FUTURE ENERGY

Electrification and Decarbonization of the Chemical Industry

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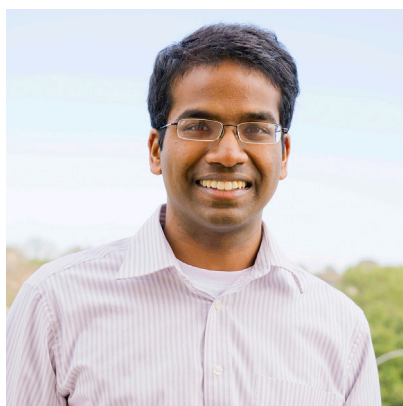
Karthish Manthiram is an Assistant Professor of Chemical Engineering at MIT. The Manthiram Lab develops technologies that enable modular and sustainable transformations of molecules. The lab is currently focused on the conversion of distributed feedstocks, such as air, water, carbon dioxide, and renewable electricity, into molecules that have an impact on our everyday lives. Examples include catalytic technologies through which farmers in developing countries can produce their own ammonia fertilizers and conversion of carbon dioxide into methanol to mitigate emissions that would otherwise contribute to global warming. Karthish received his bachelor's degree from Stanford University in 2010 and his Ph.D. from UC Berkeley in 2015, both in Chemical Engineering. Most recently, he was a postdoctoral researcher at the California Institute of Technology.

Renewable energy sources, such as solar and wind, have become increasingly prevalent and helped drive progress toward decarbonization of electricity. Renewable energy sources are often discussed in the context of the electrical grid, transportation, and household devices. However, the commodity chemical industry is a large consumer of energy and a major contributor to global greenhouse gas emissions. Decarbonizing the chemical industry would have a significant impact on global carbon dioxide emissions, and electrification of the industry using renewable sources is a possible step toward reducing the carbon footprint of chemicals.

Electrification of the chemical industry requires identifying clear targets for chemical processes that would have a large impact at the energy-carbon nexus (Figure 1A). The top five commodity chemicals with both the largest production volume and energy consumption are ammonia, ethylene, propylene, methanol, and benzene/toluene/xylene (BTX).[1] These high-volume commodity chemicals are transformed into other commodity chemicals, specialty chemicals, or finished products. For instance, ammonia is necessary for the production of acrylonitrile, hydrazine, phenol, nitric acid, and urea; it is eventually incorporated into fertilizers, cleaners, and plastics.

Energy consumption itself is not necessarily a problem, but it is a relatively clear indicator of undesired greenhouse gas emissions (GHGs), as the chemicals with the largest energy consumption also have large GHG emissions (Figure 1B). Two sources of GHG emissions during the production of these commodity chemicals are the combustion of fossil fuels and the production of feedstocks such as hydrogen. Ammonia, ethylene, propylene, methanol, and BTX production all require energy to raise temperatures, apply pressures, or separate products, and this energy generally comes from burning fossil fuels, leading to GHG emissions. In addition, some synthesis routes, including those for ammonia and methanol, require hydrogen gas as a feedstock. Hydrogen gas is generally produced by steam reforming of methane, in which water and natural gas are converted to hydrogen and carbon monoxide. Using the water gas shift reaction, carbon monoxide and water are then converted to additional hydrogen and carbon dioxide, producing GHG emissions.

