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A COMPARATIVE TECHNO-ECONOMIC ANALYSIS OF RENEWABLE METHANOL SYNTHESIS PATHWAYS FROM BIOMASS AND CO_2

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ABSTRACT

Global demand for methanol as both a chemical precursor and a fuel additive is rising. At the same time, numerous renewable methanol production pathways are under development which, if commercialized, could present significant environmental benefits over traditional methanol synthesis pathways. There is a need to harmonize the analyses of renewable pathways using a consistent techno-economic approach to evaluate the potential for commercialization of various pathways. This analysis considers economic and environmental factors critical to market acceptance of three renewable pathways versus a commercial baseline. We suggest that biomass gasification to methanol represents a near-term viable pathway with high technology readiness level and commercially competitive market price. However, long-term solutions should consider CO_2 electrolysis pathways which offer further improvements in sustainability metrics to support global decarbonization efforts.

Keywords: Methanol, carbon dioxide, techno-economic analysis, biomass, hydrogenation, power-to-liquids (PTL), waste carbon conversion

NONMENCLATURE

Abbreviations	
TEA	Techno-economic analysis
PTL	Power-to-liquids
MSP	Minimum selling price
FE	Faradaic efficiency
TRL	Technology readiness level

1. INTRODUCTION

The call to reduce global CO_2 emissions is at the forefront of research and development in the transportation and petrochemical industries. A potential solution which intersects both sectors is the adoption and commercialization of renewable technologies for methanol production. Currently, methanol is gaining popularity as a possible fuel additive, and as a polymer precursor via established methanol-to-olefins (MTO) routes which are increasing in capacity and utilization, putting methanol in the spotlight and global methanol production on the rise. Specifically, from 2006 to 2016, global methanol demand doubled from 40 to 80 million metric tonnes annually [1], without including potentials from MTO routes. Recent data projects the demand to continue to grow at an average annual growth rate of 4.3% through 2026 [2].

As a result, novel process designs for renewable methanol synthesis seeking to mitigate conventional emissions are accumulating in literature. Significant research is underway for catalytic CO_2 hydrogenation with renewable H_2 (hydrogen) [3-8]. More mature renewable technologies such as biomass to methanol are also reported [9-11], contrasting with newly emerging technologies such as direct electrolysis [12] and others. Despite the abundance of literature available on the subject, it is unclear what near-term and long-term commercialization strategies are most feasible.

In this study, we identify four key process metrics to evaluate the feasibility of commercializing a renewable methanol synthesis technology versus a commercial baseline of natural gas to methanol. The four metrics selected include minimum selling price (MSP), carbon efficiency, energy efficiency, and technology readiness level (TRL). Of the numerous potential renewable pathways to analyze, we have selected three: biomass gasification to methanol, indirect conversion of CO_2 to methanol via a CO intermediate, and direct conversion of CO_2 to methanol via electrolysis. Developing a consistent baseline and generating a cross-comparison between metrics distinguishes the near-term versus long-term potential of each pathway.

