

Manufacturing Energy and Greenhouse Gas Emissions Associated with United States Consumption of Organic Petrochemicals

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ABSTRACT: Th	e production of commodity	organic chemical	s today is both	Curront		Benchmark Data

primarily sourced from and powered by fossil carbon resources. Toward decarbonization of this key global economic sector, it is imperative to quantitatively understand the contributions to energy usage and greenhouse gas (GHG) emissions along the petrochemical manufacturing supply chain, which can inform judicious policy development and impactful technology options to improve or reimagine existing manufacturing practices. To that end, here we use the Materials Flows through Industry (MFI) tool to estimate the supply chain energy and GHG emissions for 51 organic petrochemicals and 6 intermediates that are globally produced at a capacity of at least 1 million metric tons (MMT) per year. This analysis focuses on supply chains in the United States, from which industrial



data are readily sourced to obtain accurate energy and GHG emission estimates. Analysis for each chemical includes contributions from sourcing chemical feedstocks, electricity use, and fuel usage for transportation and manufacturing. This analysis predicts that process fuel, which is primarily used for heating, dominates GHG emissions in all cases except for chlorochemicals, where electricity is used extensively for the chloroalkali process and results in a large electricity GHG emission contribution ranging from 7 to 54% of total GHG emissions. Additionally, the contribution of electricity to GHG emissions ranges from 6 to 63%, representing the decarbonization potential in the transition toward renewable electricity with existing manufacturing processes. Taken together, these data serve as a critical baseline toward industrial decarbonization of the organic chemical sector, against which to compare changes to the electrical grid and industrial heat sources, improvements to existing technologies to manufacture the same chemicals, and new technologies to source alternative feedstocks to manufacture direct or functional replacement chemicals.

KEYWORDS: chemicals, supply chain modeling, industrial decarbonization, energy efficiency, manufacturing energy

INTRODUCTION

Organic petrochemicals are integral to essentially every dimension of modern life, and the manufacturing scale and associated energy demands required to supply the variety of chemicals used by humankind are concomitantly immense with more than 500 million metric tons (MMT) of material from fossil fuels to various chemical products annually.^{1,2} For the United States (U.S.) alone, according to the Manufacturing Energy Consumption Survey (MECS) from the U.S. Energy Information Administration, the U.S. chemical industry (defined under North American Industry Classification System code 325) consumes approximately 7.1 quads of energy, which is roughly 37% of all manufacturing energy consumption in the U.S.³ Furthermore, reported greenhouse gas (GHG) emissions attributed to U.S. chemical manufacturing totaled 186 million metric tons (MMT) in 2019,⁴ or approximately 2.8% of total estimated GHG emissions in the U.S. in 2019.⁵

Toward mitigating climate change, there is concerted effort in the global community to identify methods of reducing energy consumption and GHG emissions in the chemical sector, $^{2,6-11}$ including prior efforts to estimate the energy requirements of manufacturing petrochemicals.^{12–17} Areas of particular interest include sourcing alternative feedstocks, implementing renewable electricity, and replacing or reducing fossil carbon-derived heat inputs, among others. For all options, it is critical to have an accurate baseline of existing technologies against which new approaches can be compared to enable meaningful industrial decarbonization.

To that end, here we estimate the baseline supply chain energy and GHG emissions for the manufacturing of organic petrochemicals in the U.S. We define supply chain as the "cradle-to-gate" scope of the chemical life cycle, from raw material extraction (cradle) through the final manufacturing step for the chemical of interest (gate). Specifically, we focus on both hydrocarbon chemicals and organic chemicals that

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contain oxygen, nitrogen, or chlorine heteroatoms. These baseline data can inform development of alternative processes for manufacturing chemicals, such as from bio-based or recycled feedstocks.^{18–20}

METHODS

This work closely follows the methodology from our previous work on polymers.²¹ We report estimated supply chain energy requirements and GHG emissions for 51 organic commodity chemicals, each with a global annual consumption exceeding 1 MMT, according to the most recent Chemical Economics Handbook reports.¹⁶ Production years for these chemicals range from 2017 to 2021. The supply chain analysis tool used in this work is Materials Flows through Industry (MFI) (version 2.2.0 (mfitool.nrel.gov)),²² which estimates the net cradle-to-gate energy-related GHG emissions and energy requirements by modeling a network of manufacturing processes that approximate the "mine-to-product" supply chain, where mine refers to any natural resources extraction process (e.g., crude oil, natural gas, etc.). The net result reflects any offsets from the production of coproducts.

