

## COMMUNICATION

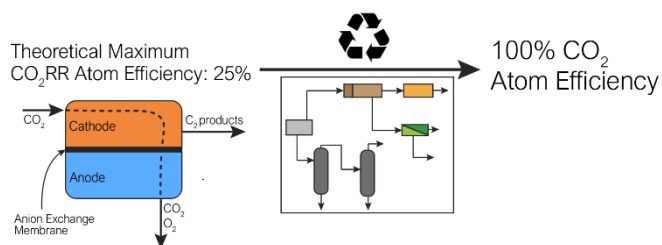
## Achieving Order of Magnitude Increases in CO<sub>2</sub> Reduction Reaction Efficiency by Product Separations and Recycling

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Accepted 00th January 20xx

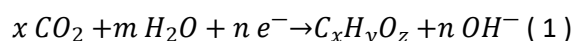
DOI: 10.1039/x0xx00000x

CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) 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 CO<sub>2</sub>RR reactors. We show that by strategic use of downstream separations and recycling of unreacted CO<sub>2</sub>, the efficiency of CO<sub>2</sub>RR can be significantly improved without changes in the electrochemical reactor.

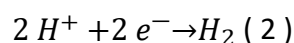
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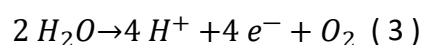
Performing CO<sub>2</sub> reduction reactions (CO<sub>2</sub>RR) using aqueous phase electrochemistry with the cathodic and anodic sides of a cell separated by an anion exchange membrane (AEM) has been widely studied.[1-6] CO<sub>2</sub>RR involves reducing carbon dioxide at a cathode using electrical 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 CO<sub>2</sub> 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 CO<sub>2</sub>RR 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, formic acid, methane or C<sub>2</sub>+ hydrocarbons), improving Faradaic efficiencies and increasing reactant conversion.[9, 11-14]

Despite the many papers on CO<sub>2</sub>RR, little attention has been given to the downstream processing of the reaction products.[15-19] This situation has led to several challenges and has largely resulted in the overall process efficiency of CO<sub>2</sub>RR 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

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

products are available.[17] This observation implies that downstream processing must be considered in any attempt to assess the energy efficiency of CO<sub>2</sub>RR processes. Second, only a fraction of the CO<sub>2</sub> at the cathode reacts, so some fraction of the CO<sub>2</sub> entering the reactor remains unused. Third, alkaline conditions must be maintained on the cathodic side of a CO<sub>2</sub>RR cell to suppress hydrogen evolution. In this alkaline environment, CO<sub>2</sub> reacts with OH<sup>-</sup> ions to produce HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>. These ions migrate to the anodic side via AEMs to maintain electroneutrality. In the acidic environment of the anode, HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> convert back to CO<sub>2</sub>. In electrochemical cells reducing CO<sub>2</sub> to C<sub>2</sub> hydrocarbons, *75% of the CO<sub>2</sub> entering the cell ultimately migrates to the anode, strongly limiting the single pass conversion of the cell* [18, 20, 21]. This feature of CO<sub>2</sub>RR processes seems almost entirely unappreciated in prior work [15, 18].

The observations above imply that in existing CO<sub>2</sub>RR processes the proportion of CO<sub>2</sub> 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<sub>2</sub> from point sources or via DAC will inevitably cost money, so emitting much of the resulting CO<sub>2</sub> from a conversion reactor without any effort to capture its value seems unwise.

The importance of considering downstream separations of CO<sub>2</sub>RR 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<sub>2</sub> conversion, cathodic Faradaic efficiency, and anodic CO<sub>2</sub> 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<sub>2</sub> will have been sourced from a dilute stream such that the cost of the CO<sub>2</sub> 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.

