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Comparison of carbon utilization technologies for decarbonization strategy in the ammonia industry

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Abstract

The ammonia industry is a carbon-intensive chemical subsector that remains highly dependent on fossil-based hydrogen and therefore requires practical decarbonization strategies. Carbon Capture Utilization (CCU) offers an attractive route by converting captured CO_2 into value-added products, but most previous studies have focused on a single utilization pathway, leaving the most suitable option for ammonia plants unclear. Therefore, this study presents a comparative analysis of three CO_2 utilization pathways, namely methanol, methane, and sodium bicarbonate, using a common simulation and assessment framework. Aspen Plus® was used to simulate each process with a fixed captured CO_2 flow rate of 71.5 ton/h based on ammonia-plant emission data. The pathways were then compared in terms of product performance, energy intensity, project economics, and net CO_2 reduction within the modeled CCU section. The results show that sodium bicarbonate provides the most balanced overall performance. It gives the lowest specific energy consumption at 0.038 MJ/kg product and 0.111 MJ/kg CO_2 converted, the strongest base-case project economics with an NPV of 1,605 million USD, an IRR of 53%, and a payback period of 2.55 years, and the highest net CO_2 reduction at 96% within the assessed process boundary. By contrast, methanol and methane are more sensitive to hydrogen cost and product-price assumptions and remain economically attractive only under favorable conditions. Overall, sodium bicarbonate is identified as the most robust CO_2 utilization pathway for the ammonia industry under the assumptions adopted in this study.

Keywords:
Ammonia Industry;
CO_2 Conversion;
Economic Feasibility;
Energy Consumption;
Process Simulation;

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INTRODUCTION

Global climate change is a crucial issue receiving significant attention due to its increasingly evident impact on the environment and human life. One of the main factors contributing to climate change is high greenhouse gas (GHG) emissions, with the transportation sector being the largest contributor. Additionally, the industrial sector also makes a significant contribution, particularly from production activities and the use of fossil fuels. While the use of fossil fuels can enhance productivity, it is also considered one of the primary sources of climate change, which could lead to various issues in the future [1].

Climate change has caused widespread adverse impacts and related losses and damages to nature and people that are unequally distributed across systems, regions, and sectors. Economic damages from climate change have been detected in climate-exposed sectors, such as energy [2]. According to the Indonesia Energy Transition Outlook 2024 report, GHG emissions from the energy sector are projected to increase from 743 $MtCO_2e$ in 2022 to 963 $MtCO_2e$ in 2030. In line with these projections and as part of its international commitments, Indonesia has set a target to achieve carbon neutrality by 2060 [3]. This requires the development of concrete and adaptive decarbonization strategies across various industrial sectors, including the chemical industry, which has a high carbon footprint.

The ammonia industry is one of the chemical subsectors that still relies on fossil fuels and contributes to significant carbon emissions. Overall, the ammonia industry accounts for nearly 2% of global carbon emissions. Each ton of ammonia production emits approximately 1.6 tons of CO_2, with a worldwide average of 2.86 tons of CO_2 per ton of ammonia [4][5]. At present, approximately 80-86% of the hydrogen used in ammonia production is derived from natural gas through Steam Methane Reforming (SMR), a process commonly referred to as gray hydrogen. Meanwhile, blue hydrogen production essentially integrates a gray hydrogen process with a CO_2 capture unit [6][7]. The level of CO_2 capture applied to the ammonia industry is reported to be up to 90% [8]. Therefore, the ammonia industry needs to implement innovative technologies and efficient solutions as part of global efforts to reduce carbon emissions.

In resolving this issue, two main strategies are present, including Carbon Capture Storage (CCS) and Carbon Capture Utilization (CCU) [9]. The CCS strategy converts CO_2 emissions from large sources, such as chimneys or directly from the air. It is then compressed, transported, and stored several hundred meters below ground level [10]. On the other hand, the CCU approach converts CO_2 emissions into valuable products such as fuel or other chemicals, thereby preventing their direct release into the atmosphere and providing economic benefits from selling value-added products [11]. This considerable potential for CCU strategies offers an opportunity to support the country’s efforts to reduce carbon emissions.

The utilization of CO_2 as a product has been widely studied and can generally be classified as energy-based (fuels) or non-energy products. Producing fuels from CO_2 offers significant benefits amid global energy resource depletion [12][13]. Power-to-Liquid (PtL) systems, like methanol, are among the most promising technologies for converting industrial CO_2 into renewable fuels for transportation and infrastructure [14]. Similarly, Renewable Natural Gas (RNG) and methane, produced via Power-to-Gas (PtG) technology, are important alternatives to fossil natural gas [15]. Carbonates such as sodium bicarbonate are also promising, as they enable long-term CO_2 storage, an essential factor for achieving positive economic and environmental outcomes in CCU technologies [16].

Most studies on decarbonizing ammonia production examine only one pathway. Many focus on a single production route, such as blue ammonia or green ammonia [17]. Others consider a single utilization outlet, such as urea, methanol, or methane. Few papers benchmark several utilization products on a shared basis. Plant-level integration further complicates single-route assessments. Impurity tolerance, pressure, and temperature matching, and compression and heat duties, can shift both capital and operating costs if routes are modeled in isolation [18]. A recent complete chain comparison of green ammonia and green methanol reaches a similar conclusion and calls for unified, comparable frameworks across carriers [17]. Recent cross-carrier comparisons note the same fragmentation across the literature [19]. Methodological guidance has likewise emphasized the problem of ‘apples vs. oranges’ comparisons and provides rules to align assumptions and improve comparability across system boundaries [20]. This issue shows the need for integrated comparisons that use consistent assumptions and common system boundaries.

Therefore, this study aims to analyze carbon utilization across multiple pathways. Methanol, sodium bicarbonate, and methane are selected as products, representing different types of typical carbon utilization products. The carbon dioxide feed stream is drawn from the already purified stream of one ammonia plant in Indonesia. Aspen Plus simulation models estimate product yield, raw material use, and utility demand. These outputs inform an economic analysis in the Aspen Process Economic Analyzer to determine NPV and IRR. An environmental analysis quantifies reductions in carbon dioxide emissions. Each case is evaluated using a single aligned simulation and assessment framework, enabling a comprehensive comparison of the most promising products. Unlike previous studies that focused on a single carbon dioxide utilization pathway, this work provides a comparative multi-pathway analysis specific to ammonia industry emissions in Indonesia.

METHOD

This section describes the approach used to assess the economic and environmental viability of carbon utilization technologies, focusing on methanol, sodium bicarbonate, and methane. In this study, the case is tailored to the actual conditions of one of Indonesia's existing ammonia industries equipped with a carbon capture system. The analysis focuses specifically on the utilization of captured CO_2 rather than the capture process itself, with the specifications of the captured CO_2 shown in Table 1.

As shown in Figure 1, the process simulation for each product is performed using Aspen Plus V14 to obtain the necessary mass and energy balances. In addition, data from the literature were required to design process flows and configurations in Aspen Plus, including determining operating conditions such as pressure, temperature, raw material ratios, and other performance parameters needed to model the production processes of the three products. Subsequently, the economic and environmental aspects were analyzed based on the results of the process simulations.

To maintain consistency with the objective of this study, the environmental assessment was limited to the CCU section and applied as a gate-to-gate comparison of the three product pathways. The system boundary starts from the captured and purified CO_2 stream supplied by the ammonia plant and includes the process operation, utility consumption, and CO_2 conversion into methanol, sodium bicarbonate, and methane. All non-CO_2 raw materials, including hydrogen, water, and sodium carbonate, were treated as externally supplied inputs. Therefore, the upstream burdens associated with raw material production, including water consumption and energy source impacts from third-party hydrogen supply, were excluded from the present boundary. Pathway-specific secondary impacts outside the modeled CCU section were also not quantified. Accordingly, the environmental results are presented as comparative net CO_2 reductions rather than as a full life cycle assessment.

