Electrochemical Conversion of Carbon Dioxide to Hydrocarbon Fuels

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Contents

Introduction

The electrochemical pathway for the production of energy dense hydrocarbons from renewable electricity, water and captured CO_2 has been proposed as a means of producing fuels from renewable electricity sources while sequestering CO_2 at the same time [A1, A2, A3]. However, few studies have investigated the feasibility of this technology, and none have been found to provide an in-depth analysis of its industrial implementation. The purpose of this study is to analyze the feasibility of applying the technology with respect to three major issues: the production of hydrocarbon fuels, the storage of excess renewable or grid electricity, and the sequestration or reduction of CO_2 emissions. The first section of this report introduces the technological aspects of the CO_2 electrochemical cell, which in many ways is similar to a water electrolysis cell but has the ability to create a potentially more useful fuel than hydrogen. Second, many aspects as to how this system can be integrated into future energy systems are introduced, such as working alongside renewable electricity production to store electrical energy when in excess or off-peak to form syn-gas, which can be a precursor to many other liquid fuels or to generate a light chain hydrocarbon such as methanol. Next, a few pathways for conversion of syn-gas are investigated for producing long-chain hydrocarbons such as Fischer-Tropsch diesel is discussed. The CO_2 and energy balance is examined to estimate how many CO_2 credits can be obtained, and to what degree this technology compares with existing renewable energy systems. Lastly, the economic factors are investigated, such as how much renewable electricity will cost, where CO_2 will be captured and at what cost, and at what expected value the final products can be sold.

Chemical energy carriers are the most effective transportation fuels, as depicted by the United States transportation sector being dependent upon petroleum for 93% of the total fuel used for transportation in 2007 [A4]. Electrolytic hydrocarbons have the ability to reduce emissions from the transportation sector by displacing fossil derived energy while providing the ability to reduce petroleum imports. The viability of this technology could be great in that it could easily be implemented into the current hydrocarbon infrastructure in comparison to its water-electrolysis counterpart. It is also apparent that renewable energy systems will not be able to support base-load power generation for time to come, thus there will be an ample supply of CO_2 emissions that can be captured. This premise is exemplified by current U.S. electric power generation which is 48% coal powered, 21% natural gas powered, 20% nuclear and the last 11% is made up through renewable and other sources [A4].

Novel Solution to the Energy and Climate Challenge

The concept overview shown in Figure 1 assists in placing the various parts of the novel fuel supply into perspective. The renewable electricity source would come from off-peak hours on an electrical grid when renewable electricity cannot be readily consumed. Waste CO_2, most likely from a coal power plant or gasification plant, is piped to the plant. The only other precursor to the reaction is water which is directly fed into the electrolysis cell.

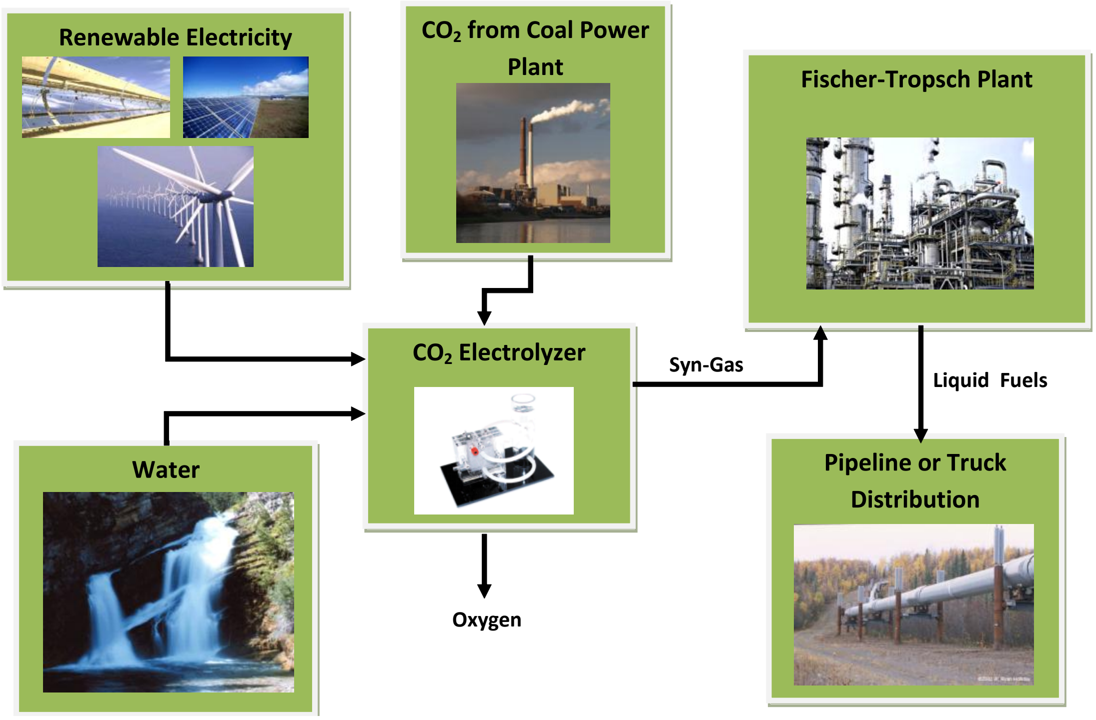


Figure 1: Concept map for proposed system

Regulations and subsidies for CO_2 reduction and renewable energy

Under the influence of the Intergovernmental Panel on Climate Change (IPCC) and successive Conference of Parties (COP) the world-scale challenge of global warming has been examined since 1988. Even though COP15 at Copenhagen could not reach an effective agreement with all the nations present, each region, such as the European Union (EU) and the Association of Southeast Asian Nations (ASEAN), has started their own actions over climate change problems, including the EU Emission Trading System (EU ETS) and ASEAN-EU Programme for Regional Integration Support (APRIS) [A5,A6]. Although the U.S. has not signed on to this protocol in the United Nations, carbon emission trading similar to EU ETS may be started in the near future. When the carbon emission trading starts, the CO_2 reduction technology will become indispensable and the technologies to reduce or consume CO_2 will have a certain value.

At the same time, there are many efforts to propagate renewable energy sources. Many states have decided their goals for a renewable energy ratio in total energy generation and phases to meet these goals [A7]. For example, Pennsylvania set their renewable ratio goal as 18 % by 2020. These policies are called Renewable Portfolio Standards (RPSs) or Alternative Portfolio Standards (APSs). To achieve these goals the Environmental Protection Agency (EPA) of the U.S. government introduced a system to enhance renewable energy using Renewable Energy Certificates (RECs) [A8]. This issues one REC for every 1000 kWh of renewable power to the electricity generators, and this REC can be traded. The REC shows that a company or organization obtained a certain amount of renewable energy through its tracking system. It can be sold via a voluntary trading market or to states that want to buy RECs to meet their goals, RPSs or APSs. The EPA also regulates emissions and wastes, including CO_2 emissions. Currently, suppliers of petroleum, natural gas, and industrial gases, as well as vehicle and engine manufacturers, have the obligation to report their green house gas emissions if they go over 25,000 metric tons [A9]. The penalty for this is not mentioned clearly in the EPA regulatory plan on fall 2009, but it may be clarified soon.

To satisfy these regulations, the CO_2 reduction process could help conventional plants, especially ones without CO_2 capturing equipment, if we use electricity from CO_2 free, or at least CO_2 neutral, power sources. Thus, we will examine renewable energy sources and conventional power plants with CO_2 capturing below.

Greenhouse Gas Emission Stabilization Strategy

The transportation sector is the second largest source of human induced CO_2 emissions in the U.S., which is due to the burning of petroleum derived fossil fuels amounting to approximately 1,800 teragrams CO_2 Eq. [A10]. While human induced CO_2 emissions (approx. 26.4 Gt) are not a significant amount of CO_2 in relation to the natural carbon cycle of Earth (approx. 440 Gt), the fact that these emissions have no new carbon sink causes the build-up of GHG emissions in the atmosphere [A11]. In result, slightly more CO_2 is being built up in the atmosphere each year which potentially has detrimental consequences to the global climate system.

EIA conclusions estimate that carbon needs to be taxed at about \$80/ton CO_2 to have a realistic chance at achieving 50% reductions in emissions by 2050. Since current market forces for CO_2 sequestration are technically and economically unfeasible, another CO_2 stabilization strategy may be necessary. It is important to appreciate that the sequestration of CO_2 from coal power plants is not the only possible route toward the required CO_2 reductions goals, as eliminating the carbon contributions from the petroleum sector would achieve even a greater reduction in CO_2 emissions, being over 60%. The potentially viable method of CO_2 electrolysis to hydrocarbons could utilize waste CO_2 from coal power plants to produce liquid transport fuels to off-set petroleum consumption, thus mitigating CO_2 emissions from the transportation sector.

Process Overview

The process proposed here produces hydrocarbons or syn-gas through the electrochemical reduction of CO_2. The cell consists of two sections, the anode and the cathode. Water is fed into the anode, where it is split into O_2 gas and hydrogen ions. The balanced anodic reaction is

$$H_2O(l) \rightarrow 0.5O_{2(g)} + \ 2H^+(aq) + \ 2e^-$$

The ions are transported by solution through the membrane and into the cathode. These ions then react with the CO_2 gas which is fed into the cathode, generally producing water and some form of reduced carbon product. A variety of products can be produced, though few experiments have produced notable amounts of species longer than one or two carbons in length. The most common reduction products have been carbon monoxide, methane, ethylene, methanol, and formic acid. Hydrogen can also be produced, though it is not desired in this situation as will be explained below. The typical cathodic reactions are listed here.

$$CO_2(g) + 2H^+(aq) + 2e^- \rightarrow CO(g) + H_2O(l)$$
$$CO_2(g) + 8H^+(aq) + 8e^- \rightarrow CH_4(g) + 2H_2O(l)$$
$$2CO_2(g) + 12H^+(aq) + 12e^- \rightarrow C_2H_4(g) + 4H_2O(l)$$
$$2CO_2(g) + 6H^+(aq) + 6e^- \rightarrow CH_3OH(l) + H_2O(l)$$
$$CO_2(g) + 2H^+(aq) + 2e^- \rightarrow HCOOH(aq)$$
$$2H^+ + 2e^- \rightarrow H_2(g)$$

Current Status

The current stage of the technology is still very experimental. The majority of tests have been performed on a laboratory scale with a purpose of either kinetic analysis or proof-of-concept to examine product distribution for different material and condition combinations [A1, A2, A3]. An advantage of electrochemical CO_2 reduction is that unlike many other hydrocarbon processes it can easily be performed at ambient conditions. However, being at the experimental level there is still considerable work to be done to bring the process up to a commercial level. Typical current densities have been on the order of milliamps per square centimeter (mA/cm^2) of electrode and catalyst surface, whereas industrial water electrolyzers operate at up to 2 A/cm^2 [A12]. This current state can be improved as it has been for water electrolysis by improved cell design and electrode configuration. However, this still has yet to be demonstrated in literature. For this analysis it has been assumed that the reduction cell can operate at the same level as typical water electrolyzers.

Cell Layout

The physical makeup of the electrochemical would be very similar to existing alkaline and proton exchange membrane (PEM) water electrolysis cells used for the production of hydrogen gas. Alkaline electrolysis uses a basic electrolyte solution in both the anode and cathode. Oxygen gas is produced at the anode, and hydroxide ions pass through the membrane into the cathode, where the ions combine to form hydrogen gas and water. The membrane is usually a porous inert material that allows the passage of electrolyte, but not the gaseous products. In a PEM electrolyzer the membrane is a proton conductor, where hydrogen ions are formed in the anode and combine to form hydrogen gas at the cathode. In this case the electrolyte is generally pure water. Membranes that conduct negatively charged ions also exist, though there are very few commercial products with performance on par with existing PEM technology.