Decarbonization and Electrification in the Current Industry

In order to decarbonize the chemical industry, we need to reduce carbon dioxide emissions by closing and moving beyond the current carbon cycle. In this context, decarbonization refers to
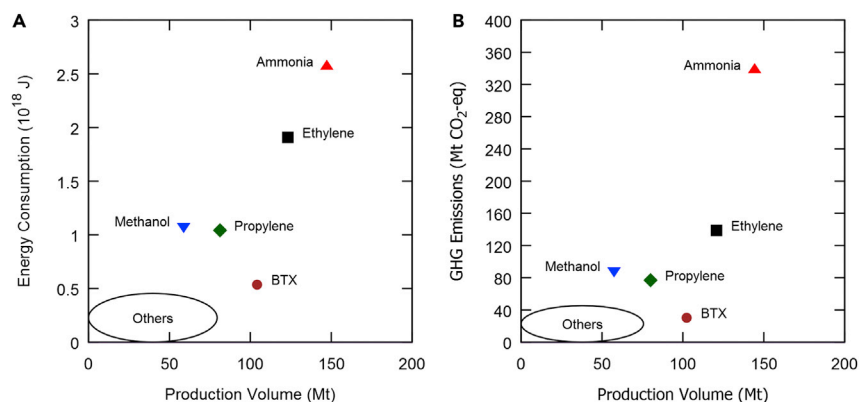
Figure 1. Energy Consumption and Carbon Footprint of High-Volume Commodity Chemicals
(A and B) Comparison of (A) energy consumption and (B) greenhouse gas (GHG) emissions versus production volume for top chemicals by volume in 2010. GHG emissions are expressed as megatonnes of carbon dioxide equivalent (MtCO$_2$-eq). The five high-volume commodity chemicals labeled on the plots have the largest energy requirements, which correspond to large GHG emissions. The region labeled "Others" shows approximately where the next 13 largest contributors fall. Figure adapted from IEA, ICCA, and DECHEMA data.[1]

the reduction of atmospheric carbon dioxide emissions. One route to decarbonization could involve converting otherwise emitted carbon dioxide into valuable commodity chemicals. A second strategy toward decarbonization would involve avoiding the generation of carbon dioxide altogether; for example, this could be achieved by sourcing hydrogen exclusively from splitting water instead of from steam methane reforming and water gas shift reactions. What both of these routes have in common is that they are likely to involve transforming species at the bottom of the free energy landscape, such as carbon dioxide, nitrogen, and water, to desirable commodity chemicals higher up on the free energy landscape, such as ammonia and methanol. Moving these commonly available feedstocks up the free energy landscape requires energy input that would ideally come from renewable sources such as solar and wind.

While trends in renewable electrification can further goals in decarbonization of chemical production, the reverse is also true: decarbonized routes for chemical production can

help to address mounting challenges for renewable electrification. The ability to transduce electrical energy into chemical bonds provides a method for storing electrical energy that helps overcome the intermittency of sources such as solar and wind.[2] Liquid fuels such as methanol and ammonia, with necessary compression or cooling, are attractive for energy storage due to their high volumetric energy density, compared with fuels such as hydrogen, and their cost-effective distribution using existing infrastructure.[3]

In the paradigm described, modular chemical synthesis devices take in nitrogen, water, carbon dioxide, and electricity from a renewable source such as solar or wind (Figure 2). This device outputs commodity chemicals, such as methanol and ammonia, providing both a means of energy storage as a fuel and desired chemical products. Without electrification of the chemical industry, the interaction between renewable electricity sources and fossil fuels used for power generation is through electrons in the grid. With carbon-neutral liquid fuels produced via electrification, the chemical and energy industries interact through

transport of liquid fuels and feedstocks, improving the fluidity and interconnectedness of both industries. Global GHG emissions from chemical and petrochemical processes were a little above 1 gigatonne of carbon dioxide equivalent (GtCO$_2$-eq) in 2010, while emissions totaled approximately 40 GtCO$_2$-eq that year.[1] By coupling the chemical and energy industries, the impact of decarbonization of chemical processes can be magnified for chemicals that are also carriers of clean energy, leading to an even greater impact on reduction of carbon dioxide emissions.

Electrification via Electrochemistry

There are many possible routes for electricity to drive a chemical reaction. For the direct transduction of electrical energy to chemical bonds, electrochemical methods are attractive and have some advantages over traditional thermochemical methods. Electrochemical methods enable bond-formation steps using electricity, which offers an alternative driving force, voltage, that can enable operation at mild temperatures and pressures. In addition, electrochemical cells often result in natural product separation due to the use of a membrane that keeps products generated at the cathode and anode separate.