2. METHODS

2.1 Process Design

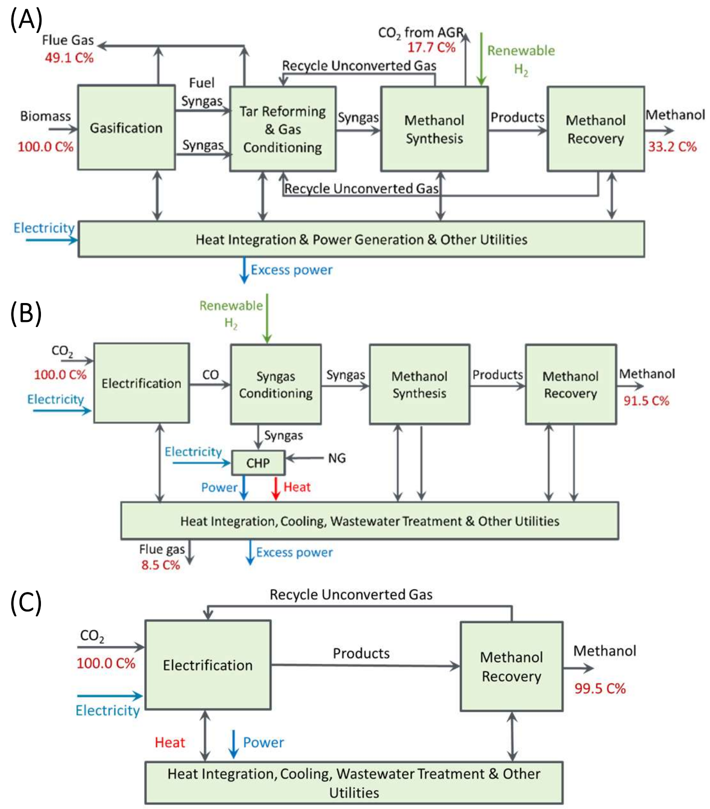

Figure 1. Process flow diagrams for the three renewable methanol synthesis pathways (A) biomass-to-methanol, (B) combined CO_2 electrolysis and H_2O oxidation for syngas conversion to methanol (indirect electrolysis), (C) direct CO_2 electrolysis to methanol.

2.1.1 Methanol synthesis via biomass feedstocks

Capitalizing on established technologies for both gasification and methanol synthesis, biomass gasification to methanol has been widely studied and, in a few cases, operated at the commercial level. In this process design [13, 14], lignocellulosic biomass is pretreated and fed to an indirect gasifier along with steam. The biomass deconstructs to syngas (CO, CO_2, H_2), tars and chars. Tars and chars are combusted as the primary source of heat for the gasifier, which is operated at 1595°F (867°C) and 2.4 atm, and syngas is routed to a gas cleanup and quench step. Following gas cleanup, the syngas is sent to an acid gas removal unit where CO_2 concentration in the syngas is limited to about 5%. Methanol synthesis is then operated isothermally at 482°F (250°C) and 49.7 atm over a commercial copper/zinc oxide/alumina catalyst [15]. Methanol is condensed and separated from the unreacted gases which are recycled to the synthesis reactor (Figure 1A).

Additional scenarios were considered to investigate the potential to increase carbon efficiency of the process. The two scenarios include a renewable electricity import case, and a renewable H_2 import and CO_2 utilization case. The renewable electricity import case seeks to offset some of the syngas diverted for process fuel use, as shown in Figure 1A, potentially increasing carbon efficiency. The CO_2 utilization case eliminates the acid gas removal step and imports renewable H_2 to include a reverse water-gas shift (RWGS) reaction to reincorporate carbon typically lost as CO_2 emissions. The RWGS reaction is shown in Equation 1.

$$CO_2 + H_2 \leftrightarrow CO + H_2O \qquad (1)$$

2.1.2 Indirect CO_2-to-methanol via syngas intermediate

Indirect CO_2-to-methanol uses a hybrid approach of low-temperature CO_2 electrolysis combined with conventional methanol synthesis (Figure 1B). Under the baseline conditions [16], CO_2 is reduced over a carbon nanotube doped Ag electrocatalyst reaching a faradaic efficiency and whole cell voltage of 98% and 3V, respectively. Acknowledging that CO_2 electrolysis is a nascent technology and will continue to improve over time, we also consider a future scenario in which the cell voltage is reduced to 2V at a faradaic efficiency of 95%. In both cases, renewable H_2 produced from PEM H_2O electrolysis [17] is imported and mixed with the CO to create a syngas mixture which then undergoes traditional methanol synthesis and purification as described in section 2.1.1.

2.1.3 Direct CO_2-to-methanol electrolysis

In the direct CO_2-to-methanol electrolysis pathway, CO_2 is reduced to methanol in a single step over a copper selenide electrocatalyst. At near ambient reaction conditions, current baseline studies have reported faradaic efficiencies of over 77% at cell voltages of 1.9 V reaching total current densities of 41.5 mA/cm^2 [18]. Reported byproducts during methanol synthesis include H_2, CO, and HCOOH which are subsequently purified via pressure swing adsorption and distillation stages and recovered for sale. Similar to the electrosynthesis of CO noted in section 2.1.2, direct methanol synthesis is an emerging immature technology which is likely to benefit from future R&D. Consequently, we also consider a future scenario which accounts for technological improvements reaching faradaic efficiencies of 95%, cell voltage of 2 V, and current density of 250 mA/cm^2.

2.2 Assumptions

2.2.1 Techno-Economic Analysis

The three renewable pathways were all modeled in Aspen Plus. Heat and mass data from the simulations were used to calculate the capital and operating expenses of a conceptual plant. The capacity of methanol production was based on the lignocellulosic biomass production at a fixed feedstock rate of 2,000 dry tonnes/day [19], therefore each model was scaled to have annual methanol production of about 96 million gallons for consistency.

