

Power-to-Liquids: Shedding Light on Levers and Uncertainties in the Process Chain

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Abstract

Power-to-Liquid (PtL) fuels produced from renewable electricity, water and carbon dioxide represent a scalable and sustainable alternative to conventional kerosene. An in-depth understanding of the entire process chain is vital to identify the levers in future scale-up scenarios for PtL capacity deployment. To this end, we shed light onto technological developments for each process step with a primary focus on energy efficiency and direct air capture (DAC). Several technologies are comparatively assessed and the learnings are integrated into a sensitivity study. Our results demonstrate the crucial importance of further DAC performance enhancements for adequate PtL production efficiencies and identify key improvement potentials.

1. Introduction

Alternative fuels play a decisive role in strategies aiming at the decarbonization of civil aviation. [1] The production of a suitable kerosene alternative needs to be scalable, while also offering adequate economic and ecological performance. Furthermore, apart from very short flights, liquid fuels are needed in aviation due to the high energy density requirements. So far, renewable aviation fuels are produced from biomass. However, limited availability of sustainable organic feedstock and decreasing cost of renewable hydrogen (H₂) production suggest that aviation fuels will increasingly be produced from non-biological resources in the future. Figure 1 illustrates that several fuels offer significant emission reduction potential [2] – among them are liquid hydrogen (LH₂) and synthetic kerosenes via Power-to-Liquid (PtL) pathways. While the former holds the promise of a comparatively inexpensive and low-emission aviation fuel, it is associated with a number of technological challenges when it comes to utilization of this cryogenic liquid aboard the aircraft and the required supply and refueling infrastructure, which differs fundamentally from currently used equipment. Further taking into account design cycles typically observed in aviation - often 20 years or longer from aircraft design to market entry – hydrogen aircrafts are not expected to contribute the bulk of the emission reduction required by 2050, even if all technological challenges and uncertainties can be overcome.

On the other hand, PtL-derived synthetic kerosene is compatible with advanced aircraft technology and airport infrastructure. By using captured carbon dioxide (CO₂), PtL-derived synthetic kerosene can be produced without the need for biogenic carbon – a limited resource – and hence holds promise for production at scale from renewable energies. Demonstration and even a first pilot plant have been built and are showcasing the technological feasibility. Current production volumes, however, are orders of magnitude lower than projected future demand. [3] An in-depth understanding of the entire process chain is key to identify the levers in future scale-up scenarios for PtL capacity deployment and optimize process efficiency, which directly affects production cost. This is not only true for the conversion and upgrading steps, but also extends to the green H₂ and carbon dioxide feedstocks required. The latter will be the main focus of the work presented herein, but first, we provide a brief overview on the production pathway and required inputs.