Process description of methanol

In this simulation, the methanol synthesis process is modeled using carbon dioxide and hydrogen as the primary raw materials. As mentioned in the preceding literature, the methanol synthesis undergoes three reactions, shown in (1), (2), and (3) [21].

$$CO + 2H_2 \rightleftharpoons CH_3OH \tag{1}$$

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \tag{2}$$

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O \tag{3}$$

The kinetic expressions for these reactions have been modelled in Aspen Plus and validated against experimental data using Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetics. Then, the validated kinetic rate expressions presented in this paper, as shown in (4), (5), and (6), are used. The value of these parameters has already been detailed for the three kinetic rate expressions, referring to the literature [21].

$$r_{(1)} = k_A \frac{K_{CO}\,[f_{CO} f_{H_2}^{\frac{3}{2}} - f_{CH_3OH} / (K_A \sqrt{f_{H_2}})]}{(1 + K_{CO} f_{CO} + K_{CO_2} f_{CO_2})\,[\sqrt{f_{H_2}} + (K_{H_2O} / \sqrt{K_{H_2}}) f_{H_2O}]} \tag{4}$$

$$r_{(2)} = k_B \frac{K_{CO_2}\,[f_{CO_2} f_{H_2} - f_{H_2O} f_{CO} / K_B]}{(1 + K_{CO} f_{CO} + K_{CO_2} f_{CO_2})\,[\sqrt{f_{H_2}} + (K_{H_2O} / \sqrt{K_{H_2}}) f_{H_2O}]} \tag{5}$$

$$r_{(3)} = k_C \frac{K_{CO_2}\,[f_{CO_2} f_{H_2}^{\frac{3}{2}} - f_{H_2O} f_{CH_3OH} / (f_{H_2}^{\frac{3}{2}} K_C)]}{(1 + K_{CO} f_{CO} + K_{CO_2} f_{CO_2})\,[\sqrt{f_{H_2}} + (K_{H_2O} / \sqrt{K_{H_2}}) f_{H_2O}]} \tag{6}$$

Table 1. CO_2 specifications in one of Indonesia's ammonia industries

Parameters	Value
Temperature (°C)	37.51
Pressure (Bar)	0.85
Mass Flowrate (ton/hour)	71.50
Composition of CO_2	99.90%

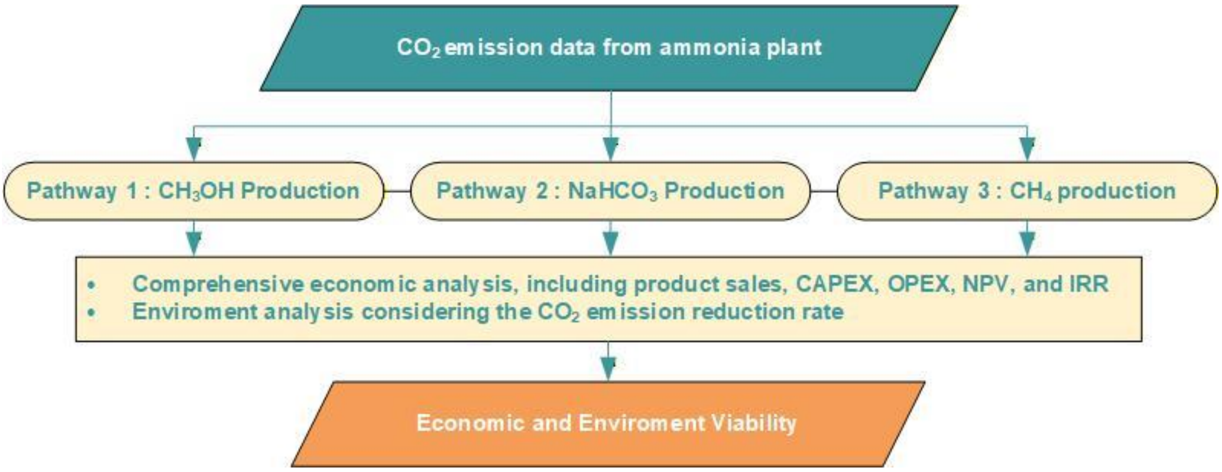


Figure 1. Framework for this study

Figure 2 shows a typical reaction–separation–recycle flowsheet for methanol production. Compressed CO_2 (100 bar, 20°C) is mixed with H_2 (45 bar, 170°C), preheated, and fed into an isothermal plug flow reactor (250°C, 50 bar) containing Cu/Zn/Al/Zr catalyst. The reactor output is cooled and separated in a flash drum (45 bar, 31°C) into a liquid (methanol-water) and a gas (mainly CO_2, CO, and H_2), with most of the gas recycled. The liquid undergoes stripping (87.6°C, 5 bar) to remove dissolved gases and is further purified in a 30-stage distillation column (45 bar), yielding pure methanol (39°C, 1.013 bar, ~12,508 kg/h) and water as a by-product.

Process description of sodium bicarbonate

The simulation process for sodium bicarbonate synthesis uses the ElecWizard platform, as the system involves inorganic carbonate-based salt solutions that are highly influenced by reaction equilibrium. Non-electrolyte models cannot accurately represent this phenomenon, so ElecWizard was chosen to ensure simulation results closely match actual industrial operating conditions. The main reaction of CO_2 soda ash carbonation is shown in (7).

$$Na_2CO_3 + CO_2 + H_2O \rightleftharpoons 2NaHCO_3 \tag{7}$$

As illustrated in Figure 3, the process starts by mixing sodium carbonate and water to form a solution. Compressed CO_2 (1.47 bar, 40°C) is cooled and reacted with the solution in a crystallizer (1.5 bar, 35°C), producing $NaHCO_3$ crystals. Excess gas is separated into a flash drum, with some recycled to the crystallizer. The crystallizer output is separated in a centrifuge, yielding $NaHCO_3$ crystals (35°C, 1 bar) as the main product and mother liquor as a by-product, while light gases are vented. The simulation shows production rates of 111.88 kmol/h $NaHCO_3$, 206.66 kmol/h mother liquor, and 34.36 kmol/h vent gas [16].

Process description of methane

The simulation of the methane formation process from carbon dioxide (CO_2) and hydrogen (H_2) feedstocks was performed in Aspen Plus V14 using the flow configuration shown in the flowsheet. The main reaction using Ni/Al(O)x catalyst was developed for the reaction of CO_2 methanation, as shown in (8) [22].

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O \tag{8}$$

The rate equation is given in (9). The parameter details for the kinetic rate expressions are taken from the literature.

$$r = \frac{k\,[p_{H_2}{}^{0,5}\,p_{CO_2}{}^{0,5}\,(1 - \frac{p_{CH_4}\,p_{H_2O}{}^{2}}{p_{CO_2}\,p_{H_2}{}^{4}\,K_{eq}})}{(1 + K_{OH}\frac{p_{H_2O}}{p_{H_2}{}^{0,5}} + K_{H_2}p_{H_2}{}^{0,5} + K_{mix}\,p_{CO_2}{}^{0,5})^{2}} \tag{9}$$

Figure 4 illustrates the process where CO_2 is compressed (9 bar), cooled, and mixed with H_2 and recycle gas before preheating and entering reactor R1 (262°C, 9 bar). In R1, catalytic methane synthesis occurs. The output is cooled, split for recycling, and directed to reactor R2 (252°C, 6 bar) for further conversion. After final cooling, the product stream enters flash separators, yielding methane (28.21 kg/h, 46°C, 6 bar) as a by-product, and the unreacted gas is recirculated to the mixer.

