

Greenhouse Gas Emissions, Energy Efficiency, and Cost of Synthetic Fuel Production Using Electrochemical CO₂ Conversion and the Fischer–Tropsch Process

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Supporting Information

ABSTRACT: This study seeks to explore whether electrochemical reduction of CO₂ (using current US average and future low carbon electricity) will become a viable route for the reuse of CO₂ for producing synthetic fuel. This paper presents the results of a technical and economic analysis conducted for a pathway that converts CO₂ released from fossil fuel-burning power plants to diesel fuel via electrochemical reduction of CO₂ to CO and the Fischer–Tropsch process. Currently achievable performance levels for CO₂ electrolyzers and the Fischer–Tropsch process were used to compute key metrics, including (i) cost of the synthetic fuel, (ii) well-to-gate CO₂ emissions, and (iii) overall energy efficiency. An engineering and economic model framework was developed for the investigation. The discounted cash flow analysis method was employed to calculate the cost of diesel fuel using a 500 MW power plant as the CO₂ source. The model takes into account capital expenditures as well as operating costs for the reactors and auxiliaries. The final cost varies from 3.80 to 9.20 dollars per gallon in 2010 US dollars depending on the projected level of technology achieved. The WTG CO₂ emissions vary from 180% (nearly twice) to a reduction of 75% compared to that of the business as usual scenario without carbon sequestration. The well-to-gate energy efficiency varies from 41 to 65%.

1. INTRODUCTION

The capture and use of CO₂ to produce synthetic fuels could have the potential to contribute to working toward a carbon neutral society. There is a significant amount of fundamental and system modeling research investigating the conversion of CO₂ to CO with reduced life cycle energy utilization and thus decreased life cycle greenhouse gas emissions.^{1–5} Here, CO serves as an intermediate energy carrier for producing other synthetic fuels. One potential pathway is electrochemically reducing CO₂ to CO and using the Fischer–Tropsch (FT) process to convert CO and H₂ into synthetic gasoline and/or diesel fuel. Using CO as an intermediate carrier in this proposed pathway is an attractive option due to the relatively high selectivity and low over-potentials for CO production during the electrochemical CO₂ reduction process. When carbon neutral electricity from wind, solar, and other carbon neutral resources becomes abundant, this pathway holds great potential to decarbonize our transportation system and industrial processes.

To date, there have only been very limited research activities attempting to understand the cost of such low carbon synthetic fuel pathways. Overall, the economic feasibility and actual environmental impact of such a pathway remains unclear, and

several important questions remain unanswered. For example, what is the real environmental impact with current and future grid electricity that may have significantly different carbon intensities? How competitive could it be economically? What are the constraints on the viability of such pathways?

This study aims at providing an analytical framework and tools to answer these questions. There are three main elements in this study: showcasing an example design of CO₂ reduction and FT fuel synthesis in an integrated system, investigating the technical and economic feasibility of the design, and assessing the well-to-gate (WTG) CO₂ emissions of this pathway. WTG means life cycle with the exclusion of the fuel use phase. The results will show the level of economic competitiveness, overall energy efficiency, and WTG CO₂ emissions for this energy pathway. In addition, the general framework and analytical tools developed in this study to accomplish these tasks can be used in evaluating other pathways for CO₂ utilization based on consistent criteria. The framework is a combination of knowledge domains including electrochemistry, general en-

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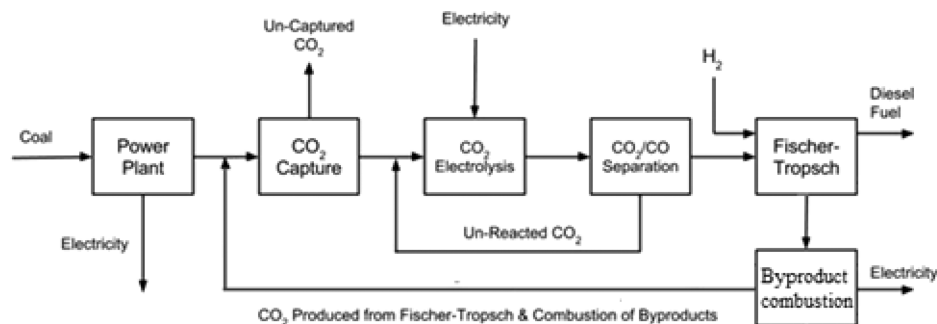


Figure 1. Proposed integrated system for liquid fuel production using CO₂ electrolysis coupled with the Fischer–Tropsch process.

gineering design, engineering economics including discounted cash flow analysis, and life cycle emission analysis. Such a framework and tools will be valuable for better guiding and prioritizing future research in CO₂ conversion and utilization.

We begin by proposing a design for an integrated system shown in Figure 1 to capture CO₂ from a coal-based power plant, electrochemically reducing it to form the CO intermediate, and producing synthetic fuel via the FT process using the CO and H₂ independently produced through electrolysis. More details on the integrated system can be found in section 2.1. A description of the electrochemical CO₂ reduction process can be found in section 2.1.4 and existing literature.^{1–3}

Next, we identify three metrics corresponding to the three elements of the study. First, we evaluate the levelized cost of fuel calculated in \$ per gallon. This provides a comparison of economic competitiveness against other current and future fuel pathways. Second, we evaluate the overall energy efficiency of the process. This includes the efficiency of all relevant components upstream of the process being directly investigated. Because the system described also produces electricity as a coproduct, we do not make direct comparisons of efficiency with existing technologies that produce only fuels. However, efficiency is still a valuable metric and calculated here because it gives a general sense of whether this technology is a good use of energy resources or not. Third, we evaluate the WTG CO₂ emissions. We compare this to the emissions of the current business as usual (BAU1) case of producing electricity and transportation fuel from fossil fuels without any significant CO₂ mitigation strategy. We can also compare this against other proposed technologies and processes for CO₂ emission reduction.

To accomplish these goals, we create an engineering and economic model in a spreadsheet representing the integrated system in Figure 1. At its core, this model solves the material and energy balance of this system and conducts an economic analysis utilizing capital and operating costs and the discounted cash flow (DCF) analysis method to calculate the levelized cost of the fuel produced. Included in the cost, material and energy balance calculations are conducted utilizing relevant electrochemistry CO₂ reduction parameters with state-of-the-art performance based on recent lab-scale research. The model enables the evaluation of the impact of CO₂ reduction technology in real environmental and economic terms. The main outputs of this model are the three metrics mentioned above under a range of proven and projected cost and performance parameters. We include a sensitivity analysis to evaluate the impact of important assumptions made to describe

which variables are most important for moving this technology toward commercialization.

