ANNUAL REVIEWS

Annual Review of Chemical and Biomolecular Engineering

Models for Decarbonization in the Chemical Industry

Yuan Yao,[1,2] Kai Lan,[1] Thomas E. Graedel,[1] and Narasimha D. Rao[3,4]

[1]Center for Industrial Ecology, Yale School of the Environment, Yale University, New Haven, Connecticut, USA; email: y.yao@yale.edu

[2]Chemical and Environmental Engineering, Yale School of Engineering and Applied Science, Yale University, New Haven, Connecticut, USA

[3]Yale School of the Environment, Yale University, New Haven, Connecticut, USA

[4]International Institute for Applied Systems Analysis, Laxenburg, Austria

Annu. Rev. Chem. Biomol. Eng. 2024. 15:3.1–3.23

The *Annual Review of Chemical and Biomolecular Engineering* is online at chembioeng.annualreviews.org

https://doi.org/10.1146/annurev-chembioeng-100522-114115

Keywords

decarbonization technologies, chemical industry, modeling, greenhouse gas emissions, industrial ecology, climate change

Abstract

Various technologies and strategies have been proposed to decarbonize the chemical industry. Assessing the decarbonization, environmental, and economic implications of these technologies and strategies is critical to identifying pathways to a more sustainable industrial future. This study reviews recent advancements and integration of systems analysis models, including process analysis, material flow analysis, life cycle assessment, techno-economic analysis, and machine learning. These models are categorized based on analytical methods and application scales (i.e., micro-, meso-, and macroscale) for promising decarbonization technologies (e.g., carbon capture, storage, and utilization, biomass feedstock, and electrification) and circular economy strategies. Incorporating forward-looking, data-driven approaches into existing models allows for optimizing complex industrial systems and assessing future impacts. Although advances in industrial ecology–, economic-, and planetary boundary–based modeling support a more holistic systems-level assessment, more effects are needed to consider impacts on ecosystems. Effective applications of these advanced, integrated models require cross-disciplinary collaborations across chemical engineering, industrial ecology, and economics.

1. INTRODUCTION

The chemical industry plays a vital role in modern society. In 2017, the industry contributed $5.7 trillion (around 7.1%) to global gross domestic product and provided 120 million jobs (1). The chemical industry is one of the largest energy consumers and greenhouse gas (GHG) emission sources. In 2020, global chemical production consumed 9% of natural gas and 13% of oil and emitted 13% of industrial direct CO_2 emissions (2–4). Decarbonization of the chemical industry is needed urgently, especially given the critical role it may play in supporting the net-zero targets of other sectors, e.g., supplying low-carbon fuels for energy and transportation.

Several global studies have explored decarbonization pathways for the chemical industry (2, 5–9). Other studies have reviewed decarbonization technologies for chemical production (10–13). Previous literature has provided quantitative assessment and data using various modeling approaches, such as process analysis, material flow analysis (MFA), life cycle assessment (LCA), techno-economic analysis (TEA), and machine learning (ML). Those methods have been reviewed individually for specific pathways, e.g., process analysis for plastic recycling (14), or for chemicals in general (15, 16). As a supplement and update to previous reviews, this article analyzes how different analytical methods have been advanced and integrated for assessing decarbonization technologies and strategies in the chemical industry, as well as how chemical engineers can leverage industrial ecology and economic tools to better understand and quantify systems-level effects of technology deployment and industrial decarbonization. This article focuses on the models that not only assess the decarbonization potential of various pathways but also evaluate the technical, environmental, and economic implications of implementing decarbonization technologies and strategies in chemical production.

There are many decarbonization pathways for the chemicals industry. This review focuses on promising pathways identified by previous studies (2, 13), including carbon capture and storage (CCS) and carbon capture and utilization (CCU), alternative feedstocks, and electrification and other process improvements. This study also includes demand-side strategies, such as circular economy practices that enhance resource utilization efficiency and reduce chemical demand. The environmental, economic, and decarbonization performances of technologies often differ by scale. The multi-scale effects must be assessed by different analytical methods (see **Figure 1**). Therefore, this review first introduces analytical methods (Section 2), followed by their applications for micro-/mesoscale (Section 3) and macroscale (Section 4) assessments of decarbonization technologies in the chemical industry.

2. ANALYTICAL METHODS

This section briefly introduces five methods that previous studies have applied for evaluating decarbonization technologies and strategies in the chemical industry. MFA and LCA are industrial ecology methods that have been applied to broad industrial activities and products. The recent MFA and LCA applications for chemicals have leveraged chemical process analysis and TEA to enable the assessment and optimization of emerging or traditional technologies considering technical, environmental, and economic performance. Among the five methods reviewed here, ML is the only data-driven method and has been applied to chemical processes when knowledge-based information is lacking. This section briefly introduces the general concepts and examples of these methods, and their applications to individual decarbonization pathways in the chemical industry are reviewed in Section 3.

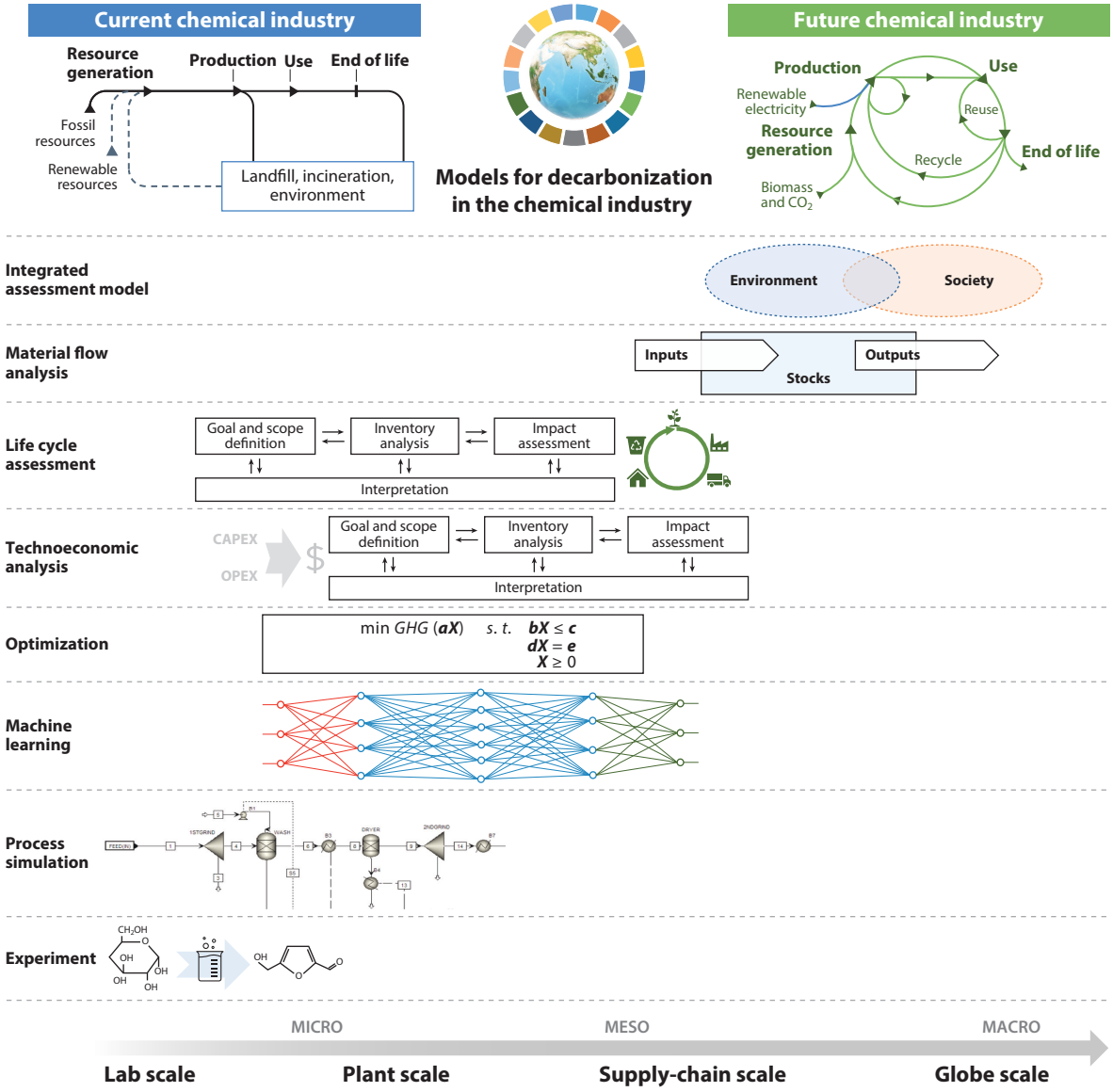

Figure 1

Micro-, meso-, and macro-level modeling techniques for decarbonization technologies and strategies in the chemical industry (17–21).

2.1. Material Flow Analysis

MFA is a key methodology in the study of the physical functioning of society. The goal of an MFA is to quantify the input and output flows of a specific material as it proceeds through its life cycle from initial mineral deposit acquisition to processing, incorporation into intermediate products (such as resins), manufacture of final goods (such as piping), incorporation into use, and (eventually) recovery for reuse or (in many cases) discard.