We can understand the impact of electrochemical versus thermochemical routes using ammonia production as a case study. Here, we specifically look at the thermodynamics of two alternative routes by calculating the reaction conversion as a function of various operating conditions (Figure 3). The equilibrium constant and corresponding conversion are calculated using tabulated thermodynamic properties of the reactants and products, accounting for the electrical work contribution of the applied potential.[4] Our system contains stoichiometric feeds, and we assume ideal liquids with unit activity and ideal gas mixtures. We
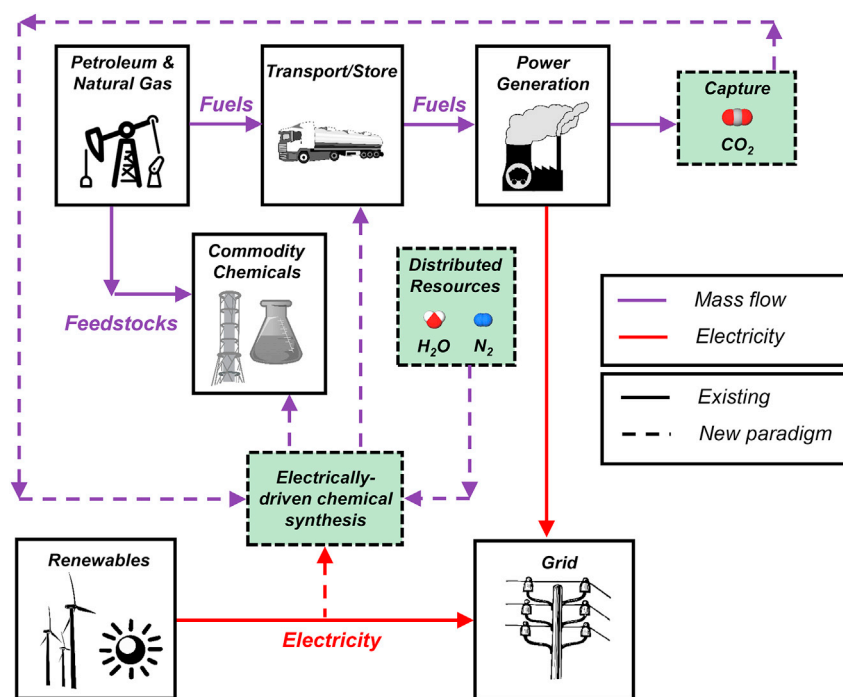
Figure 2. Current and Envisioned Coupling of the Chemical and Energy Industries
Purple lines indicate mass flow and red lines indicate electrical energy transport. Solid lines indicate the current state of the industries and dashed lines indicate how the proposed methods of electrification and decarbonization could be incorporated. Specifically, an electrically driven chemical synthesis device would allow chemicals such as ammonia or methanol to act as either energy carriers for renewable electricity or intermediates for producing other chemicals and products. Such an electrical device would further connect the energy and chemical industries and help close and replace the current carbon cycle.

also assume water is in the gaseous phase if the vapor pressure is greater than the operating pressure at the conditions studied and liquid phase otherwise.

We first consider the case in which nitrogen and hydrogen react to form ammonia (Equation 1):

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
(Equation 1)
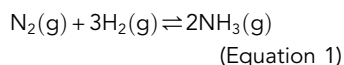
Running this reaction thermochemically is simply the commercially practiced Haber-Bosch process (Figure 3A). Although equilibrium conversion can be much higher at low temperatures and ammonia is thermodynamically favored at ambient conditions, the kinetics are only favorable at high temperatures, and high pressures are

necessary to achieve reasonable conversions at those high temperatures. As a result, the standard operating conditions for the Haber-Bosch process are around 450°C and 200 bar. Replacing pressure with voltage in an electrochemical route to drive conversion to ammonia, the thermodynamics of the system become favorable without the use of elevated pressures (Figure 3B); the voltage may also help to accelerate the kinetics with a suitably designed catalyst.

To achieve low-carbon ammonia synthesis, the electrochemical route would need to use hydrogen gas sourced from splitting of water, perhaps also through an electrochemical route. Instead of first splitting water to generate hydrogen and then reacting this hydrogen with nitrogen in a separate

electrochemical reactor, it is appealing to react nitrogen and water directly in a single reactor (Equation 2):

$$2N_2(g) + 6H_2O(g,l) \rightleftharpoons 4NH_3(g) + 3O_2(g)$$
(Equation 2)
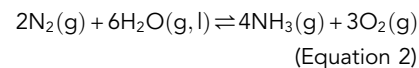
Thermochemically, the reaction of water and nitrogen is not feasible at mild conditions (Figure 3C). However, when a voltage of greater than 1.17 V is applied at ambient temperature and pressure, ammonia is thermodynamically favored compared to nitrogen and water (Figure 3D). This route could lead to significant decarbonization of ammonia synthesis, as water is used as the hydrogen source instead of natural gas, and the process is driven by renewable electricity.

