MinnesotaCorn
RESEARCH & PROMOTION COUNCIL

FINAL REPORT

PROJECT TITLE: **Techno-Economic Analysis of Carbon Dioxide-to-Fuel in Corn Ethanol Plants**
PROJECT NUMBER: 6081-22D
PRINCIPAL INVESTIGATOR AND CO-INVESTIGATOR(S): Will Northrop

ABSTRACT

This project investigates the techno-economic feasibility of converting CO_2 emissions from corn ethanol refineries into renewable fuels, focusing on methanol and gasoline production. Using Aspen Plus simulation software, the project team at the University of Minnesota developed a comprehensive plant model encompassing hydrogen production, methanol synthesis, and Methanol-to-Gasoline (MTG) processes. Three pathways for methanol synthesis were evaluated: Direct Hydrogenation (DH), Indirect Hydrogenation (IDH), and Ethanol Dry Reforming (EDR). Among these, EDR emerged as the most effective and economically viable method, utilizing CO_2 more efficiently and requiring less external hydrogen due to its unique ability to produce hydrogen from ethanol, a byproduct of corn fermentation. This capability reduces dependence on external hydrogen sources, lowering operational costs and enhancing process sustainability.

Parametric studies on various ethanol-gasoline blends, including E85 and E98, demonstrated that EDR optimizes fuel. A sensitivity analysis further confirmed that EDR maintains economic viability even when hydrogen prices fluctuate, making it particularly suited for large-scale implementation in ethanol refineries. By integrating CO_2 conversion technologies, corn ethanol refineries can reduce emissions and valorize a previously wasted byproduct. For corn farmers, this project provides a dual advantage: it enhances the economic stability of ethanol plants, a key market for their corn, and contributes to a sustainable energy future, ultimately supporting the long-term demand for corn-based biofuel. This approach aligns with the goals of reducing carbon emissions in agriculture and maximizing the economic value of corn as a renewable resource.

INTRODUCTION

Biofuels, particularly bioethanol, present a promising alternative to mitigate harmful emissions by partially replacing fossil fuels. Unlike petroleum-derived ethanol, bioethanol is increasingly sourced from renewable plant-based feedstocks, driven by environmental regulations and growing demand for sustainable, bio-based products.[1] First-generation biofuels, primarily developed in the USA, Brazil, and the EU, rely on crops like sugarcane, beet, and various oils, utilizing CO_2 recycling through photosynthesis to reduce net emissions[2][3][4]. Although biofuels face challenges such as lower oxidation stability and reduced calorific value, these can be improved with additives or through blending with conventional fuels [5][6][7].

The U.S. ethanol export industry, the third-largest globally, is crucial to this market, exporting 1.43 billion gallons annually [8]. With a projected growth for ethanol from USD 87.71 billion in 2022 to USD 135.07 billion by 2030, bioethanol's role in energy markets continues to expand, especially in North America, which holds a substantial share [1]. In the United States, where corn is the primary feedstock, emissions from corn-based bioethanol production are notably high [9]. Therefore, efforts to decarbonize corn ethanol production present an impactful opportunity to reduce emissions in the transportation sector.

The stability of CO_2 and its high activation energy make its conversion into valuable products a thermodynamic and catalytic challenge [13]. Among the various CO_2 conversion processes, hydrogenation has shown promise as a pathway for converting CO_2 into transportable fuels and chemicals, such as methanol or methane.[14], [15], [16] Although CO_2 utilization may not directly offset GHG emissions, it contributes to a circular carbon economy by transforming CO_2 into products with industrial or fuel applications.[17] Methanol, a versatile industrial chemical, can be synthesized from CO_2-enriched syngas and further converted into gasoline-range hydrocarbons via the Methanol-to-Gasoline (MTG) process, offering a pathway to substitute traditional gasoline with renewable alternatives.[18], [19]
Key CO_2 Conversion Processes include:

For methanol-based gasoline production, the MTG process developed by ExxonMobil in 1987 offers an efficient alternative to heavier hydrocarbon synthesis like Fischer-Tropsch. This process includes methanol dehydration to dimethyl ether (DME) followed by conversion to gasoline-like hydrocarbons in the presence of ZSM-5 catalysts.[23] A key advantage of MTG is its high selectivity for gasoline-range hydrocarbons, making it ideal for ethanol refineries aiming to produce renewable gasoline.[24]

Ethanol Dry Reforming (EDR) provides an alternative route for syngas (a mixture of CO and H_2) production, essential for producing various hydrocarbons and chemicals. EDR is a catalytic process that converts ethanol and CO_2 into syngas, utilizing high temperatures and specific metal-based catalysts to enhance efficiency and minimize unwanted byproducts like coke [25][26]. The overall EDR reaction is:

$$C_2H_5OH + CO_2 \rightleftharpoons 3CO + 3H_2 \, \Delta H = 296.7 \, kJ/mol \, (298K)$$

From hydrogen and carbon monoxide, methanol is synthesized according to:

$$CO + 2H_2 \rightleftharpoons CH_3OH \;\; \Delta H = -166 \, kJ/mol \, (298K)$$
$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O \, \Delta H = -49.5 \, kJ/mol \, (298K)$$
$$CO^2(g) + H^2(g) \rightleftharpoons CO(g) + H^2O(l) \Delta H = 41.2 \, kJ/mol \, (298K)$$

Ethanol acts as both a hydrogen and carbon source in this reaction, while CO_2 enhances syngas production [27], [28], [29], [30]. Metal-based catalysts such as nickel (Ni), noble metals (e.g.,Rh,Pt,Pd), and bimetallic combinations (e.g.,Ni-Co,NiCu) are commonly used to drive the EDR reaction, reduce coke formation, and improve efficiency. Optimized conditions for EDR include high temperatures (1200-1300 K) and a CO_2:ethanol molar ratio of approximately 1.2 to 1.3, achieving over 94% H_2 and 97% CO yields.[31]

EDR offers advantages over conventional steam methane reforming by reducing external hydrogen requirements and creating a syngas with high CO content, ideal for subsequent hydrocarbon synthesis via Fischer-Tropsch or Methanol-to-Gasoline (MTG) processes. In the MTG process, methanol is dehydrated to dimethyl ether (DME), which is then converted into gasoline-range hydrocarbons in the presence of ZSM-5 catalysts, providing a feasible route to renewable gasoline [23][24].

This project investigates CO_2 capture and conversion in corn ethanol plants to produce renewable fuels and chemicals. By combining CO_2 hydrogenation with Ethanol Dry Reforming (EDR), we aim to generate methanol and syngas, ultimately using the Methanol-to-Gasoline (MTG) process to create gasoline-range hydrocarbons. This approach reduces emissions and offers economic benefits under Section 45Q, supporting a circular carbon economy for Minnesota's ethanol refineries.

Our research focuses on using fermentation-derived CO_2 for transportation-ready fuels. We compare the EDR process with traditional indirect hydrogenation methods to reduce reliance on renewable hydrogen and optimize the H2/CO ratio for methanol synthesis, creating a more efficient pathway for CO_2 conversion.

OBJECTIVE AND GOAL STATEMENTS

This project evaluates the feasibility and benefits of converting CO_2 emissions from ethanol refineries into valuable fuels, such as methanol and e-gasoline. The objectives, as outlined in the original proposal, are as follows:

1. **Build a Plant Model**
   Develop a comprehensive process model for hydrogen production, methanol synthesis, and the methanol-to-gasoline (MTG) process, building upon the validated Chippewa Valley Ethanol Company (CVEC) plant model.
2. **Conduct Parametric Studies**
   Perform parametric studies using the developed model to evaluate renewable ethanol blends and fuel quantities. Parameters such as CO_2 flow rates, hydrogen sources, energy requirements, and the impact of government incentives (like Section 45Q) will be explored to determine optimal operational conditions and benefits.
3. **Determine Optimal E85 Blending Hydrocarbons**
   Use engine modeling to identify the most effective hydrocarbons for blending with ethanol to create renewable E85. Although the performance testing of the blends is out of scope, simulating their production will provide valuable insights into the potential for renewable ethanol fuel blends.
4. **Finalize Cost Benefits and Return on Investment**
   Calculate the operational expenses, cost benefits, and return on investment (ROI) for implementing the CO2-to-fuel system at various scales. This analysis will account for the costs of hydrogen production, CO_2 capture, and methanol synthesis, as well as the financial impact of tax incentives.
5. **Revise Reactor and Disseminate Findings**
   Adjust reactor models as needed based on simulation results and parametric studies. The final results will be shared through conference presentations, journal publications, and discussions with ethanol plant operators to encourage the adoption of CO_2-to-fuel conversion technologies.

MATERIALS AND METHODS

1. Calculation Of Feedstock

Ethanol Dry Reforming (EDR) and Indirect Hydrogenation (IDH) aim to produce gasoline-range hydrocarbons from CO_2, with differences in hydrogen dependency and conversion processes. The goal of these calculations is to determine the amounts of ethanol, CO_2, and hydrogen needed for each pathway, optimizing for economic feasibility and sustainability.

1. Ethanol Dry Reforming (EDR) Pathway

The EDR pathway leverages the use of ethanol and CO_2 to produce synthesis gas (syngas), a mixture of hydrogen (H_2) and carbon monoxide (CO), which is subsequently processed into methanol and then converted to gasoline through the Methanol-to-Gasoline (MTG) process. This pathway reduces the need for external hydrogen by deriving some hydrogen directly from ethanol, thereby increasing the process's energy efficiency.

Key Reaction for EDR:

$$C_2H_5OH + CO_2 \rightarrow 3CO + 3H_2$$

This reaction shows that 1 mole of ethanol (C_2H_5OH) reacts with 1 mole of CO_2 to yield 3 moles each of CO and H_2.

EDR Calculations:

The amount of hydrocarbons required, based on a target yield, is calculated as:

$$Hydrocarbons\ Needed = x \times ethanol\_amount \times hc\_per\_ethanol$$

where x is the fraction of ethanol converted, ethanol_amount is the total ethanol input, and hc_per_ethanol is the yield ratio (kg hydrocarbons per kg ethanol).

Total Material Balance:

$$Total\ Combination = (1 - x) \times ethanol\_amount + Hydrocarbons\ Needed$$

CO_2 and Hydrogen Requirements:

CO_2 Requirement: The amount of CO_2 needed to produce the hydrocarbons is:

$$CO_2\ Required = Hydrocarbons\ Needed\ /\ hc\_per\_co2$$

Hydrogen Requirement: The amount of H_2 needed is calculated as:

$$H_2\ Required = Hydrocarbons\ Needed\ /\ hc\_per\_h2$$

2. Indirect Hydrogenation (IDH) Pathway

The IDH pathway involves a two-step process where CO_2 is first converted to syngas using the Reverse Water-Gas Shift (RWGS) reaction, followed by methanol synthesis and subsequent conversion to gasoline. Unlike EDR, this pathway requires an external hydrogen source to drive the conversion reactions.