The capital and operating expenses were used in a discounted cash flow rate of return (DCFROR) analysis. The minimum methanol selling price is the minimum price that methanol must sell for to generate a net present value of zero for a 10% internal rate of return, assuming a 30-year plant life, 21% income tax rate, and 2016 U.S. dollars.

2.2.2 Modeling Assumptions

Key parameters used for process modeling are quantified in Table 1. Note the values presented are those for the baseline case for each pathway. Variations on these metrics are noted in the respective pathway descriptions in section 2.1.

Table 1. Summary of Metrics for Process Modeling

Pathway/Metric	Assumed Value	Ref.
CO_2-to-CO Electrolysis		
Cell Voltage (V)	3.0	[16]
Faradaic Efficiency (%)	98.0	[16]
Current Density (mA/cm^2)	350.0	[16]
CO_2-to-MeOH Electrolysis		
Cell Voltage (V)	1.9	[18]
Faradaic Efficiency (%)	77.8	[18]
Current Density (mA/cm^2)	41.5	[18]
PEM H_2O Electrolysis		
Cell Voltage (V)	2.0	[17]
Faradaic Efficiency (%)	99.0	[17]
Current Density (mA/cm^2)	1600.0	[17]
Methanol Synthesis		
Temperature (C)	250.0	[19]
Pressure (bar)	50.0	[19]
CO_2 Free MeOH Selectivity (%)	100%	[19]

3. RESULTS

3.1 Minimum Selling Price (MSP)

A comparison of the minimum selling price of methanol for each pathway is shown in Figure 2. The underlying economic assumptions for each of the modeled renewable pathways were held constant to ensure a uniform baseline. The commercial baseline cost for methanol averages $0.33/kg [20] with feedstock and operating expenses contributing most of the cost.

The biomass to methanol pathway is competitive with commercial pathways at a baseline cost of $0.39/kg. The greatest cost reduction is achieved with the CO_2 utilization case, achieving an MSP of $0.35/kg. However, it is important to note that this value is highly sensitive to renewable H_2 import cost. If H_2 costs are high, the MSP increases by 28% from the baseline scenario.

The baseline case for the indirect CO_2-to-methanol pathway exhibits an MSP of $0.90/kg. Reducing cell voltage and keeping faradaic efficiency nearly constant reduces the electricity requirement of the process, decreasing both the operating expenses and capital expenses of electrolysis. Decreasing cell voltage from 3V to 2V reduces MSP by nearly 8%.

The direct CO_2-to-methanol pathway is in the very early stages of development. As such, methanol production via direct electrolysis exhibits variation across experimental baseline results. Therefore, we present two MSP baseline cases and two MSP future cases, utilizing two sets of experimental results [18]. Current baseline results for both cases of the direct pathway are extremely capital intensive due to the low reported current densities. Our projections show the MSP of the first baseline direct case (Baseline-1) as $11.20/kg with 75% of the cost contributions coming from capital expenses associated with the electrolyzer and baseline-2 even greater at $17.26/kg. The second case (Baseline-2) exhibits slightly lower product selectivity towards methanol, increasing cost, and decreasing carbon and energy efficiency. Increasing the current density in both future cases essentially increases the productivity. This results in greater yield of methanol per unit area, significantly reducing the capital expenses of the process, resulting in a future MSP of the first case (Future-1) of $1.01/kg, which is nearly 3-fold of the current methanol market price, and for Future-2 an MSP of $1.57/kg.

3.2 Carbon Efficiency

Carbon efficiency highlights the technical limitations unique to each pathway as it applies to carbon loss due to selectivity, feedstock challenges, and maximum theoretical yield. Carbon flows normalized by carbon in the feedstock for each scenario are displayed in Figures 1A-1C. The exiting carbon flow as methanol is equal to the process carbon efficiency. As a baseline for comparison, current commercial pathways exhibit carbon efficiencies ranging from 68%-75% [20].