The anode electrolyte and electrode would mimic those already in use for water electrolysis. For the cathode the electrode and electrolyte compositions vary depending on the desired products. We have chosen to focus on production of methanol, methane, and syngas as our primary fuels. These can readily be utilized in the existing fuel infrastructure, assuming the syn-gas has been processed into a fuel such as diesel. The operating conditions have been chosen based on some of the most promising results that were found out the literature investigated and can be seen in the table below. It should be noted that the total efficiencies tend to fall less than 100%. This generally occurred for two reasons. The first was due to resistive losses in the cell, where the electricity was dissipated as heat. The second reason was that many experiments only analyzed select products, meaning that certain products were left unaccounted. Methane production was based off results from Kanaco et al., where copper was used for the cathode electrode catalyst and LiI in methanol for the electrolyte [A13]. Syn-gas production was modeled based on Yamamoto et al. using a carbon fiber/Ni gas diffusion electrode (GDE), where no liquid electrolyte was present in the cathode [A14]. Two different results were modeled for methanol production, both using an aqueous $KHCO_3$ electrolyte solution. Bandi et al. [A15] obtained results at a larger current density using Ru/Ti oxides for the catalyst, while Kobayashi et al. [A16] obtained a much higher efficiency using a Cu/Zn/Al alloy, though at considerably lower current densities. The majority of these catalyst materials would be cheaper than the noble metals, such as Pt, found in PEM electrolyzers, and would be about as expensive as the more common metals, such as Ni, used in alkaline electrolysis.

Table 1: Modeled conditions for CO_2 electrolysis. *a* = product not listed in literature;
* = value estimated from similar literature

Fuel	**Cell Potential**	**Current Density**	**Product Selectivity**					
			Methane	Ethylene	Methanol	Formic Acid	CO	H2
Methane	4.95 V	0.0655 A/cm^2	65.50%	9%	*a*	*a*	14.90%	<1%
Methanol 1	2.85 V	0.005 A/cm^2	*a*	*a*	29.80%	4.20%	*a*	50% *
Methanol 2	1.85 V	0.00025 A/cm^2	*a*	*a*	90%	*a*	*a*	*5% **
Syn-gas ($2 H_2$:1 CO)	2.5 V	0.1 A/cm^2	0%	0%	0%	0%	33.33%	66.67%

It is important to note the cell potentials listed in the table above. They range between 1.85 V to 4.95 V, compared to the 1.6 V to 2.2 V often used in water electrolysis [A12]. The potential is higher for three typical reasons. First, all of the processes listed above still require the electrolysis of water to occur in parallel to CO_2 reduction. Second, additional power must then be consumed to drive the resulting reduction. Finally, the cells used were generally of an inefficient design. Efficient industrial cells are designed to minimize the spacing between the electrodes and membrane as much as possible. Increased spacing results in more current having to pass through the solution, which has a higher resistance that the electrical circuit. This results in the need to apply a much larger potential, which in turn increases the energy required. Since hydrogen can be produced more efficiently in a standard water electrolysis cell it is viewed as an undesired byproduct here, as it increases the power consumption of the cell.

A basic schematic of the likely system is shown in the figure below. The feed streams would consist of CO_2, water, and electricity. For this analysis the CO_2 would likely be captured at a coal fired power plant operating under sequestration and purchased as feed. While this could provide a cheap source of reactant, the stream would probably contain trace amounts of NO_x and SO_x. The NO_x could lead to acidic conditions in the cell, changing the reaction conditions and possibly increasing the material corrosion of the cell. Presence of SO_x would be more detrimental to operation, as it is a well-known catalyst poison. For these reasons the CO_2 feed would likely have to be filtered and the contaminants removed. This would further increase the capital and energy costs of the system, though it is not included in this analysis. The water feed could be standard industrial water. This would need to be filtered, but since it is standard procedure for electrolysis cells it should not increase the system costs. Since most of the systems require an aqueous electrolyte a management system would need to be in place to control the pH and conductivity of the solution. This provides an issue, as this is common in alkaline electrolysis but not in PEM electrolysis. For a PEM cell the advantage is that the more expensive membrane material usually reduces the need for an electrolyte solution, removing the need for the additional processing equipment found in alkaline cells. Since our cell would likely require both this would further increase the capital and operating costs of the system.

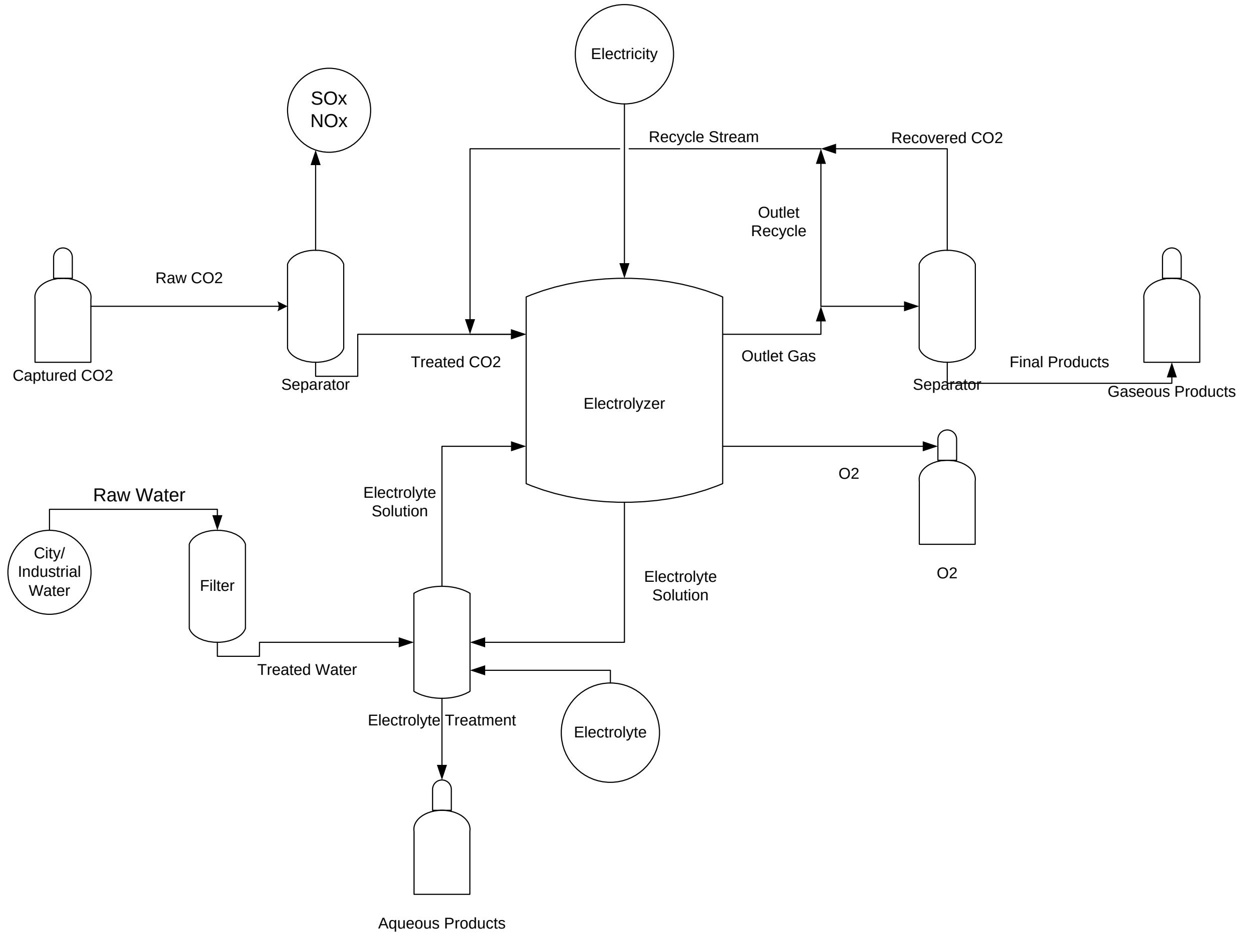


Figure 2: Schematic of proposed electrochemical system

Auxiliary Processes

Upon exiting the cell the products would need to be separated and stored. Pure oxygen is the only product at the anode, and it can simply be compressed and stored for sale. The cathodic products would be a more complicated issue. It is very unlikely that all of the CO_2 would fed into the cathode would be reacted. In order to reduce the load on the final product separation a recycle feed would likely be implemented. In most systems any products more reduced than CO_2 or CO have been found to be inert and unreactive in the cell. The resulting gaseous products would still require removal of the remaining CO_2, followed by further separation of the product mixture. It should be noted, however, that syn-gas productions only gives CO and H_2, meaning that no separation would be necessary. Aqueous products, such as methanol and formic acid, would be even more difficult to remove. Since they would be present in the electrolyte additional processing would be required for their recovery. In the case of methanol, this separation is usually done through distillation. It should be noted that currently the resulting methanol concentrations have been found to be on the order of 10 mM, or around 0.0014% by volume

[A17]. A quick calculation shows that a concentration on the order of 100 mM, or around 0.016% by volume, would be required just to recover the energy required to run the distillation. This again demonstrates the physical hurdles present before potential commercialization of this process. The additional separation is not common in water electrolysis, and would further increase the system costs. In order to provide a simplified and best-case scenario for this analysis the additional capital and energy costs of separation have been neglected here, but should be considered when examining the final results.

Product Refining

Basic F-T Chemistry

Carbon monoxide and hydrogen exothermically react on the surface of appropriate catalyst at varying high temperatures to form various liquid fuels which is coined the Fischer-Tropsch (F-T) reaction (Reaction 1). The products can include alkanes, alkenes, alcohols, methane and potentially many others useful chemicals. The products are a function of the operating conditions such as H2/CO/CO_2 ratio, temperature, pressure and residence time, catalyst utilized. The F-T product is always a mixture of many different hydrocarbons, which may or may not need further upgrading to achieve adequate purity for use in modern engines.

$8\ CO + 17\ H_2 \rightarrow C_8H_{18} + 8H_2O$ (Delta H = -1282 kJ/mol) (Reaction 1)

While Iron (Fe) catalysts are less expensive, While several types of catalyst can be used, in order to produce a relatively pure diesel fuel with high conversion, Cobalt based catalysts are desired to maximize diesel fuel. This is because Co based catalyst are more reactive for hydrogenation to produce straight chain aliphatic hydrocarbons instead of unsaturated hydrocarbons which are found in the product stream of Iron based catalyst. Fe catalysts also promote the water gas shift (WGS) reaction (Reaction 2). The WGS reaction is not desired for the CO_2 electrochemical process since the desired syn-gas ratio was already optimized for diesel fuel production, which is 2.13:1 H2:CO. [A18]

$CO + H_2O \rightarrow CO_2 + H_2$ (Delta H = -38.9 kJ/mol)

F-T Parameters for Maximum Diesel Fuel Production

In order to maximize diesel fuel production, the Anderson-Schulz-Flory (ASF) distribution is maximized to obtain the largest chain length hydrocarbons as seen in equation 1. The selectivity for long chain alkanes is then determined through ASF which is shown in Figure XX by the optimization of the reaction conditions.

$C_n = \alpha^{n-1}(1-\alpha)$ (Equation 1)

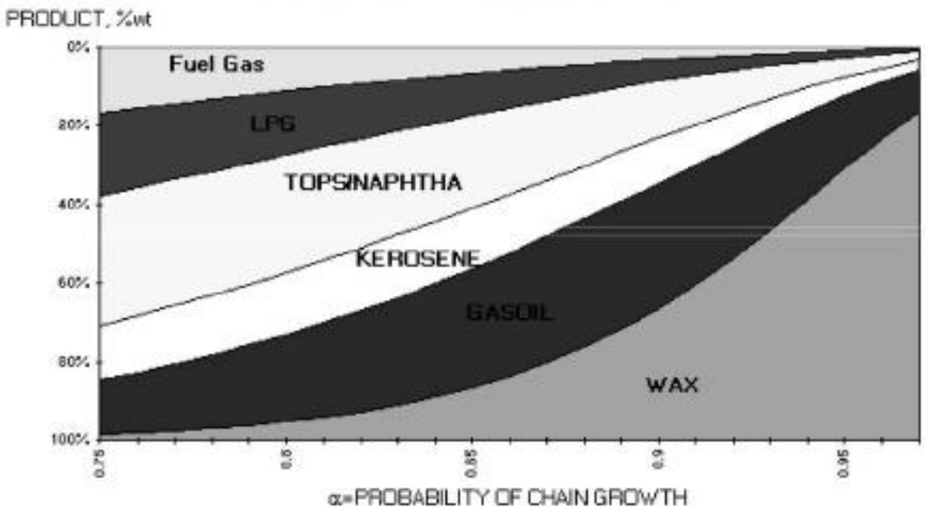


Figure 3: Heavy Paraffin Product Distribution [R28]

For direct production of diesel fuel, low temperatures and pressures are desired for the processing conditions, as shown below in Table 2 [R3].