Key Reactions for IDH:

Reverse Water-Gas Shift (RWGS):

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$

Methanol Synthesis:

$$CO + 2H_2 \rightleftharpoons CH_3OH$$
$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O$$

These reactions imply that 1 mole of CO_2 requires 3 moles of H_2 to form methanol.

IDH Calculations:

The amount of hydrocarbons required is calculated similarly to EDR:

$$Hydrocarbons\ Needed = x \times ethanol\_amount \times hc\_per\_ethanol$$

CO_2 Requirement: For methanol synthesis, the CO_2 needed is calculated by:

$$CO_2\ Required = Hydrocarbons\ Needed\ /\ hydrocarbon\_per\_co2$$

Hydrogen Requirement: Given the external hydrogen dependency in IDH, the hydrogen requirement is:

$$H_2\ Required = Hydrocarbons\ Needed\ /\ hydrocarbon\_per\_h2$$

2. Process Simulations Using Aspen Plus®

This study employs Aspen Plus® software to simulate various CO_2 conversion processes aimed at producing gasoline-range hydrocarbons from CO_2 captured during ethanol fermentation. The simulations evaluate multiple pathways for converting CO_2 into methanol, which is subsequently processed into gasoline via the Methanol-to-Gasoline (MTG) process. Simulated scenarios consider different hydrogen production methods and gasoline-ethanol blends to determine the most economically and environmentally viable pathway.

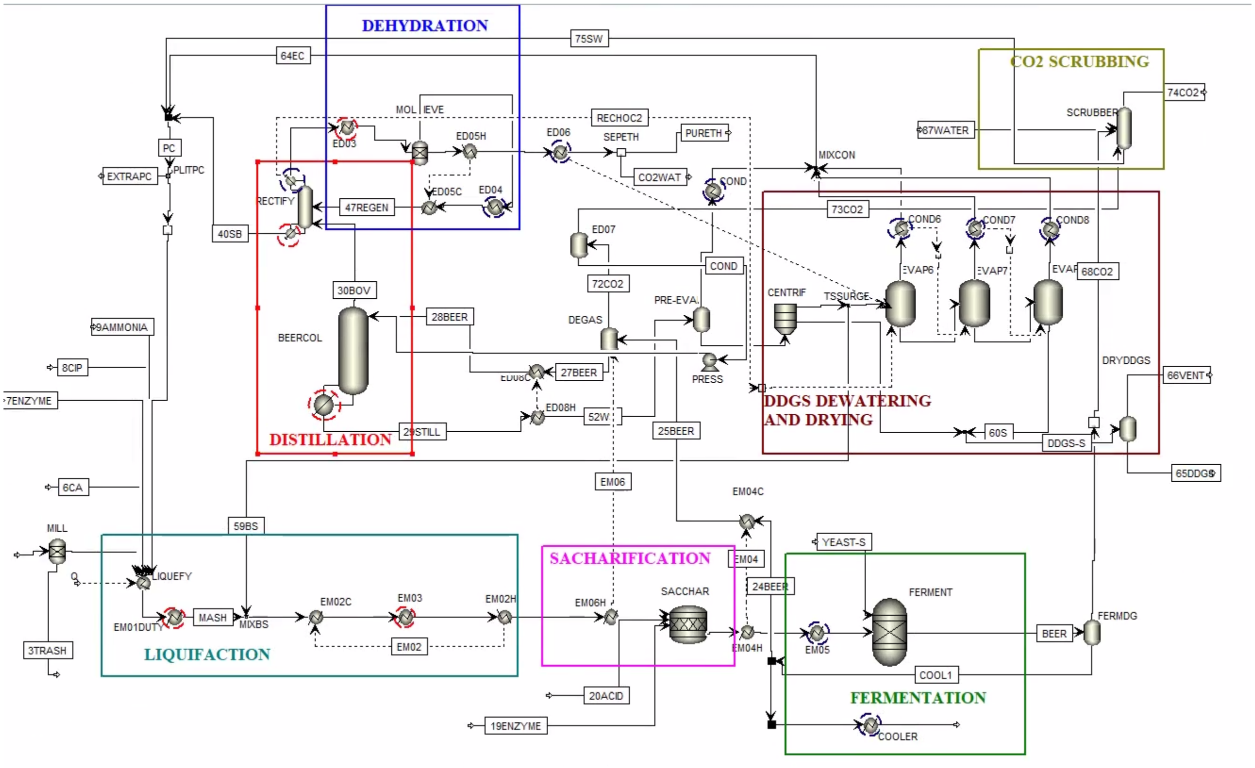

Figure 1 Flow Sheet of Ethanol Refinery in Aspen Plus

3. CO_2 Source and Capture

The CO_2 used in this study is sourced from the fermentation process at a corn ethanol refinery with a production capacity of 100 million gallons per year (MGY). All the information can be found at Table 1.

Table 1 Ethanol Refinery Information

Parameter	Units	Value
Ethanol Production	MGY	50.1
Ethanol Production	L/h	22,079
Corn Consumption	t/day	1,344
Ethanol Yield from Corn	L/Ton	394.27
Natural Gas Use	GJ/day	3,623
Steam Use	Kg/L	1.8
Thermal Energy Use	MJ/L	6.83
Electricity	kWh/L	0.16
Water Consumption	L/L EtOH	2.1
DDGS Moisture	%	10.5

Ethanol Concentration in Beer	Mass %	14.2
CO_2 from Scrubber	ACFM	5,890.75
CO_2 from Scrubber	kg/hr	19,775.23
Bushels of Corn	#/hr	2,000
Product Revenue and Costs		
Ethanol Revenue	$/gal	$1.65
Ethanol Hourly Revenue on Ethanol Basis		$9,623.79
Total Ethanol Revenue per Gallon		$9,623.79
Oil Revenue	$/gal	$0.14
Total Oil Revenue per Hour		$816.56
DDG Revenue	$/gal	$0.40
Total DDG Revenue per Hour		$2,333.04
Costs		
Utility Cost	$/gal	($0.17)
Utility Total Cost per Hour		($991.54)
Labor Cost	$/gal	($0.04)
Labor Total Cost per Hour		($233.30)
Corn Cost		($8,500.00)
Denaturant Cost		($262.40)
Net Revenue per Gallon		($363.46)
Total Net Revenue per Hour		$2,786.15

During fermentation, CO_2 is released as a byproduct, which is then captured and scrubbed for further use in conversion processes. The captured CO_2 is compressed and cooled before being fed into the methanol synthesis reactors. Capture efficiencies and production rates are modeled using data from the CVEC ethanol refinery.

4. Hydrogen Production

Hydrogen is a critical component for all CO_2 conversion pathways in this study. To support sustainable production, hydrogen is assumed to be generated via water electrolysis powered by renewable energy. The study evaluates the economic impact of producing hydrogen on-site versus purchasing it externally. Hydrogen costs range from \$1.5/kg (onsite production) to \$6.5/kg (market rates), with sensitivity analyses conducted to assess the influence of these cost variations on the overall economic feasibility of each CO_2 conversion pathway.

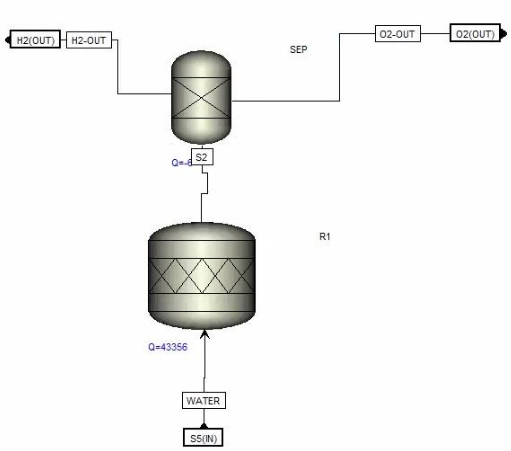

Figure 2 Flow Sheet of a stack For Alkaline Electrolysis in Aspen Plus

5. CO_2 Conversion Pathways

- Pathway 1: Indirect Hydrogenation (IDH)

This pathway involves converting CO_2 and H_2 into syngas via the Reverse Water-Gas Shift (RWGS) reaction at 500°C and 50 bar, following this reaction:

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \quad \Delta H = 41\,kJ/mol\,(298K)$$

Syngas is then passed into a reactor for methanol synthesis via the reactions:

$$CO + 2H_2 \rightleftharpoons CH_3OH$$

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O \quad \Delta H = -49.5\,kJ/mol\,(298K)$$

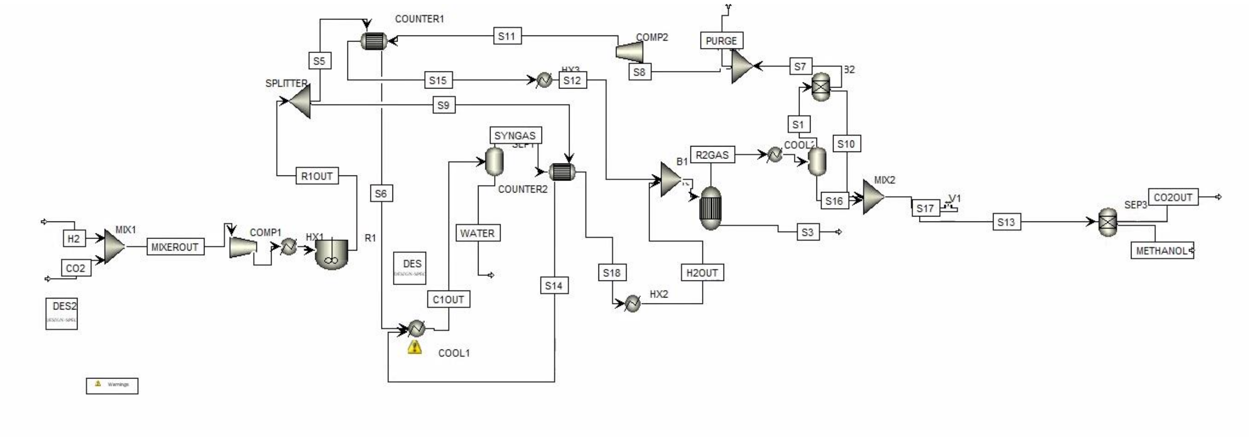

Figure 3 Flow Sheet of Indirect Hydrogenation of Carbon Dioxide in Aspen Plus

- Pathway 2: Direct Hydrogenation (DH)

This pathway directly hydrogenates CO_2 into methanol in a single-step process. CO_2 and H_2 are compressed to 78 bar and fed into a fixed-bed adiabatic reactor operating at 210°C. Methanol is separated via distillation, with yields directly affected by hydrogen availability.