The MFI database and inventory data are combined from proprietary sources (primarily ecoinvent and the IHS Process Economics Program Yearbook) and public sources including the U.S. Life Cycle Inventory and the life cycle assessment (LCA) literature.^{23–25} MFI uses the directed network of unit processes to compute and aggregate the material and energy inputs required to produce a final product, outputting the supply chain energy and GHG emissions related to transportation fuel, renewable electricity, fuel for electricity, process electricity, and, for energy consumption specifically, chemical feedstocks. Here, we distinguish chemical feedstocks as those fossil fuels (e.g., natural gas, crude oil, and their derivatives) that are consumed in the production of the final product not via combustion. Meanwhile, process fuel is defined as the fuel required to heat the process, fuel for transportation is the fuel used in moving the chemicals, and fuel for electricity is the fuel energy used to provide electricity. Therefore, by definition, no combustion GHG emissions are ascribed to this type of fossil feedstock use and process emissions (i.e., CO₂ produced during reaction) are not considered. An important assumption and distinction from more traditional LCA methods is that the "technology mix" used for each species of interest is specifically curated to reflect current production patterns in the United States, sourced from both publicly available and proprietary market data. This approach is considered valid because most of the assessed chemicals are produced domestically; only 10 chemicals are imported at rates greater than 10% of U.S. consumption. For all electricity inputs, the 2016 nationally averaged U.S. grid mix is assumed.²⁶ The output of this approach reflects how the energy is consumed between supply chain nodes. For the work presented here, the output is ultimately an energy-containing feedstock material (e.g., a fossil feedstock converted to a chemical or chemicals), and thus, this work provides a representative U.S. industry average for the supply chain energy and GHG emissions of the 51 chemicals utilizing a consistent framework.

Below, we present the MFI data in a series of case studies that group classes of chemicals together based on functional groups. These case studies include (1) platform hydrocarbons; (2) carboxylic acids and anhydrides; (3) alcohols and diols; (4) ketones, aldehydes, and ethers; (5) nitrogen-containing chemicals (including ammonia for reference); and (6) chlorine-containing chemicals. In general, all chemicals in the latter case studies derive from chemical transformation of the platform hydrocarbons. We excluded compounds such as ethanol and glycerol, which, while important industrially, are derived primarily from bio-based sources. For each case study, we report supply chain energy consumption and GHG emissions for producing each chemical on both a per unit mass and an absolute basis, the latter by scaling the per unit mass results by annual U.S. consumption levels. We also report global consumption values for each chemical in the SI.

RESULTS

Platform Chemicals, Additional Hydrocarbons, and Intermediates. The most abundant platform chemicals are the primary output from refining crude oil, natural gas, and synthesis gas, and include methanol, ethylene, propylene, butadiene, benzene, toluene, and xylenes. As the fundamental organic building blocks of the petrochemical industry, these compounds are produced at a combined 64 million metric tons per year (MMT/yr) as of 2020 in the U.S., of which ethylene production is approximately half.¹⁶ These chemicals serve as the starting point for production of essentially all other organic chemical products (both commodity and specialty). Transformations for the chemicals in this study are provided in Figures S1–7.

Estimates of supply chain energy and GHG emissions of U.S. platform hydrocarbon production are presented in Figure 1 and provided in Tables S1-3, with chemical representations of the molecules in Figure 1A. As shown in Figure 1B,C, energy and GHG emissions range from 37 MJ/kg and 0.4 kg CO₂-e/kg (methanol) to 128 MJ/kg and 2.3 kg CO₂-e/kg (butadiene). Similar fossil feedstock energy intensity (denoted as "chemical feedstocks") of approximately 50-60 MJ/kg is exhibited across all platform hydrocarbons, or approximately 71-77% of the overall supply chain energy, with the exceptions of butadiene, which is 95 MJ/kg, and methanol, which is not a hydrocarbon and is 30 MJ/kg. Process fuel energy (for process heat) is lower for ethylene and propylene and generally higher for the larger molecules (butadiene, benzene, toluene, xylenes). Electricity and transportation energy requirements are relatively low for all, relative to more functionalized compounds (vide infra). For combustion GHG emissions, emissions from process fuel dominate, at between 0.45 and 1.71 MJ/kg (56–84%). Note that feedstock energy does not have corresponding GHG emission impact because, by definition, the feedstocks are not combusted but rather converted to products downstream.