Table 2: F-T diesel operating conditions

Parameter	**Low-Temperature F-T**
Temperature (^{o}C)	220-250
Pressure (bar)	25-60
CO+H_2 Conversion (%)	60-93
Chain Growth Probability	0.8
S_{C5+}	78%

Biomass to Liquids Comparison

While biomass to liquids could be a major source of energy in the future, there are currently many technological problems associated with the induction of this technology. Since biomass is inherently less energy dense, the biosyngas plant must be constructed near biomass plantations or close to ports and waterways to alleviate the transportation of the biomass. Moreover, biomass has many pretreatment steps that are not well developed such as milling biomass to small particles in an energy efficient manner so that biomass particles do not plug feeding lines. Some technologies such as torrefaction or pyrolysis are being investigated to alleviate these problems [A20]. While coal gasification is a well developed technology, biomass has many inherent differences than coal such as a higher reactivity which allows the gasifer to operate at a lower temperature. The main issue with biomass derived syn-gas is the gas clean up steps, which is causes by different ash and slag behavior and tar formations which go downstream of the gasifier[A21]. There are also many other impurities that need to be addressed which are shown in the Table 3 below [A22].

Since the syn-gas derived from the electrochemical process will of high enough quality to enter the F-T catalyst reactor without cleaning, this pathway shows many benefits over the traditional biomass to liquids process. Furthermore, instead of transporting biomass over large distances to a centralized BtL facility, electricity will be transferred instead. The following pathways show how electrochemical derived syn-gas can be converted into a liquid fuel, such as F-T Diesel or methanol.

Table 3: Syn-gas Purity Constraints for Catalytic Conversion to Liquid Fuel

Catalytic Reactor	**Methanol**	**Fischer-Tropsch**
Catalyst	Cu/ZnO/Al_2O_3	Fe/CO
Poisons:		
Ash/dust	<0 ppm	0 ppb
Tars	< dew point	0 mg/Nm$^{\wedge 3}$
S (H2S + COS)	<1 ppmV	<10 ppb
N (HCN – NH_3)	< 1ppmV	<20 ppb
Alkalines	<10 ppb	< 10 ppb
Halogens (HCL + HF)	< 10 ppb	< 10 ppb

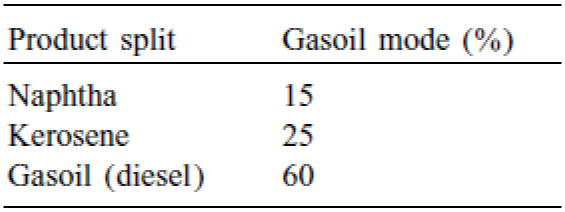
The typical cleansing techniques utilize sorbents, scrubbers, filters and reforming catalysts. The biomass gasification industry is attempting to move away from traditional scrubbing to filters, sorbents and reforming catalysts to alleviate operating costs and waste streams [A23].

Outputs

Diesel Fuel

With the F-T conditions prescribed in the previous section, the syn-gas can yield the following distributions of fuel in a single pass. Diesel was chosen to be maximized to increase the efficiency of the end-use of the renewable fuel.

Table 4: Product Distribution for Maximum Diesel Production [R28]



Product split	Gasoil mode (%)
Naphtha	15
Kerosene	25
Gasoil (diesel)	60

Diesel engines average a 33% efficiency increase over gasoline engines, which would correspond to 26.6 mpg instead of 20 mpg SUV. Furthermore, the modern light-duty diesel vehicle averages 39 mpg. Recently there have been many stringent regulations of diesel engines which made auto manufactures enhance the emissions of diesel engines. These works have allowed for the emissions to be even better than gasoline engines in terms of GHG emissions. The recent innovations include diesel particulate filters and NO_x removal traps in many new diesel engines. It is also important to realize that F-T diesel will see an 8% decrease in energy density over petroleum diesel. This fact is accounted for in the following life-cycle GHG emissions analysis.

Grid Integration of Renewable Electricity

The following section discusses the key issues that arise when utility grids continue to add more renewable energy.

California 2010 and 2020 Goals: A Case Study

California has the most extensive renewable energy implementation in the US which is due to state incentives to reach their renewable portfolio standard. California's grid integration for renewable energy could be the country's gold standard in terms of a first-of-a-kind methodology. Furthermore, California has a great potential for renewable energy due to their abundant natural resources. Thus if renewable energy integration does not work in California, it may look even more bleak in other states.

As shown in Figure 4 below, natural gas is the main source of electricity at 45.2% of the total 306.5 GW-h in 2008. The ability of natural gas ramping adds extra flexibility for integration of intermittent renewable energy sources. California has also tapped out its existing large hydropower facilities which accounts for 11% of total system power. [A24]

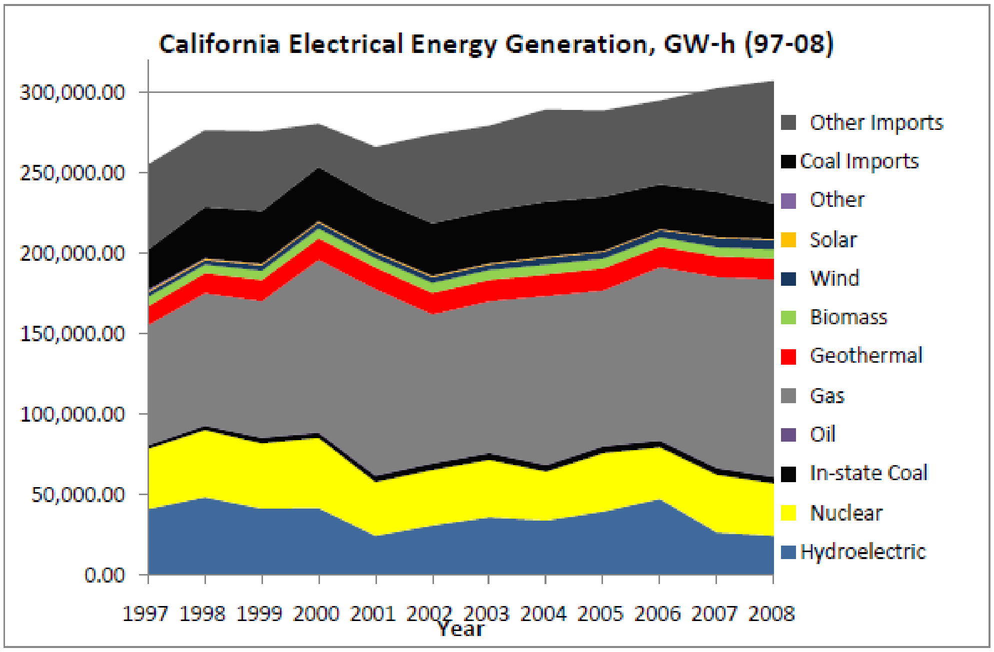


Figure 4: California's Electrical Energy Generation [A24]

Through incentives, California achieved their 2010 goal of providing 20% of their total electrical energy through renewable resources. Figure 5 below depicts the breakdown of the contributions for different forms of renewable energy.

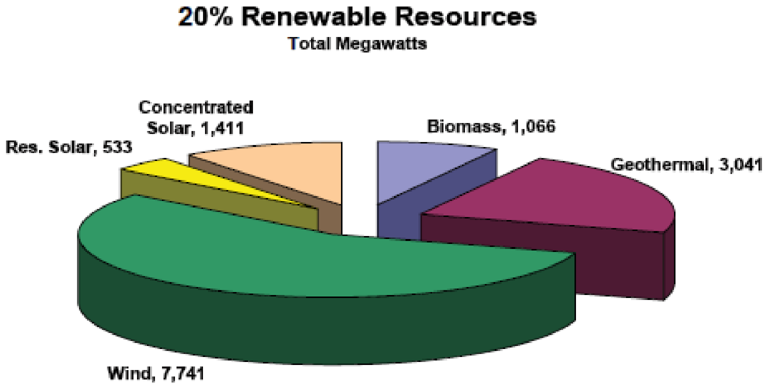


Figure 5: California 2010 RPS [A25]

The California Independent Service Operator (CAISO) released a report in 2007 which depicted the issues that needed to be addressed for the grid integration of the varying energy sources[A25]. It was found that the 2010 variability of wind and solar generated energy production is usually less than the variability in system load changes. Thus, with their current system design they did not have many issues with ramping production in relation to consumption.

California's 2020 goal is still on schedule to be reached, with many wind projects being planned throughout the state. While wind energy is expected to increase from 7.7 to 12.8 GW, the photovoltaic contribution is expected to be the hardest to reach. This is due to only 533 MW being currently on-line while 3,000 MW will be required[A25]. The renewable contribution for the 2020 33% RPS is shown below in Figure 6.

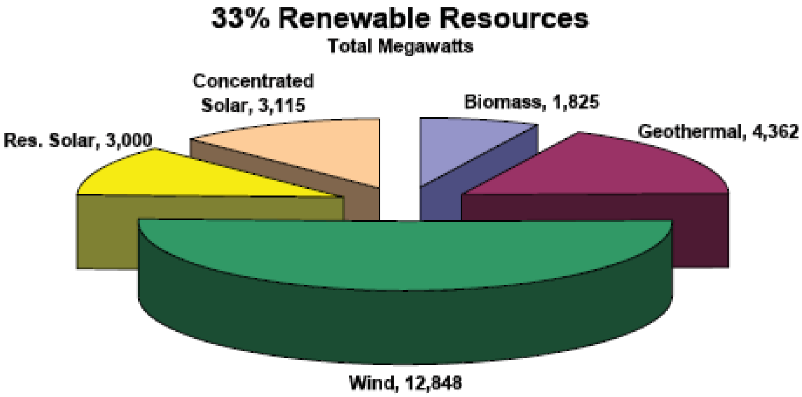


Figure 6: 33% California RPS[A25]

While CAISO has not released a report for the 2020 RPS integration, many key issues were discussed since some instability issues were expected with the 2010 RPS. Overall, the outlook for the 2020 goal of 33% renewable power production showed many signs of grid instability due to a much larger contribution of intermittent wind and solar energy. The instability of the grid increases non-linearly because of the capacity factor of wind and solar energy. Thus, it is expected that moving from the 20% RPS to the 33% RPS could more than double integration problems and costs[A25].

Renewable Electricity

Most life on earth was created by the constant supply of dispersed energy from the sun. Consequently, most types of energy that humans take advantage of today was originated by the trapping of solar energy through primary producers, and over millions of years it has become conveniently energy dense. At this time in the hydrocarbon age, it is of essence to move away from these conventional forms of carbon based energy resources to lessen our impact on the environment and adhere to the suns never-ending potential. The sun's diffuse energy can be captured through many natural forms such as wind, biomass, waves, and hydropower. Alternately, the sun's power can be utilized directly as heat or through the photoelectric effect, and subsequently transformed into a more practical and desired form of energy, electricity.

Renewable energy technology has a great advantage in that the energy source is free or can be recycled. Once the facility is constructed it does not need any input cost except maintenance, or for the case of biomass which needs to gather or grow biomass. If we have a high efficiency and enough electricity comparable to a conventional power plant, we could get stable energy sources and deal with global warming. Taking these factors into account, we can assume a "Levelised cost of energy (LCOE)" of each power plant. Making this LCOE more competitive to other conventional power generation systems needs more research to increase the efficiency and lower the capital cost. Here we show the reference LCOE values of renewables in Figure 7.