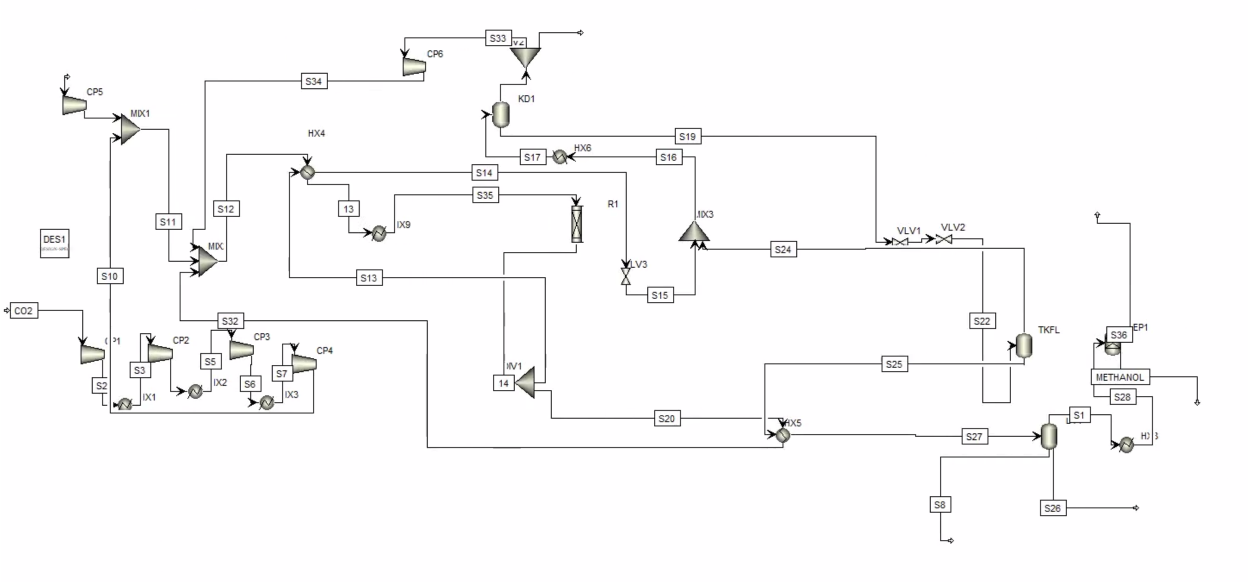

Figure 4 Flow Sheet of Direct Hydrogenation of carbon Dioxide in Aspen Plus

- Pathway 3: Ethanol Dry Reforming (EDR)

EDR combines ethanol and CO_2 to produce syngas, reducing the reliance on external hydrogen. As shown in Figure 5 ethanol (C_2H_5OH) and CO_2 react in an RGibbs reactor at 927°C and 1 bar:

$$C_2H_5OH + CO_2 \rightleftharpoons 3CO + 3H_2 \ \Delta H = 296.7\ kJ/mol\ (298K)$$

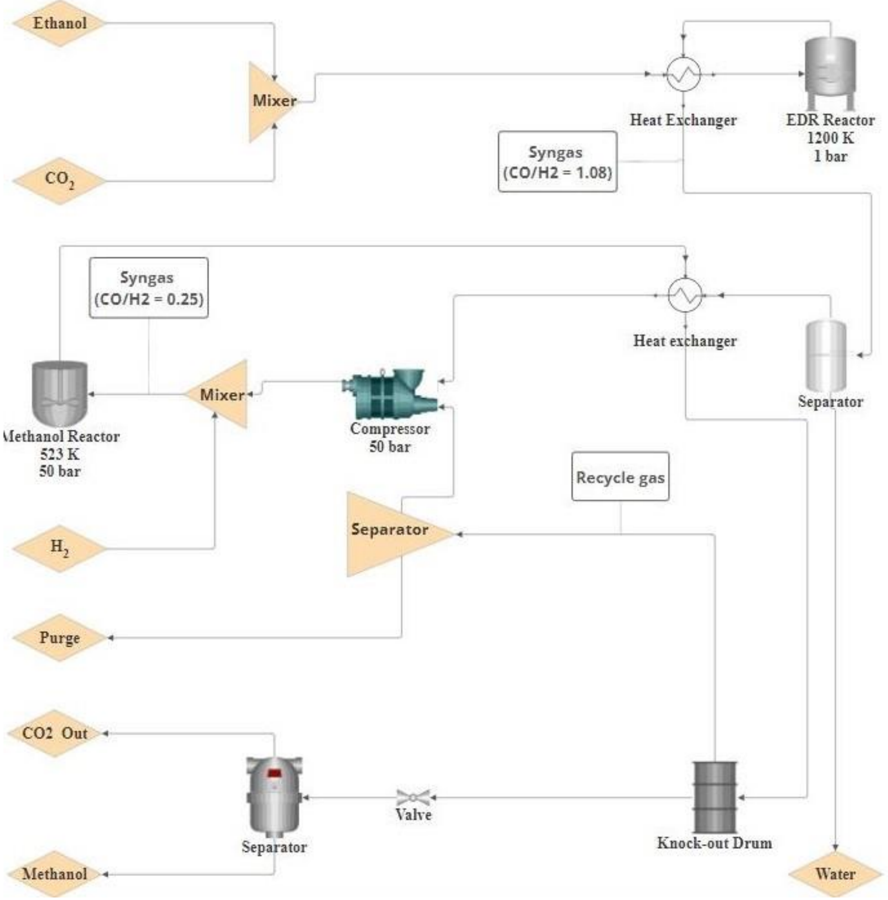

Figure 5 Process Flow Diagram of Ethanol Dry Reforming Followed by Methanol Synthesis

The resulting syngas is compressed and heated for methanol synthesis, following the same steps as in the IDH process. EDR’s primary advantage is its reduced hydrogen requirement due to the partial hydrogen contribution from ethanol itself.

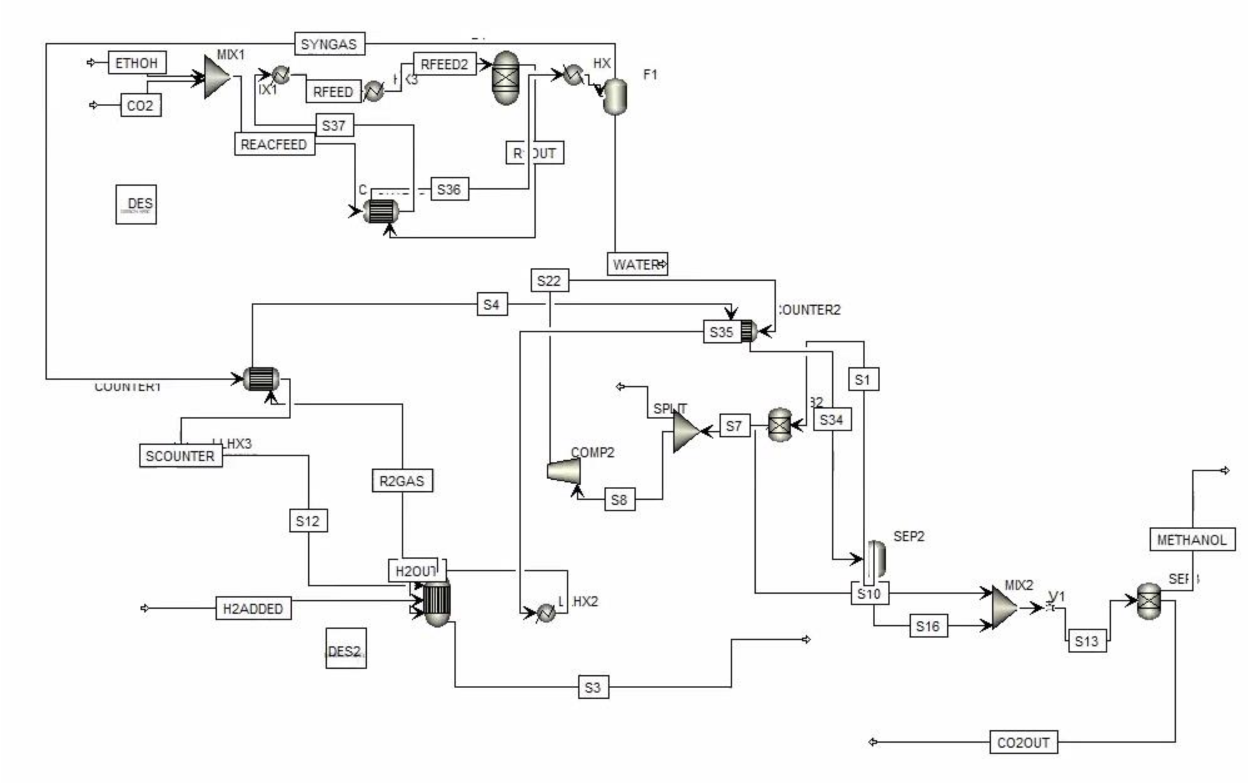

Figure 6 Flow sheet of Ethanol Dry Reforming and Methanol Synthesis from product Syngas in Aspen Plus

6. Methanol-to-Gasoline (MTG) Process

The MTG process converts methanol to gasoline and other hydrocarbons. Methanol is first dehydrated in a γ-Al_2O_3-catalyzed reactor at 27 bar and 310°C to form dimethyl ether (DME):

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O$$

DME is then processed in a second reactor with ZSM-5 catalyst, yielding gasoline-range hydrocarbons.