More fundamental research will be needed to achieve the full potential of CO₂ electrochemical reduction. Optimization of an integrated power plant, CO₂ capture, CO₂ reduction, and the FT fuel process would also be important to improve the environmental and economic performance of the system. This study is intended to be a first pass at broadly understanding the potential and limits of the viability of this technology. As will be seen, the results help identify the key cost, energy requirement, and CO₂ emission issues that can guide future research and thinking around this and other CO₂ utilization schemes.

2. METHODOLOGY

2.1. Process Description. **2.1.1. Overall Process.** It is assumed that the CO₂ source is a 500 MW pulverized coal power plant and that the CO₂ is captured using the current postcombustion acid gas removal process using chemical absorption and monoethanolamine (MEA) as the solvent.^{6,7} The CO₂ is sent to an electrochemical CO₂ reduction (ECR) process. This process is shown in Figure 1. It is assumed that the CO₂ electrolyzer is similar to a standard alkaline electrolyzer design used in water electrolysis for H₂ production.⁸ There are some differences between a CO₂ electrolyzer and a water electrolyzer, such as differences in catalysts. Such discussion can be found in existing literature.³ Unreacted CO₂ is separated from CO and recycled back through the CO₂ electrolyzer to increase the overall conversion of CO₂ to CO. The CO is combined with H₂ and sent to the FT process for fuel synthesis. We assume that H₂ is also produced via electrolysis in this analysis, but the model and process design are flexible and can be used to evaluate other H₂ sources as well. In the FT process, CO and H₂ are reacted to form a mixture of hydrocarbons that can be refined to produce synthetic diesel.⁹ For simplicity, we assume that the fuel produced has the same chemical composition as regular diesel.⁹ Hydrocarbon byproducts can be combusted and the heat can be used for electricity generation, and this electricity can be recycled for use again in electrolysis.⁹ Additionally, CO₂ produced as a byproduct of the FT process and by the combustion of the hydrocarbon byproducts can be recycled back through the process to increase the yield of fuel.

2.1.2. Fossil Fuel Power Plant (FFPP). The analysis baseline in this study is a 500 MW pulverized coal power plant. Full life cycle operations excluding the fuel end use phase associated with this integrated system are included in our energy efficiency and WTG CO₂ analyses, including all energy efficiency and WTG CO₂ effects upstream of the FFPP, such as coal extraction and transportation, and electricity production in the 500 MW plant.⁷ This study did not explicitly include the cost of the FFPP in the analysis. Electricity is a feedstock for the CO₂ reduction and fuel production. The cost of the FFPP is included implicitly in the cost of electricity purchased from the grid for the CO₂ reduction and hydrogen production. Evaluating the economics of synthetic fuel using current and projected future electricity prices provides a clear basis for evaluating competitiveness with other possible fuel options and elucidates well the parameters

most important for future research on CO₂ conversion to synthetic fuels.

2.1.3. CO₂ Capture. As mentioned in section 2.1.1, the CO₂ is captured using a postcombustion chemical absorption solvent MEA. The postcombustion MEA absorption system absorbs CO₂ from the power plant flue gases and then desorbs the CO₂ from the solvent by direct contact with steam. Energy is required to generate the steam for the desorption process.^{6,7} Parasitic electric loads for equipment such as blowers also consume energy. The capital and operating costs as well as the energy requirement of this CO₂ capture process are extracted from the existing literature and presented in Tables 1 and 2 and the Supporting Information.^{6,7}

Table 1. Base Case and Low and High Performance Values of Key Variables^a

key variables	high performance	base case	low performance
CO ₂ electrolysis cell voltage, V	−1.5	−1.8	−3
CO ₂ electrolysis current density, mA/cm ²	600	400	250
CO Faradaic efficiency, %	98	98	75
reference electrolyzer cost, \$/m ²	1221	2442	4884
energy loss for CO ₂ capture, %	27	27	27
FTL configuration	with recycle	no recycle	N/A ^b
FTL conversion (yield of fuel), %	80	34	34
percent reduction in grid CO ₂ emissions, %	90	0 (current grid)	N/A ^c
capital cost multiplier for CO ₂ separation and capture	0.5	1	1.3
capital cost multiplier for CO ₂ /CO separation after CO ₂ electrolysis	0.5	1	2
capital cost multiplier for FTL	0.5	1	1.5
after tax real IRR, %	7	10	20
cost of electricity, \$ kWh ^{−1}	0.03	0.06	0.09
cost of H ₂ , \$ kg ^{−1} H ₂	3	5	5

^aFor sensitivity analysis, one deviation from the base case value for one parameter represents one case. For example, for the electrolyzer cell voltage variable, there are two cases in addition to the base case: low and high performance values (all other parameters are held at the base case value). For the FTL configuration variable, there is only one deviation from the base case configuration, which is “with recycle” (all other parameters are held at the base case value). Another special case is the “percent reduction in grid CO₂ emissions” variable. Because we assume the grid emission will improve over time, there is really no low performance value for this parameter. ^bFor the “no recycle” FTL configuration, unreacted CO and H₂ mixture is combusted to generate electricity rather than recycled for the FT process. ^cReduction in grid CO₂ emissions by 90% could represent a grid dominated by renewables and/or other carbon neutral power production. It is assumed that all the processes in the system operate constantly. It is worth noting that coal plants currently operate almost constantly. The variability of renewables is addressed by a portfolio of solutions including hydro, battery, and natural gas plants that have operational capacity flexibility. In the case of high level penetration of renewables, it is possible that 10% of coal plants in the electricity mix operate constantly, and they do not have to operate 10% of the time.

