High pressure electrochemical CO_2 reduction to ethanol – Downstream separation process and economics

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1. Introduction

Recycling of emitted CO_2 is a crucial approach to reduce CO_2 emissions and prevent the associated global warming. Since the electrochemical reduction of CO_2 (CO_2RR) is very flexible and offers a high product diversity, it is one of the most attractive recycling options.[1] In research, CO_2RR at high pressure and ambient pressure are currently being investigated. The CO_2RR is typically performed in an electrolysis cell. The cell is divided by a membrane into two sections, the cathode and anode compartments. In the anode compartment, H_2O is reduced to H^+ ions and O_2. The H^+ ions diffuse through the membrane and reduce CO_2 to organic products at the cathode. This results in two independent product streams that require downstream processing for further use. In the product stream from the cathode compartment, a variety of products such as alcohols, carboxylic acids, aldehydes, alkenes, carbon monoxide and hydrogen can be found. The product stream from the anode compartment essentially contains water and oxygen. In order to improve the electrolysis process, there is currently a high need to improve the product selectivity of the reaction. Furthermore, the overall product yield, which depends on the current density, must be improved.

Despite the great need for improvement in the reaction system, it makes sense to develop and evaluate processes for product separation now, as these can significantly influence the cost-effectiveness of the overall process. Various techno-economic assessments for CO_2 reduction already exist in the literature. Different target products, such as formic acid, carbon monoxide, ethylene or ethanol, are used as the basis for evaluation. [2,3,4] In addition, either literature values of the reaction or idealized reaction systems are used as a basis for calculating the product stream composition.[3,4] To our knowledge there are no references that compare the downstream processes of a high-pressure and low-pressure CO_2RR.

Therefore, this work will compare the downstream processes for CO_2RR at high pressure with those at low pressure. For this purpose, an idealized reaction is assumed in order to illustrate the influence of the downstream process on the overall system even under ideal reaction conditions. A current density of 300 mA/cm², an ethanol faraday efficiency of 80% and water, hydrogen and oxygen as by-products are assumed.

2. Materials and Methods

The Aspen Plus® software is used to design the downstream processes. The mass and energy balances and the size of the equipment are also determined using Aspen Plus®. With these balances, the downstream process of high- and low-pressure electrochemical reduction can be evaluated according to the Technical Readiness Level TRL 3-4. The investment costs of the entire downstream process are determined according to the guidance for "techno-economic evaluations based on the TRL" by Buchner et al.[5] Finally, the energy consumption for the reaction and downstream process are compared.

3. Results and discussion

Even though the separation process under high pressure and low pressure differ from each other when viewed in detail, the processes run similarly in basic principle. Therefore, a principle flow diagram is shown in figure 1. First, carbon dioxide is fed to the cathode compartment of the reactor and water is fed to the anode compartment. After the reaction, the oxygen-water mixture exiting the anode compartment is separated using a flash evaporator. For the cathode compartment, the liquid products

water and ethanol are separated from the gases carbon dioxide and hydrogen also in a flash evaporator. The gases are then separated by cryogenic distillation, while the azeotropic mixture of ethanol and water is purified by three different methods. These are the vacuum rectification, pressure swing
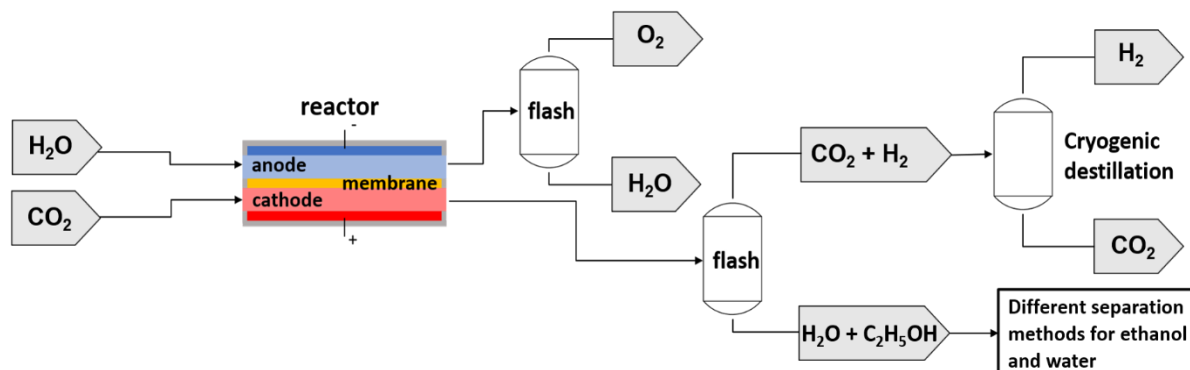

Figure 1. Basic flow diagram of the downstream process.

rectification and extractive rectification. These three processes achieve different yields and purities of the target product ethanol. In addition, the energy consumption per kilogram of ethanol produced is different. The values are compared in Table 1. It should be noted that the values always refer to the entire downstream process (separation of H_2O-O_2, CO_2-H_2, water-ethanol). The reaction is not considered.

Table 1. Comparison of the purification methods at ambient pressure.

Separation method	Yield of Ethanol	Purity of Ethanol	Energy demand [MJ/kg]
Vacuum rectification	85 %	96.9 %	10.91
Pressure swing rect.	9 %	99.9 %	14.53
Extractive rectification	83 %	99.9 %	15.01

Vacuum rectification achieves the highest ethanol yield with the lowest energy requirement, but the maximum purity is just 96.9 %. If a higher purity is required, the pressure swing rectification can reach a purity of 99.9 % with 33 % higher energy requirements but only at a yield of 9 %. In comparison, extractive rectification requires slightly more energy (15.01 MJ/kg) than pressure swing rectification but also achieves 99.9 % purity and a yield of 83 %. Apart from this, there is an additional special possibility with the extractive rectification. In the low-pressure range, ethylene glycol is used as the extractant. In the high-pressure range, it is possible to use CO_2 as the extractant, which is needed anyway due to the reaction.

When comparing the energy demand of the downstream processes with that of the reaction, which is 94 MJ/kg, it can be seen that product preparation requires only about 10-14 % of the total energy demand.

4. Conclusion

Based on the results, it can be seen that the energy requirement for the downstream process is significantly lower than for the reaction itself. The comparison of the downstream process at high pressure with that at low pressure is currently in progress.

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