Figure 2 illustrates a typical (although complex) MFA: plastics in the United States in 2015 (22). Seven specific plastics and one plastics group are followed quantitatively step by step from

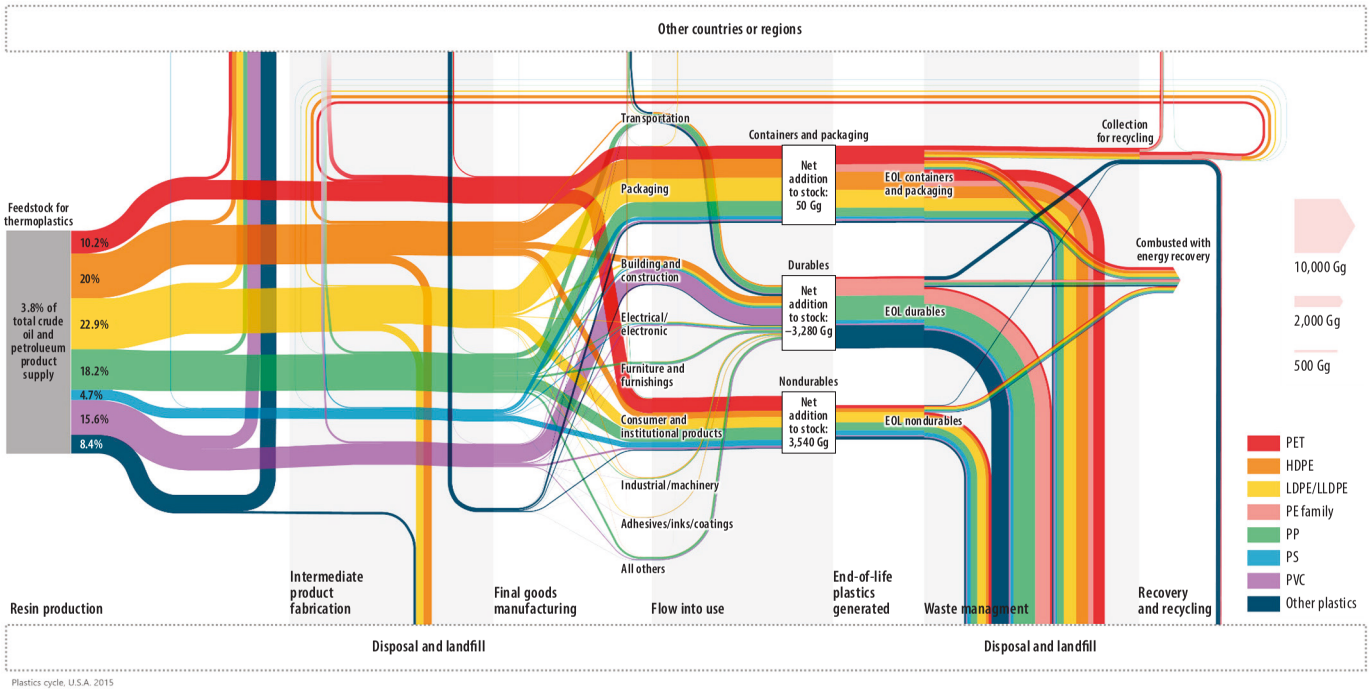

Figure 2

Material flow analysis of plastics supply chains in the United States. Abbreviations: EOL, end of life; HDPE, high-density polyethylene; LDPE, low-density polyethylene; LLDPE, linear low-density polyethylene; PE, polyethylene; PET, polyethylene terephthalate; PP, polypropylene; PS, polystyrene; PVC, polyvinyl chloride. Figure reproduced with permission from Reference 22; copyright 2021 Elsevier.

the initial feedstocks to final disposal. Plastic flows are divided into three categories: containers and packaging, durables, and nondurables. Following eventual discard, the fate of most plastic products in the United States is disposal.

Figure 2 is a Sankey diagram, named after the Irish engineer who originated it in the late eighteenth century. In such diagrams, line widths provide a visual picture of the relative flow magnitudes. Other examples of MFA related to the chemical industry include Levi & Cullen's (23) comprehensive industrial carbon study and Chaudhari and colleagues' (24) plastics supply chains analysis.

2.2. Life Cycle Assessment

LCA is a standardized method to evaluate environmental impacts across the life cycle of a product or service, including raw material acquisition, production, use phase, and end of life (cradle to grave) (25). LCA includes four phases: goal and scope definition, life cycle inventory (LCI) analysis, life cycle impact assessment, and interpretation. During the goal and scope definition phase, the purpose of an LCA (e.g., intended use and audience of the study) and scope (e.g., functional unit, system boundary, environmental impact categories) must be defined and determined clearly. During LCI analysis, relevant inputs and outputs of processes (e.g., mass and energy balances) within the system boundary are collected. The compiled LCI results are converted to specific environmental impacts in the life cycle impact assessment phase. Finally, the results are interpreted based on the goal and scope of the study, and necessary sensitivity checks and quality evaluations are conducted before conclusions and recommendations are made. Kleinekorte et al. (16) and Bakshi (15) have reviewed LCA applications for the sustainable design of chemical products, processes, and supply chains.

Carbon accounting and carbon footprint analysis are based on LCA methods but focus only on GHG emissions and sinks. Different GHGs, such as CO_2, CH_4, N_2O, and fluorinated gases, often are aggregated based on their global warming effects across a time horizon relative to CO_2 and reported in the unit of CO_2 equivalent (26). The Intergovernmental Panel on Climate Change (26) publishes characterization factors of non-CO_2 GHGs for different time horizons (e.g., 20, 100, and 500 years). Carbon accounting can be applied at product, process, corporation, landscape, national, and global levels and often classifies GHG emissions into three scopes. Scope 1 includes direct, on-site GHG emissions; Scope 2 includes GHG emissions associated with purchased electricity; and Scope 3 GHG emissions are related to upstream (e.g., material acquisition) and downstream (e.g., end-of-life) operations (27).

2.3. Process Analysis

Process analysis in the chemical industry analyzes the process performance of chemical production, e.g., investigating material and energy balances, process variables, and properties of process materials (28). Because many decarbonization technologies have low technology readiness levels (TRLs), industrial-scale process information (e.g., mass and energy balances, environmental emissions) needed by LCA and TEA is often lacking. Process analysis provides engineering-rigorous assessments of potential large-scale production based on lab-verified data and/or process simulations, offering a robust means to address the data challenges of TEA and LCA. For low-TRL systems with alternative reaction and process pathways, superstructure-based process design, synthesis, and optimization methods have been developed in process systems engineering, which generates process flowsheets with conditional flow paths and computes an optimal structure for one or multiple objectives, e.g., to maximize or minimize specific performance indicators (29). As

Figure 1 shows, process analysis can scale up conceptual/lab-scale exploration to a computational level relevant to real-world chemical production and supply chains.

2.4. Techno-Economic Analysis

TEA evaluates the economic performance of a product, process, or service based on its technical performance (21). TEA has been used widely to assess the economic viability of emerging technologies and products, commonly at the process or plant level. A TEA framework similar to the four phases of LCA has been proposed (21). In the phase of goal and scope definition, the overall goal is defined along with the determined scope of the TEA. In the inventory phase, the technical data (e.g., mass and energy balances, process variables or parameters) and economic data (e.g., equipment cost, labor cost) are collected and analyzed. In the calculation phase, technical and economic performance results are generated based on selected indicators (e.g., minimum selling price, net present value, energy efficiency). And in the interpretation phase, the technical and economic performance results are interpreted based on the goal and scope of the TEA study (21).

2.5. Machine Learning

ML is defined as a computer program that "is said to learn from experience (*E*) with respect to some class of tasks (*T*) and performance measure (*P*), if its performance at tasks in *T*, as measured by *P*, improves with experience *E*" (30, p. 2). Common ML techniques include artificial neural networks, support vector machines, and random forest (31). In a typical ML workflow, a model is trained and validated using data collected from experiments or literature and then used for prediction or optimization. ML has been used to develop surrogate models for chemical processes or production systems (e.g., based on process simulation data or operating data), optimization, process control, and fault diagnosis (31, 32). Several studies have reviewed ML applications in the chemical industry (31, 32). Therefore, this review includes mainly ML applications that enhance MFA, LCA, TEA, and process analysis of decarbonization technologies in the chemical industry.

3. MICRO- AND MESO-MODELING FOR DECARBONIZATION TECHNOLOGIES

This section discusses micro- and mesoscale modeling for three decarbonization pathways in the chemicals industry: carbon capture, utilization, and storage (CCUS); alternative feedstock; and electrification and other process improvements. Microscale modeling simulates unit operations or a chemical plant equipped with one or multiple decarbonization technologies. Mesoscale modeling includes interconnected manufacturing activities or groups, such as the supply chain or life cycle of a chemical, or chemical plant networks.

3.1. Carbon Capture, Utilization, and Storage

CCUS refers to a suite of technologies involving the capture of CO_2 from diverse sources (carbon capture, CC), storing CO_2 in underground geologic formations (carbon storage), or the chemical transformation of CO_2 into a product (carbon utilization) (33). CO_2 can be sourced from industrial facilities or directly from the air. Different CC strategies exist, including postcombustion, precombustion, and oxy-fuel combustion. Common techniques to capture/separate CO_2 include chemical/physical absorption and adsorption, and ionic liquids (ILs) and hybrid systems are emerging (34). CO_2 can be transported by pipeline, ship, rail, or truck. Deep geological formations for storing CO_2 include depleted oil and gas reservoirs and saline reservoirs. CCS provides long-term CO_2 storage, and the best practices for monitoring and verification to ensure the storage permanence have been discussed widely (2, 33). For CCU systems, the fate of

CO_2 and climate change mitigation benefits highly depends on CO_2 utilization options (35). For instance, CCU for long-lived products (e.g., construction materials) can provide relatively long-term carbon storage and achieve net carbon negative if CO_2 is from biogenic sources or direct air/water capture; on the contrary, carbon in CCU for short-lived products (e.g., fuels and chemicals) will be released to the atmosphere in a short time. However, CCU provides opportunities to replace fossil carbon with existing or new products and chemicals, enabling a circular carbon economy that brings additional social, economic, and environmental benefits that CCS alone cannot achieve. Chemical plants for carbon-intensive commodity chemicals (e.g., olefins, methanol, aromatics, ammonia and derivatives) are often considered for CCS implementation, given their GHG-intensive production processes (these chemicals account for >70% of global GHG emissions from the chemical industry) (2). The carbon sources of CCU can be from the chemical industry or other sectors (e.g., the power sector). The chemical products from CCU have large variations, but most of them are still in fundamental research. Commercial CCU products are very limited; a few examples include methanol, dimethyl ether, carbon monoxide, and some polymers (33). Both CCS and CCU will be needed to decarbonize the chemical industry and support a net-zero society.

3.1.1. Material flow analysis. In studying any material flow system, the first step is to identify and quantify mass flows, and thus reveal the most important components. **Figure 3** provides such an analysis for the entire global chemical and petrochemical sector in 2013. The Sankey diagram immediately shows the relative flows of the feedstocks, the upstream and downstream chemicals, and the principal chemical products. Given these perspectives, it becomes straightforward to develop approaches to decarbonize the chemical industry while considering control aspects such as CCUS (2, 7, 8, 36).