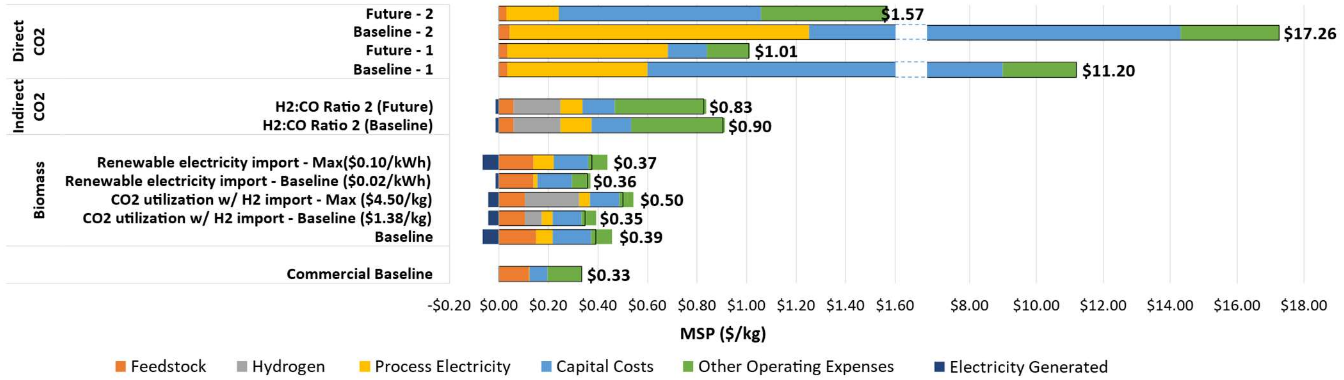

Figure 2. Minimum selling price comparison for renewable pathways versus commercial baseline. The biomass scenario includes additional sensitivity cases for either high or low H_2 and electricity costs, respectively. Commercial baseline data derived from IHS [20].

Out of the four cases, the biomass to methanol pathway displays the lowest carbon efficiency, regardless of scenario. The carbon efficiency of the biomass pathway in the base case was 33.2%, significantly lower than the commercial baseline. Importing H_2 into the synthesis loop to reincorporate carbon lost to CO_2 provides some improvement in carbon efficiency, up to 46.6%, while the renewable electricity case, which diverts less syngas to process fuel, only shows minimal gains in carbon efficiency (36.1%).

Both the indirect and direct conversion of CO_2 to methanol have the potential for improved carbon efficiency over the biomass and commercial cases, achieving greater than 90% carbon efficiency in both cases. The indirect case achieves a carbon efficiency of 91.5% and carbon loss is primarily due to a small slip stream in the synthesis recycle loop, and light hydrocarbons separated out in the methanol recovery step. Carbon lost in the indirect case is routed to the combine heat and power system (CHP) and is burned as process fuel.

3.3 Energy Efficiency

Calculated energy efficiencies are reported for the four studied methanol synthesis pathways showing a range of 41.0% - 66.3% depending on the specific case and assumptions. In comparing the three renewable pathways to the commercial base case, we show that the energy efficiencies are all lower, under both current baseline and future case assumptions. Amongst the renewable cases, the direct CO_2-to-methanol case was the highest performing pathway at 56.1% - 57.8% followed by biomass utilization at 47.8% - 51.1% and then indirect CO_2-to-methanol at 41.0% - 47.1%.

With the baseline biomass case relying predominantly on the energy inherent within the biomass as the main energy input, the lower energy efficiency can largely be traced back to the poor carbon efficiency as noted in Figure 1A. Specifically, much of the inherent energy in the incoming feedstock is lost to char, tars, and other light species and not recovered for process use. Further, the biomass case employs several energy intensive unit operations such as the tar reformer, acid gas removal, and methanol synthesis which further drive up energy usage. Process efficiencies are modestly improved through the usage of renewable electricity; however, are only expected to reach ~51.1%.

For the direct and indirect electrolysis CO_2-to-methanol cases, the most significant differences in energy efficiency are related to the electrolysis operating assumptions. Although both processes require the transfer of six electrons to reduce CO_2 to methanol—shown in Equation 2 for the direct pathway and Equations 3-5 for the indirect pathway—differences in assumed cell voltage significantly impact the total energy demand.

$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O \quad (2)$$

$$4H^+ + 4e^- \rightarrow 2H_2 \quad (3)$$

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \quad (4)$$

$$CO + 2H_2 \rightarrow CH_3OH \quad (5)$$

The assumed cell voltage for direct methanol synthesis is 1.85 V based on recent experimental data whereas the cell voltages for the H_2O oxidation and CO_2 to CO electrolysis are higher at 2.0 and 2.1V, respectively. Thus, despite requiring the same number of electrons per product (i.e., current), when multiplied by voltage to get total power demand, the differences in voltage significantly impact energy efficiency. Further, after forming the two syngas components via electrolysis, additional heat and pressure are required in the indirect case for the thermochemical conversion process to convert the syngas to methanol whereas the direct case operates at near-ambient conditions.