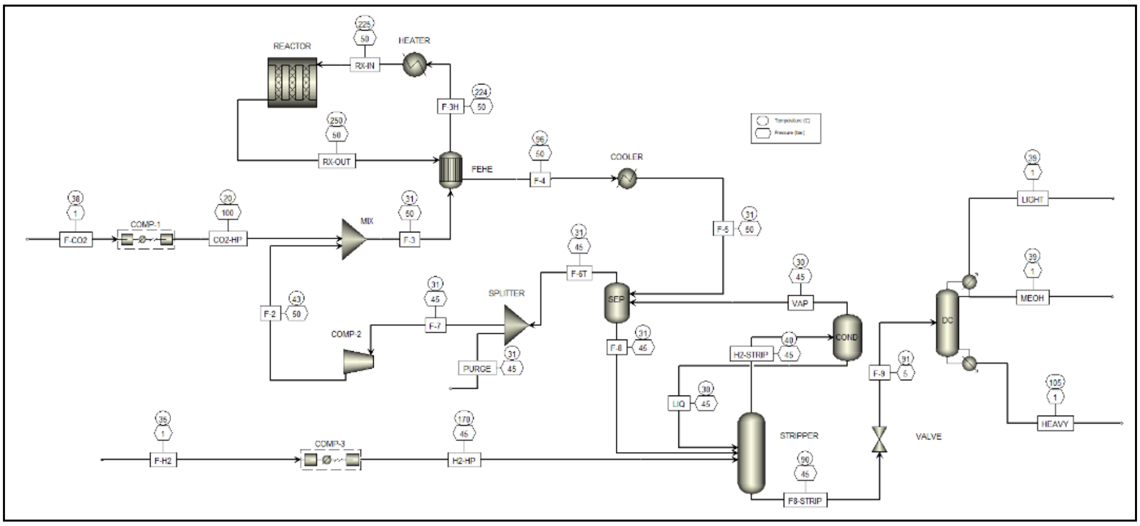


Figure 2. Simulation flowsheet of methanol using Aspen Plus V14

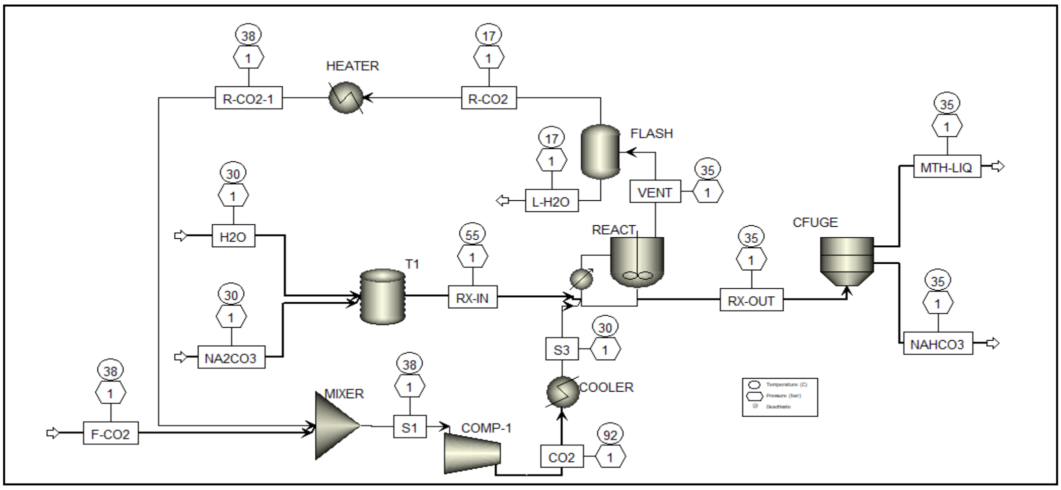


Figure 3. Simulation flowsheet of sodium bicarbonate using Aspen Plus V14

RESULTS AND DISCUSSION

The objective of this study is to identify CO_2 utilization pathways by comparing products with the highest economic potential and carbon-emission-reduction potential in the ammonia industry.

Model Validation

To ensure the accuracy of the simulation model used in this research, validation was conducted by comparing simulation results with reference data. The comparison between the two results was performed by calculating the Relative Root Mean Square Error (RRMSE). Meanwhile, RRMSE normalizes the average magnitude of differences between predicted and actual values by dividing by the dependent variable's range, yielding a relative measure of error. The RRMSE values can be calculated using (10) [23].

$$\text{RMSE} = \sqrt{\left(\frac{1}{m}\right)\sum_{i=1}^{m}\left(A_{v_i} - P_{v_i'}\right)^2} \qquad (10)$$

Where m is the number of data points (samples/observations), A_{v_i} is the actual value at the i-th data point, $P_{v_i'}$ is the predicted value at the i-th data point

Table 2 shows that the mass flow obtained from the methanol product validation process has an RRMSE of 3.691%. The minimal deviation between the simulation results and the reference values indicates that the developed model accurately represents the actual process and can therefore be considered reliable for further analysis and scenario evaluation.

As indicated in Table 3, the obtained mass flow for the sodium bicarbonate production process has an RRMSE value of 3.912%. Although the error obtained is higher than that in the methanol validation, the difference is still within an acceptable range. Thus, the simulation results can still be used as a representative basis for performance evaluation and further process development.

The deviation of simulated methane production is presented in Table 4, indicating that the molar flow obtained from the methane product validation process has an RRMSE value of 0.891%. The relatively small overall error means that the simulation results are sufficiently close to the reference data, confirming the model's validity. This provides confidence that the developed model can be further utilized to analyze process behavior and optimize operating conditions in subsequent studies [23].

Table 2. Methanol product validation

Stream	Simulation Results	Reference Results	Error
RX-IN	122,003.00	122,002.00	0.000%
RX-OUT	122,003.00	122,002.00	0.000%
F-9	19,870.00	19,867.00	0.011%
LIGHT	11.38	12.52	9.042%
MEOH	12,509.00	12,508.00	0.002%
HEAVY	7,349.00	7,346.00	0.040%
RRMSE			**3.691%**

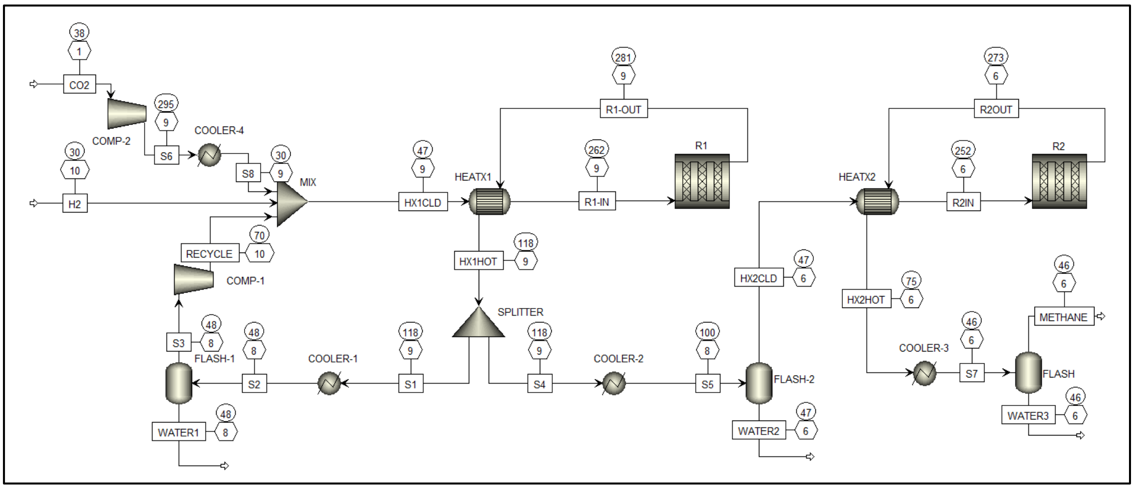


Figure 4. Simulation flowsheet of methane using Aspen Plus V14

Table 3. Sodium Bicarbonate product validation

Stream	Simulation Results	Reference Results	Error
VENT	297.15	297.14	0.006%
$NaHCO_3$	1,029.41	1,091.25	5.667%
MTH-LIQ	1,725.74	1,663.92	3.715%
RRMSE			**3.912%**

