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*Review*

# Design of Sustainable Biofuel Processes and Supply Chains: Challenges and Opportunities

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**Abstract:** The current methodological approach for developing sustainable biofuel processes and supply chains is flawed. Life cycle principles are often retrospectively incorporated in the design phase resulting in incremental environmental improvement rather than selection of fuel pathways that minimize environmental impacts across the life cycle. Further, designing sustainable biofuel supply chains requires joint consideration of economic, environmental, and social factors that span multiple spatial and temporal scales. However, traditional life cycle assessment (LCA) ignores economic aspects and the role of ecological goods and services in supply chains, and hence is limited in its ability for guiding decision-making among alternatives—often resulting in sub-optimal solutions. Simultaneously incorporating economic and environment objectives in the design and optimization of emerging biofuel supply chains requires a radical new paradigm. This work discusses key research opportunities and challenges in the design of emerging biofuel supply chains and provides a high-level overview of the current "state of the art" in environmental sustainability assessment of biofuel production. Additionally, a bibliometric analysis of over 20,000 biofuel research articles from 2000-to-present is performed to identify active topical areas of research in the biofuel literature, quantify the relative strength of connections between various biofuels research domains, and determine any potential research gaps.

**Keywords:** biofuels; sustainability; sustainable biofuel supply chain; next generation biofuels; bibliometric analysis; multiobjective optimization; multiscale modeling; life cycle assessment

## 1. Introduction

Chemical technologies and the chemical process industry provide a range of useful and valuable products derived from biobased resources for use in personal care products, health products, agrochemicals, and transportation fuels. However, the production of these products is accompanied by generation of vast quantities of wastes and a range of harmful emissions to air, water, and soil. There is increasing realization that resource consumption and anthropogenic-derived impacts can have long-standing consequences on global ecological systems, and place strain on the natural biogeochemical cycles that support human life. Published findings from the millennium ecosystem assessment (MEA)—an international collaboration designed to assess the impact and widespread consequences of environmental change for human and ecological well-being, indicate that in the second half of the 20th century anthropogenic-derived resource degradation and overconsumption of natural capital have changed ecosystems more rapidly and extensively than in any comparable period in human history [1]. Rockstrom and colleagues assessed that the Earth has transgressed planetary boundaries for climate change, biodiversity, nitrogen cycle balance and is fast approaching the limit of safe operating space for global freshwater use, land use change, ocean acidification and global phosphorous cycle balance [2–5].

Traditional methods of chemical process design have primarily relied on finding the economic optimum subject to physical constraints, namely satisfying the heat and material balances and thermodynamic limitations. However, concerns over the depleting fossil energy sources, mounting regulatory compliance and the resulting push towards environmentally conscious process design are forcing designers to consider reduced environmental impact as one of the product design objectives. Business leaders have begun to realize that such a shift towards more sustainable design practices can not only minimize the environmental impact of industrial activity but is also crucial for long term success and sustainability of their enterprises.

The emerging field of sustainability science and engineering is developing tools to recognize, quantify, and reconcile resource limitations; human needs, and optimize global and human benefit. The concept of sustainability is multifaceted; encompassing the entirety of the human enterprise, interfacing with environmental, social, political, and economic issues, and as such is highly interdisciplinary. The outstanding challenge facing the chemical industry is the incorporation of environmental and sustainability objectives along with traditional design objectives in the development of emerging chemical processes. The rapid development of biofuels as a potentially sustainable and cleaner replacement for conventional fuels represents a unique challenge for the chemical industry that requires simultaneous consideration of economic, social, and ecological aspects and thus exemplifies an excellent content in which to understand the challenges and opportunities for designing sustainable supply chains.

## 2. Emerging Biofuel Pathways

Global climate change, volatile petroleum prices, energy security issues, and resource depletion have driven nations to consider adding renewable and alternative energy options to their energy portfolios. Transportation as well as the power and electricity generation sector constitute the two largest greenhouse gas (GHG) emitting sectors in the United States, accounting for 27% and 31% of total GHG emitted in 2013 respectively [6]. Accordingly, this has prompted the development of United States (U.S.) regulatory programs as well as European directives designed to mitigate GHG emissions from the transportation and power generation sector while concurrently increasing domestic energy independence and security. In 2007 the U.S. congress passed the Energy Independence and Security Act (EISA) [7], which mandates the production of 36 billion gallons of biofuels by the year 2022, and stipulates that a percentage must be derived from conventional, cellulosic biofuel, biomass-based diesel, and advanced biofuels. Additionally, EISA sets yearly volumetric biofuel production targets and requires renewable fuels achieve minimum reductions in overall life cycle GHG emissions relative to baseline petroleum fuels. Similarly, in 2009 the European Union (EU) passed the renewable energy directive (RED) [8]. This legislation requires that the EU obtain 20% of its total energy consumption from renewable sources, and derive 10% of energy consumption within the transportation sector from renewable resources by 2020. Furthermore, the EU imposed a 5% cap on the amount of food crop-derived biofuels used to meet the EU's 2020 goal, in an effort to mitigate the potential social and economic impacts of competition between crops for food *vs.* fuel. The RED sets minimum life cycle GHG emission reductions targets of 35% relative to baseline petroleum fuels for the year 2010, increasing to 50% in 2017 and 60% in 2018.

