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Reaction Efficiency by Product Separations and Recycling**

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Achieving Order of Magnitude Increases in CO₂ Reduction Reaction Efficiency by Product Separations and Recycling

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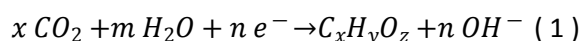
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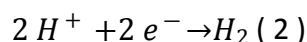
CO₂ reduction reaction (CO₂RR) systems are the heart of many proposed e-refinery schemes. There have been few studies on the separation systems that will be needed to complement CO₂RR reactors. We show that by strategic use of downstream separations and recycling of unreacted CO₂, the efficiency of CO₂RR can be significantly improved without changes in the electrochemical reactor.

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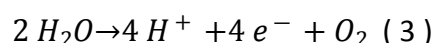
Performing CO₂ reduction reactions (CO₂RR) using aqueous phase electrochemistry with the cathodic and anodic sides of a cell separated by an anion exchange membrane (AEM) has been widely studied.[1-6] CO₂RR involves reducing carbon dioxide at a cathode using electrical energy:



These reactions are often accompanied by production of hydrogen,



These cathodic reactions are accompanied by oxidation of water at the anode



This series of reactions present an opportunity to convert CO₂ from post combustion capture, direct air capture, or other sources to useful products via renewable energy and is therefore a potential basis for future for e-refineries.[7-10]. A very large literature exists exploring the many catalytic features of CO₂RR that affect the efficiency of this process.[1-5] These features include developing catalysts with improved selectivity for specific products of interest (for example, carbon monoxide, formate/formic acid, methane or C₂+ hydrocarbons), improving Faradaic efficiencies and increasing reactant conversion.[9, 11-14]

Despite the many papers on CO₂RR, little attention has been given to the downstream processing of the reaction products.[15-19] This situation has led to several challenges and also has largely resulted in the overall process efficiency of CO₂RR being overlooked. First, practical electrochemical cells produce a mixture of products at the cathode, often with low yields, requiring additional processing steps before high purity reaction products are available.[17] This observation implies that downstream processing must be considered in any attempt to assess the energy efficiency of CO₂RR

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processes. Second, only a fraction of the CO_2 at the cathode reacts, so some fraction of the CO_2 entering the reactor remains unused. Third, alkaline conditions must be maintained on the cathodic side of a CO_2RR cell to suppress hydrogen evolution. In this alkaline environment, CO_2 reacts with OH^- ions to produce HCO_3^- and CO_3^{2-} . These ions migrate to the anodic side via AEMs to maintain electroneutrality. In the acidic environment of the anode, HCO_3^- and CO_3^{2-} convert back to CO_2 . In electrochemical cells reducing CO_2 to C_2 hydrocarbons, 75% of the CO_2 entering the cell ultimately migrates to the anode, strongly limiting the single pass conversion of the cell. [18, 20-25] This feature of CO_2RR processes seems almost entirely unappreciated in prior work [15, 18].

The observations above imply that in existing CO_2RR processes the proportion of CO_2 entering the reactor that forms desired products is often 10% or less. From an atom efficiency perspective, the observation that a majority of the reactant of interest leaves the process in an unreacted state is a glaring inefficiency. From a cost perspective, capturing CO_2 from point sources or via DAC will inevitably cost money, so emitting much of the resulting CO_2 from a conversion reactor without any effort to capture its value seems unwise.