As shown in Figure 1D, with their high production volumes of 32 and 15 MMT/yr, respectively, ethylene and propylene stand out on both energy and GHG impacts on an absolute basis, with energy consumption values of 2,000 and 1,000 PJ/ yr, respectively, and GHG emissions of 26 MMT CO_2 -e/yr and 15 MMT CO_2 -e/yr, respectively. Butadiene, while having the highest per mass intensity, exhibits the lowest absolute impact given its relatively low 1.3 MMT/yr production level. The relative intensity of butadiene manufacturing is due to the extraction of butadiene from C4 alkanes, which currently relies on extractive distillation with either *N*-methylpyrrolidone or dimethylformamide but historically also used copper salts.¹⁶

We additionally estimated the supply chain energy and GHG emissions of other hydrocarbons, namely, ethane, propane, butane, styrene, and isoprene. These results are presented in Figure 1E–H with numerical values presented in Tables S4–6. Akin to the chemicals in the subsequent case studies, the main use of the chemicals is for polymer applications; however, propane and butane also find use in heating applications. Ethane and propane are often dehydrogenated to their respective platform molecules, while both isoprene and butadiene are key components of elastomeric materials (e.g., rubber for tires). Styrene is used in the polymerization of polystyrene and as a comonomer in many other polymers such as acrylonitrile–butadiene–styrene

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Figure 1. Platform hydrocarbon chemicals. (A) Chemical structures, names, and abbreviations for the platform hydrocarbons. (B) Per unit mass supply chain energy requirements in megajoules per kilogram of chemical (PJ/kg), classified by energy type. (C) Per unit mass supply chain combustion GHG emissions in kilograms of carbon dioxide equivalent per kilogram of chemical (kg CO_2 -e/kg), classified by emission source. (D) U.S. annual production-scaled supply chain energy requirements in petajoules per year (PJ/yr) and annual production-scaled supply chain combustion GHG emissions in millions of metric tons of carbon dioxide equivalent per year (MMT CO_2 -e/yr). Additional hydrocarbon chemicals. (E) Chemical structures, names, and abbreviations for the additional hydrocarbons. (F) Per unit mass supply chain energy requirements in megajoules per kilogram of chemical (MJ/kg), classified by energy type. (G) Per unit mass supply chain combustion GHG emissions in kilograms of carbon dioxide equivalent per year (G) Per unit mass supply chain combustion GHG emissions in kilograms of carbon dioxide equivalent per kilogram of chemical (kg CO_2 -e/kg), classified by emission source. (H) U.S. annual production-scaled supply chain energy requirements in petajoules per year (PJ/yr) and annual production-scaled supply chain combustion GHG emissions in millions of metric tons of carbon dioxide equivalent per year (MMT CO_2 -e/yr). Production numbers for ethane, propane, and butane are based on a conversion from the annual heating value of these chemicals. Figures S1–7 provide the chemical transformations relevant to each platform chemical. Tables S1–6 provide the numerical data in this figure and the U.S. annual consumption values.

(ABS), styrene-butadiene rubber, and unsaturated polyester resins.

In addition to the platform chemicals and other hydrocarbons, we also examined major intermediates used in key chemical transformations to produce many of the molecules presented below, namely, synthesis gas (syngas, a mixture primarily of carbon monoxide and hydrogen), hydrogen, methane, chlorine gas, nitric acid, and ammonia. These intermediates are either used in the production of the platform chemicals (e.g., syngas for MeOH) or used to incorporate heteroatoms (e.g., nitric acid to functionalize benzene with NO₂ groups), and the supply chain energy and GHG emissions for each are reported in Tables S7 and S8. Of note is that the production numbers for these compounds are not published as they are components of other product streams.