3.4 Technology Readiness Level (TRL)

An assessment of the TRL for each pathway was generated from the U.S. Department of Energy's (DOE) Technology Readiness Assessment Guide [21]. The TRL is a qualitative assessment of the current state of research and development and is a useful indicator for estimating time to commercialization with lower TRLs requiring significant development efforts. Commercial installations of biomass gasification plants ranging from pilot scale to demonstration scale since as early as 1990 suggest a high TRL for the biomass gasification pathway, on the order of 7-9 [22]. The indirect pathway consists of essentially three technologies, CO_2 reduction to CO, H_2O electrolysis to H_2, and syngas conversion to methanol. Water electrolysis and syngas conversion to methanol are both commercialized and mature technologies [23]. However, CO_2 to CO is around 4 in TRL level and is thus the limiting factor in time to commercialization. Finally, the data used to derive the direct CO_2-to-methanol case is from small scale, first principles experimentation. Therefore, the direct pathway is at a TRL of about 1 and will require significant R&D efforts to reach commercial scale deployment.

4. DISCUSSION

Analyzing minimum selling price, carbon efficiency, energy efficiency and TRL simultaneously helps to identify the factors which are most important for near-term or long-term deployment of renewable methanol technologies.

The biomass gasification to methanol pathway has been highly optimized for cost efficiency. Comparatively, lower TRL technologies such as the waste CO_2 pathways, which are more focused on proof-of-concept process design, are not yet optimized for cost or for sustainability.

One of the challenges in comparing baseline data across products, such as CO and methanol, is that experimental conditions can be optimized for different metrics which can highly impact TEA results. In the case of direct CO_2-to-methanol synthesis (lowest in TRL), the reported current density, another key metric for commercialization, is comparably very low at only approximately 40 mA/cm^2. By contrast, the reported commercially relevant current densities for CO_2 to CO and H_2O to H_2 were at hundreds of mA/cm^2 which act to drive down both footprint of the electrolyzer and capital cost. This tradeoff is clearly illustrated in Figure 2 which shows that despite the higher energy efficiency of the direct pathway, the indirect pathway has a significantly lower calculated production cost of \$1.05/kg methanol compared to \$11.20/kg methanol from direct conversion of CO_2.

However, when comparing the future electrolysis cases which account for improvements in technical parameters and a more like-for-like comparison, we find that the direct case approaches price parity with the indirect case while maintaining a higher energy efficiency. A significant limitation in the biomass to methanol pathway is carbon lost to tars and chars in the gasification step (about 31%). Higher operating temperatures could form less char, and thus would increase carbon efficiency of biomass to gaseous product, but gasification would require an external fuel source to provide heat, decreasing the energy efficiency of the process. In contrast, the CO_2-to-methanol pathways exhibit very high theoretical carbon efficiencies, accomplished through the elimination of other carbon sinks via highly selective electrocatalysts.

5. CONCLUSION

Commercial methanol pathways operate at large scale, at low cost, and with moderate carbon and energy efficiencies. Therefore, a viable renewable methanol technology should meet or exceed the current commercial metrics to drive adoption at scale. Our analysis shows the biomass gasification to methanol pathway is capable of meeting market competitive costs and displays a high TRL, and of the studied pathways is the most promising technology for the near-term. However, sustainability metrics are key elements for impactful change in the ongoing global decarbonization efforts. Both indirect and direct CO_2-to-methanol pathways present energy efficiencies comparable to commercial pathways and exceptional carbon efficiencies, but at a cost. The direct CO_2 pathway is comparatively much lower in TRL and requires the most substantial R&D efforts pushing commercialization feasibility the farthest into the long-term, while the indirect CO_2 pathway may be achievable in less R&D time if electrolysis costs can be reduced.

Near-term commercialization will largely be driven by TRL and market acceptance through cost parity. As global priorities begin to shift and greater consideration is given to sustainability metrics for commercial deployment of technologies, long-term solutions will require both improved carbon and energy efficiencies over the commercial baseline which may be possible through the indirect and direct electrolysis pathways. Consequently, future analyses should consider process designs that are optimized across a variety of economic and environmental metrics rather than solely economic drivers.

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