The importance of considering downstream separations of CO_2RR products has been explored recently by Alerte et al. [15], who considered a process that aimed to generate high purity streams of key products. Alerte et al. [15] made energy estimates for separations systems based on industrially mature large-scale separation processes, namely cryogenic distillation, amine absorption, and tri-ethylene glycol dehydration based on the reaction products from experiments reported by Gabardo et al. [5]. They performed a principal component analysis of the contributions of CO_2 conversion, cathodic Faradaic efficiency, and anodic CO_2 crossover on downstream energy requirements and concluded that separation of anodic gas mixture is the most energy intensive step in the processing and it would be more energetically favorable to simply vent this mixture than to use natural gas-based heating to recapture it. However, as noted above, this CO_2 will have

been sourced from a dilute stream such that the cost of the CO_2 will be one of the key cost drivers in the overall e-refinery process. This suggests that alternatives other than venting of the anodic gas mixture must be explored to reduce e-refinery process costs. There have been notable works that have investigated the possibility of eliminating the need for the CO_2/O_2 separation by making changes in the reactor itself or via the use of dual-reactor systems. Ramdin et al. [18] analyzed a two-step reaction pathway for production of C_2 hydrocarbons where CO_2 is reduced to CO in the first electrochemical cell which is then reduced to ethylene/ethanol in the next. This eliminated the need for maintaining alkaline conditions at the cathode but introduced an extra CO_2/CO separation step before CO could be fed into the second cell. Xie et al. [26] replaced oxygen evolution at the anode with an all-liquid organic oxidation reaction and achieved an overall CO_2 conversion of 75%.

In this paper, we present a separation strategy that can enable dramatic efficiency increases in CO_2RR . Most importantly, we develop concepts associated with recycling of downstream CO_2 into the electrochemical CO_2RR process. The concept of recycling partially reacted products into a reactor is a key concept in chemical process development [27], but remarkably it does not seem to have been considered in the development of CO_2RR processes. [1-4] An important implication of considering processes that include reactant recycling is that the single pass efficiency of the reactor, a focus of much of the existing CO_2RR literature, is only one of many variables controlling the overall process efficiency and that maximizing single pass conversion is unlikely to be the best overall strategy. Shin et al. [28] reported a techno-economic analysis of production of carbon monoxide, formic acid, ethylene and ethanol via carbon dioxide electrolysis and highlighted the need to account for separation processes and recycling of unreacted CO_2 . The work, however, also focused on single pass CO_2 conversion and presented design guidelines for achieving profitable manufacture of C_2 products from the standpoint of reactor and catalytic design and stability as opposed to

optimal downstream separation strategies which are the focus of this work.

In addition to considering process schemes with CO₂ recycling, we describe a process based on separations that are expected to be more energy efficient than those analyzed by Alerte et al. In particular, we examine the use of adsorption- and membrane-based separations.[29] In addition to offering a way to reduce the energy intensity of the separations considered by Alerte et al., these choices are readily scalable. Moreover, they are well suited to laboratory implementation on the scale at which much of the research on CO₂RR is being performed.

We consider the same reaction specifications as considered by Alerte et al.[5, 15], with slight modifications, with the aim to develop a process focused on ethylene production. We included estimated concentrations of CH₄ and C₂H₆ in the product stream, since evolution of these gases has been observed along with C₂H₄ in several cases [3, 6, 11, 12]. Ethane evolution is less common than other products included in the mixture but C₂H₄/C₂H₆ is a challenging separation[30-32] that has the potential to bottleneck downstream separation systems. We therefore felt it was useful to consider the role of ethane in our proposed separation processes to make this approach widely applicable.

In addition to ethylene, we considered syngas, acetic acid, and alcohols as value-added byproducts of the process. As noted above, the CO₂ reduction in this reactor [5] is carried out in alkaline conditions using membrane electrode assembly. This suggests that carboxylic acids produced in the reaction will dissociate almost completely into their ionic forms [33] and are likely to migrate across the AEM. Neutral molecules are also expected to diffuse owing to a gradient in chemical potential. Gabardo et al.[5] found formate only at the anode whereas a significant quantity of ethanol was detected at the cathode outlet. Only formate ions were appreciably oxidized at the anode. For this reason, we do not include formate or formic acid in our downstream analysis. Commercially, acetic acid is a more attractive product than acetate salts. Formation of

salts would also require constant replenishment of electrolyte which would serve as the cation source[33]. Attempts to convert carboxylate anions to their respective acids have been done in the past, both within the cell using a modified 3 compartment configuration using protons from the anode[34] or using electrodialysis post CO₂RR. Hence, for our analysis we would consider acetic acid as the product and for the sake of simplicity assume it to be present in our cathodic tail.