Table 4. Methane product validation process

Stream	Simulation Results	Reference Results	Error
R1 IN	0.13	0.13	0.000%
R1 OUT	0.03	0.03	1.022%
R2 IN	102.72	104.10	1.319%
R2 OUT	102.25	102.90	0.628%
RRMSE			**0.891%**

Simulation Results

A common carbon dioxide source from ammonia, with a purity of 99.99%, was used in three utilization routes, namely methanol, sodium bicarbonate, and methane. The comparison focuses on CO_2 conversion into several products, with emphasis on product rate, product purity, byproduct formation, economic feasibility, and net CO_2 reduction within the modelled CCU section. To maintain that scope, the CCU capacity was fixed according to the CO_2 specification in Table 1, all non-CO_2 raw materials were assumed to be purchased from third parties, and the environmental comparison was limited to net CO_2 reduction within the modelled process boundary. Upstream burdens associated with raw-material production, including water consumption and energy-source impacts from hydrogen supply, were excluded, and pathway-specific secondary impacts outside the modelled CCU section were not quantified. In all cases, unreacted gases were recycled to minimize losses and maintain a common CO_2 capacity basis across the three pathways.

In the methanol route, carbon dioxide reacts with hydrogen to form a liquid methanol product stream with a total mass flow rate of 52,443 kg/h and a purity of 99.15%, as shown in Table 5. Reactor kinetics follow a Langmuir, Hinshelwood, Hougen, and Watson approach [21]. The vapor phase is handled using the RK Soave cubic equation of state, and liquid-phase splitting uses the NRTL activity model. The main byproduct is water (99.99%), which is primarily left in the distillation section. Light gases are returned to the reactor loop to maintain conversion, while the distillation duty is focused on meeting the methanol specification. A recent study suggests that the methanol yield from inlet carbon dioxide is 70.52%. Compared with the simulation results of this study, the 73.37% yield indicates a higher methanol production. However, the hydrogen-to-carbon dioxide ratio is slightly higher than reported in the literature at 0.14, rather than 0.15 in this study [21]. The slight differences indicate a trade-off in hydrogen demand within the system, and the simulation results for methanol production remain aligned with the recent publication.

The sodium bicarbonate pathway converts carbon dioxide into a solid sodium bicarbonate product stream with essentially complete purity. The electrolyte thermodynamics are treated with the ELECNRTL model, while the gas phase uses a cubic equation of state for consistency with the recycle header [16]. Table 6 shows that crystals are recovered by solid-liquid separation at a rate of 207,921 kg/h. At the same time, the remaining solution, containing water along with sodium and bicarbonate ions, is processed at a rate of 407,159 kg/h. Gas recycle maintains near complete capture of the entering carbon dioxide. Compared to the existing literature on sodium bicarbonate production, this study achieves a higher purity, reaching almost unity, compared to 93.4%. This improvement is achieved by rerouting CO_2 vented from crystallization for recycling back into the system [16].

For the methane route, carbon dioxide reacts with hydrogen at a rate of 12,609 kg/hr over a nickel catalyst. The thermodynamic method is Peng-Robinson. The design uses a two-reactor loop with an internal gas recycle. Condensed water is removed between steps to maintain catalyst performance and to enhance methane concentration [22]. Table 7 shows that a high purity (91.23%) of methane is produced at a rate of 27,496.3 kg/hr, and unreacted gases are recycled to raise overall conversion. Benchmarking the results against the existing literature suggests a lower methane purity in this study, at 91.23%, compared to 96% in the literature. This lower result is attributed to the lower hydrogen inlet of this simulation as compared to the literature [22]. The low amount of hydrogen used aims to maintain the economics of this process.

Overall, the technical results obtained in this study are in reasonable deviation from the referenced literature, and the observed deviations can be explained by differences in the hydrogen-to-CO_2 ratio, recycle strategy, and pathway-specific process configuration. Across the three routes, sodium bicarbonate provides the largest mass of saleable product at very high purity, methanol provides a high-purity liquid intermediate with a relatively straightforward separation sequence, and methane yields a moderate-purity gaseous product with substantial co-produced water removal. The corresponding breakdown of process water, steam, electricity, and cooling water demand for each pathway is presented in Table 8. These utility data were then used to determine total utility cost in the economic analysis and utility-related CO_2 emissions in the environmental analysis.

As a steady-state comparative assessment, the present work does not explicitly model catalyst deactivation over time. For the methanol route, recent studies on $Cu/ZnO/Al_2O_3$ have shown that long-term performance can decline during CO_2 hydrogenation, with sintering identified as a major cause of activity loss [24]. For the methane route, Ni/Al_2O_3 methanation catalysts have also been reported to undergo measurable deactivation during extended operation, which may reduce long-term methane productivity [25]. By contrast, the sodium bicarbonate pathway considered here is not catalyst-driven, although sodium carbonation routes can still face process-level limitations such as sluggish kinetics, solvent evaporation, product-purity constraints, and secondary-waste generation [26]. Therefore, the comparative results reported in this study should be interpreted as steady-state pathway indicators, while future work should further evaluate catalyst stability and long-term operability, especially for the methanol and methane routes.

Utility Demand and Energy Intensity

In addition to product yield and utility demand, the three pathways were compared in terms of energy intensity to provide a process-level basis for broader pathway evaluation. Table 8 presents the utility inventory for methanol, sodium bicarbonate, and methane pathways, including electricity, steam, cooling water, and process water. In this study, electricity and steam were treated as the main direct energy carriers for comparative analysis, whereas cooling water and process water were retained as supporting utilities for subsequent economic and environmental evaluations. This treatment follows recent benchmarking approaches that separate direct energy carriers from supporting utilities to improve comparability across industrial process configurations [27].

The total direct energy input was calculated from the electricity and steam demand, as shown in (11). The specific energy consumption per unit product was calculated by dividing the total direct energy input by the product mass flow rate, as shown in (12). Similarly, the specific energy consumption per unit of CO_2 converted was calculated by dividing the total direct energy input by the mass flow rate of CO_2 retained in the product, as expressed in (13).