Carboxylic Acids and Anhydrides. Both carboxylic acids and anhydrides are reactive with water, alcohols, epoxides, and amines, which has led to their widespread use for multiple applications. For instance, acetic acid is commonly used as a solvent, and up to 40% of its annual production is consumed to manufacture acetic anhydride for use as an acetylation agent.²⁷ Phthalic anhydride is commonly used to make plasticizers and thermal stabilizers for poly(vinyl chloride) (PVC), and it is also used as a monomer in the synthesis of alkyd resins.^{21,28}



Figure 2. Acids and anhydrides. (A) Chemical structures, names, and abbreviations. (B) Per unit mass supply chain energy requirements in megajoules per kilogram of chemical (MJ/kg), classified by energy type. (C) Per unit mass supply chain combustion GHG emissions in kilograms of carbon dioxide equivalent per kilogram of chemical (kg CO_2 -e/kg), classified by emission source. (D) U.S. annual production-scaled supply chain energy requirements in petajoules per year (PJ/year) and annual production-scaled supply chain combustion GHG emissions in millions of metric tons of carbon dioxide equivalent per year (MMT CO_2 -e/yr). Figure S9 provides the relevant transformations to produce the chemicals in this case study. Tables S9–11 provide the numerical data in this figure and the U.S. annual consumption numbers.

Meanwhile, maleic anhydride,²⁹ adipic acid,³⁰ terephthalic acid, and isophthalic acid³¹ are used in the synthesis of polymers, including unsaturated polyesters, alkyd resins, nylon-6,6, and poly(ethylene terephthalate) (PET).

Supply chain energy and GHG emission impacts for carboxylic acids and anhydrides are shown in Figure 2 and provided in Tables S9-11. Per unit mass intensity impacts range from 37 MJ/kg and 1.2 kg CO₂-e/kg (both acetic acid) to 137 MJ/kg and 4.5 kg CO₂-e/kg (isophthalic acid and adipic acid, respectively). There is a general trend of increasing impact intensities (for both energy and GHG emissions) as the carbon number of the acid or anhydride increases. As shown in further case studies below, such as the alcohols and diols, this trend is not always so clear. Feedstock energy accounts for between 36% (adipic acid) and 64% (maleic anhydride), which is lower than that of the hydrocarbon chemicals. Generally, as more processing steps are needed to synthesize a final chemical product, the greater the nonfeedstock proportion of energy requirements becomes.

Adipic acid exhibits highest per kg GHG intensity due to the the upstream cyclohexanol-cyclohexanone (KA oil) air oxidation process from cyclohexane using nitric acid, which is the dominant route to adipic acid in the U.S. and globally.³⁰ Process fuel contributes the largest share (54–81%) of combustion GHG emissions for all other molecules in this case study.

Impacts related to the production of terephthalic acid (a precursor for PET) stand out on an absolute basis, at 240 PJ/ yr and 7.5 MMT CO_2 -e/yr for supply chain energy and GHG emissions, respectively. Acetic acid and adipic acid are

estimated to require 92 and 73 PJ/yr of supply chain energy, respectively, and emit 3.0 MMT CO_2 -e/yr and 3.1 MMT CO_2 -e/yr, respectively. These two chemicals represent the next two highest chemicals on an absolute basis and both are less than half the value of TPA. Maleic anhydride and isophthalic acid exhibit the lowest absolute impacts due to their relatively low U.S. production levels of 0.292 MMT/yr and 0.147 MMT/yr, respectively.

Alcohols and Diols. Alcohols and diols are an important class of chemicals as intermediates, for use in materials, and as solvents. Isopropanol,³² *n*-butanol, and isobutanol³³ in particular are common solvents for industrial processes and use in household products such as inks and paints. These alcohols are used extensively as solvents due to their volatility, which enables facile removal, and their amphiphilic nature, which can compatibilize aqueous and organic mixtures. Another primary use of alcohols and diols is in polymers. Generally, these applications exploit the propensity for alcohols to react with carboxylic acids or other functionalities to form more complex products in which their functionality and application can be tuned by the coreactant. Ethylene glycol (EG), sometimes referred to as monoethylene glycol, is used both as a coolant and in plastics such as PET.³⁴ 1,4-Butanediol (1,4-BDO) is used in polymer applications,³⁵ and is commonly used as a precursor to tetrohydrofuran (THF).³⁶ Phenol has multiple uses, and it is also commonly converted to other chemicals³⁷ or, with acetone, to bisphenol-A (BPA), which is used as the primary component in polycarbonates and epoxy resins.³⁸ 2-Ethylhexanol can be esterified by reaction with