Decarbonizing the chemical/petrochemical sector will require that the system not only captures carbon but also develops feasible and affordable approaches to reuse it (7, 37, 38). Doing so at the required scale is an enormous challenge in technology development, industrial participation, and global collaboration. Previous studies have used MFA to track carbon flows within one chemical plant or across chemical networks, enabling the identification of main GHG emission sources, and pairing carbon sources and sinks for effective decarbonization. For example, Yao et al. (39) analyzed GHG flows in a representative petroleum refinery to estimate the cost and mitigation potential of different CC implementation strategies, and Kaiser & Bringezu (40) modeled carbon flows for material use in Germany to evaluate the potential of CO_2 utilization to close the carbon cycle of the chemical industry.

An important but often overlooked aspect of decarbonization of the economy is that such a transition must address at least two potentially confounding issues: (*a*) carbon in products such as cosmetics and coatings that often dissipate or disintegrate during use (41) and (*b*) commercial goods and packaging that are often lost during or after use (41), thus making a fully circular chemical industry very difficult. Efforts to surmount these challenges will thus be needed (22, 24).

3.1.2. Process analysis and optimization. Process simulation and other chemical engineering computer-aided tools have been explored in microscale process analysis, e.g., for pilot plant or industrial-scale operations (42). Roh et al. (42) presented a systematic procedure for using these tools, including screening CCU routes using stoichiometry-based methods, calculating mass and energy balances using flowsheet-based process simulators (e.g., Aspen Plus, HYSIS, CHEMCAD), and leveraging primary data collected from lab-scale experiments. Their study highlighted that the accuracy of these models for low-TRL CCUS depends strongly on process design and performance that often rely on theoretical evidence or expert judgment.

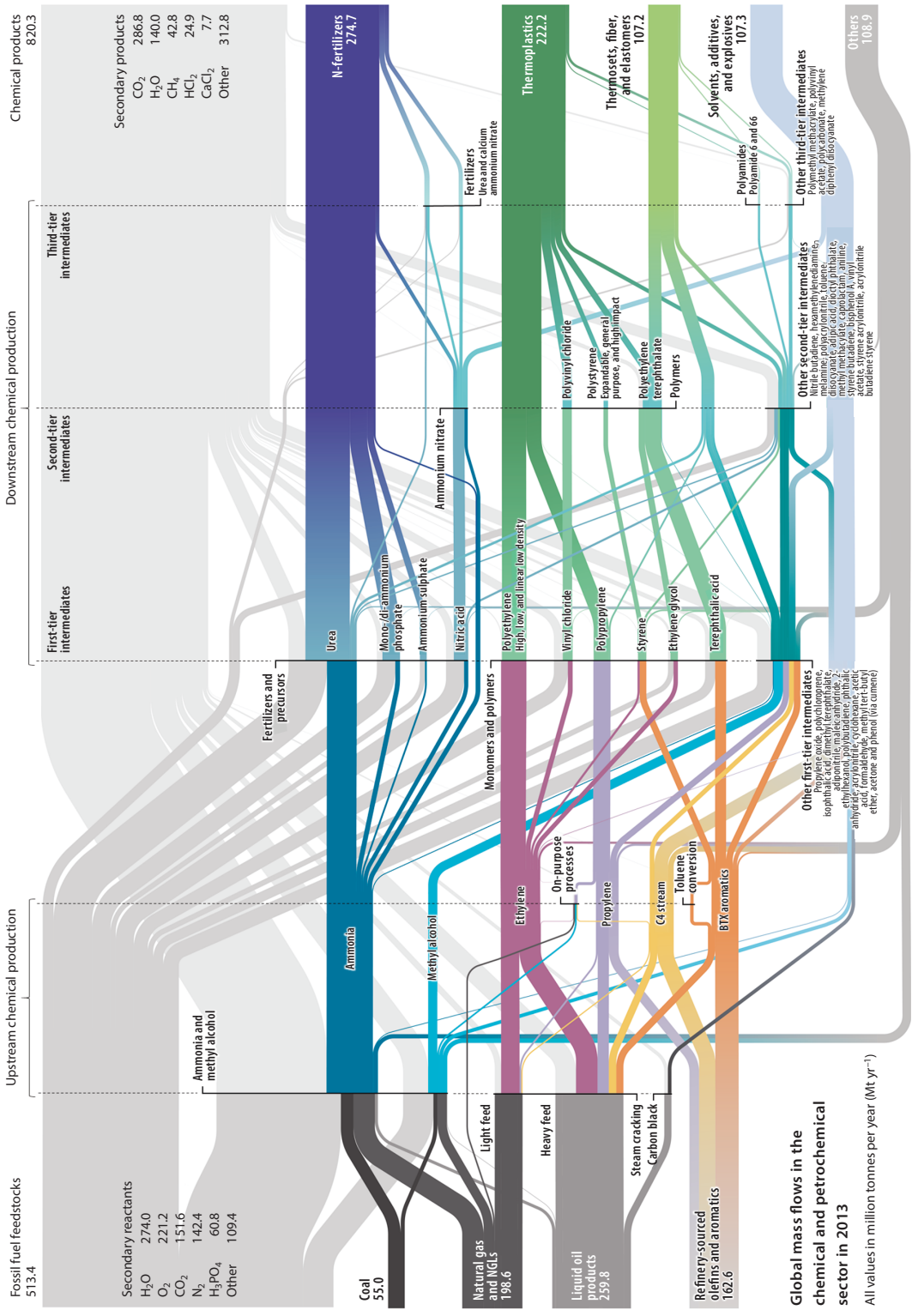

Figure 3

The global chemical and petrochemical sector from feedstocks through chemical products. The analysis is for 2013, but the main features (relative flows, secondary reactants, principal products) have changed little since that time. Abbreviations: BTX, benzene, toluene, and xylene; NGLs, natural gas liquids. Figure reproduced with permission from Reference 23; copyright 2018 American Chemical Society.

Many process systems engineering studies have developed superstructure-based models for exploring alternative designs and addressing uncertainties for CCUS system synthesis and optimization (29). One example is ArKaTAC^3, a tool to explore combinations of carbon sources, CC process options, and final products and optimize the superstructure for maximum profits and net CO_2 reduction using mathematical programming (43). Other studies have linked microlevel models of CCUS systems with carbon sources (e.g., fossil power plants) or with meso-level models for supply chain management across CC, transport, and storage/utilization at various temporal and spatial scales (44). These linked models are helpful in assessing and optimizing large-scale CCUS deployment and supporting policy and industrial decision making. In contrast, other studies have linked process-level models of CCUS systems with smaller-scale (e.g., molecule-level) models for screening and optimizing CC materials (e.g., absorbents and adsorbents), which are helpful for research and development (44). Multi-scale models are computationally challenging, given the high computational costs and extensive knowledge required to develop and use process models.

ML has been deployed to address computational and knowledge challenges. Microlevel ML applications allow for a sequential, bottom-up approach to screen many materials and technologies before conducting a process analysis (44). For instance, Wang et al. (45) screened different ILs based on ML-predicted viscosity and melting point and developed process simulations only for the best ILs selected by ML (45). Similar applications for different CC systems have been reviewed (46). Furthermore, ML supports interlinked micro- and meso-models of CCUS networks by providing computationally cheaper surrogate alternatives that address the challenges in solving nonlinear algebraic and partial differential equations for optimizing dynamic, cyclic CC processes (e.g., pressure swing adsorption) (44) or constructing input–output relationships when data and knowledge gaps exist (47). ML training data can be measured data (48) or come from process simulations (e.g., Aspen Plus or gPROMS) (47). Most ML applications in process analysis are limited to the individual life cycle stage of CCUS (e.g., CC or CO_2 utilization). More universal workflows for ML applications across the CCUS life cycle and development of hybrid knowledge-based/data-driven models are needed to facilitate a holistic assessment of CCUS.

3.1.3. Techno-economic analysis. CO_2 removal and avoidance costs are two common performance indicators that were widely assessed in previous microscale TEA models for CCS systems. CO_2 removal cost is calculated as the increased production cost divided by removed CO_2 (49); CO_2 avoidance cost is the increased production cost divided by reduced CO_2 emissions compared to chemical production without CCS (49, 50). Because CCU systems generate marketable products, previous CCU TEAs have focused on evaluating product-oriented and profit-relevant indicators, such as internal rate of return, net present value, capital investment, discounted payback period, and minimum selling price of CO_2-drived chemicals (51). Besides microlevel analysis, TEA models have been coupled with optimization models to evaluate the mesoscale economic performance of CCUS networks that connect CO_2 sources and applications or consider carbon policy interventions (52, 53).

TEA models for CCUS systems suffer from substantial uncertainties in technology performance and costs, given their low TRL and limited large-scale projects in operation. Because TEA models rely on mass and energy balance data from process simulators, conducting uncertainty and sensitivity analysis, especially for global sensitivity analysis, can be challenging (54). Recent efforts to address this challenge include design under uncertainty by optimizing system variables according to one or several targeted objectives related to the output distribution of cost performance modeled in TEA (e.g., minimizing the mean value of cost or uncertainty range of cost distribution) (54). Another effort to address the challenge is developing surrogate models using ML methods such as Artificial Neural Network to avoid intense computational demands in uncertainty analysis

(55). Another gap is the lack of standardized TEA methods for CCUS systems. Recent efforts include TEA guidelines for CCUS published by Zimmermann et al. (21) and Langhorst et al. (56).