The anode composition is calculated assuming 100% Faradaic efficiency of the oxygen evolution reaction and CO₂ crossover of 0.5 mol CO₂/mol electron. These values are conservative estimates, since in a real system the Faradaic efficiency will be less than 100% and the CO₂ crossover is likely to be higher than our estimate. The gas mixtures are assumed to be at 100% relative humidity. Figure 1 shows the composition of mixtures exiting the cathode and anode.

Figure 2 shows the overall schematic of the process we consider. Detailed mass and energy balances are described in the SI. The aim is to separate the mixture of products exiting the cathode to ultimately obtain ethylene, syngas, acetic acid, and ethanol as pure products while recycling carbon dioxide back to the reactor. The remaining unseparated mixture contains methane, carbon monoxide, and ethane. Instead of further separating these gases, the proposed process uses them as combustion fuel to obtain energy for the separation processes.

The anode mixture contains oxygen along with water and “crossover” CO₂, which as mentioned above accounts for the majority of CO₂ fed into the reactor. This mixture is first fed to a flash tank to remove water.

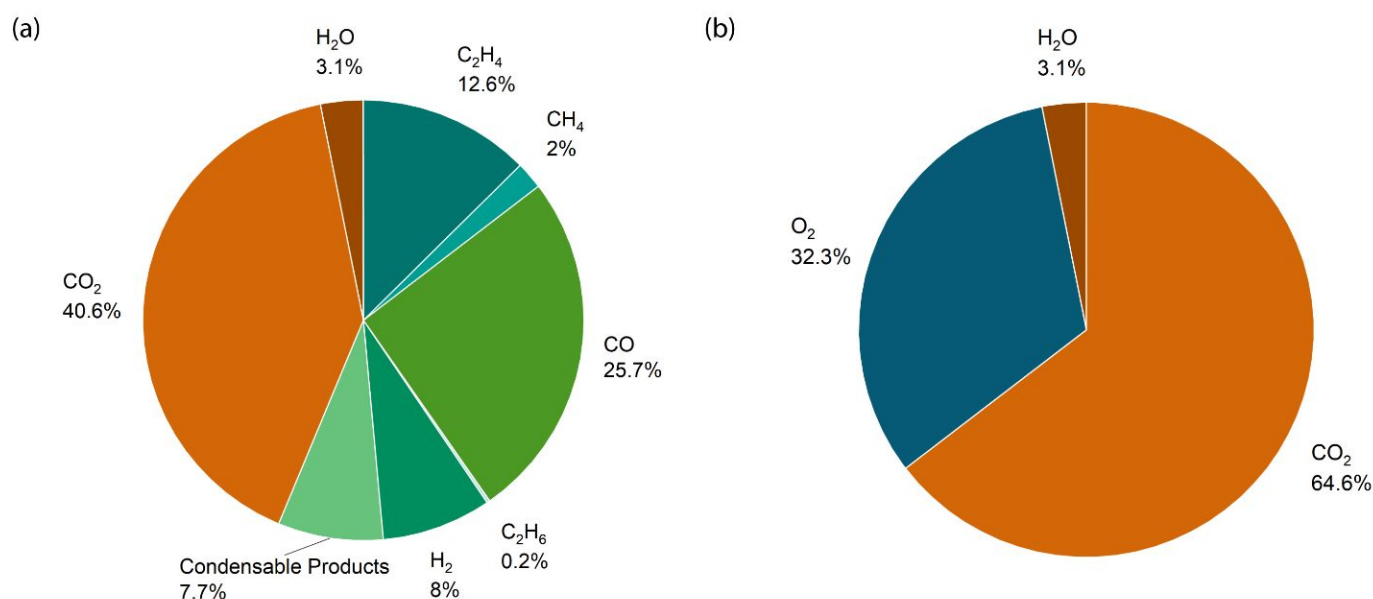


Figure 1: Estimated composition in mole percent of mixtures exiting the (a) cathode and (b) anode in CO₂RR. The condensable products in (a) include acetic acid and alcohols, here, ethanol and propanol.