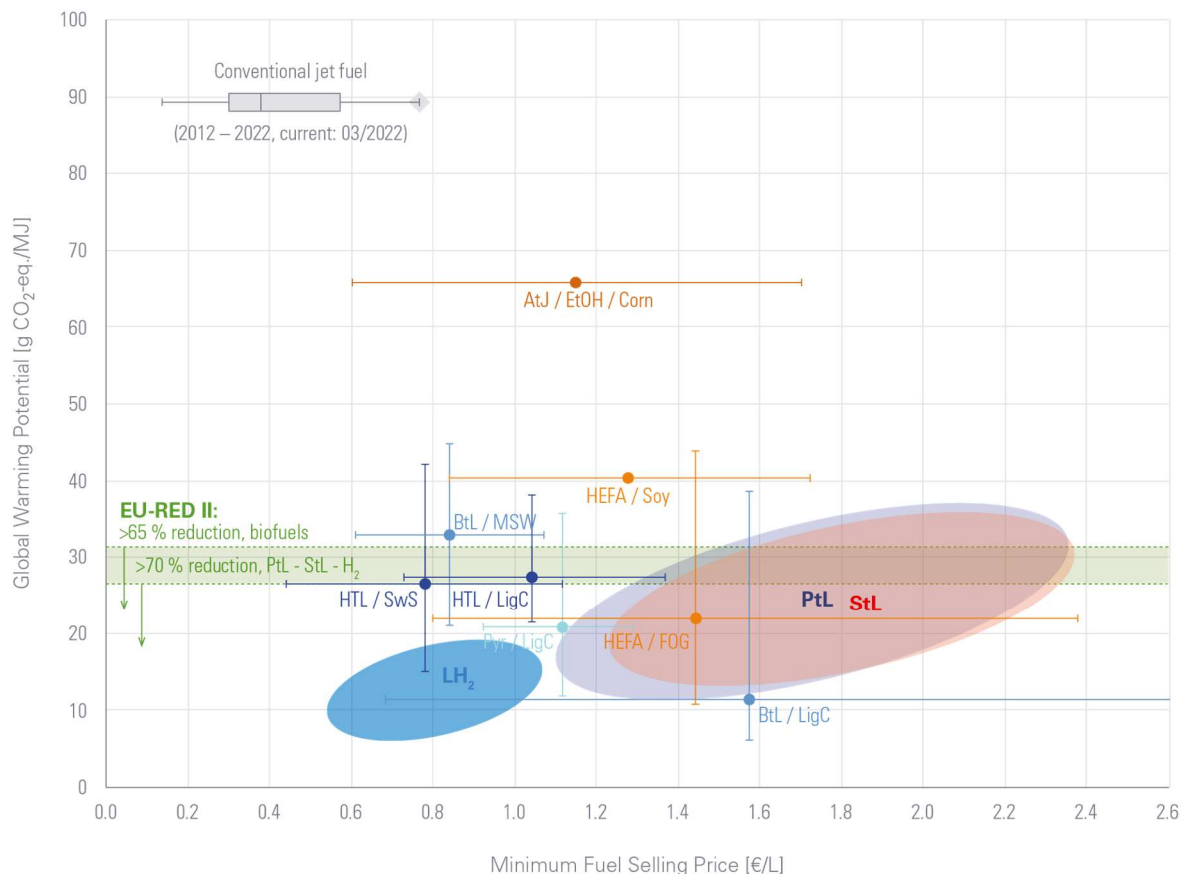


Figure 1: Global warming potential versus minimum fuel selling price for a number of fuel pathways. Reproduced with permission from [2]. Price estimates for LH₂ are given in Liter kerosene equivalent.

1.1 PtL Production Pathways

PtL fuels are produced from renewable electricity-derived H₂ and CO₂. Different processes have been proposed for fuel synthesis from these reactants, the predominant ones are the Fischer-Tropsch (FT) pathway and methanol (MeOH) based synthesis routes, which are schematically illustrated in Figure 2a and b, respectively. The FT process converts carbon monoxide (CO) and H₂ into a mixture of hydrocarbons that is further upgraded to yield suitable fuels. CO is obtained from CO₂ and H₂ undergoing the reverse water gas shift (RWGS) reaction. In the MeOH pathway, on the other hand, MeOH can be synthesized from CO₂ and H₂. Further conversion and upgrading steps then yield hydrocarbon fuel. An in-depth review of reaction conditions including process and reactor design can be found e.g. in Ref. [4]. Notably, both MeOH synthesis and the FT reaction are exothermic allowing a use of waste heat e.g. for H₂ production or carbon capture.