3.1.4. Life cycle assessment. LCA has been used to assess the carbon footprint and other environmental impacts of CCUS systems (e.g., eutrophication and human health impacts). LCAs for CCS systems have focused on CO_2 from direct air capture, industrial sources, and biomass systems. The best practices for CCS LCA are available in the literature (57) and a guideline published by the US Department of Energy (58). CCU systems have more methodological challenges than CCS. One main issue is the multifunctionality—the question is how to attribute the environmental burdens between CO_2 (which is emitted to the environment in the absence of CC) and primary products of the point sources (e.g., electricity produced by a power plant) (59). The literature shows substantially different GHG results between stand-alone CCU systems using CO_2 from any source and systems integrating CO_2 point sources (60). ISO standards (25) recommend system expansion to avoid allocation. A recent review assessed different methods and recommended substitution, a mathematically equivalent method of system expansion. The substitution method subtracts the environmental impacts of the CO_2 sources without CC, to avoid suboptimal choices of CO_2 sources using other methods such as allocation (59). This method has been used in consequential LCA (CLCA) studies for CCU systems. For example, Thonemann & Pizzol (61) included avoided environmental impacts of the marginal production of conventional chemicals (to be replaced by CO_2-derived chemicals) and changing marginal suppliers of CO_2 and H_2 in the near and long term scenarios (61). CLCA and attributional LCA are two broad LCA types. Attributional LCA attributes environmental impacts to the functional unit of a studied system, whereas CLCA assesses impact changes in response to a decision or action (62). CLCA is more decision relevant than attributional LCA. However, because the CO_2 market has not been established, determining marginal suppliers that would respond to a small increase in demand could be challenging.

Advanced LCA models have been developed to enhance the policy relevance and engineering utility of CCU LCA. For example, Thonemann & Schulte (63) present a prospective LCA model that couples the CLCA of a lab-scale CCU system with a scale-up scheme leveraging flowsheet development and process simulation to understand future impacts at a full operating scale. Hoppe et al. (64) estimated raw material inputs and total material requirement, two common indicators used in MFA, using a cradle-to-gate LCA for CO_2-based production of methane, methanol, and derived polymers. This insight into resource utilization may be useful for policymakers in understanding the role of CCU in supporting a more resource-efficient society. Another study developed a stochastically determined climate return on investment metric using the carbon footprint results of CCU LCA, which helps identify research and development priorities toward CCU products with the greatest climate benefits even with uncertainty—one of the largest concerns for assessing low-TRL technologies (65).

Recent developments in coupling process analysis, TEA, and LCA have advanced sustainability-informed design and optimization for CCUS. De Luna et al. (66) conducted TEA and a simple LCA for prospective renewable energy–powered electrosynthesis pathways of converting CO_2 and water into commodity chemicals (e.g., diesel and alcohol). This allows simultaneous comparison of the market and GHG-reduction potential of CO_2-derived and fossil-based chemicals, as well as exploration of how technical performance and market potentials would affect the comparison. Another example (67) is an integrated assessment that couples process flowsheet, LCA, and TEA for a CO_2 refinery design that converts CO_2 from direct air capture to methanol and its derivative olefines and aromatics, supporting a holistic evaluation of technical, economic, and environmental performances of different CCU implementation strategies for chemical production in different regions.

3.2. Alternative Feedstock

Biomass and H_2 have been explored extensively as alternative feedstocks for chemical production. These two have overlaps, as H_2 can be made from biomass. This section discusses advanced micro- and meso-modeling for biomass-based chemicals (including H_2) and H_2 from water electrolysis.

3.2.1. Biomass. Biomass can be converted to value-added chemicals through different platforms (e.g., syngas and C6 sugar) and conversion pathways (e.g., thermochemical and biochemical conversion). Given the large number of biomass feedstocks, platform chemicals, conversion technologies, and chemical products, identifying the optimal pathways is challenging but needed for scaling up. Knowledge-based microscale process analyses have been used to compare alternative pathways and combined with TEA and LCA to support pathway screening (68). One example is an optimization-based process synthesis framework that combines process analysis with LCA and TEA using MINLP (mixed-integer nonlinear programming) to explore the economic and life cycle GHG emissions of converting three biomass feedstocks to liquid transportation fuels through different combinations of biomass conversion units, operational conditions, and upgrading processes (69). In addition, previous studies have used green chemistry and engineering principles to guide biorefinery design and pathway screening (70).

ML has been used to overcome both computational and knowledge barriers in sustainable synthesis and design for biomass conversion processes, products, and supply chains. Previous reviews (71, 72) found that most ML applications for biomass systems have focused on optimizing either technical performance (e.g., yields of chemical products) or part of the life cycle (e.g., only biomass conversion). A few studies have demonstrated the powerful use of ML to support sustainability assessment for bio-based products. For example, Liao et al. (73) combined a kinetic-based process simulation with Artificial Neural Network models trained from experimental data collected from the literature to predict GHG emissions and energy consumption of pyrolysis and steam activation across a wide range of woody biomass feedstock for biochar and activated carbon production (73). Another study trained ML models using data from biomass conversion process simulations and leveraged a knowledge-based decision tree to automate the initial process design of separation and product recovery, allowing for fast evaluation of economic, technical, and environmental performance (74). A recent perspective presents a promising integration of bench-scale digitation (enabled by ML methods such as text mining) and automatic laboratory experiments and multi-scale modeling (from molecular to process level) for LCA and TEA, which can accelerate the identification and optimization of biomass system design for sustainable chemical production (68).

Large-scale biomass utilization impacts land use and ecosystems, which often are not considered in engineering-based models. Land use change (LUC) can be direct (e.g., forest converted to cropland) or indirect [e.g., induced LUC (ILUC) caused by changes in biomass supply and demand]. LUC can result in net carbon emissions or sinks. For instance, a study for bioenergy with CCS identifies LUC as the main factor determining whether bioenergy with CCS is carbon positive or negative (75). Because ILUC is an ongoing research field, different models (e.g., GTAP-BIO and GLOBIOM) may provide different GHG emission estimations (76). In contrast to bioenergy literature, LCAs of biomass-based chemicals rarely have considered LUC. A few studies have considered land requirements based on biomass yields (77, 78), but the LUC GHG emissions are not included. Eerhart et al. (79) used GHG emission factors of ILUC associated with corn-based ethanol biofuel for bio-based polyethylene furandicarboxylate and showed significant impacts of ILUC on the GHG mitigation benefits of polyethylene furandicarboxylate compared to petroleum-based counterparts. Waste biomass has been highly recommended, because it does not drive LUC as dedicated crops (e.g., corn) (80). However, removing waste

biomass (e.g., agricultural residues) may lead to soil organic carbon losses, which have been explored in biofuel literature (81), but not bio-based chemicals. More research and modeling efforts are needed to understand the large-scale impacts of biomass use for chemical production on ecosystems.

3.2.2. H_2. H_2 is used widely in the chemical industry as a feedstock (e.g., ammonia production). Thus, decarbonizing H_2 production and application will benefit the chemical industry. Microscale process analysis for H_2 production typically relies on knowledge-based simulations leveraging the literature and experimental data to assess and optimize process performance for various technology pathways, e.g., electrolysis (82–84), thermochemical (85), biochemical (86), and electrochemical (84). Data-driven models mainly use ML techniques, and their outputs are process performance indicators (e.g., H_2 yield and energy consumption). ML training data can be collected from lab-scale experiments (87), plant operation (88), simulation models (89), and the literature (90). These data-driven models can be used further for process optimization [e.g., maximizing H_2 yield (91)] and uncertainty/sensitivity analysis that is challenging to execute in process simulators (88). Furthermore, they can be integrated with LCA or TEA for fast environmental and economic assessment (92). Compared to traditional models, the benefits of ML models include no need for initial solutions or guesses for the simulation model (88), greater ability to model complex phenomena (e.g., convection, conduction, and radiation among the burner–flame guide–steam methane reforming reactors for H_2 production) than equation-based models (88), higher prediction accuracy for H_2 production under nonequilibrium conditions (91), and less computational intensity (91, 92).

Models for H_2 applications have focused on either microscale applications or mesoscale optimization for H_2 networks. For microscale applications, one emerging area is power-to-fuel using CO_2 and H_2 to produce energy products (e.g., methanol, methane, and fuel). These studies integrated the models of CC, H_2 production via electrolysis, and conversion together for a holistic assessment (93–95). Mesoscale models evaluate the GHG reduction potential or optimize the low-carbon hydrogen supply chain for industrial uses. For example, Chisalita et al. (96) used LCA to evaluate the environmental impact of ammonia production with different H_2 production scenarios across supply chains (e.g., via steam methane reforming, chemical looping, or electrolysis), and Ibrahim & Al-Mohannadi (97) used MILP to identify the minimum cost of the low-carbon H_2 supply chain networks in industrial clusters and displayed the trade-offs between levelized cost and CO_2 emission reductions. Simultaneously, many MILP-based models for H_2 supply chain network design exist in the transportation sector (98), where the methods can be applied to H_2 used for chemical production.

3.3. Electrification and Other Process Improvements

There are two types of electrification: direct electrification that changes only energy infrastructure and indirect electrification that relies on electrochemistry to synthesize alternative feedstocks (99). Because direct electrification does not change existing chemical processes, previous studies typically began by analyzing existing systems, followed by estimating energy and GHG emission changes after implementing electric facilities. For example, Chen et al. (99) developed a knowledge-based process simulation and TEA for a traditional methanol plant and then modified the model for heat pump implementation and estimated energy reduction benefits. Leveraging public databases, Schoeneberger et al. (100) characterized GHG emissions and energy consumption of existing industrial boilers, then estimated the GHG reduction benefits of replacing them with electric boilers. Similar approaches, such as that of Jabarivelisdeh et al. (101), have been used to analyze other incremental process improvements that do not alter chemical processes.

Indirect electrification requires substantial changes in chemical process design (93, 99). For example, using electrochemistry, methanol can be made from CO_2 through direct CO_2 electrolysis or CO_2 hydrogenation with H_2 derived from water electrolysis, both of which require substantially different design of reactor and feedstock treatment from traditional methanol synthesis via thermochemical conversion of natural gas (93). Thus, it is more challenging to conduct process analysis, TEA, and LCA. The level of modeling details depends on the analysis purpose and scale. For example, process optimization studies often start from reactor or process design and then use LCA and TEA to identify optimal process design (84, 102). Other studies have used LCA and TEA in a streamlined fashion without detailed process analysis to identify technical conditions or chemical product targets with the largest potentials in terms of markets and GHG reduction (e.g., 99).

Electrification allows for integration of renewable energy, such as solar and wind, into chemical production (103). On the other hand, the carbon impacts of decarbonizing the chemical industry can propagate and be magnified through chemicals' use as clean energy carriers (e.g., low-carbon H_2 and methanol) (11). Understanding such impacts requires integrated modeling for both the energy and chemical sectors. Macro-level modeling, discussed in the following section, can be helpful.