2.1.4. CO₂ Electrolysis. CO₂ electrolysis is the new process in the integrated system. The other processes including CO₂ capture and FT are technologies that are either commercial or demonstrated at small or medium scales. To date, most fundamental research for CO₂ electrolysis utilizes a 3-electrode cell or microfluidic devices, and several types of bench-scale reactors have been tested.^{10,11} CO₂ electrolysis research focuses on improving three parameters: cell voltage (*V*), the potential difference across the anode and cathode; current density (*I*), typically measured in mA/cm²; and the Faradaic

Table 2. Key Parameter Values for the Base Case and Optimistic Case (Costs are in 2010 US dollars)

key parameters	base case value	optimistic case value
CO ₂ electrolysis cell voltage, V	−1.8	−1.5
CO ₂ electrolysis current density, mA/cm ²	400	400
CO Faradaic efficiency, %	98	98
reference electrolyzer cost, \$/m ²	2442	2442
efficiency loss for CO ₂ capture after the CO ₂ electrolyzer, %	27	27
FTL configuration	no recycle	no recycle
FTL conversion (single pass), %	34	80
percent reduction in grid CO ₂ emissions, %	0 (current grid)	90 ^b
capital cost multiplier for CO ₂ capture	1	1
capital cost multiplier for CO ₂ /CO separation	1	1
capital cost multiplier for FTL	1	1
after tax real IRR, %	10	10
cost of electricity, \$ kWh ^{−1}	0.06	0.03
cost of H ₂ , \$ kg ^{−1} H ₂	5	3

efficiency (FE). FE is a measurement of the amount of energy input into the cell that actually ends up as chemical energy in CO.

Electrochemical CO₂ reduction occurs at a three-phase boundary among gaseous CO₂, liquid electrolyte, and solid catalyst.^{10,11} As a result, achieving a high reaction rate with high efficiency is quite difficult, and developing a catalyst to efficiently accomplish this remains elusive. Although this paper is not meant to prescribe an exact benchmark, the results of the analysis should yield a general sense of where state-of-the-art lies relative to a state promising for commercialization.

The energy required for each unit of CO₂ reduction can be calculated as

$$J = V/FE \times C$$

where *J* is energy in joules per unit of CO₂ reduction, *V* is voltage, and *C* is charge measured in Coulombs. According to Faraday's law, *C* is directly correlated to moles of CO₂ reacted or CO produced. The result is a measurement of energy input per unit CO produced, which is directly dependent on voltage *V*. Energy use is also dependent on FE. When FE is lower, more energy is wasted in byproduct production, increasing the energy necessary to produce a given amount of CO.

Current through the system is directly correlated to reaction rate according to Faraday's law. Thus, when a fixed rate of CO₂ is input for CO production, total current through the system is fixed. As a result, current density, *i*, defines the total electrode area necessary to achieve the specified CO production rate. It is assumed that the capital cost of a CO₂ electrolysis unit is dependent on the electrode surface area, and thus *i* is a crucial parameter for determining the capital cost of the CO₂ electrolysis equipment. It is worth noting that, in this study, the CO₂ electrolyzer capital cost is dependent only on the current density for CO production (this is a reasonable approximation when no detailed cost data are available at the current R&D stage). Thus, current density does not affect the mass or energy balances. It is also assumed that some CO₂ is separated from CO and recycled back through the CO₂ electrolyzer. More details about separation of the CO₂ and CO stream can be found in section 2.1.5.

The cost estimate of a CO₂ electrolyzer is based on the cost of an alkaline water electrolyzer in the H2A model published by the U.S. Department of Energy (DOE).⁸ The H2A model published standard rates of H₂ production for an electrolyzer. Using current densities common in alkaline water electrolyzers obtained from the literature, the H2A production rate, and Faraday's law, one can estimate the electrode area in a single electrolyzer in the DOE analysis.⁸ Using the electrode area and the cost per electrolyzer, one can then calculate a cost per electrode area for a water electrolyzer. This study assumes that

a CO₂ electrolyzer resembles an alkaline water electrolyzer and applies the cost per electrode area of a water electrolyzer to that of a CO₂ electrolyzer.

Although an alkaline water electrolyzer and a CO₂ electrolyzer share similarities, they may require different design and materials for catalyst and electrodes, rendering a different cost per electrode area for the two electrolyzers. The sensitivity analysis in this study addresses the uncertainty in this cost assumption.

It is worth noting that there are other types of water electrolyzers, such as PEM electrolyzers. The mechanism of these water electrolyzers is similar. The main difference between the alkaline and PEM electrolyzers is the use of different electrolytes. The PEM contains precious metal, platinum, which adds some cost. Recent advances in manufacturing technology significantly reduced the required amount of platinum, and the cost of the two electrolyzers is comparable. The CO₂ electrolyzers are still in the early development stage; it is too early to predict which type of electrolytes will be commercialized in the future. CO₂ electrolyzers do not require a precious metal such as platinum. In this sense, they are more similar to alkaline electrolyzers. In addition, a large margin is used in the sensitivity analysis based on electrolyzer cost, which addresses the uncertainty in the CO₂ electrolyzer capital cost.

This study assumes that electrochemical performance on a laboratory scale can be achieved on an industrial scale as well. A 10% efficiency loss is included in extrapolating lab scale operations to an industrial scale system to account for other parasitic aspects of plant operations, such as blowers and the control system.

2.1.5. Separation of the Stream of CO₂ and CO. The CO₂/CO separation after the CO₂ electrolyzer is achieved through the pressure swing adsorption (PSA) technology.¹² The parameters associated with this process are obtained by surveying industry experts (Linde, personal communication). The survey provided capital and installation cost and energy input for a reference CO₂/CO separation unit with specified size. These parameters are then scaled to the sizes evaluated in this study. More specifically, the size of the reference unit has a total flow rate of 4.40×10^6 mol/h. The reference composition of the feed stream to the CO₂/CO separation unit is 50% CO₂, 45% CO, and 5% H₂ on a molar basis. The capital and installation cost is given as \$77,064,498 for the reference size, and it is assumed that electrical power of 10 kW is required to operate the unit. The unit would lose a few percent of CO and H₂ to the CO₂ stream and a few percent of CO₂ to the CO and H₂ stream. As a result, 97% of CO₂ stream feed to the electrolyzer is assumed to be converted to CO.