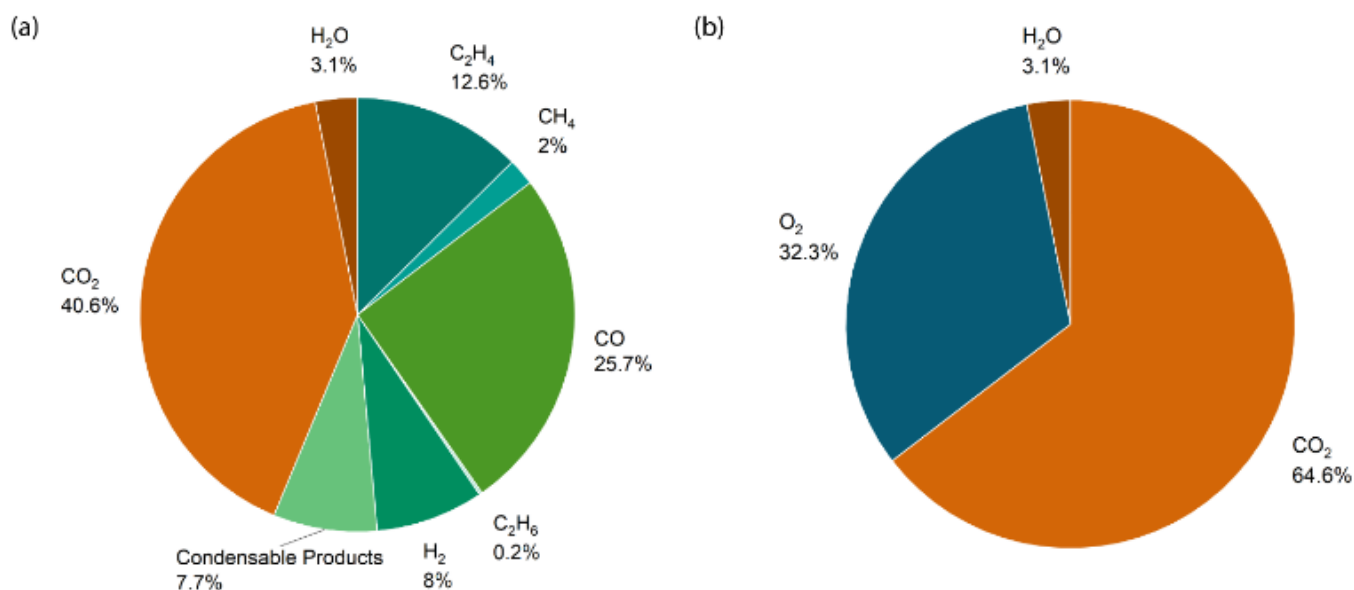
In this paper, we present a separation strategy that can enable dramatic efficiency increases in CO<sub>2</sub>RR. Most importantly, we develop concepts associated with recycling of downstream CO<sub>2</sub> into the electrochemical CO<sub>2</sub>RR process. The concept of recycling partially reacted products into a reactor is a key concept in chemical process development[22], but remarkably it does not seem to have been considered in the development of CO<sub>2</sub>RR 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<sub>2</sub>RR 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.

In addition to considering process schemes with CO<sub>2</sub> 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[23]. 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 CO<sub>2</sub>RR 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  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  in the product stream, since these gases are commonly obtained from side reactions along with  $\text{C}_2\text{H}_4$  [3, 6, 11, 12]. In addition to ethylene, we considered syngas, acetic acid, and alcohols as value-added byproducts of the process. The anode composition is calculated assuming 100% Faradic

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”  $\text{CO}_2$ , which as mentioned above accounts for the majority of  $\text{CO}_2$  fed into the reactor. This mixture is first fed to a flash tank to remove water. As previously mentioned, the estimates by Alerte et al. [15] showed that separating  $\text{CO}_2$  and  $\text{O}_2$  is by far the



**Figure 1:** Estimated composition in mole percent of mixtures exiting the (a) cathode and (b) anode in  $\text{CO}_2\text{RR}$ . The condensable products in (a) include acetic acid and alcohols, here, ethanol and propanol.

efficiency of the oxygen evolution reaction and  $\text{CO}_2$  crossover of 0.5 mol  $\text{CO}_2$ /mol electron. These values are conservative estimates, since in a real system the Faradaic efficiency will be less than 100% and the  $\text{CO}_2$  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.