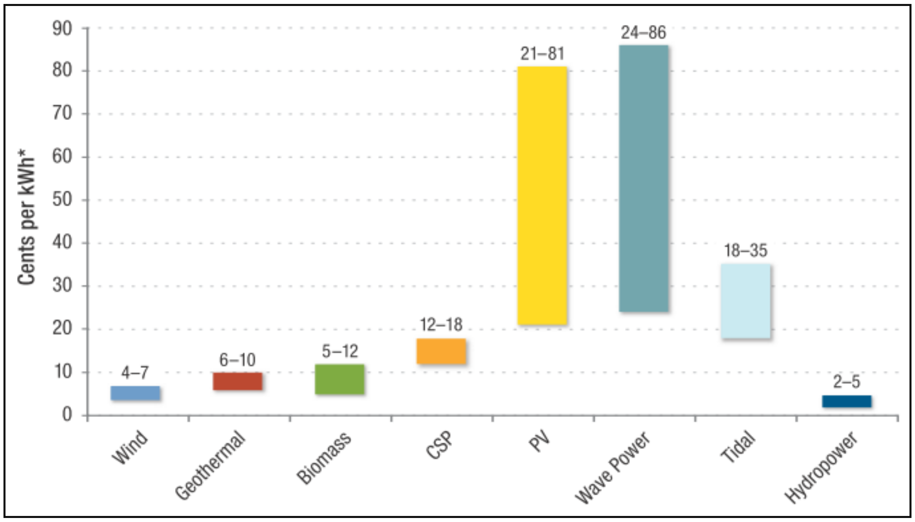


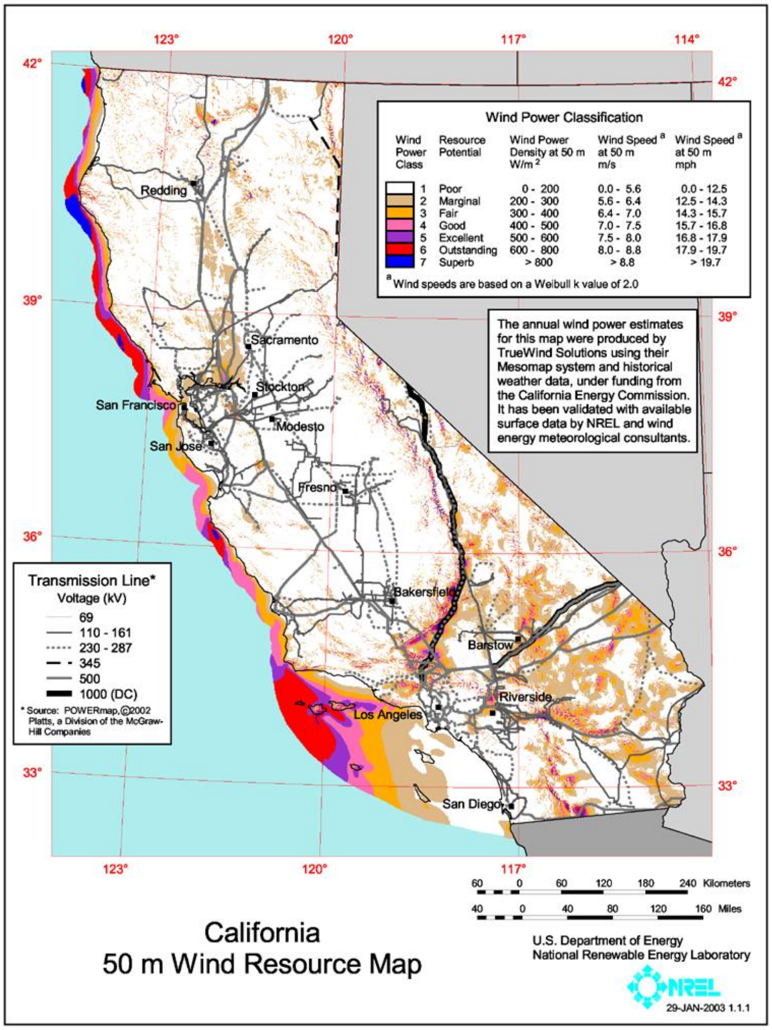
Figure 7: Leverised cost of renewable energy [A26]

In Figure 7, we see that the photovoltaic (PV) power generation and the wave power have a broad range of costs compared to others. In this report, we take wind, concentrating solar power (CSP), and PV as our electricity sources.

Wind

Wind energy, the world's fastest growing renewable source of electric power, has been proven to be a pertinent short term goal for our industrialized society [A27]. California's renewable energy initiative has regarded wind energy as a must. In 2007, wind energy farms in California accounted for 6.8 GWh of electricity, providing 2.3% of the state's total electricity demand[A27]. Projected research breakthroughs and reduced turbine production, construction and operation and maintenance costs can reduce the cost of wind power to 3.5 cents per kWh[A27]. Alongside federal government incentives and California's Existing Renewable Program, wind power technology has become commercially desirable under multiple situations.

California as a whole has a great potential for wind power projects, especially due to the prevailing winds from the ocean. Much of the on-shore wind is located in the southeastern portion of the state along ridgelines. The figure below from the US DOE shows that the mountains east of San Diego become much higher in magnitude through the mountainous region, ranging from class 1 (poor) to class 6 (outstanding) at 50 meters in height .The wind speed at 100m is greater than 7.5 m/s over approximately 60 meters of ridgeline.[A28] This corresponds to a wind class rating of 5 (excellent).



Wind Power Classification

Wind Power Class	Resource Potential	Wind Power Density at 50 m W/m ^{2}	Wind Speed [a] at 50 m m/s	Wind Speed [a] at 50 m mph
1	Poor	0 - 200	0.0 - 5.6	0.0 - 12.5
2	Marginal	200 - 300	5.6 - 6.4	12.5 - 14.3
3	Fair	300 - 400	6.4 - 7.0	14.3 - 15.7
4	Good	400 - 500	7.0 - 7.5	15.7 - 16.8
5	Excellent	500 - 600	7.5 - 8.0	16.8 - 17.9
6	Outstanding	600 - 800	8.0 - 8.8	17.9 - 19.7
7	Superb	> 800	> 8.8	> 19.7

[a] Wind speeds are based on a Weibull k value of 2.0

The annual wind power estimates for this map were produced by TrueWind Solutions using their Mesomap system and historical weather data, under funding from the California Energy Commission. It has been validated with available surface data by NREL and wind energy meteorological consultants.

Transmission Line*
Voltage (kV)
69
110 - 161
230 - 287
345
500
1000 (DC)

* Source: POWERmap, ©2002 Platts, a Division of the McGraw-Hill Companies

Figure 8: California wind resource map

Concentrated Solar Power

The southwestern United States and many other parts of the globe located in the "sun-belt" possess a large, untapped solar energy resource. The southwestern United States alone could support Concentrated Solar Power (CSP) plants totaling several thousand GW [A29]. The following figure shows the yearly direct normal insolation available in the United State which shows why CSP has only been developed in the southwestern United States.

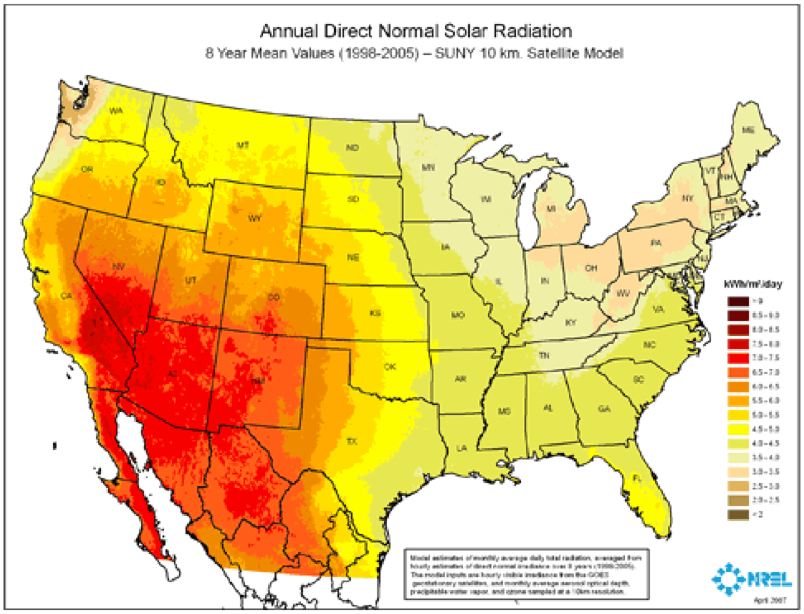


Figure 9: Incident Solar Radiation in the United States

High direct solar insolation is a necessity for parabolic trough power plants because it drives the economics of this technology. An analysis done by the NREL identified the pristine areas that are eligible for CSP technologies in the USA. Their assessment was a function of having high solar insolation, level land, land type, environmental sensitivity and in proximity to energy demand. The following figure of the southwestern United States depicts these areas that could total to 200GW of power production, assuming a need for 5 acres/MW. This is equivalent to approximately 17% of the total U.S. current electricity consumption[A30].

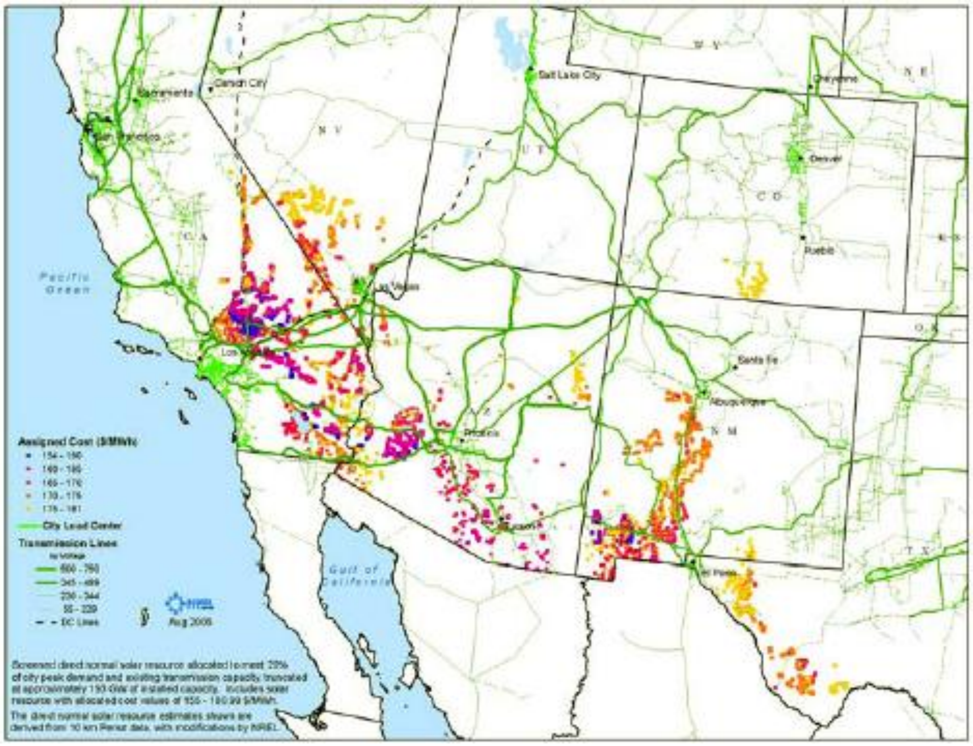


Figure 10: Eligible Areas for CSP in Southwestern United States

Grid Stabilization

Coupling energy storage technologies with solar and wind power resources can solve many of the operational issues such as renewable energy's non-coincident peak, it's non-dipatchability and the stability of the power supplied due to their inherent fluctuating nature [A31, A32]. Due to the large integration of renewable technologies into California's grid, short and fast start facilities will need to increase the 3-hour morning ramp by another 1 GW, increasing the morning 3-hr ramp to 8.49 GW and the evening 3-hr ramp to 9.8 GW for the 20% renewable integration goal [A25]. It is then expected that the ramp will also increase significantly for the 33% integration goal, for approximately another 1-3 GW. The main reason ramping is increased due to renewable energy is shown below in Figure 11, where load drops off as wind energy begins to pick up.

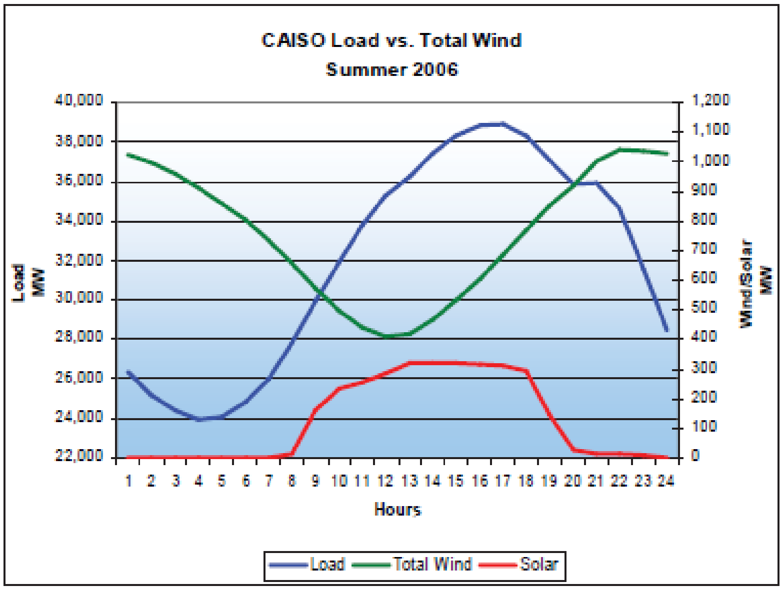


Figure 11: Grid Loading Alongside Renewable Energy Sources [A25]

To further depict the contrast of peak wind power not matching peak energy demand, Figure 12 below shows wind energy production over a span of time and red dots show when the grid needs energy the most. It is concluded that integrating 20% renewable is achievable alongside high efficiency wind forecasting, but with the 33% goal, energy storage technologies must be employed.

