Supplementary Information (SI) for RSC Sustainability.

Decarbonizing Specialty Chemical Manufacturing: Opportunities for Electrochemists

SUPPLEMENTARY INFORMATION

Robert J. Hacku, Thomas J. Henry, Michael A. Kane, Maxwell J. Vance, Zachary J. Sebastian, Glenn Cormack, Tyler Petek, Elisa Sedon, and James R. McKone

Table S1: electrochemical reactions used for scoping study

Reaction	Class of Reaction	General Overall Reaction	Example	Reactor setup	Working Electrode	FE of product	No. of publications
CO2 --> methane	Reduction	$CO_2 + 2H_2O \rightarrow CH_4 + 2O_2$	Zhang et al.[1]	H-Cell	$Cu_3(PO_4)_2$	76%	>100
CO2 --> ethylene	Reduction	$2CO_2 + 2H_2O \rightarrow C_2H_4 + 4O_2$	Zhang et al.[1]	H-Cell	$Cu_3(PO_4)_2$	67%	>100
CO2 --> acetylene	Reduction	$4CO_2 + 2H_2O \rightarrow 2C_2H_2 + 5O_2$	Song et al.[2]	H-Cell	Cu-IO	3%	<10
CO2 --> propylene	Reduction	$6CO_2 + 6H_2O \rightarrow 2C_3H_6 + 9O_2$	Lee et al.[3]	H-Cell	Cu_2O	1%	>10
CO2 --> n-butane	Reduction	$8CO_2 + 10H_2O \rightarrow 2C_4H_{10} + 13O_2$	Lee et al.[3]	H-Cell	Cu_2O	1%	>10
CO2 --> acetone	Reduction	$3CO_2 + 3H_2O \rightarrow C_3H_6O + 5O_2$	Yuan et al.[4]	GDE	N-Gr.O GDE	10%	>10
CO2 --> methanol	Reduction	$2CO_2 + 4H_2O \rightarrow 2CH_3OH + 3O_2$	Munir et al.[5]	H-Cell	Cu-ZnO	70%	>100
n-butane --> maleic anhydride	Oxidation	$C_4H_{10} + 3H_2O \rightarrow C_4H_2O_3 + 7H_2$	Ye et al.[6]	Solid Oxide Membrane	V-PO	8% yield*	<10
propylene --> acrylic acid	Oxidation	$3C_3H_6 + 2H_2O \rightarrow C_3H_4O_2 + 3H_2$	Winiwarter et al.[7]	H-Cell	Pd	11%	<10
acetone --> MIBK	Oxidation	$4C_3H_6O \rightarrow 2C_6H_{12}O + O_2$	Pauwels et al.[8]	H-cell	Pt	15%	<10
nitrobenzene --> aniline	Reduction	$2C_6H_5NO_2 + 2H_2O \rightarrow 2C_6H_5NH_2 + 3O_2$	Li et al.[9]	H-Cell	Carbon Nanotube	45%	>10
cyclohexane --> cyclohexanone	Oxidation	$C_6H_{12} + H_2O \rightarrow C_6H_{10}O + 2H_2$	Zhang et al.[10]	Membrane PFR	V_2O_5/Ti	30%	>10
methanol --> formaldehyde	Dehydrog-enation	$CH_3OH \rightarrow CH_2O + H_2$	Childers et al.[11]	Undivided Cell	Pt/C	36%	>10
cyclohexanone --> adipic acid	Oxidation	$C_6H_{10}O + 3H_2O \rightarrow C_6H_{10}O_4 + 3H_2$	Wang et al.[12]	MEA	V-NiOOHi/Ni foam	82%	>10

