CO2 hydrogenation to methanol over Cu/ZnO/Al2O3 commercial catalyst: a techno-economic-environmental study

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ABSTRACT

In this work, the sustained catalytic hydrogenation of CO2 to methanol using the commercial catalyst Cu/ZnO/Al2O3 is investigated. The process uses pure CO2 from cryogenic, while hydrogen is purchased. The process which was simulated using Aspen Plus yielded methanol with purity ≥o 99 %, as well as a methanol selectivity of 99 %. The process was further researched economically and environmentally and findings showed that the proposed process is a viable option for use in the biomass value chain.

Keywords: CO2 capturing, feasibility, added-value products e

1 INTRODUCTION

Carbon dioxide (CO2) is the most significant contributor to global greenhouse gas emissions, which contribute to climate change. CO2 emissions to the atmosphere can occur naturally or because of human activity such as the industrial use of fossil fuels and derivatives, electricity generation, heat production, and transportation (Ahmad & Upadhyayula2020a). As a result, carbon capture and storage (CCS) and carbon capture and utilization (CCU) technology deployment are critical (Ahmad & Upadhyayula2020b).

Because of the maturity of existing catalyst systems, CO2 hydrogenation to methanol has been one of the most promising CO2 utilization processes in the industry over the past 10-15 years. Methanol can be utilized as a solvent and feedstock in the chemical industry, as well as a cleaner transportation fuel (Wang et al., 2017). By 2025, the worldwide methanol market is expected to reach $26 billion.

Methanol can be made from CO2 utilizing both homogeneous and heterogeneous catalytic systems, with the reaction route mostly determined by the catalyst (Yang Et al., 2010). As a result, this feasibility study presents a techno-economic-environmental assessment of the CO2 hydrogenation to methanol process employing the commercial Cu/ZnO/Al2O3 catalyst. Finally, the optimized process is assessed in terms of environmental and economic factors.

2 1. PROCESS DESCRIPTION

Figure 1 depicts the suggested CO2 utilization of methanol. At 12.3 °C and 47.63 pressure, this uses 76.46 kmol/hr of CO2. Additionally, 535.22 kmol/hr of hydrogen supplied at 25 °C and 30 bar is required as a feedstock for the process. The CO2 hydrogenation to methanol process consists of three main sections: (1) feed preparation to meet reaction conditions; (2) catalytic CO2 hydrogenation reaction to methanol in a single reactor; and (3) methanol purification to achieve methanol purity greater than 98%.

The compressed and heated CO2/H2 mixture fed to a single fixed bed plug flow reactor, with inlet specifications of 75.7 bar and 21, For catalytic CO2 hydrogenation to methanol, the compressed and heated CO2/H2 mixture was fed to a single fixed bed plug flow reactor with inlet specifications of 75.7 pressure and 210 °C. Both isothermal reactors use 44,500 kg of commercially available Cu/ZnO/Al2O3 catalyst and are simulated and tested for comparison. Table 1 shows the characteristics of the catalyst that was employed in the simulation. 0 °C, for catalytic CO2 hydrogenation to methanol. Isothermal reactors are simulated and tested for comparison wherein both reactors utilize 44,500 kg of the commercially available Cu/ZnO/Al2O3 catalyst. The characteristics of the catalyst used in the simulation are illustrated in Table 1.

Table 1 Catalyst characteristics (Van-Dal & Bouallou,

Density	1775 Kg_{cat}/m^3_{cat}
Fixed bed porosity	0.5
Mass	34.8 g
Pellet diameter	0.0005 m

The gases leaving the reactor are then fed to a knock-out drum (KO101) to separate the unreacted reactants from products.

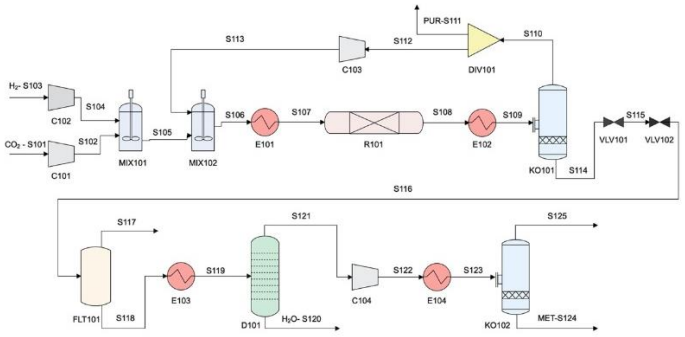

Figure 1: CO2 to methanol process flowsheet created by aspen plus

3 RESULTS AND DISCUSSION

The simulation results indicate that optimal operating feed conditions of 210 °C and 75 bar resulted in CO2 conversion of 99% and methanol yield of 98%. Fundamentally, recycling a fraction of unreacted gases back to the reactor contributed in reaching achieving higher CO2 conversion as previously reported by Leonzio et al. (2019). On the other hand, in the proposed process, increasing the feed pressure up to 75.7 bar and specifying reactor pressure at 75 bar played a vital role in enhancing the synthesis of methanol as the forward reaction is more favorable based on le chatelier's principle.