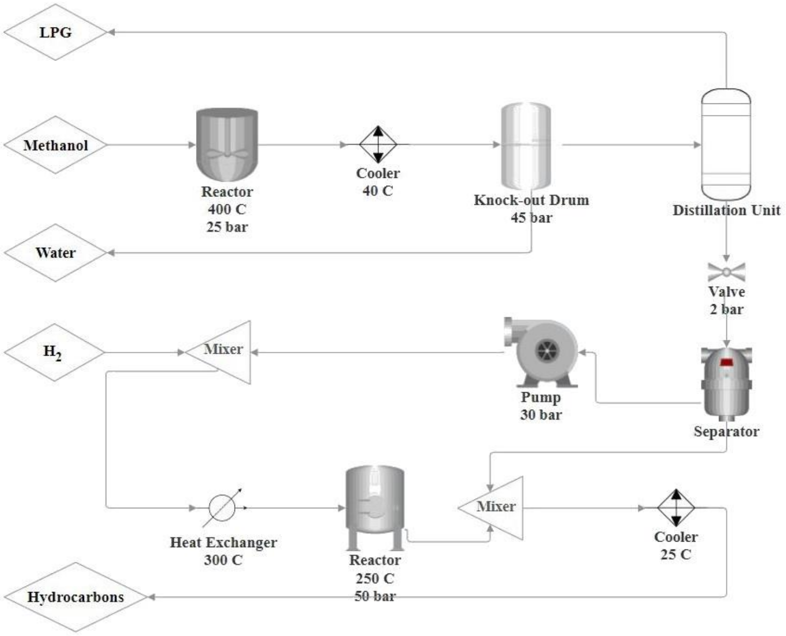

Figure 7 Process Flow diagram of methanol to gasoline Process

As shown in Figure 7 the final product is separated into gasoline, LPG, and heavier components. This MTG process optimizes gasoline yield and selectivity.

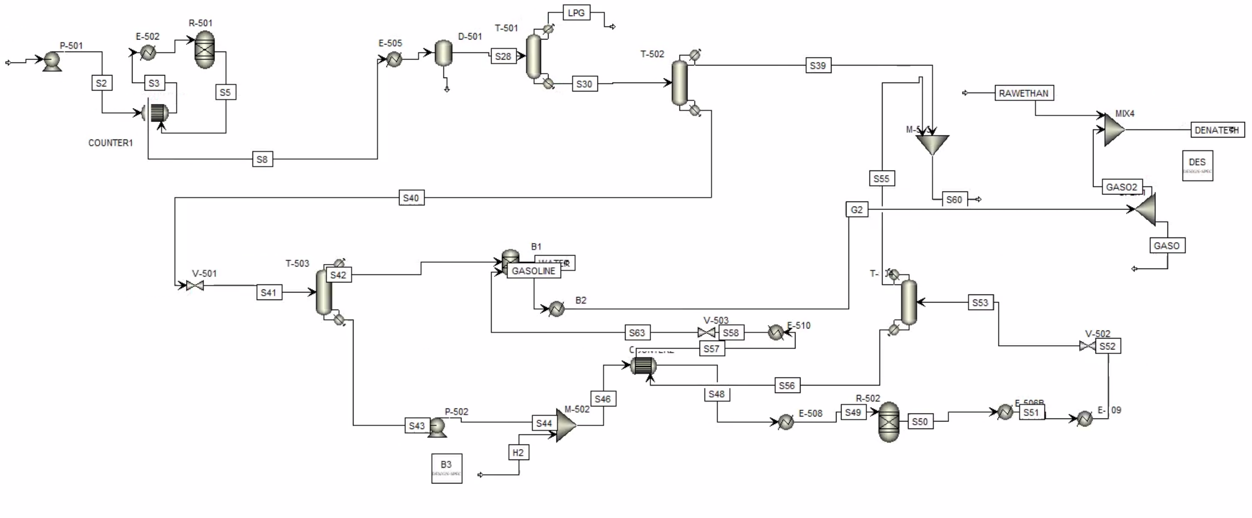

Figure 8 Flow sheet of MTG Process in Aspen Plus

7. Control Scenario: CO₂ Sequestration

CO₂ sequestration is used as a control scenario. Here, captured CO₂ is compressed and stored long-term.

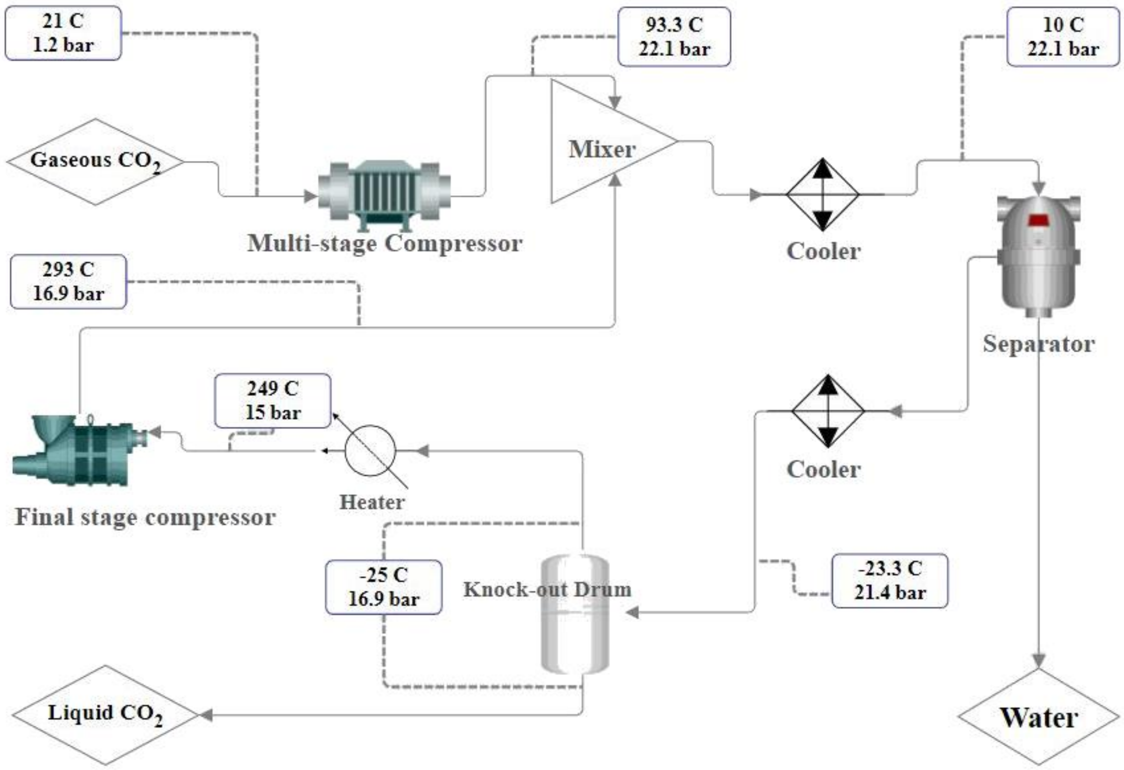

Figure 9 Process Flow Diagram of Conversion of Gaseous Carbon dioxide to Liquid

This process includes cooling, compression to 18 bar, and liquefaction at -25°C and 16.9 bar. The process flow diagram has been shown in Figure 9. This baseline scenario serves as a comparison to the utilization pathways.

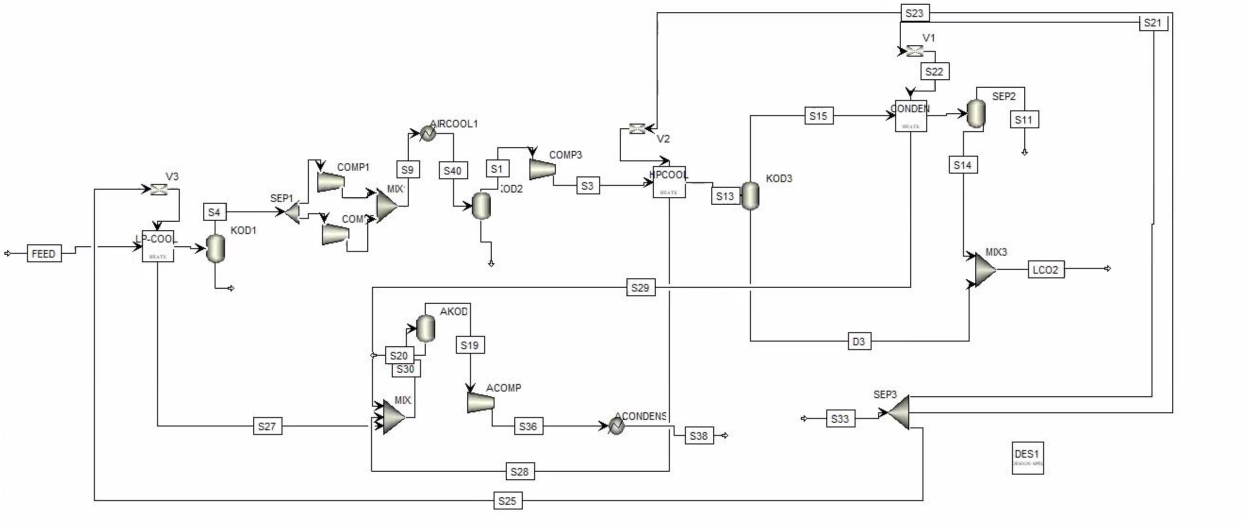

Figure 10 Flow sheet of Conversion of Gaseous Carbon dioxide to Liquid in Aspen Plus

8. Gasoline-Ethanol Blends

Simulations also examined the production of gasoline-ethanol blends such as E10, E20, E85, and E98. For each blend, the study calculated the hydrogen requirement, CO_2 demand, and production costs. The analysis provides insights into the financial and environmental impacts of various gasoline-ethanol blends in each pathway.

9. Economic and Environmental Metrics

- Energy Efficiency: Calculated as the ratio of the lower heating value (LHV) of products (methanol, gasoline) to total energy input.

$$EE\ (\%) = \frac{\left(LHV_{output} \times \ Mass_{output}\right)}{(LHV\_input\ \times\ Mass\_input\ +\ Heating\ Load\ +\ Electrical\ Load)} \times\ 100$$

Carbon Selectivity: Assessed by comparing the amount of CO_2 fed into the system versus the CO_2 converted into useful products.

$$Carbon\ Selectivity\ (\%)\ =\ (\frac{\left(CO_{2_{in}} - CO_{2_{out}}\right)}{CO_{2_{in}}})\ \times\ 100$$

Operating Expenses (OPEX): Factors include hydrogen costs, utility expenses, and product revenue.

$$OPEX\ =\ (Price_{E98} \times\ Mass_{E98})\ +\ \ (Price_{E85} \times\ Mass_{E85}) -\ Utility\ Costs\ +\ Tax\ Incentives\ -\ (Mass\_H_2\ \times\ Price\_H_2)$$

Cost per Gallon of Gasoline: The economic feasibility of gasoline production was determined using the following equation:

$$Cost\ per\ Gallon\ of\ Gasoline\ = \frac{Total\ Operating\ Expenses(H_2, Utility, Raw\ Material)}{Total\ Gasoline\ Output\ (gallons)}$$

RESULTS AND DISCUSSION

1. Build a Plant Model for Hydrogen Production, Methanol Synthesis, and M2G Processes

In this study, we developed a detailed plant model for methanol synthesis from CO_2 and its subsequent conversion into gasoline using Aspen Plus. This model is based on three different methanol synthesis pathways: Direct Hydrogenation (DH), Indirect Hydrogenation (IDH), and Ethanol Dry Reforming (EDR).