Figure 3. Alcohols and diols. (A) Chemical structures, names, and abbreviations. (B) Per unit mass supply chain energy requirements in megajoules per kilogram of chemical (MJ/kg), classified by energy type. (C) Per unit mass supply chain combustion GHG emissions in kilograms of carbon dioxide equivalent per kilogram of chemical (kg CO_2 -e/kg), classified by emission source. (D) U.S. annual production-scaled supply chain energy requirements in petajoules per year (PJ/year) and annual production-scaled supply chain combustion GHG emissions in millions of metric tons of carbon dioxide equivalent per year (MMT CO_2 -e/yr). Figure S10 provides the relevant transformations to produce the chemicals in this case study. Tables S12–14 provide the numerical data in this figure and the U.S. annual consumption numbers.

carboxylic acids to produce fragrances, surfactants, moisturizers, lubricants, adhesives, coatings, and plasticizers for PVC.³⁹

Supply chain energy and GHG emissions to produce the alcohols and diols examined here are provided in Figure 3 with numerical data presented in Tables S12–14. Per unit mass intensity impacts range from 45 MJ/kg and 1.1 kg CO₂-e/kg (EG) to 136 MJ/kg and 4.6 kg CO₂-e/kg (1,4-BDO). Unlike with the acids and anhydrides, there is no clear trend of increasing impact intensities as the carbon number of the alcohols or diol increases. Despite having the lowest per unit mass intensities, EG exhibits the highest absolute supply chain energy and combustion GHG impact primarily due to its substantial production volume (31 MMT/yr).⁴⁰

Aldehydes, Ketones, and Ethers. Aldehydes, ketones, and ethers are an important class of chemicals due to their use as precursors to other organochemicals or polymers. The inherent reactivity of these compounds enables reactions with water, alcohols, amines, and electron-deficient aromatic carbons. These chemicals are also used as building blocks for the other molecules in the case studies presented here (e.g., ethylene oxide is used to manufacture EG,⁴¹ acetone reacts with phenol to form BPA,⁴² KA oil is used to form multiple chemicals including caprolactam⁴³ and adipic acid).³⁰ THF can be used as a monomer precursor to polyols for polyurethanes but predominately finds use as a solvent in household products (alongside other chemicals) and in PVC production.³⁶ Formaldehyde and ethylene oxide both serve as polymer precursors, with formaldehyde used predominantly in phenolbased resins (>89% of total demand)⁴⁴ and ethylene oxide being used as a prominent precursor in the synthesis of polyethers.⁴¹ As these building block molecules are often used for specialty chemicals, they are routinely transformed to other molecules that do not individually exceed a market size > 1 MMT/year.

Supply chain energy and GHG emission impacts to produce aldehydes, ketones, and ethers are provided in Figure 4 with numerical data presented in Tables S15-17. Per unit mass intensity impacts range from 47 MJ/kg and 0.7 kg CO₂-e/kg (formaldehyde) to 159 MJ/kg and 6.0 kg CO₂-e/kg (THF). Fossil feedstock energy intensity across the chemicals included in this case study range from 36 MJ/kg for formaldehyde to 78 MJ/kg (THF) across a range of 35% (KA oil) to 77% (formaldehyde).

GHG emission intensities are mostly attributed to process fuel, with the exception of ethylene oxide, which has an electricity-intensive manufacturing supply chain where electricity accounts for approximately 63% of supply chain combustion GHG emissions. The dominant route for ethylene oxide production is the oxidation of ethylene using highly pure oxygen gas (instead of the air-based oxidation employed in older plants), which is produced by air separation in an electricity-intensive process.⁴¹ Excluding ethylene oxide, process fuel accounts for between 60% (methyl tert-butyl ether (MTBE)) and 69% (methyl iso-butyl ketone (MIBK)). On an absolute basis, formaldehyde and ethylene oxide exhibit the highest absolute impacts, with acetone and MTBE at approximately half of the former group's absolute supply chain energy impact and two-thirds of the former group's absolute supply chain GHG emission impact. Notably, acetaldehyde production is low and declining. Previously, acetaldehyde was commonly used in the production of acetic acid, but alternative routes, mostly the carbonylation of methanol, are now more widespread, which attributes to its lower absolute impact.⁴⁵

