Techno-economic analysis of a co-electrolysis-based synthesis process for the production of hydrocarbons

Gregor Herz⁎, Erik Reichelt, Matthias Jahn
Fraunhofer IKTS, Fraunhofer Institute for Ceramic Technologies and Systems, Winterbergstraße 28, 01277 Dresden, Germany

HIGHLIGHTS

• A coupled process of co-electrolysis and Fischer-Tropsch synthesis was developed.
• Heat integration allows for an energetic efficiency > 60%.
• Economic feasibility can be improved when valuable products are focused.
• Availability and price of renewable energy are crucial for industrial application.

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ABSTRACT

The paper is focused on the development and techno-economic assessment of a sustainable process for the production of valuable hydrocarbons from CO₂ and H₂O. With help of process modeling tools an advantageous and highly integrated process design is identified. The application of co-electrolysis for direct syngas production as well as the implementation of advanced heat integration concepts allow for an energetic efficiency of ηen > 0.6. Additionally, the amount of reactors and heat exchangers in the proposed process is reduced in comparison to other Power-to-X concepts. The high efficiency and the focus on valuable products like waxes is also beneficial for the economic feasibility of the process. The implications of product value as well as availability and costs of renewable electricity are discussed in the context of a potential market entry of Power-to-X technologies.

1. Introduction

The utilization of renewable energy for the sustainable production of chemical products from CO₂ and H₂O is of increasing interest worldwide. Different process concepts based on the coupling of electrolysis and a chemical synthesis step are summarized under terms like Power-to-Gas, Power-to-Fuel or Power-to-Chemicals. The variety of electrolysis technologies (alkaline, polymer electrolyte membrane and solid oxide electrolysis) and potential synthesis steps (e.g. methanation, methanol synthesis, Fischer-Tropsch synthesis) allow for several different process concepts. However, so far the technical demonstration of such Power-to-X concepts is particularly focused on the production of methane. Here several demonstration plants exist [1]. Plants for the production of liquid fuels are only operated by Carbon Recycling International [2] and Sunfire [3].

Especially the production of liquid fuels is believed to play a crucial role in a future energy and transport system [4]. However, for the mass market of transportation, production costs are of high importance. As recent studies show, the production costs for so-called electrofuels are considerably higher than the production costs for fossil fuels [5]. For the necessary reduction of production costs, an increase in efficiency of the Power-to-X technologies is of vital importance.

As the market entry of Power-to-X technologies on a mass market like transportation is expected to be more difficult, first applications should be focused on niche markets, where advantageous products are able to achieve high prices. Potentially interesting products are waxes produced via Fischer-Tropsch synthesis. Due to the absence of aromatic and polycyclic aromatic compounds as well as sulfurous substances, Fischer-Tropsch waxes are especially feasible for cosmetic applications [6]. The increasing demand for waxes [7] and the sustainable production makes this synthesis route an attractive option for a first market entry of Power-to-X technologies.

Established electrolysis technologies like alkaline and PEM (polymer electrolyte membrane) electrolysis are only capable of converting H₂O to H₂ [8,9]. The direct conversion of H₂ and CO₂ to hydrocarbons is limited to only few reactions (e.g. methanation, methanol
synthesis) [10]. For more complex and more valuable products, syngas is necessary as feed. In this case, an additional reverse water-gas shift reaction step is necessary for syngas production [3]. A highly efficient alternative is the application of solid oxide electrolysis cells (SOEC). This technology allows for the direct production of syngas from CO₂ and H₂O in a so-called co-electrolysis.

The source of the CO₂ used as feed is important for Power-to-X processes. Potential point sources of CO₂ are industrial emitters (e.g. steel mills, cement plants) and power plants. The separation of CO₂ from the diluted flue gas streams of these emitters is costly. Expected costs for the separation depend on the emitter and differ considerably in the range of approximately 25–300 €/t CO₂ [5,11,12]. The utilization of CO₂ from the mentioned emitters would allow for a reduction of crude oil usage and would therefore lead to an emission reduction. However, to achieve the ambitious CO₂ reduction goals of the climate summit in Paris in 2015, the utilization of fossil fuels must be significantly reduced. The increasing share of renewables in electricity generation [13] and novel production processes, e.g. in the steel industry [14,15] will be used. The increasing share of renewables in electricity generation [13] and novel production processes, e.g. in the steel industry [14,15] will be used. The increasing share of renewables in electricity generation [13] and novel production processes, e.g. in the steel industry [14,15] will be used. The increasing share of renewables in electricity generation [13] and novel production processes, e.g. in the steel industry [14,15] will be used. The increasing share of renewables in electricity generation [13] and novel production processes, e.g. in the steel industry [14,15] will be used. The increasing share of renewables in electricity generation [13] and novel production processes, e.g. in the steel industry [14,15] will be used.