Additionally, we could have considered acetate/acetic acid in our anode tail but the lack of exact reported crossovers and compositions of anode and cathode liquid mixtures provide no basis for this estimation. In that case, our liquid stream from this flash tank would be mixed with the cathodic liquid effluent. Regardless, we do not expect significant differences in the liquid separation energy.

As previously mentioned, the estimates by Alerte et al. [15] showed that separating CO₂ and O₂ is by far the most energy intensive operation in their proposed downstream purification process to the point that these authors recommended simply venting this CO₂-laden mixture. Instead of applying an energy-intensive separation to this CO₂/O₂ mixture, our process instead uses this mixture as oxyfuel for combustion of the unseparated hydrocarbon mixture from the cathodic products. Stoichiometrically, the amount of oxygen produced at the anode is greater than amount of oxygen required for this combustion process. Our process therefore adds additional methane to the combustion mixture to ensure that all oxygen entering the combustor is consumed. This combustion not only

eliminates an energy-intensive separation but also generates enough energy to drive the separation processes and, in principle, some excess energy that could be used for upstream direct air capture of carbon dioxide. CO₂ and H₂O produced as a result of combustion are recycled back to the reactor. We could consider hydrogen, instead of methane as the fuel but methane is cheaper and none of the CO₂ produced is vented to the atmosphere, hence, we chose methane over hydrogen. Future iterations of this design should consider the use of H₂, and the energy/carbon footprints of that process as compared to the CH₄-driven one shown here.

No CO₂ remains in the streams exiting the process in Fig. 2. We noted above that the atom efficiency for the CO₂RR reactor considered here is at best 10% (i.e., the single pass conversion). The addition of the downstream separations and CO₂ recycle in our process increases this atom efficiency by approximately an order of magnitude to nearly 100% overall conversion of CO₂. The process uses CH₄ combustion as part of the downstream processes, but this combustion does not lead to net CO₂ emissions because all CO₂ in the process is converted to products.