Table 5. Material streams data of the proposed process for methanol synthesis

Parameter	**Input**		**Output**		
	F-CO_2	**F-H_2**	**LIGHT**	**CH_3OH**	**HEAVY**
Temperature	37.50	35.00	39.00	39.00	105.05
Pressure	0.85	1.10	1.01	1.01	1.10
Mass Flow (kg/h)	71,500	11,047.00	46.29	52,443.00	30,036.10
Mass Frac CO_2	0.99	-	1.682E-05	4.09E-08	2.44E-36
Mass Frac H_2	-	0.89	0.1236	1.99E-06	5.03E-32
Mass Frac CO	-	-	-	-	-
Mass Frac H_2O	0.0001	0.11	0.0022	0.008	0.99
Mass Frac CH_3OH	-	-	0.8741	0.992	2.18E-13

Table 6. Material streams data of the proposed process for sodium bicarbonate

Parameter	Input			Output	
	F-CO_2	H_2O	Na_2CO_3	$NaHCO_3$	MTH-LIQ
Temperature	38.35	30.00	30.00	35.00	35.00
Pressure	0.85	1.47	1.47	1.47	1.47
Mass Flow (kg/h)	71,499.97	376,595.82	167,375.92	207,920.83	407,159.04
Mass Frac Na_2CO_3	-	-	1	-	-
Mass Frac H_2O	0.01	1	-	-	0.86
Mass Frac CO_2	0.99	-	-	-	0,004
Mass Frac H_3O^+	-	-	-	-	5.85E-10
Mass Frac Na^+	-	-	-	-	0.0296
Mass Frac $NaHCO_3$	-	-	-	1	0.0325
Mass Frac HCO_3^-	-	-	-	-	0.0757
Mass Frac CO_3^{--}	-	-	-	-	0.0014

Table 7. Material streams data of the proposed process for methane

Parameter	Input		Output			
	CO_2	H_2	CH_4	WATER-1	WATER-2	WATER-3
Temperature	37.5	30.00	45.80	47.50	47.40	45.80
Pressure	0.85	10.01	6.00	8.00	6.20	6.00
Mass Flow (kg/h)	71,500	12,609	27,496.3	46,431.7	10,152.4	28.35
Mass Frac CO_2	0.99	-	0.0715	8.98E-06	6.98E-06	6.60E-06
Mass Frac H_2	-	1	4.28E-07	7.71E-11	5.92E-11	7.75E-13
Mass Frac CH_4	-	-	0.9123	1.22E-05	9.47E-06	8.75E-06
Mass Frac H_2O	0.01	-	0.0161	0.99	0.99	0.99

Specific energy consumption is commonly expressed as the energy required per unit mass of the product. However, recent CCU studies also report specific energy consumption per kilogram of converted CO_2 to compare alternative conversion routes on a common carbon basis [28][29].

$$E_{total} = E_{elec} + Q_{steam} \tag{11}$$

$$SEC_{product} = \frac{E_{total}}{m_{product}} \tag{12}$$

$$SEC_{CO_2} = \frac{E_{total}}{m_{CO_2 converted}} \tag{13}$$

where E_{total} is the total direct energy input in MJ/h, E_{elec} is the electricity demand converted into MJ/h, Q_{steam} is the steam duty in MJ/h, $\dot{m}_{product}$ is the product mass flow rate in kg/h, and $\dot{m}_{CO_2,converted}$ is the mass flow rate of CO_2 retained in the product in kg/h.

Table 9 shows clear differences in direct energy demand among the three CO_2 utilization pathways. Methanol has the highest total direct energy input, followed by methane, while sodium bicarbonate requires the lowest. When normalized to product output, the specific energy consumption reaches 4.564 MJ/kg product for methanol, 0.606 MJ/kg product for methane, and only 0.038 MJ/kg product for sodium bicarbonate. A similar trend is observed on a carbon basis, where the specific energy consumption per kilogram of CO_2 converted is 3.348 MJ/kg CO_2 for methanol, 0.239 MJ/kg CO_2 for methane, and 0.111 MJ/kg CO_2 for sodium bicarbonate.

For methanol, the obtained utility intensity is comparable to recent CO_2 hydrogenation studies. One study reported electricity demand of about 550 kWh/t methanol and steam consumption of 0.48–1.16 t steam/t methanol for low-energy hydrogenation flowsheets, which is close to the present result of about 573 kWh/t methanol and 1.15 t steam/t methanol [30]. For methane, recent Power-to-Gas studies report much higher energy intensities, such as 39–50 MJ/kg CO_2 in integrated electrolysis and methanation systems and 40.5–42.4 MJ/kg CO_2 avoided in thermally integrated synthetic natural gas production [31]. The lower value obtained in this study is expected because the present comparison is limited to the modeled CCU section and excludes upstream hydrogen production and CO_2 capture burdens. or carbonate-based CCU, Belinchón et al. reported specific energy consumption in the range of 8.4–15.7 MJ/kg CO_2 for cyclic carbonate production, which remains substantially above the sodium bicarbonate route obtained here [29]. Although the product class is not identical, the comparison still supports the low energy demand of carbonate-type carbon fixation relative to hydrogenation pathways. Overall, the energy analysis confirms that the three pathways have distinct process-intensity characteristics, with sodium bicarbonate showing the lowest direct energy demand, methanol the highest, and methane an intermediate profile. These findings are used in the next sections to support the broader comparison of economic and environmental performance.

Table 8. Utility consumption and associated basis for economic and environmental analysis

Utility	Unit	Methanol	Sodium Bicarbonate	Methane	Unit Cost ($/ Unit)	Emission Basis (kg CO2e/ Unit)
Electricity	kWh	30,039.14	1,861.47	4,749.25	0.068	0.181
Steam	ton/hour	60.12	0.57	0.00	5.125	115.703
Cooling Water	ton/hour	6,058.88	372.34	7185.95	0.149	3.156
Process Water	ton/hour	0.00	376.60	0.00	2.000	3.156

Table 9. Comparative energy performance of the CO_2 utilization pathways

Parameter	Unit	Methanol	Sodium Bicarbonate	Methane
Electricity Demand	MJ/hour	108,140.90	6,701.27	17,097.29
Steam duty	MJ/hour	131,207.03	1,240.88	-
Total direct energy input	MJ/hour	239,347.93	7,942.16	17,097.29
Specific energy consumption per kg product	MJ/kg product	4.564	0.038	0.606
Specific energy consumption per kg CO_2 converted	MJ/kg CO_2 converted	3.348	0.111	0.239

Economic Feasibility Analysis

Economic analysis was carried out to evaluate pathway feasibility under the market and policy conditions considered in this study. Operating costs consist of raw materials and utilities. The main raw materials are purchased green hydrogen and soda ash, while the utilities include processing water, steam, electricity, and cooling water. Utility prices were kept fixed across all scenarios because they were obtained from the literature and local tariff references. The adopted values were 2 USD/ton for processing water and 5.1 USD/ton for steam [16][32]. Electricity and cooling water prices were fixed at 0.0679 USD/kWh and 0.15 USD/ton, respectively [32]. By contrast, selected raw-material prices, product selling prices, CO_2 supply costs, and carbon incentives were varied to test the robustness of project feasibility under market and policy uncertainty.

The scenario analysis follows three cases, namely pessimistic, base, and optimistic. The base case represents the reference condition used in the main economic evaluation, whereas the pessimistic and optimistic cases represent unfavorable and favorable conditions within the reported literature and market ranges, respectively. For revenue variables, the optimistic case corresponds to a higher product selling price and carbon incentive. For cost variables, the optimistic case corresponds to a lower purchase price or CO_2 supply cost. The corresponding assumptions are summarized in Table 10 [33].

The revenue variables include methanol, sodium bicarbonate, and methane selling prices, along with carbon incentives. Methanol price assumptions were selected from reported market-based studies and recent reference prices [34][35]. The optimistic methanol case was represented by a higher market reference value [36]. The sodium bicarbonate price varied within the reported industrial price range in recent studies [37][38]. The upper scenario also reflects moderately high industrial prices [39]. The methane price was varied using reported market and literature-based assumptions [40][41]. Conventional natural gas values were used to avoid overstating the methane production value. Carbon incentives have been evaluated under low, moderate, and strong policy support conditions [42][43].