Figure S1: alternative version of maintext Figure 5 plotted on linear axes

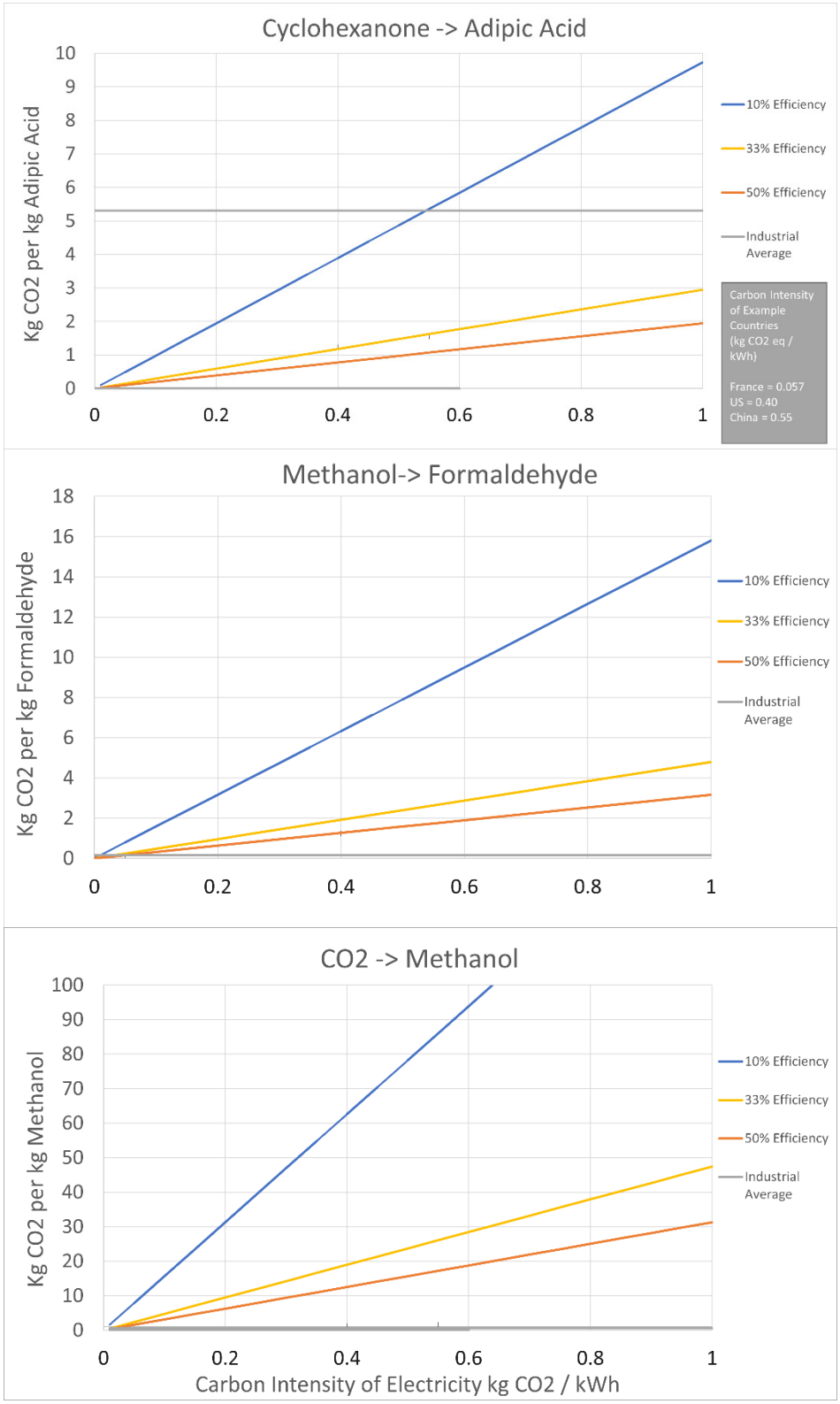