The above considerations show that economic feasibility of Power-to-X plants is highly influenced by several factors. Some of these factors can be influenced by legislation, e.g. by remunerations for avoided CO₂ emissions or reduced electricity costs for Power-to-X plants. However, in order to allow for a future application of such processes, concepts with optimized energy and cost efficiency have to be found. Therefore, in this paper, a novel highly integrated process for the co-electrolysis-based production of chemicals is proposed. The efficiency of the process is calculated with help of process modeling tools and compared to other concepts. Based on these results, the economic feasibility of the process is evaluated. The influence of availability, electricity price and product fraction is considered and discussed. The results not only allow for an evaluation of Power-to-X processes, but also give an indication which potential tools might support the market entry of Power-to-X technologies.

2. Process and model development

2.1. Process scheme

Generally, a Power-to-X process can be divided into three main process steps: syngas production, synthesis step and product separation. A simplified process scheme is depicted in Fig. 1.

There are various different means of implementing these process steps. They are discussed in Section 2.2. This section focuses on general concepts for recirculation and heat integration.

Power-to-X processes have been studied in the literature by several authors and it was found that by-product utilization is crucial in order to reach an efficiency competitive with other sustainable hydrocarbon synthesis processes.

In a process concept proposed by Cinti et al. [19], two different means of by-product utilization were implemented (Fig. 2a). In this process scheme all by-products (water, tail gas) are recycled via a long recycle into the syngas production step and reform (as opposed to a short recycle into the synthesis step). The conversion of by-products via internal reforming as well as in a reverse water-gas shift step were considered. The simulation results showed a slightly higher efficiency for internal reforming in comparison to the case of reverse water-gas shift reaction for tail gas conversion. In both cases, a significant increase in efficiency compared to a once-through process was observed.

Even though the process concept proposed in Ref. [19] allows for a high overall efficiency, it would have to be altered in order to be technically implemented. For example the necessity for a purge stream to avoid the accumulation of inert components was not considered. However, the proposed concept highlights the importance of by-product recirculation for process efficiency.

The potential of heat integration via utilization of the purge gas was evaluated by Becker et al. [20]. A simplified flowsheet of the proposed process concept is depicted in Fig. 2b. In this case, by-products and unconverted syngas are combusted in order to supply thermal energy to the syngas production step.

The purge gas is combusted with anode off-gas in order to reach high exhaust temperatures, which significantly improves heat integration. Furthermore, thermal losses caused by inert nitrogen can be minimized. The hot exhaust gas is first used to pre-heat the inlet streams of cathode and anode side of the SOEC. After exiting the pre-heating steps, the exhaust gas can be used to pre-heat carbon dioxide, evaporate feed water and supply heat to syngas pre-heating, product upgrading and an electric generator.

In this process concept, the possibility of separating the hydrogen from the tail gas was also introduced (not included in Fig. 2b in order to aid comparability). A fraction of this hydrogen is fed to the SOEC to avoid degradation [21,22], while the rest is considered as a marketable product. This separation step significantly increases overall process complexity and is therefore not reasonable for a technical realization.

A process concept proposed by König et al. [23] incorporates both mentioned possibilities of tail gas utilization but utilizes a water electrolysis and a reverse water-gas shift step. A part of the tail gas is recycled and again converted into syngas in the reverse water-gas shift step while the rest is combusted to supply heat to the RWGS reactor. The ratio between these two streams is adjusted, so that the heat demand of the syngas production step is met. While this approach allows for a very flexible process management, not all advantages of high temperature electrolysis were considered, such as co-electrolysis or internal reforming. Additionally, in this concept the heat of the exothermic Fischer-Tropsch synthesis is not utilized.

The main characteristics of the aforementioned process concepts are listed in Table 1. This summary illustrates the variety of different implementation methods for coupled processes of high temperature electrolysis and Fischer-Tropsch synthesis. In the process concept depicted in Fig. 3, the aforementioned possibilities for tail gas utilization (short recycle (a), long recycle (b) and tail gas combustion (c)) are combined. Additionally, a concept for the utilization of the heat produced in the exothermic synthesis step introduced by Verdegaaal et al. [3] was included. The heat is used to evaporate the feed water supplied to the process. This reduces the thermal energy demand for reactant conditioning significantly, as shown in Section 3.1.2. This form of heat integration has so far not been implemented into a model of a Power-to-X process.

The process scheme in Fig. 3 is the base for the process design study in this paper. With help of process modeling an advantageous process design for the highly efficient production of waxes from renewable energy is developed.

2.2. Modeling

The process was modeled using the flowsheet based simulation

![Fig. 1. Simplified process scheme of a Power-to-X process.](image-url)
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