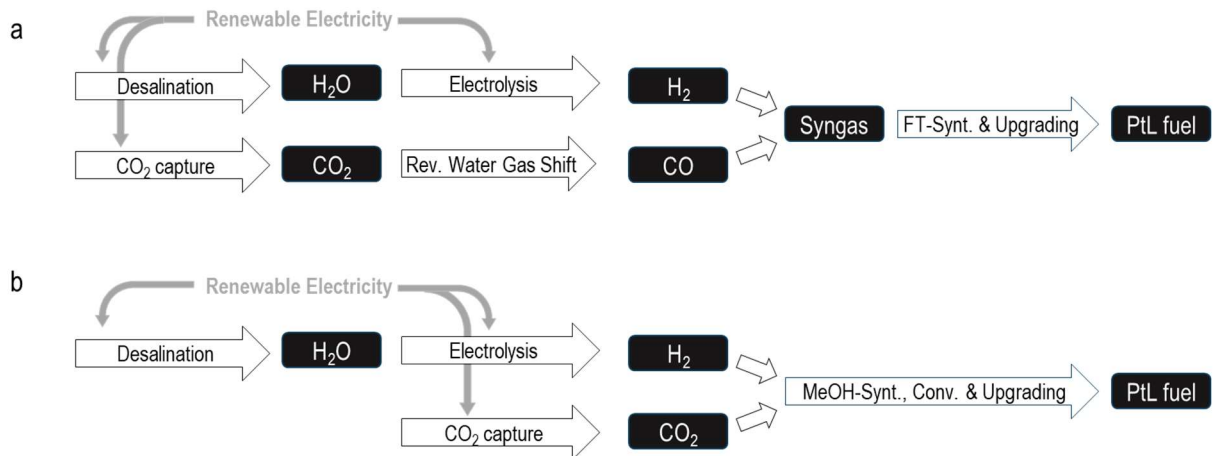


Figure 2: Schematic illustration of fuel production via (a) the FT and (b) the MeOH pathway.

1.2 Renewable Electricity

Renewable electricity with low greenhouse gas emission-intensity is key to sustainable e-fuel production from green H₂. As the energy system transition from fossil resources towards renewable energy carriers will be accompanied by an increased reliance on renewable power generation in several economic sectors, [5] the latter has been denoted a bottleneck, especially for certain geographic regions.

Against this backdrop, putting the electricity demand for PtL jet fuel in perspective and comparing it to technical renewable electricity potentials is vital. For Europe, this potential has been estimated to amount to ~22 000 TWh/a far exceeding the ~3 000 TWh/a of current electricity use, [3] cf. Figure 3. The remaining available electricity would surpass the expected renewable power requirements for meeting 2050s PtL demand by about an order of magnitude. [3] For Germany, renewable power potentials have been determined to be ~2 100 TWh/a, which is faced with ~620 TWh/a of current demand. Similarly, this results in a significant excess that could theoretically substitute the current jet fuel demand of ~11.8 Mt (in 2019 [6]) with PtL-production.

Notably, while renewable energy potentials are substantial and seemingly sufficient, actual supply will depend on scale up and economic considerations. Furthermore, it is to be expected that also other currently fossil-dependent sectors will become increasingly large consumers of renewable electricity. A detailed discussion of the magnitude of these sectors' demands is, however, beyond the scope of this manuscript.

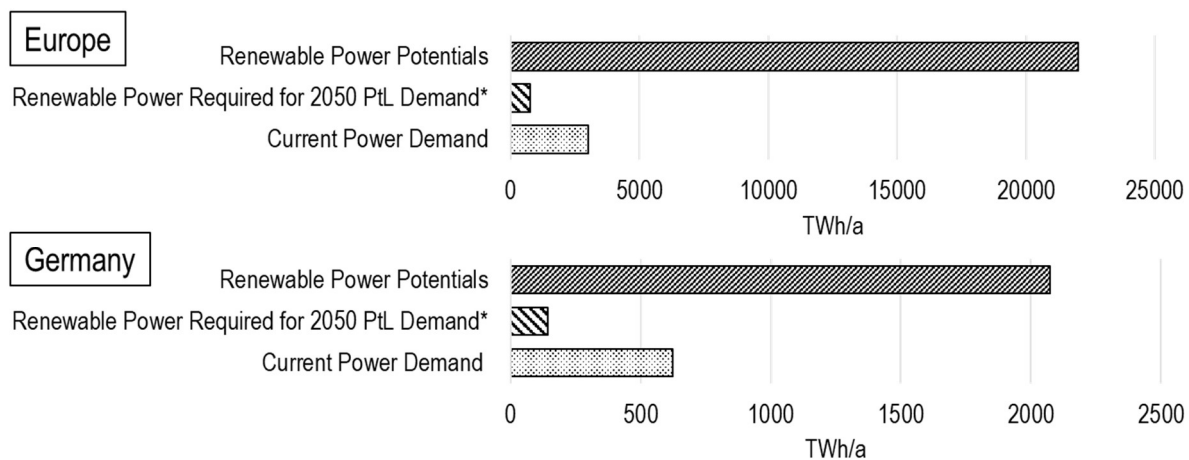


Figure 3: Europe's and Germany's renewable power potentials, renewable power required to meet the expected 2050 synthetic kerosene demand (*if all synthetic kerosene were produced via the PtL process) and current power demand. [3,7–9]

1.3 Hydrogen Source

Hydrogen (H_2) for the PtL process is provided via electrochemical conversion of renewable electricity and water to H_2 and O_2 . Compared to biomass-based fuel pathways, PtL water demand is low: ca. 4 L per L jet fuel have been estimated, which is orders of magnitudes lower than what is required to produce the same amount of biofuel. [3]

