected, but also taking into account their capability and likelihood to deployment on large scale. These factors are assessed through the Life Cycle Sustainability Assessment (LCSA) procedure, aiming to obtain results that are as comprehensive as possible.

Particular attention will be given to a specific application of these transition technologies: e-jet fuel. Sustainable Aviation Fuels (SAF) are expected to play a crucial role in the upcoming years, particularly in Europe. An additional aim of this study is to provide an overview of current and promised policies, identifying common ground and possible blind spots.

2. State-of-the-art

In this chapter, the intention is to depict the current state of the petrochemical industry in terms of product output, employed processes and their characteristics. This will be accomplished initially from a global perspective, followed by a focus on the European Union (EU) to gain insights from developed economies. This approach will prove valuable when considering future policies and alternatives.

The petrochemical industry stands as one of the foundations of modern society. This assertion is confirmed by both the direct and indirect utilization of its products in our everyday lives, supported by data. In fact, the chemical/petrochemical industry (hereafter, the terms will be used interchangeably) is the leading industry in terms of energy consumption, ranks third in Greenhouse Gas (GHG) emissions [2] , holds the 8th position in economic industries with revenue exceeding 5 trillion USD (United States Dollars)(considering only the oil refinery and gas industry) [3] , and is responsible for approximately 95% of all manufactured goods.

a. Global overview

In this section, the global chemical market will be analyzed once again, focusing on output and industrial processes. This task proves to be challenging, not only due to the sheer volume of data required but also because of the lack of reliable sources. An illustrative example of this challenge is evident when tracking final products. This process involves small-scale businesses that are seldom connected to national or international databases.

As this report does not have the means to generate highly accurate results but instead adopts a general and broader approach, the focus is directed towards the main products (primary chemicals, diesel, and jet fuel) and primary processes. The analysis concept adopts an upstream perspective for this complex industry (i.e., Cradle to Gate). The intention is to emphasize the significance of downstream steps in more comprehensive studies, which are essential for developing complete models, forecasts, and assessments.

The magnitude of the chemical industry is evident, especially in the upstream flows concerning feedstocks. Notably, the chemical industry stands out as one of the largest consumers of fossil fuels. Approximately 3% of global coal consumption, 14% of oil consumption, and 9% of gas consumption are attributed to this industry. The global demand for fossil fuels demand is illustrated in Figure 1.

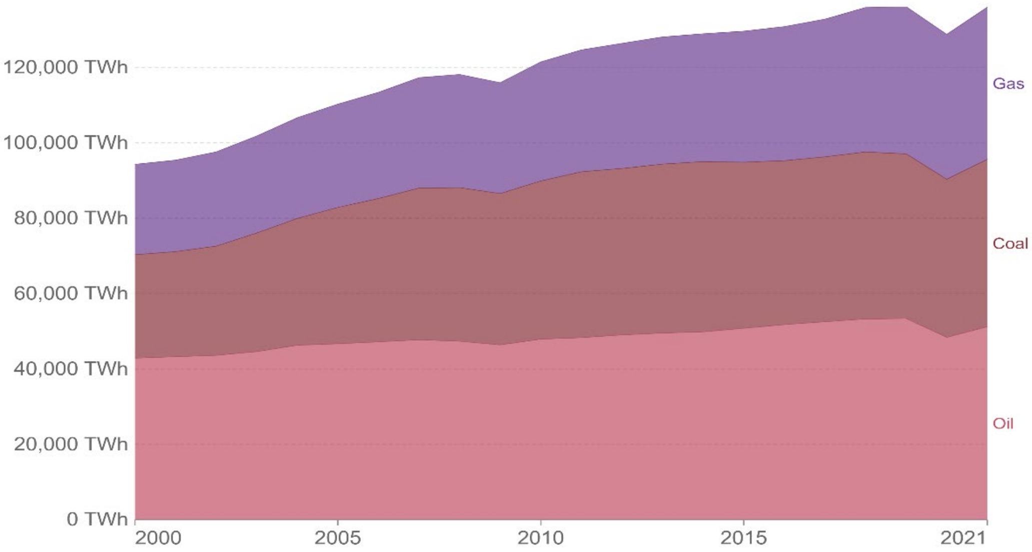


Figure 1 Global fossil fuels consumption in the past 2 decades [4]

Interestingly, despite these shares being accounted for as "energy demand", the majority is required as feedstock rather than for typical energy purposes. This distinctive aspect arises from the necessity for carbon and hydrogen atoms, the primary constituents for most chemicals, as inputs. Specifically, approximately 60% of the "energy demand" manifests in the form of feedstock. In this context, the various fuels are not consumed to produce energy but are processed and integrated into the chemical structure of various products. Furthermore, owing to the advancements in efficiency and process integration, the proportion of inputs used as feedstock has been on the rise over the years (see Figure 2).

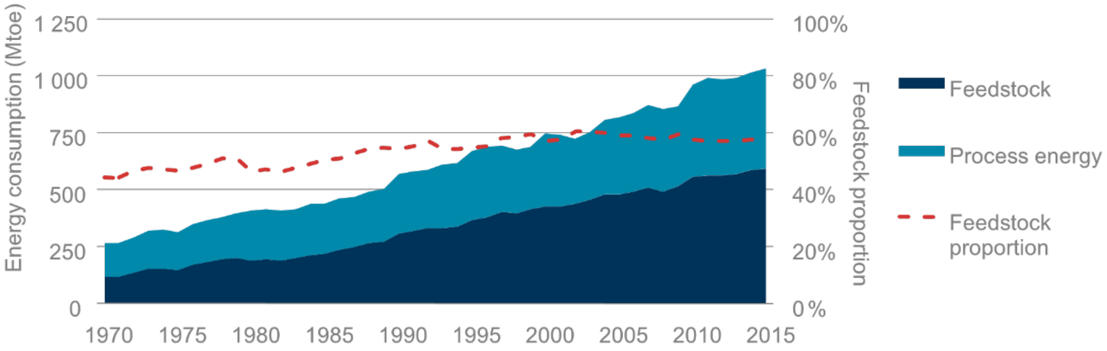


Figure 2 Feedstock and process energy consumption in the chemical sector.[6]

As specific energy consumption tends to decrease, the utilization of feedstock is less affected by technological improvements, primarily due to the theoretical limit imposed by stoichiometry. This is a crucial aspect to highlight when discussing the transition of the petrochemical sector. Given the intrinsic need of carbon atoms in the production of these goods, referring to this transition as decarbonization might be misleading. Instead, it would be more appropriate to characterize it as achieving carbon neutrality.

The overall emissions of the petrochemical sector rank as the third highest among industries (see Figure 3), despite the considerable consumption of fossil fuels. This is partially explained by the concept elucidated earlier. The assessment of GHG emissions is intricate, relying on LCAs that consider all externalities from upstream to downstream, encompassing both direct and indirect impacts.

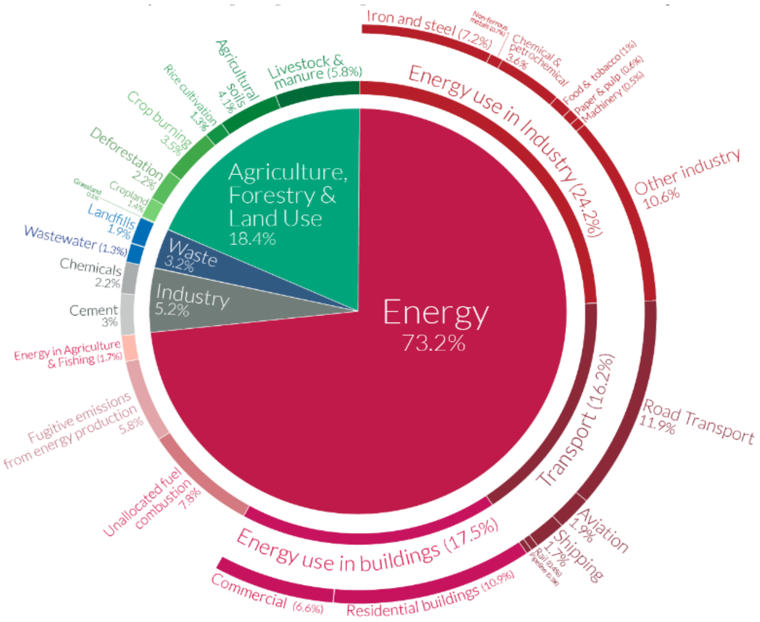


Figure 3 *Global emissions of CO_2 eq. by sector (2016)* [7]

In a more precise breakdown, emissions are categorized into scopes 1, 2, and 3. Scope 1 emissions, or direct emissions, encompass all emissions generated on-site, such as those resulting from the combustion of hydrocarbons. As depicted in Figure 4, direct emissions account for less than one-third of all emissions [8] . Within this category, the largest share is attributed to the production of primary chemicals[2] . Scope 2 and scope 3 emissions are considered indirect emissions. Scope 2 emissions are associated with the production of electricity, while scope 3 emissions encompass all the remaining indirect emissions linked to raw materials, transportation, distribution, etc. Indirect emissions are more complex to compute, primarily due to the extensive range of products (see Figure 6), end uses, and other variables influencing results, such as transportation means and the carbon footprint of electricity.

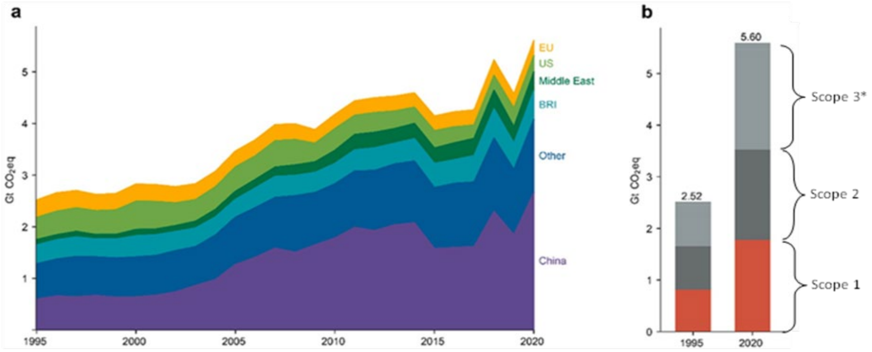


Figure 4 *GHG emissions from chemicals (a) by country and (b) by scope** [8]

*Only upstream emissions, neither downstream nor end of life emissions are accounted

Furthermore, the results illustrated in Figure 4 pertain to the situation in 2013, and as the years pass, the demand and production paradigm undergo changes. Figure 5 illustrates the growth of the chemical sector over the past 50 years in terms of output compared to other sectors.

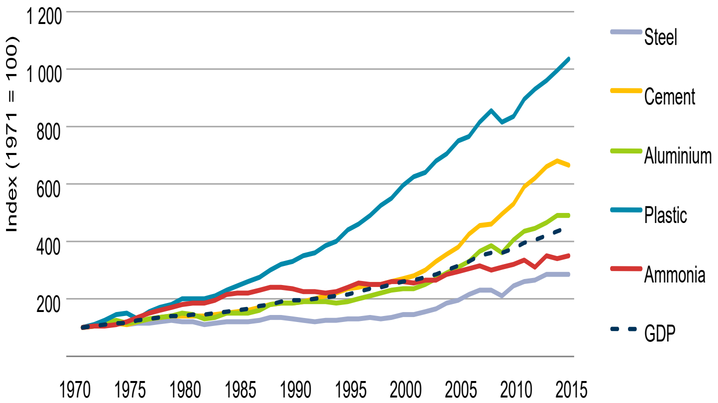


Figure 5 Demand evolution of the main industries' outputs (1970-2015).[6]

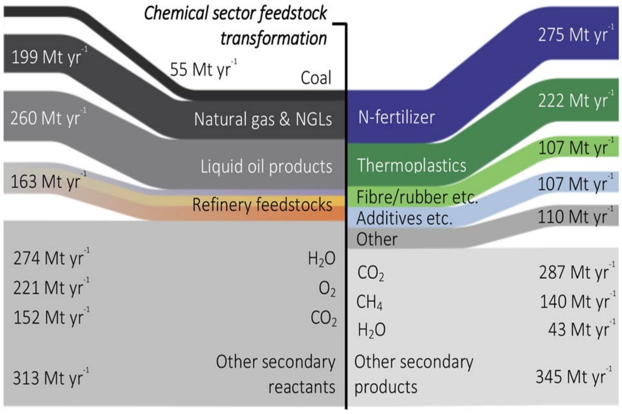


Figure 6 Global balance of feedstock and products.[1]

This growth is driven by multiple factors, with the main ones being the increase in population and GDP (Gross Domestic Product), which, when combined, contribute to a general expansion of the market. Moreover, technological advancements in various sectors, particularly those reliant on plastic products, significantly impact demand. The proliferation of plastic products across different industries is attributed to their advantageous physical and chemical characteristics, including water resistance, durability, workability, and cost-effectiveness. Additionally, some of the technological benefits offered by these new materials are considered undeniable and unmatched. Taking the transport industry as an example (see Figure 7), the progressively stringent regulations regarding fuel consumption and emissions necessitate vehicles to be as light as possible. This objective is presently achieved by substituting most of the interiors and parts of the chassis with plastic equivalents.

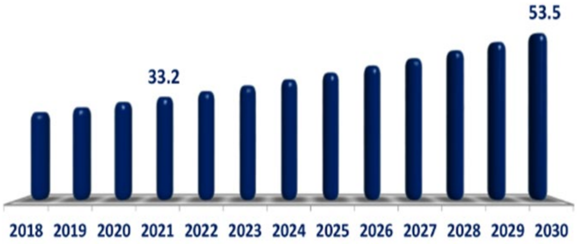


Figure 7 Global automotive plastics market (USD Billions) [10]

Other examples of increased plastic usage can be found in the building and construction sector, which has seen a rise in plastic utilization in recent years. The most common chemical product employed in this context is PVC, which, along with other plastics (e.g., PUR) constitutes nearly 95% of thermal insulating materials. This trend is qualitatively consistent across most sectors, leading to a dilemma. While the use of these plastics can result in lower direct emissions in various sectors (e.g., lighter vehicles leading to reduced combustion emissions), this benefit needs to be weighed against the indirect emissions originating from the supply chain of these products. As a result, no general result can be drawn to determine whether the use of these chemicals is "good or bad". Some of the determining factors include the type of plastic employed and its end use, which significantly impacts the product's life span and, consequently, the interrelated emissions. Therefore, assessing whether the use of plastics has a net positive or negative effect requires a tradeoff, specific to each case, where the achieved emissions reduction must be compared with the life cycle emissions of the plastic used. As a general result, the shorter the lifespan of a plastic, the higher the impact generated. For example, packaging plastics raise more concern compared to plastics used in the transportation sector due to the substantial difference in lifetimes observed in Figure 8.

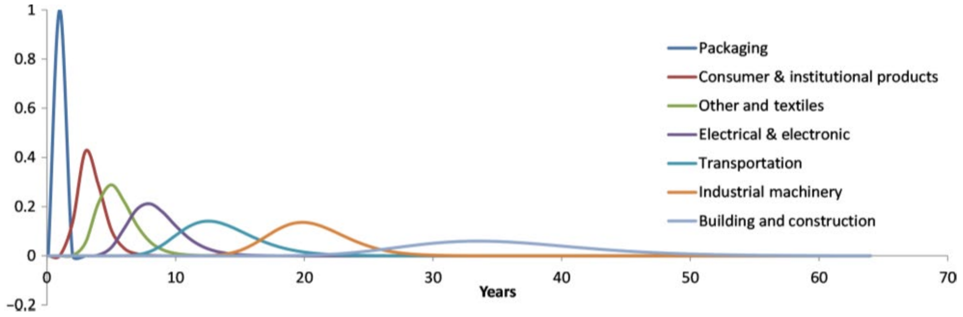


Figure 8 Product lifetime distribution for different products and end-use [11] .

b. A Europe insight

In this section, the focus shifts to the EU market. A local approach is crucial when problem-solving, albeit more complex and time-consuming. The EU was the second largest market for chemicals in 2011, totaling 516.8 billion euros [12] , following China's lead at 761.6 billion euros. Over the years, the EU's market share decreased from 19% in 2011 to 15% in 2021 [12] maintaining its position as the second largest market (see Figure 9) and ranking as the third largest producer of primary chemicals.

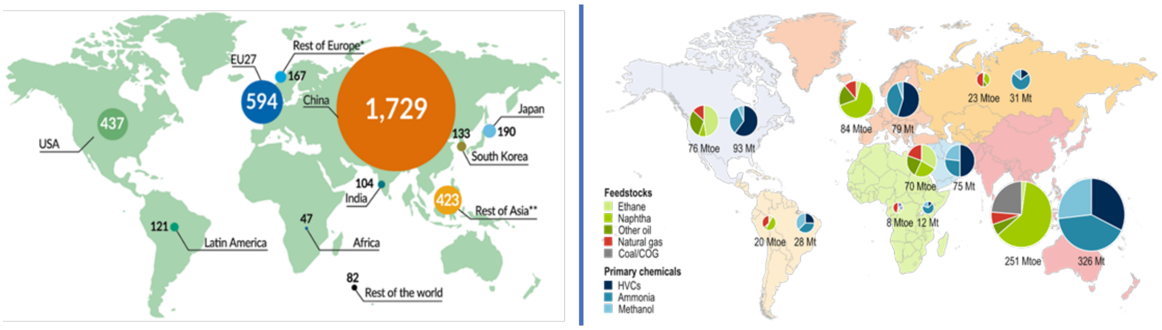


Figure 9 Global chemicals' market distribution (left, billion$) [12] *, global primary chemicals production and relative feedstocks (right)* [6]

The same trend can be observed in other developed countries, such as USA and Japan, where they registered a 4.4% and 1.6% decrease in market share, respectively. Another major difference among regions is the feedstock employed. Figure 10 illustrates fossil fuel production in each region of the world, and this tends to determine feedstock preferences. In Russia, more than half of the feedstock comes from Natural Gas (NG), followed by South America and the Middle East in terms of share. Asia Pacific, on the other hand, stands alone in the use of coal. Each region is characterized by its unique production and trade of each source, significantly influencing the cost and feasibility of processes as well as the Research and Development (R&D) of different technologies, such as Methanol to Hydrocarbons (MTH) technologies in China.

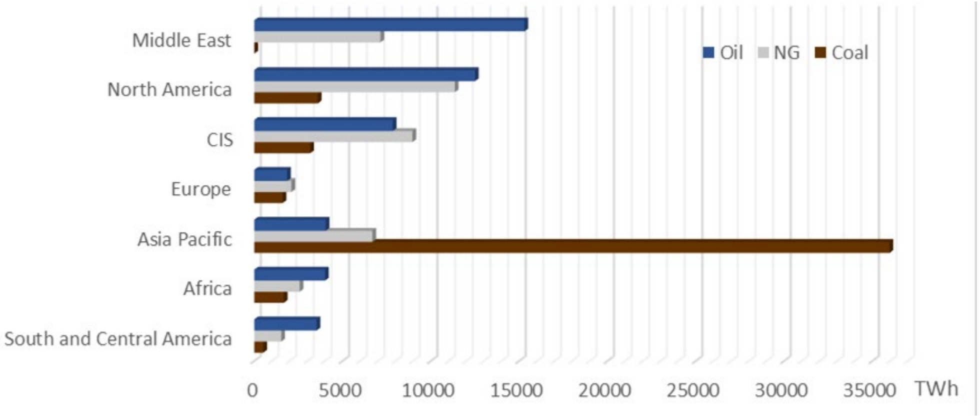


Figure 10 Global fossil fuels production by region [4]

c. Main products and corresponding processes

Now, it is time to specifically focus on the main products of the petrochemical industry, aiming to provide an overview of the production processes. The production of end-use products, including plastics resins and others, relies on relatively few feedstock inputs. Primary chemicals serve as the starting point for nearly all processes and, in some cases, can be used directly as final products (primarily methanol and ammonia). Thus, gaining an understanding of their impact at various levels provides valuable insights into the nature of the petrochemical industry.

These primary chemicals can be regarded as the elemental building blocks that constitute all other products in the chemical industry. These iclude ammonia (NH3), methanol (CH3OH), and other olefins and aromatics known as High-Value Chemicals (HVCs). Figure 11 provides a summary of the CO_2 emissions associated with the production of primary chemicals and outlines the main applications for each one of them.

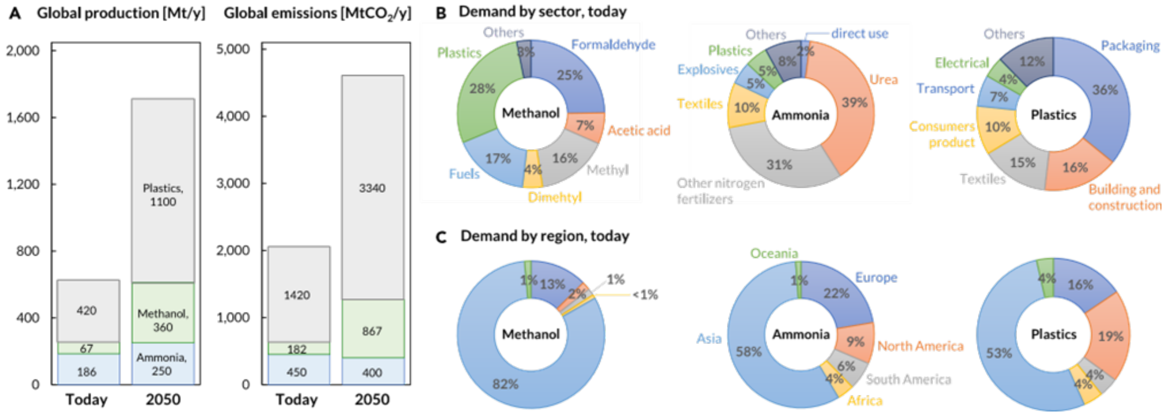


Figure 11 Global production and CO_2 emissions associated with the primary chemicals in 2020 and 2050.[9]

i. Ammonia

Ammonia is one of the primary chemicals, constituting approximately 28% of the industry's output. While ammonia can be directly used as a product in specific applications such as a refrigerant or cleaning product (around 2%), its predominant use is in the fertilizer industry, accounting for about 70%, with nearly 40% directed towards urea production. It is worth noting that about half of the world's food production relies on fertilizers [6] , and consequently, fertilizer consumption tends to increase with the growth of the population and the development of a region (see Figure 12).

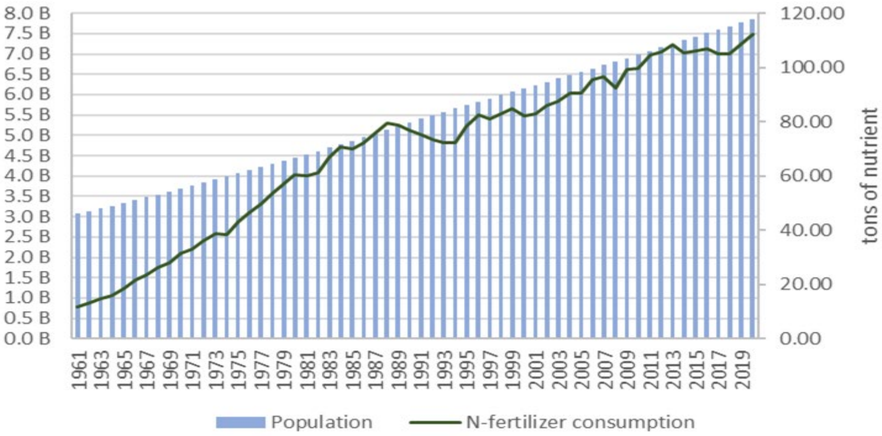


Figure 12 Trends of population growth and N-fertilizers consumption compared [16] [17] .

Production processes

Ammonia was first discovered in 1774 by Priestley and later synthesized by Frank and Caro in 1898 through hydrolyzation of calcium cyanamide:

$$CaO + 3C \leftrightarrow CaC_2 + CO \quad (1)$$

$$CaC_2 + N_2 \leftrightarrow Ca(CN)_2 + C \quad (2)$$

$$Ca(CN)_2 + 3H_2O \leftrightarrow CaCO_3 + 2NH_3 \quad (3)$$

Since then, the most significant discoveries and implementations were made by Haber, the first to synthesize ammonia from streams of nitrogen and hydrogen, and Bosch, one of the chemists to discover the best iron catalyst for the process as well as the required equipment to withstand high pressures and temperatures (approximately 500 °C and 200 bar). This discovery is arguably one of the most important of the last century, paving the way for sustaining progress and the society we now live in. It is estimated that more than 50% of the world's population is fed thanks to fertilizers. The breakthrough occurred at a crucial moment in history, as the supply of the former natural fertilizer (i.e., bird's guano extracted in the Chincha islands offshore of Peru) was dwindling. Figure 13 illustrates the main sections of the ammonia synthesis process.

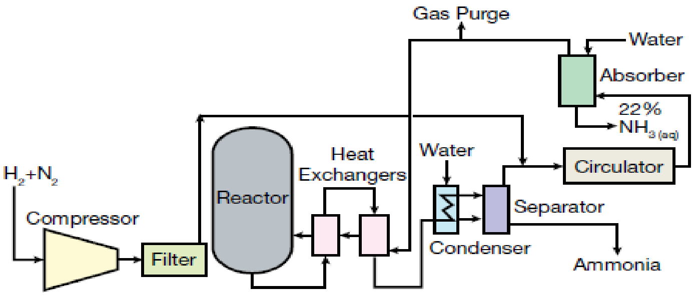


Figure 13 Simplified flow scheme of the first BASF ammonia production process [15]

In the past 100 years, various improvements have been patented by different companies, mainly aiming to enhance the energy efficiency and capacity of the sequence of processes. Variations among processes arise from differences in reformer type, machinery employed, and purification section. Figure 14 compares a conventional process to a Linde ammonia concept. The Linde concept, with the inclusion of a Pressure Swing Adsorption (PSA) unit and an Air Separation Unit

(ASU), eliminates the need for a separate purification step.

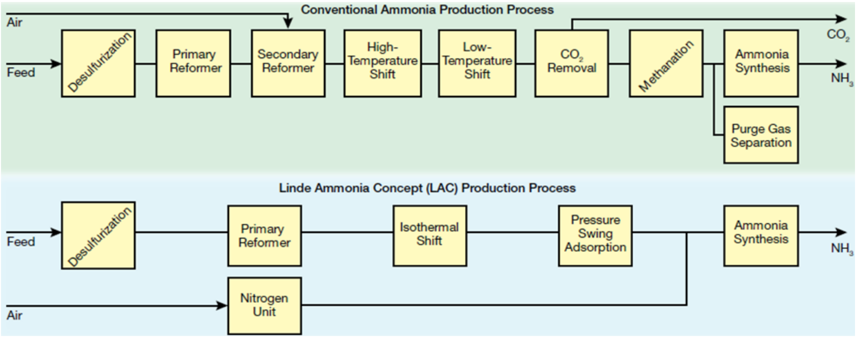


Figure 14 Comparison between conventional process and LAC, the latter using PSA and ASU to obtain high purity streams. [15]

Another significant difference among processes is the feedstock employed. Currently, natural gas is the most widely used feedstock, offering the highest efficiency (see Figure 15). Coal follows with the majority of the installations in China, and secondary sources such as biomass and green hydrogen. Regarding biomass and coal, the processes differ from NG-based ammonia because a gasification step is required to convert solid fuels into synthesis gas. The energy consumption reported in Figure 15 serves as an indicator of the conversion efficiency, and despite some routes (e.g., coal) being less efficient than others (NG) there's no unique preferred feedstock.

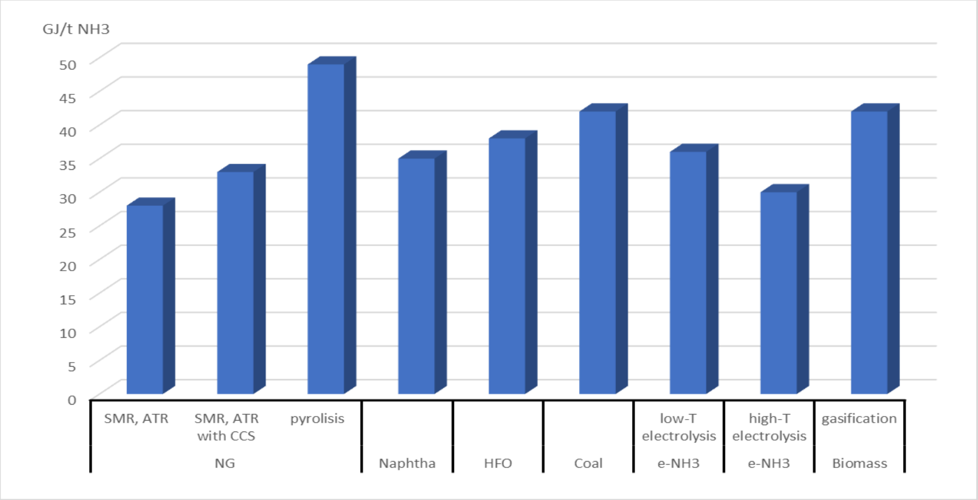


Figure 15 Typical energy consumption for different ammonia production routes[13] .

The selection of the feedstock depends on four major factors: availability, cost of the feedstock, capital intensity, and policies' compliance. While coal can be considered one of the cheapest feedstocks available, ranging from 0.47 to 2.37 \$/GJ, especially when compared to natural gas, which is in the range of 1.9 to 9.48 \$/GJ, its capital intensity is significantly higher, around 2,900 \$/y/installed capacity, compared to natural gas's 1500-2000 \$/y/installed capacity [13] . This substantial difference can be attributed to two main aspects. First, the coal-based plants require equipment for the gasification step, such as a gasifier and air separation unit, and additional purification equipment (see Figure 14) that is not necessary in NG-based plants where only the sulfur removal unit (SRU) is required. Secondly, the installed capacity of coal-based plants is about 100-300 kt_{NH3}/y, much lower than the installed capacity of NG-based plants, which can reach 1.3 Mt_{NH3}/y, benefiting from greater economies of scale [13] .

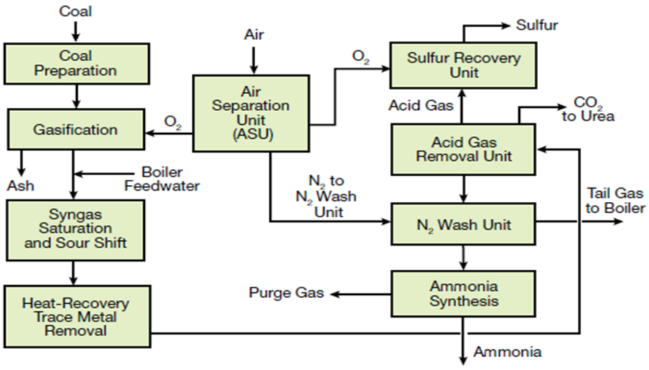


Figure 16 Flow scheme of ammonia production from coal. [15]

These differences result in a cost of ammonia of 225-315 \$/t_{NH3} for coal-based plants and of 110-340 \$/t_{NH3} for NG-based plants [13] . These results do not consider carbon taxes, which vary significantly from region to region. In the EU, considering an average of 75\$/t_{CO2}, the price of NG-based ammonia rises to 272-505 \$/t_{NH3}, while in China, no effective carbon tax has been implemented yet. Such a tax would bring the price into the range of 525-615 \$/t_{NH3}, higher than the expected prices for renewable ammonia in China for 2030 (below 500 \$/t_{NH3}).

ii. Methanol

Methanol, the simplest among alcohols, is the primary chemical with the steepest increase in production and demand from the late '00s to now (see Figure 17). The direct use of methanol is relatively narrow on a global scale. Direct-use applications include fuel cells, specifically Direct Methanol Fuel Cells (DMFCs), and fuel blends in gasoline to increase the Octane Number (ON). About 40% of the produced methanol is used to synthesize formaldehyde. Of this formaldehyde produced, about half is meant for direct use, with the remainder used as a feedstock to produce resins and plastics. The steep increase in the demand for this chemical is predominantly driven by its use as a fuel in the transport sector, either alone (M100) or blended (M85), for heating and cooking (stoves and boilers to assist the transition in developing countries), and in the naval sector.

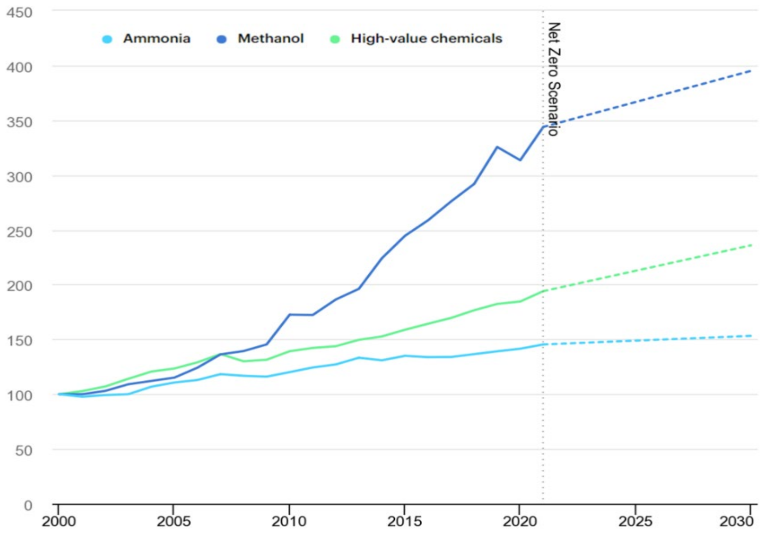


Figure 17 Increase of primary chemicals consumption normalized to 2000's values, and projected trends for net-zero scenario [2]

Production processes

As with ammonia, the synthesis process for methanol is now standardized, at least from a chemical standpoint. Methanol synthesis occurs by reacting hydrogen and carbon monoxide through a series of steps, which can be summarized by Eq.(4) and Eq.(5), and combined, they give Eq.(6).

$$CO+2H2\leftrightarrow CH3OH \tag{4}$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O \tag{5}$$

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \tag{6}$$

Once the syngas is obtained, whether from coal or natural gas, it is sent to the reactor in which a Cu/ZnO-based catalyst is present. The operating conditions are currently low temperature and pressure, around 200-250 °C and 50-100 bar, respectively.

While the synthesis process is generally the same, there are several technologies that differ in the pathway followed from feedstock to syngas. Currently, most methanol plants are based on natural gas, with coal being the second most common feedstock. The remaining percentage covers alternative feedstocks, such as biomass or CO_2/electricity.

Starting with natural gas as a feedstock, a reforming process is required to produce syngas. Different reformer configurations can be employed: Fired Tubular Reformer (FTR), Auto-Thermal Reformer (ATR), Dry Methane Reformer (DMR), Combined Methane Reformer (CMR). FTR, DMR, and CMR are endothermic processes that require a significant amount of heat to maintain the internal temperature above 700°C, while ATR is adiabatic or slightly exothermic. This heat is provided by the combustion of natural gas, making the processes highly OPEX intensive. To increase the overall efficiency, these processes are generally integrated with electricity generation capable of recovering some of the heat rejected through flue gases.

In a study by Blumberg[82] conventional technologies, FTR and ATR, were compared to more innovative layouts. With the EU average prices of electricity and natural gas (65 US$/MWh and 5 US$/GJ, respectively) the Levelized Cost of Methanol (LCOM) is 625 US$/$t_{MeOH}$ for the FTR, and 365 US$/$t_{MeOH}$ for the ATR- higher than the average contract selling price, approximately 300 $/$t_{MeOH}$ in EU. This significant difference is related to the higher efficiency of the ATR, resulting in lower fuel consumption and lower capital investment required. Moreover, the ATR benefits from higher economies of scale, and the resulting LCOM is less sensitive to natural gas prices than the LCOM of FTR system (see Figure 18). Overall, the average contract selling price for MeOH is approximately 400 $/$t_{MeOH}$ in North America and 300 $/$t_{MeOH}$ in the EU.

