Conceptual Process Design for Hydrogenating Carbon Dioxide to Produce Ethanol

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Abstract

Global warming and the energy crisis have become some of the most significant challenges facing the world today. With the finite nature of fossil fuels and ever-increasing carbon emissions, there is an urgent need to transition to renewable energy sources to mitigate the irreversible impact on our planet. This study aims to design a process flowsheet for ethanol synthesis by carbon dioxide hydrogenation using Aspen Plus. Ethanol serves a dual purpose as a renewable energy carrier and a fuel, aligning with Carbon Capture and Utilization (CCU) and contributing to carbon reduction efforts.

**Keywords**: Global warming, CO2 hydrogenation, Ethanol synthesis, Process design, Aspen Plus.

* 1. Introduction

Nowadays we are facing the challenges of global warming and energy shortages. Conventional energy production methods, such as fossil fuels, are major contributors to increased CO2 emissions, a primary greenhouse gas. In response to these issues, this study focuses on hydronation of CO2 to synthesize ethanol, which satisfies the concept of Carbon Capture and Utilization (CCU). Ethanol serves two primary purposes. Firstly, ethanol’s liquid state under normal conditions and its limited flammability in the air make it a potential candidate for energy carrier within the renewable energy supply chain. However, a comprehensive evaluation is needed when compared to other energy carriers like methanol and ammonia. Secondly, ethanol can also function as a fuel, combusting with oxygen. Moreover, CO2 hydrogenation to synthesize ethanol doesn't compete with food supplies, a key distinction from conventional starch fermentation. Thus, the investigation into ethanol synthesis through CO2 hydrogenation is a promising studying.

The overall framework is shown in Figure 1,including both export and import sides, and illustrates the entire ethanol supply chain. The process uses two reactants - hydrogen and carbon dioxide. Hydrogen comes from renewable energy sources through water electrolysis and carbon dioxide comes from carbon capture. Once ethanol has been synthesized, the intermittent nature of most renewables means that the storage and transport part is essential. When ethanol as an energy carrier arrives on the import side, it can be used in two ways as described above. This study will focus on the synthesis part of ethanol.



Figure 1. The overall framework of the synthesis and use of ethanol

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		1. Thermodynamic Models & Chemical Reactions

The process of hydrogenating carbon dioxide is simulated by Aspen Plus using two thermodynamic models: the Peng-Robinson equation of state in the reaction section and the UNIQUAC model with Henry’s constant in the separation section.

A total of three reactions are considered in this study: the reverse Water Gas Shift reaction (rWGS), the ethanol (EtOH) synthesis, and the Methane Steam Reforming (MSR). All have been verified, and further details are given below. The rWGS reaction is provided in the work of Zhang *et al.*[ 4 ] and Vendas and Maria[ 5 ].

|  |  |
| --- | --- |
| $$ CO\_{2}+ H\_{2} ⇌CO+ H\_{2}O$$ | (1) |

The EtOH synthesis reaction includes five reactions provided by Portillo *et al.*[ 6 ]. All of them are assumed to be irreversible except the rWGS reaction (6).

|  |  |
| --- | --- |
| $$ CO+ 2H\_{2}\rightarrow CH\_{3}OH$$ | (2) |
| $$ CO+ 2H\_{2}+CH\_{3}OH\rightarrow C\_{2}H\_{5}OH+H\_{2}O$$ | (3) |
| $$ CO+ 2H\_{2}+C\_{2}H\_{5}OH\rightarrow C\_{3}H\_{7}OH+H\_{2}O$$ | (4) |
| $$ H\_{2}+CH\_{3}OH\rightarrow CH\_{4}+H\_{2}O$$ | (5) |
| $$ CO+ H\_{2}O ⇌CO\_{2}+ H\_{2}$$ | (6) |

The MSR reaction includes two reactions, which utilize the power-law model (Eq. 7 - Eq. 8) provided by Chen *et al.*[ 7 ].

|  |  |
| --- | --- |
| $$ CH\_{4}+ H\_{2}O\rightarrow CO +3H\_{2}$$ | (7) |
| $$ CH\_{4}+2H\_{2}O\rightarrow CO\_{2}+4H\_{2}$$ | (8) |

* + 1. Process Statements

This study includes two distinct designs, each detailed in the process block flow diagrams shown in Figure 2 and Figure 3.