As the technological development of electrolysis is not in the focus of this article, the interested reader is referred to other focused reviews, e.g. [10–12]. Herein, only a very brief overview will be provided: Several types of water electrolyzers exist and are present in the industrial landscape: Alkaline electrolysis has been the prevailing technology for decades; further suitable alternatives are emerging. Among them, polymer electrolyte water electrolysis (PEWE) and solid oxide electrolysis (SOE) are currently the most prominent contenders. While the former represents a so-called low-temperature (LT) approach ($T \sim 60\text{--}80^\circ\text{C}$), the latter is operated by temperatures around $800\text{--}1000^\circ\text{C}$ to ensure adequate conductivity of the solid electrolyte. When it comes to electrical efficiency, SOE far outperforms LT-electrolysis with target values nearing 100% [11,13], but additional high-quality thermal energy has to be provided, which can represent a significant penalty. Limited scalability of PEWE and SOE is often considered a hurdle, which, however, is tackled with rising success in large-scale pilot plants up to 20 or 0.25 MW, respectively. [14,15]

For a competitive performance of PtL fuel produced from green H_2 , the associated production cost needs to substantially decrease. In this context, data from large-scale alkaline electrolysis plants indicate that capital expenditure significantly drops with increased system size and capacity roll-out. [16] As H_2 is considered a key energy carrier in a future energy system compatible with climate targets, H_2 production and distribution infrastructure is in the center of recent research and infrastructure initiatives. [1,17,18] Consequently, significant scale-up is expected for the next decade and, therefore, green hydrogen (H_2) production and distribution will unlikely represent a key bottleneck in PtL production.

1.4 Carbon Source

As illustrated in Figure 2, CO_2 is employed as the carbon source in the PtL process. CO_2 can be provided in several ways, whereby for the PtL pathway mainly CO_2 captured from point sources or directly from the air is considered (when CO_2 from biomass gasification is employed, the process is typically referred to as PBtL instead, [19] which is not considered herein).

Capturing CO_2 from industrial point sources benefits from relatively high CO_2 concentration, which facilitates extracting significant quantities with a comparatively low energy penalty. Nevertheless, the utilization of conventional point sources needs to be carefully assessed from an economic and environmental perspective as only renewable CO_2 sources can close the carbon cycle. With respect to the latter, biogenic point sources are preferable for aviation fuel synthesis. What is more, the availability of accessible CO_2 -rich streams as a resource is limited: Zitscher et al. [20] have estimated the amount of CO_2 emissions for Germany in 2017 to be 143 Mt. If, however, only process related emissions are considered that cannot be substituted by renewable alternatives this number shrinks to 26–66 Mt CO_2 in 2050, which is insufficient for the substitution of PtL demand in light of regional disparity of CO_2 point sources with renewable electricity potentials and potential further demand from other sector.

Direct CO_2 capture from air (DAC), on the other hand, is a potential solution for sustainable CO_2 provision at scale. It effectively closes the carbon cycle (cf. Figure 4) and enables decoupling the carbon source from fossil infrastructures and biomass. Decentralized capture units would further reduce the need for CO_2 transportation and logistics. Data availability, however, is comparatively low, as DAC is a novel technology and only a small number of operational plants with a total annual output of around 10 kt have been realized [21] – orders of magnitude lower than what would be required in a net-zero emission scenario. Consequently, DAC, while representing a corner stone in a scalable Power-to-Liquids process chain, is associated with considerable uncertainties when it comes to its potential for future widespread application. This is why, herein, we will take a closer look at DAC, including technological options, associated energy demand and integrability in the PtL process.

