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Conceptual design of pre-treatment units for co-electrolysis of CO_2 and water

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Abstract

Reaching our climate goals will require urgent advancements in the development of fossil-free technologies. Solid-oxide electrolysis (SOE) at high-temperature is a promising candidate for combining CO_2 utilization and renewable electricity use. Explorative techno-economic analyses are being performed to understand the full plant design requirements for integrated SOE systems. However, there is still a lack of understanding of the potential impact that the pre-treatment of CO_2 will have on the overall design and economics of a SOE-based system. To address this knowledge gap, as a first step, the process model of the pre-treatment units needed to purify CO_2 from a bioethanol plant is developed in Aspen Plus in the current work. Based on the preliminary results of this paper, the equipment costs mainly stem from the units related to the removal of sulfur (~65%) and alcohols (~32%). The energy costs are almost entirely related to the cryogenic distillation step required for the removal of non-condensable gases (~96%).

Keywords: solid-oxide electrolysis, co-electrolysis, syngas, pre-treatment, ex-ante techno-economic analysis, low carbon technologies

1. Introduction

Net-zero CO_2 emissions must be reached by 2050 to reduce the disastrous effects of climate change (IEA, 2020). Carbon dioxide electrochemical reduction (CO_2ER) has the potential to mitigate CO_2 emissions as it combines CO_2 utilization and renewable (intermittent) electricity for the synthesis of chemicals. A specific type of CO_2ER technology is the solid-oxide electrolyzer (SOE). Co-electrolysis of CO_2 and water in a SOE has a technology readiness level (TRL) between 5-7, and it can be used to generate syngas (Zheng et al., 2017). To reach higher TRLs and eventually large-scale commercial deployment, explorative techno-economic analyses (TEAs) are underway to better understand the full plant design requirements (for example, Gao et al., 2020; Herz et al., 2018).

SOE TEAs assume that future CO_2-based plants will be operated using CO_2 from industrial point sources or direct air capture (DAC). It is also often assumed that this CO_2 stream is pure and available at the gate of the SOE plant. However, this may not be the case. The CO_2 purity level of several industrial sources can vary between ~30-96 mol% (Verma et al., 2019). Some SOE TEAs mention that purifying the CO_2 will be needed before entering the electrolyzer as experimental studies have indicated that even a slight concentration of impurities (for instance, sulfur or heavy metals) can alter the catalytic performance significantly or deactivate the catalyst entirely (Gao et al., 2020; Kibria et al., 2019). However, neither the target purity levels nor the required types of purification steps have been specified or modeled in SOE TEAs literature.

Therefore, there is currently a lack of understanding of the potential impact of pre-treatment units on the design and economics of SOE plants. To address this knowledge gap, in this study an ex-ante TEA of the pre-treatment units for a CO_2 stream from a bioethanol plant for co-electrolysis via SOE to produce syngas is performed. The aim of this paper is therefore twofold: 1) to propose a conceptual design for pre-treatment units of CO_2 for future SOE plants, and 2) to evaluate the plant performance. In the upcoming section, the scope, modeling, and evaluation steps are described. In the subsequent sections, the preliminary results are discussed.

2. Methodology

2.1. Scope

The current techno-economic analysis consists of a 'gate-to-gate' ex-ante assessment. Figure 1a presents an overview of the overall SOE-based plant, and the current system boundaries. The electricity is considered to be continuous and acquired from the grid.

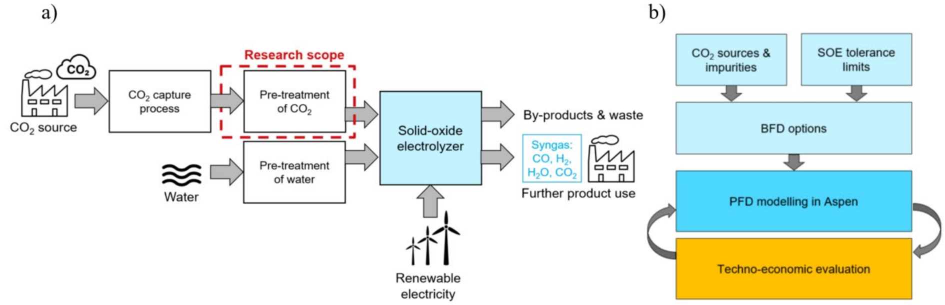

Figure 1: a) System boundary definition, focus on pre-treatment of CO_2. b) Methodological steps for modeling and evaluation (BFD: block flow diagram, PFD: process flow diagram).

The methodological framework for this research follows the approach for analyzing future "N-of-a-kind" (NOAK) plants (Roussanaly et al., 2021). Since this research involves an ex-ante analysis of a low TRL technology, this means that the entire analysis is based on a "what-if" approach where the SOE is treated as if it was already commercially available today. It is assumed that the performance at industrial scale is the same as currently demonstrated in lab conditions. The model considers a CO_2-based plant located in Northwestern Europe and installed in 2019. The scale of the plant corresponds to the production of 1 tonne of pure CO_2 per year (8000 hours).