4. MACRO-LEVEL MODELING FOR DECARBONIZATION TECHNOLOGIES

Various modeling approaches have been used to understand and identify the decarbonization potential of the chemical industry that accounts for its broader impact on supply chains (e.g., energy supply) at a national or global level. This section discusses these approaches with specific application examples and highlights their strengths and limitations.

4.1. Industrial Ecology Models

Industrial ecology models have been used to analyze chemical industry decarbonization at the macro-level. In this section, two categories of industrial ecology models are discussed, namely material flow analyses and bottom-up macro-level models.

4.1.1. Material flow analyses and scenario analysis. MFAs (discussed in Section 2.1) are based on data gathered from domestic sources on flows of materials, import/export information, and statistics or estimates of reuse or loss. MFAs are very useful in illustrating the quantitative life cycle of a particular element; nonetheless, they are stories of the past.

An approach that suggests the future is termed material future scenarios (MFSs). MFSs begin with recent MFAs and build upon those foundations to provide informed stories of one or more possible futures regarding material supply, demand, utilization, and loss over time, often for several decades. A typical MFS addresses a particular geographic scope (country, region, planet); a material group of interest; and a storyline that describes material demand, technology development, societal evolution, and national/international policy over the MFS time period. To allow for various visions of possible futures, MFAs generally involve several scenarios that differ substantially in attributes such as anticipated changes in supply and demand, political stability level in countries that are suppliers or users of the material in question, and perhaps technological or societal evolutions.

Several scenarios specifically related to plastics have been published, with foci on plastics production (104), plastics pollution (105), plastic-related CO_2 emissions (5), and industry transitions toward net-zero CO_2 emissions by mid-century (2, 7). There is general agreement that without significant transition of the industry toward net zero, the CO_2 emissions and impacts on

natural ecosystems will at least double by 2050. Studies such as these do not, of course, provide political pathways toward such a transformation, but they do provide the scientific justification for moving to implement those pathways for the good of people, the environment, and the planet.

4.1.2. Bottom-up macro-level modeling of chemical industry decarbonization. Bottom-up decarbonization analysis scales up understandings from microlevel analysis by considering chemical demand and technology adoption. Previous bottom-up analyses began by analyzing the process-level or chemical-specific impacts of an individual technology (or technology group) on the GHG and energy intensity of chemical production (e.g., CO_2e/t and GJ/t of chemicals), which were then scaled up based on chemical production and technology adoption. For example, Van der Hoeven et al. (106) investigated the improvement potentials of catalytic processes for producing individual chemicals and scaled up the impacts by chemical demands. Woodall et al. (8) used a similar approach to estimate the cost and GHG mitigation of supply-side (e.g., low-carbon energy supply and CCUS) and demand-side (e.g., reduced consumption of derivative chemicals) strategies and estimated the US decarbonization potential by assuming technology-specific adoption rates in the chemical industry. Many studies have focused on on-site GHG emissions without considering the life cycle GHG emissions. Bottom-up, prospective LCA addresses this challenge by including chemical life cycles (107). For instance, Yao et al. (108) integrated LCA with a prospective analysis model (which projects future ethylene demand, feedstock supply, and technology adoption) to quantify the cradle-to-gate GHG emissions and energy consumption of the US ethylene industry from 2015 to 2040 and identify the main factors (e.g., fugitive emissions from upstream natural gas production) influencing the decarbonization potential of the US ethylene industry.

Bottom-up models can be used together with top-down approaches (as hybrid methods). One example is a decarbonization study for the UK chemical sector (109) that used a bottom-up approach to model individual chemical processes and a top-down approach to disaggregate nation-level steam and electricity consumption data. The decarbonization potential was then analyzed through a bottom-up technology roadmap combined with different technology adoption scenarios. Most previous studies, whether bottom-up, top-down, or hybrid, relied on assumptions of individual technology adoption, which overlooks the possible competition and synergies among different technologies.

Several global decarbonization analyses have considered technology competition using optimization models, such as a technology choice model that addresses the uncertainties associated with technology choices in CLCA (110). A global analysis for plastic life cycles used this method to consider different technology choices (including CCU and biomass) with the objective function of minimizing system-wide GHG emissions (111). Other studies have considered the techno-economic potentials of different decarbonization choices. For instance, Yang et al. (112) conducted TEA for decarbonizing chemical/petrochemical production based on representative CO_2 refinery processes and their CO_2 emissions, as well as the technical feasibility and costs of typical CC and biomass systems. The authors estimated the best CO_2 emission reduction options under 100 €/CO_2 for the entire sector (112).

4.2. Integrated Assessment Models

Integrated assessment models (IAMs) model the interaction of the chemicals industry with the rest of the economy, particularly the energy sector and its transformation through climate policies. IAMs project future demand for different energy carriers that are used (as feedstock or as energy services) and produced (e.g., hydrogen) by the chemicals industry. Industry decarbonization

pathways are a relatively recent development in IAMs (N. Bauer, S. Moreno, H.-S. de Boer, D. Fragkiadakis, P. Fragkos, et al., manuscript submitted). Some IAMs model the chemicals industry separately, but with various degrees of detail. For instance, only four of seven global IAMs that model industries represent CCUS in the chemical industry (N. Bauer, S. Moreno, H.-S. de Boer, D. Fragkiadakis, P. Fragkos, et al., manuscript submitted). IAMs typically rely on generic international reports for sources of technological information, such as the International Energy Agency for TRLs and the Intergovernmental Panel on Climate Change WG3 AR6 bottom-up assessments for abatement cost estimates (113). They also lack regional heterogeneity in technology and process sophistication, which gain importance with the need for different regional solutions in emerging and industrialized economies. Regional or national IAMs (e.g., GCAM-China) may enable a less burdensome way to break out the chemicals sector (114) and model location-specific carbon sequestration potential (115).

Stronger coupling between IAMs and micro- and meso-models in industrial ecology can improve the representation of decarbonization pathways in both types of models. The industrial ecology models can provide IAMs with improved process innovations, recycling, lightweighting, and other material efficiency strategies to broaden the spectrum of emissions mitigation strategies (116). IAMs balance the incorporation of detail in industrial processes against computational and data limitations, as well as structural constraints in balancing macro-level energy statistics and monetary flows. One example of such coupling is the embedding of a plastics supply chain model in the IMAGE IAM (PLAIA), wherein the former provides a detailed representation of plastics production, and the IAM enables a broader set of carbon mitigation options (e.g., circular economy) that can also account for trade-offs with other sectors (e.g., land use in biogenic carbon sequestration) (5).

The IAMs, in turn, provide industrial ecology studies with future projections of energy mixes and prices, decarbonization scenarios in other industry sectors, and socioeconomic futures that drive chemicals demand. Coupling IAM with industrial ecology methods offers opportunities for cross-sectional prospective analysis (116) and supports prospective LCA studies of emerging technologies in chemical production. For example, Lamers et al. (117) presented an open-source framework (LiAISON) to link future energy mix scenarios derived from IMAGE with LCA of emerging technologies that consider future technology improvements and scale-up. The framework was applied to power-to-hydrogen and steam methane reforming, demonstrating how future transitions in power, cement, steel, and fuel industries could reduce the environmental impacts of hydrogen production. Another study explored the country-specific decarbonization potential of biomass-derived drop-in (e.g., fast pyrolysis) and hydrogen-based biofuels with and without CCS in Europe by linking LCA models with the outputs from REMIND IAM, which projects future technology mixes in power, transportation, and industries in a specific policy scenario by 2050 (118). Furthermore, other studies have integrated LCA-based, technology-specific insights into IAM. Examples include work by Pehl et al. (119), who integrated LCA-derived embodied energy use coefficient and indirect CO_2 emissions (e.g., from construction and land use change) into REMIND IAM, and McDowall et al. (120), who integrated indirect CO_2 emissions derived from environmentally extended input–output analysis (a top-down IE approach) into the European TIMES IAM model. Both studies found that including indirect GHG emissions affects the results of the optimal power sector mix given by IAM. Because the chemical industry is an important energy demand sector while producing energy carriers (e.g., hydrogen and biofuels), there are many research opportunities in leveraging IAM to better understand the role and impacts of chemical decarbonization technologies in global and regional contexts and cross-sectoral mitigation strategies.

4.3. Planetary Boundary–Based Environmental Sustainability Assessment

An emerging research field is absolute environmental sustainability assessment (AESA), which compares the environmental impacts of anthropogenic systems to their assigned nature's carrying capacity based on planetary boundaries (PBs). PBs are defined as the safe operating space for human development and are represented by nine essential earth system processes, including climate change, land-system change, and biochemical flows (121). Many studies have used AESA in combination with LCA; for example, Tulus et al. (122) analyzed 492 chemicals and found that 99.4% of them transgress at least one PB. Because PBs are global, AESA of chemical production requires downscaling PBs or upscaling local impacts. A recent study used a bottom-up model to upscale the life cycle environmental impacts of 14 largest-volume plastics in 2030 to the global level, which were compared with safe operating space downscaled to the plastic industry (6). Their analysis showed that climate-optimal pathways may lead to transgression of other PBs, and a balanced solution requires combinations of bio-based and CCU-based plastics with maximum recycling (6), which demonstrates the benefits of LCA-based AESA in providing insights beyond climate change. Meng et al. (2) integrated various models for the global chemical industry to identify pathways to net-zero GHG emissions. They modeled global chemical demand based on the existing knowledge of improving resource efficiency and circularity; the authors also modeled the technology mix using a bottom-up plant-level optimization model (2). They incorporated PBs and resource availability as modeling constraints, pinpointing decarbonization pathways that do not transgress PBs (2).

Most scaling methods used in PB-based AESA rely on sharing principles (e.g., principles based on global and regional environmental impacts, gross value added, and final consumption expenditure), limiting the use of biophysical information that may be more accurate for region-specific assessment (123). Bakshi et al. (124) developed a techno-ecological synergy framework that directly compares human demand for ecosystem services (e.g., GHG emissions or resource uses) with the carrying capacity of ecosystems estimated by biophysical models and data rather than scaling methods. Techno-ecological synergy allows for exploring technological systems co-located with ecosystems and can be integrated with LCA for multi-scale assessment, as demonstrated by previous studies (125, 126). Decarbonization technologies affect ecosystems through natural resource utilization (e.g., biomass, lands, and water) and environmental emissions. Spatially explicit ecosystem modeling and data need to be incorporated into LCA and AESA to support region-specific decision making.