The supply chain energies and GHG emissions for this group of chemicals also exhibit some trends with molecule complexity. Formaldehyde exhibits the lowest impact of the ketones and aldehydes, but as the carbon number increases from acetaldehyde to MIBK, the resultant supply chain energies and GHG emissions increase. KA oil follows a similar



Figure 4. Aldehydes, ketones, and ethers. (A) Chemical structures, names, and abbreviations. (B) Per unit mass supply chain energy requirements in megajoules per kilogram of chemical (MJ/kg), classified by energy type. (C) Per unit mass supply chain combustion GHG emissions in kilograms of carbon dioxide equivalent per kilogram of chemical (kg CO_2 -e/kg), classified by emission source. (D) U.S. annual production-scaled supply chain energy requirements in petajoules per year (PJ/year) and annual production-scaled supply chain combustion GHG emissions in millions of metric tons of carbon dioxide equivalent per year (MMT CO_2 -e/yr). Figure S11 provides the relevant transformations to produce the chemicals in this case study. Tables S15–17 provide the numerical data in this figure and the U.S. annual consumption numbers.

trend with GHG emissions, but not with supply chain energy, as the production of NO_x species disproportionately contributes to emissions.⁴⁶ The ethers meanwhile do not exhibit any trends associated with carbon number or complexity. Indeed, THF exhibits the highest GHG emissions for the oxygenated compounds, which is the result of THF being formed from the dehydration and cyclization of 1,4-BDO, which also exhibits high supply chain energies and GHG emissions, as noted above.

Organonitrogen Compounds. Most of the organonitrogen compounds that meet the market size for inclusion in this work are used as precursors for other materials or exist within the same supply chain. Acrylonitrile is used in many polymer applications (e.g., acrylic fibers and ABS account for >70% of its use) and as a precursor for carbon fiber,⁴⁷ caprolactam is used to make nylon-6,⁴³ hexamethylenediamine (HMDA) is used with adipic acid to synthesize nylon-6,6,48 and the isocyanates are used in polyurethanes.⁴⁹ Aniline, which is formed from nitrobenzene, is used primarily as a precursor to dyes, monomers (e.g., methylene diisocyanate), and pharmaceuticals.⁵⁰ Dinitrotoluene⁵¹ is used to produce toluene diamine (TDA),⁵² which in turn is used with phosgene to produce toluene diisocyanate (TDI), which is the primary isocyanate used in polyurethanes. Overall, the nitrogen groups in these compounds lead to their use as building blocks in multiple commodity applications.

Supply chain energy and GHG emission impacts to produce organonitrogen compounds are provided in Figure 5 with numerical data presented in Tables S18–20. Per unit mass intensity impacts range from 44 MJ/kg (TDA) and 1.2 kg CO_2 -e/kg (nitrobenzene) to 180 MJ/kg (HMDA) and 7.9 kg

 CO_2 -e/kg (methylene diphenylene isocyanate, MDI). Like 1,4-BDO above, HMDA is made predominately from acrylonitrile but can also be synthesized from the hydrocyanation of butadiene. Both production routes thus contribute to a higher supply chain energy and greater GHG emissions than its counterparts.⁴⁸

There are no distinct trends between the complexity of the chemicals in this group and their supply chain energies or GHG emissions. However, some supply chain effects are apparent in the chemicals that are chemical transformations of other chemicals found in this group. As an example, nitrobenzene is converted to aniline and exhibits a lower supply chain energy and GHG emission as it is a precursor.⁵⁰ Meanwhile, dinitrotoluene is converted to TDA, which is converted to TDI, and finally methylene diisocyanate, in a manufacturing supply chain that exhibits increasing GHG emissions with the addition of each step.^{49,53} The notable increase between TDA and TDI can be attributed to the use of phosgene as a stoichiometric reagent, plus additional base, to form the isocyanate.