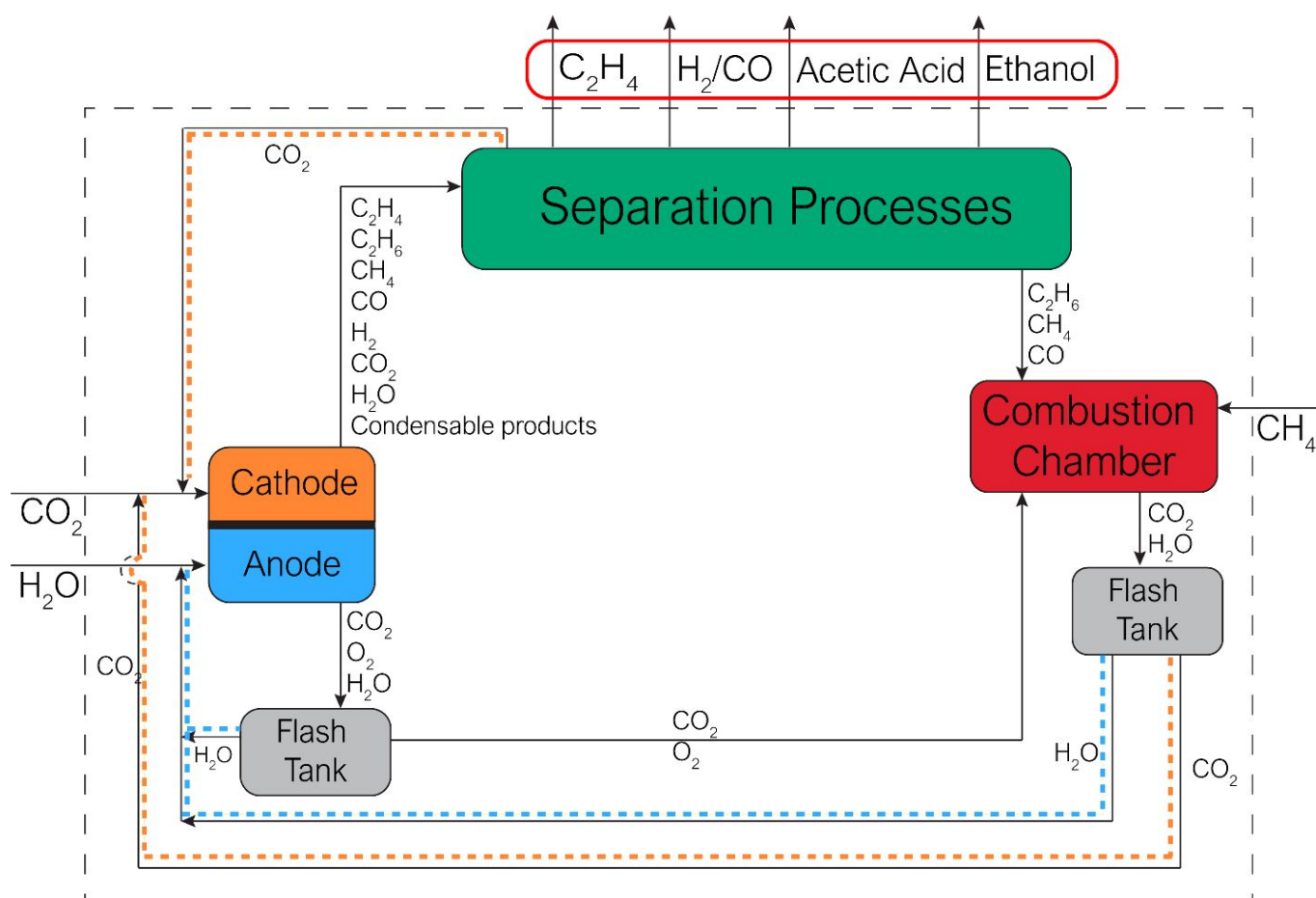
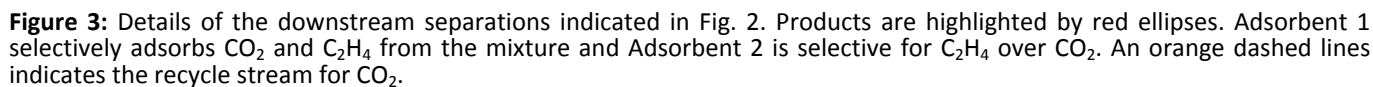


Figure 2: Schematic process flow diagram for a combined CO₂RR reaction and separation system allowing recycling of CO₂. The anodic gases are used as oxyfuel for CH₄ combustion, which provides heat and power to the separation systems. Products are circled in red. The CO₂ and H₂O recycle streams are accompanied by dashed orange and blue lines respectively to assist in tracing the streams.

To perform quantitative mass and energy balances, details of the separations processes in Fig. 2 need to be specified. The separation unit operations we used for these calculations are illustrated in Figure 3. The cathodic products are separated into gaseous and liquid streams using a flash tank. The gas mixtures comprising of C₂H₄, C₂H₆, CH₄, CO, H₂ and CO₂ are then separated by a combination of adsorption and membrane separations. The mixture is first passed over molecular sieves to ensure that any trace water in the effluent gas stream from the flash tank is removed. The mixture is then passed through an adsorbent bed. This first adsorbent should be able to selectively adsorb C₂H₄ and CO₂. Literature data indicates that zeolite CaX fits this requirement well[35]. The mixture of C₂H₆, CH₄, CO and H₂ obtained above is then passed through a hydrogen

selective polymeric membrane like cellulose acetate or polyimide[36, 37] to obtain syngas.