2.1.6. FT Fuel Synthesis. The FT process produces hydrocarbons of varying lengths using CO and H₂ as feed stock. The raw product from the FT process includes naphtha, middle distillate, wax, and a gas stream of unreacted syngas, CO₂, and light hydrocarbons. The majority of the FT hydrocarbons can be further converted to synthetic diesel fuel and other transportation fuels through hydrotreating and hydrocracking.^{9,13–15} Some of the carbon input into the process ends up as hydrocarbon byproducts that cannot be refined into diesel fuel. These hydrocarbons can be combusted to produce electricity, and the electricity can be recycled for use in CO₂ electrolysis, decreasing the amount of electricity needed as input. In this study, this electricity is counted as a byproduct credit in the DCF analysis. The combusted hydrocarbon also produces CO₂. As a result, the final output of the FT process is synthetic fuel and a CO₂-rich gas stream. The CO₂ can either be released to the atmosphere or recycled back to the initial CO₂ capture unit.

The mixture of the raw product from the FT reaction varies depending on the catalyst, H₂ to CO ratio, operating temperature, and pressure. The fuel producers can control these parameters and the subsequent hydrotreating or hydrocracking processes to generate the desired fuel products. This study focuses on analyzing the complex integrated synthetic fuel production system. The FT process is a subsystem of the integrated system. The FT and hydrotreating and hydrocracking processes are commercially established processes, and a significant amount of literature exists for further reference.^{9,10,13–15} Therefore, the details of the FT process are not discussed here, and a simplified representation and key FT parameters from the literature

are used to model the FT subsystem. Readers can refer to the aforementioned references for further details of the FT process.

H₂ for the FT process is produced onsite by water electrolysis. The energy consumption associated with this process is derived from the H2A model.⁸ The electricity usage and its upstream EE and CO₂ effects are included in the mass and energy balances. As a result, the mass and energy balances include electricity input into this system for both CO₂ and water electrolysis. However, the detailed cost analysis of H₂ electrolysis is not included. Rather, a fixed cost per unit of H₂ is used for the fuel cost analysis. This allows us to explore the effect of H₂ cost with more flexibility to account for other H₂ production methods, such as steam reformation of natural gas.

2.1.7. Carbon Intensity of Grid Electricity. The motivation for the synthetic fuel system under study is to reduce CO₂ emissions and improve our energy independence. In the base case in this study, electricity for CO₂ and H₂ electrolysis is purchased from the current U.S. grid. Whether the integrated system will achieve the life cycle CO₂ reduction goals will depend on its performance and the CO₂ emission rate or carbon intensity of grid electricity. In the alternative cases, this study evaluates the CO₂ emissions impact in response to improvements in efficiency and emissions rate in a grid with varying CO₂ emission rates. This is important to understand the full potential of CO₂ reduction technologies in the future because there have been increasing electricity decarbonization efforts in many countries and regions. For example, both Germany and California have a target of 50% renewable electricity by 2030. In addition, Germany has a target of 80% renewable electricity by 2050, and California is also expected to set higher renewable electricity targets post 2030.

One possible future scenario would be if most grid electricity is produced by renewable or other carbon neutral energy sources, and FFPP is still utilized to meet some of the demand as necessary or industry and transportation sectors still rely on hydrocarbon fuels. This study investigates the benefits to the synthetic fuel system with increasing efficiency and reduced CO₂ emissions associated with grid electricity production. Reducing emissions and improving efficiency are accounted for simultaneously using a scale of improvement from 0–100%. 0% improvement corresponds to the efficiency and emissions in the current electricity grid. 100% improvement corresponds to zero emissions and 100% efficiency. Renewables such as wind, solar, and hydro are considered as having zero emission. (It is worth noting the manufacturing process of renewable equipment emits CO₂. The actual life cycle CO₂ emissions of renewables are not zero, but such CO₂ emissions are expected to be relatively small.) An efficiency of 100% for renewables is used in calculating the effective efficiency of grid electricity because renewables such as wind and sunlight are inexhaustible and free, and efficiency is less of an issue for renewables.

2.1.8. Energy Efficiency. In the model developed in this study, the energy usage per unit CO and synthetic fuel produced affects all three of the target metrics: fuel cost, energy efficiency, and WTG CO₂ emissions. The cost of this input energy is considered in the DCF analysis, and its usage is taken into account in the WTG energy balance and CO₂ emission analysis.

The energy efficiency is defined as

$$\text{energy efficiency} = \text{energy in all useful products} / \text{total energy input}$$

The energy in all useful products is the sum of the energy in fuel, electricity from combustion of nonfuel products of the F-T process, and electricity from fossil fuel power plants. The total energy input includes energy input to fossil fuel power plants including upstream consumption, energy for CO₂ capture, and energy input to CO and H₂ electrolysis including upstream. As explained in section 2.1.7, nuclear and renewable grid electricity is assumed to have an efficiency of 100%. For example, based on 2014 U.S. Energy Information Administration data, the US grid mix is 39% coal, 28% natural and other gas, 19% nuclear, 1% petroleum, and 13% renewables. Assuming the efficiency for coal, natural gas, and petroleum is 41, 60, and 41%, respectively, the overall efficiency of the grid electricity would be 65.2%. The higher the percentage of nuclear and renewables, the higher the grid

Table 3. Summary of Key Results for the Analyzed Cases

	levelized fuel cost, \$ per gallon	WTG CO ₂ emission, million, t y ⁻¹	energy efficiency, %	change in levelized fuel cost against BAU1, %	change in WTG CO ₂ emission against BAU1, %	change in WTG CO ₂ emission against BAU2, %
base case	9.2	11.3 (2.56 × 10 ⁸ kmol y ⁻¹)	53	230	180	1355
optimistic case	3.8	1.1 (2.61 × 10 ⁷ kmol y ⁻¹)	55	36	-75	-8

electricity efficiency would be, and thus the higher would be the energy efficiency for the synthetic fuel system.

2.2. Model for Process Analysis. *2.2.1. Model Description.* The model developed has two integrated modules: a high-level mass and energy balance modeling module and a cost analysis module. The mass and energy balance module enables the calculations of energy efficiency and WTG CO₂ emissions by solving the mass and energy balances for the system outlined in Figure 1. The mass and energy balance module provides inputs such as the CO flow rate during fuel production for the cost analysis module for the calculations of synthetic fuel cost.

The mass and energy balance module is developed under this study. All of the energy input associated with the fuel cycle is considered in the mass and energy balance module. This means that only the energy associated with the fuel use phase and the construction of conversion facilities are not included. The processes including CO₂ capture, electrochemical CO₂ reduction, CO₂/CO separation, and FT synthesis are represented in a high-level, simplified way using parameters from previous studies. The upstream energy efficiency and CO₂ effects are included using data from the H2A model, which was originally obtained from the GREET database.¹⁶ Details regarding the key parameters for the processes can be found in Tables 1 and 2 and the Supporting Information.

