Techno-Economic and Environmental Analysis for Direct Catalytic Conversion of CO\textsubscript{2} to Methanol and Liquid/High-Calorie-SNG Fuels

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Abstract: Catalytic hydrogenation of CO\textsubscript{2} has great potential to significantly reduce CO\textsubscript{2} and contribute to green economy by converting CO\textsubscript{2} into a variety of useful products. The goal of this study is to assess and compare the techno-economic and environmental measures of CO\textsubscript{2} catalytic conversion to methanol and Fischer–Tropsch-based fuels. More specifically, two separate process models were developed using a process modeler: direct catalytic conversion of CO\textsubscript{2} to Fischer–Tropsch-based liquid fuel/high-calorie SNG and direct catalytic conversion of CO\textsubscript{2} to methanol. The unit production cost for each process was analyzed and compared to conventional liquid fuel and methanol production processes. CO\textsubscript{2} emissions for each process were assessed in terms of global warming potential. The cost and environmental analyses results of each process were used to compare and contrast both routes in terms of economic feasibility and environmental friendliness. The results of both the processes indicated that the total CO\textsubscript{2} emissions were significantly reduced compared with their respective conventional processes.

Keywords: CO\textsubscript{2} catalytic conversion; methanol synthesis; Fischer–Tropsch; environmental analysis; economic analysis

1. Introduction

Global warming, which occurs due to climate change, is one of the most pressing challenges the world is facing, and tackling global warming requires serious determination and focus on research. Fossil fuel energy sources are a major source of CO\textsubscript{2}. To minimize CO\textsubscript{2} emission, efficient utilization of fossil fuels as well as CO\textsubscript{2} capture should be addressed. Recent research has shown CO\textsubscript{2} to be a potential carbon source rather than an expensive waste; therefore, the carbon capture and utilization (CCU) concept has developed \cite{1,2}.

Researches on producing renewable synthetic fuels from liquefied biomass processes are also being carried out \cite{3}. In addition, renewable power generated from solar and wind energies is being increasingly developed to reduce dependence on fossil energy and CO\textsubscript{2} emissions. As a result, technologies that combine renewable power and CO\textsubscript{2} hydrogenation to liquid fuels or synthetic natural gas have been recently developed with extensive efforts. These technologies can be categorized as power to liquid (PTL) and power to gas (PTG). The demand of renewable fuels for transport, households, as well as industry, can be the main driver for PTG and PTL. The concept of PTL or PTG for the production of synthetic fuels is briefly explained in Figure 1. These technologies constitute three main steps. The first is water electrolysis to produce hydrogen. The electrochemical splitting of water into hydrogen and oxygen by supplying electrical and thermal energy is known as water electrolysis. It is a key process that can be used for the production of high-quality (purity) hydrogen from water. The second is CO\textsubscript{2} capture from
industrial processes such as coal, steel, and cement industries. The third is hydrogenation of CO$_2$ to generate hydrocarbons [4]. CO$_2$ hydrogenation can be divided into direct and indirect routes based on the CO$_2$ conversion pathway. Indirect CO$_2$ hydrogenation routes require generation of synthesis gas and subsequent conversion of synthesis gas to hydrocarbons or oxygenated products such as methanol via the Fischer–Tropsch process or via methanol synthesis. In indirect CO$_2$ hydrogenation, two separate reactions occur in two separate reactors: (1) reversible water gas shift reaction to produce synthesis gas and (2) conversion of synthesis gas. Therefore, two separate reactors are required for indirect CO$_2$ hydrogenation [5,6]. Direct routes use single reactors to perform CO$_2$ hydrogenation reactions simultaneously. The use of a single reactor for multiple reactions provides an additional benefit for many processes. The direct route is economic and environmentally benign compared to the indirect route [6,7].

**Figure 1.** Concept of power-to-liquid or power-to-gas for the production of synthetic fuels (re-used with permission from C. Panzone et al. [6]).

Recently, many researchers developed PTL processes that can convert CO$_2$ to liquid fuels via the indirect route using renewable power. For example, J. Kim et al. conducted process simulation and techno-economic analysis of a PTL process for the production of light hydrocarbons from CO$_2$ and H$_2$ with a CO$_2$ reduction rate of 1.85 kg CO$_2$ per kg of hydrocarbon produced [8]. The net production cost was estimated to be 3.58 USD/kg. M. Pérez-Fortes et al. proposed a PTL process that produces methanol from CO$_2$, and it is capable of reducing 2.71 million tons of CO$_2$/year emission [9]. C. Zhang et al. studied the hybrid PTL/PTG process and PTL process [10]. Their research considered economic and environmental comparison of these processes, and they concluded that the hybrid PTL/PTG process is more economically competitive compared to the PTL process.