Currently ethanol from corn is the most widely produced and utilized biofuel in the United States. However, critical concerns have been raised about the potential of corn ethanol and other first generation biofuels in mitigating climate change and reducing dependence on fossil fuels. It has been contended that the direct and indirect land use change effects may possibly negate the GHG reduction potential of first generation biofuels possibly resulting in overall higher life cycle GHG emissions relative to baseline petroleum fuels [9–11]. In addition, first generation biofuels require changes in the existing transportation infrastructure such as modifications to vehicle engines and fuel pipelines. Further, the production and use of first generation biofuels have resulted in deleterious impacts on ecosystem goods and services such as soil erosion, water and air pollution, and loss of biodiversity, and thus have prompted the development of next generation biofuels [12].

A myriad of feedstocks and conversion platforms pathways are currently under development for next generation biofuel production, shown in Figure 1. Common biofeedstocks include sugarcane and corn, lignocellulosic biomass, algae, and oil-seeds. Lignocellulosic feedstocks include agricultural residues such as corn stover and forest residues; energy crops such as switchgrass, *Miscanthus*, and poplar; and industrial/municipal solid wastes. Additionally, several non-food lipid sources including algae and *Jatropha* are being considered for biofuel production. The "Billion Ton Study" jointly conducted by the US Department of Energy (DOE) and the US Department of Agriculture (USDA) provides a detailed quantification of available biomass in the US for producing fuels and biobased products, and estimates that up to 1.6 billion tons of dry biomass can be produced annually in the contiguous U.S. for meeting growing energy demands without displacing critical food, fiber, or feed crops [13]. These findings are compelling as they suggest that the U.S. has the capacity to support a large-scale domestic biofuels and bioproducts market.

