materials proceedings

Proceeding Paper

Exergy Analysis of Methanol Production Plant from Hydrogenation of Carbon Dioxide †

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† Presented at the 6th Conference on Emerging Materials and Processes (CEMP 2023), Islamabad, Pakistan, 22–23 November 2023.

Abstract: Reducing greenhouse gas (GHG) emissions through carbon capture and conversion to fuel and other useful products is a focus of recent research. Among all fuels, CO_2 to methanol stands out for its efficiency and promise. To make the CO_2-to-methanol (CTM) process sustainable and efficient, it needs to be analyzed with respect to its thermodynamic potential. Conventionally, energy analysis was used, but exergy analysis is an advanced tool used for this purpose. In this study, the Aspen Plus-based CTM model was developed, and its exergy analysis was carried out. Physical exergy data are taken from Aspen Plus V.11, while an interface between Aspen Plus and Excel was used to calculate the exergy destruction, exergy efficiency, and the improvement potential of the process. All three sections of the CTM model were compared and it was observed that the separation section has the highest exergy destruction of 37,225.89 KW with an exergy efficiency and exergetic improvement potential of 76.17% and 8870.75 KW, respectively.

Keywords: CO_2 to methanol; exergy analysis; exergy destruction; exergy efficiency; improvement potential

Citation: Zulkefal, M.; Ayub, A.; Sethi, H. Exergy Analysis of Methanol Production Plant from Hydrogenation of Carbon Dioxide. *Mater. Proc.* **2024**, *17*, 15. https://doi.org/10.3390/materproc2024017015

Academic Editors: Sofia Javed, Waheed Miran, Erum Pervaiz and Iftikhar Ahmad

Published: 12 April 2024

1. Introduction

Human-made carbon dioxide emissions have seen a dramatic rise over the past century, primarily due to industrial processes. Reducing these CO_2 emissions is essential because its escalating emission has resulted in global warming, leading to adverse consequences like rising temperatures, melting glaciers, abnormal climate patterns, and elevated sea levels, potentially submerging coastlines and low-lying areas [1]. To tackle this issue, carbon capture and storage (CCS) and carbon capture and utilization (CCU) are the two pathways used, with CCU as the most promising one because solely capturing and storing CO_2 emissions can be energy-intensive and costly (CCS) [2], but transforming CO_2 into valuable chemicals (CCU) or fuels like methanol offers a more sustainable and economically viable approach. Methanol serves as a versatile platform chemical used in various industrial processes, including the production of olefins, formaldehyde, acetic acid, dimethylether, and methylamine [3]. By converting CO_2 into methanol, a waste product is effectively converted into a valuable resource, addressing both environmental and economic challenges. To enhance the thermodynamic efficiency of this process, exergy analysis can be employed. Exergy analysis can help to make the process efficient as exergy analysis, following the second law of thermodynamics, helps pinpoint inefficiencies in energy conversion processes by identifying where and why they occur [4]. It quantifies the maximum work possible from a reversible process when a system reaches equilibrium with its surroundings. Applying exergy analysis leads to process improvements, ensuring the sustainable use of limited natural resources and, consequently, the sustainability of various industries like cement [5], power generation [6], pulp and paper [7], steel [8], chemical [9,10], and food [11]. In this particular study, the CO_2-to-methanol (CTM) process exergy analysis is carried out to pinpoint the inefficiency of the process so that they can be addressed to optimize and make the process efficient. For the CTM process, Yang et al. [12] carried out advanced exergy analysis using Graaf's kinetic model and the Aspen Plus model with multistage hydrogen compression, while in this study, Vanden Bussche's kinetic model with a different Aspen Plus model having multistage CO_2 compression instead of hydrogen was used [13].

2. Materials and Methods

In this section, a brief explanation of process description and exergy analysis will be discussed.

2.1. Process Description

Aspen Plus software is used to develop a model for the CTM process. The CTM process is divided into three sections. In the preheating section, the carbon dioxide is compressed in four stages with intercooling. The compressed CO_2 is combined with compressed hydrogen and recycled gas. In the reaction section, this feed is reacted over a $Cu/ZnO/Al_2O_3$ catalyst to synthesize methanol. In the separation section, the reactor output is first cooled in heat exchangers, with heat integration to the distillation feed. Then, untreated gases are separated and largely recycled. The liquid stream is then depressurized and further purified in a distillation column to produce high purity methanol product. Heat is exchanged between the reactor output and column feed. The gaseous methanol product is then compressed, cooled, and sent to a flash tank to remove residual gases, yielding the final liquified methanol product. Figure 1 shows the CTM process flowsheet.