Methanol and Gasoline Production Comparison:

The bar charts (Figure 11) Comparing methanol and gasoline production per bushel of corn shows that EDR produces the highest amount of methanol, followed by IDH and DH. Gasoline production is also maximized with EDR, which reflects its superior capacity for CO_2 utilization when compared to DH and IDH.

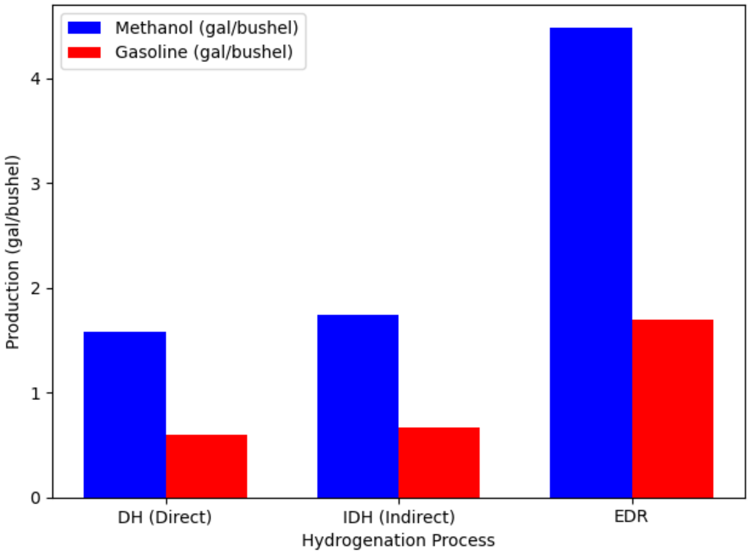

Figure 11 Methanol and following Gasoline output from different Methanol Synthesis Processes

Based on the results, we observe that there is no significant difference between IDH and DH in terms of carbon selectivity and energy balance. As a result, we selected IDH for further analysis as it is already widely used in industrial processes and offers practical benefits.

Hydrogen Requirements: The radar plot in Figure 22 Provides a normalized comparison of key performance indicators (KPIs), demonstrating that EDR and IDH require significantly different amounts of hydrogen, with EDR being more hydrogen-efficient than gasoline production.
This plant model has been successfully built and validated for different methanol synthesis pathways, providing a foundation for further economic and energy assessments.

2. Conduct Parametric Studies Using the Developed Model for Renewable Ethanol Blends and Fuel Quantities

Parametric studies were conducted to analyze the energy efficiency, production outputs, and energy requirements for different gasoline-ethanol blends, including E98, E85, E60, E50, E20, and E10. The goal was to assess each blend's economic and environmental performance using the IDH and EDR pathways.

Production and Energy Output:
In Figure 12, the bar charts show the production of E85 and E98 blends and the remaining ethanol for denaturing. The results highlight the trade-offs between maximizing gasoline production and preserving ethanol for other uses. In E85 scenarios, significantly more ethanol is converted into gasoline, while in E98 scenarios.

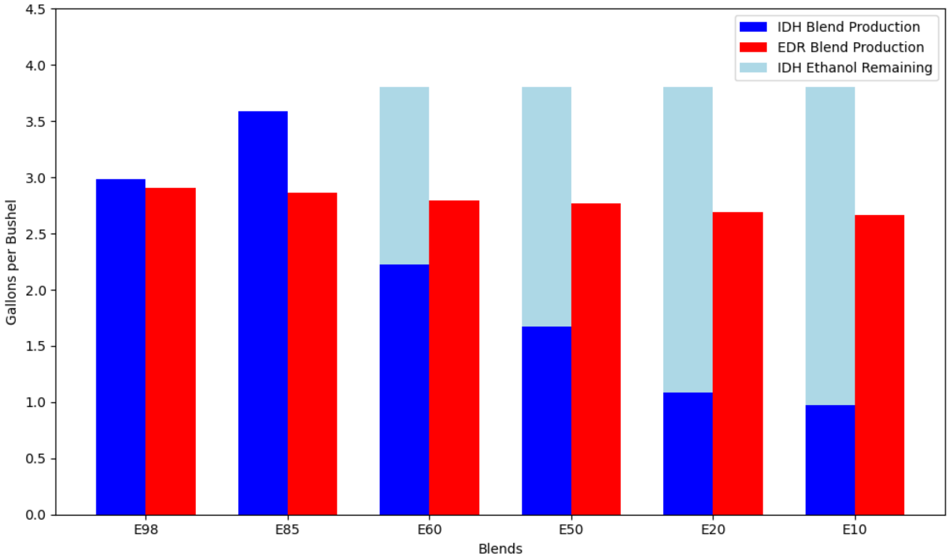

Figure 12 Volumetric Production Comparison per Bushel by Blend and Conversion Method

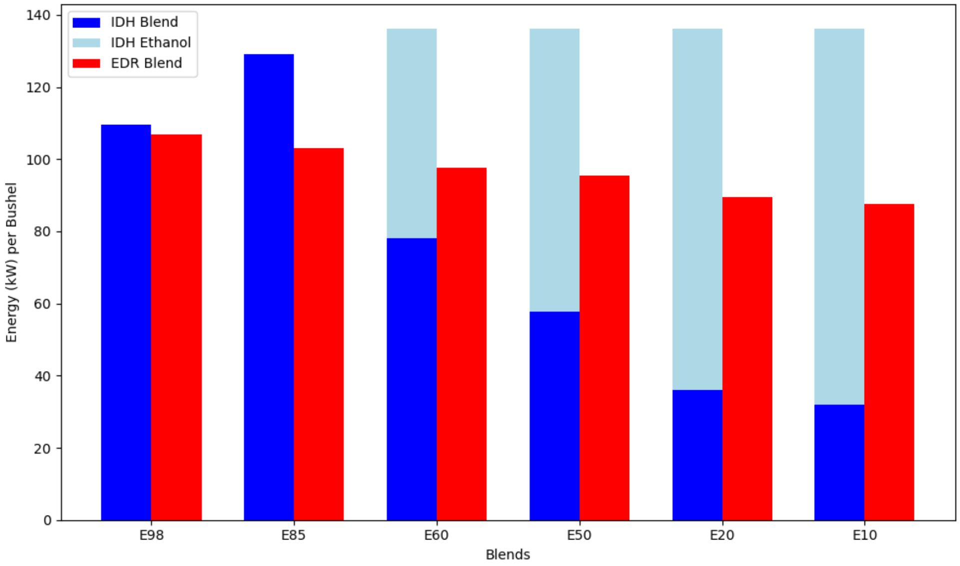

Figure 13 Energy Consumption per Bushel by Blend and Conversion Method

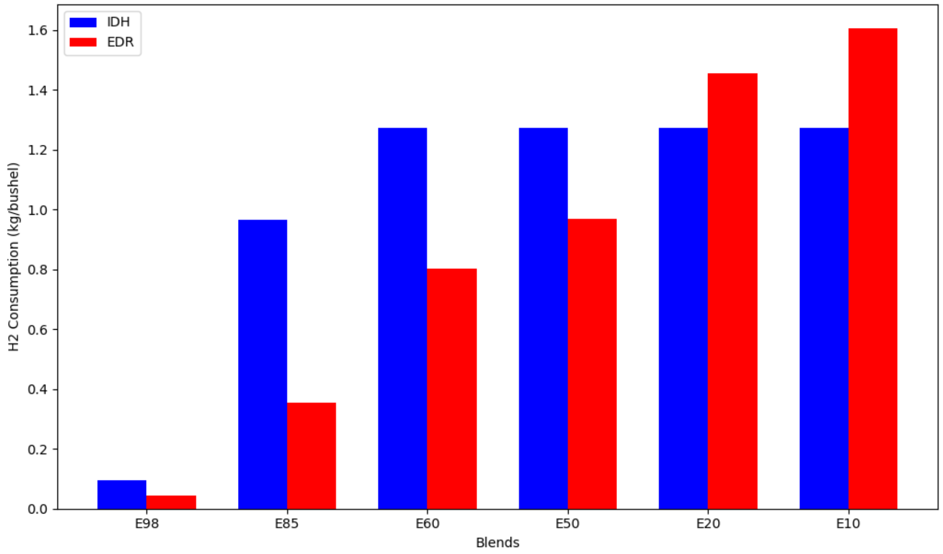

Figure 14 Hydrogen Consumption per Bushel by Blend and Conversion Method

The second chart (Figure 13) on energy content per bushel further supports these findings, showing that IDH and EDR processes result in varying levels of energy output depending on the blend ratio.

The Figure 14 illustrates the hydrogen requirements for different fuel blends. It is observed that, as the proportion of gasoline in the blend increases, the hydrogen requirement also rises. For blends of E98, E85, E60, and E50, the hydrogen requirement for EDR is less than that for IDH. Conversely, for blends of E20 and E10, the situation is reversed.

The primary reason for this difference is that to convert all carbon dioxide into gasoline while blending with ethanol, the resulting blend would be E77. Lower ethanol blends cannot be achieved, necessitating the denaturation of any remaining ethanol. Therefore, after reaching E77, the maximum hydrogen requirement capacity will be fulfilled, while this capacity is influenced by both ethanol and carbon dioxide levels.

Efficiency: The radar chart (Figure 22) also demonstrates efficiency variations between processes and ethanol blends, showing how EDR performs better in terms of energy efficiency compared to IDH and DH.

Hydrogen Price Sensitivity: The contour plots (Figure 20, Figure 21) provide a detailed view of total earnings based on hydrogen price and the ratio of ethanol conversion to E85. This analysis reveals a clear sensitivity to hydrogen prices, with lower prices leading to better economic outcomes, especially for EDR.

This objective has been comprehensively addressed by evaluating various fuel blends and the impact of critical parameters like hydrogen price and CO_2 utilization.

3. Determine Optimal E85 Blending Hydrocarbons for Internal Combustion Engine Performance Through Engine Modeling

Although the direct connection to internal combustion engine performance metrics was not explicitly modeled in the results, the production outputs for E85 and E98 (Figure 11 and Figure 12) allow for an assessment of which blends are optimal for maximizing fuel production from CO_2 and ethanol.