Based on our previous works, we now propose a base case PTL process that directly converts CO$_2$ to methanol, and a hybrid PTL/PTG process that directly converts CO$_2$ to liquid fuels and high-calorie synthetic natural gas (SNG) simultaneously [1]. In this work, two separate models for direct catalytic conversion of CO$_2$ to Fischer–Tropsch-based liquid fuels/high-calorie SNG (hybrid PTL/PTG) and direct catalytic conversion of CO$_2$ to methanol were developed. The objective of this research is to compare and contrast both routes in terms of economic feasibility and environmental friendliness as well as identify the route with better results. The techno-economic and environmental measures of direct CO$_2$ catalytic conversion to methanol and liquid fuels/high-calorie SNG were assessed. The cost and environmental analyses results of each process were used to compare and contrast both the routes in terms of economic feasibility and environmental friendliness. There are previous studies on the techno-economic assessments in both direct hydrogenation of CO$_2$ to hydrocarbons and to methanol [2,8–17]. However, it was not possible to compare the results due to the fact that the models were developed with considering different assumptions, methodology, and level of details. In this study, similar methodology, level
of detail, and key assumptions were considered to make the model results comparable in terms of economic factors and environmental factors.

2. Results

2.1. Model Validation

For the methanol synthesis process, the experimental results from A. A. Kiss et al. [18] were used to validate the model data. This model considered both CO and CO$_2$ as the carbon source of methanol. The simulated CO$_2$ conversion (%) and methanol yield (%) of the reactor were compared with the reference data, as shown in Table 1. The simulated data of this study are similar to the reference data. These results suggest that the model can provide reasonable accuracy in predicting the economic and environmental investigations.

Table 1. Comparing simulation results between the reference data and the model by varying the reaction temperature at 50 bar, 5900 (mL/gcat·h).

| Temperature (°C) | CO$_2$ Conversion (%) | Methanol Yield (%) |
|-----------------|-----------------------|--------------------|
|                 | [18]                  | This Work | [18] | This Work |
| 210             | 12.44                 | 12.38       | 11.52 | 11.47     |
| 230             | 19.57                 | 19.50       | 15.97 | 15.92     |
| 250             | 23.98                 | 23.98       | 15.30 | 15.30     |
| 270             | 24.04                 | 24.05       | 10.58 | 10.59     |

For the liquid/high-calorie-SNG fuel synthesis process, the comparison between the experimental and simulated reactor outlet stream is presented in Table 2. It can be observed that the simulated results closely match the experimental results. These results suggest that the model can provide reasonable accuracy for the economic and environmental analysis.

Table 2. Comparison between simulated and the experimental reactor outlet stream for Liquid/high-calorie-SNG fuel synthesis process.

| Parameters | FT Reactor Stream Outlet (This Work) | FT Reactor Stream Outlet [19] |
|------------|--------------------------------------|------------------------------|
| Temperature| 320 °C                               | 320 °C                       |
| Pressure   | 20 bar                               | 20 bar                       |
| Yield      | 12.2% (liquid fuel)                  | 12.2% (liquid fuel)          |
|            | 32.2% (high-calorie SNG)             | 32.2% (high-calorie SNG)     |

2.2. Economic Analysis Results

The estimated total capital investment costs for the methanol synthesis process are shown in Figure 2. The total equipment cost is 17.01 M$ (million USD). The main portion (approximately 41%) of the total equipment cost is dominated by compressors. This is because the operating pressure of the methanol synthesis reactor was high (80 bar). The CO$_2$ feed was compressed from 1 bar to 80 bar, and the H$_2$ feed was compressed from 30 bar to 80 bar; therefore, consecutive compressors were required. The total capital investment of the methanol synthesis process was computed based on the total equipment cost. As a result, the methanol synthesis has 102.80 M$ total capital investment.