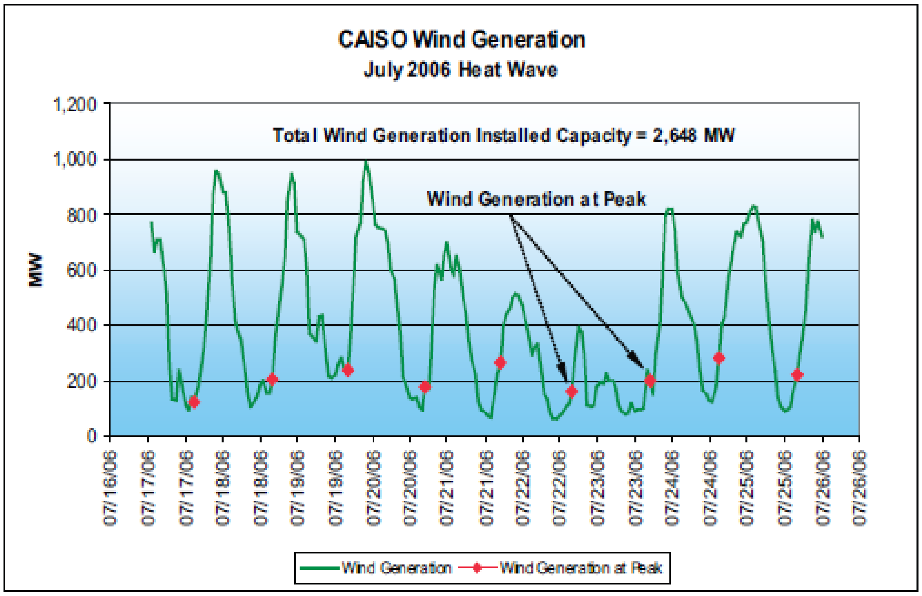


Figure 12: Wind Energy Peak Matching [A25]

Dispatchability

Dispatchable power is a block of power that can be transmitted in a reliable and controlled fashion. For many wind power sites, up two 67% of the total wind power resource is outside of the peak demand period (9AM-5PM) since most wind power is available in the morning and evening [A33].The mismatch of renewable energy resources to power demand significantly impacts profitability since wholesale electric power prices vary throughout the day.

Capacity Factor

Renewable energy such as wind and solar is intermittent (timing, intensity variability), wind and solar has an average utilization capacity factor of 20-37% of the nameplate capacity, thus for every 100 MW of installed capacity only 30 MW will be achieved yearly. Therefore, to increase the amount of energy available from renewable energy sources from 20% to 33% requires approximately a doubling of the installed capacity. The electricity grid system stability can be compromised when wind resource penetration reaches approximately 15% of an area's supply [A33]. In comparison, other renewable technologies have high capacity factors such as biomass and geothermal resources, with capacity factors of 89% and 90%, respectively.

Over-generation

One of the concerns of CAISO grid operators is that intermittent renewable energy (especially wind) can ramp unexpectedly causing an imbalance between load and generation. The conditions for over-generation are usually seen in the spring with light load conditions, all nuclear plants are on-line at maximum production, hydro generation is at maximum capacity due to rapid snow melt, and long-start thermal generation units are on-line to get ready for future hours. While little excess energy available in 2010 scenario (500 MW for 100 hours/year), this problem will be exaburated with the 2020 RPS goal. The CAISO will need to take action by sending dispatch notices to wind generation facilities for their operators to reduce generation at wind facilities by taking turbines off-line. In turn, a potentially large portion of renewable energy could go unutilized which decreases the revenue of the wind farm investment. The CO_2 electrochemical process would allow for a guaranteed revenue stream with or without the introduction of energy storage mechanisms to the California energy grid.

Energy Storage Mechanisms

Electricity is the highest quality energy carrier, but one of the most troublesome aspects of the electric power industry is that electricity must be produced when it is needed and used once it is produced. Furthermore, electricity may not play a major role in transportation due to the high cost and low energy density of batteries. With the overarching goals of U.S. energy policy makers to increase the use of domestic renewable energy, energy storage options must be considered for various reasons. Energy storage mechanisms can also mitigate over-generation of electricity when generation is high and demand is low. Many proponents of renewable energy do not realize that energy storage is key for making raw, intermittent renewable power technically feasible. Energy storage is seen to the grid operator as a load, as there are efficiency losses for storing and dispatching this energy. The high capital cost of energy storage technologies is a hidden cost of renewable energy and needs to be addressed when states decide to integrate large fractions of renewable power into the grid.

Some of the main requirements of energy storage include the rapid access, versatility, high cycle efficiency and economic feasibility. For the storage of high- energy sources (i.e. electrical or mechanical energy) either a high cycle efficiency or highly useful energy is required of the storage medium. Thermal energy storage is not suitable for high cycle efficiency because the Carnot limits the efficiency of electricity regeneration, combined with the losses during storage, and thus is not considered in the following analysis [A34]. The following table depicts many forms of stored energy for use as either a transportation fuel or for electricity re-generation.

Pumped Hydro Storage

PHS provides a rapid access (½ -3 min startup), high cycle efficiency pathway for grid stability and dispatchability for a large amount renewable energy by charging renewable energy during off peak hours and releasing that energy at more cost-effective times of the day. There is currently 90 GW of installed PHS capacity in the world distributed among over 200 different sites [A35] . A successful PHS project was implemented in Alta Mesa, CA to store off-peak wind energy [A33]. A 70 MW PHS facility associated with a 54 MW wind park with a cycle efficiency of 70%. The hydraulic head utilized was 1,250 ft of 113 MM gal storage capacity allowing for the distribution of 420 MWh (over 6 hours) each day during peak demand, increasing the overall value of the intermittent wind energy source.

Some of the drawbacks of PHS include the dependence on specific geological formations that will suffice for adequate energy storage. Since an adequate formation has a large amount of head, most PHS sources are found in remote mountainous areas where there is no current power grid. Some of the other potential PHS sources include underground hydro storage where the upper reservoir may be a lake or ocean and the lower reservoir is either an excavated or natural cavity. Furthermore, the capital cost of PHS is massive since there are many large formations required in the construction, the cost of the turbines and pipes all while mitigating environmental damage. The estimated cost for large scale PHS is between 200-1,500 million dollars in the 1k-3k MW capacity range (electricity storage, PHS). Furthermore, as shown in Table 4 the energy density of PHS is low, requiring 1000 gallons of water 100m high to deliver 1 kWh [A36]. Finally, in the context of integrating PHS with solar and wind sites across the U.S., it seems improbable that ample PHS sites could be found in suitable locations.

Batteries

Hybrid electric vehicles (HEV) such as the Toyota Prius, Honda Insight as well as plug in hybrids (PHEV) like the Chevy Volt are highly beneficial because they combine advanced electronics with conventional drive trains. The smart electronics allow for less fuel consumption due to the ability of the vehicle to shut down the IC engine in traffic or during idling. The batteries also capture the kinetic energy during braking for enhanced fuel efficiency. Some new models of the PHEV can run solely on electricity between 20 to 60 miles before an IC recharge is required or to be plugged back into the grid. This is sufficient for the average American's daily commute, who's range is only 33 miles [A37]. When considering plug-in electric hybrids or pure plug in-electric vehicles, some major issues such as charging the car during peak load times during the day and potentially causing the creation of new coal fired power plants. This problematic scenario could be addressed by moving forward to implementing a vehicle known as vehicle-to-grid (V2G). Batteries of EV could be used as an energy storage source (V2G). A V2G plug-in vehicle would communicate with the grid to know when the best time to charge is at the cheapest price while reducing peak load demand [A38]. The NREL study for V2G found that there would be many advantages and potential disadvantages of integrating electric vehicles to the grid [A39]. It was found that there could be great savings in buying off-peak electricity which could amount to $200-450/yr. This would be due to the high efficiency and capacity battery, which can hold 7.2 kWh of electricity. The proposed vehicles can utilize 9-10 kWh which is equivalent to 1 gal of gasoline. Furthermore, this would allow grid operators to balance fluctuations in load by charging and dispactching the batteries when required. Some of the main disadvantages would be the requirement to increase home transformer feeder capacity to accomdate the charging and discharging of batteries in a condensed community. Another downfalls of the electric vehicle are the emissions and discharges of lead from manufacturing facilities and the necessary disposal process for lead-acid batteries. [A40] Lastly, several regulations would need to be put in place to require when the consumer can charge their battery to prevent grid overloading as depicted in Figure 13.

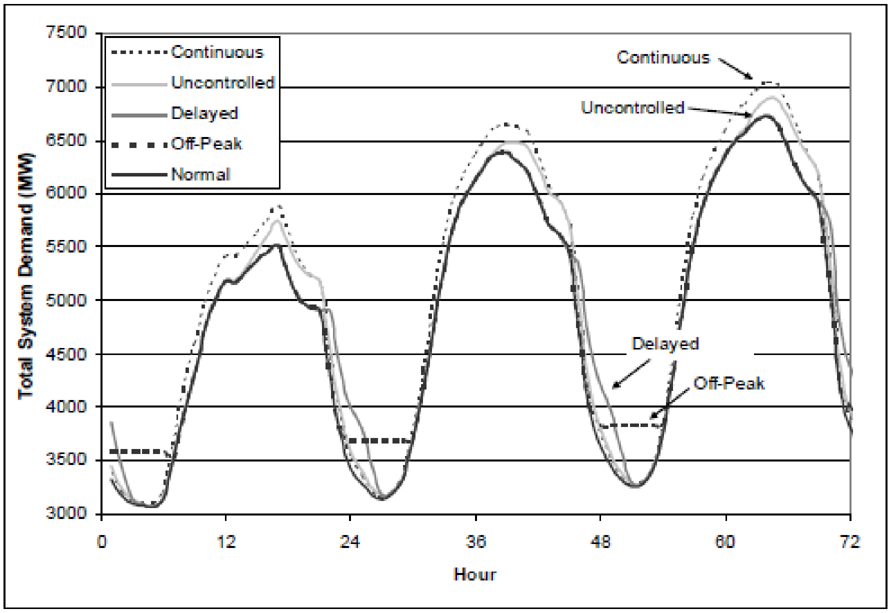


Figure 13: Battery Load and Discharge Contribution to Grid [A39]

Compressed Air Energy Storage

The premise of CAES is taking advantage of the compressibility properties of gases such as air, hydrogen or methane for the small to large-scale energy storage of renewable energy to provide stability and dispatchability to the electric power grid. This storage mechanism provides a fast start-up time of approximately 12 minutes [A41]. For large-scale applications salt domes, cavities in rock formations and aquifers are considered [A34]. As shown in Table 5, the energy density of a CAES operation is only 15 MJ/m$^{\wedge 3}$ with an overall cycle efficiency of 40-50% when compression is allowed to reach 1000-1500 psi. This requires a very large cavern, such as the 300,000 m$^{\wedge 3}$ Huntorf CAES plant in Alabama which provides 110 MW capacity. A major issue when investigating the application of CAES is the risk associated with the stability of the underground storage area to support an elevated pressure. Sample analysis and pressure tests may not provide certain applicability until actual full-scale pressure tests have been conducted. The stability of a cavern is influenced by temperature variations and pressure variations of the compressed gas storage media. The cavern wall temperature can be kept ambient by cooling the gas as it is compressed or carrying out the compression slowly. The costs associated with CAES are alleviated when an ideal cavern is already available, such as the 10,000,000 m^3 cavern being developed by Norton Energy Storage LLC to cost between 50 and 480 million dollars for between 200-480 MW capacity [A42].