The cost variables include the green hydrogen purchase price, soda ash price, and CO_2 supply costs. The hydrogen price was varied according to the reported ranges for green hydrogen purchase [12][44]. The soda ash base case was taken from the literature, whereas the pessimistic and optimistic cases were generated by applying a ±20% variation around that value [16]. The CO_2 supply cost was included as a proxy for the upstream capture and conditioning costs [43][45]. Its scenario range was selected from recent Aspen-based techno-economic studies, while the system boundary of the present work remained focused on the CCU section rather than a detailed capture process design [46].

Based on the scenario assumptions in Table 10, the operating economics results in Table 11 and Figure 5 show that the three pathways respond differently to changes in market and policy conditions. Sodium bicarbonate remains profitable in all scenarios, whereas methanol and methane are unprofitable in the pessimistic and base cases and become profitable only in the optimistic case. Figure 5 further shows that the gap between total revenue and total operating cost remains consistently positive for sodium bicarbonate, while methanol and methane only reach a positive margin under favorable conditions. This pattern indicates that hydrogen-based CO_2 utilization routes are more sensitive to feedstock cost and product selling price, as also reported in previous techno-economic studies [12][47]. By contrast, sodium bicarbonate shows a more robust economic profile because it does not depend on hydrogen as the principal reactant and has previously been associated with stronger economic performance in carbonate-based CO_2 utilization studies [16][48]. Therefore, sodium bicarbonate is identified as the most robust pathway under the market and policy ranges considered in this work.

Project-level economic feasibility was further evaluated using net present value (NPV), internal rate of return (IRR), and payback period (POT). NPV was calculated by discounting the annual net cash flow over the plant lifetime and subtracting the fixed capital investment, as shown in (14). IRR, as shown in (15), was determined as the discount rate at which the NPV becomes zero [20]. For comparison with similar CCU studies, discounted payback period was considered where relevant and presented in (16) [16].

$$NPV = -FCI + \sum_{t=1}^{n} \frac{CF_t}{(1+r)^t} \tag{14}$$

$$0 = -FCI + \sum_{t=1}^{n} \frac{CF_t}{(1+IRR)^t} \tag{15}$$

$$POT = \min\left\{t \middle| \sum_{k=1}^{t} \frac{CF_k}{(1+r)^k} \geq CAPEX\right\} \tag{16}$$

The economic analysis assumes a plant life of 20 years, an interest rate of 10%, and a discount rate of 12%, which are standard values commonly adopted in chemical process evaluations. The initial investment cost was estimated using the Aspen Process Economic Analyzer. The major components of the investment include the Purchased Equipment Cost (PEC) and the Installed Direct Cost (IDC). Additional Non-installed Direct Costs (NIDC) were also considered, consisting of building construction at 0.29 × PEC, yard improvements at 0.12 × PEC, and land acquisition at 0.06 × PEC. The Total Direct Cost (TDC) is calculated as the sum of IDC and NIDC, while the Indirect Cost is estimated at 0.255 × PEC. Consequently, the Fixed Capital Investment (FCI) is determined as the sum of IDC and TDC, with a start-up cost assumed to be 0.05 × FCI to cover the initial operation phase [49].

Table 12 shows that the discounted project-economics results are more selective than the operating-economics trends in Table 11. Methanol remains infeasible in the pessimistic and base cases and becomes only marginally feasible in the optimistic case, with an IRR of 12% and a POT of 19.10 years. Methane shows a similar pattern, remaining infeasible in the pessimistic and base cases but becoming feasible in the optimistic case, with an IRR of 57% and a POT of 2.40 years. In line with techno-economic assessment guidance, these indicators should be interpreted together with NPV and operating profit rather than using IRR alone [20]. This pattern is also consistent with previous studies showing that hydrogen-based CO_2 utilization routes are highly sensitive to feedstock cost and market assumptions [12][47].

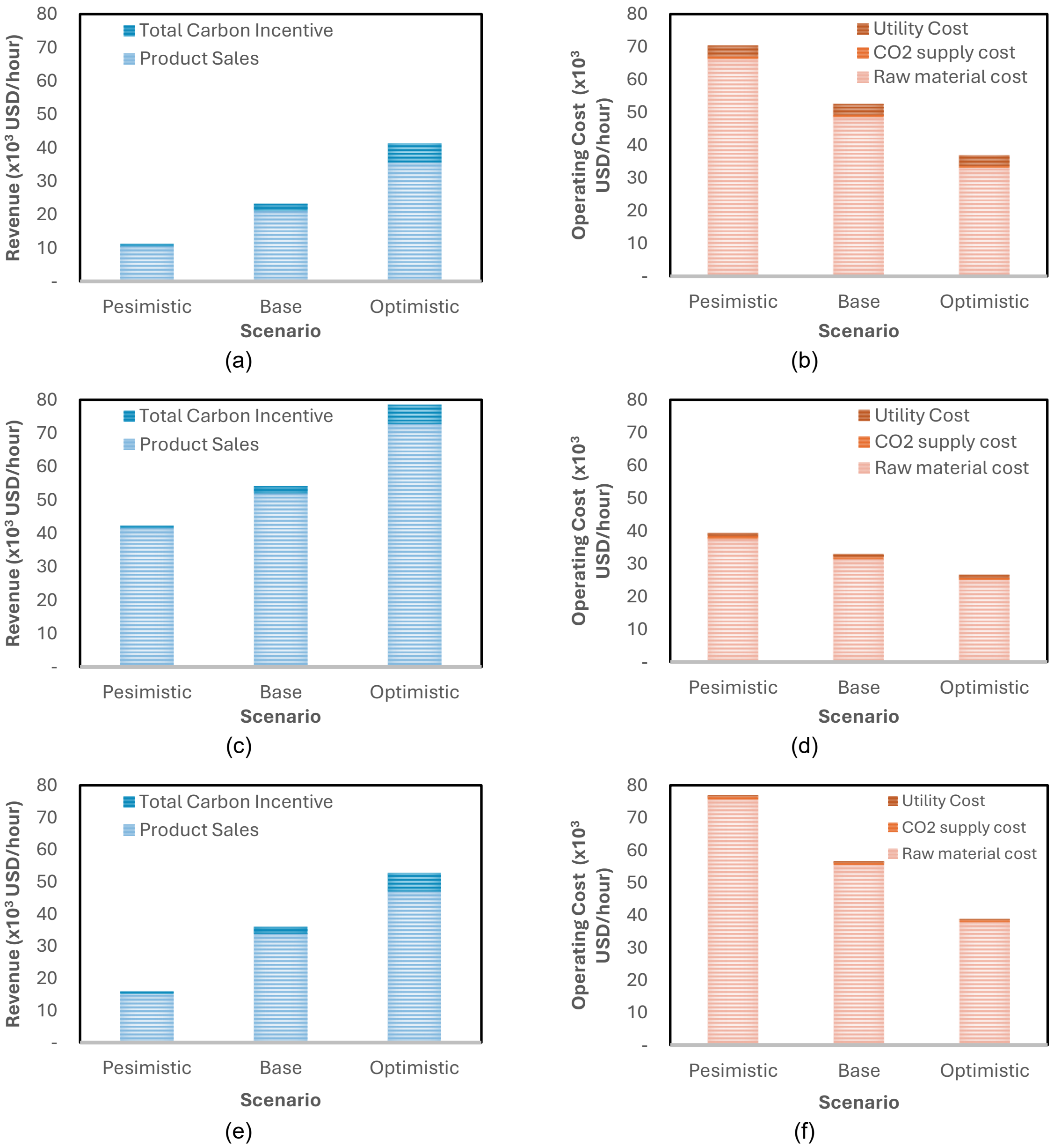
By contrast, sodium bicarbonate gives the strongest discounted performance among the three pathways. In the base case, it reaches an NPV of 1,605 million USD, an IRR of 53%, and a POT of 2.55 years, which improves further in the optimistic case. This result is consistent with the stronger operating margin already observed in Table 11 and with previous carbonate-based CO_2 utilization studies that reported favorable economic performance for sodium bicarbonate pathways [16][48]. Therefore, the discounted project economics confirm that sodium bicarbonate is the most robust pathway under the market and policy ranges considered in this study. The shorter POT obtained in this study compared with some literature values should be interpreted carefully. A higher POT in previous studies does not invalidate the present result, because payback period is strongly affected by system boundary, cost-year basis, raw material and product price assumptions, hydrogen sourcing, and the inclusion of additional cost items such as taxes, labor, maintenance, and financing charges [20].