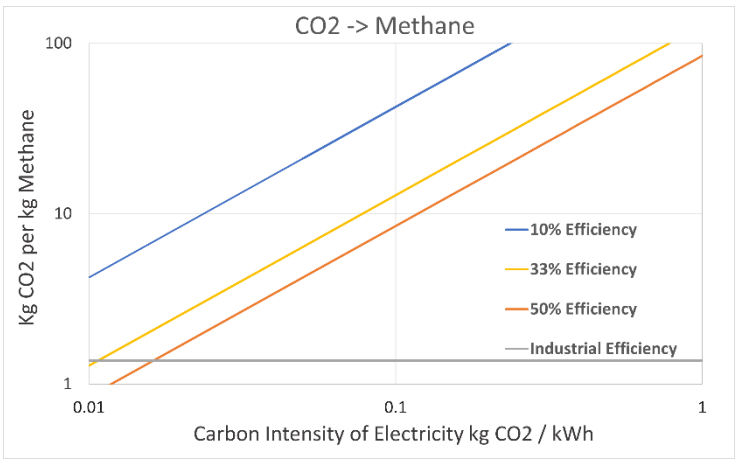
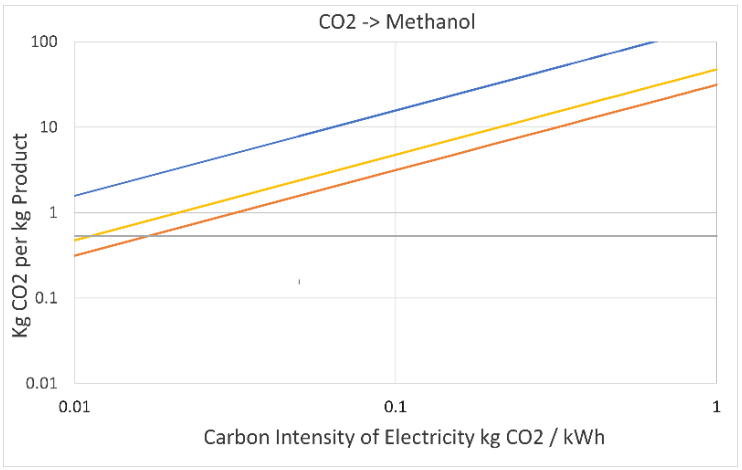
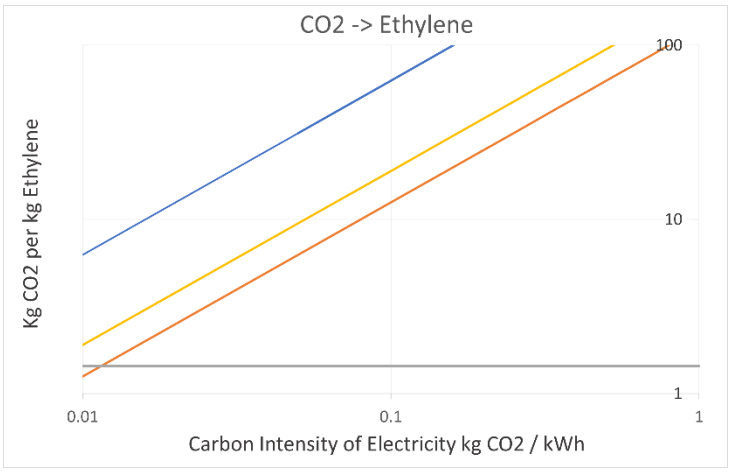


