The Conversion of Carbon Dioxide to Methanol Simulated by Aspen Plus

(Litong Wang 2023 J. Phys.: Conf. Ser. 2608 012048)

Literature review & Simulation reproduction submitted:

For

Applied Process Engineering-IV (CH309G)

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AIM:

This report presents a simulation study of the conversion of carbon dioxide (CO_2) to methanol (CH_3OH) using Aspen Plus V10, based on the methodology described by Litong Wang (2023). The primary objectives are:

- To replicate the original Aspen Plus process for methanol synthesis.
- To perform sensitivity analysis for process optimization.
- To improve methanol product purity from 96.0 wt% to 99.97 wt%.

This is achieved by adjusting key process parameters, including reactor conditions and distillation column specifications (such as the number of stages and reflux ratio), with a focus on enhancing purity, energy efficiency, and overall process performance.

In our literature review, we aim to analyse this paper and reproduce the Aspen simulation ourselves, to understand the process better.

THEORY:

This report presents a simulation study of the conversion of carbon dioxide (CO_2) to methanol (CH_3OH) using Aspen Plus V10. The model is based on the methodology described by Litong Wang (2023). The objective is to reproduce the original Aspen Plus process, perform sensitivity analysis for optimization, and achieve high-purity methanol production. The study includes process design, model assumptions, simulation settings, and energy analysis, culminating in improved methanol purity from 96.0% wt to 99.97% wt.

1. **Introduction**: With growing concerns over climate change and increasing levels of greenhouse gases, carbon capture, utilization, and storage (CCUS) has emerged as a critical technology for mitigating anthropogenic emissions. Among the greenhouse gases, carbon dioxide (CO_2) is the most significant contributor, primarily due to large-scale industrial

activities, fossil fuel combustion, and deforestation. In response, scientists and engineers are increasingly focusing on sustainable strategies to reduce and repurpose CO_2 emissions. One promising CCUS route is the conversion of captured CO_2 into valuable chemicals and fuels, providing both environmental and economic benefits. Among the various products that can be synthesized from CO_2, methanol (CH_3OH) stands out as a versatile and widely used chemical. Methanol is an important building block in the chemical industry, used for manufacturing formaldehyde, acetic acid, and various plastics. Additionally, methanol serves as an alternative fuel and hydrogen carrier due to its high energy density and liquid-state storage advantages.

Methanol synthesis from CO_2 is typically achieved through catalytic hydrogenation using a source of hydrogen gas (H_2). This process not only captures and utilizes CO_2 but also offers a pathway for integrating renewable energy, particularly when green hydrogen (from electrolysis powered by solar or wind) is used. However, the process must be carefully optimized to ensure high conversion efficiency and product purity while minimizing energy consumption and operational costs.

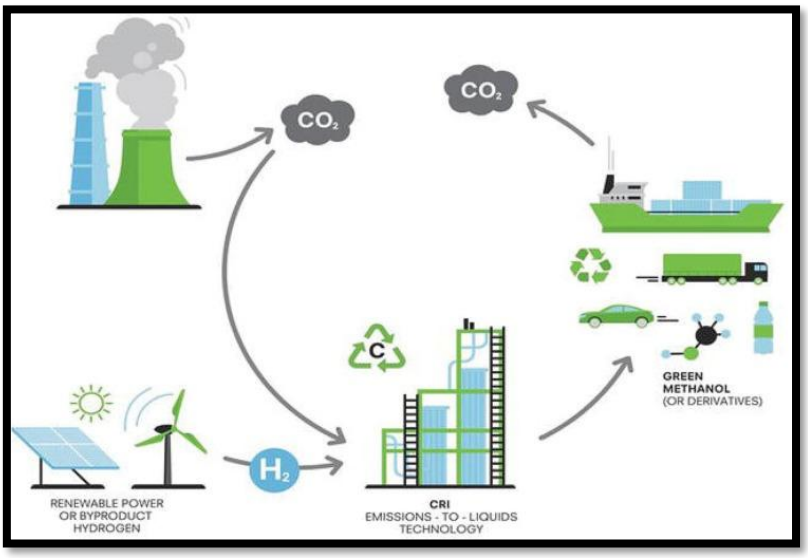

Fig 1: *Available challenges and recent progress in carbon dioxide capture, and reusing methods toward renewable energy, Zhang et al, Sustainable Energy Technologies and Assessments*