5. FUTURE RESEARCH

This article reviews the advanced and integrated use of engineering, industrial ecology, techno-economic, and ML models to assess promising decarbonization technologies and strategies in the chemical industry. The selection and combination of these models are purpose and scope dependent. Micro- and mesoscale models support engineering and supply chain design and optimization. Macroscale models provide high-level insights for policy and industrial decision making.

Most process analysis, LCA, and TEA are conducted at the microlevel and rely on the knowledge of process configurations, environmental emissions, and economics, leading to computational challenges and knowledge barriers to scaling up microlevel models to meso- and macroscales. ML addresses this challenge by providing data-driven approaches when knowledge gaps exist or providing computationally cheaper surrogate models. However, previous ML applications were limited to one or two life cycle stage(s) of decarbonization technology (e.g., the CC process only rather than the entire CCUS life cycle) or a single aspect of sustainability (e.g., economic). More research is needed to effectively combine ML with existing systems analysis models to support

holistic assessment and optimization of decarbonization technologies. MFA has been used for both micro- and macro-level analyses and is particularly useful for circular economy pathways. Two critical issues need to be included in future models for a decarbonized circular economy. One is the carbon in products that dissipate or disintegrate during use; the other are products and packaging lost during or after use.

Assessing decarbonization technologies and strategies requires forward-looking, robust models of future chemical production and relevant industrial systems (e.g., energy systems). Previous prospective studies have developed different scaling-up scenarios to explore what-if situations. However, most are limited to chemical production without considering future changes in other industrial systems (e.g., electricity grid), economics (e.g., changes in feedstock supply and prices), and society (e.g., human behavior). LCA and TEA of emerging technologies is a fast-growing field, and recent developments in prospective, anticipatory, and consequential approaches are promising to address this challenge (62, 127, 128). Application of these new tools requires close collaboration between chemical engineers, industrial ecologists, and economists for tailored modeling strategies to ensure the usefulness of the results with reasonable levels of technical detail and data.

Climate change is not the only grand challenge society faces. Many resources and environmental challenges must be addressed for a more sustainable future. This review includes two recent developments, IAM- and PB-based AESA, that have not been used widely by chemical engineers but provide a means of linking the chemical industry with the environment and society. IAM provides forward-looking, cross-sectional insights on industrial decarbonization beyond the chemical industry, which can be combined with micro-/mesoscale models to understand how technology-specific decarbonization pathways would affect regional and global industries and society. PB-based AESA considers nature's carrying capacity and includes environmental aspects beyond climate change, allowing for a more holistic assessment of decarbonization technologies and strategies in terms of sustainability. More research is needed for seamless integration of these methods to provide useful insights for different audiences. This review does not include social impact assessment; however, methods such as social LCA (129) are under development and should be considered in future assessment of emerging decarbonization technologies.

DISCLOSURE STATEMENT

The authors are not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

ACKNOWLEDGMENTS

The authors thank the funding support from Yale University and the US National Science Foundation. This work is partially supported by the National Science Foundation under grant no. 2038439. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation.

LITERATURE CITED

1. Econ. Consult. Team. 2019. *The global chemical industry: catalyzing growth and addressing our world's sustainability challenges*. Rep., Oxford Econ., Oxford Univ., Cambridge, UK
2. Meng F, Wagner A, Kremer AB, Kanazawa D, Leung JJ, et al. 2023. Planet-compatible pathways for transitioning the chemical industry. *PNAS* 120(8):e2218294120
3. Int. Energy Agency. 2022. *Tracking industry 2021*. Int. Energy Agency, Paris. **https://www.iea.org/energy-system/industry#tracking**

4. Int. Energy Agency. 2022. *Chemicals—analysis*. Int. Energy Agency, Paris. **https://www.iea.org/energy-system/industry/chemicals**
5. Stegmann P, Daioglou V, Londo M, van Vuuren DP, Junginger M. 2022. Plastic futures and their CO_2 emissions. *Nature* 612(7939):272–76
6. Bachmann M, Zibunas C, Hartmann J, Tulus V, Suh S, et al. 2023. Towards circular plastics within planetary boundaries. *Nat. Sustain.* 6(5):599–610
7. Huo J, Wang Z, Oberschelp C, Guillén-Gosálbez G, Hellweg S. 2022. Net-zero transition of the global chemical industry with CO_2-feedstock by 2050: feasible yet challenging. *Green Chem.* 25(1):415–30
8. Woodall CM, Fan Z, Lou Y, Bhardwaj A, Khatri A, et al. 2022. Technology options and policy design to facilitate decarbonization of chemical manufacturing. *Joule* 6(11):2474–99
9. Mallapragada DS, Dvorkin Y, Modestino MA, Esposito DV, Smith WA, et al. 2023. Decarbonization of the chemical industry through electrification: barriers and opportunities. *Joule* 7(1):23–41
10. Xia R, Overa S, Jiao F. 2022. Emerging electrochemical processes to decarbonize the chemical industry. *JACS Au* 2(5):1054–70
11. Schiffer ZJ, Manthiram K. 2017. Electrification and decarbonization of the chemical industry. *Joule* 1(1):10–14
12. Chung C, Kim J, Sovacool BK, Griffiths S, Bazilian M, Yang M. 2023. Decarbonizing the chemical industry: a systematic review of sociotechnical systems, technological innovations, and policy options. *Energy Res. Soc. Sci.* 96:102955
13. Gabrielli P, Rosa L, Gazzani M, Meys R, Bardow A, et al. 2023. Net-zero emissions chemical industry in a world of limited resources. *One Earth* 6:682–704
14. Nicholson SR, Rorrer JE, Singh A, Konev MO, Rorrer NA, et al. 2022. The critical role of process analysis in chemical recycling and upcycling of waste plastics. *Annu. Rev. Chem. Biomol. Eng.* 13:301–24
15. Bakshi BR. 2019. Toward sustainable chemical engineering: the role of process systems engineering. *Annu. Rev. Chem. Biomol. Eng.* 10:265–88
16. Kleinekorte J, Fleitmann L, Bachmann M, Kätelhön A, Barbosa-Póvoa A, et al. 2020. Life cycle assessment for the design of chemical processes, products, and supply chains. *Annu. Rev. Chem. Biomol. Eng.* 11:203–33
17. US Dep. Energy. 2022. *Industrial decarbonization roadmap*. Rep. DOE/EE-2635, US Dep. Energy, Washington, DC. **https://www.energy.gov/sites/default/files/2022-09/Industrial%20Decarbonization%20Roadmap.pdf**
18. Zimmerman JB, Anastas PT, Erythropel HC, Leitner W. 2020. Designing for a green chemistry future. *Science* 367(6476):397–400
19. Ioannou I, D'Angelo SC, Galán-Martín Á, Pozo C, Pérez-Ramírez J, Guillén-Gosálbez G. 2021. Process modelling and life cycle assessment coupled with experimental work to shape the future sustainable production of chemicals and fuels. *React. Chem. Eng.* 6(7):1179–94
20. Farmahini AH, Krishnamurthy S, Friedrich D, Brandani S, Sarkisov L. 2021. Performance-based screening of porous materials for carbon capture. *Chem. Rev.* 121(17):10666–741
21. Zimmermann AW, Wunderlich J, Müller L, Buchner GA, Marxen A, et al. 2020. Techno-economic assessment guidelines for CO_2 utilization. *Front. Energy Res.* 8:5
22. Di J, Reck BK, Miatto A, Graedel TE. 2021. United States plastics: large flows, short lifetimes, and negligible recycling. *Resour. Conserv. Recycl.* 167:105440
23. Levi PG, Cullen JM. 2018. Mapping global flows of chemicals: from fossil fuel feedstocks to chemical products. *Environ. Sci. Technol.* 52(4):1725–34
24. Chaudhari US, Johnson AT, Reck BK, Handler RM, Thompson VS, et al. 2022. Material flow analysis and life cycle assessment of polyethylene terephthalate and polyolefin plastics supply chains in the United States. *ACS Sustain. Chem. Eng.* 10(39):13145–55
25. ISO. 2006. *ISO 14044: Environmental management, life cycle assessment, requirements and guidelines*. Guidel. 14044, ISO, Geneva. **https://www.iso.org/standard/38498.html**
26. Myhre G, Shindell D, Bréon F-M, Collins W, Fuglestvedt J, et al. 2013. Anthropogenic and natural radiative forcing. In *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*, ed. TF Stocker, D Qin, G-K Plattner, M Tignor, SK Allen, et al. Cambridge, UK: Cambridge Univ. Press