2.2. Data collection, modeling & evaluation

The methodology followed for the data collection, modeling and evaluation of the pre-treatment configuration for future SOE plants is illustrated in Figure 1b. A targeted literature review was performed to collect information regarding (i) possible CO_2 sources and their compositions, and (ii) the electrolyzer's tolerance levels per contaminant (considering a SOE Ni/YSZ cermet fuel electrode). Assumptions were made based on existing literature for solid-oxide fuel cells and water electrolysis, and information from experts in the field. Next, a screening of potential cleaning technologies for the removal of contaminants was done based on heuristics, temperature and pressure considerations to create a block flow diagram (BFD). For the current bioethanol case, the pilot plant study from McKaskle et al., the research on purification units from Quevedo et al., and a CO_2 purification patent by Gupta et al. served as a starting point (Gupta, 1999; McKaskle, 2018; Quevedo, 2021). The subsequent process flow diagram (PFD) was created in Aspen Plus. The model was validated, unit-by-unit, using data from literature. The Aspen model was used to generate data on the equipment dimensions, mass and energy balances. Finally, key performance indicators (KPIs), i.e. CO_2 losses during the process, energy needs, and bare equipment costs, were calculated.

3. Results & discussion

The main impurities in the selected bio-based CO_2 stream are non-condensable gases (NCDS), such as oxygen and nitrogen, as well as sulfur components, water, alcohols, and other hydrocarbons (see Table 1). The investigation into the target purity levels for SOE revealed that even trace levels of sulfur components are likely to negatively affect the degradation rate of the electrodes (Caliandro, 2018; Rinaldi, 2019). The other identified contaminants from the bioethanol plant are expected to be less problematic for the SOE, but experimental data on the effect of these components is still limited in the current literature, for instance, for alcohols. In the current work, it is considered a conservative goal to reach at least ppb-level of the contaminants that are less known.

Table 1: Overview composition of the CO_2 stream from a bioethanol plant (i.e., the fermentation off-gas from an ethanol plant using corn as the biomass source) including major and trace impurities alongside tolerance limits for SOE (Caliandro, 2018; McKaskle, 2018; National Academies of Sciences, Engineering, 2022; Rinaldi, 2019; Yokokawa et al., 2008).

Composition	Bioethanol plant	Unit used	Degradation type	Tolerable amount	Unit used
CO_2	90	%	C-poisoning		
CO	1	ppm	C-poisoning		
H_2O	5	ppm			
CH_4	3	ppm	C-poisoning		
SO_x	1	ppm	S-poisoning	<2	ppm
NO_x	1	ppm			
O_2	100	ppm		<5	%
H_2S	1	ppm	S-poisoning	~0.05	ppm
N_2	98768	ppm			
Ar	-	ppm		~100	µmol/mol
Heavy metals	-	ppm	Metals	-	ppb-level
Cl	-	ppm	Cl-poisoning	<5	ppm
Alcohols	3-950	ppm			
Other hydrocarbons	1	ppm	C-poisoning	~2	µmol/mol
Aromatics (benzene, toluene, xylene)	3	ppm			
Carbonyl sulfide	1	ppm	S-poisoning	<2	ppm
Dimethylsulfide	1	ppm	S-poisoning	<2	ppm
Ethers	1	ppm			
Ketons	1	ppm			
Mercaptans	1	ppm			

Figure 2 shows the design of the preliminary CO_2 purification train for the removal of the contaminants listed in Table 2. In total, four different purification sections are needed to achieve this level of purity, namely (i) alcohols removal, (ii) sulfur removal, (iii) moisture removal, and (iv) non-condensable gases removal. The global property method Redlich-Kwong-Soave (RKS-BM) was selected in Aspen Plus, which is suitable for gas processes.

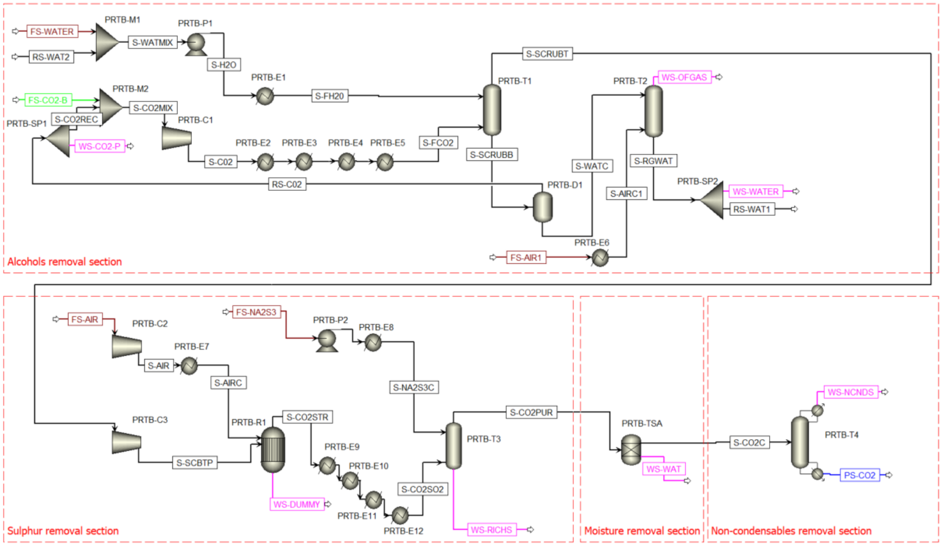

Figure 2: Aspen PFD for the purification of a CO_2 stream from a bioethanol plant to reach SOE purity levels.