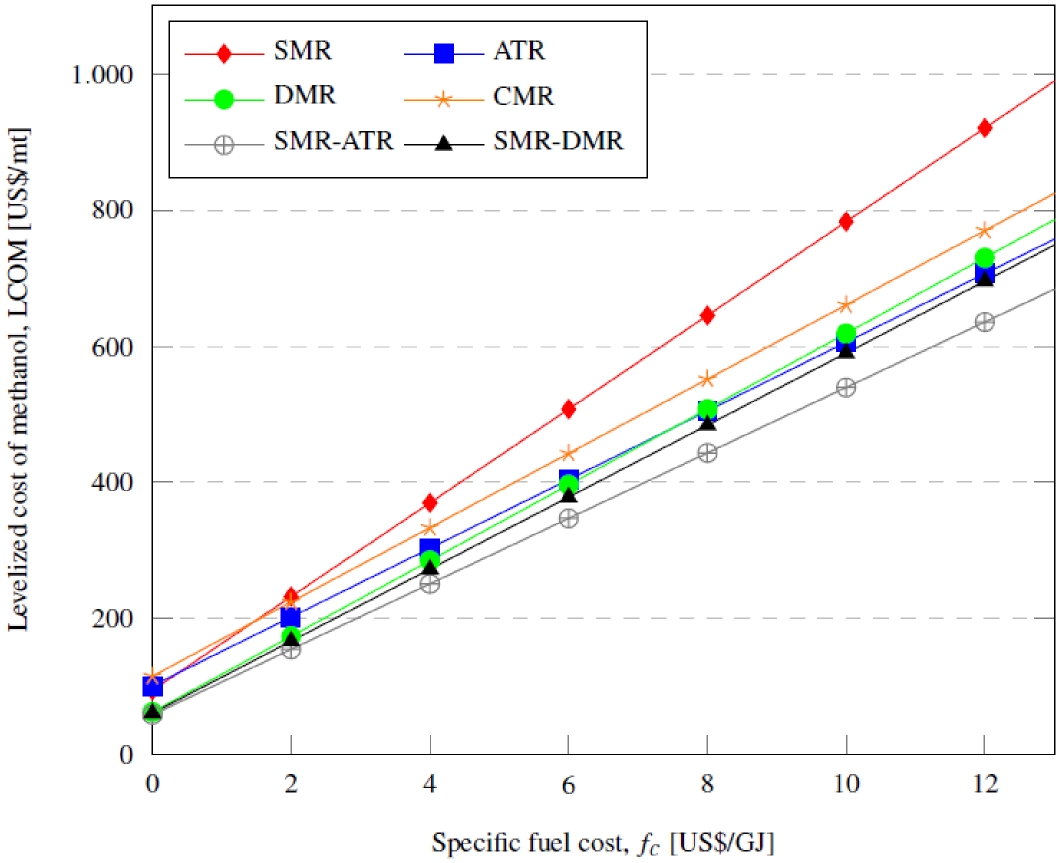


Figure 18 Impact of the price of NG on the LCOM for different processes.[82]

About 35% of methanol is produced from coal, with most of this production situated in China. Using coal as a feedstock requires higher capital investment attributable to the gasification and the syngas clean-up steps, and the process efficiency is about 10-20 percentage points lower than NG plants (50-60% compared to 70%)[26] .

iii. High Value Chemicals

Unlike ammonia and methanol, HVCs are not a singular compound but a family of chemicals. High-Value Chemicals is the name given to a group of compounds used as a starting point in the chemical/manufacturing industry. These HVCs include light olefins (ethylene and propylene) and BTX aromatics (Benzene, toluene, and mixed xylenes).

Main use

The direct use of HVCs is very rare, except for specific applications such as solvents. The market is heavily dominated by the chemical industry. As mentioned earlier, these compounds are the core of all plastic production. Despite the large number of final products that employ HVCs as feedstock, there are few that account for most of the final output. All of these are thermoplastics, meaning that they can be more easily recycled multiple times at the end of life. In Table 1, they are reported with the respective code, and the main applications are listed.

Table 1 List of the most diffused thermoplastics [6]

01 PET	Poly-ethylene Terephthalate (PET) is primarily used to manufacture polyester fiber, but its other key end-use is in food and beverage packaging. Its key properties include its high crystallinity and strength.
2 HDPE	High-Density Polyethylene (HDPE) is one of the most versatile plastics, used in a wide range of products from shampoo bottles to hard hats. It is made entirely of ethylene and is among the most recycled plastics.
03 PVC	Polyvinyl Chloride (PVC) is a tough resin that is most frequently used in construction. PVC is commonly used for windows, doors, and pipes on construction sites and in buildings throughout the world.
4 LDPE	Low-Density Polyethylene (LDPE) was the first polyethylene plastic to be invented and is another key plastic used for packaging. It is the key constituent of most plastic carrier bags.
05 PP	Polypropylene is a versatile plastic with many end-uses. Because it has a higher melting point than some other key polymers, it is often used in automotive applications where high temperatures can be encountered.
06 PS	Polystyrene comes in three main forms: “general purpose”, “high impact”, and “expandable”. The latter is used in packaging applications to protect goods during transport and storage.
07 O	Other thermoplastics include polycarbonate, acrylonitrile butadiene styrene, styrene-acrylonitrile, polymethyl methacrylate, polyacrylonitrile, polyvinyl acetate, and many others. They have a wide range of uses, but each is produced in much smaller volumes than those mentioned previously (01-06).

Production routes

There are several pathways followed to obtain HVCs because of the multitude of products and specific applications. Various ways to classify these processes can be adopted. The first difference, once again, stands in the feedstock, which in this case are predominantly oil refinery products (naphtha, LPG-Liquified Petroleum Gasses, etc.), and in the process layout. Naphtha and ethane cover most of the industry’s feedstock, followed by propane, methanol, and biogas.

Steam cracking is the most widely used process for naphtha, LPG, ethane, and gasoil. The general structure of a steam cracker, as shown in Figure 19, comprises three main sections. The first section is the pyrolysis section, in which the feedstock is preheated and sent to a pyrolysis furnace where it evaporates thanks to superheated steam reaching 750-900°C. The residence time depends on the severity chosen (which affects the product yield) which can range between 0.5 and 1 second. After leaving the furnace the gas is cooled down to 300°C and sent to the second section. The second section consists of primary fractionation to separate heavier compounds and a compression section. Before being sent to the product fractionation, the last section, the compressed gases pass through a cleanup section. Through product fractionation hydrogen, methane, C_2, C_3, and C_4 hydrocarbons are separated. The main difference between processes with different feedstocks is mainly in the middle section. Indeed, for ethane as a feedstock no primary fractionation is needed [19] .

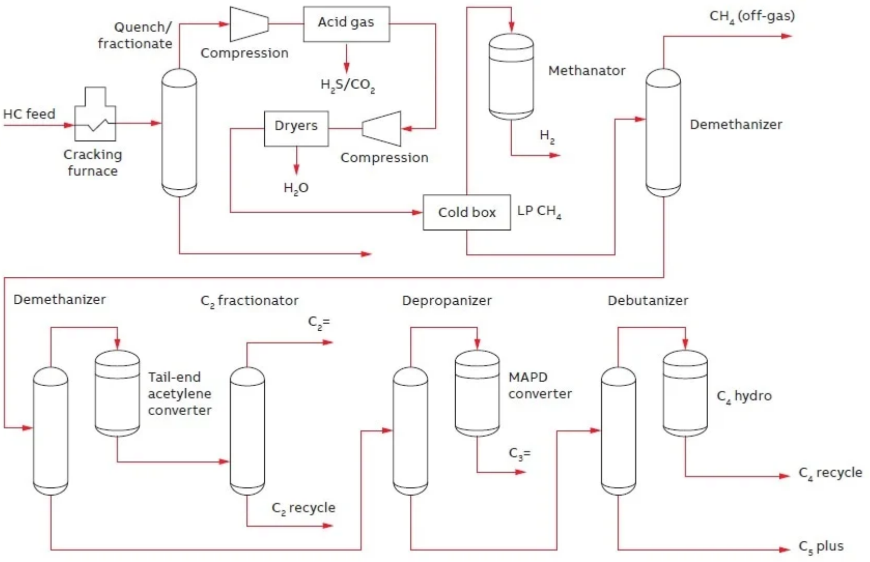


Figure 19 Flow scheme of a steam cracker.

A variation of this process is the naphtha catalytic cracking (NCC), developed with the goal of increasing the propylene yield. This necessity originated from the fractional yield obtained when ethane is used as feedstock. During the shale revolution in the USA (2010-2017), the situation aggravated when the supply of ethane increased, leading to a fall in prices, which favored a shift to ethane steam crackers. In addition, naphtha is increasingly requested to increase the production of diesel and gasoline in the transport sector. All this inevitably shook the market with a fall in ethylene prices and a rise in propylene prices.

For the same reasons, a set of other processes have been developed using methanol as a feedstock. Among these Methanol-To-Olefins (MTO) and Methanol-To-Aromatics (MTA), first brought to fruition by China, are alternatives to oil in the production of refinery products such as diesel or gasoline.

iv. Diesel & Jet fuel

The output of the petroleum industry is dominated by diesel and gasoline (nearly 85%). In this work, diesel and jet fuel, two of the many outcomes of the oil refinery process train as depicted in Figure 20, are included due to their implication in the net-zero transition related to their application. Diesel is the second most diffused fuel in the transportation sector, accounting for 36% of the total share[27] , while jet fuel is the primary fuel in the aviation sector. Both sectors are significant players in the global economy and in terms of GHG emissions, accounting for 12% and 2.4% of global emissions, respectively.

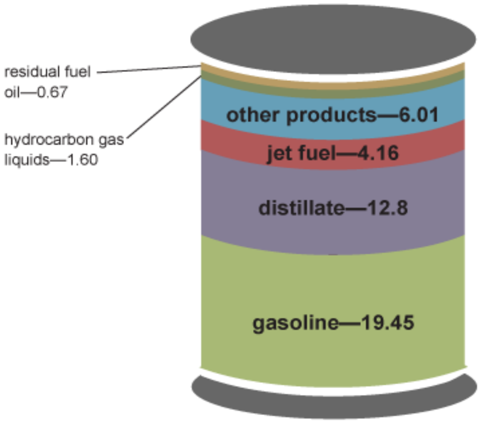


Figure 20 Refinery products distribution (gallons) of a 42 gallons U.S. oil barrel, 2022[53]

Main uses

More than 80% of total final consumption of diesel fuel, or gasoil, is employed in the transportation sector. Road vehicles are the largest consumers and are projected to increase, especially long-haul and heavy-duty vehicles. Other uses comprehend the agricultural sector, coming in second with about 13% of the share, followed by the energy sector with less than 5%. Jet fuel is instead used in the aviation sector, with a registered consumption of 7 million b/d or 38.9 PJ/d in 2023. It represents only 17.7% of the airline's operating cost.

The focus of this work is directed towards applications considered hard to mitigate, so for the sake of better understanding, it is necessary to identify these more challenging scenarios. Compared to road transportation, where other mature technologies are already available (e.g., BEV-Battery Electric Vehicles), some of these are not suitable for agriculture, aviation, and energy security (continuity). In the agricultural sector, gasoil is used to run tractors and other machinery which require a high level of reliability that is difficult to reach with alternative solutions. For energy production, similar results can be drawn with different considerations. The use of diesel genset is widespread in remote locations with generically unfavorable weather, like Alaska or the Asia Pacific. Unlike the EU where gensets are mostly used as backup generators, in other regions, there aren't economic advantages or resource availability to justify the transition to alternative technologies. Finally, in the aviation sector, electrification is not even technologically feasible, thus the solutions proposed in this work are the only proxy to conventional technologies based on fossil fuels.

Production pathways

Petroleum products are produced through crude oil refining. The overall refinery process is complex and involves several steps, such as distillation, cracking, treating, and blending. Due to the large and increasing demand for gasoline and gasoil by the transportation sector, research and development over the years have focused on increasing the yield of these two products through processes such as catalytic cracking, hydrocracking, and alkylation.

Both diesel and jet fuel combustion properties are expressed in terms of Cetane Number (CN), which is an indicator of the ignition quality of the fuel. This parameter is especially important in Internal Combustion Engines (ICE) but is not the only defining characteristic of these products. There are several chemical and physical properties that are required for each specific application. For example, freezing point and viscosity are crucial for safety reasons in jet engines. Some of these properties affect the CN, so for general description, the fuels can be classified using only this parameter. The cetane rating required for diesel for road transport is in the range of 45-55, while for jet fuel, it is in the range of 40-50. The CN is obtained by direct comparison with a reference fuel obtained by the mix of n-cetane and iso-cetane. The higher the cetane rating, the faster the ignition process, and higher ratings are favored by the presence of paraffinic compounds and hindered by the presence of aromatic and cyclic hydrocarbons.

The production pathway for diesel and jet fuel requires multiple steps, and it is not always the same between different refineries. According to a study by Elgowainy et al.[73] , conducted on 43 US refineries, the average specific production efficiency was found to be 90.9% for diesel and 95.3% for jet fuel. These results were obtained using an energy allocation method. The higher efficiency of jet fuel can be attributed to the fact that it is obtained almost directly as a straight run from the distillation tower, requiring only hydrotreatment to eliminate heteroatoms. On the other hand, diesel is partially recovered from the heavy residue treatment units, leading to higher hydrogen consumption and, consequently, higher energy expenditure.

The carbon intensity of the fuels varies globally, and different analyses yield different results depending on the focus of the study. According to Elgowainy et al., using an energy allocation method, the carbon intensity was found to be 86 for jet fuel and 92 gCO_2/MJ for diesel. Refinery direct and indirect emissions account for around 5% of total Life Cycle Emissions (LCE), while end-life emissions (combustion) contributed to 80% of total emissions, with the remainder attributed to crude oil recovery. Similar results were obtained by the Joint Research Centre, EUCAR and Concawe (JEC) in the Well-to-Tank report v5[28] , estimating the carbon footprint of fossil diesel at 18.9 gCO_2/MJ_{diesel} and the energy expenditure at 0.26 MJ/MJ_{diesel} in a Well-to-Tank approach.

3. Projections

As highlighted in the "Global Warming 1.5°C" report by the International Panel on Climate Change (IPCC), a pivotal step to mitigate the impacts of global warming involves a 50% reduction in global emissions by 20230, steering our world towards net-zero reality by 2050. The petrochemical industry, as emphasized in the first chapter, plays a crucial role in this transition. To facilitate the effective delineation of the transition pathway, two essential elements are required. Firstly, projections concerning various global equilibria (such as demand, population, prices, etc.), are necessary. Secondly, a collection of viable and implementable solutions is indispensable. In this chapter, modeled scenarios will be presented with a specific focus on market evolution and technological development. Additionally, various assessment techniques will be discussed as the primary tools for informing policy-making decisions.

a. 2050 Scenarios

Projected scenarios rely on models that incorporate key variables such as population growth, existing policies, or those that have been announced, as well as learning and growth curves. To finalize the model several assumptions are necessary, introducing the possibility of variations in the resulting scenarios. Primarily concentrating on market evolution, these models aim to predict future demand.

i. Reference Technology Scenario

In the 2018 IEA report on "*the future of petrochemicals*", a decision-based model known as Reference Technology Scenario (RTS), was employed [6]. Figure 21 below illustrates the demand trend for key plastics from 2017 to 2050 within this scenario. In general, the anticipated growth in primary chemicals demand by 2050 is approximately 60%, resulting in a corresponding 30% increase in CO_2 emissions.

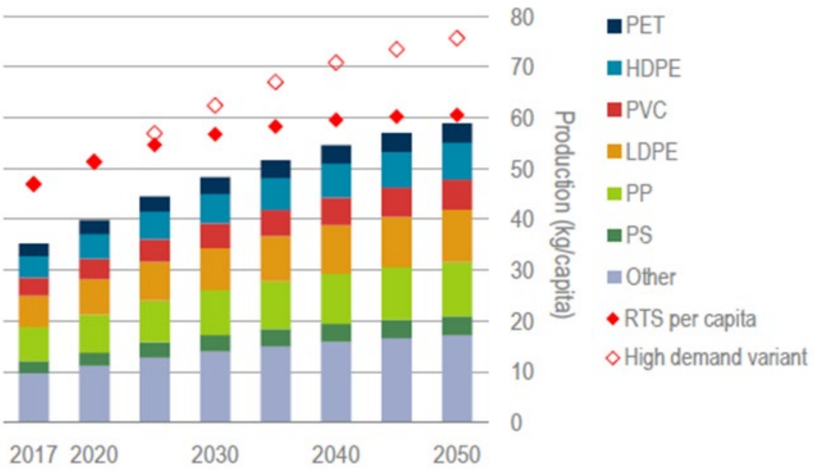


Figure 21 Production of key thermoplastics in the RTS [6] .

Ammonia demand

Remarkably, ammonia stands out as the primary chemical with the slowest global increase, experiencing a 30% rise evenly distributed from 2020 to 2050. The intriguing findings extend to the regional distribution of ammonia demand. In developing economies like the Middle East and Africa, production nearly doubles, whereas in developed regions such as Europe, demand reaches a plateau and eventually declines. This phenomenon can be attributed to the agricultural sector, which continues to be the primary driver. The reduction in fertilizer use in developed countries stems from a combination of lower population growth rates and the increased efficiency in fertilizer utilization.

Methanol demand

In this scenario, methanol remains the chemical with the most pronounced surge in demand, nearly doubling by 2050. Notably, 60% of this increase is concentrated in the Asia Pacific region, with China alone accounting for 50% of global production. This growth is primarily attributed to the highlighted usage of methanol in fuel applications, both as a blend and in MTO and MTA processes.

High Value Chemicals demand

A substantial 60% increase in demand for HVCs is anticipated, predominantly driven by the demand for plastics. Similar to fertilizers, the growth in plastics demand is distributed unevenly across regions. Per capita demand for packaging and single-use plastics tends to decrease in developed countries while showing an upward trend in the rest of the world. Nevertheless, certain plastic applications are observed to proliferate globally.

ii. IEA World Outlook

The International Energy Agency, in its Energy Outlook, has formulated three distinct scenarios: STEPS (STatEd Policies Scenario), APS (Announced Pledges Scenario), and NZE (Net Zero). These projections[59] exhibit notably diverse outlooks for oil demand by the year 2050, ranging from 76 Mbl/d in the STEPS scenario to 16.4 Mbl/d in the NZE scenario. In NZE scenario, the energy demand of the transport sector is forecasted to be 79 EJ [61] in 2050, a result achieved through a combination of demand-side measures and increased efficiency. The EU's energy demand is estimated to be 9.6 EJ.

The International Civil Aviation Organization (ICAO) has employed a model to project for the growth in jet fuel consumption, anticipating a total demand slightly exceeding 16 EJ in 2050[60] , with approximately one-fourth of this demand originating from the EU.

iii. IRENA

In the "World Energy Transitions Outlook 2023: 1.5°C Pathway" published by IRENA[62] , the 1.5°C scenario is juxtaposed with the Planned Energy Scenario (PES) concerning energy demand and GHG emissions. The projected energy demand for 2050 sees a reduction from 159 EJ in the PES to 91 EJ in the 1.5°C scenario. The share of renewable-based fuels is estimated at 23%, with the aviation and shipping sectors contributing 39% and 31%, respectively. Direct electrification accounts for 52% of total final energy consumption. Across all sectors, renewable electricity production in 2050 (1.5°C scenario) is approximately 294.4 EJ and e-fuels production increases to 63 EJ. Table 2 provides values specifically for the three primary sectors: industry, building, and transport.

Table 2 Energy demand by sector in the 1.5°C 2050 scenario

Sector	Direct electrification (EJ)	e-fuel consumption (EJ)
Industry	50.49	40
Building	79.8	0.14
Transport	47.3	21.84

b. Life Cycle Impact Assessment

The main challenge confronting policymakers is the identification of the most advantageous solution for society from among numerous options. The process of doing so presents difficulties on various levels, particularly considering that all impact assessment procedures carry some degree of inaccuracy, and there is no singular or standardized methodology. The term "Life Cycle Assessment" (LCA) refers to a family of assessment procedures designed to evaluate the performance of a specific scenario or technology, adopting a comprehensive approach throughout its entire life cycle. While the term is commonly associated with environmental impact assessments, LCA has a broader scope encompassing all three spheres: economic, environmental, and social. Consequently, the contemporary discussion often revolves around Life Cycle Sustainability Assessment (LCSA). To ensure consistency in the the procedure, the structure of LCA studies is defined by ISO 14044 as follows:

- **Goal and scope definition:** In this phase, the objectives (goals) of the study are declared, along with the conditions and the assumptions (scope) made for the assessment. While this stage is data-free, it holds crucial importance as it establishes the system and defines its boundaries.
- **Life Cycle Inventory (LCI):** Following the definition of the system with its primary flows (exchanges with the surrounding environment), , the subsequent step involves collecting the data necessary for conducting the impact assessment. In this phase, various software and databases are typically consulted to gather information on elementary flows, encompassing material and energy exchanges with the environment. The data collected extend beyond environmental impact and include financial quantities as well.
- **Life Cycle Impact Assessment:** In this phase of the study, impact assessment software and methodologies are utilized to determine impacts expressed as indicators. A crucial aspect of this step is the diverse ways to quantitatively represent the produced impact. Indicators are classified into midpoint indicators and endpoint indicators. Midpoint indicators, being easier to calculate, provide more accurate results. These indicators do not directly signify the generated impact but consider individual consequences. For instance, the emissions of greenhouse gases can be readily calculated, and the direct consequences of these emissions are expressed by midpoint indicators, such as water acidification or temperature rise. These indicators represent a midpoint in a chain of cause and effect. Endpoint indicators, on the other hand, focus on final consequences categorized into three categories: Human Health (HH), Resource Scarcity (RS), and biodiversity. Although not formally considered as an impact during this phase, an economic analysis is also conducted, and the results are generally presented

in terms of specific costs, such as the specific cost of a product or the CCA (Cost of CO_2 Avoided).

- **Results interpretation:** The concluding step of an LCA involves the interpretation and discussion of the results obtained in the preceding phases. This encompasses comparisons among scenarios, conducting sensitivity analyses to identify the primary contributors to different impacts, and an examination of uncertainties. The analysis of uncertainties relies on statistical methods such as the Monte Carlo method. In essence, this probabilistic method entails creating a dataset of inputs modeled through a probabilistic distribution (whether gaussian, square, or double triangular distribution). Subsequently, multiple simulations are executed based on inputs randomly chosen from the dataset (modeled as explained before) to generate a set of results. Finally, a statistical analysis of the obtained results enables the evaluation of the magnitude of uncertainty generated by the assumptions and the inputs, propagated throughout the algorithm.

As mentioned earlier, LCSA results are not uniform, primarily due to differences in assumptions and the procedures. Regarding the procedure employed, the most significant variations arise from the way impacts are assessed, attributed to a product/process, and the defined boundaries of the system. During the impact assessment two pathways can be followed. The first approach is attributional modeling, which was one of the earliest developed and is sometimes the most straightforward. In this approach, the impact is attributed by considering the system at the state-of-the-art. Essentially, an average value is calculated, defining the impact produced by the functional unit. This approach is useful for comparing the impact generated by different technologies at the time of the study, as is often necessary in the case of carbon accounting. However, this approach lacks the ability to assess the viability of an option in the future.

The alternative modeling approach is referred to as marginal or consequential, and it centers on attributing the impact generated by changes in production resulting from decisions, policies, market dynamics, etc. These changes, generally market-driven, pertain to the foreground system (such as the demand for a product), which in turn influences the background processes. Assessing the consequences of decisions and policies under this approach is highly intricate because it necessitates forecasting the evolution of the market and the entire supply chain. For instance, when evaluating the impact of PV panels through the marginal approach, it involves accounting for the impact generated by the expansion of the supply chain, including aspects like raw material extraction and transportation.

This approach proves beneficial in cases where new prospectives are compared to traditional technologies or Business As Usual (BAU) scenarios.

Another source of divergence among LCAs arises from the allocation method, i.e., the manner in which the impacts are assigned to a specific product in a system with multiple outputs. A category of allocation methods is based on the weight of each product, and this weight can be evaluated using mass, energy, or economic share. Another allocation method is known as avoided burden. In this scenario, all impacts are assigned to the functional unit, and to account for all byproducts, the impacts of the system are compared to the impacts generated by a fictional system where each byproduct is produced individually using conventional means. For instance, in a process where outputs consist of the functional unit and excess electricity (a byproduct), the latter is considered an avoided burden. When calculating the emissions of the process, these emissions are subtracted by the emissions generated by an equivalent system producing only electricity using conventional technology.

c. Technology learning curves & growth curves

When dealing with projections, a static approach runs the risk of offsetting the results. Therefore, a "marginal" approach necessitates considering the effect of large-scale deployment of a technology on its production cost. This phenomenon has been observed numerous times in the past, and a theory formalized by Theodore Wright in 1936 sheds light on it. In his paper "Factors Affecting the Costs of Airplanes", Wright discusses the relationship between production capacity and the cost of airplanes. Wright's Law posits that the production cost reduction rate for doubling the capacity remains constant. The result of this theory is learning curves, which graphically represent this relationship.

Learning curves find application in various technologies including renewables and lithium-ion batteries. The reduction in costs is attributed to an increase in experience. By experience, we mean a combination of economies of scale and R&D, giving rise to a virtuous circle. Essentially, when the cost of a particular technology decreases, demand tends to rise, leading to increased production and subsequently reduced production costs. Furthermore, R&D efforts expand the fields of application, further driving up demand. Figure 22 illustrates the example of PV panel cost as a function of cumulative installed capacity, showcasing a learning rate is 20.2%.

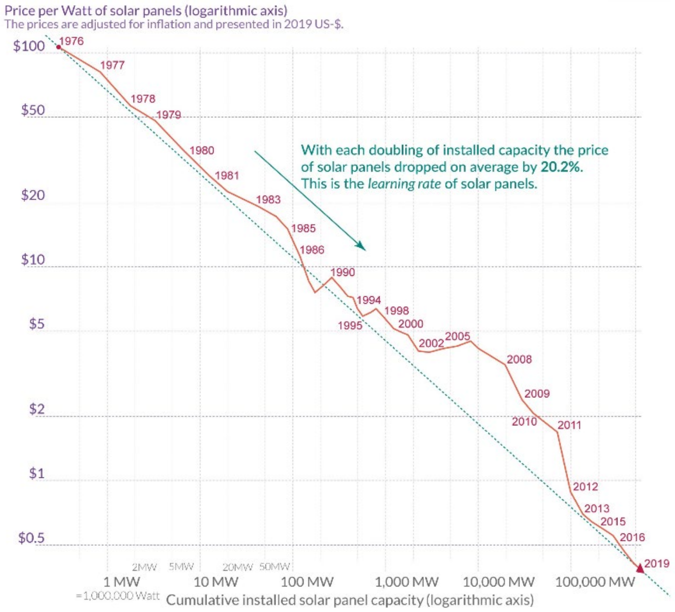


Figure 22 Wright's Law applied to the PV panels case.[63]

The S-curve, depicted in Figure 23, illustrates an important phenomenon that captures the relationship between resources invested (time, money, etc.) and output (performance, specific capacity, etc.). The shape of the curve can be attributed to the three distinct sections it comprises. The first section is associated with the initial stages of development, marked by the technology's early discoveries. During this phase, research focuses on refining the theory behind the technology and attempting practical implementation through trial and error. This stage demands significant resources with comparatively little return, potentially acting as a barrier for the technology due to the challenge of attracting investors. In contrast to the first section, the second section is characterized by substantial gains in performance with relatively low investment. The rapid growth in this stage is facilitated by acquired knowledge and "predictable" improvements. Despite the advantages and enhancements obtained, there are inherent risks. Due to the extensive opportunities for capitalizing on these technologies, projections tend to be overestimated, assuming continuous linear growth. After the takeoff, the technology enters a saturated condition where substantial investments are required to achieve additional improvements. At this plateau, the technology is considered mature. Understanding these sections helps navigate the complexities and challenges associated with the development and maturation of technologies.

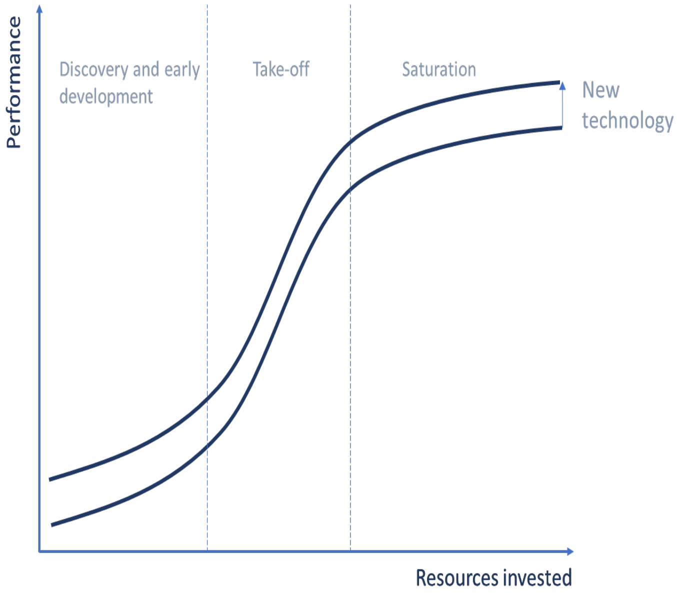


Figure 23 Technology growth curve.

4. Available technologies and practical pathways

As mentioned earlier, a successful transition necessitates, among other factors, a range of technologies and alternatives to supplant conventional technologies. In this chapter, various options and categories of processes will be compared, with a specific focus on the most mature technologies and alternatives that show the best prospects.

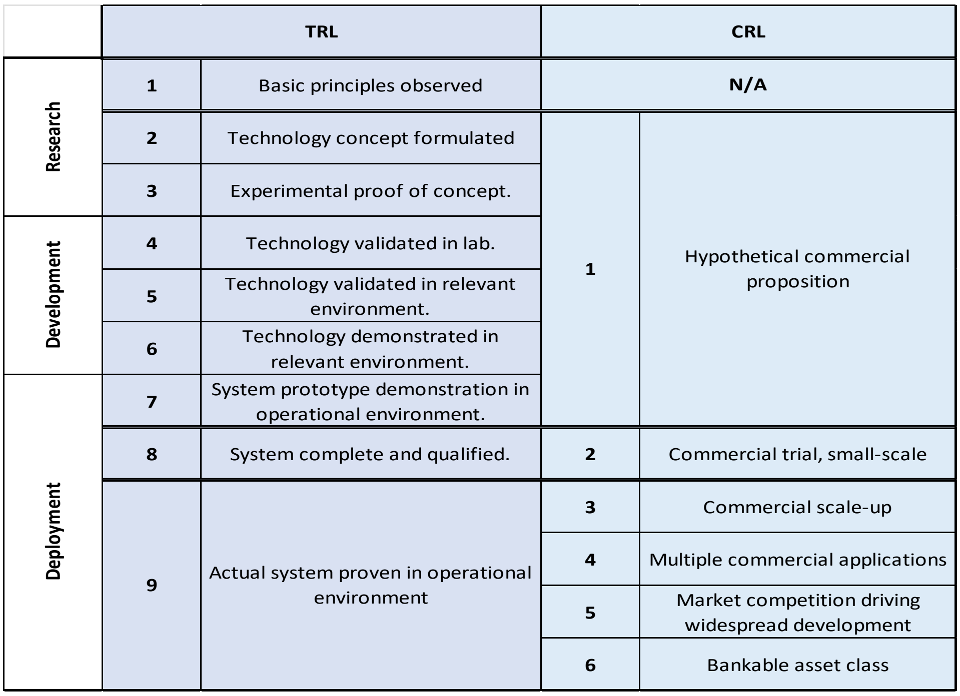
Achieving net-zero emissions poses a more intricate challenge in the petrochemical sector compared to other sectors like energy. This complexity arises primarily from the pervasive presence of carbon atoms in the chemical structure of most chemical products. Therefore, two crucial aspects must be considered: the origin of carbon atoms and the fate of these carbon-based products at the end of their life cycle.

To gain a clearer understanding of the various pathways toward the goal, the presented solutions can be classified based on different determinants:

- **Upstream or downstream approach**: This classification depends on the specific step within the production chain that is the focal point. Recycling, for instance, is an example of a downstream approach.
- **Mitigation or abatement techniques**: This categorization distinguishes between techniques that prevent the generation of emissions (mitigation) and those applied downstream to a process to capture the CO_2, preventing its release into the atmosphere (abatement).
- **Green or blue technology**: This classification differentiates between green processes, which rely entirely on green energy and feedstocks, and blue technologies, which employ fossil fuels but capture and store their emissions.
- **TRL/CRL** (Technology Readiness Level/Commercial Readiness Level): The Technology Readiness Level (TRL) serves as an indicator of a technology's state of development. In the context of global-scale solutions, the most feasible solutions are those with the highest TRL. It is important to note that a technology with a TRL of 9 is not guaranteed to be commercially ready for widespread implementation. To address this, another indicator, the Commercial Readiness Level (CRL), was developed by Australian Renewable ENergy Agency (ARENA). The CRL focuses more on the

potential for commercializing a technology. As summarized in Table 3, ensuring commercial spread and scale, requires a technology that is ready and proven in the operational environment. However, to attain a "bankable asset" status- meaning technology with proven and expected standards and performances- multiple steps are necessary.

Table 3 TRL and CRL integration



	TRL		**CRL**	
Research	**1**	Basic principles observed	**N/A**	
	2	Technology concept formulated	**1**	Hypothetical commercial proposition
	3	Experimental proof of concept.		
Development	**4**	Technology validated in lab.		
	5	Technology validated in relevant environment.		
	6	Technology demonstrated in relevant environment.		
Deployment	**7**	System prototype demonstration in operational environment.		
	8	System complete and qualified.	**2**	Commercial trial, small-scale
	9	Actual system proven in operational environment	**3**	Commercial scale-up
			4	Multiple commercial applications
			5	Market competition driving widespread development
			6	Bankable asset class

a. Downstream techniques

In this section, a brief description of various approaches applied at the end of the production chain will be provided. These approaches focus on the end of the life cycle of goods, or, in other words, their destiny once they have been used.

i. Demand-side measures

Undoubtedly, the most impactful action to reduce emissions is to decrease the demand for chemical products. This is particularly true for commonly used products or those with the shortest lifespan (refer to Figure 8). Examples of demand-side measures include the prohibition of single-use plastic plates, cutlery, straws, balloon sticks, and cotton buds in European markets from July 3rd, 2021. Additionally, many countries, such as Australia, Thailand, Mexico City, Rwanda, have banned single-use plastic bags. The United States has also banned microbeads in cosmetics and personal care products. The EU expects this policy to result in a 50% reduction in marine littering, a decrease of 3.4 Mt of CO_2 emitted annually, and approximately 22 B€ in savings in environmental damage [22] .

Another crucial demand-side measure is recycling, which can be enhanced through increased awareness and incentives. Europe has been at the forefront of recycling rates and yields. Policies regarding recycling set ambitious targets, aiming for 55% of all plastic packaging to be recycled by 2030 and limiting the landfill to 10% in mass percentage of municipal waste by 2035 [23] . It is important to note that there are various types of recycling routes:

- **Reuse:** Reuse stands out as a technique with substantial gains. Raw material consumption, emissions, and cost can drastically decrease due to an increase in the lifetime of products. Reuse can be directly implemented by customers or facilitated by suppliers through incentives for collecting and returning specific plastic goods.
- **Back to polymer:** This is a form of mechanical recycling that involves grinding the plastic and melting it to create another product. The challenge with mechanical recycling lies in the quality of the secondary plastic, which is negatively affected by the presence of additives such as colors and other impurities. In some cases, achieving "closed-loop recycling" becomes impossible, meaning that the resulting plastic has lower quality than the virgin material, making it no longer possible to produce the original product. When downcycling (as previously explained) is the only option, the focus shifts towards products that require lower quality standards (e.g., PET fibers). It is worth noting that downcycling is an "open loop" scenario, and it has fewer advantages than closed loop recycling.
- **Back to monomer:** This form of chemical recycling involves decomposing the material to obtain the building block of the plastic once again. This method allows the quality of secondary plastic to be nearly equal to that of the virgin material. However, chemical recycling is characterized by higher energy demand and process complexity compared to mechanical recycling.

In terms of advantages, not all plastics are the equal, and recycling is not feasible for every type of plastic. The feasibility largely depends on the lifespan of products (refer to Figure 8). Packaging plastics such as PET and LDPE are the most widely used, and therefore, an effective recycling policy for these would have the most significant impact in terms of emissions. Their lifespan is also relatively short, allowing for an effective replenishment of feedstock for the chemical industry. On the other end of the spectrum, plastics used in the building sector, like PVC, have a lifespan too long to guarantee a balance between input and output of the industry.

ii. Supply chain management

The production of goods aligns with the demand trends, but this does not imply that all chemicals are actually used. This unbalance results from the wastage throughout the supply chain. In many cases, chemical consumption and the associated emissions could be reduced without compromising productivity if a more efficient use is implemented. One of the notable examples of this is evident in the food industry.

Presently, the use of fertilizers plays a crucial role in supporting global food production and ensures food security, which would have been challenging otherwise. However, this industry is substantial, accounting for 26% of global GHG emissions. It is important to note that not all these emissions are a necessary evil. Numerous studies conducted in various countries have emphasized the inefficient use of fertilizers and poor management of the supply chain, contributing to food wastage.

It is estimated that approximately 35% of emissions could be mitigated with very small impact on crop yields (less than 1%) [24] . An important indicator is the Nitrogen Use Efficiency (NUE), calculated as the ratio between the nutrients found in the crop and the nutrients input. Figure 24 emphasizes developed regions as having the highest wastage of fertilizer to meet the market demand. The image on the left illustrates the efficiency with which fertilizers are currently used, while on the right side shifts the focus toward the theoretical amount required to satisfy current demand.

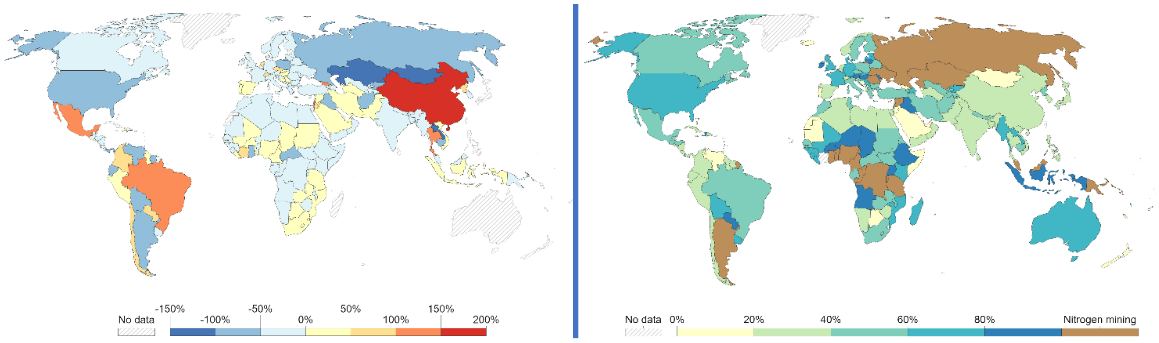


Figure 24 NUE by region (right), overapplication of fertilizer by region (left) [24]

Food waste, on the other hand, contributes to 6% of global GHG emissions, with two-thirds of these emissions occurring throughout the supply chain (refer to Figure 25). Additionally, this wastage implies a squandering of resources such as water and land. Addressing this issue could be achieved through consumer awareness and education, as well as by establishing a better correspondence between the demand and supply sides of the food chain.