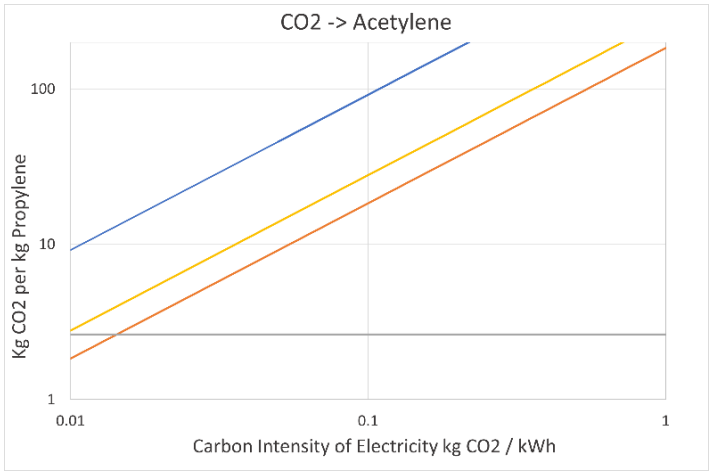
Figure S2: Carbon intensity of electrochemical products with varying carbon intensity of input electricity for transformations investigated in Step 2 of the scoping analysis

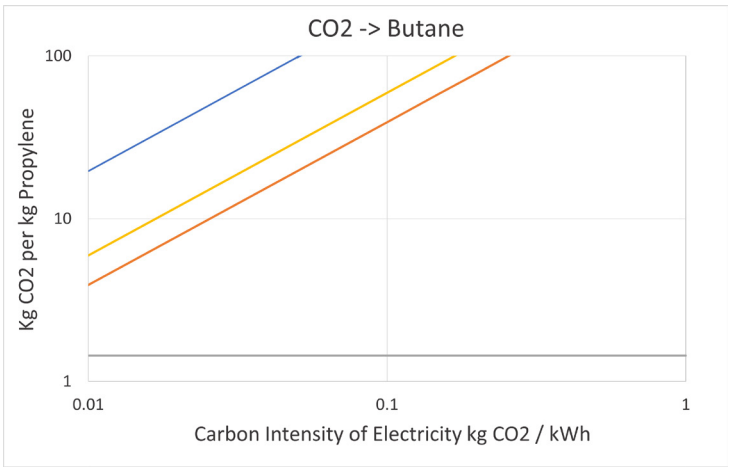
(NOTE: The legend displayed for CO_2 conversion to methane (upper left) applies to all graphs in this section)