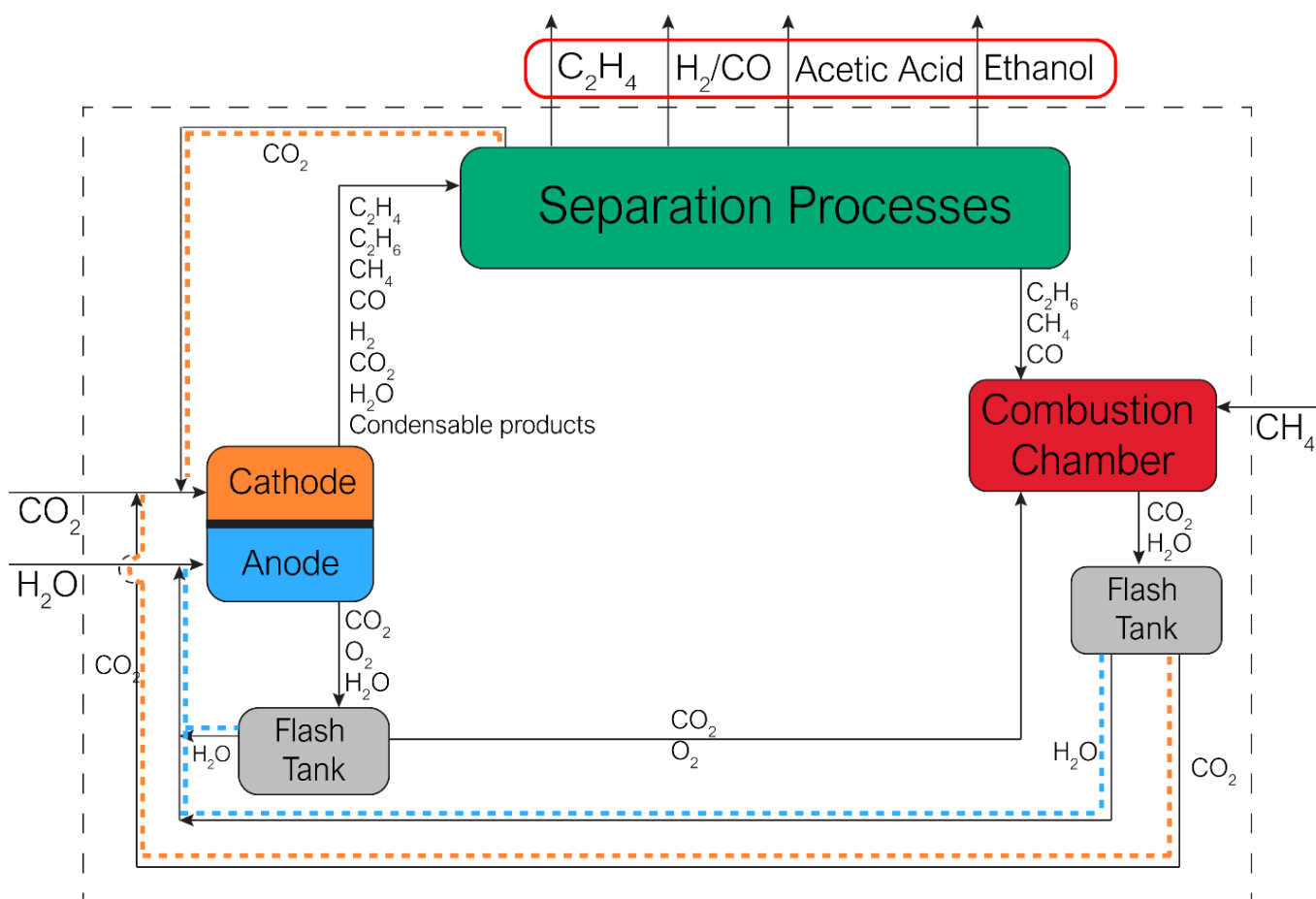
Figure 2 shows the overall schematic of the process we consider. Detailed mass and energy balances are described in the SI. The aim is to separate the mixture of products exiting the cathode to ultimately obtain ethylene, syngas, acetic acid, and ethanol as pure products while recycling carbon dioxide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

most energy intensive operation in their proposed downstream purification process to the point that these authors recommended simply venting this  $\text{CO}_2$ -laden mixture. Instead of applying an energy-intensive separation to this  $\text{CO}_2/\text{O}_2$  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.  $\text{CO}_2$  and  $\text{H}_2\text{O}$  produced as a result of combustion are recycled back to the reactor.