The cost analysis module is based on a DCF analysis adapted from the H2A model.^{8,17} The H2A model includes standard cost inputs for materials and utilities taken from U.S. EIA data. Calculation methods are left unchanged, but the model is modified to use the results of mass and energy balances from the mass and energy balance module as inputs for sizing the equipment and calculating the capital and operating and maintenance (O&M) cost of all of the processes. The H2A model is expended under this study to include the capital and O&M cost of all of the processes, including CO₂ capture, electrochemical CO₂ reduction, CO₂/CO separation, and the FT process. All capital costs are calculated using aggregated industry data from references^{8,17} and adjusted to the dollar value of reference year 2010 using the consumer price index (CPI) and the chemical engineering plant cost index (CEPCI). The H2A model includes many important financial parameters as inputs, which are left unchanged in this study. This includes a real 10% after tax internal rate of return (IRR). More details regarding the key cost parameters for the processes can be found in Tables 1 and 2 and the Supporting Information.

2.2.2. Cases Analyzed. This study evaluates the CO₂ to synthetic fuel system shown in Figure 1 through case studies. As a base case, state-of-the-art performance parameters are utilized for all components in the synthetic fuel system. The base case is compared with two reference scenarios. The first reference scenario considered is referred to as business as usual case 1 (BAU1). This is the current-day scenario in which the equivalent amount of electricity is produced from coal without CO₂ capture and sequestration (CCS), and the equivalent amount of fuel is produced from petroleum using current day oil refining technologies. The second reference scenario is referred to as business as usual case 2 (BAU2) in which CCS is utilized during the production of the electricity from the coal plant.

The purpose of analyzing the synthetic fuel system is mainly to explore an alternative liquid fuel pathway at lower WTG CO₂ emissions while producing the same amount of electricity from the power plant compared to the BAU1 and BAU2 cases. The WTG CO₂ emission for the base case is compared against that of the BAU1 and BAU2 cases. Across all comparisons, the amount of electricity produced and the amount of diesel fuel produced are held equivalent.

The results of these comparisons show by how much the synthetic fuel system under study is either increasing or decreasing the rate of CO₂ emissions compared to the BAU cases.

The levelized cost of synthetic fuel in the base case and other cases analyzed is compared to the price of petroleum diesel fuel in BAU1. This comparison indicates the competitiveness of the synthetic fuel system relative to those of BAU1 and BAU2. According to statistics of the U.S. Energy Information Administration (EIA), the average wholesale price of petroleum diesel fuel in 2014 was \$2.80 per gallon.¹⁸

In all three cases, the systems produce two products, electricity and diesel fuel, and the grid electricity has multiple sources including fossil fuels, nuclear, and renewables. Thus, the definition of energy efficiency in this study is defined based on the multiple energy products and primary sources as discussed in section 2.1.8. This is different from the traditional definition of energy efficiency of a fossil fuel power plant, which has electricity as the single product. The achievement of a meaningful direct comparison on overall efficiency among the three cases would be debatable. Nevertheless, energy efficiency is still a valuable metric and gives a general sense of whether a technology is a good use of energy resources or not. Therefore, a value for energy efficiency of the base case is reported for a general sense of how resources are utilized only and not for a direct comparison among the three cases. More discussion on this can be found in section 3.1.

As mentioned before, the base case is derived from current state-of-the-art values for key parameters of all components. A sensitivity analysis is conducted to better understand the significance of the assumptions in the model and to identify the parameters that have the largest impact on overall performance as measured with the three metrics. Table 1 shows the key parameters in the model and their values of the base case. A range of values corresponding to the lower and upper bound system performances is also presented in Table 1. The lower and upper performance bounds of the parameters are not arbitrary, and in general, they represent an estimate at a high confidence level. Several references are reviewed in determining the values of the parameters: CO₂ electrolysis cell voltage,¹⁰ CO₂ electrolysis current density,^{17,19,20} CO Faradaic efficiency,¹⁰ reference electrolyzer cost,¹⁷ energy loss for CO₂ capture,⁷ FTL configuration,^{9,15} and FTL conversion (yield of fuel).^{10,13,15}

The key parameters of the H₂ electrolysis process are consistent with the H2A model, which is well-documented and can be found in refs 8 and 17.

Sensitivity analysis was conducted with the key parameters in Table 1, as shown in section 3.2, to better understand the performance of the synthetic fuel system with a range of conditions for these variables and to identify key areas for improvement.

There is significant continuing effort on the research, development, and demonstration of all subsystems in this study, specifically, CO₂ capture, CO₂/CO separation, CO₂ electrolysis, and FT synthesis. These effort and resulting improvement on the performance of the subsystems are not necessarily for the purpose of the fuel system in this study but will contribute to improving the performance of the integrated fuel system. An optimistic case is thus developed in this study to represent a future scenario where plausible improvement is achieved for the key parameters of the integrated fuel system. In the optimistic case, favorable conditions for key variables identified in the sensitivity analysis, namely, FT fuel yield, grid electricity CO₂ emission rate, and H₂ and electricity price are applied, and the impact is evaluated. The optimistic case results require drastic improvement in the key variables. Details on the values of key parameters for the base case and optimistic case are given in Table 2.

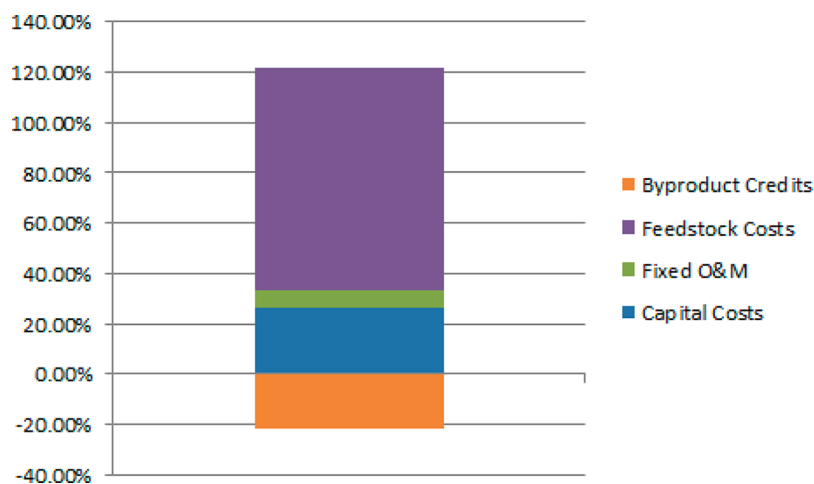


Figure 2. Percent contribution of the cost components for the synthetic fuel production.