The estimated total capital investment costs for the PTL/PTG hybrid process is also presented in Figure 2. The total equipment cost is 44.25 M$. The major portion (approximately 65%) of the total equipment cost is the separation systems employed, like PSA used to recover H$_2$ from the gaseous product and recycle it back and CO$_2$ adsorption for CO$_2$ recovery. The total capital investment of the Fischer–Tropsch process was computed based on the total equipment cost. As result, the Fischer–Tropsch process has 267.45 M$ total capital investment cost. Additional details in the economic analysis result is found in the Supplementary Materials.
of the proposed processes.

Renewable H$_2$ produced by water electrolysis is highly expensive under the current technological status due to the high electricity consumption during generation. The technological developments to lower the price of renewable H$_2$ can lower the total operating cost of the proposed process.

The total operating cost of the methanol synthesis process is shown in Figure 3. The cost breakdown of the total operating cost indicates that the H$_2$ cost is the dominant operating cost, and it covers over 85% of the total operating cost. The total operating cost of the Fischer–Tropsch process is also shown in Figure 3. The cost breakdown of the total operating cost indicates that the H$_2$ cost is the dominant operating cost, and it covers over 80% of the total operating cost. The main reason for such a high operating cost of H$_2$ is due to the high price of H$_2$. Particularly in this study, the renewable H$_2$ produced from water electrolysis is assumed to be used as the raw material for the CO$_2$ catalytic hydrogenation (with a price of 3.53 $/kg). Renewable H$_2$ produced by water electrolysis is highly expensive under the current technological status due to the high electricity consumption during generation. The technological developments to lower the price of renewable H$_2$ can lower the total operating cost of the proposed process.

Figure 2. Total capital investment cost breakdown of methanol synthesis and Fischer–Tropsch process models (MeOH indicates the methanol synthesis process model and FT indicates the Fischer–Tropsch process model).

Figure 3. Total operating cost breakdown of methanol synthesis and Fischer–Tropsch process models.
Sensitivity Analysis

Sensitivity analysis was also conducted in both the models to investigate the effects of fluctuations on the prices of H\textsubscript{2}, CO\textsubscript{2}, CAPEX, and utility cost. Parametric analysis was conducted by changing one input variable to its low or high value while keeping all other variables constant. The plant parameters that most influence the total production cost are identified according to the sensitivity results. As is shown in Figures 4 and 5, hydrogen price raises a significant level of uncertainty compared to the other parameters. Overall, it can be observed that the most crucial parameter is the H\textsubscript{2} price; in fact, a 20\% change (increase or decrease) in the H\textsubscript{2} price can change the total unit production cost by 17.45\% for the methanol synthesis process and a 20\% change in the H\textsubscript{2} price changes the total unit production cost by 16.8\% for the Fischer–Tropsch process. The technological developments to lower the price of renewable H\textsubscript{2} can lower the total unit production cost of the proposed processes.

![Figure 4](image1.png)

**Figure 4.** Sensitivity analysis of selected parameters for the methanol synthesis process model.

![Figure 5](image2.png)

**Figure 5.** Sensitivity analysis of selected parameters for the Fischer–Tropsch process model.
2.3. Environmental Assessment Results

The result of the GWP for methanol synthesis process was 1.67 kg CO$_2$-eq per kg of methanol. This indicates that 1.67 kg CO$_2$-eq is emitted per 1 kg of methanol produced. The CO$_2$ capture system accounts for more than 75% of the GWP.

The conventional methanol synthesis plant used for the comparison was fossil-based (coal) methanol production [20]. As can be observed from the results shown in Figure 6, the developed methanol process showed lower CO$_2$ equivalent emission compared to the conventional fossil-based (coal) methanol production due to the fact that the sources of electricity for H$_2$ generation used in this process were renewable resources (wind).

The result of the GWP for the Fischer–Tropsch process model process was 3.95 kg CO$_2$-eq per kg of the product. This indicates that 3.95 kg CO$_2$-eq is emitted per 1 kg of the synthetic fuel produced. The CO$_2$ raw material accounts for more than 70% of the GWP. The conventional Fischer–Tropsch process plant used for comparison was fossil-based (coal) plant. The GWP of the conventional plant was 4.10 kg CO$_2$-eq per kg of the product [21]. As can be observed from the results, the developed Fischer–Tropsch process showed lower CO$_2$ equivalent emissions compared to the conventional fossil-based (coal) Fischer–Tropsch process due to the fact that the sources of electricity for H$_2$ generation used in this process were renewable resources (wind).