No  $\text{CO}_2$  remains in the streams exiting the process in Fig. 2. We noted above that the atom efficiency for the  $\text{CO}_2\text{RR}$  reactor considered here is at best 10% (i.e., the single pass conversion). The addition of the downstream separations and  $\text{CO}_2$  recycle in our process increases this atom efficiency by approximately an order of magnitude to nearly 100% overall conversion of  $\text{CO}_2$ . The process

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  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{CH}_4$ ,  $\text{CO}$ ,  $\text{H}_2$  and  $\text{CO}_2$  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  $\text{C}_2\text{H}_4$  and  $\text{CO}_2$ . Literature data indicates that zeolite CaX fits this



**Figure 2:** Schematic process flow diagram for a combined  $\text{CO}_2\text{RR}$  reaction and separation system allowing recycling of  $\text{CO}_2$ . The anodic gases are used as oxyfuel for  $\text{CH}_4$  combustion, which provides heat and power to the separation systems. Products are circled in red. The  $\text{CO}_2$  and  $\text{H}_2\text{O}$  recycle streams are accompanied by dashed orange and blue lines respectively to assist in tracing the streams.

uses  $\text{CH}_4$  combustion as part of the downstream processes, but this combustion does not lead to net  $\text{CO}_2$  emissions because all  $\text{CO}_2$  in the process is converted to products.

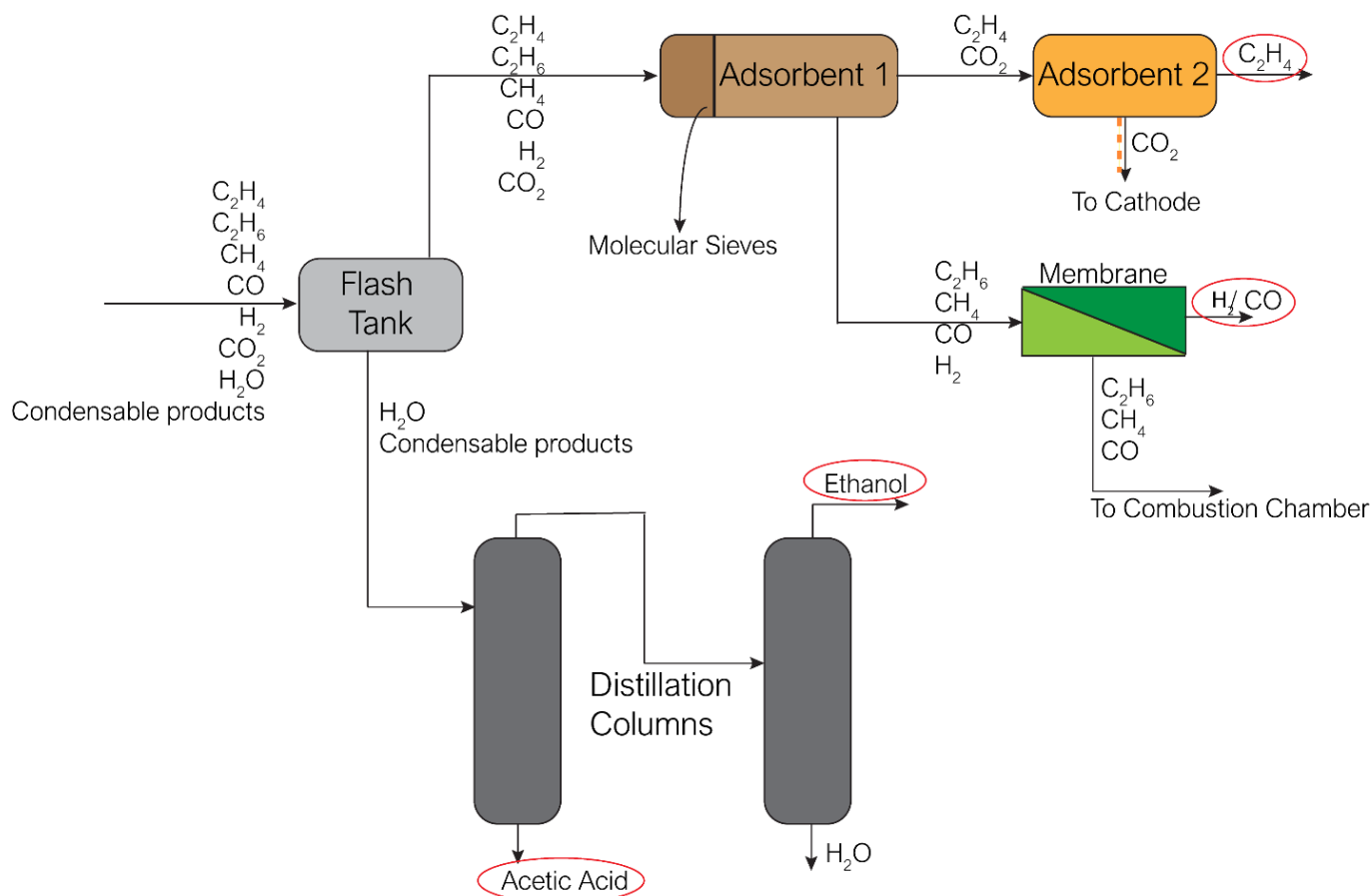
To perform quantitative mass and energy balances, details of the separations processes in Fig. 2 need to be specified. The separation unit operations we used for