The other output from the first adsorbent bed is a mixture of C₂H₄ and CO₂. This mixture of is fed into a second adsorbent bed with the aim of separating the two components. Metal Organic Frameworks (MOFs) with unsaturated metal sites seem potential candidates for this separation as they can use π electron interactions to selectively adsorb ethylene.[38] Bachman et al. [35] reported single component isotherms of C₂H₄ and CO₂ at room temperature for open metal site MOFs from the M₂(m-dobdc) (M = Fe, Mn, Ni, Mg, Co) series. We used Ni₂(m-dobdc) as the second adsorbent in our process model. Mn₂(m-dobdc) and Fe₂(m-dobdc) MOFs show higher selectivity than Ni₂(m-dobdc) but require inert atmospheres for



The aqueous mixture of condensable products leaving the cathode-side flash tank in Fig. 3 are separated to obtain useful fractions via distillation. These columns produce acetic acid and azeotropic mixture of alcohols (here, mostly ethanol) as byproducts.

CO₂, CO and CH₄ for CaX and Ni₂(m-dobdc) were digitized (Figure S3 and S4) and fitted to a Dual Site Langmuir-Freundlich Isotherm equation (Table S5 and S8). Ideal Adsorbed Solution Theory [40, 41] was employed to obtain estimate gas adsorption isotherms for all mixtures. We assumed that hydrogen does not adsorb in CaX at these conditions. The heats of adsorption reported by Bachman et al. were used to estimate of energy requirements for regeneration of adsorbents. Heats of adsorption provide minimum thermodynamic estimate of the process. In this work, we assume the actual energy required to be 1.5 times this thermodynamic minimum. The choice of membrane determines the ratio of H₂ and CO in the syngas produced by our process. We assumed the use of a cellulose acetate membrane[36] with a H₂/CO separation factor of 21 operated at an upstream pressure of 35 bar at 35 °C. The distillation columns were used to achieve > 99% purity of acetic acid and an

azeotropic mixture of alcohols (~90% alcohol) (more details are given in the Supporting Information). The energy produced from combustion was calculated using the heats of combustion values for the gases.[42, 43].

Figure 4 shows the energy consumed by each separation process described above. Among the four separations in the process, adsorption requires the most energy, followed by distillation, membrane separation, and flash tanks. Even though separation of the cathodic gaseous mixture by adsorption requires ~34.5 GJ/tonne of C_2H_4 produced, this energy is significantly lower than the energy input required by a combination of amine absorption, tri-ethylene glycol dehydration and cryogenic distillation for the same purification reported by Alerte et al., which is about 68.9 GJ/tonne C_2H_4 . [15]. Combusting the components that do not exit the process as purified products produces 25.44 GJ/tonne C_2H_4 which is less energy than is required for the separations. Thus, we would need additional chemical energy to drive the separation processes. Our process uses input methane equivalent to approximately 80 GJ/tonne ethylene but only a fraction from this energy goes into the separation processes and this source accounts for the total energy input associated with separations.

A key part of our proposed process is the use of CH_4 combustion to avoid an energy-intensive separation of CO_2 and O_2 . Xie et al. [26] demonstrated that oxygen fraction of over 1.8% in the cathode feed diminished CO_2RR selectivity. Therefore, it is important that all of the oxygen is combusted and we ensure that by tuning the amount of methane added as required stoichiometrically, although we recognize that an excess of CH_4 would be needed for complete O_2 combustion. Moreover, the need for a very pure inlet CO_2 stream means that if anodic tail gas separations were to be carried out instead of combustion, they would incur significant energy costs irrespective of the separation method employed. It can be seen in Fig. 4 that as a result the combustion process theoretically *produces* excess energy of 52.38 GJ/tonne C_2H_4 . All of this energy cannot be converted into useful form but the inefficiencies that would inevitably exist would not be a bottleneck since