Figure 15 demonstrates how thermodynamic efficiency varies, primarily due to the significant thermal load used in EDR, which is less efficient from a thermodynamic perspective.

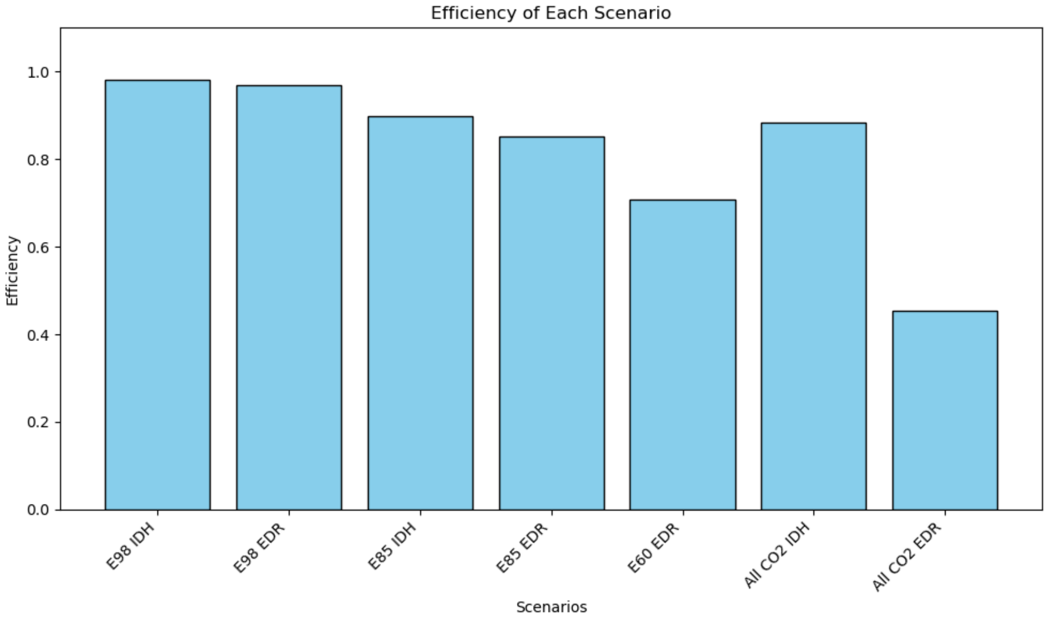

Figure 15 Thermodynamic efficiency of different scenarios

The Table 2 below shows the octane numbers of different blends, indicating that blends with higher ratios of ethanol yield higher octane numbers.

Table 2 Octane Number of Different Blends Calculated by Aspen Plus

	RON	MON	Average
E85	100.5	84.8	92.7
E98	108.2	89.5	98.9
E10	92.6	80.4	86.5
E20	72.1	68.4	70.3
E50	76.2	70.8	73.5
E60	88.5	78.0	83.3

Hydrocarbon Production Cost:

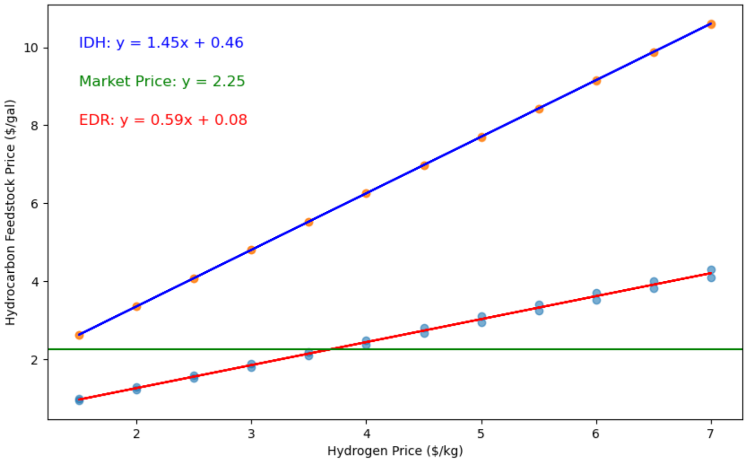

Figure 16 Hydrogen price influences on cost of gasoline production via two methods of methanol synthesis EDR and IDH

Figure 16 displays the relationship between hydrogen price and the cost of hydrocarbon production for IDH and EDR. EDR consistently shows a lower cost per gallon of gasoline than IDH, indicating its superior economic efficiency when producing gasoline blends like E85. The IDH process, while more commercially established, has higher production costs.

This suggests that the EDR pathway may be more cost-effective when large-scale E85 production is prioritized.

Given the production outputs and cost analyses, E85 made via EDR presents itself as a more feasible option from a production and economic standpoint, aligning to optimize E85 blending hydrocarbons.

4. Finalize Cost Benefits and Return on Investment at Various Scales of Implementation

The cost-effectiveness of each process was evaluated through detailed financial analyses, including operational expenses (OPEX), hydrogen price sensitivity, and product revenues.

Operating Expenses (OPEX):

The OPEX results presented in Figure 17, Figure 18, Figure 19 illustrate the net operating expenses in relation to hydrogen prices. A comparison of the IDH and EDR scenarios—which includes sequestration and utilization incentives—demonstrates that the EDR scenario yields a better economic outcome at lower hydrogen prices. Specifically, at a hydrogen price of $2/kg, EDR becomes economically viable, resulting in net positive earnings per bushel of corn.

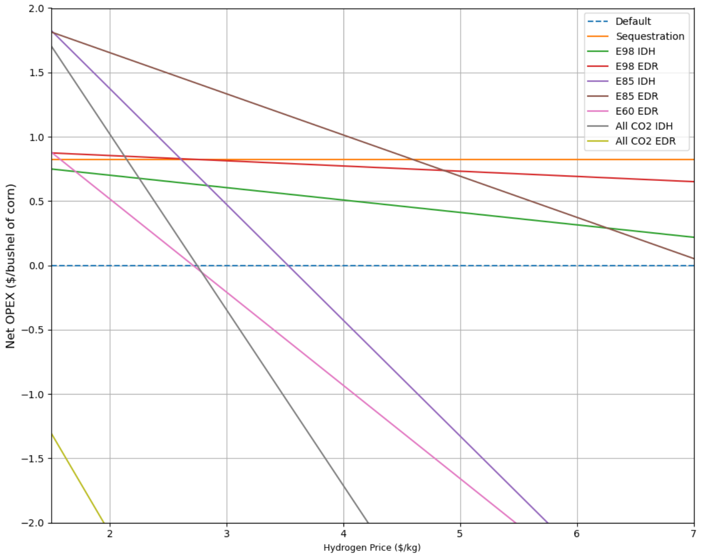

Figure 17 Earning within different scenarios and different Hydrogen prices with sequestration of remained carbon dioxide

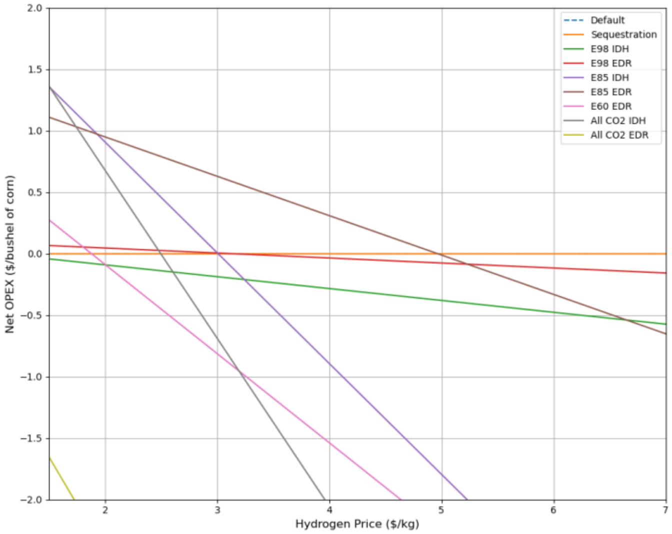

Figure 18 Earning within different scenarios and different Hydrogen prices without considering a utilization tax incentive

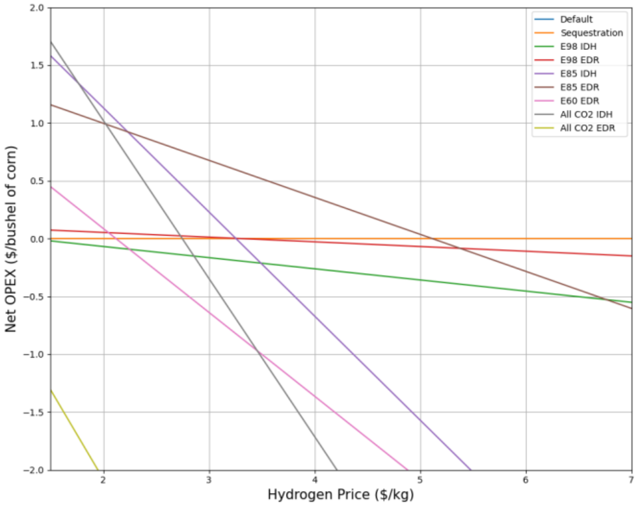

Figure 19 Earning within different scenarios and different Hydrogen prices with considering a utilization tax incentive

The financial breakdown provided in Table 3 details the raw material, utility, and product earnings for each scenario. Raw material costs significantly impact the profitability of each process, with both EDR and IDH benefiting from CO_2 utilization incentives. It is important to note that the price of hydrogen production is assumed to be \$3/kg. Additionally, the side products from the corn ethanol refinery, including DDGS and corn oil, are included in the product earnings

Table 3 breaks down of expenses

Scenario	Utility ($/bushel)	Raw Material ($/bushel)	Utilization Incentive ($/bushel)	Utilization Incentive with Renewable Electricity ($/bushel)	Sequestration Incentive ($/bushel)	Product ($/bushel)	Earnings ($/bushel)
Base	0.61	4.38	0.00	0.00	0.76	6.30	1.31
E98 IDH	0.64	4.54	0.02	0.08	0.70	6.30	1.14
E98 EDR	0.62	4.37	0.01	0.05	0.73	6.30	1.32
E85 IDH	0.90	6.95	0.23	0.40	0.22	7.76	0.14
E85 EDR	0.66	5.21	0.05	0.08	0.60	7.80	1.98
All CO_2 IDH	1.05	8.35	0.35	0.60	0.00	10.01	0.96
All CO_2 EDR	0.81	8.89	0.35	0.36	0.00	7.01	-2.34

The Figure 20 and Figure 21generated for IDH (Indirect Hydrogenation) and EDR (Ethanol Dry Reforming) methanol synthesis pathways show the total earnings (in \$/bushel) as a function of hydrogen price and the ratio of ethanol converted to E85. These contours provide valuable insight into the sensitivity of each pathway to changes in hydrogen cost and ethanol conversion ratios.
In the IDH contour plot, earnings sharply decrease with rising hydrogen prices, showing potential for positive earnings at low prices (below \$2/kg) and high E85 conversion ratios. However, profitability is heavily constrained by hydrogen costs, making it less scalable if prices are high or fluctuate.