Table 10. Price and policy assumptions for the economic scenario analysis

Parameter	**Unit**	**Scenario**			**References**
		Pessimistic	**Base**	**Optimistic**	
Revenue Variable					
Methanol selling price	USD/ton	200	402	679	[34, 35, 36]
Sodium bicarbonate selling price	USD/ton	200	250	350	[37, 38, 39]
Methane selling price	USD/ton	550	1230	1710	[40][41]
Carbon incentive	USD/ton	10	30	80	[42][43]
Cost Variable					
Green hydrogen purchase price	USD/ton	6000	4400	3000	[12][44]
Soda ash price	USD/ton	224	187	150	[16]
CO_2 supply cost	USD/ton	12.38	10.10	7.90	[43, 45, 46]

Table 11. Operating economics across all pathways and scenarios (in 10^3 USD/hour)

Parameter	Methanol Pathway			Sodium Bicarbonate Pathway			Methane Pathway		
	Pessim.	**Base**	**Optim.**	**Pessim.**	**Base**	**Optim.**	**Pessim.**	**Base**	**Optim.**
Product Sales	10.49	21.08	35.61	41.58	51.98	72.77	15.12	33.82	47.02
Total Carbon Incentive	0.72	2.15	5.72	0.72	2.15	5.72	0.72	2.15	5.72
Total Revenue	**11.20**	**23.23**	**41.33**	**42.30**	**54.13**	**78.49**	**15.84**	**35.97**	**52.74**
Raw material cost	66.28	48.61	33.14	37.49	31.30	25.11	75.65	55.48	37.83
CO2 supply cost	0.89	0.72	0.56	0.89	0.72	0.56	0.89	0.72	0.56
Utility Cost	3.25	3.25	3.25	0.87	0.87	0.87	0.38	0.38	0.38
Total Operating Cost	**70.42**	**52.58**	**36.96**	**39.25**	**32.90**	**26.55**	**76.92**	**56.58**	**38.77**
Operating Profit	**(59.22)**	**(29.35)**	**4.37**	**3.05**	**21.23**	**51.95**	**(61.08)**	**(20.61)**	**13.97**



(a) (b) (c) (d) (e) (f)

Figure 5. Total revenue and total operating cost of the methanol (a,b), sodium bicarbonate (c,d), and methane (e,f) pathways under pessimistic, base, and optimistic scenarios

Table 12. Process economics across all pathways and scenarios

Pathway	Scenario	Operating Profit (10^3 USD/year)	CAPEX (10^3 USD)	NPV (10^3 USD)	IRR (%)	POT (year)
Methanol	Pessimistic	(426,348.37)	230,177.88	(5,841,875.38)	n.a.	n.a.
	Base	(211,344.09)	230,177.88	(3,770,224.64)	n.a.	n.a.
	Optimistic	31,474.55	230,177.88	148.75	12%	19.10
Sodium Bicarbonate	Pessimistic	21,944.53	228,428.20	(152,896.86)	4%	n.a.
	Base	152,854.78	228,428.20	1,605,602.43	53%	2.55
	Optimistic	374,019.41	228,428.20	4,566,656.26	111%	1.27
Methane	Pessimistic	(439,772.61)	137,834.70	(5,837,812.30)	n.a.	n.a.
	Base	(148,425.30)	137,834.70	(2,253,220.13)	n.a.	n.a.
	Optimistic	100,573.19	137,834.70	1,080,486.33	57%	2.40

Therefore, the discounted project economics confirm that sodium bicarbonate is the most robust pathway under the market and policy ranges considered in this study, whereas methanol and methane remain much more sensitive to favorable economic conditions.

In addition to project economics, implementation in an existing ammonia plant also depends on retrofit integration and supply-chain readiness. Because the present study applies a pathway-level comparative framework, a detailed brownfield cost estimate, implementation schedule, and pilot-scale validation were not developed. Nevertheless, the integration roadmap can be outlined conceptually. The first step is the connection of the CCU unit to the existing purified CO_2 stream, followed by assessment of feed preparation, storage, and utility integration, including electricity, steam, cooling water, and process water. For the methanol and methane pathways, additional attention is required for continuous low-carbon hydrogen supply, compression, storage, and process safety, while methanol also requires liquid-product storage and methane requires suitable off-take or gas-distribution infrastructure. By contrast, the sodium bicarbonate pathway is less dependent on hydrogen logistics but requires reliable soda ash supply together with solid handling, storage, and transport. Therefore, the economic indicators reported in Table 12 should be interpreted as a preliminary basis for pathway prioritization, while detailed retrofit design, supply-chain validation, and large-scale implementation assessment should be addressed in future work through site-specific engineering study and industrial demonstration [18][20].

Environmental Analysis

The environmental assessment in this study was conducted as a gate-to-gate comparison of the modelled CCU section. The analysis focused on net CO_2 reduction because this parameter can be evaluated consistently across the methanol, sodium bicarbonate, and methane pathways under a common process boundary.

The calculation considers the captured CO_2 feed entering the utilization section ($mCO_{2(in)}$), the amount of CO_2 retained in the product stream ($mCO_{2(out)}$), and the CO_2 associated with utility use during the process operation ($mCO_{2(utility)}$), as shown in (11) [50]. Upstream burdens from externally supplied raw materials, including hydrogen production, water consumption outside the plant boundary, and other life cycle impacts, were not included. In addition, pathway-specific secondary impacts outside the modelled CCU section, such as wastewater burden and potential chemical waste generation, were not quantified in this study. Therefore, the environmental results should be interpreted as a comparative carbon reduction assessment rather than a full life cycle assessment.

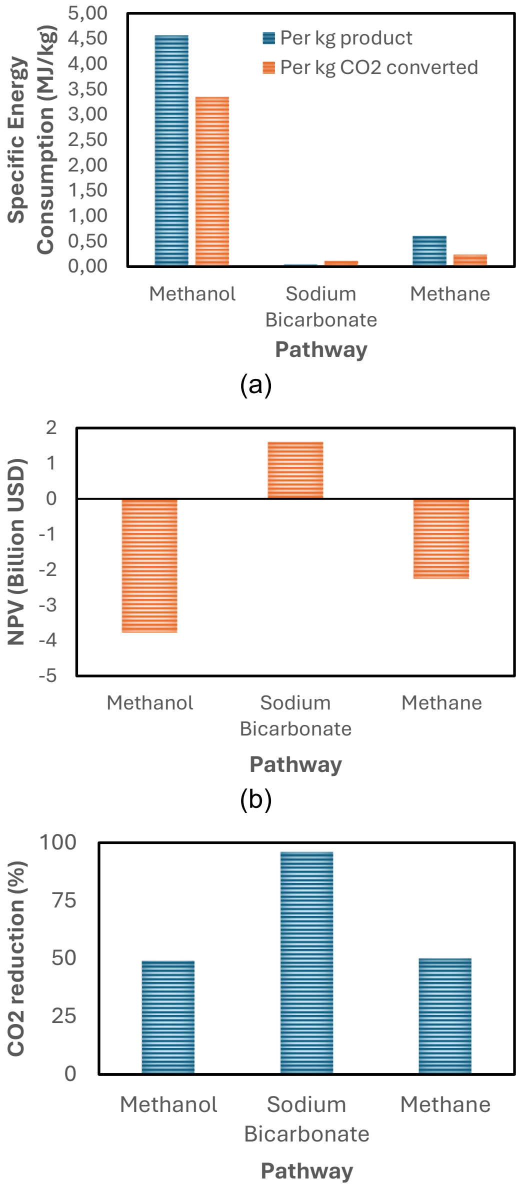
$$CO_2\ reduction = \frac{m_{CO_2(in)} - m_{CO_2(out)} - m_{CO_2(utility)}}{m_{CO_2(in)}} \qquad (11)$$