This report aims to replicate and analyze the CO_2-to-methanol conversion process described by Litong Wang (2023) using Aspen Plus. The simulation is used to explore the effect of process parameters such as reactor conditions and distillation column specifications. By adjusting the number of stages and the reflux ratio in the RadFrac distillation column, the study targets an enhancement in methanol purity. In doing so, the report provides insights into the feasibility and efficiency of this sustainable chemical pathway, highlighting opportunities for process improvement, energy integration, and future scalability.

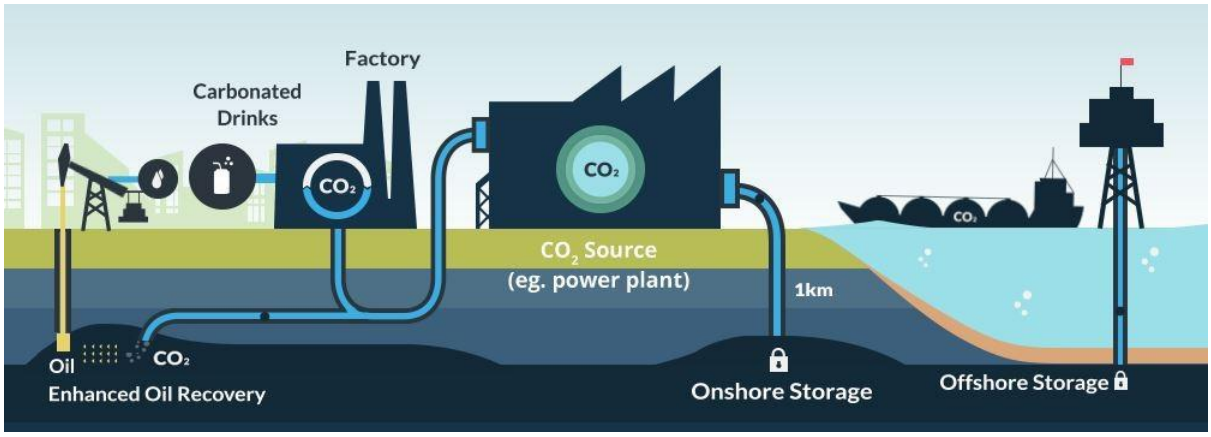

Fig 2: *CCUS Schematic: Ministry of Energy and Energy Industries, Trinidad & Tobago*

2. Methodology:

2.1.Objectives:

- Simulate the CO_2 hydrogenation process to methanol using Aspen Plus.
- Accurately reproduce the simulation from Wang (2023).
- Analyze and optimize process parameters for maximum methanol purity.
- Evaluate energy requirements and propose energy-saving modifications.
- Conduct a preliminary economic feasibility assessment.

2.2.Reaction Chemistry: The simulation considers three principal reactions involved in methanol synthesis:

- $CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O$ $\Delta H = -49.7$ kJ/mol (exothermic)
- $CO_2 + H_2 \rightleftharpoons CO + H_2O$ $\Delta H = +41.0$ kJ/mol (endothermic)
- $CO + 2H_2 \rightleftharpoons CH_3OH$ $\Delta H = -90.6$ kJ/mol (exothermic)

These reactions are implemented in an R-Plug reactor, with equilibrium conversion modelled under isothermal conditions.

2.3.Assumptions and Operating Conditions:

- The system operates under steady-state conditions.
- All gas species behave as ideal gases.
- Reactions occur in a single-phase vapor system.
- Heat losses and pressure drops in pipelines are negligible.
- The reactor operates at a fixed temperature (280°C) and pressure (77 atm).
- Pure CO_2 and H_2 streams are used as feed inputs.