CO_2 Electrochemical Reduction as Energy Storage

When comparing the CO_2 electrolysis liquid fuel products to other energy storage forms, it is apparent that a liquid hydrocarbon fuel is a much more efficient energy carrier by weight and volume than thermal, mechanical, battery and hydrogen energy storage. The CO_2 electrochemical liquid fuels are comparable to fossil fuels and biochemical fuels. Yet, storage of electrical energy to a liquid fuel has a downside of not being accessible for electricity regeneration to provide grid stability, dispatchability and peak power reduction unless it is used as a fuel-based back-up such as a diesel generator (which would be less than ideal). An upside of storing energy as a hydrocarbon is that the CO_2 electrochemical cell can run at any time, thus providing the renewable energy source a pathway for economic viability to gain revenue when renewable power is in excess or being generated at off-peak hours. An integrated CO_2 electrochemical hydrocarbon transportation sector complements renewable systems by providing a flexible use for excess renewable electricity while reducing overall emissions from fossil based transportation fuels.

Comparison

Table 5: Comparison of Different Forms of Energy Stores. N/A = Not Applicable.NF: Value not found in literature. SS: Only utilized on small scale. ; * = value estimated from similar literature

Energy Storage Type	**Energy Density**		**Cycle Efficiency**	**Capacity (MW)**	**Capital ($/kW)**	**Source**
	kJ/kg	MJ/m$^{\wedge 3}$				
Fossil Fuels						
Crude Oil	42,000	37,000	N/A	N/A	N/A	[A34]
Coal	32,000	42,000	N/A	N/A	N/A	[A34]
Gasoline	46,400	34,200	N/A	N/A	N/A	[A44]
Diesel	46,000	37,300	N/A	N/A	N/A	[A44]
CO$_2$ Electrolysis Products						
Methane	53,600	39	.122	SS	SS	[A44]
Methanol	21,000	17,000	.488	SS	SS	[A45]
F-T Diesel (HHV)	47,400		.368	SS	SS	[R21]
Syn-gas (2:1 CO:H2) (HHV)	24,700		.473	SS	SS	[R21]
Biochemical Pathway						
Ethanol	28,000	22,000	0.6	N/A	N/A	[A34]
Biodiesel	38,600	34,000	0.8	N/A	N/A	[A45]
Thermal						
Water (100C → 40C)	250	250	0.4-0.5	NF	NF	[A34]
Inorganic Salt, heat of fusion (> 300C)	>300	>300	0.6-0.7	NF	NF	[A34]
Mechanical						
Pumped Hydro, 100m head	1	1	0.65-0.8	1000-3000	500-1500	[A34]
Compressed Air		~15	0.4-0.5	200-500	250-1000	[A34]
Flywheel, steel	30-120	240-950	0.8-0.95	20-40	100-300	[A34]
Electrochemical (Battery)						
Lead-Acid	40-140	100-900	0.7-0.8	400-100	NF	[A34]
Lithium ion	700	1400	0.7-0.9	200	600	[A34]
Water Electrolysis						
Hydrogen, gas	120,000	10	0.4-0.6	100	800	[A34]
Hydrogen, liquid	120,000	8,700	NF	NF	NF	[A34]
Hydrogen, metal hydride	2,000-9,000	5,000-15,000	NF	NF	NF	[A34]

The energy density by weight and volume are key factors when considering the suitability of the energy storage medium (how much energy is available in a small space or a light weight). Fossil energies from crude oil and coal are shown as a reference for comparison to other forms of energy storage, which illustrate that they are the most convenient forms of chemical energy storage for transportation and electricity generation. The cycle efficiency was defined with the assumption that the initial energy source is an electric or mechanical energy source. The cycle efficiency shown for hydrogen assumes water electrolysis was the first step of the storage cycle.

The dispatchable types of energy storage will stabilize the grid in many ways such as mitigating over-generation, assisting in large ramps in the morning and evening, transferring off-peak power to peak power, and matching system load with off-peak power. The main downsides are that most of the energy storage mechanisms addressed are highly capital intensive, investors do not see the necessity of energy storage for renewable energy induction, there is always an efficiency loss, and some of the energy storage technologies require ideal geographic land features and are thus site specific.

Efficiency and Life Cycle Analysis

Overall Efficiency

With current small-scale technology for CO_2 electrochemical reduction, the conversion of electrical energy to chemical energy is adequate to produce liquid fuels economically. Table 6 shows the overall HHV efficiencies of the three potential products of the electrochemical cell. The F-T Diesel efficiency shows the efficiency loss from converting syn-gas into F-T liquid diesel and gasoline.

Table 6: Conversion efficiencies for electrochemical cell

Product	Conversion Efficiency (HHV), %
H2:CO @ 2:1 Ratio	47.25
F-T Diesel	36.8
Methane	12.2
Methanol	48.81

To compare this technology with other gas to liquid facilities, two processes will be addressed. The first are methane to F-T Diesel and the second is a novel technology proposed by Doty Energy which converts electricity to alcohols. Plant efficiencies for producing GTL diesel from natural gas have reached 65% recently [A46]Doty energy proposed an optimum design for obtaining efficiencies above 72% for productin of mid-alcohols (such as ethanol and butanol) from H2 and recovered CO_2 [A47].

Overall GHG Emission Reductions

For every barrel of diesel or gasoline produced from the CO_2 electrolysis facility, one barrel of imported oil will be displaced. Since we are under the assumption that our electricity source is carbon neutral, our product is also carbon neutral. Our group went a step further and found that the majority of our imported oil is sourced from Canadian tar-sands, shown in Figure 14 below.

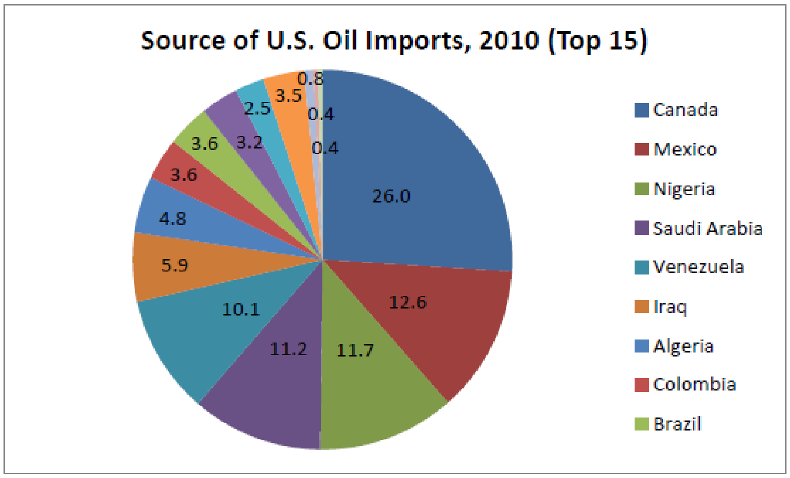


Figure 14: Crude Oil and Petroleum Imports, 2010 [A48]

Petroleum sourced from Canadian oil sands are even more environmentally unfriendly than conventional oil ,but was found to have approximately the same CO_2 emissions per barrel [A49.] The life cycle analysis carried out recently by the DOE found that 0.54 ton CO_2 is emitted per barrel of oil sourced from Canada. In comparison, 0.96 ton CO2/bbl of F-T diesel derived from coal is released [A50]. The life-cycle study assumed 24.4 mpg for the g CO2/mile given in Figure 15 below.

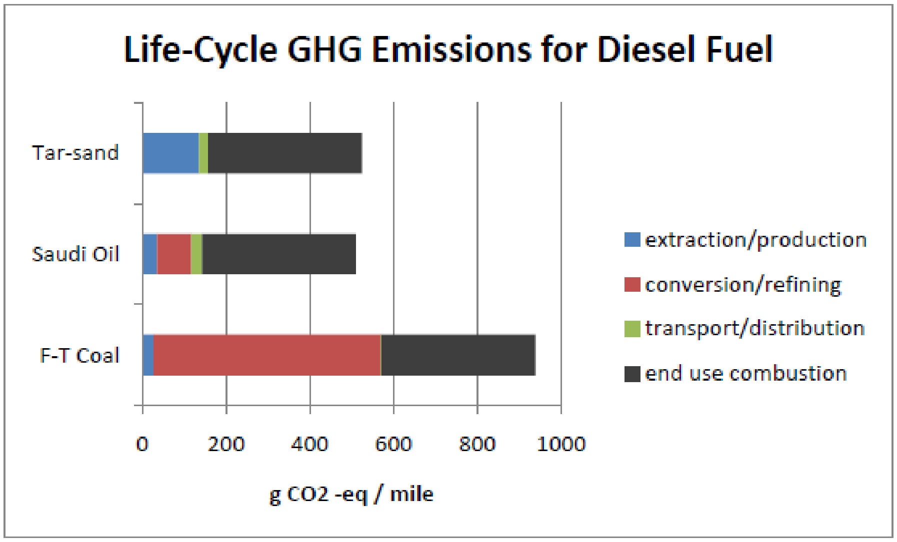


Figure 15: Life-Cycle GHG Emissions for Diesel Fuel [A50]

Economic Aspects of Products

In this section, we will define the CO_2 electrolyzer model in order to estimate how much production we will have for a set electrical input. Then, the value of our inputs (investments) and outputs (revenues) will be clarified. Finally, the breakeven analysis will be performed under a sample condition.

Models for CO_2 electrolyzer

The CO_2 reduction process can make a wide variety of products. We prepared four electrolysis models: the syn-gas/Fischer-Tropsch (F-T) model, the methanol model, the hydrogen model, and the methane model. In the syn-gas/F-T model we assume that we produce syngas from the electrolyzer and convert it to fuels via the F-T process. The products are diesel, gasoline, and kerosene, with diesel ad the primary desired product. Production yields and efficiencies were calculated using the balanced electrochemical reactions with Faraday's Law and the cell potential and product current efficiencies stated earlier. Production was normalized to a set power rate. Here the rate was set on the order of MW in order to allow for easier viewing of the values.

The efficiencies of the electrolysis can be written as the ratio of the higher heating values (HHVs) of the products to the applied electrical energy. The HHV efficiency of each product for every model is shown in Table 7 below. It can be seen that the more efficient methanol model has the highest energy efficiency, with syn-gas (without F-T conversion) following closely. Methane had the lowest efficiency of all. This is mostly due to the very high cell potential, almost 5 V, required to drive the reaction.

Table 7: The HHV efficiency and the production rates in the electrolysis models

	F-T model	Methanol model	Hydrogen model	Methane model
Methanol		48.81 % (77.4 kg/hr)	10.56 % (16.76 kg/hr)	
Methane				12.19 % (7.90 kg/hr)
Ethylene				1.77 % (1.27 kg/hr)
Formic acid			8.61 % (9.64 kg/hr)	
Carbon monoxide	15.63 % (55.66 kg/hr)			3.56 % (12.67 kg/hr)
Hydrogen	31.63 % (7.96 kg/hr)	3.20 % (0.807 kg/hr)	20.80 % (5.23 kg/hr)	

Revenues

For our revenues, we have sale of the products and a gain for CO_2 avoidance or sequestration. Our possible products were have diesel, gasoline, and kerosene via the F-T process, and methane, methanol, ethylene, formic acid, hydrogen, and oxygen from the electrolysis cell. The reference prices were obtained mainly through the Chicago Mercantile Exchange [A51] and are shown in Table 8 below.

Table 8: Reference market selling prices of the products.

	Prices $/kg
Diesel	0.96
Gasoline	1.03
Kerosene	1.01
Methane	0.389
Methanol	0.366
Ethylene	0.726
Formic acid	0.700
Hydrogen	6.82
Oxygen	0.0166

Since there are a variety of products in our electrolyzer, price estimation for the future is difficult. In the break even analysis, the fluctuations of these products will not be included.

In addition to these product sales we can take the CO_2 avoidance gain into account. According to our reference, CO_2 avoidance cost is estimated to keep increasing 4-5 % per year [A51]. Since we consume CO2 in our system, we are able to count this avoidance cost as a part of our revenues. In this report, we will use 0.025 $/kg CO_2 which increases 4 % a year.

Investments

As the investment, we have the capital cost, manage and operating (M&O) cost, the electricity cost, and the industrial water cost. The capital cost of the CO_2 electrolyzer was estimated with the capital cost of hydrogen producing electrolyzers [A53]. The M&O cost of the electrolyzers were estimated to be 32.5 % of the capital cost for every year [A54]. The M&O cost includes the replacements for the system and the labor-cost, and it is related to the capital cost. When the capital cost reduces, the M&O cost will shrink as well.