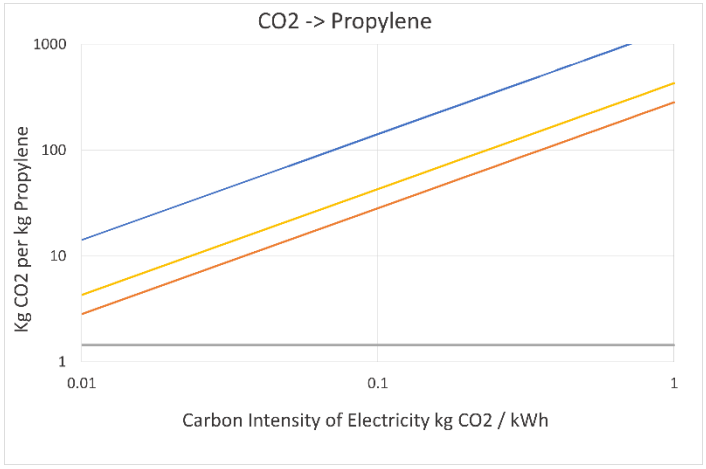


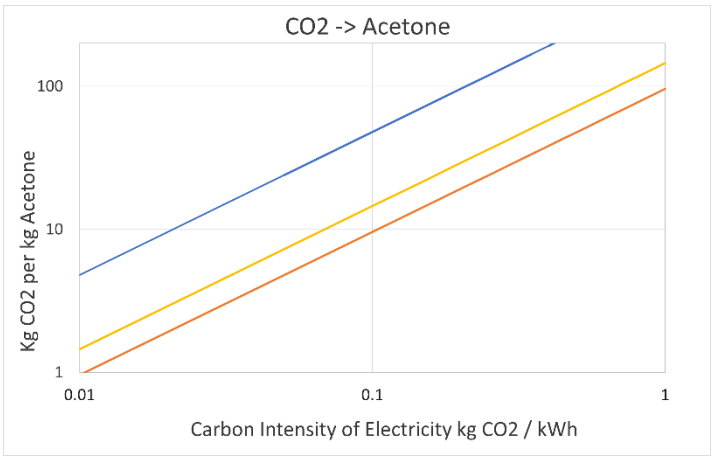


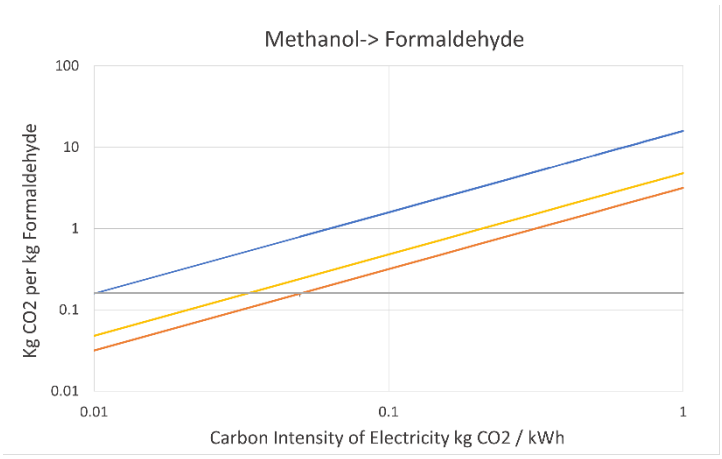


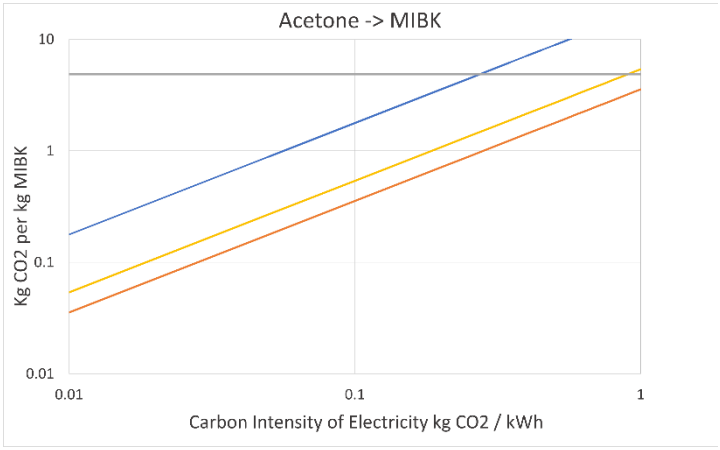


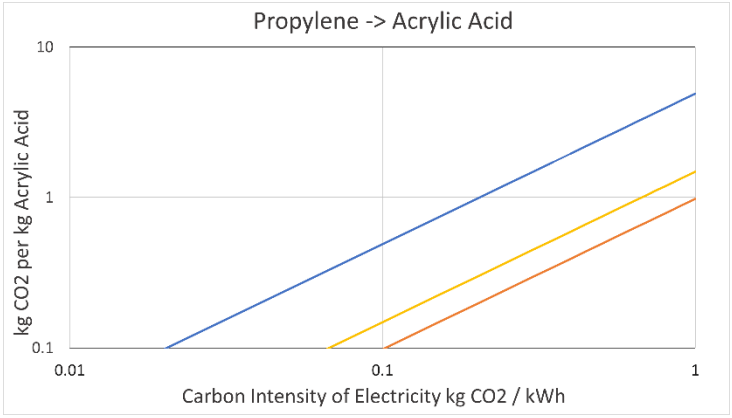


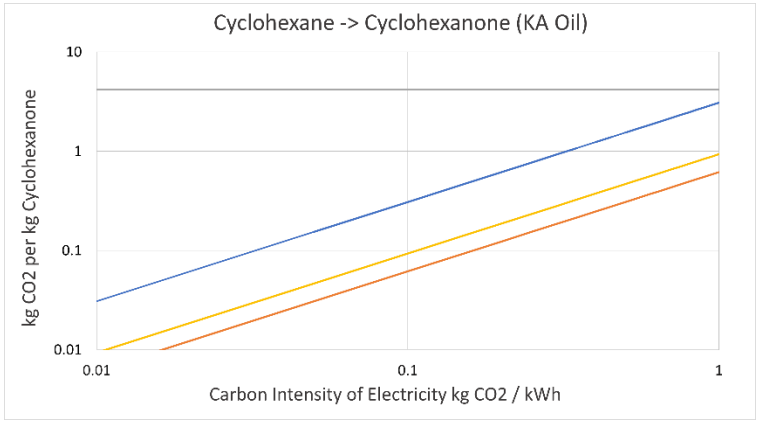


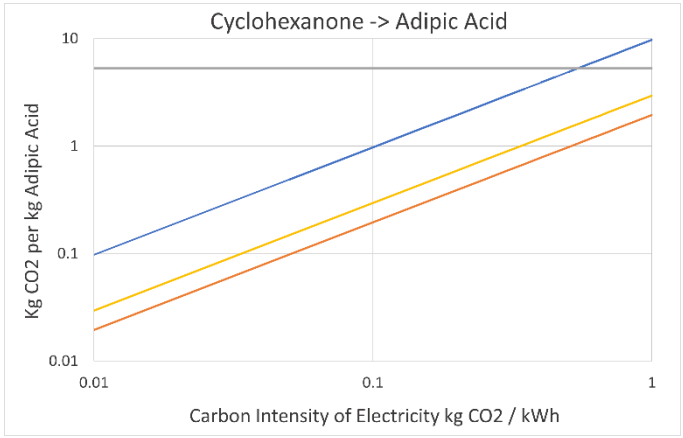

CO2 -> Acetone
Kg CO2 per kg Acetone
100
10
1
0.01
0.1
1
Carbon Intensity of Electricity kg CO2 / kWh

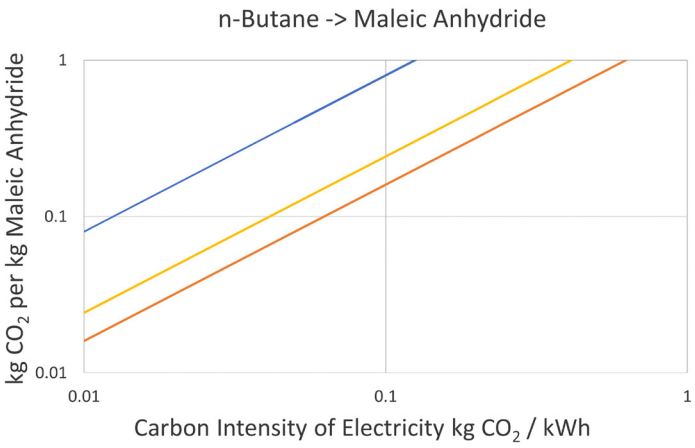

Methanol-> Formaldehyde
Kg CO2 per kg Formaldehyde
100
10
1
0.1
0.01
0.01
0.1
1
Carbon Intensity of Electricity kg CO2 / kWh


Acetone -> MIBK
Kg CO2 per kg MIBK
10
1
0.1
0.01
0.01
0.1
1
Carbon Intensity of Electricity kg CO2 / kWh


Propylene -> Acrylic Acid
kg CO2 per kg Acrylic Acid
10
1
0.1
0.01
0.1
1
Carbon Intensity of Electricity kg CO2 / kWh


Cyclohexane -> Cyclohexanone (KA Oil)
kg CO2 per kg Cyclohexanone
10
1
0.1
0.01
0.01
0.1
1
Carbon Intensity of Electricity kg CO2 / kWh


Cyclohexanone -> Adipic Acid
Kg CO2 per kg Adipic Acid
10
1
0.1
0.01
0.01
0.1
1
Carbon Intensity of Electricity kg CO2 / kWh


n-Butane -> Maleic Anhydride
kg CO2 per kg Maleic Anhydride
1
0.1
0.01
0.01
0.1
1
Carbon Intensity of Electricity kg CO2 / kWh