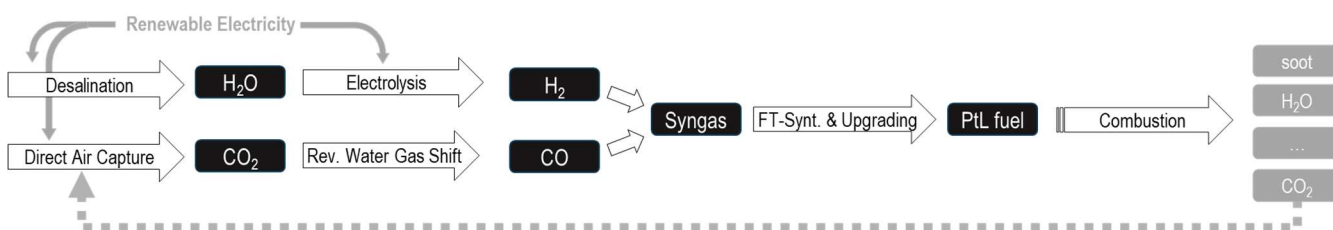


Figure 4: Schematic illustration of a closed carbon cycle enabled by DAC (at the example of the FT-pathway).

2. Direct Air Capture for Carbon Provision

Capturing CO₂ from air for the purpose of fuel production or geoengineering represents a concept that has attracted considerable attention only recently. In the last decade, growing awareness of the need for negative emission technologies (NETs) for reaching climate targets [22,23] has increased efforts towards the development and deployment of DAC for carbon capture and storage application.

Several technology options based on solid or liquid sorbents exist, employing different temperature ranges and typically demanding significant amounts of thermal and electrical energy. [24–32] CO₂ is present in the air only in low concentration (currently ca. 418 ppm [33]), which means that a minimum of roughly 1600 t of dry air have to be processed to yield 1 t of CO₂). The minimum thermodynamic separation work of separating a two-component gas mixture would amount to ~ 22 kJ/mol (or about 3-4 times higher than for flue gas). [34,35] Real sorption/separation processes are considerably more complex and require consideration of the co-presence of other species (e.g. H₂O [36]). Published total energy requirements for realized DAC units range from 240 to well above 800 kJ/mol, i.e. energy for CO₂ separation far exceeds the quoted thermodynamic minimum. Even though this minimum is not technologically realizable, the mismatch indicates a significant improvement potential. When compared to typical enthalpies of ~ 650 kJ/mol -CH₂- in kerosene range alkane molecules, the minimum thermodynamic separation work corresponds to less than 4% of the energy stored in the corresponding amount of kerosene product (neglecting carbon losses); this share increases to ≥37% for the energy requirements derived from modelling real processes. Consequently, it is important that the energy requirement for DAC is met by renewable sources and/or energy streams that are recuperated from the fuel conversion processes.

Providing enough CO₂ to be used as a renewable carbon feedstock – for aviation and beyond – and further employing DAC for carbon removal in CCS concepts, will require a drastic scale-up of production capacities for DAC systems. As the most suitable technology depends on the location, the unit scale required and available integration options with other processes, a number of technologies may coexist. In the following, we briefly introduce the main characteristics of each of the currently most prevalent technologies and provide a comparative assessment alongside the most relevant metrics in the context of PtL production.

2.1. Low-Temperature Adsorption

This technology is based on the adsorption of CO₂ on a solid sorbent. For the release of CO₂ from the sorbent, temperature, vacuum or humidity swings (or a combination thereof) are employed. The process is typically realized in small, modular capture units, which are cycled between capture and release conditions. As operating temperatures are comparatively low (typically ≤100 °C [32]), low-grade waste heat can be used to cover the thermal energy demand. Studies show that sorption kinetics are the main factor influencing productivity and cost of this capture method – consequently, they represent an important lever on increasing process efficiency. [26] Research efforts aim at inexpensive, yet kinetically favorable solid sorbents that can be produced at large scale. While various sorbent chemistries are under investigation, amine-based systems are currently prevalent.

2.2. High-Temperature Absorption

In this case, a liquid sorbent solution is employed for CO₂ capture instead of a solid sorbent. The process is run continuously in comparatively large capture units. This method is commonly used for flue gas CO₂ capture and, consequently, the sorption process is well understood for point source application. For DAC, on the other hand, the technology is in development. NaOH and KOH are the predominantly used sorbents, both of which are base chemicals and available at large scale. During the so-called alkali scrubbing, the respective carbonate is formed. To regenerate the sorbent and release the CO₂, high temperatures of ca. 900°C are required. Hence, low-grade waste heat temperatures do not suffice in this case.