![Graph showing GWP results comparison](image)

Figure 6. GWP model results comparison with conventional fossil-based methanol production and conventional fossil-based Fischer–Tropsch process.

2.4. Economic and Environmental Assessment Result: Comparison of Methanol Synthesis and Fischer–Tropsch Process Models

As the sensitivity analysis indicated, the H$_2$ cost was the most sensitive parameter in both the Fischer–Tropsch and methanol synthesis processes. Therefore, an additional case study on the hydrogen cost reduction to compute the defined payback time was conducted to further study the effect of H$_2$ cost in both processes as well as to compare the processes based on the payback time. The base cost of H$_2$ used in both processes was 3.53 $/kg [8]. It is not possible to obtain the defined payback time at the base cost. Therefore, five scenarios (Table 3) were set based on the reduced H$_2$ cost that can provide the defined payback time (non-negative value). Based on the results of the case studies on the payback time shown in Figure 7, if the H$_2$ cost is reduced by 65% (1.24 $/kg) from the base cost (3.53 $/kg), as in scenario 1, a payback time of nine years is obtained for the Fischer–Tropsch process and
three years for the methanol process, which indicates that the methanol synthesis process can be economically more viable than the Fischer–Tropsch process.

From the environmental point of view, the GWP results of both the methanol synthesis and Fischer–Tropsch process models indicate that utilizing the renewable technology throughout the process could reduce the CO₂ emissions compared to their respective conventional processes that rely mainly on fossil fuels. The GWP of the methanol synthesis model (1.67 kg CO₂-eq per kg of methanol) is much lower compared to the Fischer–Tropsch process of the synthetic fuel synthesis model (3.95 kg CO₂-eq per kg of synthetic fuel produced). The stoichiometry of the reactions and simulation result indicate that the methanol synthesis process produces less water and more product compared to the Fischer–Tropsch process of the synthetic fuel synthesis model, which affects the revenue economically and the GWP environmentally as the GWP also depends on the production quantity.

Table 3. Reduced hydrogen cost scenarios considered for the defined payback time case study.

| Scheme | 1 | 2 | 3 | 4 | 5 |
|--------|---|---|---|---|---|
| % Reduction of H₂ Cost | 65 | 70 | 75 | 80 | 85 |
| Reduced H₂ Cost ($/kg) | 1.24 | 1.06 | 0.88 | 0.71 | 0.53 |

Figure 7. Payback time for both the Fischer–Tropsch process and the methanol synthesis at reduced H₂ cost scenarios (MeOH indicates the methanol synthesis process model and FT indicates the figure.

3. Process Description and Design

3.1. Assumptions

Purchased CO₂ and H₂ were used as raw materials. Water electrolysis and CO₂ capture technologies are commercially available; therefore, they were excluded from this study. The CO₂ capture and transport, H₂ generation and transport, and further purification steps of the CO₂ stream are outside the scope of this work. Both the streams entering into the plant were assumed to be 100% pure. The scale of the Fischer–Tropsch process plant was equivalent to an average representative of PTL/PTG plant. The scale of the methanol plant was set to be equivalent to the Fischer–Tropsch process plant for comparison purposes. The Chemical Engineering Plant Cost Index (CEPCI) and Economic Analyzer software were used to determine the equipment purchase cost. Production time of 8000 h per year was assumed.
3.2. Methanol Synthesis

A simplified process model for the methanol process mainly dealing with the compression, CO$_2$ hydrogenation, product separation, and recycling units was studied. Figure 8 shows simplified process flow diagram of the methanol synthesis process. The thermodynamic calculation method used for the methanol process model was the Redlich–Kwong–Soave with the modified Huron–Vidal mixing rule (RKSMHV2) for higher than 10 bar, which has high accuracy on high pressure and Non-Random-Two-Liquid (NRTL) for pressures lower than 10 bar, which is recommended for polar non-electrolyte system at low pressures.

![Diagram](image-url)

**Figure 8.** Schematic diagram of the methanol synthesis process. Major equipment: (B2, B4, B6, B7, B9) compressor for feed compression; (B3, B5, B8) compressed feed cooler; (B10, B11) heat exchanger for feed preheating; (B12) methanol synthesis reactor; (B13, B14) heat exchanger (cooler); (B15, B19) flash separator; (B20) distillation column.