Conversely, the EDR contour plot indicates that earnings are less negatively affected by hydrogen price increases. By utilizing ethanol as a partial hydrogen source, EDR demonstrates greater economic resilience, maintaining closer-to-zero or slightly positive earnings across a wider range of prices and conversion ratios.

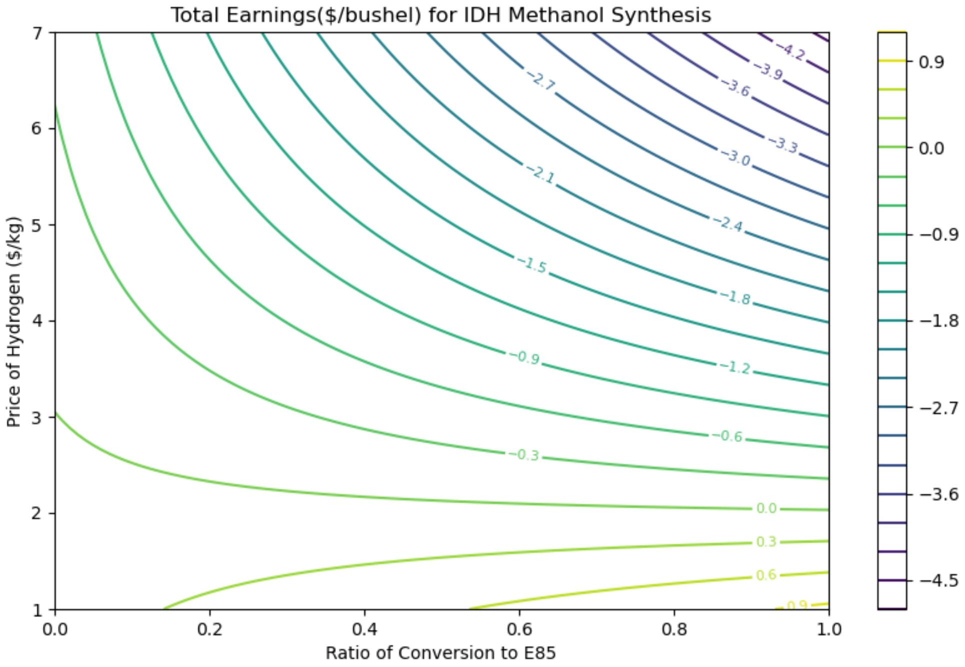

Figure 20 Total Earnings Based on Hydrogen Price and Ratio of Ethanol Conversion to E85 with Sequestration of Remained Carbon Dioxide By IDH.

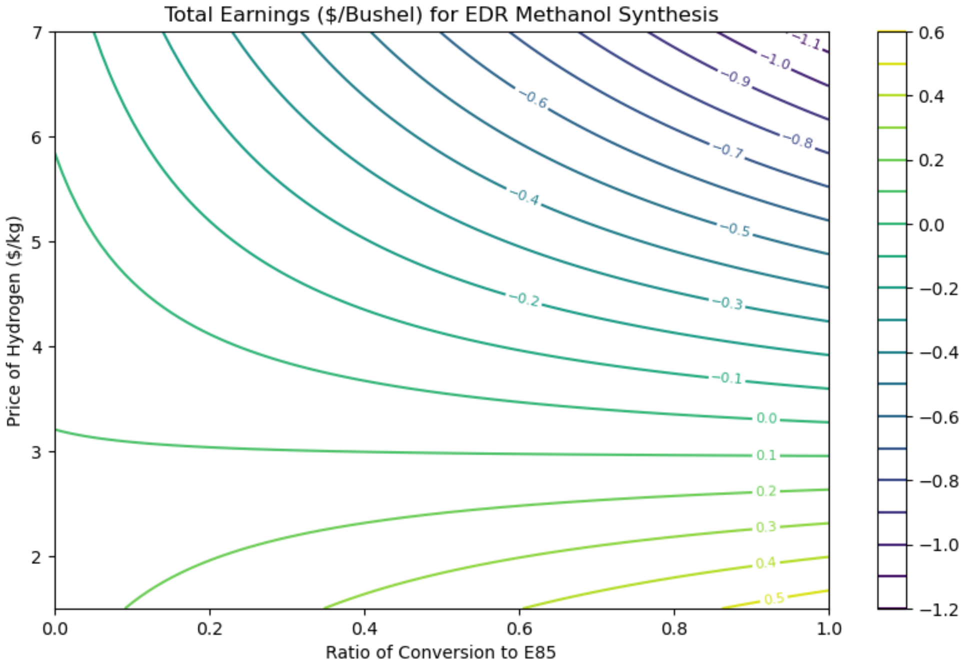

Figure 21 Total Earnings Based on Hydrogen Price and Ratio of Ethanol Conversion to E85 with Sequestration of Remained Carbon Dioxide By EDR.

The analysis suggests that EDR offers more reliable economic performance than IDH, especially at high hydrogen prices. EDR's reduced sensitivity to hydrogen costs and broader feasibility range makes it a better option for large-scale implementation, while IDH may only be viable in specific conditions. EDR's potential for stable returns is enhanced with tax incentives and financial support for CO_2 utilization. These results provide a detailed assessment of the cost benefits, showing that hydrogen price and raw material costs are the most significant factors affecting profitability. The results support the conclusion that EDR is more cost-effective for large-scale implementation, especially when hydrogen prices are low and CO_2 utilization incentives are high.

5. Revise Reactor as Needed and Disseminate Findings

As we continued our analysis, it became evident that a key element in the effective transformation of CO_2 into fuel is the preliminary conversion into intermediate compounds. Additionally, the expense of raw materials—especially hydrogen—significantly influences the economic feasibility of this process. The sourcing of hydrogen emerges as one of the largest cost factors in the CO_2-to-fuel conversion pathway, highlighting the importance of strategies that lessen hydrogen dependence.

To address this issue, we concentrated on adopting Ethanol Dry Reforming (EDR) within our process. Utilizing EDR allows us to extract hydrogen directly from ethanol, which is produced through corn fermentation, to facilitate the CO_2 conversion. This method not only maximizes the utilization of renewable hydrogen but also reduces the dependency on external hydrogen sources, enhancing the sustainability and economic viability of the CO_2-to-fuel pathway. This realization emphasizes the need to refine reactor models to improve EDR integration and showcases the potential of EDR in lowering overall costs and boosting process efficiency.

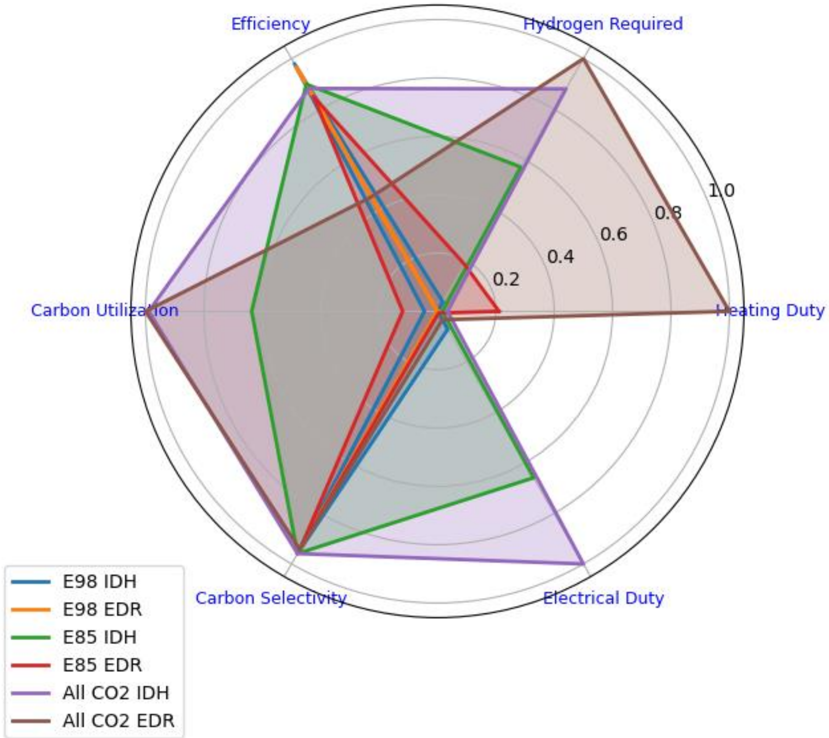

Figure 22 Normalized comparison of Key Performance Indicators (KPIs) among Scenarios

In the context of CO_2 Utilization and Sequestration: Figure 22 features a radar plot that offers a comprehensive perspective on carbon utilization efficiency, selectivity, and overall system performance.

This plot illustrates the trade-offs between various performance indicators, indicating opportunities for optimizing reactor conditions or process flows to further enhance overall efficiency.
All analyzed pathways for carbon dioxide from ethanol refineries to vehicle fuels are illustrated in the Figure 23.