Figure 25 Global greenhouse gas emissions from wasted food [25]

b. Upstream techniques

This section delves into practical upstream techniques, those capable of reducing emissions through mitigation or abatement. These approaches often directly impact the process layout and performance. The various technologies presented, ranging from more mature to innovative ones, are compared by investigating their techno-economic and environmental implications.

i. Carbon Capture and Storage

The abatement of emissions is achieved through Carbon Capture and Storage (CCS), one of the most mature and widespread industrial technologies in the transition. Similar to all mitigation technologies, CCS implies the continuous use of fossil fuels, which is unsustainable in the long term. Despite this conceptual flaw, CCS technologies play a crucial role in the transition of all sectors. They provide a quick and relatively easy fix that can be applied in almost all sectors, buying time for the transition to occur. Currently, they are also the only feasible solutions in hard-to-abate sectors like steel and cement manufacturing. CCS technologies can be grouped into two families: Concentrated or Point Source Capture (CCS from now on) and DAC (Direct Air Capture).

CCS is applied to gas streams with concentrated amounts of CO_2 such as the exhaust from gas turbines or the chimneys of coal-based water boilers. The capture of CO_2 is based on adsorption or absorption technologies, generally involving chemisorption using amine solutions or physisorption (Selexol, Rectisol). In theory, this technology can be applied to any kind of process with concentrated streams, but it has a negative effect on the process's energy efficiency. The capture of CO_2 requires a substantial amount of heat for the regeneration of the chemical solvent, approximately 4MJ/kg_{CO2}. The additional costs come from the capital cost of the equipment, the increase in fuel consumption, and the cost of transportation and storage, which can be several thousand kilometers away from the capture site. CO_2 is transported either by ships to the storage site or through pipelines. The latter is the most capital-intensive option because new pipelines need to be constructed to connect the capture hub to the storage. The average energy expenditure for CO_2 compression is around 0.378 MJ/kg, a small fraction (<10%) of the regeneration heat. The source of this energy is crucial. Depending on the distance to the storage site, recompression along the way may be required. Pipeline pressure is set at a minimum of 150 bar, so CO_2 is injected at pressures around 200 bar. On-site energy is generated internally, depending on the process itself (e.g., combined cycle). Recompression, however, relies on natural gas-powered turbines to drive the compressor, which could be replaced by electric motors powered by renewables. This concept is extended to all pipeline infrastructures, including hydrogen.

In a net-zero scenario, DAC becomes necessary to balance emission leakages throughout the supply chain, particularly in hard-to-mitigate processes like steel and cement production, where even if CCS is applied, small amounts of CO_2 are released into the atmosphere. DAC also has the advantage of decoupling the generation site of emissions from the capture site, allowing for the installation of DAC facilities near to storage sites and reducing transportation costs. However, this configuration maintains local air quality at the same as if there were no capture at all. From a human health perspective, CCS outperforms DAC, and the Cost of CO_2 Captured (CCC) is approximately four times lower for CCS. The higher cost for DAC is mostly attributed to its higher energy consumption, ranging from 7 to 9 MJ/kg_{CO2}.

DAC sorbents

DAC is based on chemisorption or adsorption. Due to the low concentration of CO_2 in the air (approximately 0.04%), the capture process can be based either on solid sorbents or liquid solutions.

High-Temperature (H-T) DAC utilizes aqueous solutions of a metal hydroxide (sodium or potassium) that can form carbonate compounds in contact with CO_2. High temperature is required during regeneration, or more precisely, during calcination. To regenerate the metal hydroxide, hydrated lime ($Ca(OH)_2$) is used to precipitate calcium carbonate. Later, this precipitate undergoes a regeneration process of calcination where, with the supply of heat at high temperature (300-900°C), CO_2 is separated from quicklime (CaO). The latter is then sent to a slaker, where the addition of water allows the formation of calcium hydroxide. Figure 26 illustrates the overall unit, highlighting the two separate cycles of calcium and the metal.

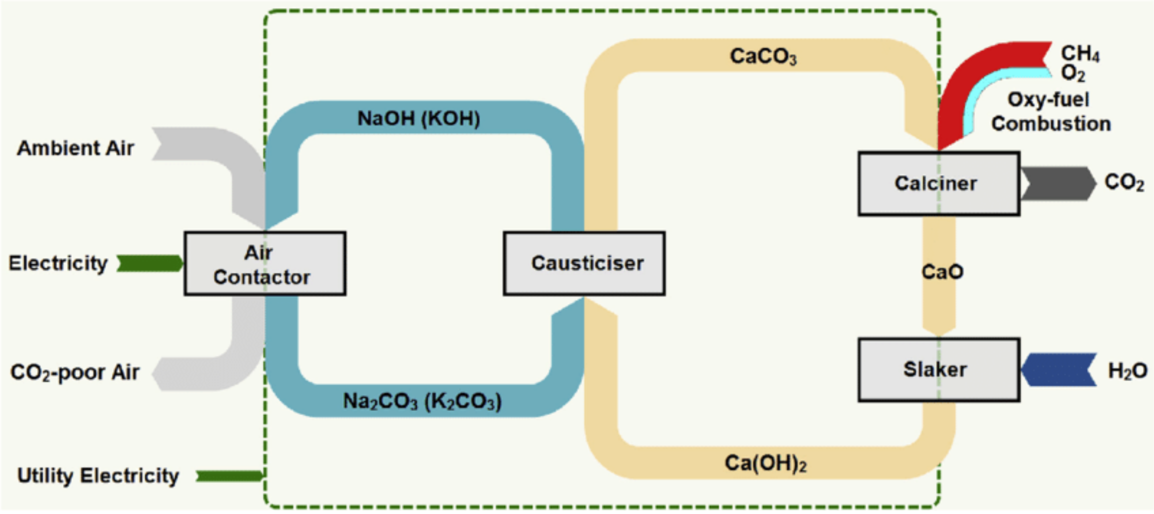


Figure 26 Scheme of H-T DAC.[55]

On the other hand, Low-Temperature (L-T) DAC employs solid sorbents such as amino-based polymers, silica, Metal Organic Framework (MOF), or potassium carbonate[55]. Unlike H-T DAC, the operation is discontinuous, as since the unit has to be switched to regeneration mode, using processes like Pressure Swing Adsorption (PSA) or Temperature Swing Adsorption (TSA), after reaching the saturation of the sorbent.

Large scale deployment

Based on the results of Gabrielli et al. [9] achieving a net-zero scenario by 2050 based on CCS technologies would require an average of 5 PWh_t/y of low-temperature heat and about 2 PWh_e/y. This corresponds to approximately 10% of the current global production of low-temperature heat and 8% of the current global electricity consumption. It is assumed that such heat will be produced through electricity and so to achieve net-zero, a green electricity source is needed. In terms of resource consumption, CCS route would lead to nearly 60 thousand km^2 of land usage and 13.5 km^3/y of blue water consumption. This resource consumption is mostly associated with the increase in electricity demand.

As mentioned earlier, in this scenario, DAC is also required. The amount of DAC required strongly depends on the carbon footprint (CF) of electricity. The slope of the lines in Figure 27 indicates the technology's carbon intensity and how much it is affected by the electricity CF. It is evident that alternative technologies require a very low CF to become competitive with fossil fuels if no DAC is employed.

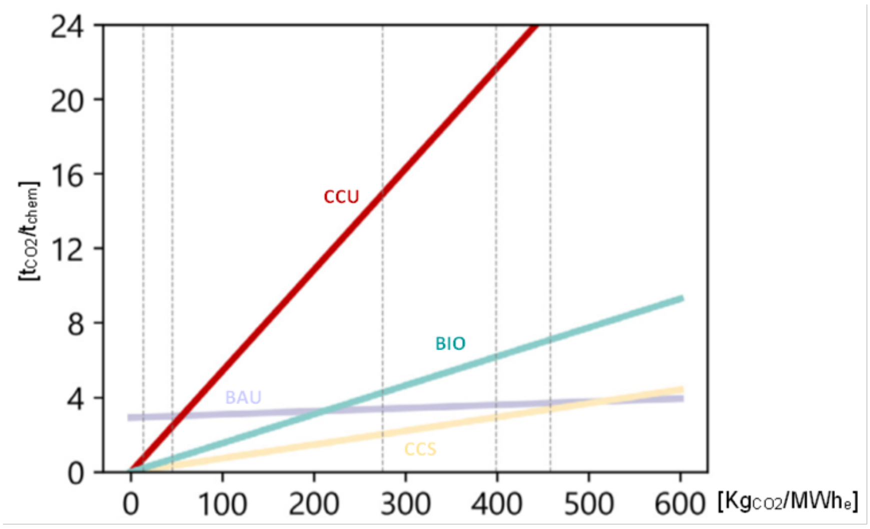


Figure 27 DAC required to reach net-zero as a function of the carbon footprint.

*BAU= Business As Usual

ii. Carbon Capture and Utilization

Carbon Capture and Utilization (CCU), different from CCS, is based on the concept of carbon circularity. In this case, the captured CO_2 is not stored but used as feedstock. This concept can be classified as a mitigation technology because the CO_2 emissions are not linked to fossil emissions but to atmospheric CO_2. Thus, contrary to CCS, CCU is sustainable in the long term if a perfect CO_2 balance is achieved (net zero). In principle, CCU does not require the use of fossil fuels, so its sustainability, as will be clear later, is highly dependent on the supply chain. The capture stage is identical to the one described in the previous section. The only difference is that the CO_2 captured is then utilized as a feedstock in various production processes where a carbon input is required (methanol, HVCs, e-fuels).

From CO_2 to syngas

As seen in section [c], CO_2 does not constitute an input to any process. Most of them require a synthesis gas, a mixture of hydrogen and carbon monoxide, instead. There are two processes able to convert CO_2 into CO. The most widely used and mature technology is the reverse Water Gas Shift (rWGS). The reaction, as shown in Eq.(7), is an endothermic process carried out at temperatures around 550 °C and ambient pressure over copper-based or supported ceria catalyst. Another possibility is the electrolysis of CO_2, which has been technologically introduced as co-electrolysis of water and CO_2. Co-electrolysis is based on SO (Solid Oxide) electrolysis, with electrode reactions reported in Eq.(8) and Eq.(9).

$$CO_2 + H_2 \leftrightarrow CO + H_2O \tag{7}$$

$$CO_2 + 2e^- \leftrightarrow CO + O^= \quad \& \quad H_2O + 2e^- \leftrightarrow H_2 + O^= \tag{8}$$

$$O^= \leftrightarrow \frac{1}{2}O_2 + 2e^- \tag{9}$$

Primary chemicals synthesis

Figure 28 depicts the Block Flow Diagram (BFDs) of e-chemicals production. The methanol production process remains unchanged because syngas is the sole input. However, there are layout changes in the syngas production section. In this case, green hydrogen and CC are employed. E-ammonia follows a process even closer to the standard production, with the only difference being that H_2 is produced through electrolysis. Despite ammonia not requiring CO_2 for its production, it is included in this section because urea, the most important ammonia-based product, can be produced through CCU.

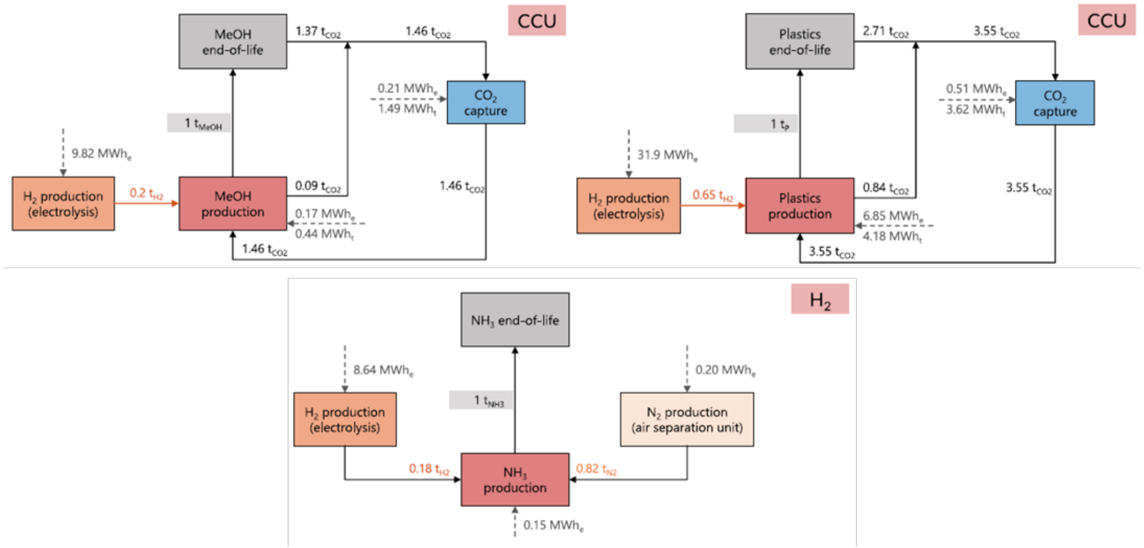


Figure 28 Block schemes of LC for three different products following the electrified route.[9]

Industrial urea production is based on the Basarov reaction, which involves two steps as reported in Eq.(10): Ammonium carbamate synthesis, and in Eq.(11): Ammonium carbamate dehydration. The overall reaction is notably highly exothermic, and due to high output recirculation, a high conversion of feedstocks is achieved. Once urea is applied to the soil, CO_2 is released through urea hydrolysis, which produces ammonia and carbon dioxide. Therefore, urea produced through CCU also relies on carbon circularity.

$$CO_2 + 2NH_3 \leftrightarrow NH_2COONH_4 \quad (10)$$

$$NH_2COONH_4 \leftrightarrow (NH_2)_2CO + H_2O \quad (11)$$

According to the IRENA report [13] , when considering a cradle-to-grave LCA, renewable ammonia comes is not without environmental cost, as illustrated in Figure 29. Over half of these costs stem from construction and materials, amounting to approximately 0.7 t_{CO2}/t_{NH3}. The report focused specifically on green ammonia and examined only the route involving renewable electricity. Consequently, no significant sensitivity to electricity CF was identified. E-NH_3 is regarded as a promising alternative fuel in the maritime transport sector, especially given the International Maritime Organization (IMO) commitment to reducing GHG emissions by 50% by 2050. Renewable ammonia is particularly relevant as it exhibits negligible Tank to Propeller (TTP) emissions and possesses favorable fuel properties. A study by Al-Aboosi et al.[34] highlights the potential for significantly lower emissions with green ammonia compared to Heavy Fuel Oil (HFO), recording 5.6 gCO_2/MJ versus 89 gCO_2/MJ for HFO. However, this comparison is nuanced due to challenges such as the incomplete compatibility of existing engines with ammonia as a fuel and, most critically, the production cost, which currently cannot compete with the affordability of HFO, standing at around 7.9 $/GJ compared to 32 $/GJ for green ammonia.

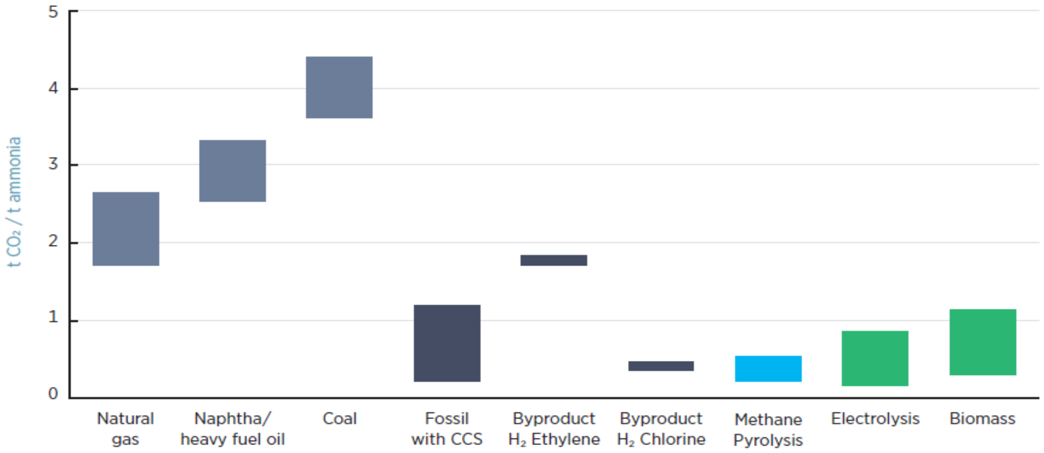


Figure 29 CO_2 emissions from different ammonia production routes [13]

The report published by Concawe in collaboration with Aramco[51] delves into various e-fuels routes, considering different locations and time horizons. A general finding suggests that more molecularly complex fuels tend to be more energy-intensive and have a greater environmental impact. In terms of LCSA, so that H_2 and NH_3 emerge as the best-performing fuels. The report aims to achieve a comprehensive LCA, presenting results on a CTG basis, and an economic evaluation for different e-fuels produced through various pathways. The environmental impact assessment primarily focuses on GWP as a midpoint indicator, and emissions are categorized into three groups:

- WTW: Well-to-Wake emissions consider direct emissions, as well as indirect emissions associated with fuel transportation, distribution, utilization, and feedstock preparation.
- O&M: Operating & Maintenance encompasses WTW emissions and includes indirect emissions associated with maintenance procedures (e.g., part replacement, filters regeneration, etc.).
- CTG emissions account for all direct and indirect emissions including construction, decommissioning, end of life, etc.

The system modeling was based on literature sources, while the LCI was retrieved from Sphera's Gabi LCI database. For the economic analysis, the Cost Of Production (COP, Eq.(12)) was obtained by summing specific costs ("sc" in Eq.(13)) of elementary inputs, which themselves are determined considering Equivalent Annual Cost (EAC) and Annual Maintenance Costs (AMC). The EAC is calculated with a discount rate of 8%, a plant lifetime of 25 years, and using the Excel built-in PMT function. The price of equipment has been adjusted using the

Chemical Engineering Plant Cost Index (CEPCI).

$$COP = \sum_n sc_n \tag{12}$$

$$sc = EAC + AMC \tag{13}$$

Since the first step for any e-fuel production pathway is hydrogen, it is logical that e-hydrogen provides the highest efficiency (approximately 75%) compared to the other routes (51-61%), and this generally reflects on emissions and cost. For the time horizon 2050, HT-DAC was assumed as the CO_2 source, SOEC (Solid Oxide Electrolyzer Cell) is used for H_2 supply, and the electricity source is consistent with the local renewable resource availability. The heat rejected by the F-T unit is integrated with the DAC unit.

In Figure 30, the breakdown of CTG emissions is presented from the LCA for various production location, namely Central EU, North EU, and South EU. Notably, F-T liquids, MeOH, and e-methane exhibit similar environmental impacts, while both H_2 and NH_3 routes show a GWP approximately 20% (1g_{CO2}/MJ) lower. The breakdown indicates that this difference is virtually negligible for O&M emissions, which appear in the CTG emissions (coming from construction and decommissioning). O&M emissions are minimal since the production process, involving CO_2 withdrawal, balances the end use, i.e., combustion. The notable emissions stem from maintenance, with wind being the major contributor. O&M in North EU (primarily wind installation) are higher than those in South EU (mostly PV installation). Construction of facilities contributes to around 85% of CTG emissions, with electrolysis (including renewable installation) responsible for 80-87%. The remaining portion is primarily covered by CO_2 capture equipment (including renewable installation to power the DAC). The impact of distribution is mainly observed in non-drop-in fuels like H2. The distribution of H2 requires a significant amount of renewable installation due to the energy intensity of the liquefaction step. In all other cases, the overall distance (assumed to be 300 km) is covered by pipelines in the main grid and trucks in the local grid.

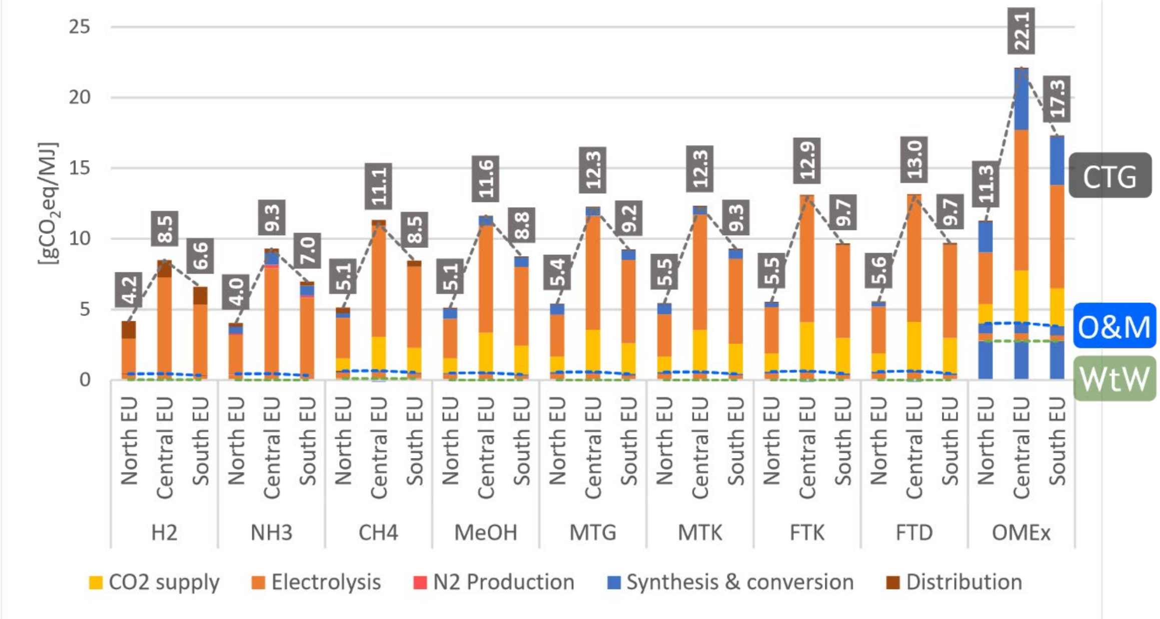


Figure 30 CTG GHG emissions for different e-fuels production based on EU 2050 scenario.[51]

In Figure 31, the embedded emissions are computed using the CF (kg$_{CO2}$/kW$_{P, installed}$) for PV and wind. These values are based on the IEA PVPS 2020 database for PV and the Wind Europe 2020 database for wind, considering the FLH. The figure presents the results for various locations analyzed in the report.

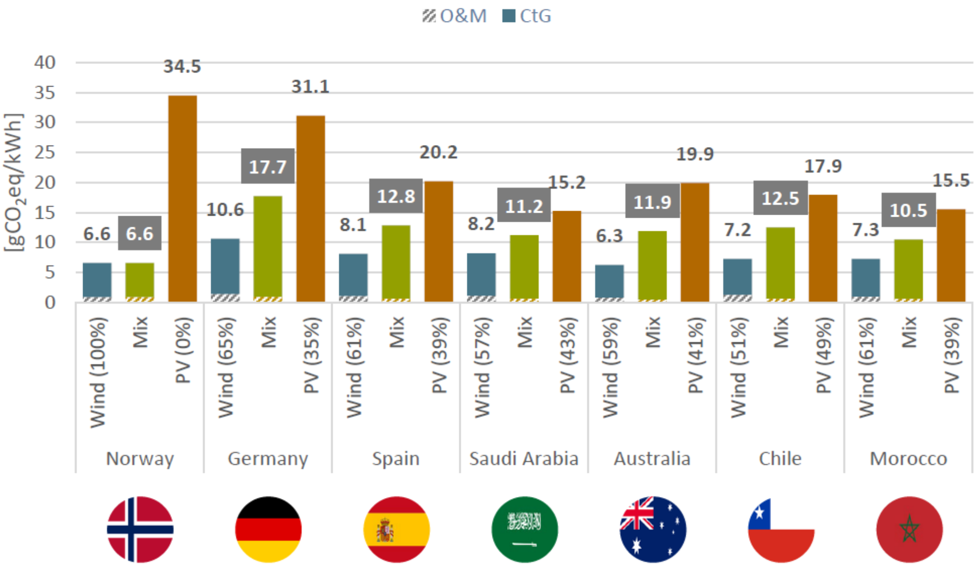


Figure 31 Renewables' embedded emissions for different locations.[51]

In Figure 32, the economic analysis results are presented. Once again, electricity costs constitute the most significant portion. The cost of electricity is calculated by taking into account the equivalent full load hours in each location. Production in North EU results in the highest cost due to the inability of the higher full load hours to offset the elevated specific cost of offshore wind. Additionally, for H2 only, the refueling station cost contributes to 30-40% of the total, mainly attributed to the high CAPEX of buffer storage and compressors. Conversely, for drop-in fuels, this cost is negligible.

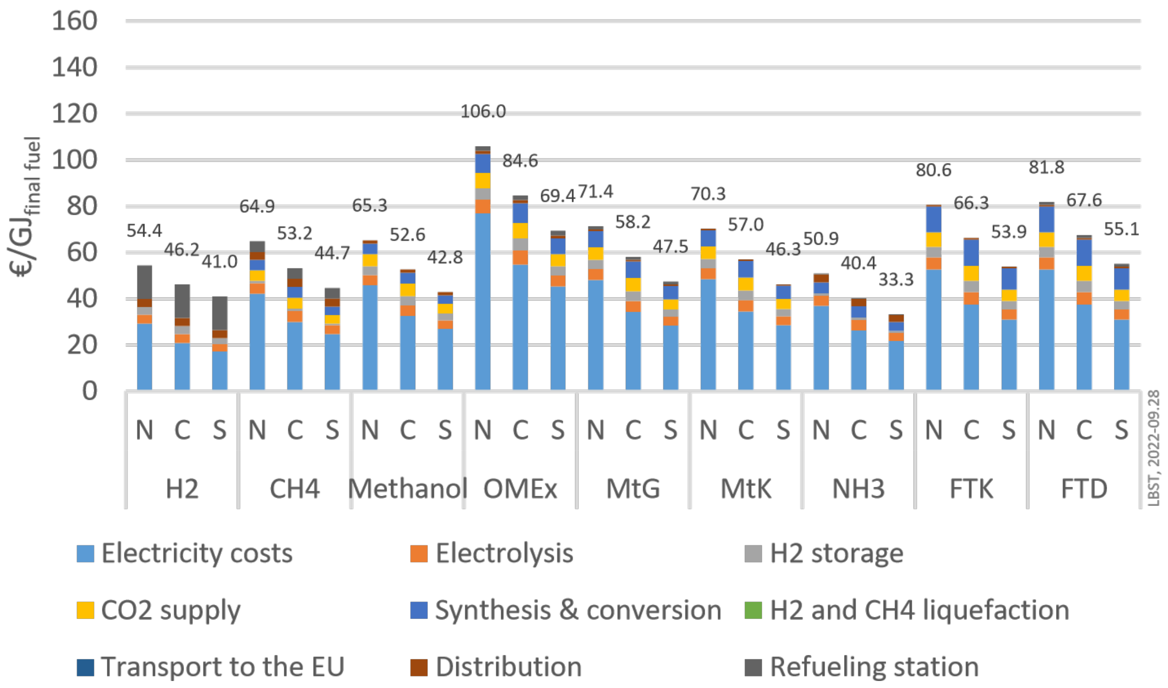


Figure 32 Cost breakdown in different EU production locations.[51]

The production of HVCs, including plastics, follows a distinct path. HVCs, and consequently, plastics are manufactured using MTH processes. E-fuels, serving as substitutes for diesel and jet-fuel, are produced through F-T synthesis or MTH processes. Both process families will be examined in the upcoming sections.

The CCU-electrification route is characterized by high energy intensity, primarily due to the substantial quantity of green hydrogen needed. In the study conducted by Gabrielli et al., the heat consumption for carbon capture nearly doubles compared to CCS, and electricity demand increases to 32 PWh_e/y. This escalation in renewable installation results in significant land and water usage, reaching 1,029 thousand km^2 and 77.1 km^3/y, respectively[9] .

e-fuels synthesis

The interest in alternative fuels varies across sectors, and the cost of these products to the end user plays a crucial role. Shifting entirely to a new technology poses numerous challenges and uncertainties, especially concerning the associated impacts. Policies with significant implications need to consider multiple variables, which are often difficult to assess in all three spheres: environmental, economic, and social. Taking electric cars as an example of an alternative to ICE vehicles, the feasibility of a market shift to this alternative must also consider all the complementary industries around the automotive sector, such as the infrastructure for fuel transportation and distribution (recharging stations in the case of battery electric vehicles). The impact generated by these drastic changes is complex to evaluate, and it is certain that they are not trivial. Therefore, drop-in technologies are generally considered the preferred option. Drop-in technologies are those that have minimal effects on the existing supply chain. E-diesel and e-jet fuel, due to their compatibility with conventional engines, do not require changes from engine manufacturers or the transportation and distribution industry. However, some solutions are technologically not feasible due to theoretical or practical limits. For instance, the electrification of long-haul flights in the aviation sector is considered unreasonable due to cost and feasibility constraints. This situation favors the adoption of Sustainable Aviation Fuels (SAF), although these alternative fuels come with several challenges.

In the study by Liu et al.[33] a cradle-to-grave LCA of F-T process coupled with DAC was conducted, based on a Carbon Engineering Ltd. (CE) pilot plant in British Columbia. The system, illustrated in Figure 33, was modeled using Microsoft Excel for material and energy balance, and Aspen Plus for the F-T synthesis, employing the Peng-Robinson model for the thermodynamic of the reactions. The modeled system has a capacity of capturing 1.1 MtCO_2/y from the air, while the pilot plant has a capacity of about 365 tCO_2/y. The DAC system by CE is based on chemical absorption with a solution of potassium hydroxide, as depicted in Figure 33.

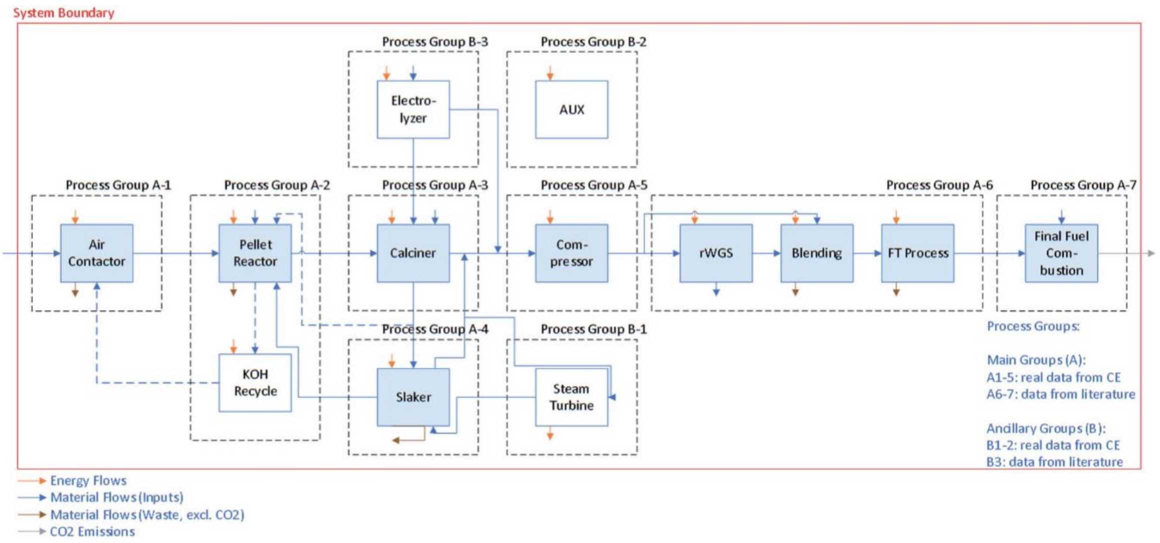


Figure 33 Flow scheme of the modeled F-T process coupled with DAC[33] .

The study adopted a cradle-to-grave approach, encompassing emissions associated with material utilization, construction, and decommissioning. The carbon footprint of electricity was a crucial factor, with a base case a value of 13 gCO_2/kWh, corresponding to a grid mix with a high penetration of renewables, such as hydroelectric power in Quebec, Canada (similarly to what was shown by Ralf et al.[32]). The study considered different functional units, including gCO_2 captured and MJ of diesel produced. In the sensitivity analysis, various allocation methods were explored, such as mass-based, market value-based, volume-based, and mole-based, accounting for potential avoided burdens. For construction and decommissioning emissions, an Economic-Input-Output (EIO) LCA was applied[42] . The EIO follows economic flow (in dollars) through different sectors. The emissions associated with plant construction, for example, are evaluated by tracing the money flow through various levels, considering the sectors involved in the production chain. The specific emissions in the Life Cycle Inventory (LCI) are expressed as $\text{kg}_{CO_2}/\$$. The eiolca.net software was used for this analysis, providing a fast yet accurate and comprehensive assessment, though limited to cradle-to-gate emissions.

The scenarios analyzed involve two different types of calciners:

- Oxy-fired natural gas calciner: It relies on an oxy-fired calciner that necessitates an ASU to produce the oxygen stream. Additionally, supplementary NG and electricity are required to obtain hydrogen and form syngas.
- Electric calciner: In this one, the calciner is powered by electricity obtained through electrolysis. The process allows the production of the required stream (i.e., H_2) with excess O_2 generated, which could potentially be sold,

leading to an avoided burden.

There are two key distinctions between the two calciner scenarios:

- Intrinsic CO2 emissions: In the oxy-fire calciner, there are intrinsic emissions of CO2 that result from the combustion of natural gas. However, these emissions are absorbed and utilized in the F-T process. As a consequence, the required atmospheric CO2 per unit of fuel produced is lower compared to the electric calciner route.
- Sensitivity to electricity carbon intensity: The electric calciner tends to be more sensitive to the carbon intensity of electricity. The relationship between the carbon intensity and the technology's carbon footprint is more pronounced in the electric calciner as indicated by the greater slope in Figure 35.

The results reported in Figure 34 indicate that, in the base cases, the modeled plant is more environmentally sustainable than traditional diesel. Moreover, when using an electric calciner, the plant exhibits slightly better environmental performance compared to other configurations.

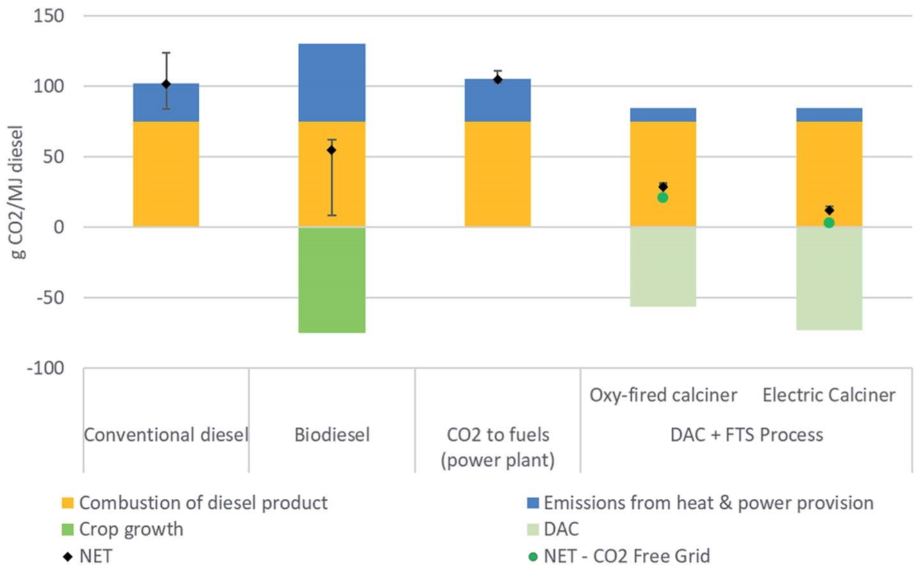


Figure 34 Specific emissions comparison among diesel production routes[33]

An important outcome of the sensitivity analysis is that the previously depicted result may not hold true considering higher electricity CF. In the case of an electric calciner, it is required a maximum CF of 144 gCO_2/kWh to make it competitive with conventional diesel, and this value drops to 74 gCO_2/kWh when compared to soybean biodiesel. Figure 35 represents the results of the sensitivity analysis focused on the CF as a variable parameter. The higher the slope of the curve, the more sensitive that technology is to the electricity CF, and this is especially true for e-fuels.