The reactant CO$_2$ is compressed from 1 bar to 80 bar, which is the operating pressure in methanol synthesis, through multi-stage compressors. Between stages, CO$_2$ is cooled to 35°C by intercoolers. H$_2$ from electrolysis is compressed from 30 bar to 80 bar. The compressed reactants are mixed together and heated to an operating temperature of 210°C. Then, the pre-heated feed enters the isothermal methanol synthesis reactor filled with a Cu/ZnO/Al$_2$O$_3$ catalyst (with gas hourly space velocity (GHSV) of 5900 mL per gram of catalyst per hour). Three reactions occur in the reactor in parallel: (1) reverse water gas shift reaction (RWGS) reactions, (2) methanol synthesis from CO, and (3) methanol synthesis from CO$_2$. In this study, both CO and CO$_2$ are considered as the carbon source for methanol synthesis, and the reaction equations are as follows [18].

- RWGS reactions: CO$_2$ + H$_2$ ⇌ CO + H$_2$O \[ \Delta H_{r}^{298K} = +41.2 \text{kJ/mol} \] (1)
- Methanol synthesis from CO: CO + 2H$_2$ ⇌ CH$_3$OH \[ \Delta H_{r}^{298K} = -90.4 \text{kJ/mol} \] (2)
- Methanol synthesis from CO$_2$: CO$_2$ + 3H$_2$ ⇌ CH$_3$OH + H$_2$O \[ \Delta H_{r}^{298K} = -49.2 \text{kJ/mol} \] (3)

Because the methanol synthesis reaction is exothermic, the reactor should be cooled to maintain the temperature for a high yield of methanol. This heat will be used to pre-heat the recycle stream. The product stream is used for heating the feed stream and the re-boiler in the distillation column by heat exchanging. After exchanging, the product stream is
cooled to 30 °C. The unreacted gas and liquid solution are separated through a flash tank. The unreacted gas is recycled with 0.5% purge ratio and mixed to the feed stream. The liquid solution is depressurized and transported to the distillation column for separating methanol from water and dissolved gas. The vapor distillate stream contains CO\(_2\) and methanol, and the liquid distillate stream contains methanol with 99 wt% purity. The purity of the bottom stream is 99.9 wt% of water. The purged gas and vapor distillate stream are combusted with air to produce steam.

3.3. Fischer–Tropsch-Based Liquid/High-Calorie-SNG Fuel Synthesis

A simplified process model for the hybrid PTL/PTG processes mainly dealing with the compression, CO\(_2\) hydrogenation, product separation, and recycling units was studied. The basic thermodynamic calculation method selected for the developed PTL/PTG process model was the Soave–Redlich–Kwong (SRK) equation of state, which is accurate in modelling a process system which contains light gases and hydrocarbons as well as operates at high pressure and temperature.

Figure 9 shows simplified process flow diagram of the Fischer–Tropsch-based hybrid PTG/PTL process. The following main operations are included: mixing of reactants with recycled feed of non-reacted hydrogen and carbon dioxide, compressing and preheating of the feed of reactants to reactor operating pressure and temperature, catalytic hydrogenation of the feed gas to 2-phase products in the Fischer–Tropsch reactor, and subsequent cooling down of the effluent/product streams for phase separation. The reactor is set based on the performance of the selected Fe-Co/K-Al\(_2\)O\(_3\) catalyst for the hydrogenation of CO\(_2\) to hydrocarbons with GHSV of 3600 mL per gram of catalyst per hour [19]. The direct catalytic hydrogenation of CO\(_2\) to hydrocarbons in the Fischer–Tropsch reactor generally occurs with two reactions in series as follows [4]:

\[
\text{RWGS reactions: } n\text{CO}_2 + n\text{H}_2 \leftrightarrow n\text{H}_2\text{O} + n\text{CO} \quad \Delta H_{\text{r}298K} = +41 \text{ kJ/mol} \quad (4)
\]

\[
\text{Fischer-Tropsch: } n\text{CO} + 2n\text{H}_2 \leftrightarrow (-\text{CH}_2\text{-})_n + n\text{H}_2\text{O} \quad \Delta H_{\text{r}298K} = -166 \text{ kJ/mol} \quad (5)
\]

\[
\text{Over all reaction: } n\text{CO}_2 + 3n\text{H}_2 \leftrightarrow (-\text{CH}_2\text{-})_n + 2n\text{H}_2\text{O} \quad \Delta H_{\text{r}298K} = -125 \text{ kJ/mol} \quad (6)
\]

Initially, as can be seen in the first step in the reaction in Equation (4), CO\(_2\) is converted into CO through the RWGS, which is a reversible as well as endothermic reaction that rapidly reaches the equilibrium [6,22–26]. In the second reaction, as can be seen in Equation (5), CO reacts with hydrogen to produce hydrocarbons through the Fischer–Tropsch reaction, which is an exothermic reaction. Equation (6) shows the overall reaction.