The CO_2 from the bio-ethanol plant enters the process at 38ºC and 0.9 atm (McKaskle, 2018) and is conditioned to 20ºC and 10 bar before being sent to a pressurized water scrubbing tower (RadFrac column –PRTB-T1) for the removal of alcohols (Abu Seman & Harun, 2019). The water scrubbing tower removes the traces of alcohols as well as ~25% of the CO_2, therefore the removed CO_2 is separated from the scrubbing water via a flash drum (Flash2 – PRTB-D1) and is recycled back (RS-CO2). The scrubbing water is regenerated using a counter-current hot air stream in a second tower (RadFrac column – PRTB-T2). Next, the CO_2 stream is mixed with air in a catalytic oxidation unit (REquil – PRTB-R1) operating at 400ºC and 22 bar to remove the hydrogen sulfide and COS by converting them into sulfur dioxide and water (Gupta, 1999). The sulfur dioxide is removed by using an aqueous solution of Na_2SO_3 in an absorption tower (RadFrac – PRTB-T3) at 38ºC and 22 bar. Then, the remaining moisture is removed using a temperature swing adsorption (TSA) unit consisting of 2-4 columns (Gupta, 1999). The TSA was modeled in Aspen Plus using a separator block (i.e., black-box model for which the energy and economic performance are not yet evaluated in the current work). Finally, the non-condensable gases are removed via cryogenic distillation (RadFrac column – PRTB-T4) at 22 bar.

Table 2 summarizes the preliminary techno-economic results of the CO_2 purification train from Figure 2. The CO_2 from the bioethanol source was purified to 99.9984 wt% with water, carbon monoxide, methane, and argon as trace impurities. The purity level is in agreement with the tolerance limits for SOE (as shown in Table 1) and matches the specifications of food-grade CO_2 (i.e., 99.9% (Parker Hannifin Ltd, 2022)). During the purification process, about ~21% of the CO_2 inlet stream is lost as gaseous emissions despite recycling efforts. Possibilities for further improvement of CO_2 recycling should be investigated to improve the process in the future.

In terms of cost, the total bare equipment costs of the purification train are almost 3M€. The analysis of the different purification sections reveals that the equipment costs related to the removal of sulfur (~65%) and alcohols (~32%) are responsible for most of the total equipment cost. The energy costs are almost entirely related to the removals of non-condensable gases (~96%) due to the cryogenic distillation step.

Table 2: Energy and economic preliminary results for the purification of the bioethanol CO_2 stream. The results are stated per tonne of clean CO_2 (VHPS: very high pressure steam at 100 bar, HPS: high pressure steam at 51 bar, MPS; medium pressure steam at 21 bar, LPS: low pressure steam at 5.5 bar, LLPS: low low pressure steam at 3.9 bar, CW: cooling water ~25-40ºC, CHILLED: chilling water ~5-7.5ºC, R50: refrigerant methane ~-162ºC, NA: energy and equipment costs not available for the TSA unit, NCDS refers to non-condensable elements such as nitrogen, argon and oxygen).

Section	Energy needs									Energy costs	Bare equipment cost
	VHPS	HPS	MPS	LPS	LLPS	CW	CHILLED	R50	Electricity		
Unit	GJ/t	GJ/t	GJ/t	GJ/t	GJ/t	GJ/t	GJ/t	GJ/t	kWh/t	€/t	k€
Alcohols	-	-	-0.06	-0.10	0.30	0.23	0.04	-	115.29	10.80	930
Sulfur	-	1.00	-0.31	-0.31	0.75	0.76	-	-	554.29	48.95	1875
Moisture	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
NCDS	-	-	-	-	2,80	-	-	3.80	-	1618.11	101
Total	**-**	**1.00**	**-0.38**	**-0.41**	**3.86**	**0.99**	**0.04**	**3.80**	**669.58**	**1677.86**	**2907**

4. Conclusion & future work

A preliminary ex-ante techno-economic assessment of the pre-treatment units for purifying CO_2 from a bioethanol plant has been performed, as a first step towards the modeling of a complete SOE-based plant for co-electrolysis of CO_2 and water to produce syngas. This study aimed to propose an initial PFD and to analyze selected KPIs. Required CO_2 purity levels for SOE were identified based mostly on solid oxide fuel cells and water electrolysis literature. Four different purification sections were proposed to purify the CO_2 stream resulting in a CO_2 purity grade similar to food-grade CO_2. The removal of sulfur (~65%) and alcohols (~32%) were the largest contributors to the overall equipment costs. The removal of non-condensable gases via cryogenic distillation was the main contributor to the overall energy costs (~96%). In future work, trade-offs will be further investigated by modeling the TSA unit using RadFrac columns and the possibilities for recycling flows, heat integration, and waste valorization will be further considered. Also, the purification of the water inlets stream will be analyzed.

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