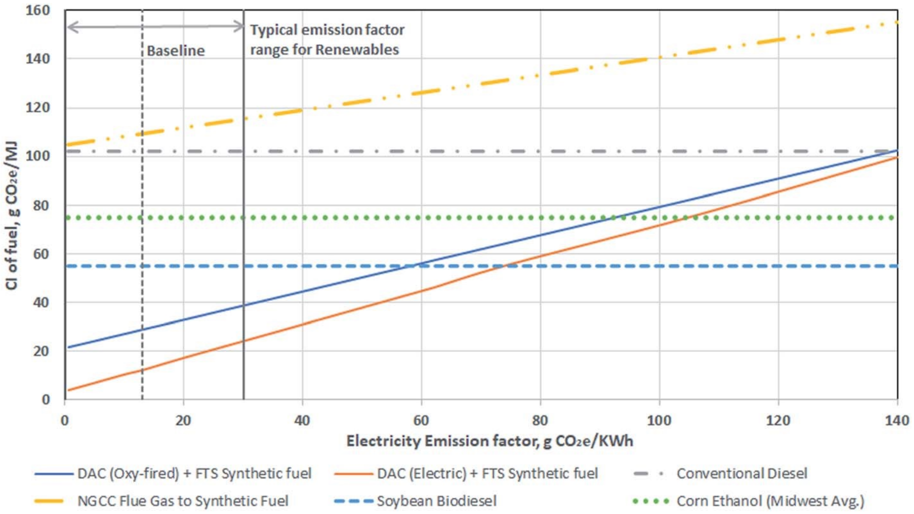


Figure 35 Sensitivity analysis of CF in different cases[33]

Ordóñez et al.[40] conducted a comprehensive LCA of e-jet fuels from different H_2 and CO_2 sources, considering five EU locations: United Kingdom (GB), Germany (DE), France (FR), Spain (ES), and Italy (IT). The considered scenarios differ in the types of technologies implemented, such as:

- **H_2:** Polymer Electrolyte Membrane Electrolyzer (PEMEL) was chosen for electrolysis. The electricity sources considered were PV, wind, or a combination of both. The model included storage of electricity (a battery) and storage for H_2 (either salt cavern or type 1 above-ground tanks). The modeling was done on an hourly basis to ensure continuous H_2 supply.
- **CO_2:** carbon capture from DAC and PSC were both considered. For DAC, two options were given: low-temperature DAC and high-temperature DAC. For PSC, two different power plants were considered: coal-fired power plant (coal-PP) and natural gas-fired power plant (NG-PP).

The production process was simulated in Aspen Plus using the Peng Robinson equation for the reactions thermodynamic. The system was modeled through a Mix-Integer-Linear-Programming (MILP), and two solvers, GAMS and CPLEX, were used to solve it. The cost of H_2 production was calculated using gAWE modeling framework, considering location-specific renewable energy availability.

The LCA was conducted using the SimaPro software with reference to the Ecoinvent database. The environmental impact (EI) assessment considered three different end-point indicators: Human Health (HH), Ecosystem Quality (EQ), and Resource Scarcity (RS). Additionally, Ballal et al.[41] implemented Near Term Climate Forces (NTCFs) to account for highly non-linear effects. In terms of economic analysis, the NPC was calculated as the Annual Capital Cost (ACC) divided by the Annual Production (AP). The ACC takes into account the Fixed Capital Investment (FCI) and Working Capital (WC), which is considered to be 10% of the Total Capital Investment (TCI). The OPEX were deemed negligible. The calculation of ACC involved using the interest rate (i) and plant lifetime (t) in the formula shown in Eq.(15). The TCI was determined according to Eq.(16), with all inputs provided in Annex C[43] . The cost of equipment was calculated using the purchased cost (PC) formula in Eq.(17), based on a reference price scaled proportionally to the size ratio with an exponent D depending on the piece of equipment. The dataset referred to 2018 prices, and the CEPCI was used to adjust the values.

$$NPC = \frac{ACC}{AP} \tag{14}$$

$$ACC = FCI\left(\frac{i(1+i)^t}{(1+i)^t - 1} + \frac{i}{9}\right) \tag{15}$$

$$TCI = FCI + WC \tag{16}$$

$$PC = PC_{ref}\left(\frac{S}{S_{ref}}\right)^D \times \left(\frac{CEPCI_{2018}}{CEPCI_{ref}}\right) \tag{17}$$

In the economic analysis, the consideration of externalities involved assessing the cost of externalities and exploring the potential for monetizing them. The monetization of externalities was evaluated by referencing the average additional price costumers were willing to pay to avoid negative consequences (Table 4). On the other hand, the cost of externalities considered carbon taxes or other penalties. The cost of abatement is determined as follows:

$$CCA = \left|\frac{NPC_{e-fuel} - NPC_{fossil\,fuel}}{GWP_{e-fuel} - GWP_{fossil\,fuel}}\right| \tag{18}$$

Table 4 Monetization indexes for externalities

Middle indexes	Monetization of externalities	Unit reference
HH	74,000 $€_{2003}$	Per 1 DALY (Disability adjusted life year)
EQ	9,500,000 $€_{2003}$	Per 1 avoided lost species per year
RS	0.862 $€_{2003}$	Per 1 USD_{2000}

The simulations results revealed two noteworthy points: firstly, the cost of e-jet fuel is currently too high to be considered competitive, necessitating a minimum carbon tax of 1125 $\$/t_{CO2,eq.}$ (which is deemed unreasonable compared to the social cost of carbon at 37 $\$/t_{CO2,eq.}$). Secondly, a phenomenon of burden-shifting was observed. This phenomenon involves a decrease in one endpoint indicator while others increase. Specifically, GWP decreases, but EQ and HH indicators increase, primarily due to carbon capture and electrolysis. The variations in results among configurations highlight that wind power outperforms other electricity generation pathways, and that salt cavern storage has less impact than type 1 tanks, which require materials and energy for production. Additionally, DAC introduces worse endpoint indicators than PSC due to its high energy intensity. These results could be subject to change based on alternations in the energy mix and, consequently, in the CF. Notably, the only scenario surpassing BAU scenario is C-PP capture with salt cavern storage in Spain.

From the NPC perspective, there is no parity with fossil fuel jet, with e-fuel NPCs ranging between 2.3 and 6.8 times higher. The major portion of this cost is OPEX, particularly H_2, except for HT-DAC where CO_2 covers the largest share. This underscores once again the significance of electricity cost and CF (see Figure 36).

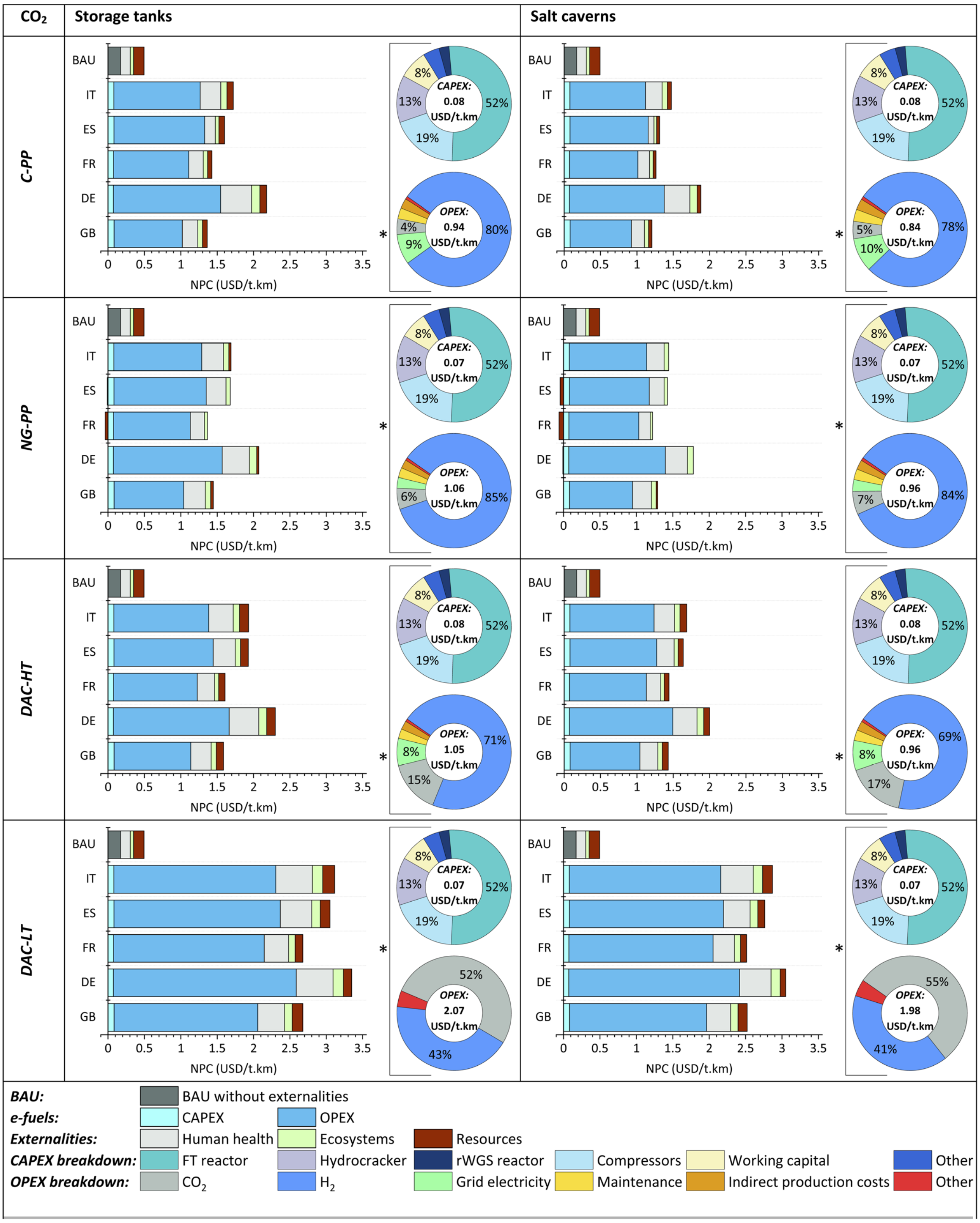


Figure 36 NPC breakdown for different scenarios compared to BAU.[40]

1. Bio-based production

Biomass serves as a feedstock applicable to various processes, involving preparation and gasification steps to generate syngas. Alternatively, biomass can undergo anaerobic digestion (AD) to produce biogas, a substitute for natural gas, or fermentation to generate bioethanol, which can be dehydrated to yield ethylene. In the case of producing HVCs, MTH processes are essential. The biomass component of production cost can be significant, reaching up to 40%, akin to electricity costs in e-chemical routes. Production costs for ammonia may range between 455-2000 $\$/t_{NH3}$, considerably higher than current cost [13] . For bio-methanol, the price may fluctuate between 300-1000 $\$/t_{MeOH}$ [26] . Biomass emerges as the route with highest land and water usage, amounting to 4,628 thousand km^2 and 4,628 km^3/y, respectively, according to the study by Gabrielli et al. [9] . Land coverage raises concerns, leading to Direct Land Use Change (DLUC) and Indirect Land Use Change (ILUC) impacts. The extent of these impacts depends on factors such as the original land use, final use, and the starting conditions of the land. The environmental impact is greater when converting forest land compared to grassland. Additionally, annual crops have a more significant impact than perennial crops. Evaluating ILUC is challenging, involving considerations about redirecting crop production in response to price changes for food crops due to the conversion of fields for biofuel crops. Calculating emission changes is complex, and the reliability of such assessments is limited, requiring a time horizon of at least 20 years.

The production of methanol from biomass has also been explored in the JEC report[28] as a potential alternative to gasoline. Therefore, the results are compared to conventional gasoline (COG1) and other pathways presented in Table 5.

Table 5 Methanol production routes code

Code	Definition
GPME1b	Piped NG (4000 km) to methanol, synthesis in EU
GRME1	Remote NG to methanol, synthesis near gas field
WxME1/BLME1	Waste wood to MeOH (W), farmed wood to MeOH (F), black liquor gasification/synthesis plant
REME1	Renewable electricity to methanol (CO_2 from flue gases)

In terms of energy consumption, bio-based routes are not competitive and even less efficient than the renewable e-methanol route. The majority of the energy required during the transformation step, which is the most energy-intensive phase, is derived from the biomass itself. Consequently, thus the Fossil Depletion (FD) factor can be exceptionally low compared to all other fossil-based routes. Figure 37 provides an energy expenditure breakdown, enabling a comparison of different routes and an estimation of the impact of transportation. Scenarios involving shipping transport (b) exhibit increased energy expenditure compared to base scenarios with road transport only (a), primarily due to the greater distance travelled. This emphasizes the sensitivity of such studies to location, indicating that concentrated production in certain regions may not be environmentally friendly due to the transport required for distribution, despite technological feasibility or resource availability at a global scale.

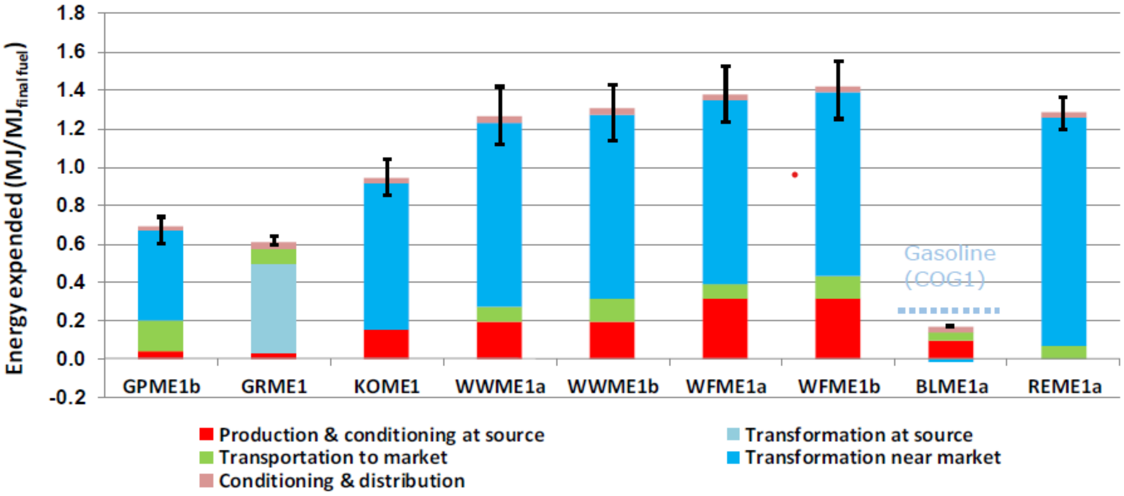


Figure 37 Energy expenditure for different alternative methanol production routes.[28]

In terms of emissions, both biomass routes and the e-methanol route surpass fossil fuel routes but remain comparable to traditional gasoline, as illustrated in Figure 38. The differences between farmed and waste wood are minimal in terms of energy efficiency and GHG emissions, but they start to widen when considering other factors such as resource depletion, land use, and the cost of avoided CO_2. Routes utilizing wasted wood remain more cost-effective than farmed wood, and the overall impact is considerably lower because it avoids competition with the agriculture industry and reduces energy expenditure. Figure 39 provides a comparison of different alternative fuels in terms of carbon emissions savings and Cost of CO_2 Avoided (CCA).

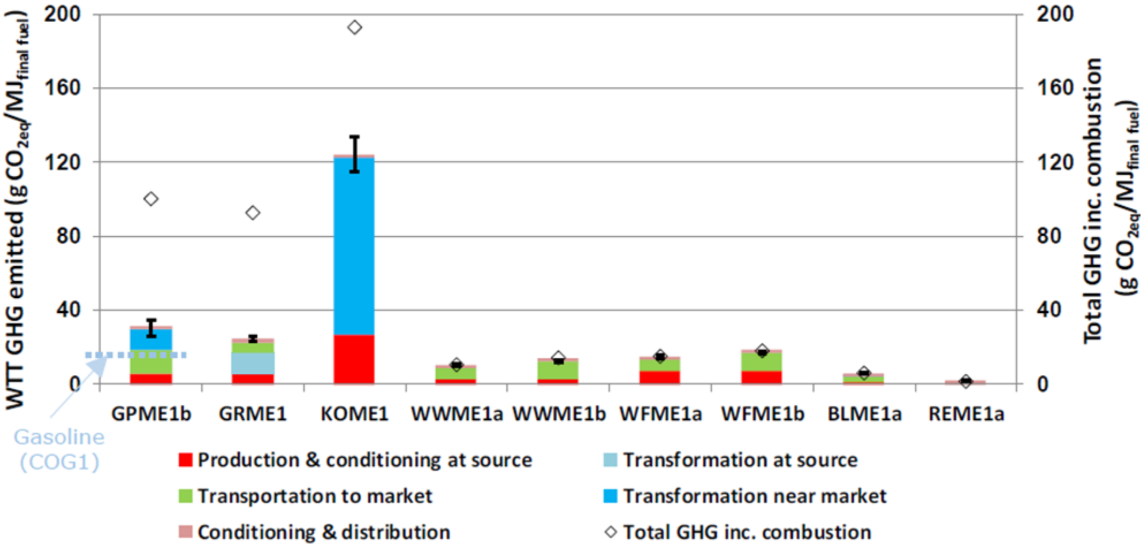


Figure 38 GHG emissions for different methanol production routes.[28]

The most significant gains are achieved through the black liquor route (BLR), surpassing even waste wood. The rationale behind this lies in process integration. Process integration is a practice applied in systems composed of different units to exploit their interconnection, aiming for higher efficiency. These procedures increase the complexity of the facility and make the fuel synthesis even more dependent on the primary industry. Similar to waste wood, in this case, the feedstock is a byproduct of a primary industry, but here, energy and mass streams rely on the main process.

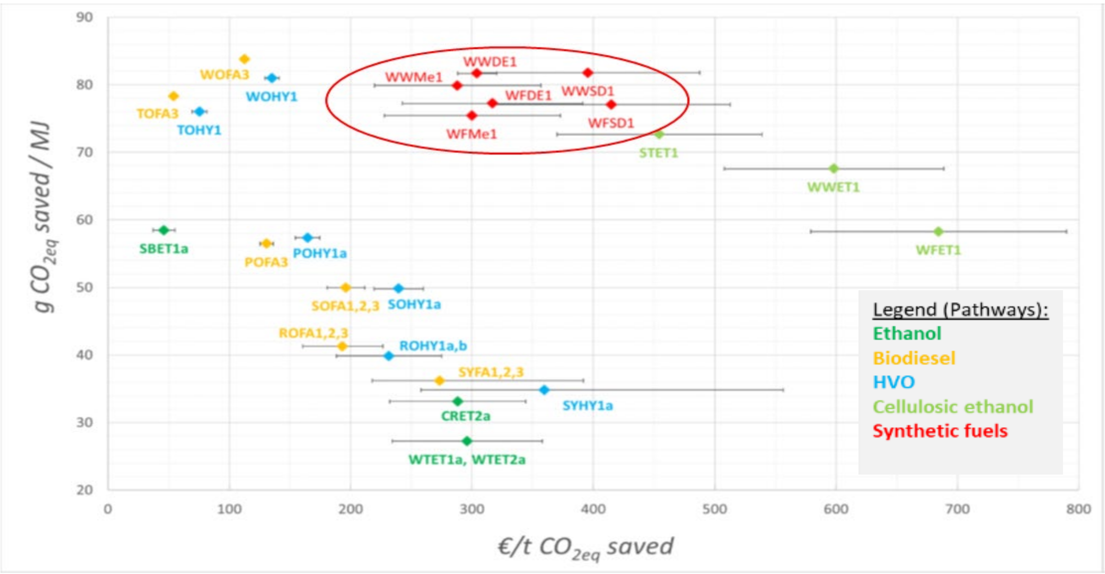


Figure 39 Specific CO_2 savings vs. specific cost of CO_2 avoided [28]

The findings of the JEC report fail to capture the true advantages of waste biomass, like waste wood, in waste-to-x configurations. The main limitation lies in assessing environmental impact solely through GWP. In reality, the situation is far more intricate, and a comprehensive LCSA is essential to discern the pros and cons of these technologies.

In a study by Li et al.[48] , it was analyzed the performance of biodiesel production based on corn stalk gasification was analyzed. The study was conducted in China, where the projected corn production for the 2023-2024 season is 280Mt[49] . Assuming a ratio of corn stalk to corn of 1.2[48] , the theoretical amount of stalk available is more than 330 Mt. The authors carried out a cradle-to-gate LCSA on the functional unit of 1 ton of jet fuel produced in a plant with a feed rate of 500 t/d. The LCSA followed the monetization methodology and the economic allocation method. The monetization methodology is based on the idea that the scarcity of a resource or the burden of pollutant treatment is reflected in the market price (e.g., a scarce resource is generally more expensive). The overall impact was expressed in terms of Indicator of Comprehensive Performance (ICP) evaluated as in Eq.(19), referred to as $B_{i,j}$ (\$/t), the total benefit of product j by process i, and α, β, γ are weighting coefficients.

$$B_{i,j} = \alpha B_{i,j}^{q} + \beta B_{i,j}^{s} + \gamma B_{i,j}^{d} \qquad (19)$$

The contributions are defined as follows:

- $B_{i,j}^{q}$ represents the Relative Economic Benefits, which is the difference in net income relative to a certain product j through the process i, compared to the traditional process (e). In the equation below, P_j^q is the market price for product j, while C_j is the production cost of product j through process i and traditional process (e).

$$B_{i,j}^{q} = \left(P_j^q - C_{i,j}\right) - \left(P_j^q - C_{e,j}\right) \qquad (20)$$

- $B_{i,j}^{s}$ is the Nonrenewable Resources Saving Benefits (NRSB) and involves the usage of non-renewable resources in producing product j through process i and consuming $Y_{i,m}$ resources except biomass:

$$B_{i,j}^{s} = \sum_{m}\left(P_m^s \times Y_{i,m}\right) - \sum_{m}\left(P_m^s \times Y_{e,m}\right) \qquad (21)$$

- $B_{i,j}^{d}$ is the Pollution Mitigation Benefits and is defined as the difference in emissions (S_n) of pollutant n during the process i producing product j compared to the emissions in the traditional process (e).

$$B_{i,j}^{d} = \sum_{n}\left(P_n^d \times S_{i,n}\right) - \sum_{n}\left(P_n^d \times S_{e,n}\right) \qquad (22)$$

The system illustrated in Figure 40 was modeled in Aspen Plus to derive energy and material balances for each process. The system can be divided into three main steps: biomass gasification (BG), F-T synthesis, and hydrocracking (HC).

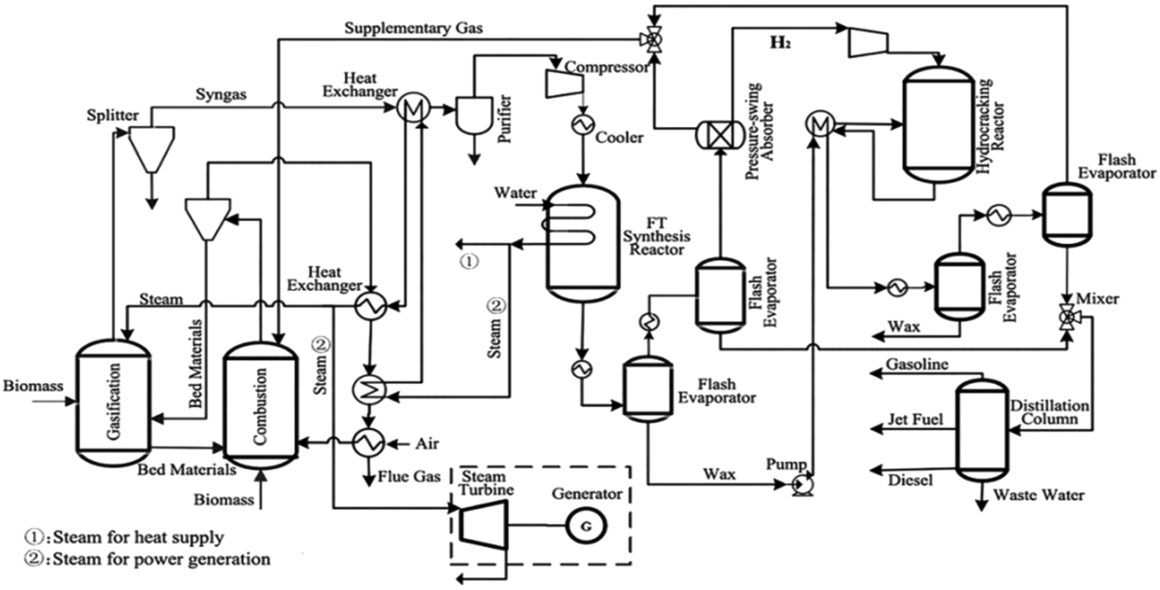


Figure 40 Flow scheme of the bio-jet fuel production process.[48]

The impact assessment relied on the Chinese Life Cycle Database (CLCD), and since stalk is a byproduct of corn cultivation, the allocation of impact was calculated as shown in Eq.(23) where MF represents the mass ratio of corn stalk and corn comb, while P denotes the market prices of corn stalk, corn and, corn comb.

$$K_{cs} = \frac{P_{cs}}{P_{cs} \times MF_{cs} + P_{cg} + P_{cc} \times MF_{cc}} \qquad (23)$$

K_{cs} is not the only allocation parameter since the system of Figure 40 produces multiple goods, mainly jet fuel (k), gasoline (g), diesel (d), wax (w), and steam obtained from rejected heat (s). Therefore, another allocation parameter is required. In Eq.(24), m represents the mass yield of each product, and q denotes the standard coal coefficients.

$$K = \frac{m_k q_k}{m_k q_k + m_g q_g + m_d q_d + m_w q_w + m_s q_s} \qquad (24)$$

The results of the analysis, depicted in Figure 41, illustrate comprehensive performance considering different weighting coefficients. The study also explored two configurations regarding heat recovery. In the ICP2 case, the steam produced from recovered heat is utilized to generate electricity, while in the base case (ICP1), it is employed for heat supply, as indicated in Figure 40. This implies a slightly different plant layout for ICP2, making the costs higher. Moreover, environmental benefits are enhanced since the avoided burden of the self-consumed electricity now accounts for the CF of the Chinese energy mix, which predominantly relies on coal power plants.

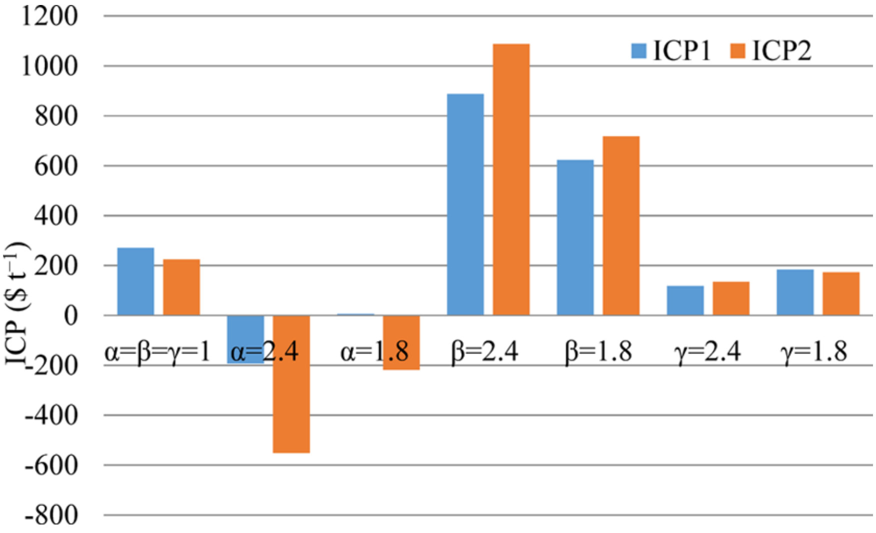


Figure 41 ICP results with different weighting coefficients.[48]

The weighting coefficients represent the significance of one indicator relative to the others. Equality among coefficients implies that the three aspects (economic, environment, resources) are valued equally. Figure 41 also presents cases where more importance is assigned to one aspect. For instance, if the economic aspect is the most important ($\alpha > 1$) , both configurations fare worse than traditional jet-fuel, being significantly more expensive in terms of production costs. Conversely, if resources or the environment are given more weight ($\beta/\gamma > 1$), both configurations outperform the traditional route. Notably, in the latter case, ICP2 demonstrates higher performance than ICP1 due to the electricity produced, which reduces the amount of drawn from the grid. However, because the system is more complex, ICP2 exhibits lower performance than ICP1 when $\alpha > 1$.

Process integration

As mentioned earlier, the black liquor route stands out as the only exception in terms of energy expenditure among the pathways considered in the JEC report. To understand why this route exhibits higher efficiency than the traditional route, it is essential to delve into its source derivation. Black liquor is a by-product of the paper industry obtained during the Kraft process (pulp extraction inside the mill), where cellulose is separated from other components like hemicellulose, lignin, and inorganic contaminants. Initially considered a waste, black liquor was disposed of into waterways until the introduction of recovery boilers in the mid-1930s. These boilers allowed for energy recovery from waste but with low efficiencies ranging between 9-14% [31] . In contrast, the gasification pathway offers much higher efficiency, approximately 45% (a selected value in the JEC report) and potentially up to 69% [31] , especially when integrated into processes to produce either electricity (Black Liquor Gasification Combined Cycle) or F-T liquids. As depicted in Figure 42, the BLGCC plant is more complex than the recovery boiler one, making it more capital-intensive but with efficiency more than tripling.

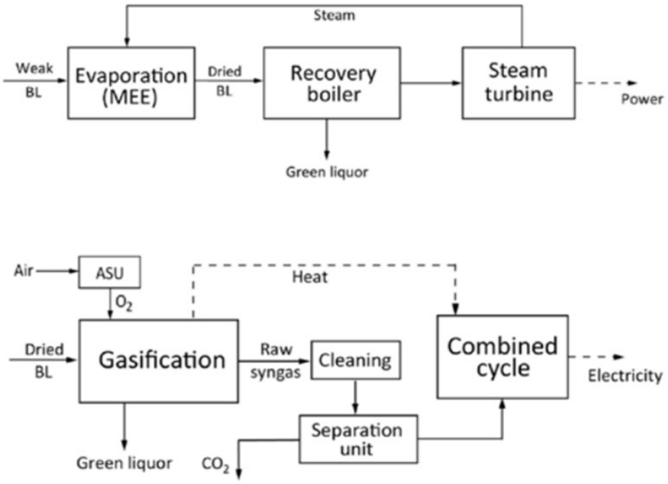


Figure 42 Flow scheme of recovery boiler (up), and BLGCC (down)

Waste biomass from the wood industry or the food industry are characterized by lower impacts, but its production and scale-up is tied to and limited by the primary industry since the amount of feedstock depends on the amount of generated waste.

Another intriguing biomass route, which could offer lower impacts and avoid issues like conflicts with the food industry, involves the redevelopment of land unsuitable for food crops. This approach was explored in the work of Okeke et al.[47] , where biomass production involved cultivating miscanthus in strip-mined-soil previously used for mining and mineral extraction. The soil, after the site is discontinued, is not suitable for hosting food crops due to factors like its acidic pH.

Figure 43 illustrates the system boundaries employed in this study, encompassing all significant processes from cultivation to the combustion of drop-in diesel. This LCA is thus a cradle-to-grave analysis. One distinctive aspect of this system, which subsequently influences the LCA results, is its energy self-sufficiency, both in terms of heat and in terms of electricity, with surplus electricity being exported. The study is centered on the cultivation of miscanthus in stripped-mined land located in Ohio, and the functional unit is the gasoline gallon equivalent (GGE) of drop-in diesel produced, corresponding to 33kg of harvested miscanthus.

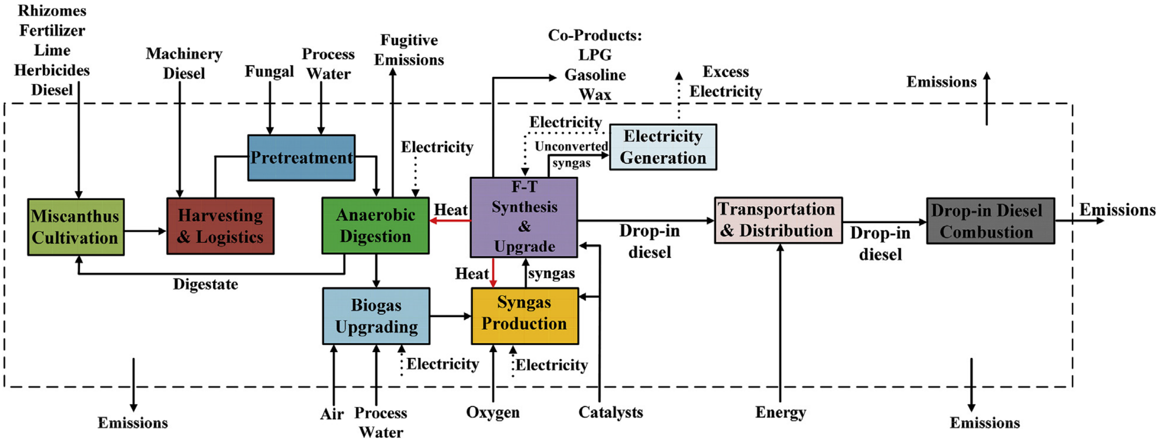


Figure 43 System boundaries with relatively major flows.[47]

The biogas production, carried out through Solid State Anaerobic Digestion (SS-AD), was simulated using parameters derived from existing studies, as outlined in Table 6. The subsequent biogas-to-liquids process, which includes the F-T slurry reactor with a Co-based catalyst, was modeled using Aspen Plus. The overall system's environmental impacts were evaluated using the SimaPro 8 and TRACI 2.0 assessment tools, utilizing the SimaPro built-in database and the GREET database.

Table 6 Main process parameters of biogas production from SS-AD

NAME	DESCRIPTION	VALUE	UNIT
Yield	Amount of miscanthus produced during cultivation	10	ton_{DM}/ha /y
VS	Volatile Solids content	87.2%	-
SOC	Soil Organic Carbon sequestrated during plant growth	0.16-0.82	ton/ha /y
MPR	Methane Production rate	0.18	m^3/kg_{VS}
Fugitive emissions	Methane leaks in the digester	3.1%	

The impact assessment results are illustrated in Figure 44, comparing ten indicators with conventional fossil diesel. As expected, drop-in diesel demonstrates better performance than fossil diesel in terms of Global Warming Potential (GWP) and Fossil Fuel Depletion (FFD). However, in some categories, the environmental impact is higher than that of fossil diesel. Notably, ozone depletion is 100% higher due to the use of a Ni-catalyst in syngas production through Steam Methane Reforming (SMR). Smog formation, which is 63% higher, results from diesel consumption in various processes such as harvesting, transportation, and distribution machinery. Acidification Potential (AP) and Eutrophication Potential (EP) are more than 90% higher than conventional diesel, primarily originating from the AD step. During AD, low-quality methane and digestate (a solid residue containing ammonia and N-compounds) are produced. The biogas stream is upgraded by removing main contaminants like ammonia and hydrogen sulfide, which are then released into the atmosphere. The Human Health (HH) impact, in terms of carcinogenic and non-carcinogenic substances, is lower compared to fossil fuel diesel due to fewer polycyclic aromatics release but is higher in terms of respiratory effects from gas leakages during biogas production.

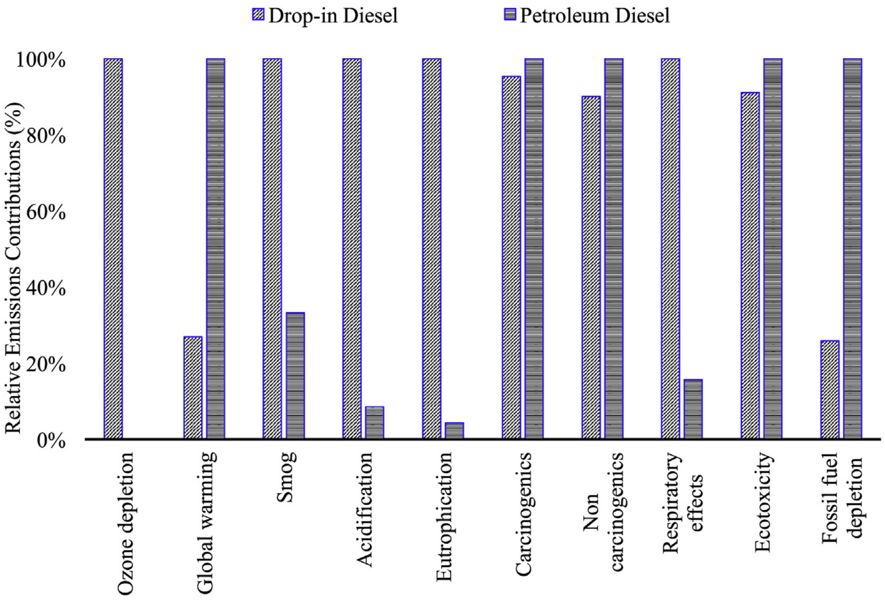


Figure 44 LCA environmental impact results compared to fossil diesel.[47]

The impact assessment breakdown highlights that a significant portion of the impact is attributed to the use of fossil diesel to power tractors, trucks, and other machinery. This observation is noteworthy because the environmental impact of drop-in diesel could be further reduced by utilizing renewable fuels, specifically those with lower impact than conventional diesel. Additionally, the study explored an alternative scenario where the digestate was internally circulated and utilized as fertilizer in the miscanthus cultivation. This practice eliminates the need for external N-fertilizer, providing substantial benefits, particularly in terms of GWP and FFD.