we produce significantly greater energy than required for separations. For instance, if 80% (30%) of the combustion energy could be converted to useful heat (electricity), the process would still produce excess heat beyond what is needed to drive the separations process. For our e-refinery separation process, we need 8.75 GJ electric energy and 44.35 GJ of heat per tonne of ethylene produced, which is obtainable using existing combined heat and power systems. This estimate of electricity required is based on the assumption that all energy associated with membrane separations and about 10% of flash tanks, adsorption and distillation combined is supplied in the form of electricity, the rest is heat. We would then have an excess of 17 GJ energy/tonne of ethylene produced in the form of useful heat. To put this in context, Alerte et al.[15] calculated a separation load (heating only) of 576 GJ/tonne C_2H_4 produced for a similar case that relied upon cryogenic distillation and absorption separations and did not include recycling of CO_2 . The excess energy could, of course, be used in a number of ways. One attractive use of this excess energy is the capture of CO_2 from the air to supply CO_2 to the e-refinery (CO_2 from the combustion system is insufficient; an external CO_2 source is still needed).

Overall, this process allows for efficient recycling of unreacted CO_2 from the electrochemical cell, which has an intrinsically low single pass conversion and generates sufficient energy in the process to power downstream operations. The product distribution can vary with the electrocatalyst and overpotential applied but this process can easily be customized to fit requirements imposed by the catalyst and reactor design. However, further research is required to develop highly selective sorbents for CO_2/C_2H_4 separation to improve process efficiency. We reiterate the need to increase focus on developing optimized separation processes for electrochemical reactions and consider separation challenges while evaluating their performance and scalability. We obtain a total carbon footprint of -0.46 g equivalent of CO_2/g ethylene produced. The details of this calculation are given in SI.