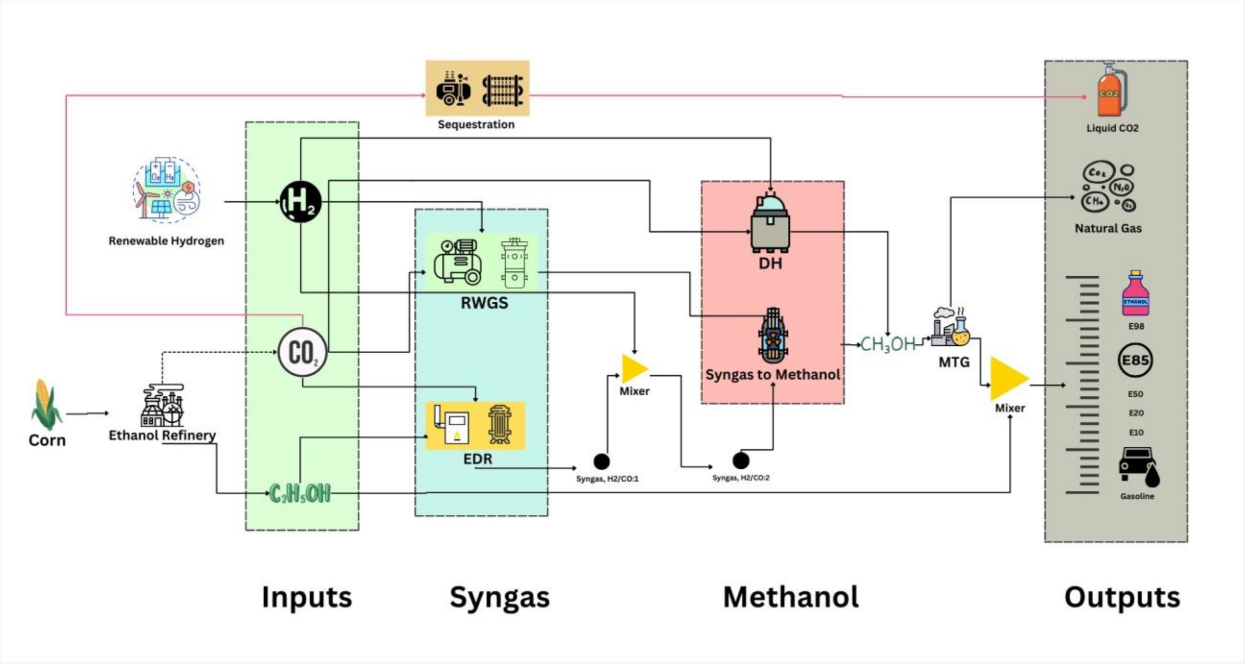

Figure 23 Process flow diagram of existing pathways

CONCLUSIONS

This study developed a plant model for hydrogen production, methanol synthesis, and gasoline conversion using CO_2 from corn ethanol refineries. It compared three methanol synthesis methods: Direct Hydrogenation (DH), Indirect Hydrogenation (IDH), and Ethanol Dry Reforming (EDR). EDR outperformed IDH and DH in methanol and gasoline production per bushel and offered significant economic advantages by reducing hydrogen dependency.

Parametric studies on ethanol-gasoline blends showed that higher gasoline content (E85) increases hydrogen requirements, while E98 maximizes ethanol preservation. Sensitivity analysis revealed that hydrogen prices greatly affect profitability, with EDR maintaining economic resilience across a wider price range than IDH.

Overall, EDR is presented as the most feasible method for large-scale CO_2-to-fuel conversion, aligning well with sustainability goals and cost-effectiveness. The study emphasizes the need to adopt EDR and integrate renewable hydrogen sources for optimal performance.

EDUCATION, OUTREACH, AND PUBLICATIONS

1) Aghaalizadeh, Aylar: Ph.D. student who worked on the project is completing a journal paper for submission to Energy Conversion and Management in early 2025. She is also planning to present the results of this report at the American Chemical Society fall meeting in 2025.

REFERENCES

[1] "Ethanol Market Size, Share & COVID-19 Impact Analysis, By Type (Synthetic and Biobased), By Application (Fuel, Industrial Solvent, Food & Beverages, Chemicals, and Others), and Regional Forecast, 2023-2030." 2023. [Online]. Available: https://www.fortunebusinessinsights.com/industry-reports/ethanol-market-101567

[2] M. F. Demirbas, "Biofuels from algae for sustainable development," *Appl. Energy*, vol. 88, no. 10, pp. 3473–3480, 2011.

[3] S. D. Fernandes, N. M. Trautmann, D. G. Streets, C. A. Roden, and T. C. Bond, "Global biofuel use, 1850–2000," *Glob. Biogeochem. Cycles*, vol. 21, no. 2, 2007.

[4] A. Singh and S. I. Olsen, "A critical review of biochemical conversion, sustainability and life cycle assessment of algal biofuels," *Appl. Energy*, vol. 88, no. 10, pp. 3548–3555, 2011.

[5] V. Shunmugam, "Biofuels—breaking the myth of 'indestructible energy'?," *Margin J. Appl. Econ. Res.*, vol. 3, no. 2, pp. 173–189, 2009.

[6] A. E. Farrell, R. J. Plevin, B. T. Turner, A. D. Jones, M. O'hare, and D. M. Kammen, "Ethanol can contribute to energy and environmental goals," *Science*, vol. 311, no. 5760, pp. 506–508, 2006.

[7] B. Hahn-Hägerdal, M. Galbe, M.-F. Gorwa-Grauslund, G. Lidén, and G. Zacchi, "Bio-ethanol–the fuel of tomorrow from the residues of today," *Trends Biotechnol.*, vol. 24, no. 12, pp. 549–556, 2006.

[8] D. of C. U.S. Census Bureau, "2023 U.S. Ethanol Exports." 2023.

[9] C. Manochio, B. Andrade, R. Rodriguez, and B. Moraes, "Ethanol from biomass: A comparative overview," *Renew. Sustain. Energy Rev.*, vol. 80, pp. 743–755, 2017.

[10] A. Parekh, G. Chaturvedi, and A. Dutta, "Sustainability analyses of CO_2 sequestration and CO_2 utilization as competing options for mitigating CO_2 emissions," *Sustain. Energy Technol. Assess.*, vol. 55, p. 102942, Feb. 2023, doi: 10.1016/j.seta.2022.102942.

[11] M. & Company, "Scaling the CCUS Industry to Achieve Net-Zero Emissions," 2021, [Online]. Available: https://www.mckinsey.com/industries/oil-and-gas/our-insights/scaling-the-ccus-industry-to-achieve-net-zero-emissions

[12] C. R. Service, "The Tax Credit for Carbon Sequestration (Section 45Q)." 2021. [Online]. Available: https://www.crs.gov/reports

[13] W. Wang, S. Wang, X. Ma, and J. Gong, "Recent advances in catalytic hydrogenation of carbon dioxide," *Chem. Soc. Rev.*, vol. 40, no. 7, pp. 3703–3727, 2011.

[14] J. Ma *et al.*, "A short review of catalysis for CO_2 conversion," *Catal. Today*, vol. 148, no. 3–4, pp. 221–231, 2009.

[15] W. C. Chueh *et al.*, "High-flux solar-driven thermochemical dissociation of CO_2 and H2O using nonstoichiometric ceria," *Science*, vol. 330, no. 6012, pp. 1797–1801, 2010.

[16] A. Baiker, "Utilization of carbon dioxide in heterogeneous catalytic synthesis," *Appl. Organomet. Chem.*, vol. 14, no. 12, pp. 751–762, 2000.

[17] G. A. Olah, A. Goeppert, and G. S. Prakash, "Chemical recycling of carbon dioxide to methanol and dimethyl ether: from greenhouse gas to renewable, environmentally carbon neutral fuels and synthetic hydrocarbons," *J. Org. Chem.*, vol. 74, no. 2, pp. 487–498, 2009.

[18] P. Sai Prasad, J. W. Bae, K.-W. Jun, and K.-W. Lee, "Fischer–Tropsch synthesis by carbon dioxide hydrogenation on Fe-based catalysts," *Catal. Surv. Asia*, vol. 12, pp. 170–183, 2008.

[19] M. Fujiwara, R. Kieffer, H. Ando, and Y. Souma, “Development of composite catalysts made of Cu-Zn-Cr oxide/zeolite for the hydrogenation of carbon dioxide,” *Appl. Catal. Gen.*, vol. 121, no. 1, pp. 113–124, 1995.

[20] X. Xiaoding and J. Moulijn, “Mitigation of CO_2 by chemical conversion: Plausible chemical reactions and promising products,” *Energy Fuels*, vol. 10, no. 2, pp. 305–325, 1996.

[21] P. J. Lunde and F. L. Kester, “Carbon dioxide methanation on a ruthenium catalyst,” *Ind. Eng. Chem. Process Des. Dev.*, vol. 13, no. 1, pp. 27–33, 1974.

[22] M. E. Dry, “Practical and theoretical aspects of the catalytic Fischer-Tropsch process,” *Appl. Catal. Gen.*, vol. 138, no. 2, pp. 319–344, 1996.

[23] Chakraborty Jyoti Prasad, Satyansh Singh and S. K. Maity, “Advances in the conversion of methanol to gasoline,” *Hydrocarb. Biorefinery*, pp. 177–200, 2022.

[24] Van-Dal Éverton Simões and C. Bouallou, “Design and simulation of a methanol production plant from CO_2 hydrogenation,” *J. Clean. Prod.*, vol. 57, pp. 38–45, 2013.

[25] B. Bej, S. Bepari, N. C. Pradhan, and S. Neogi, “Production of hydrogen by dry reforming of ethanol over alumina supported nano-NiO/SiO2 catalyst,” *Catal. Today*, vol. 291, pp. 58–66, 2017.

[26] M.-N. N. Shafiqah *et al.*, “Advanced catalysts and effect of operating parameters in ethanol dry reforming for hydrogen generation. A review,” *Environ. Chem. Lett.*, vol. 20, no. 3, pp. 1695–1718, 2022.

[27] P. Osorio-Vargas, N. A. Flores-González, R. M. Navarro, J. L. Fierro, C. H. Campos, and P. Reyes, “Improved stability of Ni/Al2O3 catalysts by effect of promoters (La2O3, CeO2) for ethanol steam-reforming reaction,” *Catal. Today*, vol. 259, pp. 27–38, 2016.

[28] A. M. Da Silva *et al.*, “Steam and CO_2 reforming of ethanol over Rh/CeO2 catalyst,” *Appl. Catal. B Environ.*, vol. 102, no. 1–2, pp. 94–109, 2011.

[29] T. S. Moraes *et al.*, “Ethanol conversion at low temperature over CeO2—Supported Ni-based catalysts. Effect of Pt addition to Ni catalyst,” *Appl. Catal. B Environ.*, vol. 181, pp. 754–768, 2016.

[30] A. de Zawadzki, J. D. A. Bellido, A. F. Lucrédio, and E. M. Assaf, “Dry reforming of ethanol over supported Ni catalysts prepared by impregnation with methanolic solution,” *Fuel Process. Technol.*, vol. 128, pp. 432–440, 2014.

[31] T. J. Siang, A. A. Jalil, A. Abdulrahman, and H. U. Hambali, “Enhanced carbon resistance and regenerability in methane partial oxidation to syngas using oxygen vacancy-rich fibrous Pd, Ru and Rh/KCC-1 catalysts,” *Environ. Chem. Lett.*, vol. 19, pp. 2733–2742, 2021.