With regard to the electricity cost, we assume three power generating costs for CSP, wind, and PV because they do not any fuel input, and they do not produce CO_2. These energy costs are levelised with possible subsidy and M&O cost. As for the water cost, we used a residential water price of $7.4\ 10^{-4}$ $/kg [A55]. Although this price would belarger than the expected industrial waterrate, it does not affect the break even analysis since the total value is much lower than the other investment prices.

For the case of producing syngas with the electrolyzer and feeding it into the F-T process, we need to include the capital cost and the M&O cost in the total investment. The capital cost for the F-T reactors was calculated based on the reference [A56]. The M&O cost of the reactors was estimated to be 30 % of the entire capital cost.

These capital costs and electricity costs will likely change in the future. Since electrolyzers are typically operated over 40 year terms, we need to consider the fluctuations of these two costs. In order to estimate them, we will apply the "learning curve estimation."

Learning curve estimation

The idea of the learning curve estimation came from a tendency that the production cost of a certain product decreases exponentially when the global cumulative production amount of that product increases. When we take the logarithmic scale of the cumulative production in the X-axis and the production cost in the Y-axis, the price will decrease linearly as shown in Figure 16.

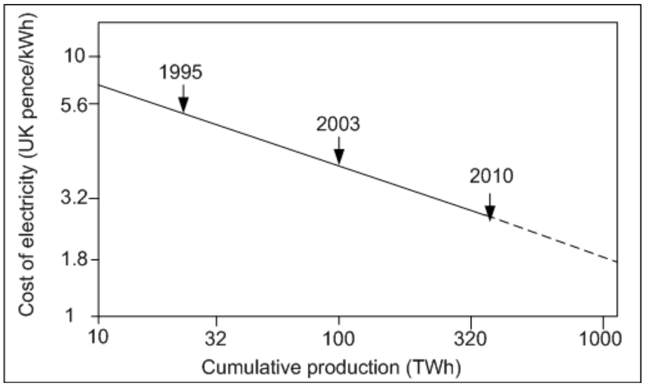


Figure 16: The example learning curve on the cost of electricity of PV generation in the United Kingdom [A57].

The cost of a certain product N years later than a certain year (C_N) is,

$$C_N = C_0 \left(\frac{n_N}{n_0}\right)^{\alpha}$$

where C_0, n_N, and n_0 represent the cost of a certain product at a certain year, the cumulative production N years later than a certain year, and the cumulative production at a certain year. α is equal to the double of the production rate (*pr*) which can be written as

$$pr = 1\text{-}\mathit{learning\ rate}\ (= 2\alpha)$$

where the learning rate is the reduction rate of the curve in the plot such as Figure 16. The learning rate tends to be in the range of 15–20 % [A57].

It is an empirical way to extrapolate future prices of a product which does not have a saturated market such that the production amount will reduce its price. This method has been used in many fields, and a number of estimations have been reported by many researchers and organizations. For example, the selling price of proton exchange membrane fuel cells, the ethanol price in Brazil, and the methanol price have been estimated in literature [A58, A59, A60]. In our economic analysis, the electricity cost of CSP, wind, and PV and the capital cost of the electrolyzers were estimated during the period of 2010-2050 with the results of some reference data [A61, A62, A63]. According to the references, the renewable electricity prices and the capital cost of water electrolyzers will decrease as shown in Figures 17 and 18 below.

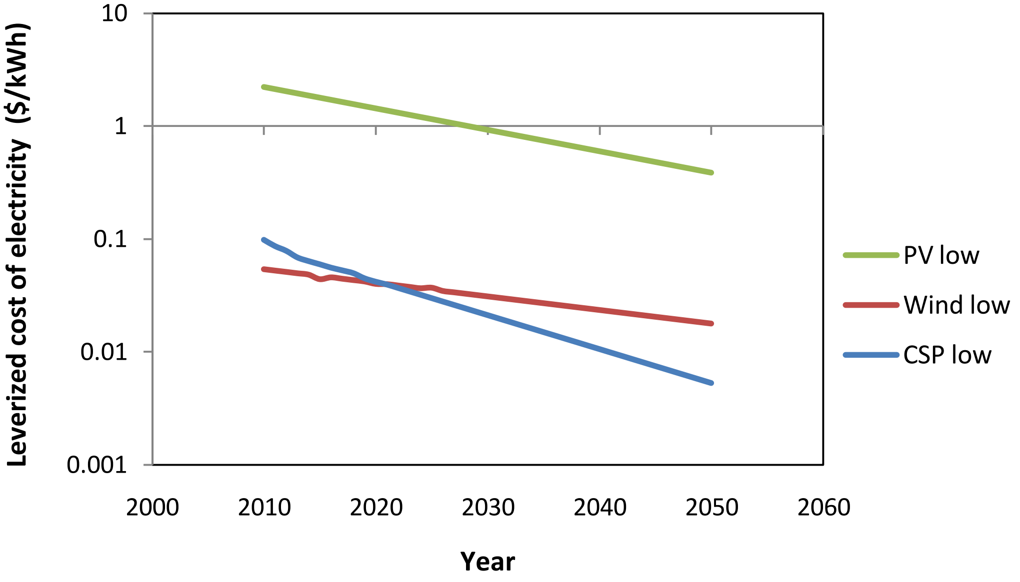


Figure 17: The learning curve estimation of the electricity cost for renewable energy sources.

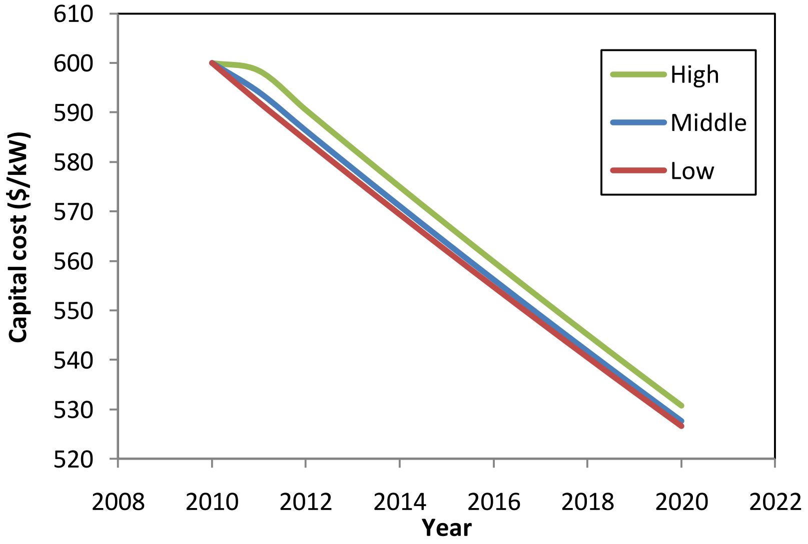


Figure 18: The learning curve estimation of the capital cost of the water electrolyzers.

From the figures above, we found that the electricity cost and the capital cost will keep decreasing as time passes by. In order to see the most promising result, we will use the CSP as the source of the electricity in the break even analysis. With regard to the capital cost, the capital cost reduction will decrease the replacement prices. As a result, the M&O cost keeps decreasing in the future.

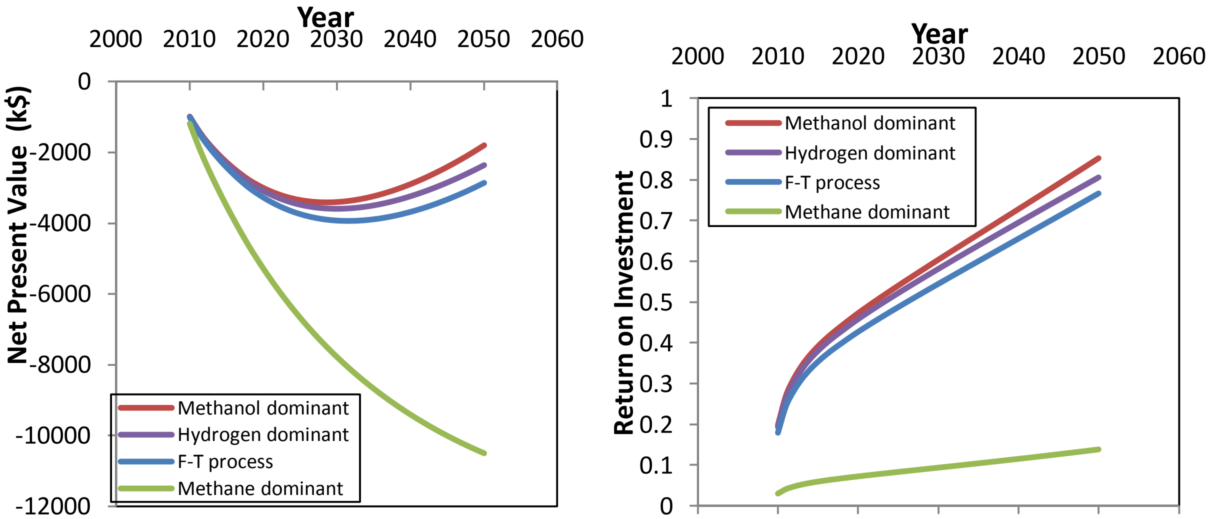
Breakeven analysis

We investigated the rate of return through the lifetime of the electrolyzers by putting the inputs into our models and obtaining the output under a sample condition. The factors in the condition in operation are shown in Table 9 below.

Table 9: Factors on the CO_2 electrolyzer operation

Factors	
The electrolyzer capacity	1 MW
Capital cost of the electrolyzer	600 $/kW
M&O cost of the electrolyzer	32.5 % of the capital cost
F-T reactor capacity	10 bbl /day
F-T reactor capital cost	0.72 $/bbl/day
Electricity sources	CSP
Operating hour	12 hours /day (capacity factor=80 %)
Lifetime	40 years
Product selling price	constant
Investment costs	Learning curve estimation

Based on the factors above and the data in Table 9, the total investment, the total revenue, and the net present value (NPV) and the return on investment (ROI) were estimated as shown in Figure 19 below.



(a) NPVs over 40 years. (b) ROIs over 40 years.

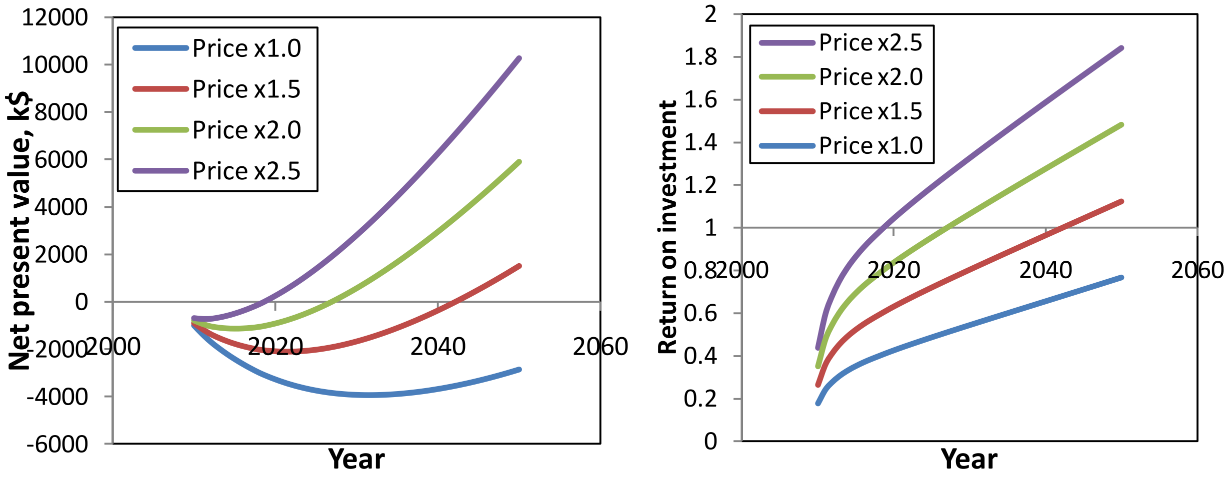
Figure 19: Breakeven analysis for four models.