For point sources, liquid sorption is also employed at intermediate temperature using aqueous amines for capture. These are regenerated by stripping with steam, which requires large amounts of low-grade heat due to the high heat capacity of the solvent. [26,37–39]

2.3. Electrochemically Mediated Capture

Adjusting the electrochemical potential represents a means of tuning the sorption properties of a sorbent, enabling rapid changes between capture and release conditions at room temperature (i.e. no thermal energy required). Furthermore, theoretically very high selectivities can be achieved. Compared to the other methods described above,

electrochemically mediated DAC is in its infancy with most approaches only conceptualized or demonstrated at laboratory scale. Many fundamental research questions, e.g. obtaining to a detailed mechanistic understanding, remain yet unanswered. However, rather fast progress is expected as learnings from other disciplines of electrochemistry can be exploited. Due to its limited technological readiness, data availability is low. Published reports indicate feasible current densities and electricity demands. [27,40–42]

2.4. Comparative Assessment

To draw a comparison between different DAC approaches in the context of PtL production, we identified several key criteria including energy requirements, productivity (i.e. defined as yield of CO₂ for a certain reactor bed volume per hour), process complexity, availability of materials and development level. Figure 5 illustrates the relative differences for the three DAC approaches discussed and sheds light onto enablers and challenges. As mentioned above, the most suitable technical solution eventually depends on a number of factors including the application case and the location of the plant. Consequently, a number of technologies may (continue to) coexist.

Notably, while the cost per ton of captured CO₂ represents a major influence on final PtL cost, the lack of (publicly available) operational data for each of the listed DAC methods, limited deployment and – especially in the case of electrochemically mediated capture – the low technological readiness level complicate the cost assessment. Most recent estimates quote capture cost in the order of 100-300 \$/tonCO₂. [24,26,43,44] These estimations, however, typically rely on economy-of-scale effects and assume learning curves for widespread deployment. As it is hard to fathom the variability of these parameters for different DAC approaches and, consequently, would be associated with considerable uncertainty, we have excluded it from direct comparison.

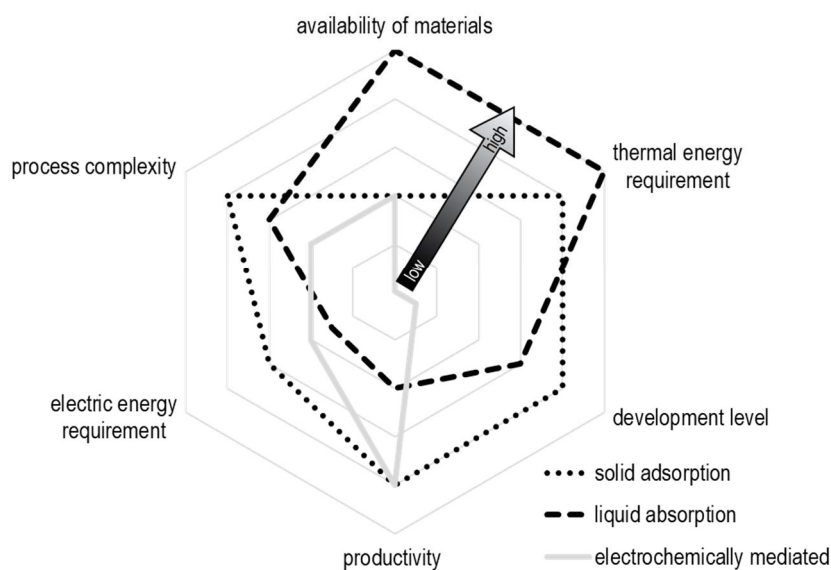


Figure 5: Comparison of different DAC methods according to relevant criteria. Electrochemically mediated approaches are marked in lighter colour as data availability is low and certain parameters had to be extrapolated or estimated.

3. Sensitivity Analysis & Discussion

In the following, we aim at illustrating levers on the overall energy conversion efficiency of the PtL process defined as the total required thermal and electrical energy input versus the fuel energy output (with respect to LHV) by means of a sensitivity analysis. For improved clarity, the following results and discussion focus solely on the FT pathway, however, we found similar dependencies for the methanol pathway.

For the base scenario, we employ assumptions derived from a meta-analysis of reports on operating pilot plants for each of the process steps (most relevant: [4,10,11,25,26,30,45–49]), which are listed in Table 1. Available waste heat was determined by internal process modelling. Further, we assumed a carbon efficiency of 90% and a total energy efficiency of 64.9 % for the conversion and upgrading steps.

Table 1: Assumptions for base case technology energy demands.