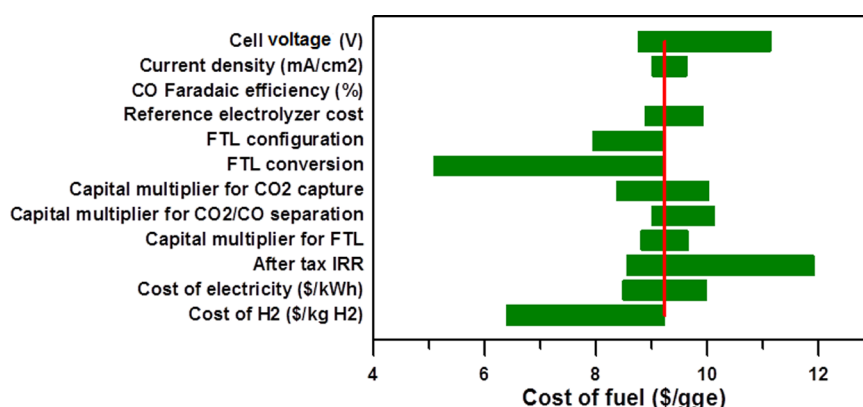


Figure 3. Sensitivity of cost of the synthetic fuel to key parameters.

3. RESULTS AND DISCUSSION

3.1. Results of the Analyzed Cases. Key model results for the base case, BAU1, BAU2, and optimistic case are summarized in Table 3. It is worth noting that for a fair comparison between the fuel costs of the base (and optimistic) case and BAU2, the cost of CCS in BAU2 should be included and properly allocated among the fuel and electricity. For simplicity, only the comparison between the base (and optimistic) case and BAU1 is provided. This is a more conservative evaluation of the relative competitiveness of this system under study because BAU2 fuel should be more expensive than the fuel of BAU1.

With the base case inputs, the model shows that the synthetic fuel is produced with a 53% overall energy efficiency, and the WTG CO₂ emission is 11.3 million tons for a 500 MW coal power plant plus the corresponding 148 million gallons of synthetic diesel fuel produced using the power plant CO₂ emissions as feed stock. The levelized cost of the synthetic fuel is \$9.20 per gallon.

On the basis of the model results, the base case WTG CO₂ emission is 180 and 1355% higher than that of the BAU1 and BAU2 cases, respectively. The levelized cost of the base case synthetic fuel is 230% higher than the \$2.80 per gallon diesel wholesale price in the BAU1 case. Figure 2 shows the percent contribution of the cost components for the synthetic fuel production. The energy efficiency of the base case, BAU1, and BAU2 cases are not directly compared here for a few reasons.

First, the synthetic fuel production system involves coproduction of both electricity and fuel, and it is not as straightforward as evaluating the efficiency of a coal power plant that generates a single energy product. Second, the energy feed stocks for the synthetic fuel production system is electricity, whose efficiency highly depends on the energy sources of the grid electricity. See sections 2.1.7 and 2.1.8 for relevant discussion.

The optimistic case WTG CO₂ emissions result in a 75 and 8% reduction compared to the BAU1 and BAU2 cases, respectively. The difference between the optimistic and BAU1 cases in the emissions depends on the carbon intensity of the grid electricity and the carbon intensity of the production process of fossil diesel. For the synthetic fuel, when the electricity is carbon free, the fuel is carbon free as well. The carbon atoms in the synthetic fuel should be attributed to the electricity generated by the coal power plant. For the fossil diesel, its carbon intensity includes two parts: the carbon emissions associated with its extraction, production, transportation and refining process and the carbon atoms in the fuels. In the optimistic case, the grid electricity has a 90% reduction in carbon emissions and is nearly carbon free, and the fossil diesel fuel is carbon intensive, and as a result, the synthetic fuel has a 75% reduction in CO₂ emissions.

The levelized cost of the optimistic case synthetic fuel is 36% higher than the diesel wholesale price in the BAU1 case. This indicates that if the reduction in the price of H₂ and electricity combined with the improved FT yield used in the optimistic case could be achieved, the price of this synthetic fuel could be

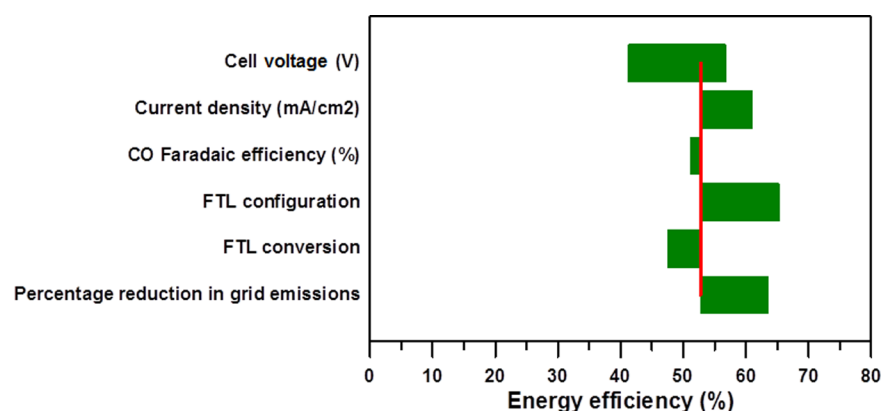


Figure 4. Sensitivity of energy efficiency on key parameters.

in a range similar (but modestly higher) than today's petroleum fuel prices. It is worth noting that the operating cost of producing this synthetic fuel is largely dependent on electricity and H₂ prices. These both are produced domestically from a range of energy sources and are not subject to the same vicissitudes of petroleum price due to geopolitical factors. Thus, the lower WTG CO₂ emission and energy independence benefits may justify the modestly higher levelized cost of the synthetic fuel. In addition, with the significantly lower WTG CO₂ emission and appropriately included carbon emission price, this synthetic fuel could potentially be competitive with petroleum fuels.