Another instance of process integration, in a sector that has experienced continuous growth in recent years, is the co-production of F-T fuels integrated with the production of bioethanol. Bioethanol is primarily generated through the fermentation of non woody biomass that contains high levels of starch and/or sugar. In Figure 45, the process of bioethanol production is described, with Dry Distiller Grains with Soluble (DDGS) serving as a by-product. In dry milling production processes, the quantity of by-product can reach 1.04t/ton of bioethanol produced. Typically, DDGS are sold as animal feed, but this necessitates transportation to the market or directly to consumers.

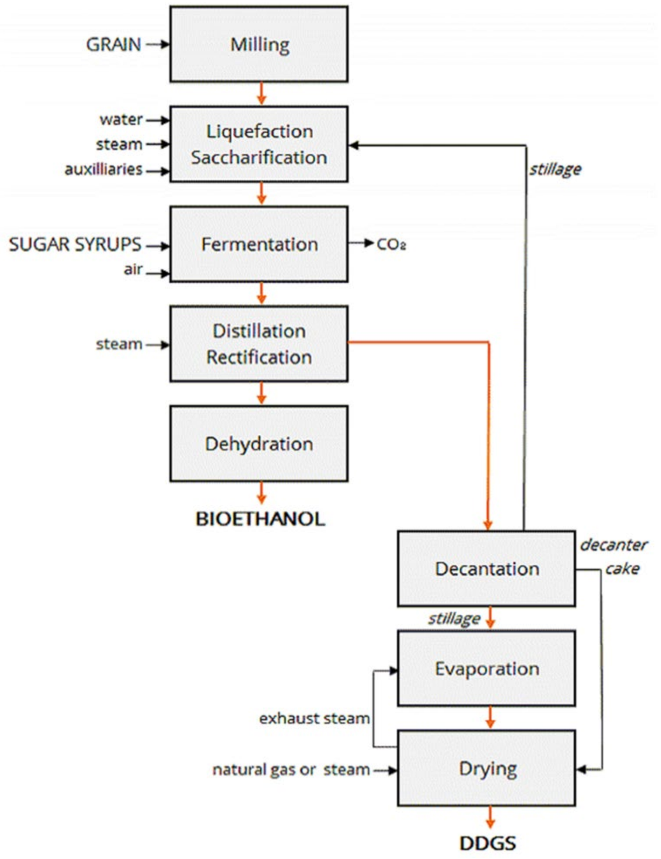


Figure 45 Block diagram of bioethanol production process.[44]

Borugadda et al.[45] investigated the potential integration of a F-T synthesis plant with an existing bioethanol production facility, utilizing DDGS as a feedstock. The initial step involves gasification to produce syngas, which is then compressed before being introduced into the F-T reactor. The study was based on a production scale of 1 ton/h of crude F-T, and the flowsheet was designed using Aspen HYSYS. In terms of process parameters, the same authors, in a previous work[46] , demonstrated the superior performances of promoted pellet iron catalysts supported on carbon nanotubes with bentonite clay loading. This specific configuration enables the achievement of an 86% CO conversion efficiency, 76% selectivity toward liquids (C_{5+}), and an H_2/CO ratio of 2. Economic assessment was carried out by sizing the plant in Aspen Icarus Process Evaluator V10, incorporating the CEPCI index. For impact assessment, defined as Potential Environmental Impacts (PEI), the WAste Reduction (WAR) algorithm software was employed.

From the simulations, the performance of the reactor aligned with the anticipated specifications outlined above, with no waxes (C_{24+}) present, rendering the hydrocracking unit unnecessary. The economic analysis yielded an Internal Rate of Return (IRR) of 107.9%, indicating a highly profitable investment, and a minimum return on investment within two years.

In the LCA, the PEI encompasses global atmospheric and toxicological impacts categorized into four subcategories: Global Warming Potential (GWP), Ozone Depletion Potential (ODP), Acidification Potential (AP), PhotoChemical Oxidation Potential (PCOP), Human Toxicity Potential by Ingestion (HTPI), Human Toxicity Potential by Exposure (HTPE), Terrestrial Toxicity Potential (TTP), and Aquatic Toxicity Potential (ATP). The overall impact was determined to be -18 PEI/kg$_{fuel}$, indicating that, overall, this integration is environmentally benign or friendly. The manufacturing of the catalyst, particularly for AP, contributes significantly to the overall impact[45] .

Biogenic Carbon Capture and Storage

In the IPCC Fourth Assessment Report, the BioEnergy Carbon Capture and Storage (BECCS) was introduced as a key technology in a net-zero scenario. The concept involves achieving negative emissions by absorbing atmospheric CO_2 during plant growth and subsequently capturing and storing CO_2 during the gasification or synthesis process.

As previously mentioned, the BECCS concept is a fundamental tool for mitigating global warming. Although it is a relatively new concept, there is not much literature on it, despite the extensive number of studies on biofuel and F-T synthesis. Additionally, most scientific papers focus on applying BECCS to power generation, but the same concept can be applied to fuel synthesis. In a study by Michaga et al.[50] , an in-depth techno-environmental analysis of F-T synthesis fuel from Forest Residue (FR) employing CCS in the system presented. The main goal of the study is to estimate the economic and environmental performance of a SAF production process based on FR gasification located in Solway Firth area, with additional CCS. The plant's capacity is set at 20 t$_{Dry}$/h or 0.16 Mt$_{Dry}$/y, based on considerations such as the percentage of FR that should be left on-site due to sustainability reasons and competition in demand from the power sector. However, the scale-up of the facility was discussed during the sensitivity analysis.

Figure 46 illustrates the system of the SAF production process defining the boundaries for both economic analysis and LCIA. The system comprises four main processes. The first step involves biomass pretreatment, although it has not been explicitly modeled, the economic and environmental impacts have been included. The biomass is then transported to the facility, where undergoes gasification in a

Dual Fluidized Bed Gasifier (DFBG). This configuration offers operational advantages, as the first bed is dedicated to gasification, while the second bed handles the combustion of unreacted char. This design limits the amount of air (N_2 and O_2) in the syngas stream. The third step involves syngas treatment to remove contaminants like CO_2, which is subsequently compressed to 153 bar and injected in the pipeline connecting the facility to the storage point. Finally, the syngas enters the F-T reactor, and the syncrude output undergoes distillation.

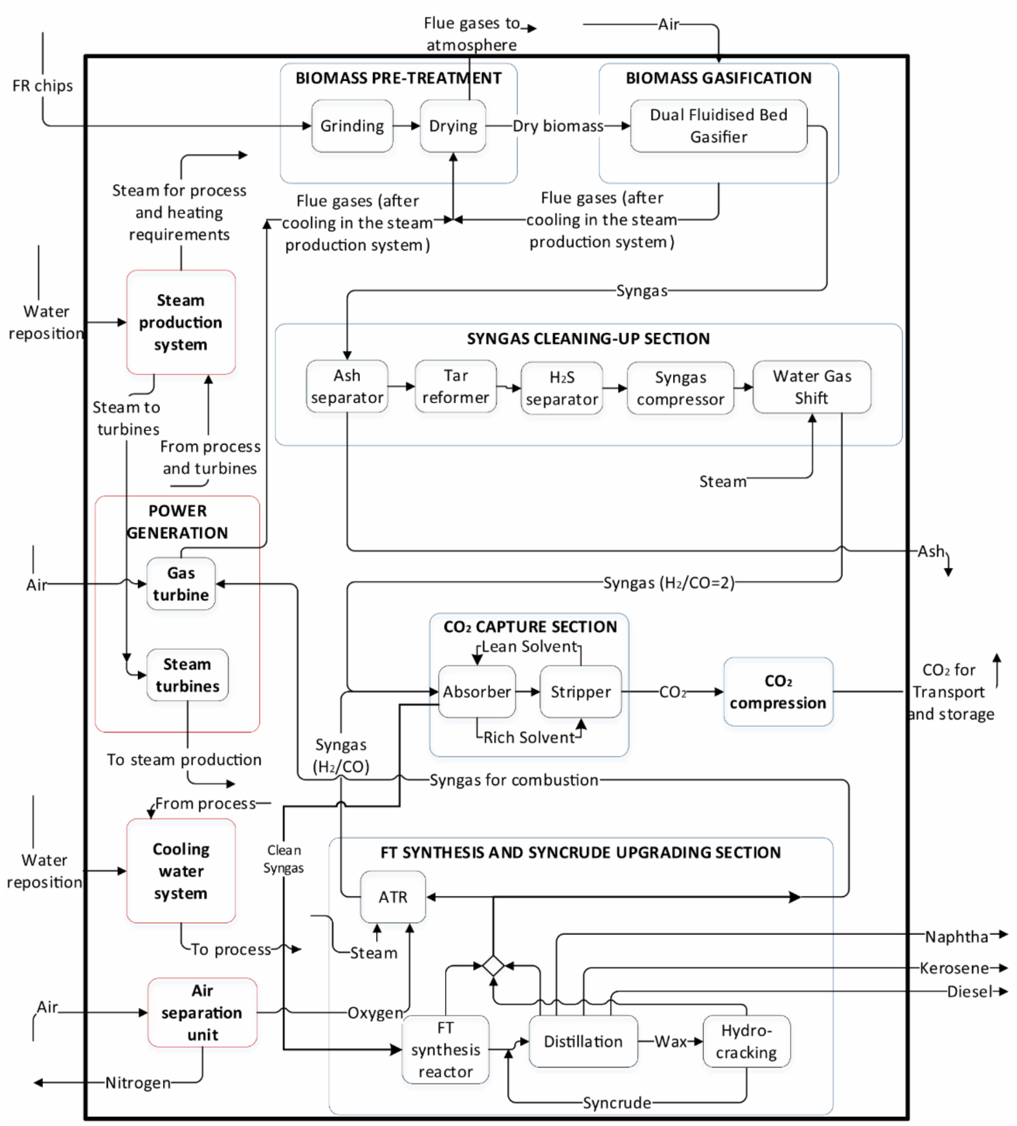


Figure 46 Blok diagram of the overall SAF production process.[50]

The main products include gasoline (C_5- C_7), jet fuel (C_8- C_{16}), and diesel fuel (C_{17}-C_{20}). These are final products, and from the distillation column, waxes (C_{21+}) are recovered. These waxes undergo hydrocracking to increase the yield of products (calculated as per Eq.(25) and Eq.(26)), and light hydrocarbons (C_1- C_4) are recirculated with the unreacted syngas exiting the F-T reactor. One unique aspect of this plant is its reliance on once-through F-T synthesis, offering two benefits. Firstly, around 15% of the unreacted syngas is directed to a gas turbine to generate electricity, meeting the plant's energy demand and enhancing overall energy efficiency (Eq.(27)). Secondly, the remainder is sent to an ATR unit and then recirculated through the CO_2 absorption unit, reducing the risk of contaminant accumulation on the catalyst and improving conversion efficiency. The final section of the system is the Combined Heat and Power (CHP) unit, consisting of a gas turbine and supplementary steam turbines running with steam produced through heat recovery across the plant.

$$yield_{overall} = \frac{\dot{m}_{gasoline} + \dot{m}_{jet\ fuel} + \dot{m}_{diesel}}{\dot{m}_{dry\ biomass}} \qquad (25)$$

$$yield_{jet\ fuel} = \frac{\dot{m}_{jet\ fuel}}{\dot{m}_{dry\ biomass}} \qquad (26)$$

$$\eta_e = \frac{\left[\sum_{fuels} \dot{m}_{fuel} \times LHV_{fuel}\right] + P_{el,produced}}{\left[\dot{m}_{dry\ biomass} \times LHV_{dry}\right] + P_{el,demand}} \qquad (27)$$

The analyses were conducted by modeling the system in Aspen Plus with Ecoinvent database for biomass treatment and transportation, as well as CO_2 compression and transportation. The functional unit for the analysis was set as 1 MJ of jet fuel. Since multiple products are obtained, two allocation methods were compared: energy allocation and system expansion. The impact assessment followed the ReCiPe methodology, incorporating assumptions such as a biomass transportation distance of 50km, jet fuel compatibility, and SAF combustion carbon neutrality. For the economic assessment, the Aspen Plus Economic Evaluator tool was utilized, complemented by data from bibliographic sources, especially for catalytic reactors. Price adjustments were made using the CEPCI index, combined with size adjustments as outlined in Eq.(28), and the .Labor OPEX were empirically calculated as a function of the plant capacity, as expressed in Eq.(29).

$$C = C_0 \left(\frac{S}{S_0}\right)^f \times \left(\frac{CEPCI_{2019}}{CEPCI_0}\right) \qquad (28)$$

$$OPEX_{lab.} = 15 \left[\frac{£}{h}\right] \times 2.13 \times n_{steps} \times Capacity_{plant} \left[\frac{kg_{out.}}{h}\right]^{0.242} \times \frac{h_{operating}}{24} \qquad (29)$$

The results of the economic analysis indicate that, without incentives or taxes, SAF cannot compete with fossil jet fuel. The Minimum Jet fuel Selling Price (MJSP) are 3.27 £/kg$_{SAF}$ and 3.03 £/kg$_{SAF}$ for the BECCS and BE (SAF without CCS) scenario, respectively, compared to the gate price to fossil jet fuel at ≈0.56 £/kg$_{fuel}$. The 7.92% difference between the MJSP of BECCS and BE scenario suggests that the integration of CCS does not drastically affect the price of SAF. The sensitivity analysis revealed that SAF is CAPEX-intensive technology, and CCS constitutes only 1.22% of CAPEX in the BECCS scenario. This is justified by the fact that the only difference in plant layout among scenarios is the compression and transportation of CO_2, as the absorption step is always required for syngas cleanup. The second major contributor to the MJSP is the feedstock cost.

These results are promising, as in the perspective of a widespread adoption of these technologies, CAPEX is expected to decrease with increased investment. Furthermore, there are potential benefits from economies of scale that could be exploited. This is demonstrated in Figure 48, where the MJSP trend tends to plateau after reaching a production scale of 100 t$_{dry}$/h.

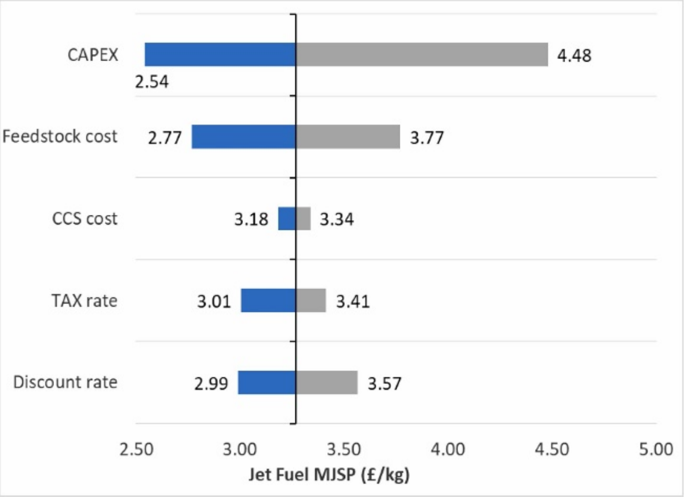


Figure 47 Sensitivity analysis of the MJSP for the BECCS scenario.[50]

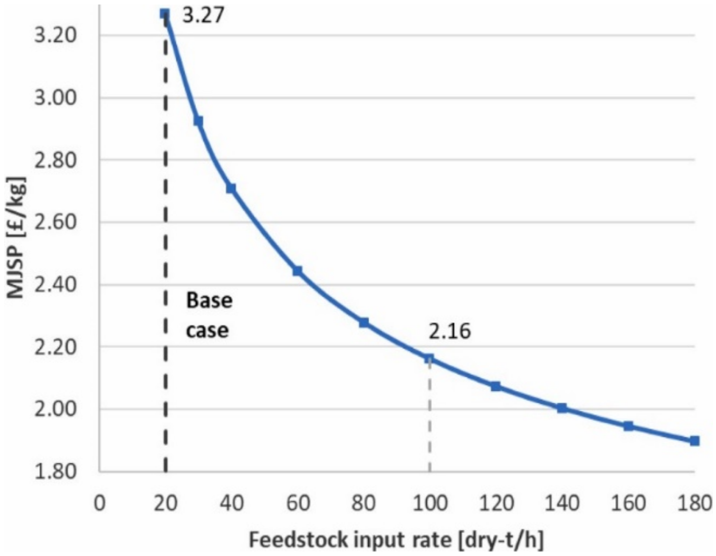


Figure 48 Effect of the plant capacity on the MJSP.[50]

The differences between BECCS and BE scenarios are substantial in the LCIA results. As depicted in Figure 49, it becomes evident that the storage step is necessary to achieve negative emissions, and the BE scenario already shows significant emissions reduction compared to fossil jet fuel (approximately 83%). Moreover, the most emission-intensive steps are jet fuel combustion and wood chips production from FR. In the end, a Monte Carlo analysis was conducted to assess the level of uncertainty introduced by the assumptions. The analysis showed a high level of confidence around the values obtained, with a 95% confidence interval between -131.26 and -106.60 g_{CO2e}/MJ_{SAF}, ensuring the robust performance of BECCS in various conditions.

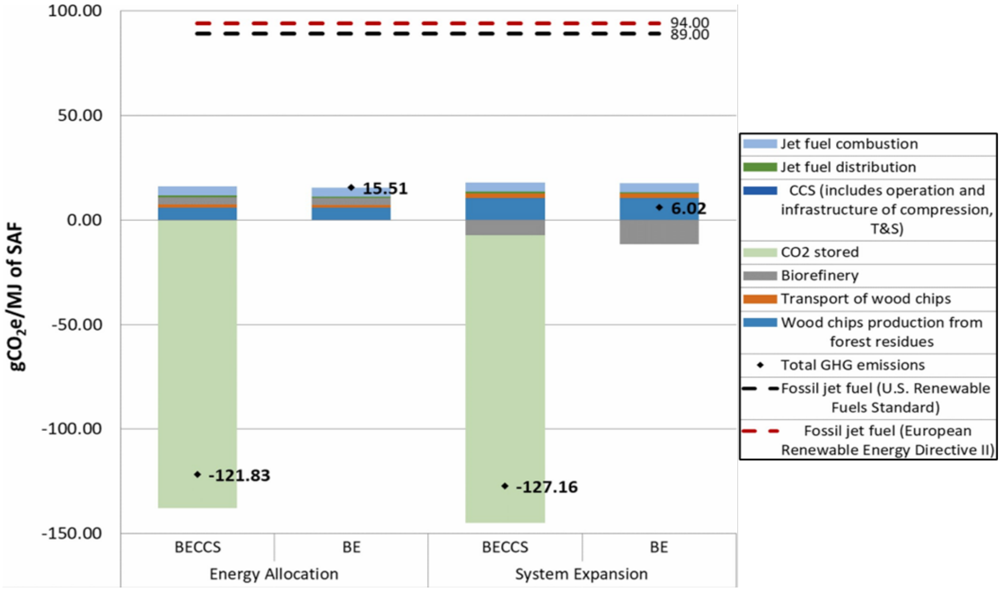


Figure 49 CO_2 equivalent emissions breakdown for both scenarios obtained with two different allocation methodologies.[50]

iii. Fischer-Tropsch processes

The Fischer-Tropsch (F-T) synthesis is a chemical process employed for producing synthetic fuels, primarily hydrocarbons, from a mixture of carbon monoxide and hydrogen, commonly referred to as synthesis gas or syngas. Below, a detailed description of the Fischer-Tropsch synthesis process will be provided, followed by reports on the system's performance based on F-T. The general structure of an F-T synthesis plant is illustrated in Figure 50.

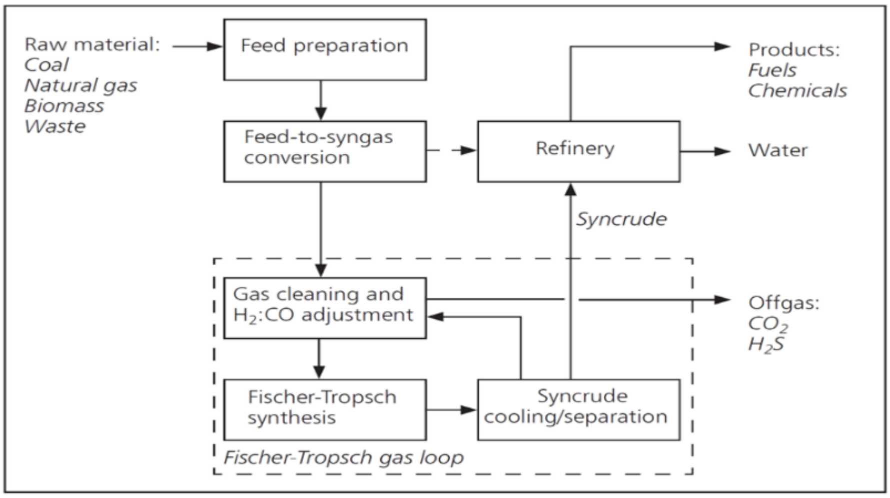


Figure 50 Block scheme of Fischer-Tropsch process.

During the 1920s, chemists Franz Fisher and Hans Tropsch developed a process that allowed the synthesis of fuels from coal, now known as Coal To Liquids (CTL). This process was developed in Germany during the Weimar Republic as a way to enhance independence from oil supplier and establish the basis for autarky, given Germany's substantial coal production at the time. After the war, these facilities were shut down, but interest in this technology has reemerged for two main reasons: first, similar to 1920s Germany, some countries like China see the opportunity to use domestic resources (like coal) to replace imported oil. The second reason stems from the potential use of Fisher-Tropsch in net-zero scenarios. In Figure 51, you can observe the locations of operating facilities and how the choice of feedstock primarily aligns with resource availability and production (see Figure 10).

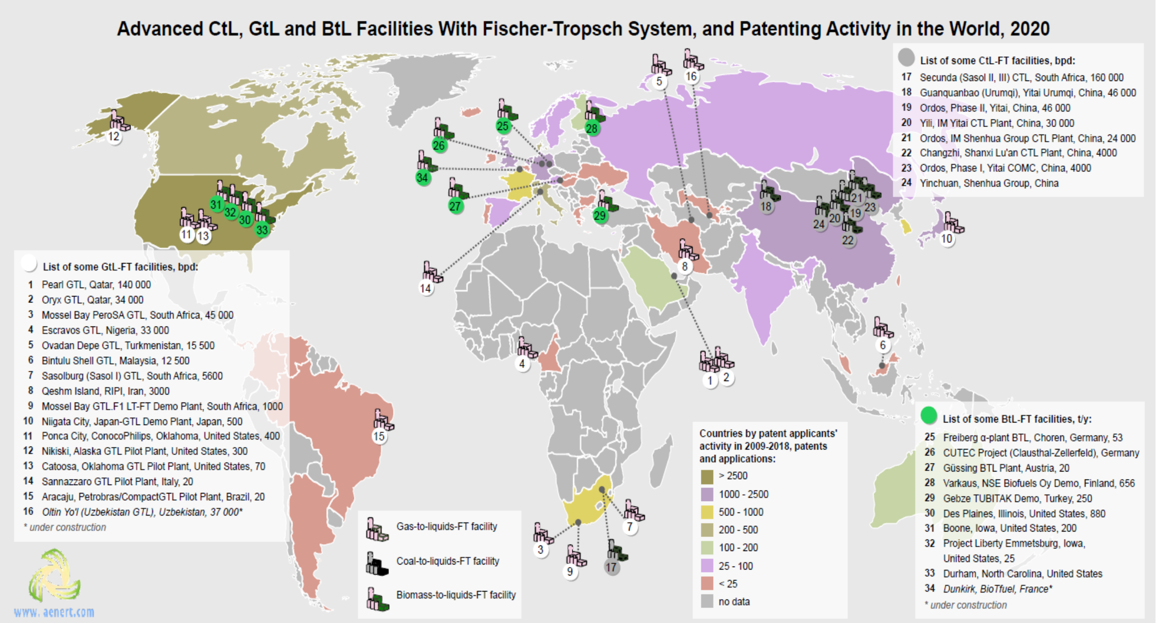


Figure 51 Worldwide distribution of GtL, CtL and BtL facilities.[29]

Process chemistry

The starting point of Fisher-Tropsch synthesis is a syngas with an H_2/CO ratio that depends on the employed catalyst. Fe-based catalysts are the only ones used on a commercial scale in CTL plants due to their lower sulfur sensitivity, the ability to catalyze Water Gas Shift (WGS) to increase the H_2/CO ratio inside the reactor, and lower cost compared to Co-based catalysts. Another option is Ni-based catalysts, which tend to be selective towards methanation[30] . Fe-based catalysts are predominantly used to produce gasoline in high-temperature fixed bed reactors, while Co-based ones are used in low-temperature slurry reactors to produce syn-diesel. The synthesis involves several reactions, and the catalyst and operating conditions affect the yield and distribution of products. The reactions of interest include methanation Eq.(30), paraffins synthesis Eq.(31), olefins synthesis Eq.(32), and WGS Eq.(33).

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \qquad (30)$$

$$nCO + (2n+1)H_2 \leftrightarrow C_nH_{2(n+1)} + nH_2O \qquad (31)$$

$$nCO + (2n)H_2 \leftrightarrow C_nH_{2n} + nH_2O \qquad (32)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad (33)$$

All these reactions are highly exothermic, rendering the overall F-T process exothermic. The heat rejected can be recovered for process integration, thereby reducing or even eliminating the energy demand of the plant.

Process performances

In this section, the results and procedures of various scientific articles focused on F-T synthesis are discussed. The emphasis is on synthetic fuels, with all processes aimed at maximizing the yield of F-T liquids.

In the JEC Well-to-Tank report v5[28] , the LCA adopted follows a consequential life cycle inventory modelling principle to compare various alternative fuels with conventional fossil diesel. The well-to-tank approach concentrates on the impact of the life stages of a fuel up to the distribution phase. Figure 52 Production steps considered in the LCA of the report.[28] , outlining the different stages required to end-user through distribution. This approach has limitations in providing a complete picture of the real impact since utilization is entirely excluded. In the report, some results attempt to address this gap by considering emissions derived from the complete combustion of the fuel, though it does not replicate real engines operation. Despite this limitation, these results remain useful, especially when comparing fuels with same end use (e.g., fossil-diesel and e-diesel).

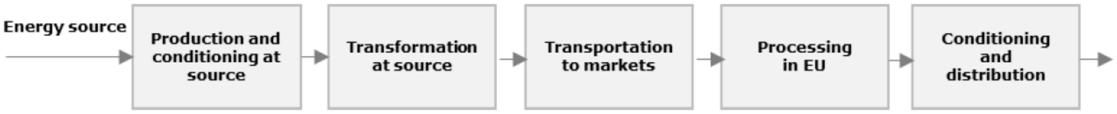


Figure 52 Production steps considered in the LCA of the report.[28]

The results were obtained using the E3database software tool, developed by LBST9, which also offers a dataset for all input data supplemented with Ecoinvent and GEMIS for the construction footprint. In the LCA, the carbon footprint for every electricity-consuming process was estimated, considering the EU energy mix, with an actual averaged value of 396 gr$_{CO2}$/kWh and a forecasted value of 268 gr$_{CO2}$/kWh. Table 7 presents the codes and associated descriptions of all the considered alternatives. Conceptually, the main difference among these products lies in the feedstock. Currently, natural gas is the most used and preferred feedstock due to lower capital intensity and a higher purity of the syngas stream. Coal comes second, with China hosting nearly all the CTL facilities, except the "Secunda CTL plant" (the world's largest CTL facility processing 40 Mt of coal per year), located in South Africa. Biomass is an alternative feedstock more prevalent in developed countries (EU, North America). In both cases, the capital intensity is much higher than natural gas due to the preparation, gasification and clean-up steps. Another feedstock possibility analyzed in the JEC report is e-diesel from wind renewable energy. Although less mature than other technologies, it represents an interesting alternative not only for diesel production but also as an Energy Storage System (ESS) in a future with a forecasted surplus of renewable energy. An additional difference between scenarios is the implementation of CCS.

Table 7 List of fuels (of the "diesel family") compared in the JEC report.[28]

Code	Definition
COD1	Crude oil from EU supply, transport by sea, refining in EU (marginal production), typical EU distribution and retail
GRSD1/1C	Remote NG to Syndiesel (GTL): GTL plant near remote gas field with/without CCS (C), Syndiesel imported into EU and incorporated into the diesel pool
KOSD1/1C	EU-mix hard coal to Syndiesel (CTL) with/without CCS (C)
RESD1	Renewable electricity to Syndiesel via methanol (CO_2 from flue gases)
RESD2	Renewable electricity to Syndiesel, SOE coupled with F-T (CO_2 from flue gases, and direct air capture)
WxSD1/1C	Farmed (F), Waste (W) wood to syndiesel with/without CCS: (a) 500 km distance travelled, (b) > 500km
BLSD1/1C	Black liquor gasification/synthesis plant: (a) 500 km distance travelled, (b) > 500km

The two impact taken into account in this study are the energy expenditure, expressed as $MJ_{\text{total primary energy input}}/MJ_{\text{diesel}}$, where total primary energy excludes the energy content of the fuel. Additionally, the environmental impact is expressed as cumulative GHG emissions, i.e., $CO_{2,\text{ eq}}$.

The energy expenditure factor is closely related to the efficiency of the process. In general, alternative pathways are much more energy-intensive than traditional fossil diesel, except for the black liquor route, which has already been discussed. The reason for this lies in the plant layout, particularly the processes involved. While in the oil route, distillation is the most energy-intensive step, natural gas, coal, and biomass require much more energy-intensive steps. In the case of natural gas, steam reforming is required to produce syngas, which is then sent to an F-T reactor, while for coal and biomass, the syngas is obtained through gasification and then sent to an F-T reactor. This dissimilarity is even more apparent considering that for oil-based diesel, the share of energy expenditure is more or less equal between production (extraction and conditioning at the source) and transformation near the market (refinery in the EU). For alternative routes, the transformation step is much more energy-intensive (see Figure 53). For these routes, the energy expended increases even more if CCS is integrated (about 15% increase), mostly due to the amine regeneration trough stripping (see Figure 53).

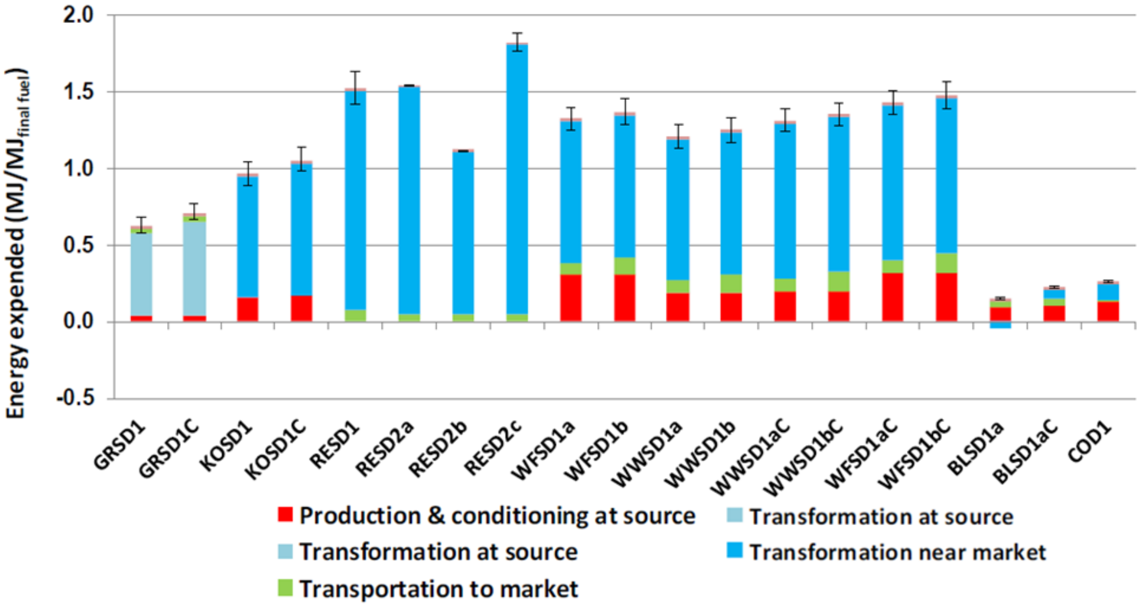


Figure 53 Comparison of energy expenditure among different alternative diesel fuels.[28]

E-diesel constitutes the most energy intensive pathway due to the production of H_2 through electrolysis, which requires about 3.75 kWh/Nm^3 of H_2. This value was obtained assuming SOE, which benefits from higher efficiency compared to low-temperature alkaline or PEM electrolyzers, at 80% vs. 65% (on a LHV basis). The higher performances mostly come from the more favorable thermodynamics of splitting steam rather than splitting liquid water and the possibility of operating at the thermoneutral Voltage (operating point at which ohmic losses equal the thermal energy demand of the cell). Moreover, the heat required to produce the steam (~0,25 MJ$_{th}$/MJ$_{H2}$) could be recovered from the F-T reactor or, in general, through heat integration. Following the results obtained by Ralf et al.[32] , the estimated costs of syn-diesel from co-electrolysis can range from 1.85 €/l to 0.94 €/l in the most optimistic case. An important result from the sensitivity analysis of this study is the weight of electricity in production cost, which amounts to about 40% of total share.

The high energy intensity is one of the main drawbacks of this route, coupled with high costs. For these reasons, e-fuels encounter resistance in being adopted as an alternative to fossil fuels. However, in a projected energy paradigm with high renewable penetration, all excess electricity (with expected prices sometimes lower than 20 €/MWh$_{el}$) can be stored and transported through synthetic fuels as energy vectors. That is the main reason why, in most studies, the LCA is conducted considering the use of renewable energy only, (wind in the JEC report, PV-wind mix in Concawe report, etc.) and not electricity from the energy mix.

The competitiveness of alternative processes is evident in terms of GHG emissions. In Figure 54, apart from CTL routes, which have a higher carbon footprint, all the other routes show similar or even lower emissions compared to conventional diesel. Of course, the e-diesel route outperforms both CTL and GTL due to the use of renewable energy. In this case, the only source of emissions arises from the transportation and distribution of the final product since embedded emissions are neglected.

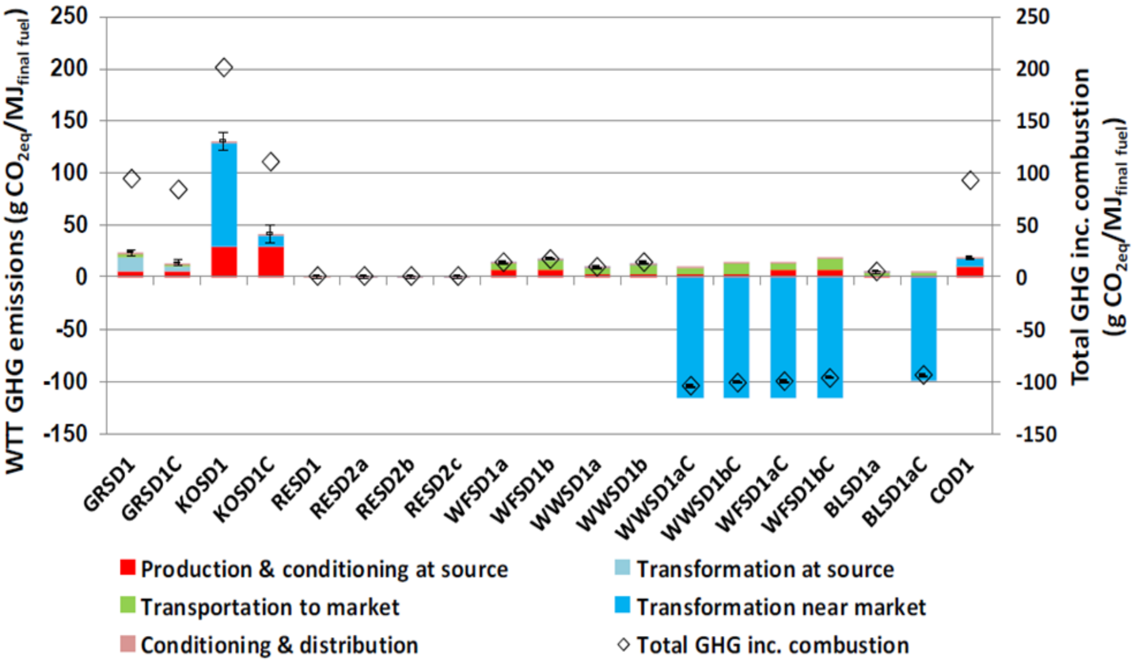


Figure 54 GHG emissions associated with different products.[28]

In the Concawe report, FTD CtG emissions range between 5.6-13 gCO_2/MJ, with production costs varying from 55.1-88.1 €/GJ, where renewable electricity cost accounts for around 63%. The range in values is attributed to different production locations. Emissions are lower in North EU and higher in South EU, mainly due to the higher carbon footprint of PV compared to wind. Interestingly, the situation is reversed when considering production costs, which are higher in North EU than in South EU, primarily because of the higher cost of wind compared to PV.

F-T coupling with fluctuating input

During the previous analysis, it was outlined that e-diesel, despite being the most energy-intensive route, could be of immense interest as an ESS. This concept is identified as a Demand Side Measure (DSM), a necessity for ancillary services considering grids with high electricity fluctuations. The optimization of the so-called Power-to-X strategies will be covered later. Instead, the focus now is on how well the F-T processes can be coupled with fluctuating input, despite electricity not being a direct feed of the process; it affects H2 production, which isa part of the overall process.