3. Process Description:

3.1.Overview: The process begins with the feeding of pure carbon dioxide and hydrogen gas streams. Both gases are compressed to the desired pressure using compressors. After compression, the gases are preheated in heat exchangers to achieve the necessary reactor inlet temperature. The streams are then mixed and introduced into a plug flow reactor (R-Plug), where methanol synthesis takes place under controlled temperature and pressure.

Post-reaction, the outlet stream from the reactor contains methanol, water, unreacted hydrogen, and carbon dioxide. This mixture undergoes a separation step using a flash separator to remove gaseous components from the liquid. The gaseous stream is

partially recycled back into the process to enhance overall conversion efficiency. The liquid stream, containing methanol and water, is fed into a RadFrac distillation column where methanol is purified based on its volatility difference with water.

3.2.Equipment and Functions:

- Compressors: Increases the pressure of gas streams (e.g., CO_2 or H_2) to desired levels for reaction or separation processes.
- Multistage Compressor: compresses gas in two or more stages, with cooling between each stage, to achieve a high overall pressure ratio efficiently and safely.
- Heat Exchangers: Adjusts the stream temperature before the reactor. Used to heat the feed mixture to the desired reaction temperature.
- Mixers: Combines two or more feed streams. In this simulation, one mixer combines CO_2 and H_2, and another combines fresh feed with the recycled stream.
- R-Plug Reactor: Simulates the chemical reactions. A Plug Flow Reactor (PFR) is used here to model methanol synthesis reactions at fixed T & P.
- R-Stoich Reactor: Simulates chemical reactions where the reaction stoichiometry and extent (conversion or yield) are user-defined — not calculated based on kinetics or equilibrium.
- Flash Separator: Splits vapor and liquid phases. It removes unreacted gases from the liquid methanol and water product.
- RadFrac Column: A rigorous distillation column used to separate methanol and water based on boiling point differences to achieve the desired purity.
- Cooler: Reduces the temperature of the compressed stream, typically used after compression to maintain safe or optimal operating conditions.

FLOWSHEET DIAGRAM:

- **Compression & Mixing**:

  CO_2 and H_2 are fed and compressed separately (via compressors B13 and B8), then mixed in mixers (B9 and B11).

- **Reaction**:

  The mixed feed enters a **Plug Flow Reactor (REA-IN)** where methanol is synthesized from CO_2 and H_2 under high pressure and temperature.

- **Separation & Recycling**:

  The reactor output enters **Flash Separator 1 (FLA1)**. Unreacted gases are split, with a portion purged (B6) and the rest recycled (RECY) back into the feed.

- **Product Purification**:

  The liquid stream proceeds to **Flash Separator 2 (FLA2)** and then to a **RadFrac Distillation Column**, which separates **methanol (DIST)** and **water (BOTTOM)**.

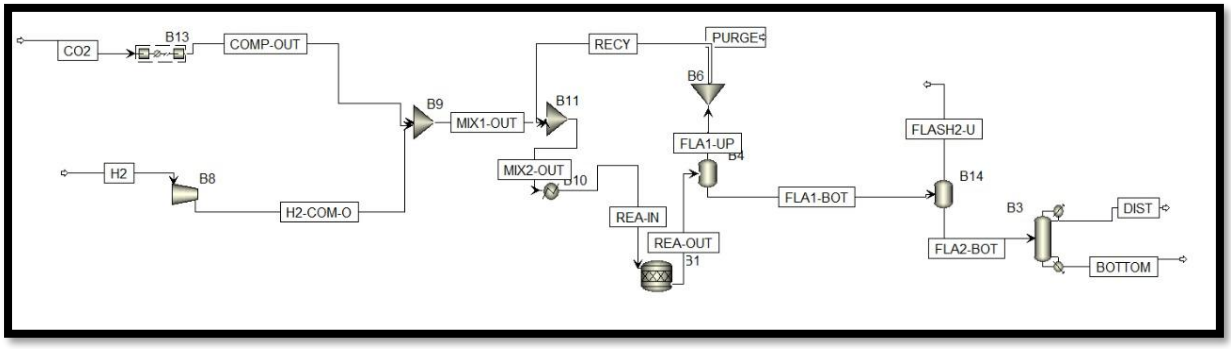

Fig.3 :- *The Simulation of the Conversion from Carbon Dioxide to Methanol.*

Data can be found by Excel file :- Excel

TABLE:

Table 1: Temperature & Pressure of all Streams

Stream Name	Temperature (K)	Pressure (atm)
MIX2-OUT	1011.69	77
MIX-1-OUT	1986.5	77
H2-Comp-out	2244.73	77
CO2	553.15	1
H2	553.15	1
REA-IN	553.15	77
Comp-out	553.15	77
Distillate	35.61	1
REA-OUT	553.15	77
Bottom	351.95	1
Flash1-Up	300.15	77
PURGE	300.15	77
RECYCLE	300.15	77
Flash1-Bottom	300.15	77
Flash2-Up	-	77
Flash2-Bottom	300.15	77

Table 2: Mole flows & Mass flows of all streams

Stream Name	Mole Flows (Kmol/hr)	Mass Flows (Kg/hr)
MIX2-OUT	1434.672452	6140.027673
MIX-1-OUT	550.594582	3400

H2-Comp-out	496.0612735	1000
CO2	54.53330849	2400
H2	496.0612735	1000
REA-IN	1434.672452	6140.027673
Comp-out	54.53330849	2400
Distillate	20	629.2634276
REA-OUT	1355.699751	6140.027673
Bottom	72.72550546	1596.456611
Flash1-Up	1262.974245	3914.307635
PURGE	378.8922736	1174.29229
RECYCLE	884.0778695	2740.027673
Flash1-Bottom	92.72550546	2225.720038
Flash2-Up	0	-
Flash2-Bottom	92.72550546	2225.720038

For Distillate,

Component	**Mass Flow (kg/hr)**
CO_2	22.73802314
Hydrogen	1.112214778
CO	8.312073893
Methanol	597.100822
Water	0.000293801

For Bottom,

Component	Mass Flow (kg/hr)
CO_2	7.10971E-20
Hydrogen	1.22646E-42
CO	3.73227E-30
Methanol	653.9751076
Water	942.4815029

For Purge,

Component	Mass Flow (kg/hr)
CO_2	70.08449174
Hydrogen	733.9976107
CO	354.1027555
Methanol	14.15336008
Water	1.954072511

Heat Duty,

	Heat Duty (kW)
Multi Compressor	-463.4487867
Heater	-5583.533771
Reactor	-514.8549954
Flash-1	-3937.807106
Flash 2	-3.84E-12
Radfrac	-1625.199392

KEY PERFORMANCE INDICATOR:

1.) Hydrogen Consumption :- The amount of hydrogen reacted to produce methanol in the unit of kgH2/kgCH3OH. = 264.891/1251.076 = 0.211

2.) Hydrogen Efficiency :- The proportion of the amount of hydrogen reacts with carbon dioxide to the feed amount of CO2. = (1000 – 733.997 – 1.112)/2400 = 0.11

3.) Product Amount:- The final methanol product mass in the unit of kilogram.

= 597.101 (distillate) + 653.975 (bottom) = 1251.076 kg

4.) Carbon Dioxides Emission :- The mass of unreacted carbon dioxide.

= 70.084 (purge) + 22.738 (distillate) = 92.822 kg

Mass fraction of Methanol in distillate = **0.948888487**

CONCLUSION:

- **Successful Simulation**: The Aspen Plus model effectively replicated the CO_2-to-methanol conversion process described in literature, validating the simulation approach and setup.
- **Purity Enhancement Achieved**: By optimizing parameters like reactor conditions and distillation column specs (e.g., reflux ratio and number of stages), methanol purity was successfully obtained as **94.88% wt.**
- **Efficient Process Design**: The integration of recycling, multi-stage compression, and rigorous separation techniques resulted in high methanol yield and improved resource utilization.
- **Sustainable Impact**: The process offers a promising method for CO_2 utilization, aligning with global goals for reducing greenhouse gas.
- **Scope for Future Work**: Further improvements can be explored through energy integration, catalyst optimization, and economic analysis for industrial-scale implementation.