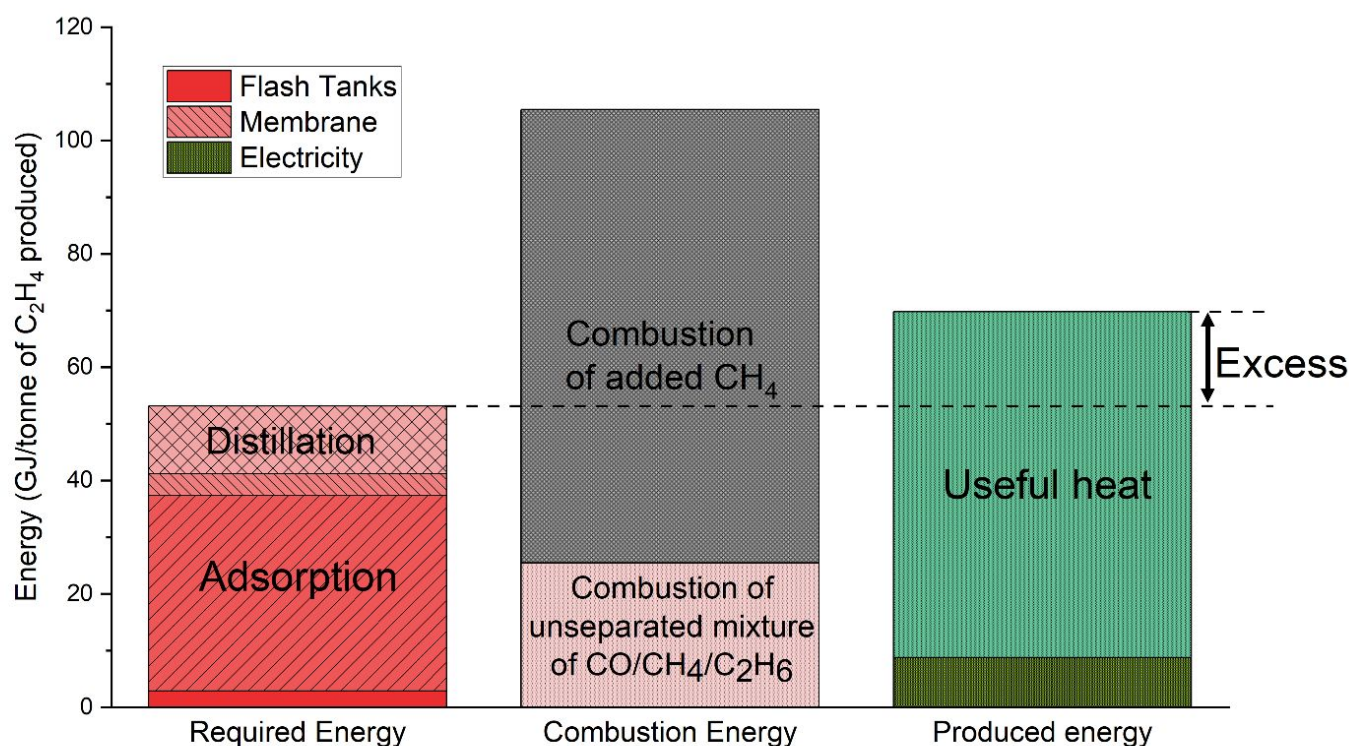


Figure 4: Breakdown of required and produced energy from the process shown in Fig. 2. The difference in required energy and produced useful heat is marked in black. This excess energy can be used to drive other processes in the plant, for example, an associated direct air capture plant to provide CO₂

Conclusions

We have shown how judicious use of downstream separations can greatly improve the efficiency of aqueous phase CO₂RR, particularly by allowing recycling of CO₂ in an electrocatalytic reactor that is not converted to desired products because of crossover to the anode or simply a lack of conversion at the cathode. We focused on a process that produces separate streams of ethylene, syngas, acetic acid, and ethanol as products. Our proposed process uses CH₄ as an input to enable combustion of some reaction products, but this combustion is performed without net CO₂ emissions and with net energy output.

Our process model made a number of simplifying assumptions, and it will of course be important in future refinement of this approach to understand the validity of these assumptions. For example, the adsorption and membrane separations we proposed were assumed to achieve highly selective separations, which led to a

process with nominally pure product streams. In practice, tradeoffs typically exist between the purity achievable with these separations and the capital and operating costs of the separations units. It will be important to explore these aspects in the future. It will also be important to test the performance of specific adsorbents or membranes for the complex chemical mixtures relevant to this process, including the presence of possible trace contaminants [16]. It is likely in a real process that achieving complete recycling of CO₂ is undesirable, since a purge stream may be required to prevent build-up of contaminants in the process. Finally, opportunities are likely to exist to increase the energy efficiency of the overall process by using careful heat integration among the multiple unit operations.

The idea of combining CO₂RR with CO₂ recycling raises several issues that are important for the burgeoning field of CO₂RR catalysts. Many reports in this area focus on the Faradaic efficiency of specific catalysts. While this quantity is of course important, our process points to

the need for catalyst studies to also report other quantities, including the product distribution of the cathodic reaction (preferably in mol %) and the amount of CO₂ crossover to the anode. Without these quantities it is not possible to consider the overall atom efficiency of CO₂RR or to quantitatively model the integration of a CO₂RR reactor with downstream separations. It is very likely that the optimal characteristics of electrochemical reactors for CO₂RR used in a process with downstream separations and recycle are markedly different from “single pass” reactors in which only a small fraction of the available CO₂ is converted to useful products.

Conflicts of interest

There are no conflicts to declare.

Additional Information

A US patent application on this process has been filed (U.S. Patent Application No. 63/340,513)

Acknowledgements

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