In the study of Wentrup et al.[37] , the authors concentrated on the performance of the F-T process under dynamic operation of the reactor due to pulsating input. The results demonstrated that not only is dynamic operation possible, but may be preferable, especially with slurry bubble reactors characterized by faster dynamics due to greater mixing. The pulsating hydrogen and the resulting catalyst drainage also provides advantages in terms of yields towards liquid products.

Impact assessment beyond GHG emissions

Reliable results from LCSA (Life Cycle Sustainability Assessment proposed by Klöpffer[38]) are crucial for effective policymaking. This assessment strategy is more comprehensive than traditional LCA because does not focus solely on environmental impact. LCSA includes LCA, LCC (Life Cycle Costing), and SLCA (Social Life Cycle Assessment). With this approach, it is possible to assess the impact on all three spheres (environmental, economic, and social), providing a more complete picture of both positive and negative outcomes of a technology. The level of detail in LCSA is crucial; for example, when considering only GHG emissions, biomass routes appear to have the lowest environmental impact. However, when encompassing factors like fresh water and land use, the results change significantly in terms of sustainability.

Similar considerations can be drawn regarding the shift from LCA to LCSA. In the LCSA conducted by Hnich et al.[39] , synthetic fuel production based on date palm waste in Tunisia was investigated. The LCA followed a cradle-to-gate approach using the ReCiPe 2016 midpoint method with a functional unit of 1 GJ (gasoline and diesel). Palm waste serves as a by-product of the agricultural industry, and economic allocation was applied in the study. For the SLCA inventory, only data concerning elements contributing to at least 2% of the total cost production were considered, sourced from the PSILCA database. This resulted in identifying several hotspots: biomass pretreatment unit and compressors from China, gasification and tar cracking unit from the USA, plant construction and maintenance in Tunisia, and Tunisian electricity production.

The LCC was based on a database reconstructed from various literature sources[39] , with values readjusted using the CEPCI parameter as follows:

$$PC = PC_{ref} \times \left(\frac{CEPCI_{2020}}{CEPCI_{ref}}\right)^{n} \qquad (34)$$

The results of the LCSA were then categorized and expressed in terms of SDGs impact. As evident from Figure 55, the alternative route can be considered "better" only in terms of GHG and FD, but overall results are considerably worse than conventional fuels. This result, like any other, is highly location-specific and time-specific. Considering the impact of electricity in Tunisia at present, most of the production is based on natural gas. If this changes in the future, for instance, with a higher share of renewable energy source (RES), the reported results will change significantly.

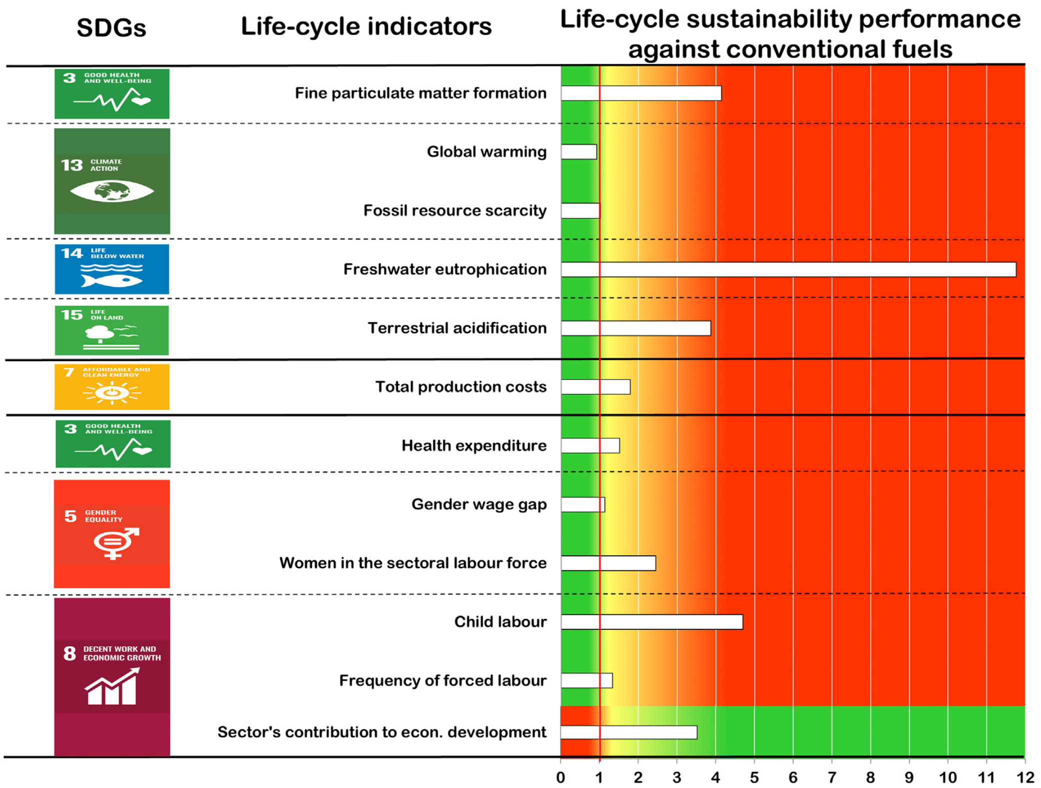


Figure 55 Impact of syn-fuels on different SDGs compared to conventional fossil-route (red vertical line).[39]

iv. Methanol To Hydrocarbon processes

The production of olefins, paraffins, naphthene, and aromatics can be achieved from syngas through processes that utilize oxygenated compounds as intermediates. Unlike Fischer-Tropsch synthesis, these processes involve at least two steps: the synthesis of oxygenated species and their subsequent conversion into olefins, paraffins, etc. The most common intermediate nowadays is methanol, but there are other options such as Dimethyl Ether (DME), which can be obtained from methanol dehydration (see Eq.(35)).

$$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O \tag{35}$$

The first step of this process corresponds to the previously discussed methanol synthesis, while the second step can generate different products depending on the operating conditions and the used catalyst.

The Methanol to Gasoline (MTG) process was the first one in a family of processes called MTH to be discovered. It was accidentally found by ExxonMobil (Mobil Oil Corporation at the time) researchers in 1977 during tests conducted on the ZSM-5 catalyst to synthesize ethylene oxide from methanol. ZSM-5 is an aluminosilicate zeolite, highly acidic, making it suitable for reactions proceeding through a carbenium ion mechanism, with pore diameter of around 5 Å. Since then, multiple processes have been developed, altering operating conditions and catalyst, such as SAPO-34 used for MTO, due to its smaller pores which hinder the diffusion of aromatics and branched alkanes.

Process chemistry

When methanol is in contact with the acidic catalyst at relatively high temperatures (around 320°C), it begins to react, forming an equilibrium mixture of DME, water, and unreacted methanol. This mixture then reacts to form the Hydrocarbons Pool (HCP), intermediate species of various composition, which ultimately produce final products such as olefins, paraffins, and aromatics. The overall stoichiometry is reported in Eq.(36), where $[CH_2]$ identifies the average composition of the products. The main process steps are outlined in Figure 56.

$$CH_3OH \leftrightarrow [CH_2] + H_2O \tag{36}$$

The MTO process is a slight variation of the MTG process, involving an anticipated stop of the reactions. This allows for the production of light olefins, mainly ethylene and propylene, while avoiding the production of gasoline range hydrocarbons.

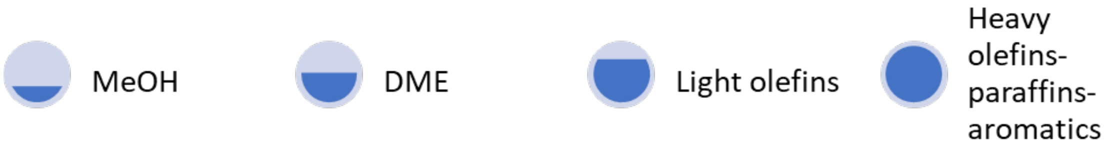


Figure 56 Main steps of the MTG process.[52]

Commercial technology

The market for this family of technologies is almost predominantly located in China. Commercially, four main processes have been patented. The DMTO-II and S-MTO technologies are MTO processes employing a fluidized bed operated at high temperature (400-500°C) and low pressure (1-3 bar). The only difference is the catalyst employed, and that the latter allows for higher yields of ethylene/propylene. The Lurgi Methanol to Propylene (MTP) process employs a four-stage train to achieve propylene yields exceeding 70%.

Process performance

The MTH pathways are slightly more efficient than the F-T process, primarily due to higher carbon conversion and selectivity towards desired products. This results in a lower required amount of both H2 and CO_2. According to the report from Concawe, MTK results show a 3% higher efficiency than FTK. This increased efficiency leads to slightly lower emissions and costs associated with electrolysis and CO_2 supply (see Figure 30 and Figure 32).

v. E-production as DSM and ESS

Renewable products, including both e-chemicals and e-fuels, have the potential to serve as modulators for the high fluctuations expected in electric grids with high renewables penetration. This section will discuss another application, whether there are any benefits in using e-fuels as ancillary support for the power sector.

In the work published by Burre et al.[35], a new definition of the Power-to-X term was introduced, encompassing three different concepts (see Figure 57):

- Demand Side Measure (DSM) is a relatively new concept based on grid modulation to attenuate frequency fluctuations, as opposed to supply side measures, such as turbine load modulation.
- E-production encompasses all production processes based on electricity, some of which have been analyzed in the previous sections.
- EES, also known as Power-to-Y-to-Power, refers to processes that enable short- or long-term energy storage without involving the exchange of material products (chemicals or fuels) with the surrounding.

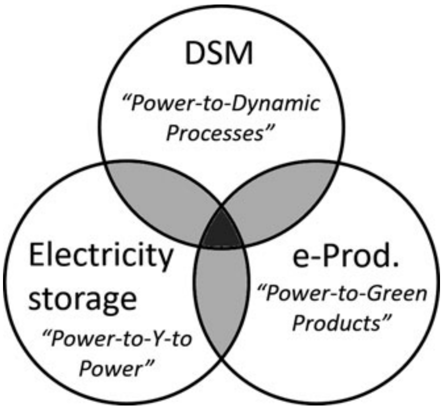


Figure 57 The three spheres of Power-to-X technologies.[35]

These concepts can be applied individually or simultaneously, forming more flexible techniques. In this study, it was also analyzed under which conditions each concept provides the most significant gains. Steady-state production is not significantly affected by fluctuation in magnitude but rather by the average price and CF, making it most convenient with very low average prices. Storage and DSM are most competitive when average prices are higher, and fluctuations are more pronounced (see Figure 58). The revenue potential of these technologies depends exclusively on the magnitude of fluctuations, as revenues are closely related to the difference between selling and acquisition prices. Combining strategies can lead to greater performances; for example, e-production with storage allows the production of e-fuels during low-price phases to be converted back to electricity during high-price phases, leaving the possibility to sell e-fuels.

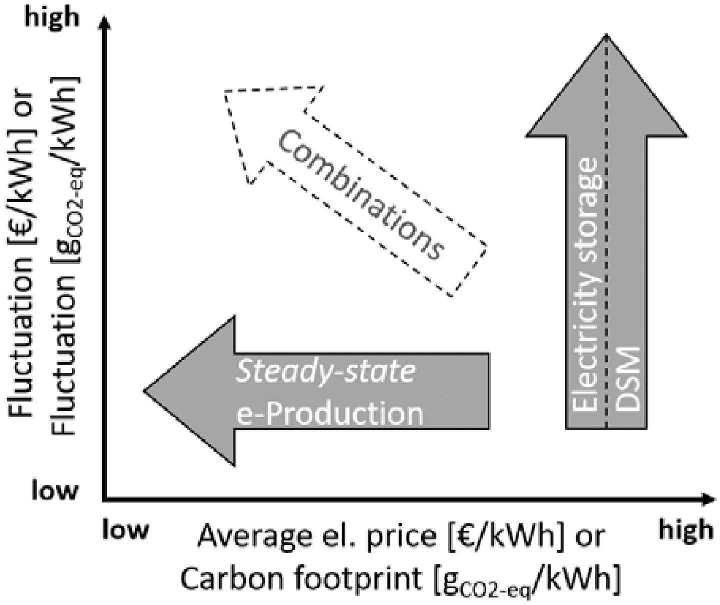


Figure 58 Competitiveness of the three modes as a function of the average value and magnitude of fluctuations of both electricity price and CF

The study explored two example cases: chlor-alkali electrolysis and storage based on ammonia with Reverse Solid Oxide Fuel Cells (RSOFC). In general, these optimized systems can increase the utilization factor of renewables but come with the cost of increased capacity to achieve sufficient operational flexibility. The selected examples focus on two high-energy-intensive processes, namely chlorine production, which accounts for 10% of global electricity consumption, and these processes have operating properties suitable for DSM. Figure 59 depicts the two operating modes of DSM-ammonia production system. Thanks to heat integration, the system is able to reach roundtrip efficiencies of 70%, with storage cost comparable to hydroelectric pump and storage plants.

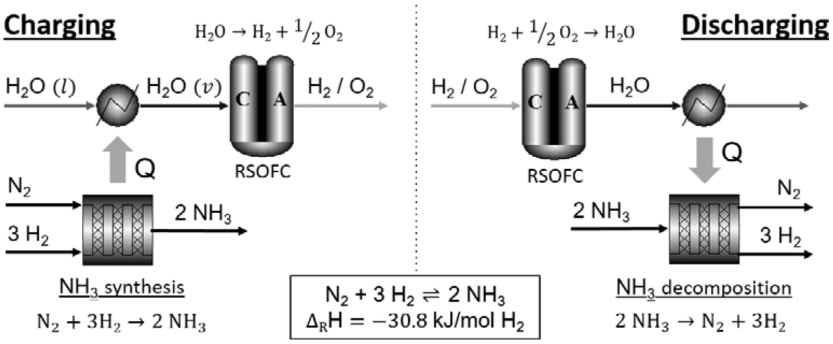


Figure 59 Operating modes of ammonia synthesis plant coupled with solid oxide electrolyzer.

Figure 60 displays the H_2-mode and O_2-mode of the chlor-alkali electrolyzer, sharing the same output., The only difference lies in the input. During O_2 operation, the electricity demand is approximately 30% lower, making it suitable for use during high-price phases. On the other hand, during H_2-operation, additional H_2 is produced, which would be optimal during low-price phases for obtaining low-cost green H_2.

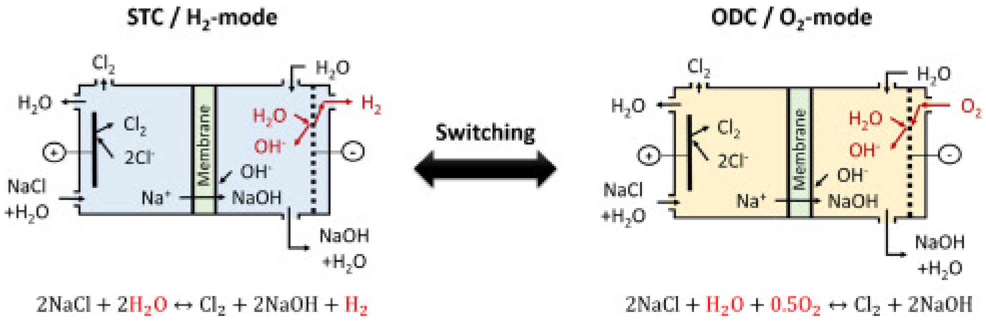


Figure 60 Flexible operation of chlor-alkali electrolysis.

Optimal dispatching and e-fuel-based energy storage were analyzed in a case study of Tsiklios et al.[36] based on facilities in North Rhine-Westphalia, Germany, scaled up to have an installed capacity of 382.57MW (the functional unit is the consumed electricity). In this study, a base case without ES was compared to four different layouts of integrated ES. All four cases involve Power-to-Power configurations, so the possibility of selling the e-product is neglected in this study. In both cases, a wind farm is considered as the renewable electricity supply.

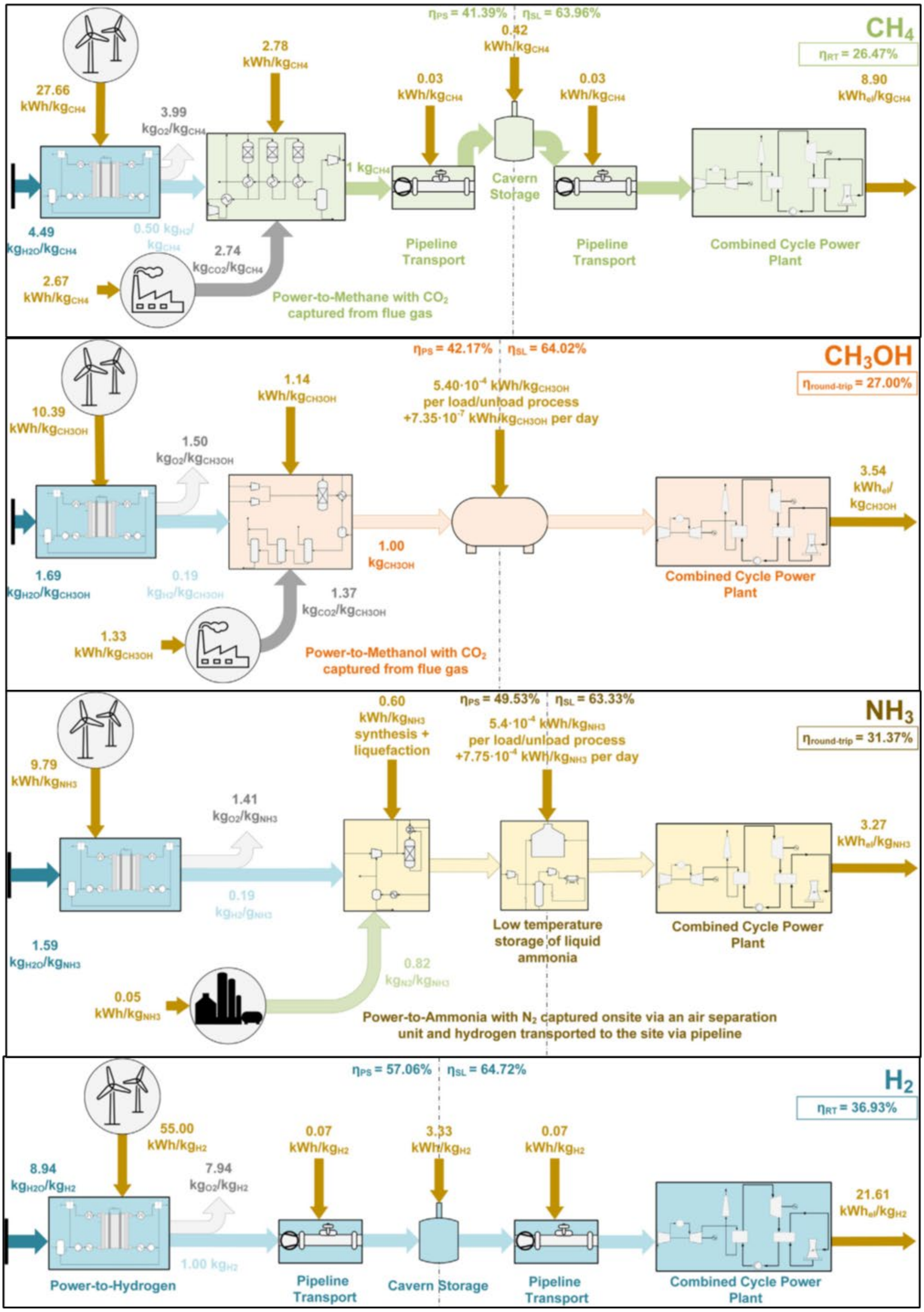


Figure 61 Mass and energy balances for PtP systems with different e-fuels. [36]

The hydrogen pathway turned out to have the highest round-trip efficiency due to the absence of CCU and/or ASU. Methanol and ammonia, on the other hand, do not require underground storage, thus avoiding transportation costs and losses, thanks to in-situ storage tanks. The goal of the study was to identify and discuss the optimal load capacity, considering two constraints: Full Load Hours (FLH) and Load Coverage (LC). Increasing capacity results in higher capital and operating costs (compression and transportation), but it allows for an increase in LC. This relationship is highly nonlinear and exhibits saturation, as shown in Figure 62, particularly due to round-trip efficiency and installed wind power. To maximize FLH, the installed wind capacity could be increased, or the generation site must be diversified.

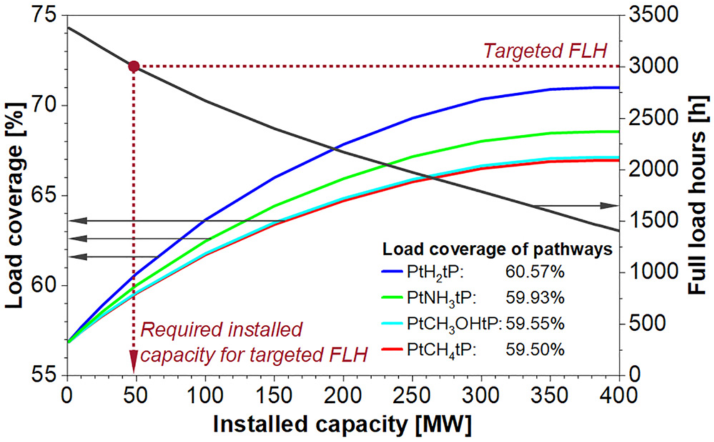


Figure 62 Load Coverage and FLH as a function of the installed capacity. Black line defines the required capacity as a function of just FLH. Colored lines refer to load coverage instead.[36]

5. LCSA calculations

After a comprehensive review of various studies exploring alternative solutions, our goal is to conduct a simplified LCSA on different SAFs. This LCSA aims to compare SAFs with conventional fossil jet fuel, focusing on production cost and carbon footprint. The assessment methodology employed is an attributional Cradle-to-Gate (CTG) LCA, supplemented by a sensitivity analysis. The study concentrates primarily on aggregated results from the production section of the supply chain (CTG), with an exclusion of distribution and end-of-life considerations for the product. Additionally, the analysis disregards any potential by-products and avoids accounting for any burdens that may have been mitigated.

a. Systems' model

In this section, the models for the four jet-fuel production systems will be presented, drawing upon various literature sources. All four systems assume the utilization of renewable energy, divided equally between PV and offshore wind sources, with a production capacity set at 10 MW_{SAF}. The electric energy produced from the power plant is assessed as a yearly average, taking into account the capacity factor (cf), which is determined from the Full Load Hours (FLH) of the chosen location (Great Britain). FLH data were obtained from renewables.ninja, and the calculations are outlined in Eq.(37) and Eq.(38). The Block Flow Diagram (BFD) of each system is presented below, and Table 8 provides the code and description of the four systems.

$$cf = \frac{FLH_{pv} + FLH_{wind}}{2 * 8760} \tag{37}$$

$$yearly\ production = Power\ installed * 8760 * CF \tag{38}$$

Table 8 Systems' code and description.

System number	CODE	DESCRIPTION
1	JF-DAC	Fossil jet fuel coupled with DAC
2	DAC-eJF	e-fuel, CO_2 from DAC
3	BioJF	Bio-jet fuel from miscanthus AD
4	CCU-eJF	e-fuel, CO_2 from PSC

System 1 (Figure 63, JF-DAC) integrates a fossil jet fuel production unit with DAC technology to achieve carbon neutrality. The CO_2 stream illustrated in Figure 63 aligns with the CF of fossil jet fuel sourced from the EU REDII, amounting to 94 gCO_2/MJ. No additional data were incorporated for the unit, except for the energy efficiency, which is derived from Elgowainy et al., set at 95.3%. This efficiency is evaluated using Eq(39) with an energy allocation method. The energy and mass balances for DAC were obtained from Ordóñez et al.[40], and the carbon capture technology employed is a HT-DAC from CE, as described in the "e-fuels synthesis" section.

$$\eta = \frac{Jet\ fuel\ energy\ content}{Energy\ input * allocation\ factor} \qquad (39)$$

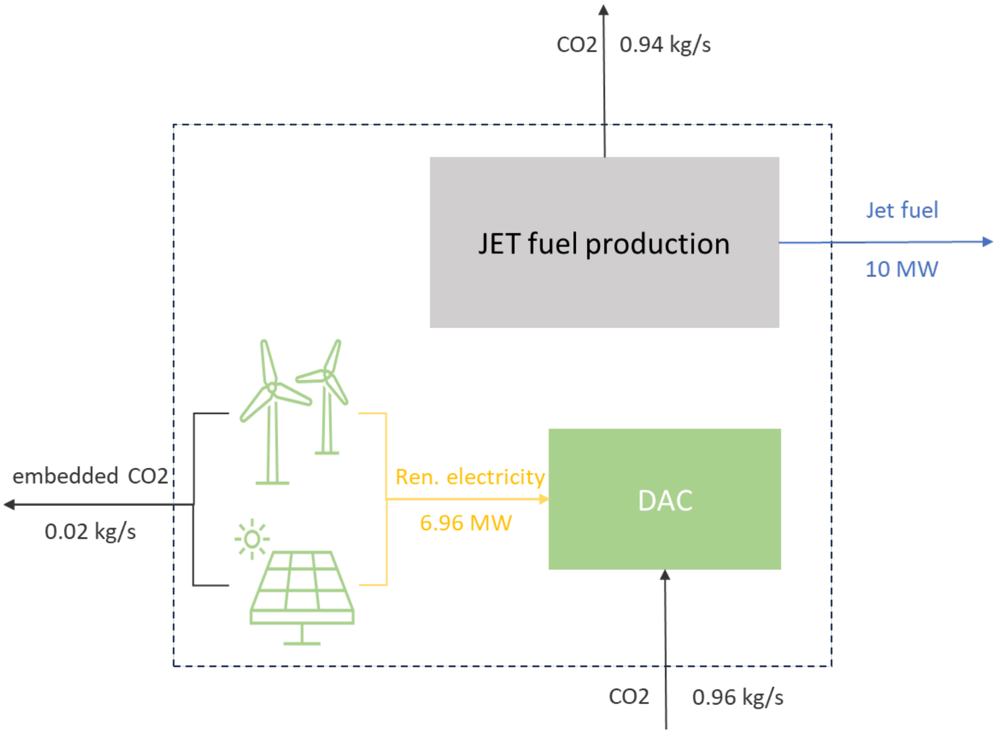


Figure 63 System 1 BFD.

System 2 (DAC-eJF), as illustrated in Figure 64, is an e-fuel production system relying on DAC as the source of CO_2. Green H_2 is produced using an alkaline electrolyzer, and the mass and energy balances for this process are derived from the Concawe report[51] . The F-T unit consists of the F-T reactor, the rWGS reactor, and the distillation unit. All equipment modeled from the Concawe report has been amalgamated into a singular unit, with inputs being H_2, CO_2, and electricity, and outputs being jet fuel and CO_2. Despite the F-T unit generating multiple outputs in the form of liquids in the gasoline range, it is assumed that the output corresponds entirely to jet fuel. The reactor employed is a slurry fluidized bed with Co-based catalyst. Both the F-T solids and gases are considered by-products. To enhance the jet fuel yield, waxes are directed to a hydrocracking unit, while gases are combusted in a boiler. The heat released from the exothermic reactions and the heat from the boiler are utilized in the DAC unit for calcination through heat integration.

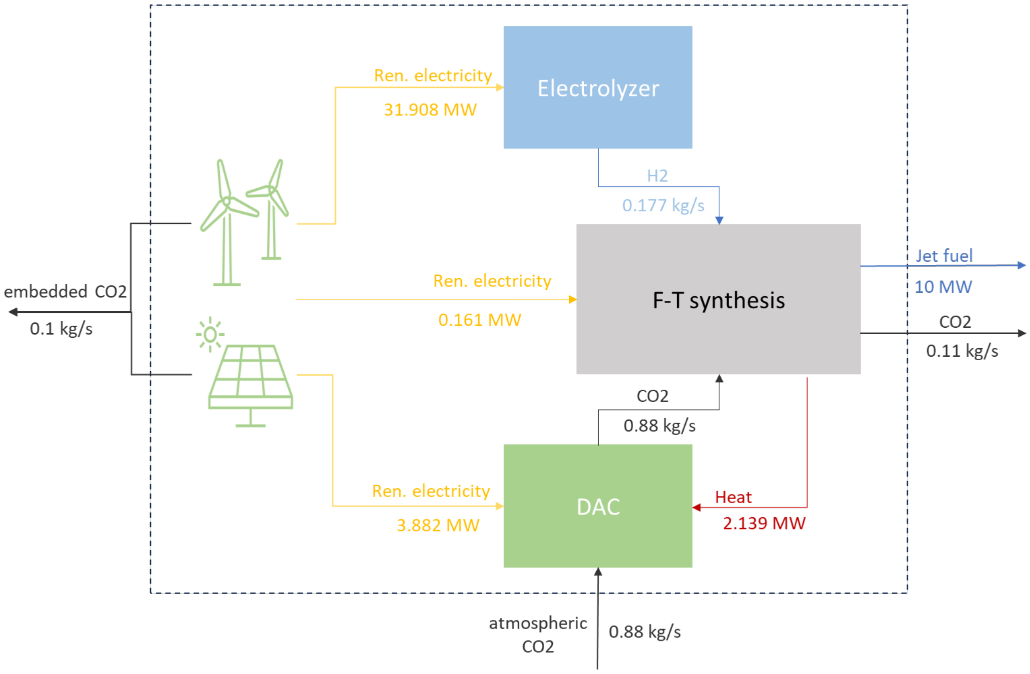


Figure 64 System 2 BFD

System 3 (BioJF), illustrated in Figure 65, involves the production of bio-jet fuel through miscanthus cultivation, AD, and steam reforming. The processes, including cultivation, harvesting, preparation, and digestion were modeled based on the study by Okeke et al.[47] . The volume of the digester was determined through a preliminary design, taking into account the most restrictive parameter, identified in the study as the Organic Loading Rate (OLR). Consequently, the minimum required volume was calculated as reported in Eq.(40). The biogas produced is directed to a steam reformer to obtain syngas, which is then sent to the F-T unit.

$$V_{min.} = \frac{VS\ mass\ flowrate\ \left[{}^{kg_{VS}}/_{d}\right]}{OLR\ \left[{}^{kg_{VS}}/_{d\,*\,m^3}\right]} \tag{40}$$

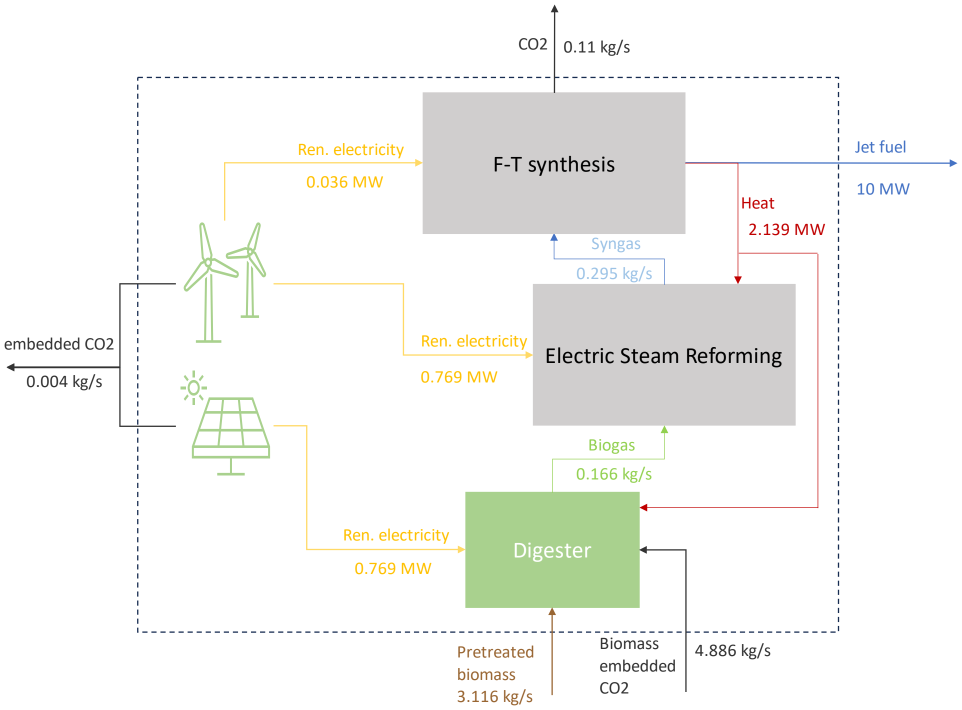


Figure 65 System 3 BFD.

System 4 (PSC-eJF), depicted in Figure 66, is an e-fuel production system utilizing PSC as the source of CO_2 extracted from flue gases. The model closely resembles that of system 2, with the primary distinction being the energy consumption of the CC unit, which is smaller in this case due to the higher CO_2 concentration in the flue gases. The CC unit is based on amine solvent with a capture efficiency of around 95% (through irrelevant for this study as the boundaries do not consider the upstream process). Similarly, in this case, the heat rejected from the F-T unit is integrated for amine regeneration.

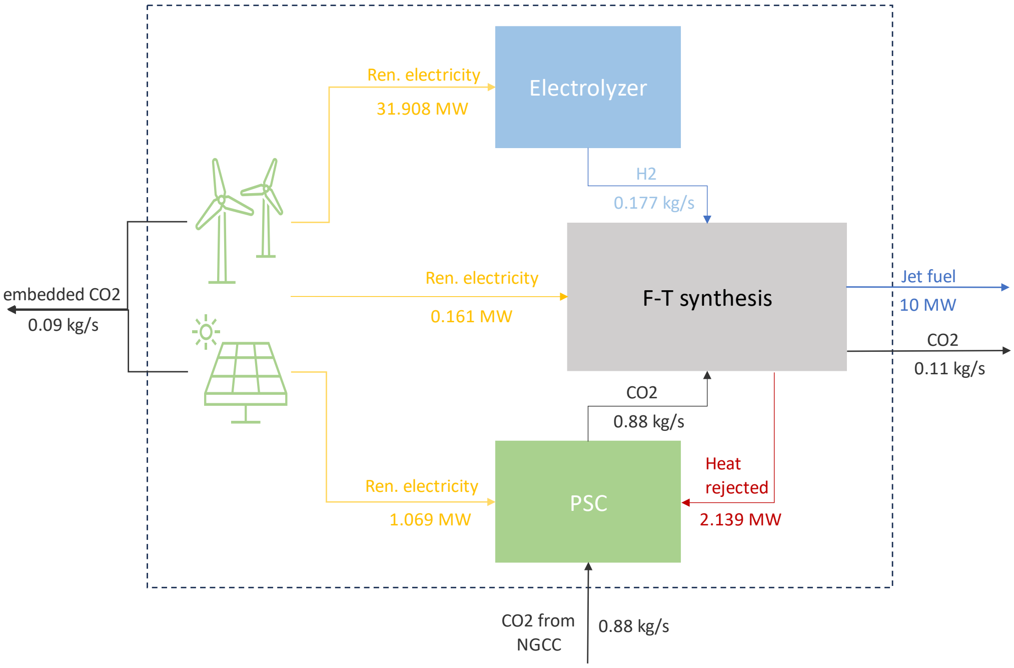


Figure 66 System 4 BFD.

i. LCI and main assumptions

After modeling of all systems was completed, data were compiled for both the LCA and the economic analysis. Table 9 presents all the data utilized for the mass and energy balances, along with their respective sources. These values roughly correspond to average values from various sources consulted for the LCI.

*Table 9 LCA data of each unit *FLH for PV and wind combined.*

LCA data	Source	Value	Unit
Jet fuel CF	EU RED II[74]	94	g_{CO2}/MJ
FLH (GB)*	renewables.ninja[75]	4138	h
FLH (FR)*	renewables.ninja[75]	5288	h
DAC energy consumption	Ordóñez et al.[40]	6.8424	MJ/kg
PSC energy consumption	Concawe[51]	3.645455	MJ/kg
PV embedded emissions	Tu et al.[76]	659.32	kg_{CO2}/kW_P
wind embedded emissions	Smoucha et al.[77]	341.6667	kg_{CO2}/kW_P
Electrolyzer efficiency	Concawe[51]	67%	-
F-T H2/CO	Okeke et al.[47]	2	-
F-T heat rejected	Concawe[51]	0.2139	$MJ/Mj_{fuel\ output}$
CO conversion efficiency	Borugadda et al.[45]	87%	-
Miscanthus yield	USDA[85]	25	$t_{harvested}$/ha/y
Carbon sequestration	BILANDŽIJA et al.[86]	39.2	t_{CO2}/ha/y
Syngas yield	Okeke et al.[47]	0.094673	kg_{syn}/kgharvested

To close the balances, several assumptions were introduced. Firstly, for the power plant, it is assumed to be installed in situ with all the other units, thereby neglecting transmission losses. The energy produced is used either directly as electricity or as heat produced with an electric heater with 100% efficiency. Additionally, no efficiency decay was considered initially, and a simplified analysis on it has been conducted in the sensitivity analysis. The energy balance itself considers energy flows of all units, and heat integration is assumed to be always possible, without a detailed analysis on the heat quality, and with no thermal losses. Regarding heat rejection, complete combustion is assumed for the F-T flue gases, so the emitted CO_2 is calculated from a stoichiometric balance. For the system production, a temporally lumped approach was adopted. To maintain continuous operation of the synthesis plant, a storage/buffer is required. This could be achieved through electricity storage, such as batteries, or through H_2 storage.

