THERMODYNAMICS OF CARBON DIOXIDE AS A FEEDSTOCK, AND ITS CONVERSION THROUGH ELECTROCHEMISTRY WITH RENEWABLE POWER

James R. Lattner*
ExxonMobil Chemical Company
Baytown, TX 77522

Abstract

In our quest to reduce carbon dioxide emissions, many have proposed using CO_2 as a feedstock to make fuels or chemicals. Owing to the extreme negative heat of formation of CO_2, a considerable amount of energy must be supplied to convert CO_2 into useful products. If the energy is supplied by combustion of a fossil fuel, the CO_2 emissions from that combustion exceed the quantity of CO_2 converted. Therefore, renewable energy must be utilized; typically renewable power from solar PV or wind turbines. However, seldom is the question asked, "what uses of renewable power have the biggest impact on CO_2 reduction?" This talk will look at the thermodynamics of utilizing CO_2 as a feedstock for chemicals or fuels, and will also look at a number of choices for using renewable power, and ranking these choices as to their impact on CO_2 emissions reduction. Of the seven choices studied for use of renewable power, the electrochemical conversion of CO_2 has the lowest impact on reduction of CO_2 emissions.

Keywords

NASCRE-4, Carbon Dioxide Utilization, Renewable Power, Electrochemistry

Introduction

Carbon dioxide production, and its potential for capture, recovery, and re-use . . . can be very emotional subjects. Government institutions, politicians, environmental activists, academics looking for funding, etc., play a major role in shaping our views of carbon dioxide. Not surprisingly, many of these policies and views do not have sound scientific bases. Proposals to convert CO_2 into fuel or chemical products receive a lot of attention and funding. In order to avoid making more CO_2 that is consumed, these routes rely on the use of renewable power and electrochemistry to drive the conversion. It is important to understand both (i) the thermodynamics of utilizing CO_2 as a feedstock for the production of fuels or chemicals, and (ii) Alternative uses of renewable power, and the CO_2 reduction potential for these alternates relative to the electrochemical conversion of CO_2.

Discussion

As a feedstock, there are very few exothermic reactions carbon dioxide will undergo to form useful products. Most routes that utilize CO_2 as a feedstock can also utilize CO as the carbon source. As CO_2 has a much lower heat of formation than CO, additional energy must be supplied to utilize CO_2 versus CO. Methanol synthesis is an excellent case to study the energetics of CO2 utilization, since methanol can be produced from either CO or CO_2. Assuming the heats of reactions are utilized perfectly, and

* To whom all correspondence should be addressed

using the water gas shift reaction to produce the additional mole of hydrogen required for the CO_2 feed case, the net impact on CO_2 is precisely zero.

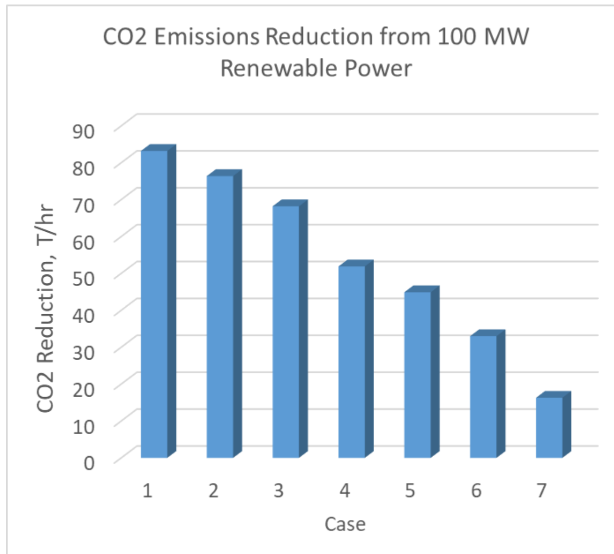
Since the shale gas boom, there have been a proliferation of ethane steam crackers to produce ethylene, with hydrogen as a byproduct. The heating value of the hydrogen can be used to provide heat for the endothermic cracking reaction and other energy requirements for the ethylene plant, avoiding the combustion of fossil fuels such as methane, and resulting in much reduced CO_2 emissions. The thermodynamics of this scheme can be calculated, and compared with the CO_2 impact of alternately using the byproduct hydrogen to back out hydrogen production from a steam-methane reformer. Again, assuming perfectly theoretical utilization of heats of reactions, the impact on CO_2 emissions from burning the hydrogen in the steam cracker, versus using the hydrogen to back out steam-methane reforming, is precisely zero.

The only method of utilizing CO_2 that results in a net reduction in CO_2 emissions is to use renewable energy for its conversion into useful products. Typically, renewable power is proposed for the electrochemical conversion of CO_2 and/or water to fuels or chemicals. Proposed electrochemical routes reduce CO_2, water, or mixtures thereof, to CO, hydrogen, and mixtures thereof, for subsequent chemistry that results in products such as methanol, formic acid, ethylene, and Fischer-Tropsch liquids. The power requirements for the electrochemistry depend upon the number of electrons involved in the reactions, and the degree of over-potential required . . . and not on the path taken. For example, in the electrochemical synthesis of methanol (plus oxygen) from CO_2 and H_2O, the power requirement is the same whether it is the H_2O or the CO_2 that is reduced (or a combination), provided the over-potentials are the same for the alternate routes.

The theoretical power required for conversion of CO_2 into useful products can be precisely calculated, and the actual power can be estimated by assuming over-potentials similar to those achieved in commercial water splitting cells. In addition, typical efficiencies of Internal Combustion Engines (ICE), Hydrogen Fuel Cell Vehicles (FCV), conventional steam boiler power plants, and Combined Cycle Gas Turbine (CCGT) power plants can be looked up. The calculations are then straightforward to look at various ways renewable power can be used reduce CO_2 emissions:

1. Renewable power to the grid, displacing power from conventional coal-fired steam boiler power plant
2. Renewable power to the grid to a (BEV), displacing fossil liquids to an (ICE) vehicle
3. Surplus renewable power to pumped water storage, with subsequent hydroelectric generation to the grid to a BEV
4. Renewable power to the grid, displacing power from conventional natural gas-fired steam boiler power plant
5. Renewable power for water electrolysis, utilizing the hydrogen to power a Hydrogen FCV, displacing fossil liquids in an ICE vehicle
6. Renewable power to the grid, displacing power from a natural gas CCGT power plant
7. Renewable power for the electrochemical conversion of CO_2 into liquid fuels for an ICE vehicle

The figure below summarizes the CO_2 emissions reduction from each of these scenarios.



Conclusions

The thermodynamic potential of CO_2 is, for all practical purposes, zero. Energy must be supplied to convert CO_2 into useful products. If the energy comes from fossil sources, then thermodynamics show it is impossible to come out ahead with respect to CO_2 emissions. Rather, renewable energy must be utilized. However, when comparing the effectiveness of various routes to use renewable power to reduce CO_2 emissions, the electrochemical conversion of CO_2 does not compete favorably compared to other uses of renewable power. Rather, renewable power is most effective at reducing CO_2 emissions through:

i. Displace fossil fuel-fired power plants, particularly coal-fired
ii. Send renewable power to the grid to a Battery Electric Vehicle, displacing fossil liquids to an Internal Combustion Engine