3.2. Sensitivity Analysis. **3.2.1. Impact of Changes in Each Individual Key Variable.** Sensitivity analysis was conducted with key variables for CO₂ electrolysis, the FT process, feedstock price, and capital cost to better understand the performance of the synthetic fuel system with a range of conditions for these variables and to identify key areas for improvement. The base case and low and high performance values of the key variables are presented in Table 1. Sensitivity cases were run using these values to assess the impact of changes in each individual key variable while holding other variables constant.

3.2.1.1. Sensitivity of Levelized Fuel Cost to Individual Key Variables. For the synthetic fuel system, the levelized cost of fuel is most sensitive to the yield of fuel from the FT process ("FT Conversion" in Figure 3). Improving FT conversion from the base case value of 34% to 80% reduces the levelized cost of fuel from approximately \$9.20 per gallon to just above \$5.00 per gallon. Some industrial-scale FT processes have reported diesel yields as high as 70%, and pilot scale reactors have reported diesel yields up to 90%. The range of values for FT conversion in this study is within the range of values found in the literature.^{9,10,13,15} CO₂ separation and electrochemically reducing CO₂ is very energy intensive, and low FT conversion results in more CO₂ processing requiring a large amount of electricity to be purchased and consumed per unit fuel produced. Additionally, the higher flow rate results in higher capital cost for the CO₂ electrolyzers.

The reduction in the price of H₂ yields the second largest improvement in the levelized cost of synthetic fuel. It is important to note the relationship of H₂ price and the CO₂ electrolyzer Faraday efficiency for CO production. When H₂ price is high, low Faraday efficiency for CO production does not significantly impact synthetic fuel cost, as H₂ is a valuable byproduct, which is used in the subsequent FT process. As the

price of H₂ decreases, the value of H₂ as a byproduct will diminish, and FE for CO production will become increasingly important.

The levelized cost of synthetic fuel is not very sensitive to the change in CO₂ electrolyzer current density. On the other hand, the levelized cost of synthetic fuel is fairly sensitive to the change in its cell voltage *V*. This indicates that without extreme sacrifices of current density, reducing cell *V* is more important than improving current density for moving this technology closer to economic viability.

If the cost of the reference water electrolyzer were increased by 100% from the base case value, the levelized cost of fuel would increase to a price of \$9.91 per gge, only a 7% increase. If the cost of the reference water electrolyzer were decreased by 50%, the levelized cost of synthetic fuel would be improved by only 3.7% (see Figure 3.) This relatively small change is because the capital cost of CO₂ electrolysis equipment is overshadowed by the capital cost of CO₂ capture equipment, FT capital costs, and operating costs including utilities and other feedstocks.

Similar sensitivity analysis is conducted as shown in Figure 3 for the capital costs of the CO₂ separation and capture equipment in the FFPP, CO₂/CO separation downstream of the CO₂ electrolyzer, and the FT equipment.

On the basis of the model results, as far as the capital cost of major components is concerned, the capital cost of CO₂ capture and separation in the FFPP is most significant, followed by FT equipment and then by CO₂ electrolysis. The model results are not excessively dependent on the assumptions of capital cost. FTL conversion yields and operating cost including H₂ and utility costs have higher influence over the model results.

3.2.1.2. Sensitivity of Energy Efficiency to Individual Key Variables. As shown in Figure 4, the system energy efficiency is fairly sensitive to the change in its cell voltage *V*. Reducing cell voltage can significantly improve the system energy efficiency. On the other hand, the system energy efficiency is not very sensitive to the change in CO₂ electrolyzer current density. This suggests that without dramatic compromise in current density, improving cell voltage is more important than improving current density for improving the overall system energy efficiency of this fuel production pathway.

FTL configuration significantly affects the system energy efficiency as well. Although there is a fixed amount of CO₂ coming from FFPL. With FTL recycling, the CO₂ from the combustion of the mixture coming out of the FT process needs

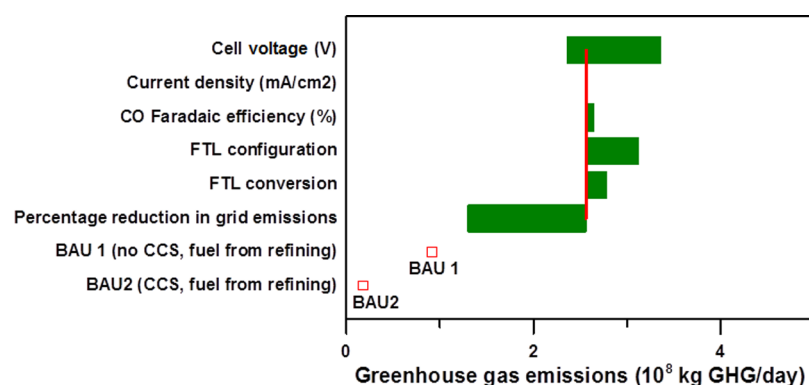


Figure 5. Sensitivity of WTG CO₂ emission to key parameters.

to be separated and sent back to the electrolyzer and the FT reactor for further processing. An appropriate amount of H₂ also needs to be produced to match with the recycled CO₂. These processes consume more electricity. However, more synthetic fuel is also produced. The higher efficiency associated with the “FTL recycle” case indicates the energy gains from additional fuel production outweigh the loss from energy consumed during the recycling process.

Significant reduction in grid electricity emissions represents a significant increase in renewables in this study, which leads to higher system energy efficiency. This needs to be treated with caution because the assumption is that the renewables are 100% energy efficient. In reality, factors such as the efficiency loss associated with manufacturing the equipment for harvesting renewables and the land use issues associated with renewables need to be taken into consideration. See sections 2.1.7 and 2.1.8 for a more detailed discussion on the treatment of renewables.

On the basis of the model results, as far as the system energy efficiency is concerned, future research can focus on improving the cell voltage for CO₂ electrolysis and FTL configuration to improve the overall system energy efficiency.

3.2.1.3. Sensitivity of WTG CO₂ Emission to Individual Key Variables. Reducing CO₂ emissions from the electricity grid has the most significant impact on the overall WTG CO₂ emission of the synthetic fuel system. This is apparent in Figure 5. When the grid electricity emissions are reduced from their current levels by approximately 90%, the synthetic fuel system achieves a WTG CO₂ emission rate that is 56% lower than that of the base case but still higher than the WTG CO₂ emission rate of the BAU1 and BAU2 cases.