Technology	Assumption
Desalination / kWh/m ³ _{H₂O}	0.03
Electrolysis / kWh/kg _{H₂}	50
DAC electrical / kWh/kg _{CO₂}	0.5
DAC thermal / kWh/kg _{CO₂}	2.7

Figure 6a illustrates the sensitivity of the overall Well-to-Gate energy conversion efficiency of the PtL process. It becomes evident that theoretically the most powerful levers are the total efficiency of the conversion (RWGS+FT) and upgrading steps, electrolysis energy demand and DAC energy demand in order of impact.

To obtain a better understanding of the potential actual impact of technology improvement, however, the learnings on sensitivities need to be put in context with the extent of potential future technology development. To this end, we conducted a thorough literature search and technology assessment and used this as a basis to derive expected improvement potentials until 2050. The energy conversion efficiency for the downstream fuel conversion processes is already close to their limitations set by the enthalpies of the involved reaction partners. Therefore, the improvement potential in terms of energy efficiency is limited (cf. Figure 6b) and research and development effort is rather needed in terms of cost reductions and an adaption of the conversion processes to typical power-generation profiles of intermittent wind and solar energy. Likewise, alkaline electrolysis is a well-established technology, where technical improvements will reduce the specific system cost rather than the energy conversion efficiency at typical operational conditions. Nevertheless, the energy efficiency of the electrolysis step can be significantly improved by a transition to high-temperature electrolysis. This is reflected in Figure 6b, which demonstrates the impact of technological improvement expected on overall process efficiency. Future reductions of electrolysis energy demand, for example, could improve PtL process efficiency by up to ~ 5%. As green hydrogen is likely to play a major role in a future energy system, there are currently immense research efforts to enhance system efficiency and ramp up system sizes and deployment of electrolysis all contributing to this significant improvement potential.

Finally yet importantly, DAC technology development has a major effect (up to ca. 7 %) on overall PtL efficiency. At the moment, while DAC can resolve issues of carbon supply from other sources as discussed above, it is associated with a pronounced energy penalty and, therefore, represents a considerable limitation. Significant reduction in energy demand could be achieved e.g. by sorbent and reactor bed optimization and tackling the currently significant inefficiencies associated with the subsystem by process optimization enabled by enhanced plant size and learnings from further deployment. Moreover, as discussed above, methods with currently low technological maturity, such as electrochemical capture approaches, present opportunities for eliminating the demand for thermal energy. This is of interest, as the available low-grade waste heat from the FT process is not sufficient to cover the thermal demand of both, solid sorption DAC (high-temperature absorption needs individual heat supply in any case as discussed above) and solid oxide electrolysis (SOE) as demonstrated by our analysis and other authors. [35,48,50] Lowering the heat demand of DAC would, consequently, allow partial or even full heat integration of SOE, aiding the exploitation of the high electrical efficiency of this electrolysis technology. Generally, it should be noted that our analysis shows that making full use of the Fischer-Tropsch waste heat is another crucial lever for high efficiency. Disregarding this source of energy results in an efficiency penalty of -4% relative to the base case.