The flash tank is used to separate gaseous products from liquid products. Gaseous products contain unconverted CO\(_2\) and H\(_2\), which need further separation from the main product, high-calorie SNG. The liquid stream coming out from the bottom of the flash separation contains liquid fuel (gasoline) and water. A decanter is used to separate water from the liquid fuel (gasoline). A user-defined model was used to simulate the absorption of non-reacted CO\(_2\), its desorption, and recycling to the reactor inlet. Pressure swing adsorption (PSA) was used for hydrogen separation from the high-calorie SNG.
Figure 9. Schematic diagram of the Fischer–Tropsch-based hybrid PTG/PTL process. Major equipment: (B2, B4, B6, B8) compressor for feed compression; (B3, B5, B7) compressed feed cooler; (B9) heat exchanger for feed preheating; (B10) 2–phase Fischer–Tropsch reactor; (B13) heat exchanger (cooler); (B12) flash separator; (B15) user-defined CO₂ adsorption desorption unit; (B14) PSA unit for hydrogen separation.

4. Process Assessment Methodology

4.1. Cost Estimation

For methanol synthesis model, the catalyst is assumed to be replaced twice a year, and the amount of annual catalyst requirement was computed based on the GHSV data obtained from the respective reference. The conventional catalyst cost was used for the cost estimation ($143.87/kg) [27]. The cost estimation method used was percentage of delivered equipment cost with the ratio factor for the fluid processing plant. The methanol selling price used for revenue calculation was $0.43/kg [21].

For the Fischer–Tropsch model, the catalyst is assumed to be replaced twice a year, and the amount of annual catalyst requirement was computed based on the GHSV data obtained from the respective reference. The conventional catalyst cost was used for the cost estimation ($2.092/kg) [8]. The cost estimation method used was percentage of delivered equipment cost with the ratio factor for the fluid processing plant. The Fischer–Tropsch based products selling price used for revenue calculation were $1/kg for the high-calorie SNG and $0.83/kg for the liquid fuel [10].

The economic estimation assumptions used for both process models are summarized in Table 4. Additional data and methodology used in the economic analysis is found in the Supplementary Materials.
Table 4. Summary of economic parameters assumptions.

| Parameter                        | Value  |
|----------------------------------|--------|
| Project lifetime                 | 20 years |
| Operating hours per period (year)| 8000   |
| Number of weeks per period (year)| 52     |
| Income tax rate                  | 35%    |
| Discount rate                    | 8%     |
| Depreciation                     | Straight line |
| Depreciation period              | 20     |
| Location                         | South Korea |
| CO\(_2\) cost                    | $0.035/kg [7] |
| H\(_2\) cost                     | $3.53/kg [7] |
| Cooling water cost               | $0.028/ton [2] |
| Electricity cost                  | $0.063/kWh [9] |

4.2. Environmental Assessment

Most of the methanol and synthetic fuel produced so far were synthesized from fossil fuels by CH\(_4\) reforming. As a result, in the process, high amounts of carbon dioxide were co-produced. Producing methanol and synthetic fuel from renewable sources throughout the process is advantageous from the environmental point of view as there will be lower fossil fuel consumption. The environmental impact of the two developed process models was assessed based on the life cycle assessment focusing on the GWP (global warming potential). GWP is the most widely used CO\(_2\) life cycle assessment method and hence it was selected for the environmental assessment in this study. The boundary conditions for the life cycle assessment considered include emissions occurring from CO\(_2\) supply, emissions occurring from H\(_2\) supply, and emissions occurring from electricity supply to the process. In other words, the CO\(_2\) supply (raw material), the H\(_2\) supply (raw material), the source of electricity required for the plant, and direct CO\(_2\) emissions from the plant were considered in the GWP assessment. The source of electricity for water electrolysis to produce H\(_2\) (in the case of H\(_2\) supply) was assumed to be wind. The source of electricity (in the case of electricity supply) for the process was heat and power co-generated natural gas combined cycle power plant. The GWP results of the proposed process models were compared to those of the conventional processes. Table 5 lists the GWP factor data used for environmental assessment.