Both adiabatic and isothermal reactors for CO2 hydrogenation were simulated under the same feed conditions, the temperature of 210°C and pressure of 75.8 bar, the same catalyst characteristics, and reaction kinetics to investigate the influence of the reactor type and characteristics on CO2 conversion and product yield. As illustrated in Table 2, the results show that an adiabatic reactor exhibited a slightly lower CO2 conversion; however, the methanol yield and selectivity were improved. Additionally, the major difference between the two reactors was the required heat duty and residence time wherein the residence time can be reduced by around 50% when choosing an adiabatic reactor. This justifies that for this process, an adiabatic reactor is favorable. Consequently, the adiabatic reactor was further analyzed under varied conditions to evaluate the impact of H2 molar flow rate in the feed, reactor temperature, and reactor pressure on methanol production.

Table 2 Simulation results of isothermal and adiabatic reactors for the CO_2 hydrogenation to methanol under fixed feed conditions

	Isothermal reactor	Adiabatic reactor
CO_2 conversion%	96.26	95.66
Methanol Yield%	98.84	99.84
Methanol Selectivity%	98.85	98.91
Heat duty (KJ/hr)	-46.46 E+5	20.94
Residence time (hr)	1.102	0.568

3. Economic Analysis

After optimizing the utilities requirements of the proposed process and reducing the total utilities by around 63%, the optimized plant was evaluated economically. The economic performance indicator, net present value (NPV) was considered to evaluate the profitability of the methanol synthesis process:

$$NPV = \sum_{t=1}^{n} \frac{CF_t}{(1+i)^t} \quad (12)$$

Where CF is the cashflow for a given year t, n is the project life in years, and i is the target rate of return on the investment. For this plant, a project lifetime of 20 years was assumed, with a return of investment of 8%.

In this plant, the revenues are mainly due sales of liquid methanol to the North American market, at an average price of 692 $/MT (Methanex Corporation, 2021). CO_2 is produced as a by-product from a parallel biogas cryogenic process and utilized to enhance the economic performance of the overall project. The economic analysis reveals that the project is profitable where an NPV of $6.5 million was estimated for the methanol plant with 23.4 kt/yr production capacity operated for 20 years. Additionally, the payback period was calculated as 9 years.

potential of algal cells for bioethanol production was investigated utilizing S. cerevisiae as a biocatalyst in a variety of fermentation processes. The goal of the project was to evaluate and improve bioethanol production from released algal sugars. Bioethanol yields are depending on algal sugars, operational temperature, and fermenter pH, according to preliminary tests. Figures 1a,b, and c illustrate sugar consumption and bioethanol generation as a function of time at three distinct pHs (4, 5.5, 6.5, and 7) and temperatures of 30, 37, and 43 degrees Celsius. Fermenters operated with algal pretreated algal biomass that has high sugar content at pH= 5.5 and a temperature of 37 °C exhibited the highest bioethanol production of 0.145 ± 0.008 g/g DAB, followed by pH = 5 and temperature of 33 and (0.122 ± 0.004 g/gDAB) and latest pH 6.0 and temperature of 42°C (0.102 ± 0.002 g/g). Fermenters operating with algal pretreatment algae biomas with high sugar content at pH= 5.5 and 37 °C produced the most bioethanol (0.145 0.008 g/g DAB), followed by pH = 5 and temperature of 33 (0.122 0.004 g/gDAB), and pH 6.0 and temperature of 42°C (0.102 0.002 g/gDAB).

4 CONCLUSION

The designed process operates at 210 ºC and 75 bar for producing high purity methanol (>99%) under the presence of the commercial catalyst Cu/ZnO/Al2O3. Utilization of the CO2 by-product for methanol synthesis result in different advantages such as reducing the number of required equipment for treating and compressions which will influence the capital and operating costs of the overall project. The adiabatic reactor showed a slightly lower CO2 conversion yet improved methanol yield. Although increase in pressure improved the CO2 yield, the kinetic parameters were restricted for an application range up to 75 bar. The results raveled that H2 supply costs influence the project's profitability significantly due to the requirement of CO2/H2 ratio of 1:7. Consequently, H2 supplied from fossil fuels is economically feasible to achieve an NPV of $6.5 Million for a plant's capacity of 2.34 kt/yr and project's lifetime of 20 years.

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6 REFERENCES

Ahmad, K., & Upadhyayula, S. (2020a). Kinetics of CO2 hydrogenation to methanol over silica supported intermetallic Ga3Ni5 catalyst in a continuous differential fixed bed reactor. International Journal of Hydrogen Energy, 45(1), 1140–1150. https://doi.org/10.1016/j.ijhydene.2019.10.156

Ahmad, K., & Upadhyayula, S. (2020b). Selective conversion of CO2 to methanol over intermetallic Ga-Ni catalyst: Microkinetic modeling. Fuel, 278, 118296.

Wang, J., Li, G., Li, Z., Tang, C., Feng, Z., An, H., Liu, H., Liu, T., & Li, C. (2017). A highly selective and stable ZnO-ZrO2 solid solution catalyst for CO2 hydrogenation to methanol. Science Advances, 3(10), e1701290.

Yang, Y., Evans, J., Rodriguez, J. A., White, M. G., & Liu, P. (2010). Fundamental studies of methanol synthesis from CO 2 hydrogenation on Cu (111), Cu clusters, and Cu/ZnO (0001 [combining macron]). Physical Chemistry Chemical Physics, 12(33), 9909–9917.