The thermodynamics of ammonia production offer a few key insights. The currently practiced thermochemical Haber-Bosch process requires high temperatures and pressures that mandate large-scale, centralized reactors to achieve economic viability. In contrast, electrification may allow nitrogen and water to form ammonia at low temperatures and pressures that are conducive to modularity. Ammonia synthesis reactors can be much smaller and located alongside renewable electricity sources. By producing the ammonia close to where it is needed, distribution costs can be reduced; even if the ammonia needs to be distributed, the transport and storage of ammonia as a liquid is cost-effective. The modularity may open up the possibility of producing ammonia-based fertilizers locally, especially in parts of Africa where infrastructure for the production and distribution of fertilizers is lacking, contributing to low crop yields and malnourishment.[5]

Although we have discussed electrification of commodity chemical production in the context of ammonia, the same principles apply to the production of other commodity chemicals. Methanol
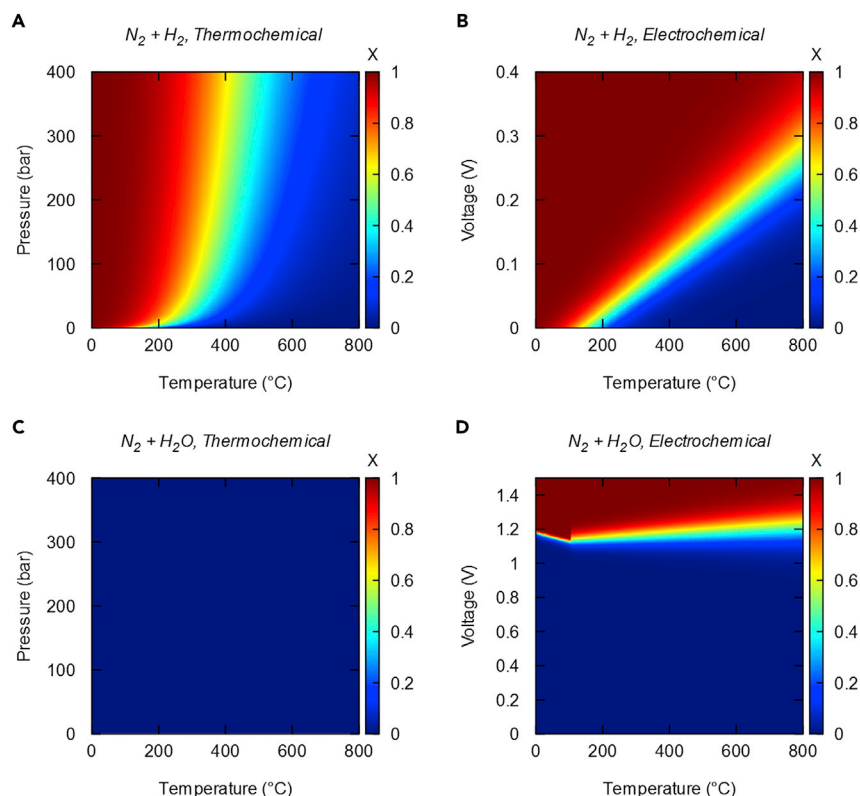
Figure 3. Calculated Equilibrium Conversion of Nitrogen to Ammonia Using Both Thermochemical and Electrochemical Routes

A conversion of 1 indicates all products and 0 indicates all reactants.

(A) The thermochemical Haber-Bosch process requires elevated pressures to compensate for the high temperatures needed to achieve fast kinetics in the reaction of nitrogen and hydrogen to produce ammonia.

(B) In an electrochemical reactor operating on nitrogen and hydrogen feedstocks, small voltages can be used to achieve high equilibrium conversions.

(C) Conversion of nitrogen and water to ammonia is negligible using temperature and pressure.