27. Greenhouse Gas Protocol. 2023. *Guidance*. **https://ghgprotocol.org/guidance-0**
28. Turton R, Bailie RC, Whiting WB, Shaeiwitz JA. 2008. *Analysis, Synthesis and Design of Chemical Processes*. London: Pearson Educ.
29. Mencarelli L, Chen Q, Pagot A, Grossmann IE. 2020. A review on superstructure optimization approaches in process system engineering. *Comput. Chem. Eng.* 136:106808
30. Mitchell TM. 1997. *Machine Learning*. New York: McGraw-Hill
31. Liao M, Lan K, Yao Y. 2022. Sustainability implications of artificial intelligence in the chemical industry: a conceptual framework. *J. Ind. Ecol.* 26(1):164–82
32. Ali JM, Hussain MA, Tade MO, Zhang J. 2015. Artificial intelligence techniques applied as estimator in chemical process systems—a literature survey. *Expert Syst. Appl.* 42(14):5915–31
33. Natl. Acad. Sci. Eng. Med. 2022. *Carbon Dioxide Utilization Markets and Infrastructure: Status and Opportunities: A First Report*. Washington, DC: Natl. Acad. Sci. Eng. Med.
34. Dubey A, Arora A. 2022. Advancements in carbon capture technologies: a review. *J. Clean. Prod.* 373:133932
35. Cuéllar-Franca RM, Azapagic A. 2015. Carbon capture, storage and utilisation technologies: a critical analysis and comparison of their life cycle environmental impacts. *J. CO_2 Util.* 9:82–102
36. Gabrielli P, Gazzani M, Mazzotti M. 2020. The role of carbon capture and utilization, carbon capture and storage, and biomass to enable a net-zero-CO_2 emissions chemical industry. *Ind. Eng. Chem. Res.* 59(15):7033–45
37. Fernández JR, Garcia S, Sanz-Pérez ES. 2020. CO_2 capture and utilization editorial. *Ind. Eng. Chem. Res.* 59(15):6767–72
38. Kothandaraman J, Lopez JS, Jiang Y, Walter ED, Burton SD, et al. 2022. Integrated capture and conversion of CO_2 to methanol in a post-combustion capture solvent: heterogeneous catalysts for selective C-N bond cleavage. *Adv. Energy Mater.* 12(46):2202369
39. Yao Y, Marano J, Morrow WR, Masanet E. 2018. Quantifying carbon capture potential and cost of carbon capture technology application in the U.S. refining industry. *Int. J. Greenh. Gas Control* 74:87–98
40. Kaiser S, Bringezu S. 2020. Use of carbon dioxide as raw material to close the carbon cycle for the German chemical and polymer industries. *J. Clean. Prod.* 271:122775
41. Ohno H, Sato H, Fukushima Y. 2018. Configuration of materially retained carbon in our society: a WIO-MFA-based approach for Japan. *Environ. Sci. Technol.* 52(7):3899–907
42. Roh K, Bardow A, Bongartz D, Burre J, Chung W, et al. 2020. Early-stage evaluation of emerging CO_2 utilization technologies at low technology readiness levels. *Green Chem.* 22(12):3842–59
43. Chung W, Lim H, Lee JS, Al-Hunaidy AS, Imran H, et al. 2022. Computer-aided identification and evaluation of technologies for sustainable carbon capture and utilization using a superstructure approach. *J. CO_2 Util.* 61:102032
44. Hasan MMF, Zantye MS, Kazi MK. 2022. Challenges and opportunities in carbon capture, utilization and storage: a process systems engineering perspective. *Comput. Chem. Eng.* 166:107925
45. Wang K, Xu H, Yang C, Qiu T. 2021. Machine learning-based ionic liquids design and process simulation for CO_2 separation from flue gas. *Green Energy Environ.* 6(3):432–43
46. Rahimi M, Moosavi SM, Smit B, Hatton TA. 2021. Toward smart carbon capture with machine learning. *Cell Rep. Phys. Sci.* 2(4):100396
47. Yan Y, Borhani TN, Subraveti SG, Pai KN, Prasad V, et al. 2021. Harnessing the power of machine learning for carbon capture, utilisation, and storage (CCUS)—a state-of-the-art review. *Energy Environ. Sci.* 14(12):6122–57
48. Jablonka KM, Charalambous C, Fernandez ES, Wiechers G, Monteiro J, et al. 2023. Machine learning for industrial processes: forecasting amine emissions from a carbon capture plant. *Sci. Adv.* 9(1):eadc9576
49. Cormos CC. 2016. Oxy-combustion of coal, lignite and biomass: a techno-economic analysis for a large scale Carbon Capture and Storage (CCS) project in Romania. *Fuel* 169:50–57
50. Xiang D, Yang S, Liu X, Mai Z, Qian Y. 2014. Techno-economic performance of the coal-to-olefins process with CCS. *Chem. Eng. J.* 240:45–54
51. Yang Y, Zhang Q, Yu H, Feng X. 2021. Tech-economic and environmental analysis of energy-efficient shale gas and flue gas coupling system for chemicals manufacture and carbon capture storage and utilization. *Energy* 217:119348

52. Al-Yaeeshi AA, Govindan R, Al-Ansari T. 2020. Techno-economic-based dynamic network design for optimum large-scale carbon dioxide utilisation in process industries. *J. Clean. Prod.* 275:122974
53. Tang H, Zhang S, Chen W. 2021. Assessing representative CCUS layouts for China's power sector toward carbon neutrality. *Environ. Sci. Technol.* 55(16):11225–35
54. van der Spek M, Fout T, Garcia M, Kuncheekanna VN, Matuszewski M, et al. 2020. Uncertainty analysis in the techno-economic assessment of CO_2 capture and storage technologies: critical review and guidelines for use. *Int. J. Greenh. Gas Control* 100:103113
55. Bailera M, Hanak DP, Lisbona P, Romeo LM. 2019. Techno-economic feasibility of power to gas-oxy-fuel boiler hybrid system under uncertainty. *Int. J. Hydrog. Energy* 44(19):9505–16
56. Langhorst T, McCord S, Zimmermann A, Müller L, Cremonese L, et al. 2022. *Techno-economic assessment & life cycle assessment guidelines for CO_2 utilization (Version 2.0)*. Guidel., Glob. CO_2 Initiat., Ann Arbor, MI
57. Terlouw T, Bauer C, Rosa L, Mazzotti M. 2021. Life cycle assessment of carbon dioxide removal technologies: a critical review. *Energy Environ. Sci.* 14(4):1701–21
58. US Dep. Energy. 2022. *Best practices for life cycle assessment (LCA) of direct air capture with storage (DACS)*. Rep., US Dep. Energy, Washington, DC
59. Müller LJ, Kätelhön A, Bringezu S, McCoy S, Suh S, et al. 2020. The carbon footprint of the carbon feedstock CO_2. *Energy Environ. Sci.* 13(9):2979–92
60. Zang G, Sun P, Elgowainy A, Bafana A, Wang M. 2021. Life cycle analysis of electrofuels: Fischer–Tropsch fuel production from hydrogen and corn ethanol byproduct CO_2. *Environ. Sci. Technol.* 55(6):3888–97
61. Thonemann N, Pizzol M. 2019. Consequential life cycle assessment of carbon capture and utilization technologies within the chemical industry. *Energy Environ. Sci.* 12(7):2253–63
62. Natl. Acad. Sci. Eng. Med. 2022. *Current Methods for Life Cycle Analyses of Low-Carbon Transportation Fuels in the United States*. Washington, DC: Natl. Acad. Press
63. Thonemann N, Schulte A. 2019. From laboratory to industrial scale: a prospective LCA for electrochemical reduction of CO_2 to formic acid. *Environ. Sci. Technol.* 53(21):12320–29
64. Hoppe W, Thonemann N, Bringezu S. 2018. Life cycle assessment of carbon dioxide-based production of methane and methanol and derived polymers. *J. Ind. Ecol.* 22(2):327–40
65. Ravikumar D, Keoleian GA, Miller SA, Sick V. 2021. Assessing the relative climate impact of carbon utilization for concrete, chemical, and mineral production. *Environ. Sci. Technol.* 55(17):12019–31
66. De Luna P, Hahn C, Higgins D, Jaffer SA, Jaramillo TF, Sargent EH. 2019. What would it take for renewably powered electrosynthesis to displace petrochemical processes? *Science* 364(6438):eaav3506
67. Ioannou I, Javaloyes-Antón J, Caballero JA, Guillén-Gosálbez G. 2023. Economic and environmental performance of an integrated CO_2 refinery. *ACS Sustain. Chem. Eng.* 11(5):1949–61
68. Batchu SP, Hernandez B, Malhotra A, Fang H, Ierapetritou M, Vlachos DG. 2022. Accelerating manufacturing for biomass conversion via integrated process and bench digitalization: a perspective. *React. Chem. Eng.* 7(4):813–32
69. Baliban RC, Elia JA, Floudas CA. 2013. Biomass to liquid transportation fuels (BTL) systems: process synthesis and global optimization framework. *Energy Environ. Sci.* 6(1):267–87
70. Moncada B J, Aristizábal MV, Cardona ACA. 2016. Design strategies for sustainable biorefineries. *Biochem. Eng. J.* 116:122–34
71. Liao M, Yao Y. 2021. Applications of artificial intelligence-based modeling for bioenergy systems: a review. *GCB Bioenergy* 13(5):774–802
72. Velidandi A, Gandam PK, Chinta ML, Konakanchi S, Bhavanam AR, et al. 2023. State-of-the-art and future directions of machine learning for biomass characterization and for sustainable biorefinery. *J. Energy Chem.* 81:42–63
73. Liao M, Kelley SS, Yao Y. 2019. Artificial neural network based modeling for the prediction of yield and surface area of activated carbon from biomass. *Biofuels Bioprod. Biorefining* 13(4):1015–27
74. Huntington T, Baral NR, Yang M, Sundstrom E, Scown CD. 2023. Machine learning for surrogate process models of bioproduction pathways. *Bioresour. Technol.* 370:128528
75. Fajardy M, Mac Dowell N. 2017. Can BECCS deliver sustainable and resource efficient negative emissions? *Energy Environ. Sci.* 10(6):1389–426