The WTG CO₂ emission is fairly sensitive to the change in cell voltage *V* and is not very sensitive to the change in CO₂ electrolyzer current density. This suggests that, without dramatic compromise in current density, improving cell voltage is more important than improving current density for moving this technology closer to environmental viability.

The FTL configuration also largely affects the WTG CO₂ emission. Comparing Figures 3 and 5, FTL configurations have different effects on the cost and the WTG CO₂ emissions of the synthetic fuel system. This indicates a trade-off between multiple factors, and careful design of the FTL configuration is required to reduce the WTG CO₂ emission without significantly increasing the synthetic fuel cost.

3.2.2. Impact of Simultaneous Changes in Multiple Key Variables. As shown in Figure 5, changing one single variable has not been sufficient to bring the WTG CO₂ emission below

the current day scenarios represented by the BAU1 case. Two or more parameters can be simultaneously changed to gain insight into their combined impact on the system performance. With an 80% improvement in the CO₂ emission rate of the grid electricity as well as an 80% yield of fuel from the FT process, the WTG CO₂ emission of the system under study is approximately 35% lower than that of the BAU1 case, resulting in a decrease in the rate of CO₂ emissions from the current day scenario. However, the WTG CO₂ emissions in this case are still over 100% higher than that of the BAU2 case. If the improvement in electricity is 100% (means net zero CO₂ emission from grid electricity), emissions are reduced from the BAU1 case by 85% and are reduced almost 50% from the BAU2 case. This demonstrates the potential role electrochemical CO₂ conversion can play in CO₂ mitigation when the electricity grid is highly renewable or decarbonized with other carbon neutral resources.

More thought must be given to evaluating the usefulness of such results. If the electricity grid is greatly improved (80–90%) in terms of CO₂ emissions compared to the current state, will there be any need for CO₂ capture and utilization? The answer is possibly yes as fossil fuel power may remain a part of our energy system. First, it is widely believed that fossil power would be needed to meet our energy needs for decades to come at a varying percentage in our electricity mix. Major energy consumption countries would want to keep some percentage of coal or natural gas in the electricity mix at least for economic and energy security reasons. Second, electricity is not the only source of CO₂ emissions, petroleum refining and some other industry processes are also significant sources of CO₂ that we need to figure out a way to manage. Assuming our transportation and industry infrastructure still rely on at least some hydrocarbon-based liquid fuels, converting CO₂ to synthetic fuel could emit less CO₂ than the mining, transportation, and refining of petroleum products if the technology could reach the state of development represented by the optimistic case in this study.

The pathway in this study is not simply a conversion of coal to diesel. The idea is to convert CO₂ that already exists to diesel fuel using low or carbon free electricity. The CO₂ can be from coal, natural gas, or other industrial sources. The value added by this pathway includes (a) alternative fuel options alleviating our dependence on petroleum and enhanced energy security, (b) potential CO₂ emission reduction on a life cycle basis, and (c) domestically produced diesel fuel, which will benefit the national economy.

Overall, this study provides a framework for analyzing different CO₂ to synthetic fuel scenarios. The coal to synthetic fuel is just one such possible scenario. By no means do the authors think this is the way future should be. Other scenarios with CO₂ from other sources can be analyzed as well using the analytical tools developed in this study to determine which pathways make more sense.

Although any organization pursuing this technology as a business venture would demand a much higher degree of precision, the general trends deduced from this analysis should hold true and will be valuable in making broad conclusions from the results. These results also help guide where further research efforts should be focused.

4. CONCLUSIONS

An engineering and economic model framework was developed and applied to an integrated system that converts CO₂ released from fossil fuel-burning power plants to synthetic diesel fuel via electrochemical reduction of CO₂ to CO and the FT process, which uses CO and H₂ (from electrolysis) as feedstocks.

On the basis of the model results, with currently achievable performance levels for CO₂ electrolyzers, the FT process, and grid electricity carbon emission rates, the synthetic fuel system has higher production cost and WTG CO₂ emission than the case of using petroleum-based fuel. This indicates that the synthetic fuel system is not economically and environmentally competitive with using petroleum-based fuel with the current system performance.

With high FT fuel yield already reported in the literature and low carbon electricity, the synthetic fuel system could reduce its WTG CO₂ emission rate below that of the BAU1 case, which is the current case of using petroleum-based diesel fuel plus electricity from coal power plants without CCS. In the case of near net zero grid CO₂ emission rate, this system reduces WTG CO₂ rates even below the BAU2 case, which is the case of using petroleum-based diesel fuel plus electricity from coal power plants with CCS. It is worth noting that these scenarios for the synthetic fuel system rely heavily on dramatic improvement of key technologies simultaneously.

With the right combination of high FT fuel yield and low electricity and H₂ price, the synthetic fuel system could produce fuels at a cost range similar to the reference year 2014 petroleum-based fuel prices. With the cost of carbon emissions being appropriately included, this electricity to synthetic fuel pathway will be even more economically competitive. This has important implications for energy security because the CO₂-based synthetic fuel can be domestically produced with low carbon electricity. The potential WTG CO₂ emission reduction with low carbon grid electricity indicates the potential role electrochemical CO₂ conversion can play in low carbon liquid fuel when the electricity grid is highly renewable or decarbonized.

From an electrolysis perspective, assuming low compromise in current density, reducing cell voltage will yield the most beneficial improvements in this technology. The levelized cost of fuel is more sensitive to the change in cell voltage than the change in current density. Additionally, reductions in cell voltage also result in improved efficiency and reduced WTG CO₂ emissions.

The analytical tools and case studies developed in this study provide important insight into understanding the economic and environmental performance of the synthetic fuel system using low carbon electricity as energy input. The tools are useful for

identifying key areas for improvement in the synthetic fuel system as well. Although not in the scope of this study, the analytical tools could be easily adapted to evaluate other CO₂ utilization processes in consistent economic and environmental terms and provide insight that would otherwise not be obtained. One example of other CO₂ utilization processes is to reduce the CO₂ directly to methanol or hydrocarbon fuels such as natural gas with comparable energy and Faraday efficiency.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.energyfuels.6b00665.

Key input and out values of the model (PDF)

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The authors declare no competing financial interest.

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