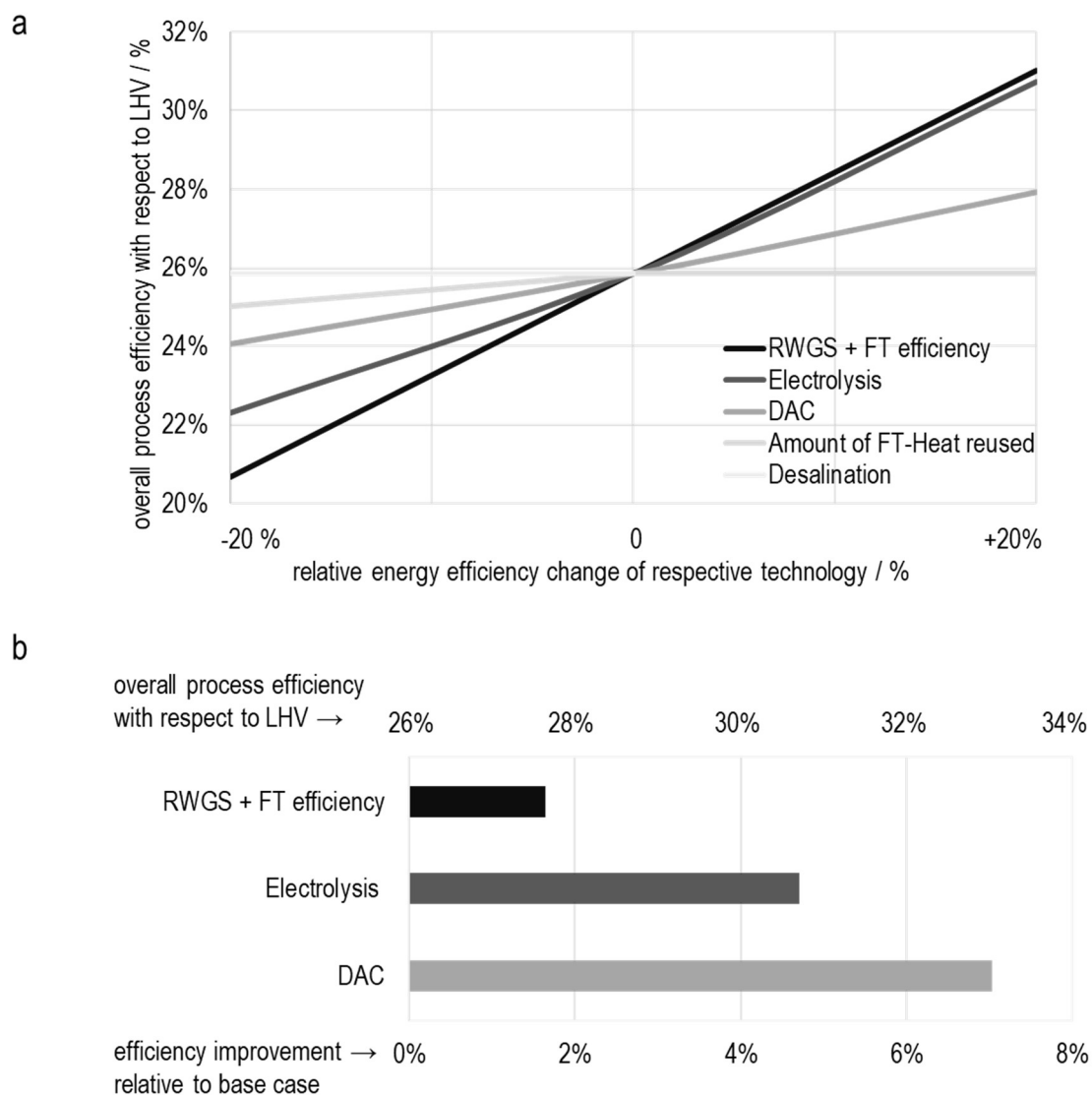


Figure 6: Impact of individual technology efficiency improvements on the overall process efficiency (a). Effect of expected technology improvement until 2050 on overall efficiency (b).

4. Summary

DAC enables utilizing atmospheric CO₂ as carbon feedstock for the production of synthetic kerosene via the PtL process. Its technological maturity and current deployment is, however, limited resulting, on the one hand, in comparatively high associated uncertainties and, on the other hand, in a large optimization and improvement potential. To that end, we have reviewed different DAC technologies and illustrated their key tradeoffs regarding relevant performance metrics. Building on the results of a thorough literature study and technological assessment, we have further investigated the sensitivities of the PtL Well-to-Gate process efficiencies to the energy demands of relevant process steps and studied the effects of expected technology improvement on the fuel production efficiency. The results demonstrate the crucial importance of further development of DAC for achieving adequate PtL production efficiencies despite making use of this low-concentration carbon source. Furthermore, a drastic scale-up for meeting demands in aviation and beyond would be necessary.

Abbreviations

LH₂ ... Liquid Hydrogen
 PtL ... Power-to-Liquids
 DAC ... Direct Air Capture
 CCS ... Carbon Capture and Storage
 CO₂ ... Carbon Dioxide
 CO ... Carbon Monoxide
 FT ... Fischer-Tropsch
 H₂ ... Hydrogen
 LHV ... Lower Heating Value
 LT ... Low Temperature
 PEWE ... Polymer Electrolyte Water Electrolysis
 SOE ... Solid Oxide Electrolysis
 RWGS ... Reversed Water Gas Shift
 NET ... Negative Emission Technology

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