requirement well[24]. The mixture of  $\text{C}_2\text{H}_6$ ,  $\text{CH}_4$ ,  $\text{CO}$  and  $\text{H}_2$  obtained above is then passed through a hydrogen selective polymeric membrane like cellulose acetate or polyimide[25, 26] to obtain syngas.

The other output from the first adsorbent bed is a mixture of  $\text{C}_2\text{H}_4$  and  $\text{CO}_2$ . 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  $\pi$  electron interactions to selectively adsorb ethylene.[27] Bachman et al. [24] reported single component

Mass and energy balances for the resulting process were performed using the ASPEN HYSYS software. These calculations make a number of simplifying assumptions, and it clearly would be interesting to further optimize these calculations in the future. Operating temperatures



**Figure 3:** Details of the downstream separations indicated in Fig. 2. Products are highlighted by red ellipses. Adsorbent 1 selectively adsorbs  $\text{CO}_2$  and  $\text{C}_2\text{H}_4$  from the mixture and Adsorbent 2 is selective for  $\text{C}_2\text{H}_4$  over  $\text{CO}_2$ . An orange dashed lines indicates the recycle stream for  $\text{CO}_2$ .

isotherms of  $\text{C}_2\text{H}_4$  and  $\text{CO}_2$  at room temperature for open metal site MOFs from the  $\text{M}_2(\text{m-dobdc})$  ( $\text{M} = \text{Fe}, \text{Mn}, \text{Ni}, \text{Mg}, \text{Co}$ ) series. We used  $\text{Ni}_2(\text{m-dobdc})$  as the second adsorbent in our process model.  $\text{Mn}_2(\text{m-dobdc})$  and  $\text{Fe}_2(\text{m-dobdc})$  MOFs show higher selectivity than  $\text{Ni}_2(\text{m-dobdc})$  but require inert atmospheres for synthesis and storage, which make them less ideal for practical use.[24, 28]

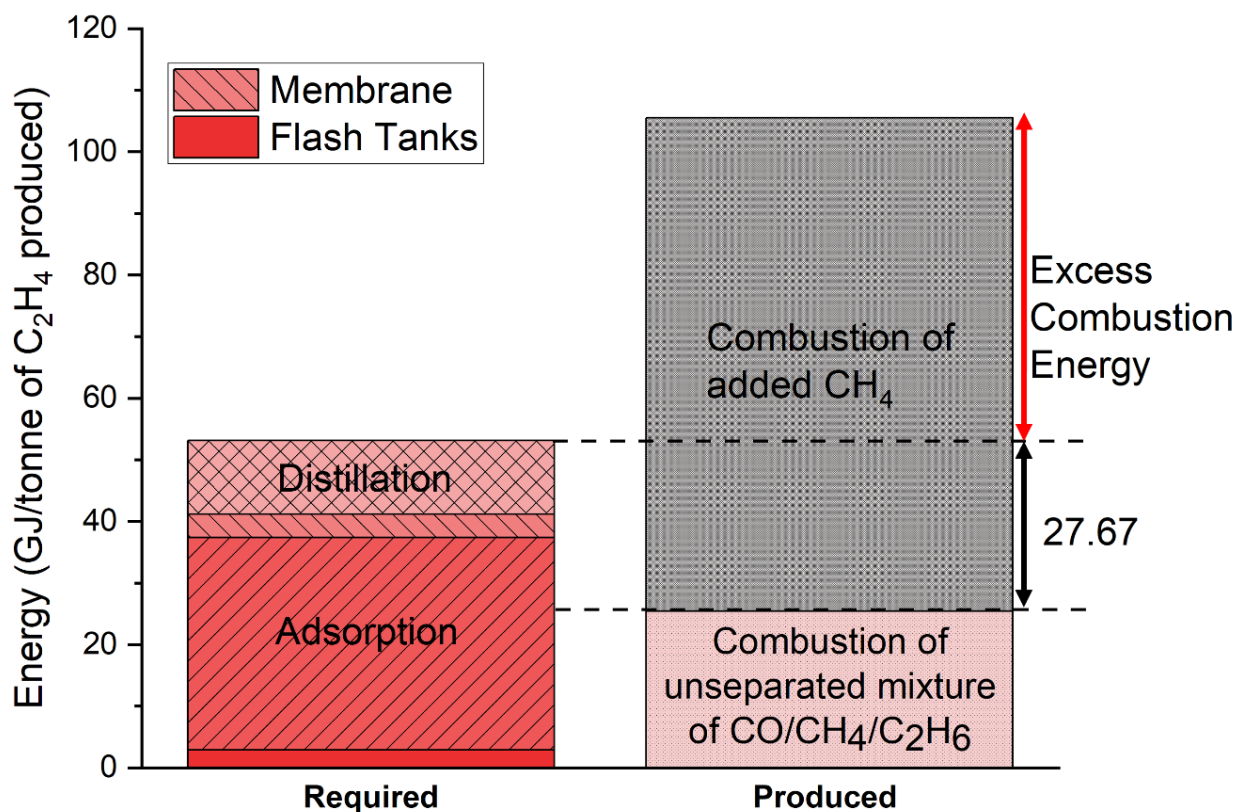
The aqueous mixture of condensable products leaving the cathode-side flash tank in Fig. 3 are separated to obtain useful fractions via distillation. These columns produce acetic acid and azeotropic mixture of alcohols (here, mostly ethanol) as byproducts.