(D) Application of a suitable potential can drive the conversion of nitrogen and water to ammonia, demonstrating the promise of electrochemical routes for producing ammonia.

and ethylene can be produced by reacting carbon dioxide and water in an electrochemical reactor, leading to decarbonization of the production of a much wider range of commodity chemicals. Producing ammonia electrochemically is an example of displacing the carbon cycle, while production of methanol from carbon dioxide provides an opportunity for closing the carbon cycle.

While we have so far only discussed the operating conditions for thermochemical and electrochemical reactors, separation of products following the reaction unit operation can also be an energy-intensive step that results in GHG emissions. In many cases, electrochemical reactions facilitate product separation since a membrane separates the oxidative and reductive half-reactions. This is already realized in the context of water electrolysis, where the product hydrogen and oxygen gases are produced at opposite electrodes and do not require further separation. In the case of the electrochemical reaction of nitrogen and water, the ammonia and oxygen products can be generated in separate compartments, avoiding an additional separation step.

Opportunities and Challenges

The discussion above focuses on equilibrium conversions that depict the thermodynamic limits; there are many challenges that remain with respect to the kinetics of these reactions that are certain to remain the focus of future research. Accordingly, the development of new catalysts is essential to electrification of the chemical industry. The field of carbon dioxide reduction has grown in recent years, resulting in improved understanding of the basic mechanisms and trends involved in catalytic carbon dioxide reduction.[6] Several companies have made significant advances toward the commercial electrochemical conversion of carbon dioxide to carbon monoxide. However, there continue to be many opportunities to develop catalysts for carbon dioxide reduction with improved activity, selectivity, and stability for liquid products such as methanol. Catalysts for low-temperature electrochemical ammonia synthesis are far less developed, although theoretical studies of catalysts and isolated experiments show promise.[7,8] For a wide range of reaction chemistries, efforts at the intersection of atomically and molecularly precise catalysts, *in situ* spectroscopy, and computational modeling of surfaces will have great impact on electrocatalyst discovery.[9] Enzymatic catalysts, such as nitrogenases and carboxylases, may also either be incorporated into or provide inspiration for the design of electrocatalytic processes.[10]

Even with the development of better catalysts, there is a significant gap between laboratory-scale research and industrial processes; the viability of electrochemical processes at scale is a key consideration. Historically, electrochemistry has been used at scale in other parts of the chemical industry, including for the chloralkali process, which uses electrolysis of sodium chloride to produce chlorine and sodium hydroxide, and for the electrolysis of

alumina to produce pure aluminum. Particular organic chemical syntheses have also been performed at scale using electrochemical routes, including acrylonitrile dimerization and fluorination of ethers.[11] In addition, hydrogen production by water electrolysis is continuing to become a more mature technology. In fact, there are multiple examples of ammonia production in the mid-20th century using hydrogen produced from water electrolysis, and this historical synthesis route offers inspiration for future carbon-neutral routes to produce ammonia as the cost of water electrolysis continues to decrease. Much can be learned from these prior examples, as well as efforts to derive chemicals from biomass, to help develop successful strategies for scale-up of electrochemically driven chemical synthesis.[12] Knowledge of scale-up constraints can also be used to inform design principles for laboratory-scale catalyst discovery.

Electrification of the chemical industry may help to match broader trends in modular and local manufacturing that have been enabled by robotic automation and additive manufacturing methods, such as 3D printing. Local production of commodity chemicals needed in these new modular manufacturing methods will help to reduce inefficiencies associated with the transportation, distribution, and storage of commodity chemicals. By using electrochemistry to react carbon dioxide, nitrogen, and water with renewable sources of electricity, such as solar and wind, one can envision locally generating the commodity chemicals needed for automated and additive manufacturing. Electrification of the chemical industry may therefore represent an opportunity for fully integrated, decarbonized, local manufacturing that starts with renewable resources and ends with desired commercial products.

AUTHOR CONTRIBUTIONS

Conceptualization, Z.J.S. and K.M.; Methodology, Z.J.S. and K.M.; Software, Z.J.S; Validation, Z.J.S. and K.M.; Investigation, Z.J.S. and K.M.; Resources, Z.J.S. and K.M.; Writing – Original Draft, Z.J.S.; Writing – Review & Editing, Z.J.S. and K.M.; Visualization, Z.J.S. and K.M.; Supervision, K.M.; Funding Acquisition, K.M.

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