For the economic analysis, the NPV method was chosen, given that the lifetime for all units was fixed at 25 years. This decision was influenced by the findings of Cui et al.[66] , who indicated in their study that the EAC is a more suitable approach when analyzing projects with varying lifetimes, while NPV is more appropriate for projects with a fixed period. The relevant data utilized in the economic analysis are detailed in Table 10.

Table 10 Economic data reported for the reference capacity.

Economic data	Source	Value	Unit	Ref. Capacity
DAC Direct cost	Liu et al.[33]	373.1	$M\$_{2016}$	1.5 Mt_{CO2}/y
PV CAPEX	Concawe[51]	637	$€_{2019}/ kW_p$	-
PV OPEX	Concawe[51]	18	$€/ kW_p /y$	-
wind CAPEX	Concawe[51]	3219	$€_{2019}/ kW_p$	-
wind OPEX	Concawe[51]	80	$€/ kW_p /y$	-
Electrolyzer CAPEX	Concawe[51]	1027	$€/ kW_{el}$	-
F-T direct cost	Liu et al.[33]	3.1	$M\$_{2016}$	0.46 Mt/y
F-T OPEX	Liu et al.[33]	3% CAPEX	$/y	-
Digester avg. CAPEX	EPA[78]	229.67	$€/m^3$	-
Reformer CAPEX	Ketebah et al.[79]	34.3	$M\$_{2016}$	1246 $MW_{LHV, biogas}$
PSC CAPEX	Concawe[51]	338	M€	346 t_{CO2}/h
Biomass cost	Witzel et al.[80]	80	€/t	-
2023 CEPCI	Web	803	-	-
2019 CEPCI	Web	607.5	-	-
2016 CEPCI	Web	541.7	-	-

For simplicity, a set of assumptions was made. The discount rate and inflation rate were standardized at 8% and 4%, respectively. It is important to note that the CAPEX and OPEX for units not detailed in the table above were excluded from this analysis.

b. Methodology

The analyses were carried out utilizing an Excel spreadsheet, where calculations for mass and energy balances were performed, followed by the assessment of NPV.

i. LCA

For the mass and energy balances, a linear program was implemented, wherein the renewable installation served as the sole variable of the model. The objective of the solver was set to the jet fuel output.

Figure 67 provides a summary of the algorithm employed to derive the CF for e-fuel systems (2 & 4). The initial step involves evaluating H_2 production, starting from the renewable installation, as depicted in Eq.(41), where cf represents the capacity factor. The subsequent stage determines the amount of CO_2 required to achieve a syngas with a H_2/CO ratio equal to two. Once the quantity of CO_2 is known, the energy consumption can be computed. Finally, utilizing the energy and mass balance of the F-T unit, fuel production is determined, alongside energy consumption, CO_2 emissions, and heat rejected. For system 3, the first two steps are replaced by the AD phase, in which the minimum required volume is calculated as shown in Eq.(40). This calculation considers the VS percentage to be 87.2%, with an OLR set at 3. The subsequent steps in the algorithm remain consistent. In contrast, for system 1, only the CC step is necessary, with the objective of achieving carbon neutrality.

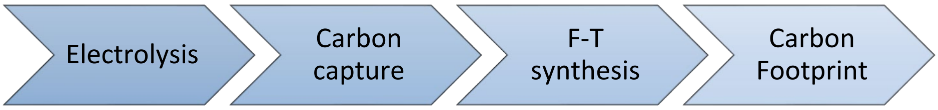


Figure 67 Block diagram of the LCA algorithm.

The CF is determined using Eq.(42), while the specific renewable electricity consumption (SREC) is calculated according to Eq.(43), where cf represents the capacity factor.

$$\dot{m}_{H_2} = \frac{\dot{P}_{inst.} * cf * \eta_{electrolyzer}}{LHV_{H_2}} \quad (41)$$

$$CF = \frac{\dot{m}_{CO_2}}{\dot{m}_{SAF}} \quad (42)$$

$$SREC = \frac{\dot{P}_{inst.} * cf}{MW_{SAF}} \quad (43)$$

ii. Economic analysis

The economic analysis aimed to determine the MJSP for the four systems utilizing the NPV methodology. The inputs for NPV include CAPEX and OPEX, which were sourced from various references detailed in Table 10. The values were adjusted to the actual capacity and converted to the same currency (€$_{2023}$) as depicted in Eq.(44), where C represents the capacity of the specific unit/equipment.

$$CAPEX_{adjusted} = CAPEX_{ref.} * \frac{C_{actual}}{C_{ref.}} * \frac{CEPCI_{2023}}{CEPCI_{ref.}} \quad (44)$$

The NPV is then computed by calculating the cumulative discounted cash flow (CDCF) at the end of life (25th year), considering the following assumptions:

- **Upfront payment and overnight construction.** This assumption simplifies the calculations by neglecting the impact of installments and interest rates, as well as O&M costs before the facility is completed.
- **Direct costs only.** Indirect costs were only considered for the electrolyzer. While indirect costs can be as high as 30% of direct costs or even more, this is not universally applicable to all units. For instance, the power plant has relatively low indirect costs compared to the F-T unit. Additionally, indirect costs are trickier to evaluate as they are more volatile than direct costs.

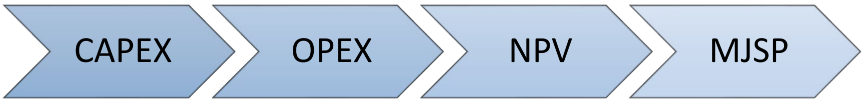


Figure 68 Block diagram of the LCC algorithm.

Eq.(45) presents the formula for the CDCF, where i is the inflation rate, and d is the discount rate.

$$CDCF = \sum_{0}^{25}(CAPEX_n + OPEX_n) * \left(\frac{1+i}{1+d}\right)^n \qquad (45)$$

Certainly, for the previously listed assumptions, the CAPEX corresponds to the initial capital investment. In other words, the CAPEX term is equal to zero for all years except the year 0. Ultimately, the MJSP is determined by imposing the break-even condition, as outlined in Eq.(46).

$$MJSP = \frac{NPV}{MW_{SAF} * 3600 * 8760 * 25} \qquad (46)$$

c. Results

In this section, the results of the LCSA will be presented, with a separate focus on the outcomes of the LCA and the economic analysis.

i. LCA results

Results from the LCA provided insights into the CF and specific renewable electricity consumption for all systems. Figure 69 illustrates the carbon footprint for different SAFs, highlighting all production stages. System DAC-JF is not displayed as its CF is, by definition, zero. All three cases share a source of negative emissions- CC for system DAC-eJF and system PSC-eJF, and biomass growth for system BioJF. They also share emissions from F-T flue gases, as the synthesis step and input are assumed to be the same (equal syngas composition). E-fuel systems (2 & 4) exhibit higher power plant emissions due to increased energy demand. System BioJF demonstrates overall negative emissions, attributed to high soil carbon sequestration despite a substantial release of biogenic CO_2 from the digester to the atmosphere. This concentrated CO_2 stream can potentially be utilized for CCS, making the system a BECCS system. Similarly, capturing F-T flue gases could lead to additional negative emissions from a Cradle to Grave perspective. The value of CO_2 sequestrated comprises the soil organic carbon (SOC), carbon biogenically stored under different forms. The variety of biogenic storage as well as the decomposition rate of these, have not been considered in the study. Contrary to geological storage, biological storage is not a stable long-term form of sequestration. Depending on soil conditions, such as ph, and on the type of the soil organic matter (SOM), the turnover time (the time required for the SOM to decompose and oxidize carbon into CO_2) can plummet to just 10 years[88]. To avoid misleading results the time horizon for soil carbon sequestration analysis should excess the cultivation lifetime. On this account several studies do not consider below ground biomass or soil carbon sequestration, but rather opt for the carbon neutrality of biogenic emissions. The emissions during the combustion of the fuel are reckoned to be balanced by the carbon sequestration in the course of biomass growth. An example of this method can be noticed in the JEC report for farmed wood pathways (see Supplementary information of reference [28]). Accordingly, if this assumption is employed, the calculations return a net positive CF of 7.78 g_{CO2}/MJ, much more in accordance with results found in the literature.

The power plant emissions are primarily embedded emissions and are nearly negligible. However, the presented results do not account for fossil emissions related to biomass transportation and fuel distribution. Only fossil emissions associated with the cultivation step (pesticides, fertilizers, tractors, etc.) are considered. Another important outcome is the estimated covered arable land, which equals 3930 ha or a specific arable land covered of 393 ha/MW_{SAF}. This large occupation of agricultural land emphasizes the need for a more comprehensive assessment, incorporating DLUC and ILUC considerations for more accurate results.

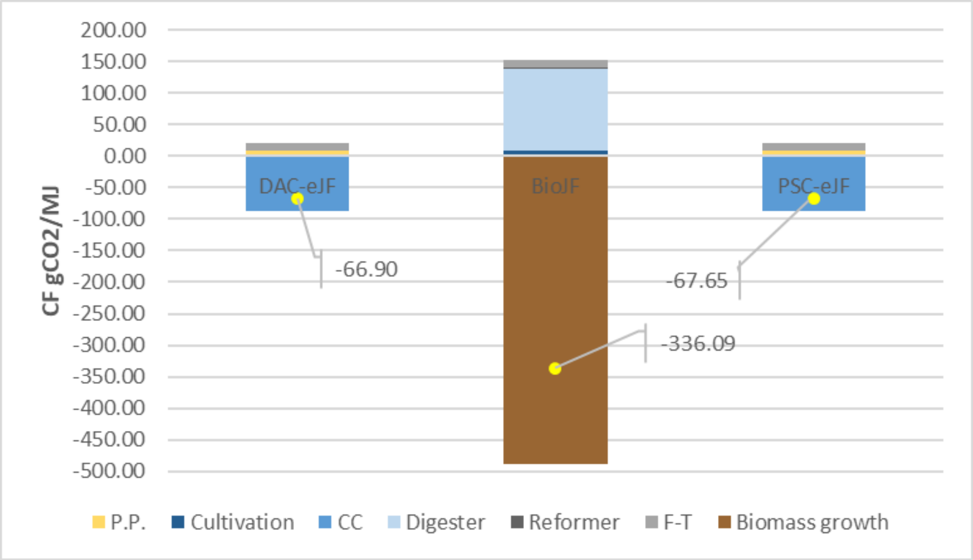


Figure 69 CF for the three SAF systems from the Cradle to Gate analysis.

Figure 70 presents the CF values, taking into account the combustion step as well. The combustion step is evaluated using a fixed value 73.32 g_{CO2}/MJ instead of stoichiometric balance. This introduces a slight mismatch between the stoichiometric balance and the actual balance, considering a negligible error due to its small magnitude and the fact that the combustion step pertains to $CO_{2,\ eq.}$ rather than CO_2. These results offer a more comprehensive view of the environmental impact, revealing the net positive CF for all systems except DAC-JF. System DAC-JF achieves net-zero emissions but is not deemed a long-term solution due to the high FD. For system DAC-eJF, net positive emissions are associated with embedded emissions since F-T-related emissions arise from carbon previously captured. It is crucial to acknowledge that these results originate from a simplified LCA, involving multiple assumptions to streamline the calculations. The CO_2 accounting procedure may fall short in representing the real impact of biofuel production, particularly in neglecting emissions related to machinery operation and transportation. Specifically, vented methane and fossil fuel combustion for trucks and tractors can subvert the results. In Figure 70 is reported system BioJFb for comparison The value of CF reported for this system was obtained considering no soil carbon sequestration, and an environmental impact for miscanthus cultivation equal to 111.8 $kg_{CO2eq.}/t_{dry\_biomass}$ [87]. Indeed, the study on which system BioJF was modeled identifies fossil fuel combustion for machinery operation as a major emission source. Additionally, emissions associated with land use are overlooked. Overall, the four systems emerge as better alternatives to fossil jet fuel from a GWP perspective even when transportation and distribution emissions are included. An average value of 5 gCO_2/MJ for fuel distribution would inflate the carbon footprint of e-fuels by 78% (reaching c.a. 11 gCO_2/MJ) and the one of system BioJFb by 14% (reaching 40.26 gCO_2/MJ).

System 4 was excluded from Figure 70 due to its distinct concept. In system 4, flue gases are considered inevitable emissions, and the system's primary goal is not carbon circularity but rather emissions' time shifting. The CO_2 embedded in the fuel originates from fossil sources and does not come from the atmosphere. Since the CO_2 captured through PSC is released into the atmosphere during e-fuel combustion, it is temporarily stored in the e-fuel and released slightly later than the generation step. Globally, the amount of CO_2 released into the atmosphere remains the same, whether or not fuel production is involved. Thus, no negative emissions are achieved. The validity of system 4 is temporary and serves as a transition measure. The environmental benefit of time shifting can be appreciated in the short and medium term, as CO_2 emitted now contributes more to GW than CO_2 emitted later in time. In the long term, this benefit tends to diminish, but it may serve an additional time-saving strategy during the transition period, especially for hard-to-abate sectors like the cement industry and steel manufacturing. Cement production unavoidably generates CO_2 during the calcination reaction in the kiln, while the inevitable CO_2 associated with steel production comes from introducing coke into the blast furnace. Research efforts are focused on finding alternatives to fossil carbon sources in these processes. For the steel industry, an interesting alternative involves substituting coke (derived from coal) with carbon coke from CCU. A 2021 study reported promising results for a breakthrough technology. Zuraiqi et al. discovered a Gallium-based liquid alloy which enables continuous CO_2 conversion at relatively low temperatures.[83]

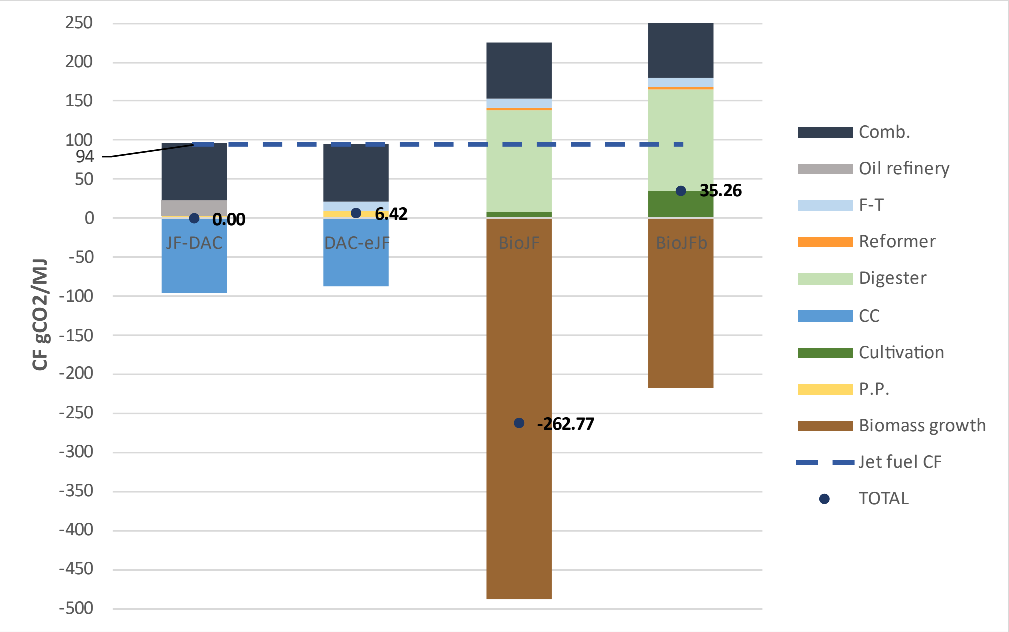


Figure 70 Weight of each step on the overall CF including combustion.

ii. Results of the economic analysis

The economic analysis, conducted through the NPV method, yielded results for the MJSP and the Cost of CO_2 Avoided (CCA). In Figure 71, the economic analysis results are presented alongside the SREC. System 1 stands out as a significantly cheaper solution compared to the others, with a production cost approximately 75% lower. In Comparison to fossil jet fuel production costs (ranging from 0.86 to 2.29 c€/MJ[68]), the System 1 production cost is about 1.43 c€/MJ higher, representing a 166% to 62% increase, respectively. E-fuels, on the other hand, are approximately 4 to 5 times more expensive than fossil jet fuel. Bio-jet fuel is considerably less expensive due to the lower SREC, leading to lower power plant CAPEX. The low SREC is a result of the high heat integration considered among all units (F-T reactor, digester, SR, pretreatment unit). The CCA ranges from 560 to 630 €/t_{CO_2} for e-SAF systems and around 140 €/t_{CO_2} in the case of System 1. The CCA indicates the carbon tax required to achieve break-even for the SAFs in comparison to fossil jet fuel. To make e-SAFs competitive, a carbon tax between 480-550 €/t_{CO_2} for higher end of fossil jet fuel production costs or between 640-710 €/t_{CO_2} for lower fossil jet fuel production costs is necessary. In contrast, for biofuel, a carbon tax of around 35 €/t_{CO_2} is required for the higher end of fossil jet fuel production costs.

Considering current carbon tax values in the EU, ranging from 0.75 €/ t_{CO_2} in Ukraine to 120 €/t_{CO_2} in Switzerland[81] , it becomes evident that e-fuels cannot break-even relying solely on carbon taxation. This underscores the importance of utilizing carbon tax as a complementary tool rather than a standalone strategy in policymaking.

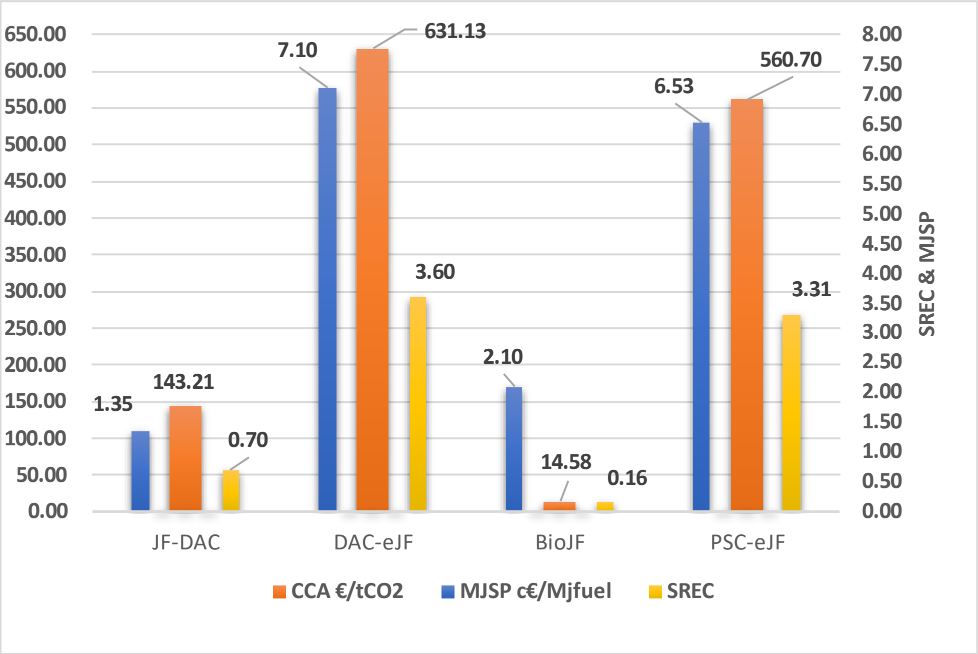


*Figure 71 Economic analysis results for all four systems. *For the CCA, the arithmetic average between the upper and lower limit of the fossil production cost range (1.58 c€/MJ) is assumed*

The SREC is a key indicator of process efficiency and takes into account heat integration. In this study, most of the electricity demand arises from the electrolyzer, followed by the DAC. While the study assumed in situ production to maximize integration among units, process integration remains crucial. In the sensitivity analysis, the possibility of co-electrolysis was explored, and ongoing research on high-performance green-H_2 production technologies, such as photoelectrochemical water splitting, is noteworthy. The heat rejected from the F-T reactor accounted for 36% of the DAC energy demand and 67% of the PSC energy demand. When DAC and the synthesis facility are installed in different locations, the rejected heat can be utilized in nearby industrial facilities requiring heat or steam, or to generate electricity. For DAC, the heat demand can potentially be met by geothermal energy, offering an alternative to renewable installations and electric heaters. Geothermal energy could be a viable option if the DAC facility is located in regions with low wind and PV FLH. The cost of geothermal energy in north America is approximately 2.5 c$/kWh$_{th}$ [70] , about one-third compared to the cost of electricity calculated in this study (7.3 c€/kWh$_{el}$). Exploring such alternatives can contribute to improving the overall sustainability and cost-effectiveness of the process.

The breakdown of the MJSP provides valuable insights into the cost structure of different systems. Figure 72 depicts the share of each factor on the production cost for all systems. E-fuels are highly CAPEX-intensive, with capital costs accounting for nearly 80% of the MJSP. The majority (90%) of the CAPEX is associated with the renewable installation in the power plant. The remaining CAPEX is mainly attributed to the electrolyzer, with minimal contributions from the CC and F-T units. The OPEX is relatively small, with the renewable installation being the primary contributor (with a 99% plus share). Similar to e-fuels, System 1 is CAPEX-intensive. Notably, the breakdown analysis for System 1 was conducted by considering the additional costs compared to fossil fuel without DAC. On the other hand, OPEX plays a significant role in System 3. Specifically, about 93% of the OPEX is attributed to the cost of biomass. This highlights the critical influence of biomass-related expenses on the overall fuel cost. Furthermore, the reliance on biomass introduces a strong dependency on the facility's location, influenced by factors such as biomass availability and transportation costs. The CAPEX structure in System 3 comprises two primary contributors: the renewable installation and the digester.

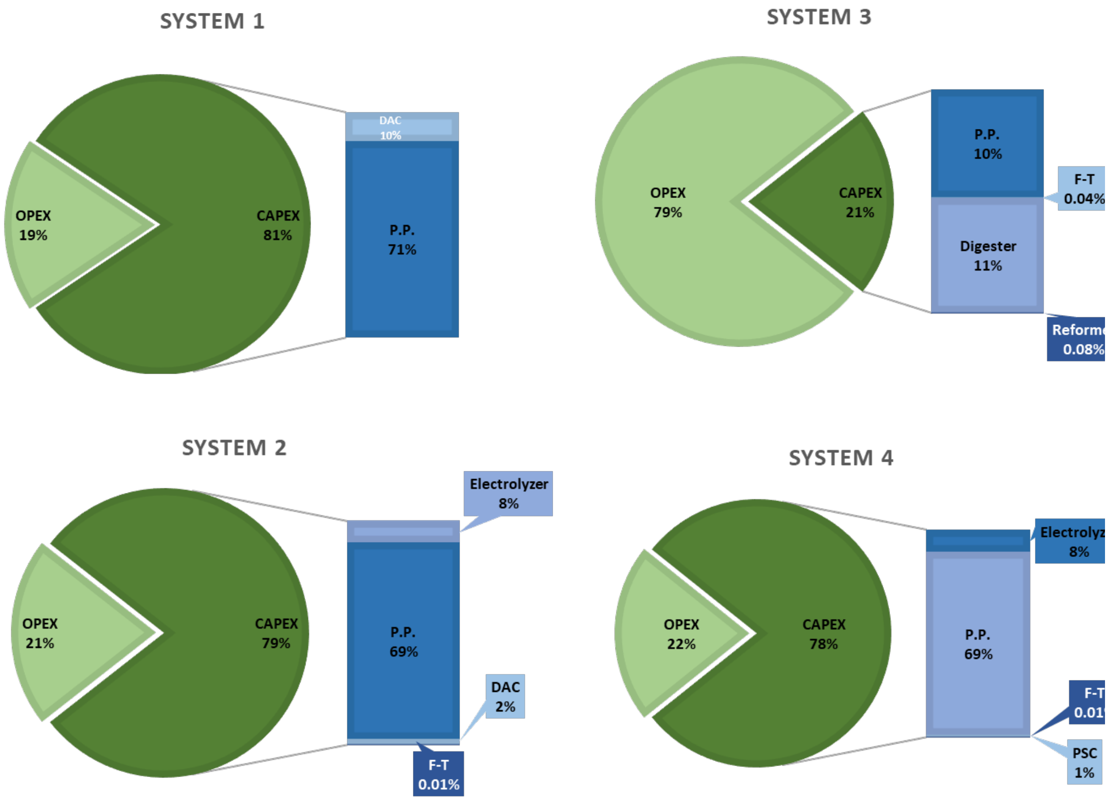


*Figure 72 MJSP breakdown. *For system 1, the additional cost due to the carbon capture has been analyzed instead of all production cost. Fossil fuel production cost is neglected.*

iii. Sensitivity analysis

Upon consolidating the outcomes of the LCA and economic analyses, a sensitivity analysis was undertaken to discern the impact of various factors on the results. The primary objective was to unveil the dependency of different factors and illustrate the performance of the system within the projected 2050 scenario, encompassing anticipated cost fluctuations and technological advancements. In Figure 73, a comprehensive depiction of the factors incorporated in the sensitivity analysis is presented, along with their respective percentage variations. Notably, for System1, the variation in MJSP remains consistent when accounting for location and renewable energy costs. This variation amounts to 10% of the total production cost, underscoring the system’s resilience to changes in these specific factors.

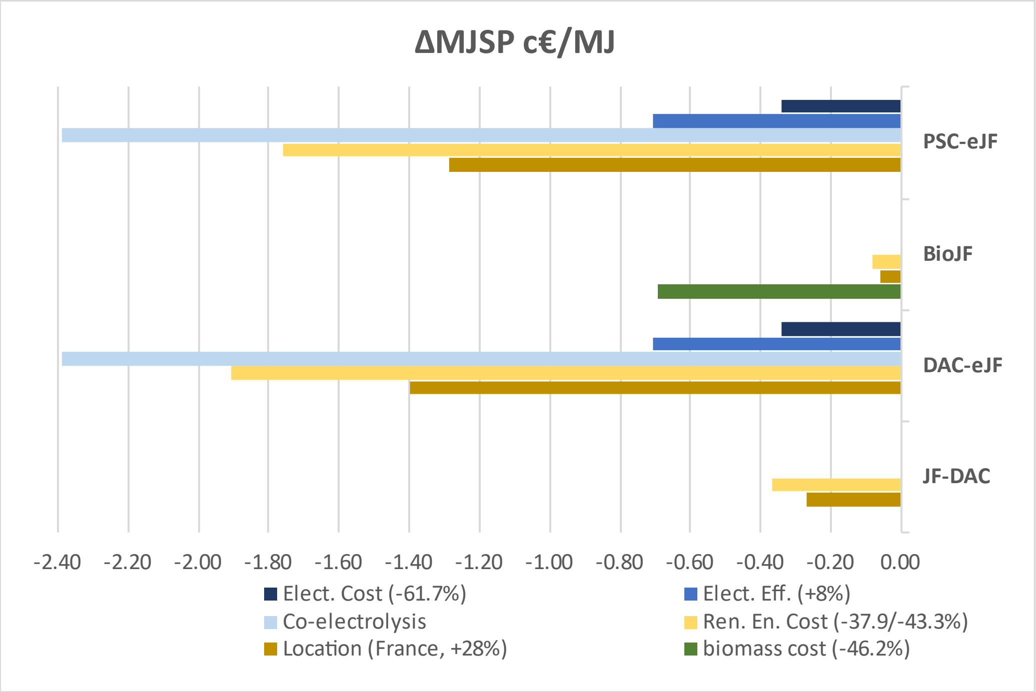


Figure 73 Results of the sensitivity analysis on the MJSP.

Figure 74 illustrates the outcomes of the sensitivity analysis on the CF, excluding System 1 due to the inherent carbon neutrality condition. The results reaffirm that location and co-electrolysis remain pivotal factors, yielding the most substantial gains attributed to lower SREC. This, in turn, contributes to diminish embedded emissions, highlighting the significance of these factors in influencing the overall environmental impact of the systems.

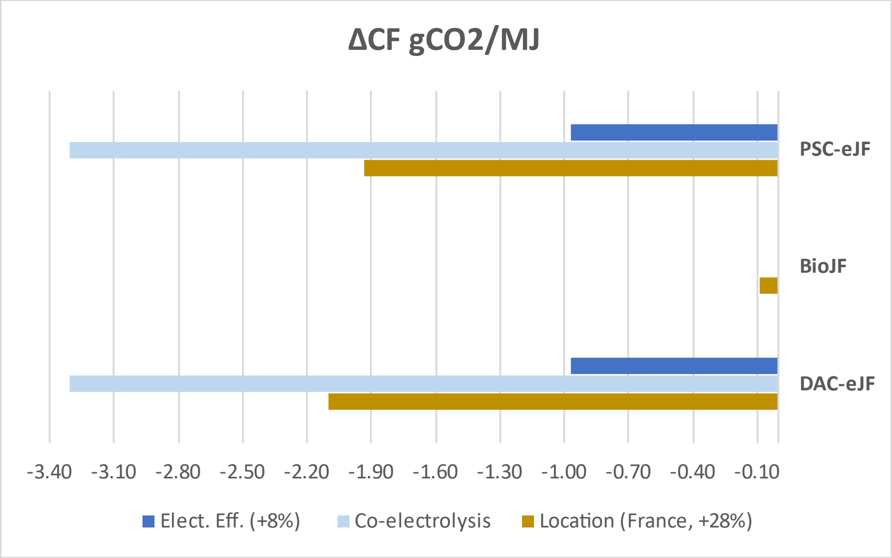


Figure 74 Results of the sensitivity analysis on the carbon footprint.

E-fuels

The sensitivity analysis on the electrolyzer unit focused on efficiency improvements, capital cost reduction, and a change in technology. A reduction of more than half in the electrolyzer's CAPEX results in a decrease of less than 0.4 cents in the MJSP. This modest impact can be attributed to the fact that the electrolyzer's CAPEX accounts for just 8%, and even with a significant reduction, the overall cost remains relatively unchanged due to the constancy of the renewable installation cost. On the other hand, an 8% increase in the efficiency of alkaline technology reduces the MJSP by 0.7 cents, indicating a more substantial impact. The most significant gain, however, is achieved by transitioning to SOEC technology, resulting in over 30% reduction in the MSJP. This notable improvement is attributed to the higher efficiency of SOEC, reaching an approximately 83% on LHV basis, coupled with heat integration and thermoneutral voltage operating condition. The substantial advantages can be related to the reduced energy demand, resulting in a subsequent decrease in the required capacity of the renewable installation.

In the power plant analysis, the sensitivity analysis focused on location and CAPEX. The alteration in location entails a significant 28% increase in FLH, predominantly due to the elevated FLH of offshore wind in French Guyana. Both factors exhibit a comparable impact on the MJSP, resulting in an approximate reduction of 1.6 cents. In the case of System 2, the sensitivity analysis also considered the efficiency decay of energy sources. Estimated at a 1.5%/y decay for wind[73] [72] and 0.5%/y for PV[71], the efficiency decay leads to a 31% increase in renewable installation, elevating the MJSP to 9.09 c€/MJ as shown in Figure 75.

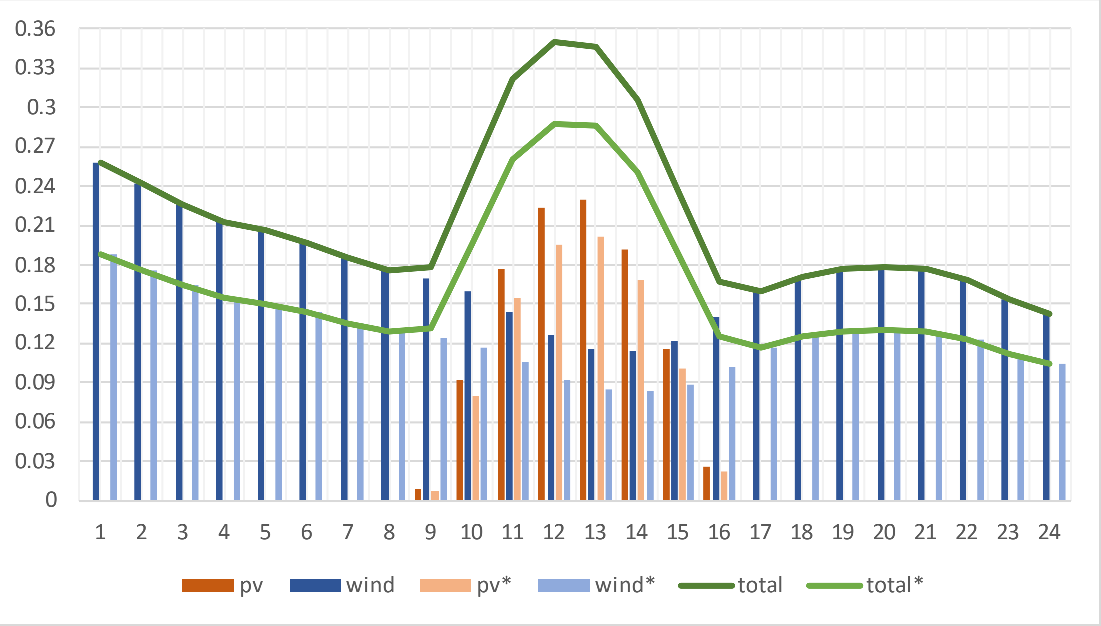


*Figure 75 Capacity factor for PV and wind in GB. *efficiency decay effect.*

For the CF analysis as well, the most influential parameters are co-electrolysis and location, primarily attributed to the reduction in renewable installation and, consequently, embedded emissions. Achieving net-zero emissions requires the comprehensive decarbonization of the entire renewables supply chain.

Biofuels

For of system 3, the most significant cost reduction is realized through a 46% decrease in feedstock cost, resulting in an approximate deduction of 0.69 cents from the MJSP. It is important to note that biomass costs are not anticipated to decrease in the 2050 scenario, unlike technologies and units that benefit of technological advancements. The biomass cost is contingent on feedstock selection and facility location, and lower biomass costs are expected for Waste-to-X technologies. The prices used in this study pertain to miscanthus cultivation, and exploring alternative feedstocks such as forest residue or agricultural residue could yield significantly different results.

For system 3, the carbon footprint is predominantly influenced by location. Additional enhancements can be achieved by substituting fossil fuels burned by tractors and other machinery with sustainable diesel and implementing CCS to transform it into a BECCS system.

6. Policies and investments

In the preceding chapters, various technologies and their performance have been discussed. LCSA studies serve as the foundation for decision-making for policymakers, and a common challenge identified in the results of the studies presented in this work is the production cost, significantly higher than corresponding fossil products. Achieving competitiveness for alternative chemicals can be pursued through various strategies:

- **Taxes**: taxes represent economic penalties designed to elevate the cost of fossil-based production or, more broadly, to discourage technologies that need replacement. While this approach may not always be highly effective, a significant challenge lies in the fact that such policies often increase the economic burden on consumers. This is because producers tend to raise the prices to compensate for the taxes imposed.
- **Subsidies**: Subsidies represent one of the most effective and efficient market-driven strategies. Unlike attempts to discredit impactful technologies, subsidies provide a boost to alternative technologies by reducing their market price. The primary advantage of these policies lies in the fact that the price reduction is borne by the government or institutions rather than producers. The effectiveness of subsidies stems from the expanded market they create, attracting increased investor interest and facilitating greater financial support for research and scale-up efforts. Ultimately, this cycle contributes to lower production costs.
- **Ban and normative restrictions**: These strategies are in contrast to the principle of the free market, as they involve government intervention to actively restrict the production and use of a particular product. Example of bans were discussed in the "Demand-side measures" section.

One example illustrating the difference in effectiveness between taxes and subsidies is presented in the study by Michaga et al.[50] . In their sensitivity analysis, the impact of a carbon tax and certificates on the MJSP was explored. Figure 76 demonstrates that as the carbon tax increases, the price of fuel also rises, whereas the addition of certificates leads to a reduction in fuel price. It is important to note that the results in Figure 76 hold more qualitative value than quantitative, owing to the inherent volatility in the certificate prices. This volatility is a characteristic feature of the free market, where these certificates are exchanged without price control.

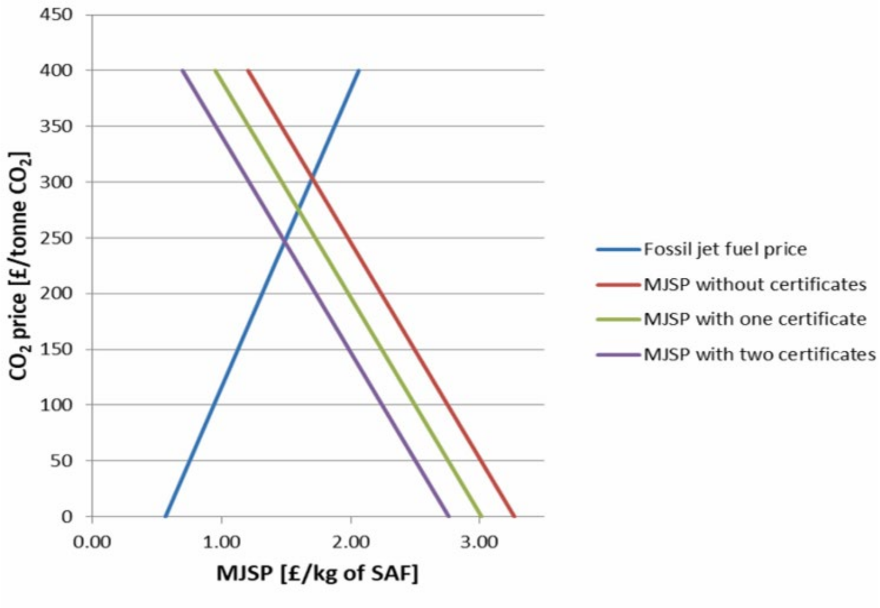


Figure 76 Sensitivity analysis of MJSP

a. Announced policies

On July 14th, 2021, the European Commission introduced the 'Fit for 55' package, which included the ReFuelEU Aviation initiative[56] . This package encompasses a series of initiatives aimed at achieving a 55% reduction in emissions from 1990 levels by 2030. The ReFuel initiative stands out as the first regulatory effort to facilitate the integration of SAFs (advanced biofuels and e-kerosene) by stipulating an escalating share of their utilization by jet-fuel suppliers. Presently, the minimum targets for SAFs are established at 2% and 5% for 2025 and 2030, respectively, increasing to 63% in 2050, with a sub-target of 0.7% for e-kerosene in 2030, escalating to 28% in 2050. The EU Commission has expressed its intention to decrease the share goal of biofuels in favor of e-kerosene.