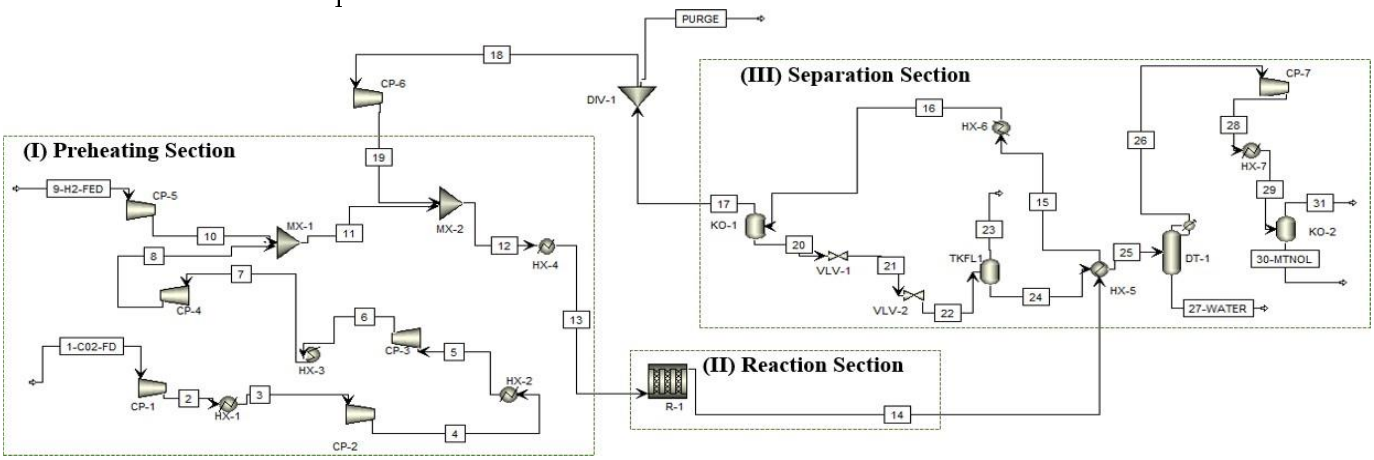

Figure 1. Process flowsheet of CO_2 hydrogenation to methanol [13].

2.2. Exergy Analysis Equations and Formulations

Exergy-based analysis integrates the principles of the first and second laws of thermodynamics to assess the energy-saving possibilities of a system. It quantifies the maximum useful work that can be extracted from a system, process, or substance when it is brought into equilibrium with its surroundings [14]. Different formulas can be used to find the exergy analysis and its performance indicators, as given in Table 1.

Table 1. Summary of formulas used in this work.

Formulas for Exergy Analysis and Its Performance Indicators	
$Ex_{ph} = m[(H - H_0) - T_0(S - S_0)]$	Physical exergy at standard conditions
$I = \sum Ex_{in} - Ex_{out}$	Irreversibility calculates the difference between exergy input and output in a process or system
$\eta = \frac{Ex_{out}}{Ex_{in}} \times 100$	Exergy efficiency measures how closely a system approaches ideal performance as a percentage
$IP = (1 - \eta)(Ex_{in} - Ex_{out})$	Exergetic improvement potential calculates the reduction in irreversibility achievable within a process

3. Results and Discussion

This section discusses the physical exergy analysis of the CTM model at 25 °C temperature and 101.325 kPa pressure.

Table 2 displays the highest six and lowest six equipment in terms of exergy efficiency for the CO_2 hydrogenation-to-methanol plant, along with their respective exergy destruction and exergetic improvement potential values. As only physical exergy is considered and chemical exergy analysis is not part of this work, because of this, the R-1* reactor has a negative exergy destruction, and its exergy efficiency exceeds 100%, as mentioned in the reported literature [15]. DIV-1 and KO-1 have perfect exergy efficiency with no exergy destruction, leaving no room for exergetic improvement potential as these are designed to carry out their functions without introducing energy losses or inefficiencies.

Table 2. Equipment's exergy destruction, efficiency, and improvement potential.

Equipment	Exergy Destruction (KW)	Exergy Efficiency (%)	Improvement Potential (KW)	Equipment	Exergy Destruction (KW)	Exergy Efficiency (%)	Improvement Potential (KW)
R-1*	−4490.86600	102.96	132.92236	CP-1	457.97617	78.44	98.71681
DIV-1	0.00000	100.00	0.00000	HX-4	53,771.94971	71.86	15,130.63269
KO-1	0.00000	100.00	0.00000	DT-1	744.69335	70.86	217.00320
MIX-1	64.17148	99.72	0.17822	VLV-1	319.34698	44.47	177.33476
CP-6	650.55879	99.45	3.54918	VLV-2	231.36874	9.53	209.32192
HX-6	782.22825	99.35	5.07421	HX-7	12,029.94934	0.25	11,999.66660

MIX-1, CP-6, and HX-6 also have good exergy efficiency with values of 99.72%, 99.45%, and 99.35%, respectively, leaving very minimum space for improvement, indicating their ability to efficiently convert input energy into useful work.