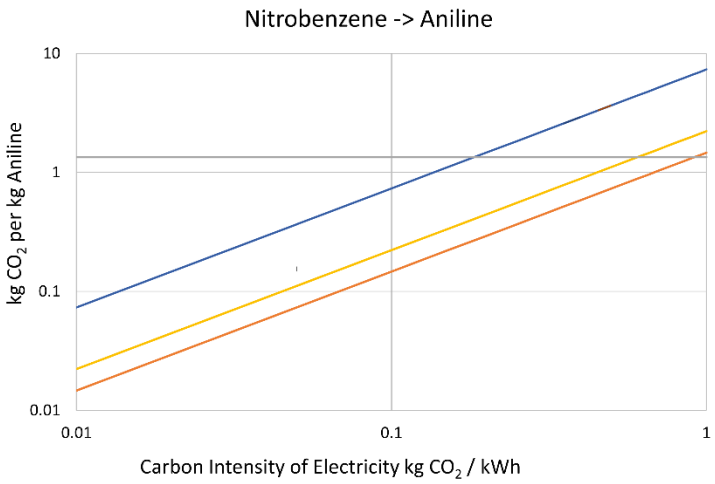
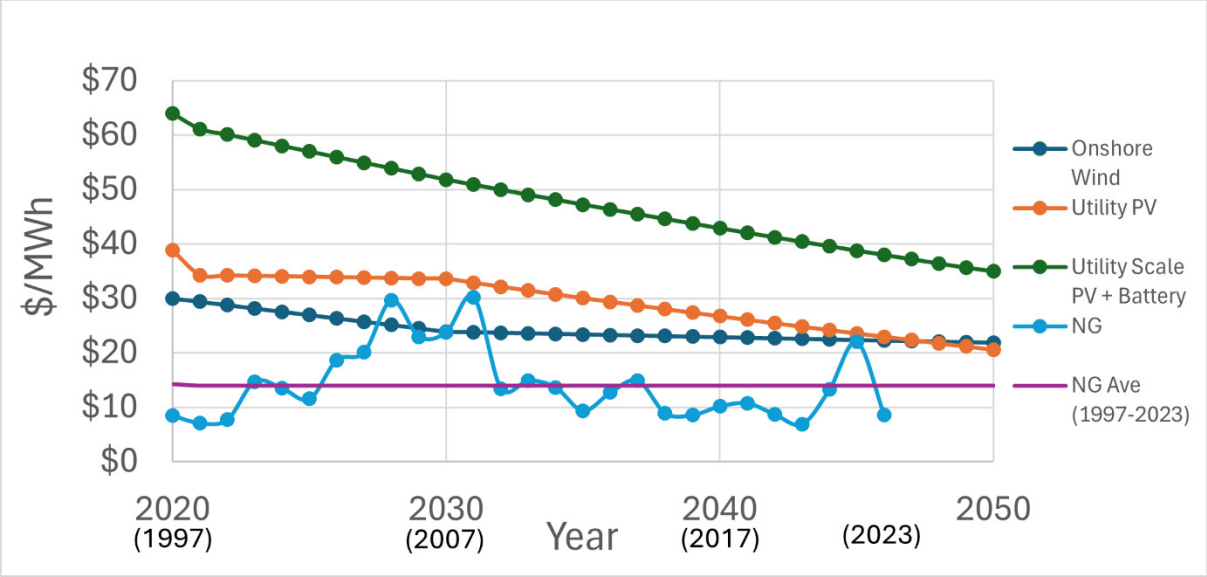

Nitrobenzene -> Aniline
kg CO2 per kg Aniline
10
1
0.1
0.01
0.01
0.1
1
Carbon Intensity of Electricity kg CO2 / kWh