In Design 1, shown in Figure 2, CO2 is hydronated to syngas in the rWGS reactor using a Pt-based catalyst. Subsequently, syngas is converted to ethanol in the EtOH synthesis reactor using an alkali-Co doped MoS2 catalyst. The low conversion of CO and selectivity of ethanol results in the need to recycle the stream exiting the EtOH synthesis reactor for sending back to the EtOH synthesis reactor. However, the development of Design 1 reveals the presence of significant methane, necessitating a purge process. The purged gas includes methane and reactants (CO2, CO, H2), leading to the wastage of valuable reactants and contributing to process inefficiency. Consequently, this finding has promoted the development of Design 2.

In Design 2, shown in Figure 3, in addition to the reactions mentioned in Design 1, we introduce the MSR reaction to solve excessive methane, turning methane into CO2, CO, and H2. This reaction occurs in the MSR reactor, positioned after the EtOH synthesis reactor, and the exiting stream of the MSR reactor is recycled to the rWGS reactor. The methane is completely consumed after the MSR reactor, eliminating the need for a purging process. Moreover, the consumption of reactants is decreased, and the amount of ethanol is increased. Thus, we can use fewer reactants to produce more ethanol. Figure 4 depicts the details of Design 2.



Figure 2. The block flow diagram of Design 1Figure 3. The block flow diagram of Design 2



Figure 4. Process flow sheet of Design 2

* 1. Conclusion

This study simulates the process of CO2 hydrogenation to ethanol, offering a promising solution to the challenges posed by global warming, carbon emissions, and the need for renewable energy sources. The reactant, CO, undergoes an initial conversion to syngas through the reverse water-gas shift (rWGS) reaction, as CO hydrogenation to ethanol is thermodynamically more favorable. Both the thermodynamic model and kinetic parameters used in the process have been thoroughly verified.

Through exploration of various reaction pathways and designs, the study evolves from an initial process (Design 1) to an enhanced version (Design 2). Design 2, incorporating the Methane Steam Reforming (MSR) reaction, effectively mitigates excessive methane production, reduces the need for a purge stream, and minimizes reactant wastage. This modification results in decreased reactant consumption, increased ethanol production, and improved purity. The simulation results, presented in Table 1, indicate a 21% reduction in H2 consumption, a 52% reduction in CO2 consumption, and a 43% increase in ethanol production compared to Design 1, and the final purity of ethanol is 99.5% (mol%) These findings underscore the potential of CO2 conversion into ethanol as a sustainable and efficient pathway for renewable energy and carbon reduction.

For future work, there is a need for in-depth research on optimizing the CO2-to-ethanol process. This involves refining and fine-tuning the various stages of the process to enhance efficiency and overall performance. Additionally, efforts should be directed towards seamless integration of CO2-to-ethanol processes into the renewable energy supply chain. This integration calls for the development of advanced methods for the storage, transportation, and reforming of ethanol. Efficient and sustainable solutions in these areas are crucial for the successful incorporation of ethanol as a renewable fuel within the broader energy infrastructure. Furthermore, exploring the multifaceted role of ethanol as an energy carrier and investigating its diverse applications within the supply chain will be paramount. By placing a strong emphasis on process optimization and integration, future research endeavours can significantly contribute to the creation of a more sustainable, resilient, and environmentally friendly energy ecosystem.

Table 1. simulation results

|  |  |  |
| --- | --- | --- |
| **Process** | **Design 1** | **Design 2** |
| **mole flow rate (kmol/h)** | **H2** | 170 | 134.5 |
| **CO2** | 105 | 50 |
| **ETOH** | 12.25 | 17.48 |
| **purity** | **ETOH** | 0.98 | 0.995 |

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