HX-4 stands out with the highest exergy destruction at 53,771.95 KW, leading to the highest improvement potential of 15,130.63 KW, despite its relatively good exergy efficiency of 71.86%. HX-7 shows the lowest exergy efficiency of 0.25%, but has an exergy destruction of 12,029.95 KW and exergetic improvement potential of up to 11,999.67 KW. The high exergy destruction of these heat exchangers is because these are exposed to significant temperature differences between process streams and because in this particular CTM model, the heat exchanger is not optimally designed and inefficient heat transfer occurs, leading to higher exergy destruction. Figure 2 shows the Grassmann diagram of all three sections of the CTM process where the line's width represents the quantity of exergy flow entering and exiting each section.

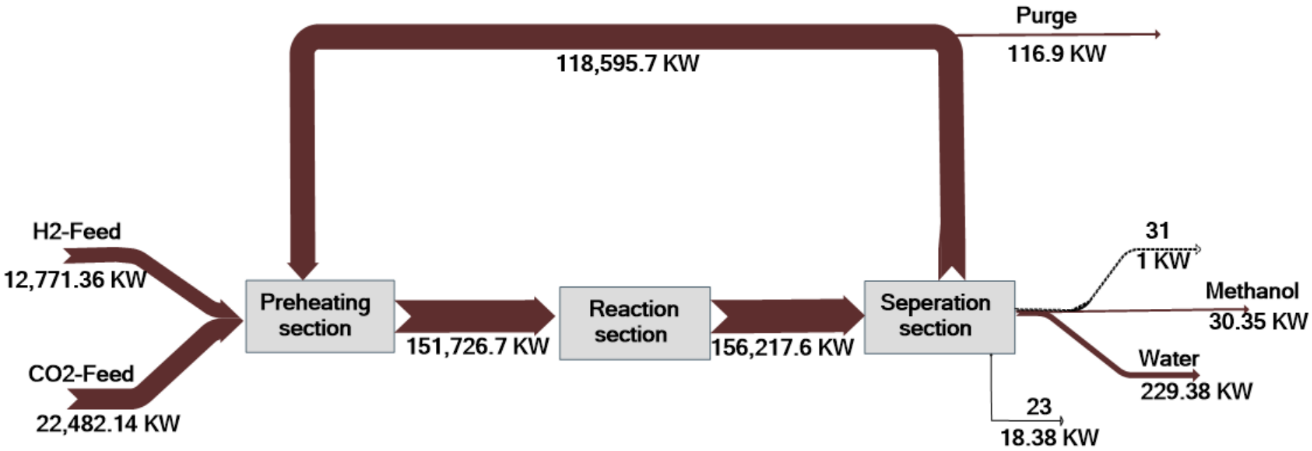

Figure 2. Grassmann diagram of all three sections of CTM plant.

4. Conclusions

The exergy analysis conducted on the CO_2 hydrogenation-to-methanol production plant helps to provide a valuable insight into its thermodynamic performance. The analysis mainly focused on physical exergy at standard conditions (25 °C and 101.325 kPa). It was observed that the equipment with the lowest exergy efficiency exhibits the highest exergetic improvement potential relative to exergy destruction. It was observed that the heat exchanger HX-7 showed the lowest exergy efficiency of 0.25%, while compressor KO-1 and DT-1 displayed perfect exergy efficiency of 100% due to its efficient isentropic compression process. This analysis helps in identifying equipment that can be optimized for improved thermodynamic performance. However, it is important to note that the analysis did not consider the chemical exergy associated with CO_2 hydrogenation reactions. Therefore, a more comprehensive evaluation in the future should incorporate chemical exergy to obtain a holistic understanding of the thermodynamic performance of the entire process.

Author Contributions: Conceptualization, M.Z.; methodology, M.Z. and A.A.; software, M.Z.; validation, M.Z., A.A. and H.S.; formal analysis, M.Z., A.A. and H.S.; investigation, M.Z.; resources, M.Z.; data curation, M.Z. and A.A.; writing—original draft preparation, M.Z., A.A. and H.S.; writing—review and editing, M.Z., A.A. and H.S.; visualization, M.Z. and A.A.; supervision, M.Z.; project administration, M.Z.; funding acquisition, M.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Dataset available on request from the authors.

Conflicts of Interest: The authors declare no conflict of interest.

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