Figure S3: LCOE for renewables compared to raw natural gas price



This figure compiles conservative projections of the levelized cost of electricity (LCOE) for onshore wind, utility scale PV, and utility scale PV with battery storage from the National Renewable energy Laboratory (NREL).[13] Natural gas prices (in unadjusted USD/MWh) from the Henry Hub Natural Gas index over the timescale from 1997 to 2023 are overlaid for comparison.[14]

As renewable electricity generation technology matures, renewable energy technology are not expected to reach the historical average for natural gas on a levelized cost basis. Hence these data illustrate that, to the extent that energy prices drive choices about chemical manufacturing technologies, regulatory mechanisms aimed at pricing in environmental externalities like GHG emissions would almost certainly need to be adopted to justify the broad adoption of renewables.

Determination of upper and lower boundaries for the efficiency factor η

To develop upper- and lower-bound estimates of the efficiency factor η applied to our carbon intensity projections, we worked from published lifecycle inventories for three electrochemical processes that are practiced on the global scale: water electrolysis, chlor-alkali manufacturing, and adiponitrile production by the Monsanto process.

For water electrolysis, the thermodynamic minimum electric work required to convert water into hydrogen and oxygen is 33 kWh/kgH_2 (free energy basis) under standard conditions. Tao et al. note that practical electrolyzers today produce H_2 with a direct electricity input of approximately 55 kWh/kg,[15] implying an overall thermodynamic efficiency of approximately 60%, which could be treated as an upper-bound estimate of $\eta \leq 0.6$. That is, the actual value of η would approach 0.6 if the input electricity accounts for the vast majority of the global warming emissions associated with the process. Notably, a granular assessment from Bareiß et al.[16] estimates a global warming potential value of 29.5 kgCO_2eq/kgH_2 using an electricity mix with GHG emissions intensity of ca. 0.5 kgCO_2/kWh, which translates to $\eta \sim 0.56$.

A more general range-based estimate of η for water electrolysis can be made based on the meta-analysis from Wilkinson et al,[17] which compiles estimates for the carbon intensity of water electrolysis using grid electricity in the range from approximately 7 to 35 kgCO_2/kgH_2. Noting that the carbon intensity of grid mixes globally vary from approximately 0.05 to 0.7 kgCO_2/kWh,[18] this leads to a bounded estimate of $0.2 < \eta < 0.66$.

For chlor-alkali production, a lifecycle inventory from the Euro Chlor industry group[19] estimates a global warming potential of 1.3 kgCO_2/kg NaOH produced—this estimate reflects the sum of all emissions associated with Cl_2, NaOH, and H_2 products on a per kg NaOH basis. The corresponding theoretical minimum electric work input is 1.88 kWh/kg NaOH, implying $\eta \sim 0.6$.

Finally, while we were unable to identify a publicly available lifecycle inventory for acrylonitrile hydrodimerization to adiponitrile by the Monsanto process, a historical account by D.E. Danly reports that the optimized process requires approximately 2.4 kWh/kg of product.[20] We further estimated a thermodynamic minimum electric work required for the hydrodimerization reaction coupled with oxygen evolution as 0.39 kWh/kg (note this value is much lower than that for hydrogen because adiponitrile is a much heavier molecule). This translates to an upper-bound estimate of $\eta \leq 0.16$ purely on the basis of the electrical efficiency for the electrochemical reaction. If we further assume the GHG emissions profile for the overall process is dominated by the emissions associated with the electric power input, the actual value of η would be close to this value. Additional energy inputs (i.e., for product purification) or emissions associated with the production and maintenance of capital equipment would translate to a lower value of η.

Based on the calculations outlined above, we chose $0.1 < \eta < 0.5$ as outer-bound estimates for our thermodynamic model estimating GWP for electrochemical conversions of specialty products. This estimate is plausible under conditions in which the GHG intensity is dominated by that of the energy inputs (i.e., electric power supply), which would be expected even for processes driven predominantly by renewable electricity.

References

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