The EU is not the sole proponent of SAFs; the U.S. government has been actively involved through the creation of the Renewable Fuel Standard (RFS) in 2005. This regulation is designed to incentivize SAFs by assigning 1.6 Renewable Identification Numbers (RINs) per gallon produced. The incentive structure relies on credits obtained during SAF production, which can subsequently be traded with non-compliant entitles of the Renewable Volume Obligation (RVO), akin to white certificates. Figure 77 provides an illustration of the transactions and key stakeholders involved. Additionally, in 2021, U.S. Congress introduced the

Sustainable Skies Act, which establishes a credit range of 1.5-2 \$/gal(US) for SAFs demonstrating a GHG savings of at least 50% compared to fossil jet fuel.

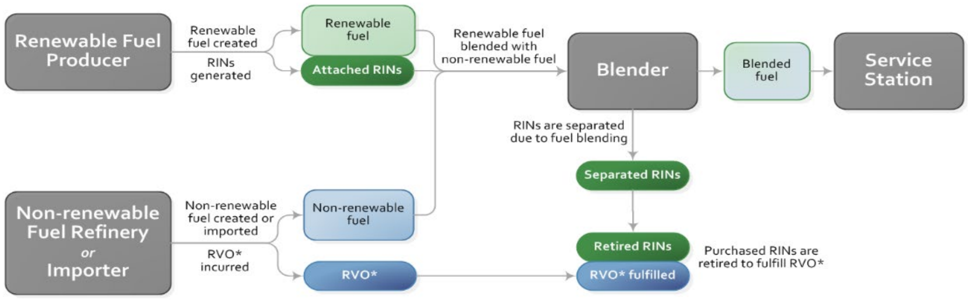


Figure 77 LC example of RINs.

b. Required investments

The estimation of required investments is crucial for policymakers and for assessing the economic feasibility of a given scenario. It is important to note that these results are inherently tied to the projections being considered. In this section, we present estimates from various sources.

i. IEA CTS scenario

In the "The Future of petrochemicals" report [6] , an alternative scenario called the Clean Technology Scenario (CTS) was developed. Similar to the RTS, the CTS was modeled with the additional constraint of achieving a 45% reduction in emissions by 2050. The total investment needed is approximately 1.5 trillion USD, with the majority allocated to core equipment (as shown in Figure 78). Within this transition, cumulative capital investment for ammonia constitutes 22% of the total, while for methanol and HVCs, the shares are roughly 10% and 68%, respectively.

In this scenario, 86% of the investment is allocated to core equipment (reactors, reformers, etc.), while the remaining 14% is distributed among carbon capture equipment, bioenergy, and electrolysis. The model incorporates two main constraints: cost efficiency and a 45% reduction in emissions, aligning the implemented technology with the most economic options. These primarily involve CCS and conventional, mature technologies. The challenge associated with resource depletion persists in the BAU scenario, and the penetration of renewables remains very limited. This outcome is likely to result from market forces if stringent policies are not enforced. Notably, a significant factor in this scenario is the savings achieved by transitioning from coal to natural gas as a feedstock in ammonia production (amounting to close to 100B$).

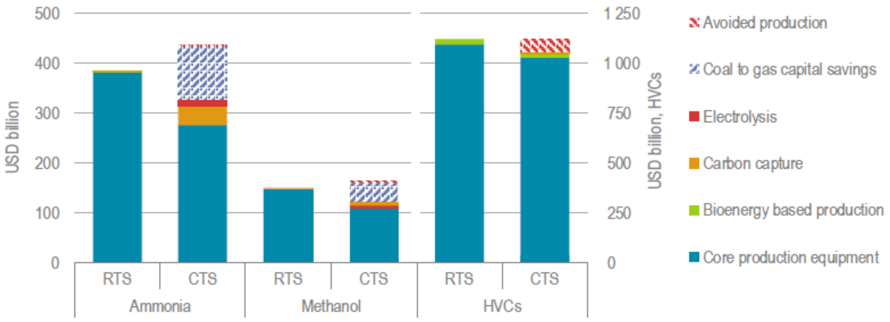
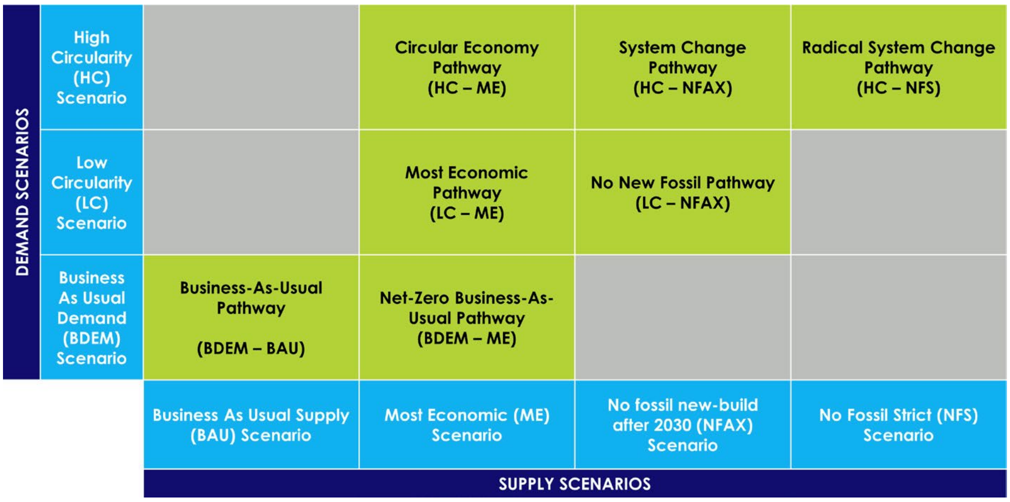


Figure 78 Investments required for the RTS and CTS scenarios.[6]

ii. Planet-compatible pathways

In the study by Meng. Et al., titled "*Planet-compatible pathways for transitioning the chemical industry*" [5] , various scenarios were examined, taking into account different constraints for demand and supply. Consequently, the investment needed for the transition shows significant variation. Figure 79 provides a summary of the seven scenarios analyzed, categorized based on the anticipated demand and the supply-side paradigm.



	Business As Usual Supply (BAU) Scenario	Most Economic (ME) Scenario	No fossil new-build after 2030 (NFAX) Scenario	No Fossil Strict (NFS) Scenario
High Circularity (HC) Scenario		Circular Economy Pathway (HC – ME)	System Change Pathway (HC – NFAX)	Radical System Change Pathway (HC – NFS)
Low Circularity (LC) Scenario		Most Economic Pathway (LC – ME)	No New Fossil Pathway (LC – NFAX)	
Business As Usual Demand (BDEM) Scenario	Business-As-Usual Pathway (BDEM – BAU)	Net-Zero Business-As-Usual Pathway (BDEM – ME)		

Figure 79 Scenarios obtained by combination of demand and supply scenarios.

The transition of the chemical sector necessitates investments in the order of 3 trillion USD. Figure 80 illustrates the economic benefits of DSM by examining the

High Circularity (HC) scenarios. in the Most Economic (ME) scenario, HC results in savings amounting to 1 trillion USD, representing a 27% reduction in the required capital investment. HC profoundly influences waste management and methanol demand. Lower waste production occurs as some "waste" re-enters the supply chain as a feedstock through recycling, while the use of methanol as the starting point for producing olefins and plastics impacts demand. Between 2.5 and 3.7 trillion USD are needed to achieve the transition of the chemical sector. However, focusing on the 2050 horizon, only HC-NFAX and HC-NFS scenarios attain a net-zero carbon footprint. Although the investments associated with these scenarios are relatively not much higher than ME scenarios, they still require robust policies and commitment to ensure that the price is not the sole market driver. Additionally, the non-renewability of the feedstock in BAU scenarios, while more than twofold cheaper than others, makes them unsustainable in the long term.

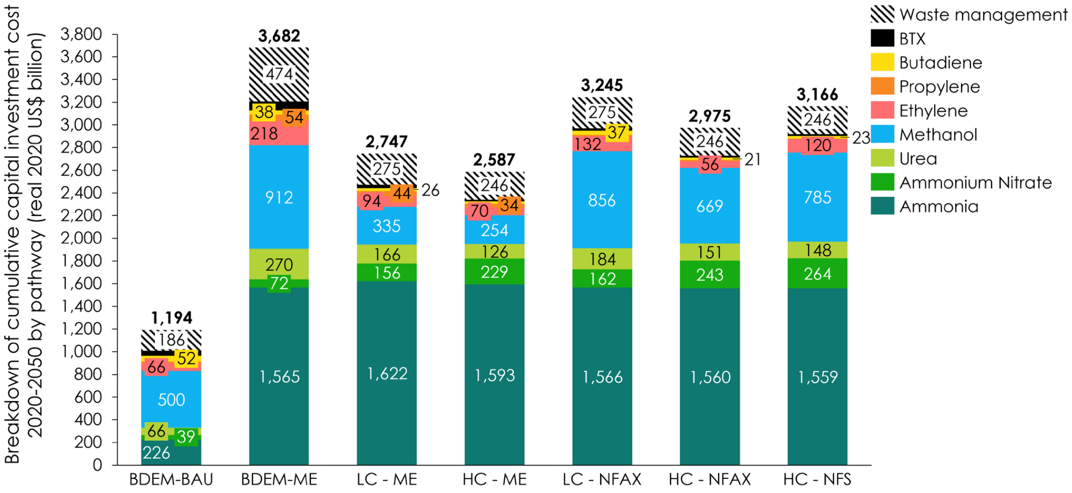


Figure 80 Components of investment required for each scenario.[5]

iii. IRENA

Under the 1.5 °C scenario, the overall cumulative investment is estimated to be around 150 trillion USD. Of this total, 43% is allocated for the power sector's transition, 23% for the building sector, 11% for the transportation sector, and the remaining portion primarily for the industry. These investments are crucial for expanding and enhancing the infrastructure of the power sector, including power grid (22 T$), H_2 infrastructure (3.7 T$), electric charging infrastructure (8.7 T$), and increasing capacity and deployment of transition technologies such as renewables, carbon capture, EVs, and more.

If the cumulative capital investment were evenly distributed throughout the transition period (2023-2050), the resulting annual average investment would be around 5.6 T$, more than four times higher than the current investment of 1.31 T$. Of the total investment in the previous years, approximately 75% originated from private sources, endorsing mostly mature technologies in developed economies due to their lower actual or perceived risks.

c. Key points of successful policies

While there is no universally optimal policy, it varies from region to region. Despite this, some common principles should form the foundation all policies:

- **RD&D:** Research is undoubtedly one of the most powerful tools against global problems and challenges. Investments in RD&D enable the improvement of existing solutions and the discovery of new, more promising routes.
- **Incentives and subsidies:** the market is typically profit-driven, and often, fossil fuels prove to be the most profitable routes. To change this trajectory and encourage a transition toward more sustainable scenarios, governments should provide incentives and subsidies to alternative technologies.
- **Taxes and ban:** Another approach to promote sustainable routes is to raise the cost of conventional routes through carbon taxes and implement bans at the consumer level.
- **Waste management and circularity:** If handled properly, "waste" could become a feedstock or a valuable resource. Moreover, the economic, social, and environmental benefits of increasing circularity are outstanding.
- **Consumer awareness:** In recent times, there has been a growing interest among people in environmental issues, significantly influencing the market and pushing producers toward more environmentally friendly production. Advertising a just transition is particularly challenging now due to fake news and greenwashing. Therefore, official governmental or international institutions should engage in education and information campaigns.
- **No one-size-fits-all solution:** Policies should target scenarios that embrace a mix of solutions rather than concentrating on one specific option. The latter might be more appealing, as it is easier to sell to the public and less resource-intensive.
- **The three spheres:** The three spheres-economic, social, and environmental-should be considered in LCSA, and similarly, policies should address all

three. Private investments, which often prioritize economic returns, should be influenced by the right policies. One approach to extend this consideration to the private market, where profit is the primary motivator, is to associate a tax with negative externalities, such as carbon tax. This way, negative social or environmental impacts are translated into negative economic impacts.

i. Public investment

An important aspect of these policies is the promotion of investment in transition technologies, and this should be in favor of public investment as well. In the last 10 years, funding resources have largely come from private investors. Both private and public investments have their pros and cons. Private investments rely on less stringent regulations, making the process quicker and more flexible. Moreover, these resources generally have specific focuses and prerogatives, which may align better with the applicant's goals. On the other hand, private investments are characterized by lower awards and aim to maximize economic return. This implies a higher tendency towards low-risk investment. Private investors are much more likely to finance projects with lower risks, corresponding to situations found in stable and developed economies with mature technologies (technology s-curve).

To promote a more equitable development scenario, substantial funds are required, especially in developing countries, surpassing the needs of developed ones. In this context, public funding can be a viable solution, taking the form of grants, subsidies, or both debt and equity. As highlighted in the IRENA report, intermediaries such as Development Finance Institutions (DFIs), banks, and NGOs play a crucial role in the redistribution of funds.

d. Challenges

From both the literature review and the calculations conducted, it is evident that market competitiveness is one of the most significant challenges, as discussed above. In this section, the focus will shift towards the other barriers that stand in the way of technology and large-scale deployment.

i. Renewable installation required.

All net-zero scenarios outlined in the "2050 Scenarios" necessitate a significant number of renewable installations, both for direct electrification and e-fuel production. According to the IRENA 1.5°C scenario, renewable installations should increase by 1,081% or by 30,403 GW. Assuming a constant yearly installation, this would result in an average of 1013 GW/y compared to the current installation rate of 295 GW/y2022. Closing this substantial gap is not anticipated in the near future, raising concerns about resource allocation. The decision of whether to prioritize e-fuels production or direct electrification is inherently market-driven and region-specific. Direct electrification is expected to spread more rapidly due to lower capital intensity, whereas the peak spread of e-fuels is anticipated after direct electrification saturates, particularly in hard-to-abate sectors with slow direct electrification diffusion. Additionally, opportunities for e-fuels are likely to grow in countries with high primary source availability, such as North EU and North Africa.

Before delving into discussions about the use of renewable installation, the primary concern lies in the installation itself, particularly in terms of land occupation. Assuming an average land coverage of 0.03 km^2/MW for PV and 0.27 km^2/MW for wind farms (with a 50/50 split between PV and wind), this would result in approximately 4,510,000 km^2 of additional land, without accounting for the fuel production facilities. To put this into perspective, the global habitable land not used for agriculture is about 37,000,000 km^2, meaning the land occupation due to the transition would account for 12.2% of the total usable land.

ii. Production capacity

Another crucial question is whether we possess the non-economic resources necessary to rapidly implement the transition scenarios. Beyond economic considerations, the production capacity of specific materials or technologies comes into focus. While the global production capacity of PV panels aligns with projections, this is not the case for other technologies. Batteries and electrolyzers, for instance, fall short by 16% and 39%, respectively, according to IEA NZE [64] . It is important to note that the production of all transition technologies relies on raw materials, adding complexity to the feasibility of the transition. In the IEA study "*The Role of Critical Minerals in Clean Energy Transitions*[84] ", the extraction of critical minerals like lithium, cobalt, and nickel needs to increase more than twenty-fold. Recycling holds promise as it could potentially reduce demand by 10%.

iii. Social acceptance

The transition to net-zero is a significant shift in technology's paradigm and is often viewed as a radical transformation of society. To mitigate public opposition, it is evident that education and transparent communication are crucial. Before addressing these concerns, understanding the roots of this resistance becomes essential. While various reasons contribute to this resistance, some are more prevalent than others and fall within the scope of this study.

NIMBY syndrome

The "Not In My BackYard" (NIMBY) syndrome is the main barrier faced by renewables in terms of social acceptance and can be applied to many transition technologies. Several factors contribute to this phenomenon, with one of the most common being the concern about the impact of these technologies on the landscape and on the local environment, including issues such as air quality and waste management.

Safety concerns

Several transition strategies will alter the everyday routines of consumers who must adapt when engaging with these novel technologies, such as Fuel Cell Electric Vehicles). (FCEV This implies a lack of knowledge on how to properly operate these technologies and an understanding of their actual risks initially. In particular, new risks tend to be overstated and considered "riskier" than those presented by conventional technology. Mature technologies are perceived as less risky due to cumulative experience, sometimes without ever encountering dangerous situations. For example, fossil fuels like gasoline pose significant dangers due to inhalation or fire outbreaks, but these risks are not considered by user nowadays since they rarely manifest. Instead, risks associated with H_2 as an alternative fuel capture people's attention because it introduces new concerns into their everyday lives.

Certainly, it is essential not to overlook the numerous safety issues associated with these chemicals. Hydrogen safety concerns stem from the risk of explosions, the ineffectiveness of safety equipment such as flame detectors in boilers, and its high diffusivity. Ammonia poses the highest risks to human health due to its high toxicity, even at low concentrations, through both inhalation and direct contact.

Drop-in technologies which serve as perfect substitutes, tend not to raise any concerns, since they are almost equal to conventional ones. Indeed, synthetic diesel is precisely equivalent to fossil diesel from a consumer point of view. Therefore, these types of technologies have the advantage of encountering low public resistance.

Environmental impact

The literature review has emphasized the significance of endpoint indicators in conducting LCSA to ensure a comprehensive and fair comparison among various technologies. Environmental impacts, particularly those related to the production of key components like batteries, electrolyzers, and renewable energy infrastructure, need careful consideration. For instance, the surge in production capacity for these technologies involves an increase in the extraction rate of raw materials such as lithium, copper, and noble metals (45% for lithium[64]). This heightened extraction rate can lead to significant environmental and social challenges associated with the energy-intensive processes required for extraction and refining. It underscores the importance of evaluating the entire life cycle, from raw material extraction to end-of-life disposal, to make informed decisions about the sustainability of alternative technologies. In doing so, a balanced and holistic approach is necessary to avoid unintended consequences and ensure that the adoption of new technologies contributes positively to sustainability goals.

Another concern is the shift in the environmental burden between GWP sources. Utilizing ammonia as a fuel allows for the avoidance of CO_2 emissions but increases nitrogen oxides emissions and PM emissions from the reaction of NO_x with ammonia. More generally, these burden shifts can occur across different spheres-social, environmental, and economic.

7. Conclusions

Achieving carbon neutrality in the petrochemical sector is a challenging yet attainable goal, with a variety of alternatives available. E-fuels, in particular, have garnered significant interest from policymakers due to their flexibility and potential for large-scale deployment. A successful transition should involve a diverse mix of solutions rather than relying on one-size-fits-all approaches. This approach becomes even more critical given the high variability in results discussed in the preceding sections, influenced by factors such as location, timeframe, and scope. Promoting a mix of solutions is not only more efficient, especially when applying the right technology to the right application, but also proves economically advantageous. This assertion is supported by projected scenarios that incorporate varying shares of each technology, such as sub targets of e-fuels in the transportation sector, and align with a market-oriented perspective. The diversity of solutions helps mitigate investment risks, attracting more investors, which, in turn, leads to increased R&D to enhance TRL and CRL of different technologies. This approach facilitates rapid development, allowing institutions to identify the most promising solutions and providing room for course corrections, such as shifting from one technology to another. Such agility is crucial, considering the dynamic nature of the industry. Rapid changes are more manageable when a range of solutions is pursued, as opposed to a scenario where a single technology is deemed the exclusive solution. Realizing this objective is imperative given that market dynamics are primarily driven by price, and the most cost-effective solution could dominate the market, potentially overlooking important social and environmental implications.

Integrating social and environmental impacts into policymaking and business decision-making is crucial for ensuring sustainable outcomes. This integration can be achieved through education, awareness-building, and economic incentives or penalties. By doing so, it becomes possible to steer the market away from defaulting to the most cost-efficient solution, often synonymous with BAU, and prevent the widespread adoption of non-sustainable alternatives. Effective management of biofuels penetration is essential to promote concepts like WtX and BECCS. This strategic approach helps avoid significant challenges related to biodiversity, potential competition with food crops, and other environmental concerns. The study’s calculations underscore the importance of a comprehensive LCSA with well-defined system boundaries. Implementing technologies with process integration is both more logical, in terms of efficiency, and cost-effective. However, emphasizing the need for localized and context-specific evaluations rather than one-size-fits-all global perspective.

a. The role of e-fuels

E-fuels, grounded in the principles of carbon neutrality and circularity, represent innovative technologies. The integration of e-fuels into today’s electric grid has been dismissed due to significantly lower conversion efficiency compared to electrification, coupled with a lack of environmental benefits. In fact, the CF of e-fuels derived from grid electricity could potentially exceed that of fossil fuels. This discrepancy arises from the additional step involved in converting primary energy sources (like fossil fuels) into electricity and subsequently into e-fuels, rather than directly transforming fossil fuels into refined products. Therefore, it becomes crucial to identify applications where e-fuels offer unique advantages over alternative solutions. This involves formulating a strategic mix that optimizes the cost-benefit tradeoff for each specific use case. This approach ensures the greatest benefits and align with overall sustainability goals.

The transportation sector emerges as the primary domain for the application of these technologies, accounting for an estimated 29% share of the total sector energy demand according to the “IEA World Energy Outlook Net Zero by 2050”. However, a comprehensive analysis in the JEC WTW report reveals that e-fuels in internal combustion engine vehicles prove to be more energy-intensive compared to BEVs, with energy expenses ranging from 5 to 7.5 times higher. This disparity is attributed to the lower conversion efficiency of the power train in e-fuel ICE vehicles and the substantial energy demand for fuel synthesis. The heightened energy intensity emerges as a significant concern, leading to larger renewable installations and increased land occupation. In terms of emissions, both technologies approach zero, as embedded emissions are not considered in the report, with slightly higher emissions from e-fuels due to transportation and distribution of the fuel itself. Hydrogen, as a fuel carrier, presents additional challenges related to handling and transportation, contributing to higher costs and emissions associated with compression and distribution. A potential mitigation strategy involves supplying energy-intensive processes (e.g., compression) with renewables instead of the assumed grid mix in the report. The heavy-duty transportation sector represents a scenario where cost comparison between electrification and e-fuel approaches equilibrium. To determine the superior alternative, a more detailed LCSA becomes essential, utilizing a marginal approach to discern potential drawbacks arising from scale-up as discussed in previous sections.

Promising prospects for adoption of e-fuels are identified in sectors that are challenging to electrify but offer a straightforward integration of these fuels. Aviation, maritime transportation, and chemical industry (as a chemical feedstock) are highlighted in this work, with a more-in-depth focus on SAFs. However, with current production costs at approximately 2.6 €/l (10 $/USgal), short term deployment is feasible only with robust policy support. Taxes alone are insufficient to meet the breakeven condition due to the high CCA, but when combined with targeted policies, such as mandates and grants, they become essential tools. The sensitivity analysis suggests that, with ongoing technology development-especially in electrolyzers- e-fuels could achieve a projected MJSP of around 4 c€/MJ. Further cost reductions are conceivable, especially considering potential decreases in renewable energy costs. The development of e-fuels raises various dilemmas concerning their environmental and social impacts during the scale-up of the supply chain. Using e-fuels as ESS and for ancillary grid services has the potential to enhance renewable penetration, increasing FLH and load coverage. Additionally, the substitution of fossil fuels with e-fuels contributes to greater energy independence, addressing uncertainties arising from shifts in geopolitical paradigms.

References

[1] Peter G. Levi and Jonathan M. Cullen, *Mapping Global Flows of Chemicals: From Fossil Fuel Feedstocks to Chemical Products*, 2018

[2] IEA *Chemicals*

[3] IBISworld, *Global Oil & Gas Exploration & Production Industry - Market Research Report*

[4] Our World in Data, *Global primary energy consumption by fossil fuel source*

[5] Menga, Wagnerb, Kremerb, Kanazawa et al., *Planet-compatible pathways for transitioning the chemical industry.*, 2023

[6] IEA, *The Future of Petrochemicals 2018*

[7] Our World in Data, *Global greenhouse gas emissions by sector*

[8] Bauer et al., *Mapping GHG emissions and prospects for renewable energy in the chemical industry document*., 2023

[9] Gabrielli et al., *Net-zero emissions chemical industry in a world of limited resources*, One Earth (2023)

[10] Acumen, *Automotive Plastics Market Size - Global Industry, Share, Analysis, Trends and Forecast 2022 – 2030*

[11] Roland Geyer, Jenna R. Jambeck and Kara Lavender Law, *Production, use, and fate of all plastics ever made*, 2017

[12] Cefic, *EU chemical industry profile*

[13] Irena, *INNOVATION OUTLOOK RENEWABLE AMMONIA*, 2022.

[14] Bicer et al., *Impact Assessment and Environmental Evaluation of Various Ammonia Production Processes*, 2017

[15] Pattabathula and Richardson, *Introduction to Ammonia production*, 2016

[16] Our World in Data, *World Population Growth*

[17] IFA, *Fertilizer Consumption - Historical Trends*

[18] Del Pozo, Cloete, Álvaro, *Techno-economic assessment of long-term methanol production from natural gas and renewables* , 2022

[19] Ren, Patel, Blok, *Olefins from conventional and heavy feedstocks: Energy use in steam cracking and alternative processes*, 2006

[20] Teng Li, Tuiana Shoinkhorova, Jorge Gascon, and Javier Ruiz-Martínez, *ACS Catalysis 2021 11 (13), 7780-7819*

[21] Peng Tian, Yingxu Wei, Mao Ye, and Zhongmin Liu, *ACS Catal. 2015, 5, 1922–1938*

[22] EU *restrictions on certain single-use plastics*

[23] EU *Waste and recycling*

[24] Our World in Data, *Can we reduce fertilizer use without sacrificing food production?*

[25] Our World in Data, *Food waste is responsible for 6% of global greenhouse gas emissions*

[26] IRENA AND METHANOL INSTITUTE (2021), *Innovation Outlook : Renewable Methanol*, IRENA, Abu Dhabi.

[27] IEA, *Transportation sector energy consumption*

[28] Prussi, M., Yugo, M., De Prada, L., Padella, M., Edwards, R., Lonza, L. *JEC Well-to-Tank report v5*, EUR 30269 EN, Publications Office of the European Union, Luxembourg, 2020.

[29] Aenert, *Fischer-Tropsch plants map in the world*

[30] NETL, *Fischer-Tropsch Synthesis*

[31] Darmawan et al., *Efficient black liquor conversion to power and H2 based on process integration and exergy recovery*, CUE2018-Applied Energy Symposium and Forum 2018: Low carbon cities and urban energy systems, 5-7 June 2018, Shanghai, China

[32] Peters, R.; Wegener, N.; Samsun, R.C.; Schorn, F.; Riese, J.; Grünewald, M.; Stolten, D. *A Techno-Economic Assessment of Fischer–Tropsch Fuels Based on Syngas from Co-Electrolysis*, 2022

[33] Liu, Sandhu, McCoy, Bergerson, *A life cycle assessment of greenhouse gas emissions from direct air capture and Fischer–Tropsch fuel production* Sustainable Energy Fuels, 2020, 4, 3129.

[34] Al-Aboosi El-Halwagi, Moore and Nielsen, *Renewable ammonia as an alternative fuel for the shipping industry*, 2021

[35] Burre, Bongartz, Brèe, Roh1, and Mitsos, *Power-to-X: Between Electricity Storage,e-Production, and Demand*

Side Management, 2019
[36] Tsiklios, Schneider, Hermesmann, and Müller, *Efficiency and optimal load capacity of E-Fuel-Based energy storage systems*, 2023
[37] Wentrup, Pesch, and Thoming, *Dynamic operation of Fischer-Tropsch reactors for power-to-liquid concepts: A review*, 2022
[38] Assen, Voll, Petersb and Bardow, *Life cycle assessment of CO2 capture and utilization: a tutorial review*, 2014
[39] Hnich, Martín-Gamboa, Khila, Hajjaji, Dufour, and Iribarren, *Life cycle sustainability assessment of synthetic fuels from date palm waste*, 2021
[40] Ordóñez, Halfdanarson, Ganzer, Shah, Mac Dowell and Guillén-Gosálbez, *Evaluation of the potential use of e-fuels in the European aviation sector: a comprehensive economic and environmental assessment including externalities*, 2022
[41] Ballal, Cavalett, Cherubini, Barbosa Watanabe, *Climate change impacts of e-fuels for aviation in Europe under present-day conditions and future policy scenarios*, 2023
[42] Liu, Sandhu, McCoy, Bergerson, *A life cycle assessment of greenhouse gas emissions from direct air capture and Fischer–Tropsch fuel production supplementary information* Sustainable Energy Fuels, 2020, 4, 3129
[43] Ordóñez, Halfdanarson, Ganzer, Shah, Mac Dowell and Guillén-Gosálbez, *Evaluation of the potential use of e-fuels in the European aviation sector: a comprehensive economic and environmental assessment including externalities supplementary informations*, 2022
[44] Bioethanol plant *block diagram*
[45] Borugadda, Kamath and Dalai, *Techno-economic and life-cycle assessment of integrated Fischer-Tropsch process in ethanol industry for bio-diesel and bio-gasoline production*, 2020
[46] Badoga, Vosoughi and Dali, *Performance of Promoted Iron/CNT Catalyst for Fischer–Tropsch Synthesis: Influence of Pellet Shapes and Binder Loading*, 2017
[47] Okeke, Sahoo, Kaliyan, Mani, *Life cycle assessment of renewable diesel production via anaerobic digestion and Fischer-Tropsch synthesis from miscanthus grown in strip-mined soils.* , 2020
[48] Li, Zhao, Xu, Y. Zhao, Yang, Tao, and Xiao, *Comprehensive Life Cycle Evaluation of Jet Fuel from Biomass Gasification and Fischer–Tropsch Synthesis Based on Environmental and Economic Performances*, 2019
[49] World grain, *China's corn production to inch up in 2023-24*
[50] Michaga, Michailos, Akram, Cardozo, Hughes, Ingham, Pourkashanian, *Bioenergy with carbon capture and storage (BECCS) potential in jet fuel production from forestry residues: A combined Techno-Economic and Life Cycle Assessment approach*, 2022
[51] Concawe, Aramco, *E-Fuels: A techno-economic assessment of European domestic production and imports towards 2050*, 2022
[52] *Review Methanol-to-hydrocarbons: process technology* by Frerich J. Keil
[53] Eia, *Oil and petroleum products explained*.
[54] Our world in data, *Learning curves: What does it mean for a technology to follow Wright's Law?*
[55] Fasihi et al., *Techno-economic assessment of CO2direct air capture plants.* , 2019
[56] EU parliament, *ReFuelEU Aviation initiative: Sustainable aviation fuels and the fit for 55 package*
[57] EPA, *Renewable Identification Numbers (RINs) under the Renewable Fuel Standard Program*
[58] IATA, *Fact Sheet: EU and US policy approaches to advance SAF production*
[59] IEA, *World Energy Outlook 2022*
[60] ICAO, *Environmental Trends in Aviation to 2050*
[61] IEA, *Transport sector energy demand NZE 2050*
[62] IRENA, *World Energy Transitions Outlook 2023: 1.5°C Pathway*
[63] Our world in data, *Learning curves*
[64] IEA, *An updated roadmap to Net Zero Emissions by 2050*
[65] Web, distribution of land use
[66] Cui, *Analysis of the Net Present Value and Equivalent Annual Cost in Optimal Machine Life*
[67] EPA, *Life Cycle Assessment and Cost Analysis of Municipal Wastewater Treatment Expansion Options for Food Waste Anaerobic Co-Digestion*
[68] IEA, *Fossil jet and biojet fuel production cost ranges, 2010-2030*
[69] Tax foundation, *Carbon Taxes in Europe*
[70] Kuru et al., *Solid sorbent direct air capture using geothermal energy resources (S-DAC-GT) – Region specific*

analysis, 2023

[71] NREL, *Photovoltaic Degradation Rates — An Analytical Review*

[72] Staffel et Green, *How does wind farm performance decline with age?* , 2014

[73] Elgowainy et al., *Energy Efficiency and Greenhouse Gas Emission Intensity of Petroleum Products at U.S. Refineries*, 2014

[74] EU, *Revised renewable energy directive 2018/2001*

[75] Renewables.ninja

[76] Tu et al., *A novel IoT-based dynamic carbon footprint approach to reducing uncertainties in carbon footprint assessment of a solar PV supply chain*, 2017

[77] Smoucha et al., *Life cycle analysis of the embodied carbon emissions from 14 wind turbines with rated powers between 50Kw and 3.4Mw*, 2016

[78] EPA, *Life Cycle Assessment and Cost Analysis of Municipal Wastewater Treatment Expansion Options for Food Waste Anaerobic Co-Digestion*

[79] Ketebah et al., *Analysis of hydrogen production costs in Steam-Methane Reforming considering integration with electrolysis and CO2 capture*, 2022

[80] Witzel et al., *Economic evaluation of Miscanthus production – A review*, 2016

[81] Tax foundation, *Carbon Taxes in Europe*.

[82] Blumberg T., *Comparative evaluation of methanol production processes using natural gas: a thermodynamic and economic assessment.* Dissertation 2018, Technische Universität Berlin.

[83] K. Zuraiqi, A. Zavabeti, J. Clarke-Hannaford, B. Murdoch, K. Shah, Michelle J. S. Spencer, C. F. McConville, T. Daeneke, and K. Chiang, *Direct conversion of CO2 to solid carbon by Ga-based liquid metals*.

[84] IEA, *The Role of Critical Minerals in Clean Energy Transition*, 2022.

[85] USDA, *Miscanthus as a Feedstock for Bioenergy in the Southeast*, 2013

[86] D. BILANDŽIJA, N. BILANDŽIJA, and Ž. ZGORELEC, Sequestration potential of energy crop Miscanthus x giganteus cultivated in continental part of Croatia, 2021

[87] LEWANDOWSKI, KIcHEnERt, and VoNIER, *CO_2 balance for the cultivation and combustion of miscanthus*, 1994.

[88] DONDINI, HASTINGS, SAIZ, JONES, and SMITH, *The potential of Miscanthus to sequester carbon in soils: comparing field measurements in Carlow, Ireland to model predictions*, 2010

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Table of abbreviations

Abbreviation	**Definition**
AD	Anaerobic Digestion
ASU	Air Separation Unit
BAU	Business As Usual
BECCS	Bio Energy Carbon Capture and Storage
BEV	Battery Electric Vehicle
CCA	Cost of CO_2 Avoided
CCC	Cost of CO_2 Captured
CCS	Carbon Capture and Storage
CE	Carbon Engineering
CF	Carbon Footprint
cf	Capacity factor
CN	Cetane Number
CRL	Commercial Readiness Level
CtG	Cradle to Grave
CTL	Coal To Liquids
DAC	Direct Air Capture
DDGS	Distilled Dry Grains with Solubles
DLUC	Direct Land Use Change
DME	Dimethyl Ether
DSM	Demand Side Measure
ESS	Energy Storage System

EU	European Union
FD	Fossil Deplition
FLH	Full Load Hours
F-T	Fischer-Tropsch
GHG	Green House Gases
GTL	Gas To Liquids
GWP	Global Warming Potential
H-T	High-Temperature
HVC	High Value Chemicals
ICE	Internal Combustion Engine
IEA	International Energy Agency
ILUC	Indirect Land Use Change
IPCC	International Panel on Climate Change
IRENA	International RENewable Agency
JEC	Joint Research Centre, EUCAR and Concawe
LC	Life Cycle
LCA	Life Cycle Assessment
LCI	Life Cycle Inventory
LCIA	Life Cycle Impact Assessment
LCSA	Life Cycle Sustainability Assessment
LPG	Liquified Petroleum Gasses
L-T	Low-Temperature

LU	Land Use
MJSP	Minimum Jet-fuel Selling Price
MOF	Metal Organic Framework
MTA	Methanol To Aromatics
MTG	Methanol To Gasoline
MTH	Methanol To Hydrocarbon
MTO	Methanol To Olefins
NCC	Naphtha Catalytic Cracking
NG	Natural Gas
NTCF	Near Term Climate Forces
O&M	Operating & Maintenance
PEM	Proton Exchange Membrane
PM	Particulate Matter
PSA	Pressure Swing Absorption
PSC	Point Source Capture
PtX	Power-to-X
R&D	Research and Development
SAF	Sustainable Aviation Fuel
SCC	Social Cost of CO_2
SCM	Supply Chain Management
SREC	Specific Renewable Energy Consumption
TRL	Technology Readiness Level
TSA	Temperature Swing Absorption

USA	United States of America
USD	United State Dollar
WtX	Waste-to-X