Organochlorine Compounds. The organochlorine compounds noted here are used as solvents or reactants for polymer precursors. As a solvent, the chloro-containing compounds are considered nonpolar and used across multiple applications due to their favorable intermediate polarity between water and alkanes.⁵⁴ As polymer and material precursors, organochlorine compounds are used either because the chlorine atom is highly reactive and can react with less reactive substituents or because the chlorine atom imparts favorable properties. BPA is reacted with phosgene to produce polycarbonates, which are strong, tough, optically clear plastics



Figure 5. Organonitrogen compounds. (A) Chemical structures, names, and abbreviations. (B) Per unit mass supply chain energy requirements in megajoules per kilogram of chemical (MJ/kg), classified by energy type. (C) Per unit mass supply chain combustion GHG emissions in kilograms of carbon dioxide equivalent per kilogram of chemical (kg CO_2 -e/kg), classified by emission source. (D) U.S. annual production-scaled supply chain energy requirements in petajoules per year (PJ/year) and annual production-scaled supply chain combustion GHG emissions in millions of metric tons of carbon dioxide equivalent per year (MMT CO_2 -e/yr). Figure S12 provides the relevant transformations to produce the chemicals in this case study. Tables S18–20 provide the numerical data for this figure and the U.S. annual consumption numbers.

with multiple applications, or with epichlorohydrin to form bisphenol-A diglycidyl ether, which is the main material precursor to epoxy resins.^{38,55} Ethylene dichloride is used in the synthesis of poly(vinyl dichloride) and mainly as a precursor to vinyl chloride for PVC manufacturing.⁵⁶

Supply chain energy and GHG emissions to produce the organochlorine compounds are provided in Figure 6 with numerical data provided in Tables S21–23. Supply chain energies range from 36 (COCl₂) to 140 MJ/kg (ECH) with GHG emissions ranging from 1.8 (COCl₂) to 7.3 (ECH) kg CO_2 -e/kg. Electricity consumption is a defining feature of the organochlorine chemical supply chain, namely, the chlor-alkali process to produce chlorine from sodium chloride is electricity intensive, even when utilizing modern membrane technology.⁵⁷ Electricity generation is responsible for between 24 and 34% of total supply chain energy among the chlorine compounds and between 43 and 53% of supply chain GHG emissions.

Among the organochlorine compounds, epichlorohydrin exhibits the highest per unit mass impacts due to a high process fuel requirement for its manufacture, as its production proceeds via the intermediate, allyl chloride.^{38,58} On an absolute basis, ethylene dichloride and the vinyl chloride monomers (both precursors in the PVC supply chain) dominate chloro-chemical impacts on an absolute basis.

DISCUSSION

The current study employs a self-consistent framework to aggregate supply chain energy and GHG emissions for all chemicals manufactured at a scale >1 MMT/year globally. The intention is for these data to serve as a baseline to design new processes or improve existing manufacturing processes to reduce GHG emissions and supply chain energies. Reductions

in these intensity metrics may come from the use of alternate forms of electricity, heating, chemicals, feedstocks, or other methods.^{8,59}

Process fuel as defined here is the energy from combustion of fossil fuels to drive a chemical process, often in the form of heat. Most commonly this accounts for the energy necessary to produce steam, which is widely used in distillation. In the case studies presented here, process fuel accounts for 7% (ethylene oxide) to 54% (adipic acid) of the supply chain energy and 17% (ethylene oxide) to 84% (benzene) of GHG emissions. Toward decarbonization of heat, Thiel and Stark recently described four methods to decarbonize heat, namely, via zero-carbon heat, electrification, zero-carbon fuels, and improved heat management.⁸

In addition to changing the heating source, it is also possible to reduce the fuel for the electricity component using alternate process designs or changing the process input from coal and natural gas sources to renewable sources such as electricity derived from solar and wind energy. Electricity commonly contributes to multiple processing operations such as cooling and nonsteam heating. Fuel for electricity contributes 1% (MeOH) to 35% (chloroform, TCM) of the supply chain energies and 6% (methanol) to 63% (ethylene oxide) of GHG emissions. While a transition in the grid mix from fossil-based electricity to renewable sources will eventually reduce the GHG impacts associated with electricity consumption,^{60,61} further reduction can be achieved by colocating future chemical plants with sources of renewable electricity. Thiel and Stark also note that there is a synergistic effect between electrifying heating processes and deriving electricity from "greener" sources to achieve a greater degree of decarbonization.8



Figure 6. Organochlorine compounds. (A) Chemical structures, names, and abbreviations. (B) Per unit mass supply chain energy requirements in megajoules per kilogram of chemical (MJ/kg), classified by energy type. (C) Per unit mass supply chain combustion GHG emissions in kilograms of carbon dioxide equivalent per kilogram of chemical (kg CO_2 -e/kg), classified by emission source. (D) U.S. annual production-scaled supply chain energy requirements in petajoules per year (PJ/year) and annual production-scaled supply chain combustion GHG emissions in millions of metric tons of carbon dioxide equivalent per year (MMT CO_2 -e/yr). Figure S13 provides the relevant transformations to produce the chemicals in this case study. Tables S21–23 provide the numerical data in this figure and the U.S. annual consumption numbers.