for the flash tanks were selected to  $-14, 4$  and  $3.6$  °C for the flash tanks for cathodic gas mixture, anodic gas mixture and post combustion mixture, respectively. The adsorbents were chosen based on the work of Bachman et al [24]. Single component isotherms for  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{CO}_2$ ,  $\text{CO}$  and  $\text{CH}_4$  for  $\text{CaX}$  and  $\text{Ni}_2(\text{m-dobdc})$  were digitized (Figure S3 and S4) and fitted to a Dual Site Langmuir-Freundlich Isotherm equation (Table S5 and S8). Ideal Adsorbed Solution Theory [29, 30] was employed to obtain estimate gas adsorption isotherms for all mixtures. We assumed that hydrogen does not adsorb in  $\text{CaX}$  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  $H_2$  and  $CO$  in the syngas produced by our process. We assumed the use of a cellulose acetate membrane[25] with a  $H_2/CO$  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.[31, 32].

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 27.67GJ/tonne  $C_2H_4$  less than is required for the separations. 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  $CO_2$ . A key part of our proposed process is the use of  $CH_4$  combustion to avoid an energy-intensive separation of  $CO_2$  and  $O_2$ . The amount of  $CH_4$  required for this purpose is driven by the stoichiometry of the process, and it can be seen in Fig. 4 that as a result the overall process produces excess energy of 52.38 GJ/tonne  $C_2H_4$ . This



**Figure 4:** Breakdown of required and produced energy from the process shown in Fig. 2. The difference in produced energy and energy obtained from combustion of unseparated species is marked in black.

excess energy could of course be used in a number of ways. One attractive use of this excess energy is the capture of CO<sub>2</sub> from the air to supply CO<sub>2</sub> to the e-refinery (CO<sub>2</sub> from the combustion system is insufficient; an external CO<sub>2</sub> source is still needed).

Overall, this process allows for efficient recycling of unreacted CO<sub>2</sub> 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<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> 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.

## Conclusions

We have shown how judicious use of downstream separations can greatly improve the efficiency of aqueous phase CO<sub>2</sub>RR, particularly by allowing recycling of CO<sub>2</sub> 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 CH<sub>4</sub> as an input to enable combustion of some reaction products, but this combustion is performed without net CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub>RR with CO<sub>2</sub> recycling raises several issues that are important for the burgeoning field of CO<sub>2</sub>RR 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 CO<sub>2</sub> crossover to the anode. Without these quantities it is not possible to consider the overall atom efficiency of CO<sub>2</sub>RR or to quantitatively model the integration of a CO<sub>2</sub>RR reactor with downstream separations. It is very likely that the optimal characteristics of electrochemical reactors for CO<sub>2</sub>RR 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 CO<sub>2</sub> is converted to useful products.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

This work was supported by the Center for Understanding and Control of Acid Gas-Induced Evolution of Materials for Energy (UNCAGE-ME), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Award No. DE-SC0012577.

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