Utility demand data in Table 8 were combined with the corresponding emission basis to estimate utility-related CO_2 emissions for each pathway. The resulting comparison is presented in Table 13, which includes the CO_2 feed entering the process, the CO_2 associated with utility consumption, the amount of CO_2 retained in the product stream, and the resulting net CO_2 reduction. Sodium bicarbonate gives the highest net CO_2 reduction within the assessed process boundary, reaching 96%, followed by methane at 50% and methanol at 49%. This result indicates that sodium bicarbonate retains a larger share of carbon in the final product under the modeled conditions, whereas methanol and methane show lower net reduction because part of the carbon remains unconverted and utility-related emissions remain significant. Therefore, within the gate-to-gate boundary used in this study, sodium bicarbonate provides the most favorable carbon reduction result among the three alternatives.

When expressed on a product basis, the present study gives reductions of 0.67 kg CO_2e/kg methanol, 0.33 kg CO_2e/kg sodium bicarbonate, and 1.27 kg CO_2e/kg methane.

Table 13. Result of environmental analysis

Environmental Parameter	Unit	Methanol	Sodium Bicarbonate	Methane
CO_2 Feed	kg/hour	71,478.4	71,499.97	71,500
CO_2 from Utility	kg/hour	36,260	1,145	7,369
CO_2 Released	kg/hour	0.08	1,720	28,233
CO_2 Reduction	%	49	96	50



(a)

(b)

(c)

Figure 6. Comparison of (a) base-case NPV, (b) specific energy consumption, and (c) net CO_2 reduction for the methanol, sodium bicarbonate, and methane pathways.

These values differ from literature ranges, which report 2.5 to 2.2 kg CO_2e/kg methanol, 0.32 to 1.04 kg CO_2e/kg sodium bicarbonate, and 3.338 kg CO_2e/kg methane [16, 22, 51]. The lower values obtained here are expected because the present assessment is limited to the modeled CCU section and excludes upstream burdens from raw-material production and hydrogen supply. Even with that limitation, the pathway ranking remains clear, with sodium bicarbonate showing the strongest environmental performance under the modeled conditions.

Comparison of CO_2 Utilization Pathways

Figure 6 summarizes the integrated comparison of the three pathways using (a) base-case NPV as the economic indicator, (b) specific energy consumption as the energy indicator, and (c) net CO_2 reduction as the environmental indicator within the assessed process boundary. When economic, energy, and environmental indicators are considered together, sodium bicarbonate delivers the most balanced overall performance among the three CO_2 utilization pathways. Economically, it is the only route that remains attractive in the base case, with a positive NPV, an IRR of 53%, and a POT of 2.55 years, whereas methanol and methane still produce negative base-case NPVs. Its process intensity is also the lowest, with specific energy consumptions of 0.038 MJ/kg product and 0.111 MJ/kg CO_2 converted, compared with 4.564 MJ/kg product and 3.348 MJ/kg CO_2 converted for methanol, and 0.606 MJ/kg product and 0.239 MJ/kg CO_2 converted for methane. These results indicate that the non-hydrogen route is inherently less energy-intensive and less exposed to cost escalation than the hydrogen-based pathways [12][16].

This difference is also reflected in the economic sensitivity of the hydrogen-based routes. Methanol and methane remain much more dependent on favorable economic conditions, especially those associated with hydrogen cost and product selling price. This trend is consistent with previous CCU studies showing that hydrogen-based fuel pathways are strongly affected by feedstock and energy costs, which can reduce or even eliminate their economic attractiveness under less favorable assumptions [20][47]. A similar observation is also reported in recent methanol studies, where green methanol remains burdened by high operating cost and unfavorable project economics under present conditions [21][52]. From the environmental perspective, sodium bicarbonate also gives the highest net CO_2 reduction within the assessed process boundary, reaching 96%, compared with 50% for methane and 49% for methanol. Therefore, under the assumptions applied in this work, sodium bicarbonate emerges as the most robust overall pathway, while methanol and methane remain more condition-dependent alternatives [16][48].

CONCLUSION

This study compared three CO_2 utilization pathways in the ammonia industry, namely methanol, sodium bicarbonate, and methane, using a common simulation and assessment framework. The comparison was performed based on process performance, energy intensity, project economics, and net CO_2 reduction within the modeled CCU section. The results show that the choice of utilization products strongly affects not only product yield and utility demand, but also the robustness of economic feasibility under changing market conditions.

From the economic perspective, sodium bicarbonate is the most robust pathway. It remains attractive in the base case, with an NPV of 1,605 million USD, an IRR of 53%, and a payback period of 2.55 years, and its performance further improves in the optimistic case. By contrast, methanol remains infeasible in the pessimistic and base cases and becomes only marginally feasible in the optimistic cases. Methane also remains infeasible in pessimistic and base cases and becomes feasible only under favorable conditions. These results indicate that the hydrogen-based pathways are much more sensitive to product selling price and hydrogen cost, whereas sodium bicarbonate is economically more stable under the scenario ranges considered in this study.

From the energy and environmental perspectives, sodium bicarbonate also shows the strongest overall performance. It has the lowest specific energy consumption, both per unit product and per unit CO_2 converted, while also giving the highest net CO_2 reduction within the assessed process boundary at 96%. In comparison, methane gives 50% net CO_2 reduction and methanol gives 49%, while both pathways show higher energy intensity than sodium bicarbonate. These results indicate that sodium bicarbonate provides the most favorable overall balance between process intensity, project economics, and carbon reduction among the three alternatives considered.

Overall, sodium bicarbonate is the most promising CO_2 utilization pathway for the ammonia industry under the assumptions adopted in this work. However, the present study is limited to the modeled CCU section and applies a scenario-based before-tax economic analysis. Upstream burdens from external raw-material supply, including hydrogen production and other life-cycle impacts, were not included.

Future work should first focus on improving pathway performance at the process level. For the hydrogen-based methanol and methane routes, this includes evaluation of catalyst stability, long-term deactivation behavior, and process intensification strategies to reduce recycled demand and energy consumption. For the sodium bicarbonate route, future work should emphasize crystallization control, mother-liquor recovery, solid handling, and mitigation of secondary waste so that the pathway can be assessed under more realistic operating conditions. In addition, the present assessment should be expanded beyond the current steady-state and gate-to-gate framework. Future studies should develop a full life-cycle assessment to capture upstream burdens associated with hydrogen supply, water use, and external raw-material production. The economic analysis should also be refined by including broader cost components and site-specific brownfield factors, such as labor, maintenance, storage, utility integration, and retrofit constraints in an operating ammonia plant. Finally, pilot-scale or industrial implementation studies are required to confirm long-term operability, supply-chain readiness, and the practical feasibility of integrating the selected CCU pathway into existing ammonia-plant infrastructure.

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