Aside from changing the chemical process to reduce the components of process fuel and fuel for electricity, alternative feedstocks can reduce the chemical feedstock portion of the supply chain energy. In the case studies presented here, chemical feedstocks represent 14-81% of the supply chain energies and overall do not directly contribute to GHG emissions. Bio-based feedstocks or waste-based feedstocks can be implemented to accomplish reductions.^{18,62-65} Bio-based chemicals also have the potential to provide reduced GHG emissions due to the carbon that is sequestered during cultivation; however, the reduction potential must be evaluated on a case-by-case basis as different separation processes will yield different results and it is possible for a bio-based chemical to have a higher energy and/or GHG impact than those of its petrochemical counterpart, especially in the cases of low atom and process efficiency.^{66–68}

Alternative chemical formulations can also provide the potential to reduce the supply chain energy and GHG emissions. As noted above, on a per kilogram basis, the organonitrogen chemicals exhibited the largest supply chain energies and GHG emissions. Isocyanates are a large source of emissions, especially when compared to their precursor molecules phosgene and various amines. Thus, in this example, chemistries that avoid the use of isocyanates offer the potential to lower the supply chain energy and GHG emissions. For example, a shift to manufacturing polyhydroxy urethanes over polyurethanes, which use amines in place of isocyanates, could enable broad reductions.^{69,70} If TDA could be used in place of TDI, a 64 and 68% reduction in supply chain energy and GHG emissions could be obtained, respectively. At the time of writing, polyhydroxy urethanes have gained traction as they exhibit better adhesion than traditional polyurethanes and

avoid isocyanates; however, multiple challenges remain to be overcome for these types of material replacements.⁶⁹

The results of this work align with other assessments of chemical manufacture. Table S24 compares the 51 chemicals and 6 intermediates presented in this study by the reported MFI GHG emission results and by global warming potentials (GWPs) calculated from ecoinvent 3.3²⁵ background data and the Tool for Reduction and Assessment of Chemicals and Other Environmental Impacts (TRACI).⁷¹ Specifically, the uncertainty range of the GWPs (estimated using in-built ecoinvent uncertainty distributions and Monte Carlo analysis with 100 runs) was compared to the MFI GHG emissions, as well as to the sensitivity range that could be obtained from MFI by assuming different production pathways. Out of the 57 chemicals, 31 exhibit overlap between the MFI sensitivity range and ecoinvent uncertainty range, and seven chemicals are not available in the ecoinvent database. Of the 19 remaining chemicals, 10 possess <20% difference between the data sets. These differences can be attributed partially to the geographical scope of the databases; namely, ecoinvent is predominantly focused on manufacturing in the EU while MFI uses U.S.-specific manufacturing routes. Additionally, differences arise because MFI does not account for process emissions (i.e., GHGs emitted due to the reaction chemistry). Most of the chemicals studied here (38 out of 51) have process emissions that are less than 10% of the total emissions; however, Table S24 notes where there are large deviations, notably in the chemicals that use nitric acid in their manufacture (e.g., adipic acid). GWPs reported by Franklin Associates⁷² for ethylene and propylene similarly fall within the sensitivity range of MFI results, with variations likely due to differences in the assumed production technology.

This study provides an important baseline for individual chemicals. However, many of these chemicals exist in the same supply chain (i.e., they are consumed in the production of other in-scope chemicals), and thus, a simple cumulative data aggregation is not representative of the organic petrochemical manufacturing industry. Overall, the results for the organic petrochemicals examined in this study will enable researchers to prioritize innovations relative to incumbent manufacturing processes for the most impact from a supply chain energy and GHG emission perspective. As new processes and associated process models are developed, comparisons of these data using self-consistent methods could ultimately enable more efficient processes and eventual decarbonization of the organic chemical manufacturing sector.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.2c05417.

Numerical data for all figures and representative chemical transformations between chemicals in this study are supplied in the accompanying PDF document (PDF)

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Notes

The authors declare no competing financial interest.

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