76. Prussi M, Lee U, Wang M, Malina R, Valin H, et al. 2021. CORSIA: the first internationally adopted approach to calculate life-cycle GHG emissions for aviation fuels. *Renew. Sustain. Energy Rev.* 150:111398
77. Dornburg V, Lewandowski I, Patel M. 2003. Comparing the land requirements, energy savings, and greenhouse gas emissions reduction of biobased polymers and bioenergy: an analysis and system extension of life-cycle assessment studies. *J. Ind. Ecol.* 7(3–4):93–116
78. Sheldon RA, Sanders JPM. 2015. Toward concise metrics for the production of chemicals from renewable biomass. *Catal. Today* 239:3–6
79. Eerhart AJJE, Faaij APC, Patel MK. 2012. Replacing fossil based PET with biobased PEF; process analysis, energy and GHG balance. *Energy Environ. Sci.* 5(4):6407–22
80. Liang C, Gracida-Alvarez UR, Hawkins TR, Dunn JB. 2023. Life-cycle assessment of biochemicals with clear near-term market potential. *ACS Sustain. Chem. Eng.* 11(7):2773–83
81. Liska AJ, Yang H, Milner M, Goddard S, Blanco-Canqui H, et al. 2014. Biofuels from crop residue can reduce soil carbon and increase CO_2 emissions. *Nat. Clim. Change* 4(5):398–401
82. Sánchez M, Amores E, Abad D, Rodríguez L, Clemente-Jul C. 2020. Aspen Plus model of an alkaline electrolysis system for hydrogen production. *Int. J. Hydrog. Energy* 45(7):3916–29
83. Ishaq H, Dincer I. 2021. Comparative assessment of renewable energy-based hydrogen production methods. *Renew. Sustain. Energy Rev.* 135:110192
84. Shaner MR, Atwater HA, Lewis NS, McFarland EW. 2016. A comparative technoeconomic analysis of renewable hydrogen production using solar energy. *Energy Environ. Sci.* 9(7):2354–71
85. Wu N, Lan K, Yao Y. 2023. An integrated techno-economic and environmental assessment for carbon capture in hydrogen production by biomass gasification. *Resour. Conserv. Recycl.* 188:106693
86. Lin PY, Whang LM, Wu YR, Ren WJ, Hsiao CJ, et al. 2007. Biological hydrogen production of the genus *Clostridium*: metabolic study and mathematical model simulation. *Int. J. Hydrog. Energy* 32(12):1728–35
87. Ozbas EE, Aksu D, Ongen A, Aydin MA, Ozcan HK. 2019. Hydrogen production via biomass gasification, and modeling by supervised machine learning algorithms. *Int. J. Hydrog. Energy* 44(32):17260–68
88. Lee J, Hong S, Cho H, Lyu B, Kim M, et al. 2021. Machine learning-based energy optimization for on-site SMR hydrogen production. *Energy Convers. Manag.* 244:114438
89. Farsi A, Dincer I, Naterer GF. 2020. Multi-objective optimization of an experimental integrated thermochemical cycle of hydrogen production with an artificial neural network. *Int. J. Hydrog. Energy.* 45(46):24355–69
90. Saadetnejad D, Oral B, Can E, Yıldırım R. 2022. Machine learning analysis of gas phase photocatalytic CO_2 reduction for hydrogen production. *Int. J. Hydrog. Energy* 47(45):19655–68
91. Zhao S, Li J, Chen C, Yan B, Tao J, Chen G. 2021. Interpretable machine learning for predicting and evaluating hydrogen production via supercritical water gasification of biomass. *J. Clean. Prod.* 316:128244
92. Ozbilen A, Aydin M, Dincer I, Rosen MA. 2013. Life cycle assessment of nuclear-based hydrogen production via a copper-chlorine cycle: a neural network approach. *Int. J. Hydrog. Energy* 38(15):6314–22
93. Sarp S, Gonzalez Hernandez S, Chen C, Sheehan SW. 2021. Alcohol production from carbon dioxide: methanol as a fuel and chemical feedstock. *Joule* 5(1):59–76
94. Parigi D, Giglio E, Soto A, Santarelli M. 2019. Power-to-fuels through carbon dioxide re-utilization and high-temperature electrolysis: a technical and economical comparison between synthetic methanol and methane. *J. Clean. Prod.* 226:679–91
95. Liu CM, Sandhu NK, McCoy ST, Bergerson JA. 2020. A life cycle assessment of greenhouse gas emissions from direct air capture and Fischer-Tropsch fuel production. *Sustain. Energy Fuels* 4(6):3129–42
96. Chisalita DA, Petrescu L, Cormos CC. 2020. Environmental evaluation of European ammonia production considering various hydrogen supply chains. *Renew. Sustain. Energy Rev.* 130:109964
97. Ibrahim Y, Al-Mohannadi DM. 2023. Optimization of low-carbon hydrogen supply chain networks in industrial clusters. *Int. J. Hydrog. Energy* 48(36):13325–42
98. Li L, Manier H, Manier MA. 2019. Hydrogen supply chain network design: an optimization-oriented review. *Renew. Sustain. Energy Rev.* 103:342–60
99. Chen C, Lu Y, Banares-Alcantara R. 2019. Direct and indirect electrification of chemical industry using methanol production as a case study. *Appl. Energy* 243:71–90

100. Schoeneberger C, Zhang J, McMillan C, Dunn JB, Masanet E. 2022. Electrification potential of U.S. industrial boilers and assessment of the GHG emissions impact. *Adv. Appl. Energy* 5:100089
101. Jabarivelisdeh B, Jin E, Christopher P, Masanet E. 2022. Model-based analysis of ammonia production processes for quantifying energy use, emissions, and reduction potentials. *ACS Sustain. Chem. Eng.* 10(49):16280–89
102. Weyand J, Habermeyer F, Dietrich RU. 2023. Process design analysis of a hybrid power-and-biomass-to-liquid process—an approach combining life cycle and techno-economic assessment. *Fuel* 342:127763
103. Liu Z, Chakraborty A, He T, Karimi IA. 2023. Technoeconomic and environmental optimization of combined heat and power systems with renewable integration for chemical plants. *Appl. Therm. Eng.* 219:119474
104. Statista. 2023. *Plastics use in the United States in 2019, with projections to 2060*. **https://www.statista.com/statistics/1339006/us-plastics-use-outlook/**
105. Lau WWY, Shiran Y, Bailey RM, Cook E, Stuchtey MR, et al. 2020. Evaluating scenarios toward zero plastic pollution. *Science* 369(6509):1455–61
106. Van der Hoeven M, Kobayashi Y, Diercks R. 2013. *Technology roadmap: energy and GHG reductions in the chemical industry via catalytic processes*. Rep., Int. Energy Agency, Paris
107. van der Giesen C, Cucurachi S, Guinée J, Kramer GJ, Tukker A. 2020. A critical view on the current application of LCA for new technologies and recommendations for improved practice. *J. Clean. Prod.* 259:120904
108. Yao Y, Graziano DJ, Riddle M, Cresko J, Masanet E. 2016. Prospective energy analysis of emerging technology options for the United States ethylene industry. *Ind. Eng. Chem. Res.* 55(12):3493–505
109. Griffin PW, Hammond GP, Norman JB. 2018. Industrial energy use and carbon emissions reduction in the chemicals sector: a UK perspective. *Appl. Energy.* 227:587–602
110. Katelhön A, Bardow A, Suh S. 2016. Stochastic technology choice model for consequential life cycle assessment. *Environ. Sci. Technol.* 50(23):12575–83
111. Meys R, Bachmann M, Winter B, Zibunas C, Suh S. 2021. Plastics by a circular carbon economy. *Science* 76:71–76
112. Yang F, Meerman JC, Faaij APC. 2021. Carbon capture and biomass in industry: a techno-economic analysis and comparison of negative emission options. *Renew. Sustain. Energy Rev.* 144:111028
113. Intergov. Panel Clim. Change Work. Group III. 2022. Climate change 2022: mitigation of climate change. In *Sixth Assessment Report of the Intergovernmental Panel on Climate Change*. Geneva: Intergov. Panel Clim. Change
114. Shao T, Pan X, Li X, Zhou S, Zhang S, Chen W. 2022. China's industrial decarbonization in the context of carbon neutrality: a sub-sectoral analysis based on integrated modelling. *Renew. Sustain. Energy Rev.* 170:112992
115. Yu S, Horing J, Liu Q, Dahowski R, Davidson C, et al. 2019. CCUS in China's mitigation strategy: insights from integrated assessment modeling. *Int. J. Greenh. Gas Control* 84:204–18
116. Pauliuk S, Arvesen A, Stadler K, Hertwich EG. 2017. Industrial ecology in integrated assessment models. *Nat. Clim. Change* 7:13–20
117. Lamers P, Ghosh T, Upasani S, Sacchi R, Daioglou V. 2023. Linking life cycle and integrated assessment modeling to evaluate technologies in an evolving system context: a power-to-hydrogen case study for the United States. *Environ. Sci. Technol.* 57(6):2464–73
118. Watanabe MDB, Cherubini F, Tisserant A, Cavalett O. 2022. Drop-in and hydrogen-based biofuels for maritime transport: country-based assessment of climate change impacts in Europe up to 2050. *Energy Convers. Manag.* 273:116403
119. Pehl M, Arvesen A, Humpenöder F, Popp A, Hertwich EG, Luderer G. 2017. Understanding future emissions from low-carbon power systems by integration of life-cycle assessment and integrated energy modelling. *Nat. Energy* 2(12):939–45
120. McDowall W, Solano Rodriguez B, Usubiaga A, Acosta Fernández J. 2018. Is the optimal decarbonization pathway influenced by indirect emissions? Incorporating indirect life-cycle carbon dioxide emissions into a European TIMES model. *J. Clean. Prod.* 170:260–68
121. Steffen W, Richardson K, Rockström J, Cornell SE, Fetzer I, et al. 2015. Planetary boundaries: Guiding human development on a changing planet. *Science* 347(6223):1259855

122. Tulus V, Pérez-Ramírez J, Guillén-Gosálbez G. 2021. Planetary metrics for the absolute environmental sustainability assessment of chemicals. *Green Chem*. 23(24):9881–93
123. Xue Y, Bakshi BR. 2022. Metrics for a nature-positive world: a multiscale approach for absolute environmental sustainability assessment. *Sci. Total Environ.* 846:157373
124. Bakshi BR, Ziv G, Lepech MD. 2015. Techno-ecological synergy: a framework for sustainable engineering. *Environ. Sci. Technol.* 49(3):1752–60
125. Martinez-Hernandez E, Leung Pah Hang MY, Leach M, Yang A. 2017. A framework for modeling local production systems with techno-ecological interactions. *J. Ind. Ecol.* 21(4):815–28
126. Liu X, Bakshi BR. 2019. Ecosystem services in life cycle assessment while encouraging techno-ecological synergies. *J. Ind. Ecol.* 23(2):347–60
127. Thomassen G, Van Dael M, Van Passel S, You F. 2019. How to assess the potential of emerging green technologies? Towards a prospective environmental and techno-economic assessment framework. *Green Chem*. 21(18):4868–86
128. Moni SM, Mahmud R, High K, Carbajales-Dale M. 2020. Life cycle assessment of emerging technologies: a review. *J. Ind. Ecol.* 24(1):52–63
129. Petti L, Serreli M, Di Cesare S. 2018. Systematic literature review in social life cycle assessment. *Int. J. Life Cycle Assess.* 23(3):422–31