Table 5. GWP factor for environmental assessment.

| Parameters               | GWP Factor | Unit               | References |
|--------------------------|------------|--------------------|------------|
| CO\(_2\) (raw material)  | 0.87       | kgCO\(_2\)-eq/kgCO\(_2\) | [20]       |
| H\(_2\) (raw material)   | 0.97       | kgCO\(_2\)-eq/kgH\(_2\) | [28]       |
| Electricity              | 0.492      | kgCO\(_2\)-eq/kWh  | [20]       |

5. Conclusions and Recommendation

In this work, two separate models for direct catalytic conversion of CO\(_2\) to Fischer–Tropsch-based liquid fuels/high-calorie SNG (hybrid PTL/PTG) and direct catalytic conversion of CO\(_2\) to methanol were developed. The techno-economic and environmental measures of the direct CO\(_2\) catalytic conversion to methanol and Fischer–Tropsch-based liquid fuels/high-calorie SNG were assessed.

The GWP for the methanol synthesis and Fischer–Tropsch conventional processes were 3.81 and 4.10 kg CO\(_2\)-eq per kg of the product respectively. The results of the GWP for the methanol synthesis and Fischer–Tropsch process models were 1.67 and 3.95 kg CO\(_2\)-eq per kg of the product respectively. From an environmental point of view, as indicated by the results of the GWP, through the chemical conversion of CO\(_2\) into useful hydrocarbon products, CO\(_2\) in the atmosphere can be significantly reduced. In addition, the GWP results of both the methanol synthesis and Fischer–Tropsch process models indicated that utilizing...
renewable technology throughout the process could reduce CO\textsubscript{2} emissions compared to their respective conventional processes that rely mainly on the fossil fuels.

From an economical point of view, as indicated by the results of economic assessment, generating positive NPV or obtaining defined payback time is not possible under the current technological and market status. Nevertheless, several technology and market developments can significantly improve the economics of the processes. A 20% change (increase or decrease) in the H\textsubscript{2} price can change the total unit production cost by 17.45% for the methanol synthesis process and a 20% change in the H\textsubscript{2} price changes the total unit production cost by 16.8% for the Fischer–Tropsch process. The sensitivity analysis indicated that the H\textsubscript{2} cost was the most sensitive parameter in both the Fischer–Tropsch process and methanol synthesis process. Therefore, the development of advanced methods to lower the price of renewable H\textsubscript{2}, such as improving the high electricity demand of electrolysis, would enable the process to become economically viable. In addition, the operating pressures of the methanol synthesis and Fischer–Tropsch reactors is high (80 bar and 30 bar, respectively). Due to such high operating pressures of the reactors, the total capital investment costs increased as more compressors were required to compress the feed to the required operating pressure. Therefore, the innovation of a catalyst which is stable, selective and capable of working at lower pressure could significantly lower the total capital investment and operating costs for both the methanol synthesis and Fischer–Tropsch processes. For economic and environmental benefits, government policies should focus on strengthening researches focusing on:

- The development of advanced methods to lower the price of renewable H\textsubscript{2}, such as improving the high electricity demand of electrolysis.
- The innovation of CO\textsubscript{2} hydrogenation catalysts which are stable, selective, and capable of working at lower pressure to insure economic feasibility.

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**Nomenclature**

| Acronym | Definition |
|---------|------------|
| CAPEX  | Capital Expenditure |
| CO\textsubscript{2}-eq | Carbon dioxide equivalent |
| CEPCI  | Chemical Engineering Plant Cost Index |
| FT     | Fischer–Tropsch |
| GHSV   | Gas hourly space velocity |
| GWP    | Global warming potential |
| LCA    | Life cycle assessment |
| MeOH   | Methanol |
| M$     | Million USD |
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NPV Net positive value
OPEX Operating Expenditure
PSA Pressure swing adsorption
PTG Power to gas
PTL Power to liquid
RWGS Reversible water gas shift reaction
SNG Synthetic natural gas
SRK Redlich–Kwong–Soave
UPC Unit production cost
yr Year

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