This Figure 19 shows that each model cannot be profitable in its lifetime of 40 years. Although the methanol-dominant model shows the highest NPV, the assumption on this model that any amount of produced methanol can be sold is not realistic. As mentioned before, methanol has to have a certain concentration to be worth the energy of separation. We need distillation or some method in order to obtain concentrated enough to be sold commercially, which will increase the investment. The less efficient hydrogen dominant methanol model and the F-T process model show better results than the methane dominant model, but they are not profitable as well. It should be noted that the less efficient methanol model obtains a considerable amount of revenue due to its hydrogen byproduct.

In our models, we assume that the product selling prices are constant. However, the prices will change in the future depending on their demands. For example, the selling price will increase when we face the depletion of crude oil. On the contrary, if competitors such as coal gasification technology or biomass gasification develop and their efficiencies are much higher than our electrolysis process, the selling prices will decrease. We will examine three scenarios that lead selling prices to rise.

Crude oil depletion and oil-derived fuel price appreciation

It is said that crude oil will deplete in the future and the price of oil-derived products will increase sharply [A64]. In order to investigate the influence of that oil depletion, we changed the product prices of diesel, gasoline, and kerosene by 1.5 to 2.5 times. The NPVs and ROIs are shown in Figure 20



(a) NPVs over 40 years.

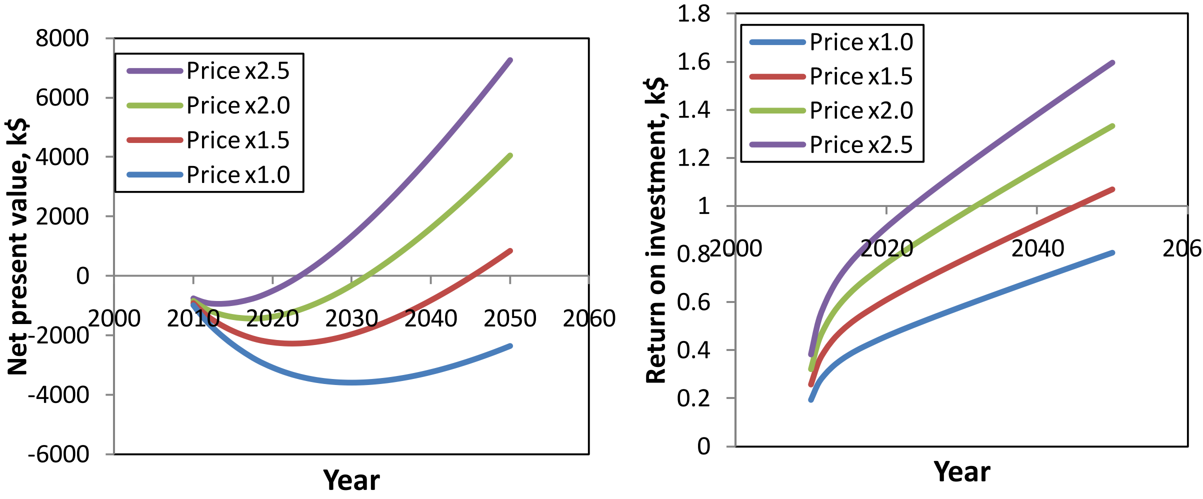
(b) ROIs over 40 years.

Figure 20: The Net Present Values of the F-T model.

This model shows that the product price have to increase over 2 times if we want to have the 15 % ROI in 25 years. When the product price is less than 1.5 times of the current price, the ROI does not reach 15 %.

Hydrogen price appreciation

The demands of hydrogen keep increasing as a energy storage run by fuel cells and the method for its production has been widely investigated [A65]. Although the price will depend on its demand and supply, the hydrogen price increase is possible because the demand itself keeps increasing. We estimated NPVs and ROIs in the same way as the oil case, changing the hydrogen price from 1.0 to 2.5 times. The results are shown in Figure 21 below.



(a) NPVs over 40 years.

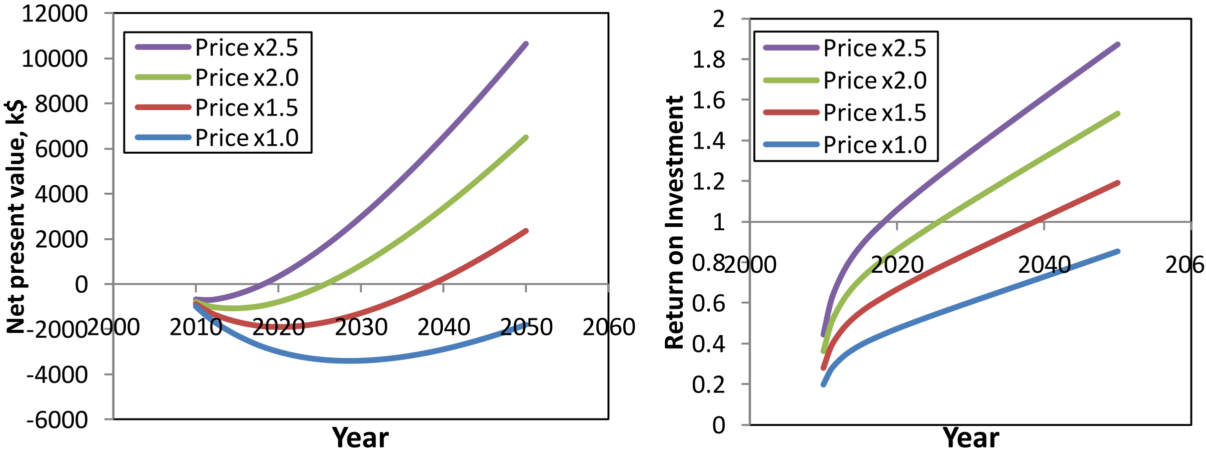
(b) ROIs over 40 years.

Figure 21: The Net Present Values of the hydrogen model.

This figure indicates that the hydrogen price has to be over 2 times if we want to have the 15 % ROI in 30 years. When the product price is less than 1.5 times of the current price, the ROI does not reach 15 % with its lifetime of 40 years.

c) Methanol price appreciation

Methanol is also gathering much attention as an energy source with direct methanol fuel cell and a fuel in combustion process with automobiles [A66, A67]. We have examined the NPVs and ROIs analysis for methanol in the same way of F-T process and hydrogen.



(a) NPVs over 40 years.

(b) ROIs over 40 years.

Figure 22: The Net Present Values of each model.

This model shows that the product price have to increase over 1.5 times if we want to have the 15% ROI in 40 years. Thus, even a little increase less than 50% in its price may cause our process profitable.

As for the case of methane, the price change of it does not affect the value of our reduction process so much as shown in Figure 22 below.

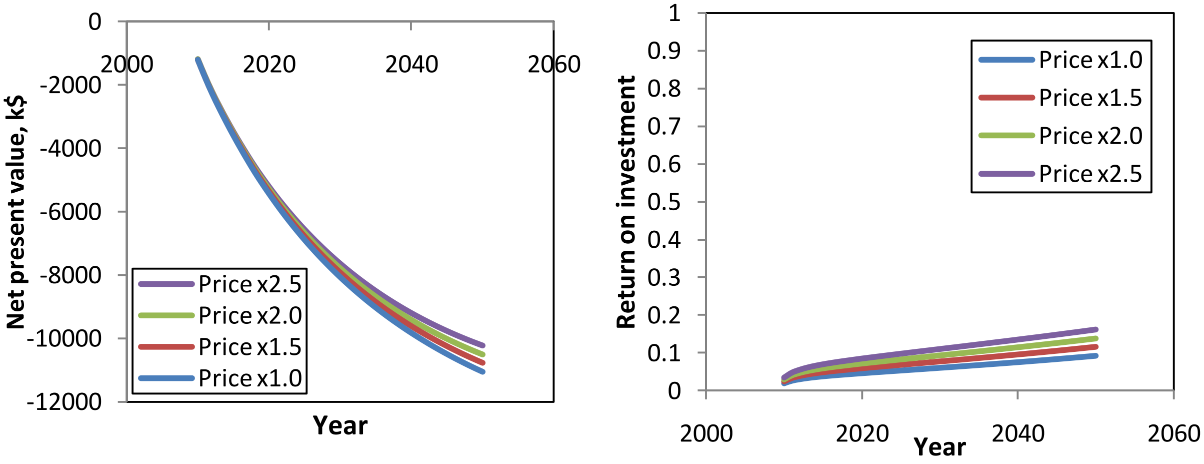


Figure 22: The Net Present Values of each model.

It is because methane is currently purified from natural gas. Natural gas is abundant and the price is low now. Therefore, it is difficult to get our process to be beneficial by producing methane.

Critical Analysis

As has been mentioned previously there are additional considerations to be made when viewing the economic and efficiency results. Foremost is the fact that this should be considered an optimistic estimation of the system. True operation would require additional separation systems for both the CO_2 feed and the final products which have not been included in this analysis. The result would be a notable increase in the capital costs, as well as a decrease in overall efficiency due to increased energy demand. Further work could be done to model these effects, but it was not considered here as it would have only made the poor return even worse. As such, this modeling would not be recommended until the economics can be made effective under the current conditions posed here.

In addition to the economic issues, it must be noted that the technology is still far from implementation. As was discussed earlier there are still significant physical hurdles to be overcome. The current density would need to be increased by several orders of magnitude. Low current density means increased capital costs in order to reach the same yield rates. This can likely be overcome, as it has already been done for fuel cells and water electrolysis through improved cell geometry and catalyst choice. The difficulty here is that the rate limiting step has been found to be the initial reduction of CO_2 to CO, which is the intermediate in the formation of hydrocarbons. Significant work still needs to be done before the processes can be considered competitive with the current state of water electrolysis. Much of the more recent improvement has been done with systems designed to produce formic acid as the product, often with the focus on use as a pharmaceutical precursor [A68,A69,A70].

Electricity costs have been found to be largest impact on profitability, as can be seen in the cost breakdown below. One path not examined here was the potential for receiving free electricity. If the cell were to be operated under the assumption that the stored electricity would normally be lost, then it could be possible to assume that the electricity had a negligible cost. This would greatly improve the economic outlook. However, this was considered unlikely for the purpose of this study.

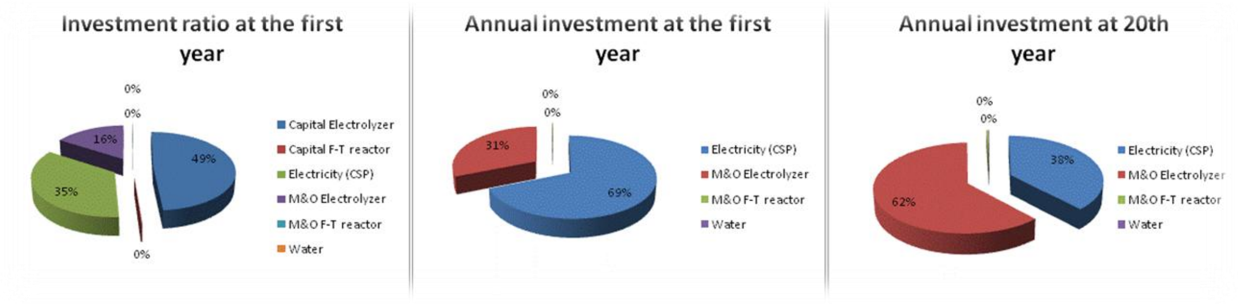


Figure 23: Cost breakdown of process over time

Conclusion

The finals results of this analysis show little promise for the process based on the current state of technology. The ratio of electricity value to fuel value is far too high to yield notable returns, even at very low estimates of \$0.04 to \$0.01/kWh over time. The cost of water was found to be negligible by comparison, and the cost of CO_2 feed was also low. Capital costs were further hampered by the stack lifetime, which for water electrolysis is typically on the order of 5 to 15 years. Significant fuel price increases, up to 200%, would be required before a 15% ROI over 20 to 30 years could be achieved. The low value and low efficiency of methane meant that there were no feasible scenarios to make its production viable. The method was also found to be an expensive means of CO_2 sequestration, as current carbon taxes or credits would need to increase by one or two orders of magnitude before they would begin to impact the costs. Low energy efficiency coupled with low conversion efficiency back to electricity reduces its potential as an energy storage method, though the capital costs of such a system could be considerably lower than some comparable battery technologies. Due to the higher operating potential required and higher potential sale value of H_2 it would be difficult to recommend this approach over water electrolysis for either fuel production or energy storage. In addition to the economic difficulties there are still considerable physic limitations that must be overcome before the system could be scaled up and commercialized.

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