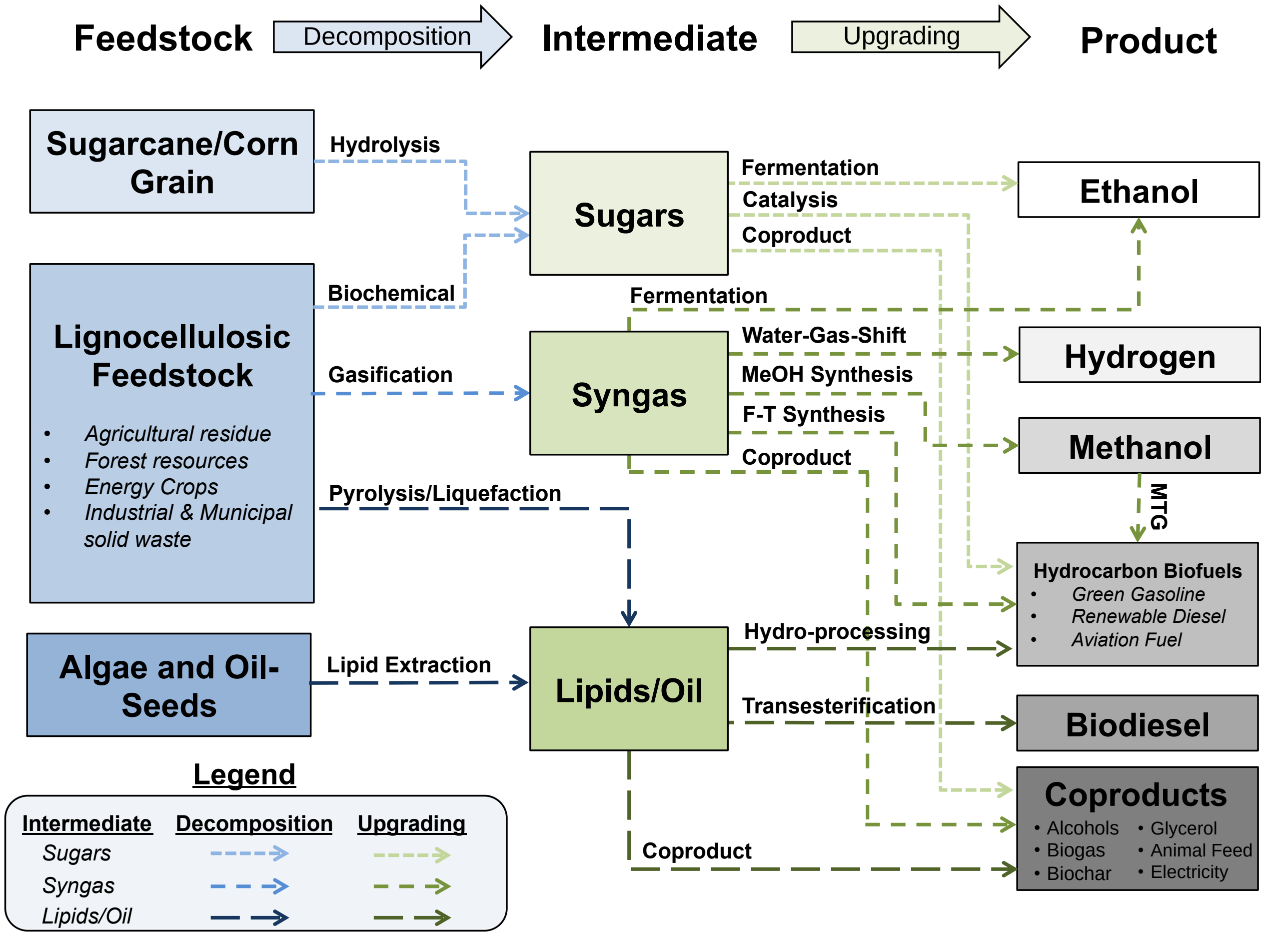

**Figure 1.** Feedstocks and conversion pathways for biofuel production. MTG: Methanol to Gasoline. F-T Synthesis: Fischer-Tropsch Synthesis.

Several comprehensive reviews of the possible catalytic, biochemical, and thermochemical conversion pathways for the production of biofuels from biomass feedstocks are available [14–17]. Traditionally, fats and oils derived from oilseed crops are converted to biodiesel via transesterification involving chemical reactions with an alcohol, such as methanol. However, biodiesel has certain undesirable properties such as poor cold flow properties, high cloud point, and roughly 10% lower energy density when compared with petroleum derived diesel fuel. Alternatively, oils and fats can be catalytically hydrotreated and converted to renewable diesel—a renewable hydrocarbon fuel that is fungible with traditional petroleum fuels. Lignocellulosic feedstocks, such as woody biomass and agricultural residues, require acid treatments to decompose cellulose and hemicellulose into sugars, which can be subsequently reformed into hydrocarbons via microbial agents [18]. Dumesic and coworkers have unraveled an entire set of catalytic reactions that convert biomass into hydrocarbon biofuels in the gasoline, diesel, and jet range [16,19–25]. Bond and coworkers successfully reported a strategy for converting γ-valerolactone, an intermediate produced from biomass carbohydrates, into liquid alkenes targeted for transportation fuels [26]. Their proposed integrated catalytic system eliminates the need for an external source of hydrogen.

Thermochemical conversion via pyrolysis or gasification has gained widespread attention as commercial platforms for biofuel production [27]. Pyrolysis involves thermochemical decomposition of organic matter at 400–600 °C in absence of oxygen and produces oxygenated bio-oil as well as biochar and non-condensable gases as coproducts [28–32]. Pyrolysis oil can be catalytically converted to high-octane hydrocarbon biofuels in the gasoline and diesel range [29,33,34], while several uses for the bio-char including (1) a soil amendment or (2) combustion to produce electricity are actively being investigated [35–41]. Agrawal and Singh presented a conceptual design of a hydrogen bio-oil process using fast pyrolysis and hydrodeoxygenation for producing liquid transportation fuels that require only modest quantities of supplementary $H_2$ [42]. Another promising thermochemical pathway is gasification, in which biomass is converted to synthesis gas (syngas)—a mixture containing CO, $H_2$, $CH_4$, $N_2$ and $CO_2$ by heating the input feed to high temperatures (>700 °C) and reacting with air, oxygen, and/or steam. Syngas can then be converted into liquid fuels by well-known reactions such as Fischer-Tropsch synthesis or synthesizing methanol and subsequent conversion to gasoline. Dauenhauer and coworkers at the University of Minnesota have combined the biomass gasification, tar cleanup, and water-gas shift into a single reactor [43].

Recently, microalgae have been touted as a promising feedstock for conversion to liquid transportation fuel due to their unique ability to utilize carbon dioxide from industrial activities [44], high photosynthetic efficiency [45], and ability to be grown on marginal or otherwise non-arable land [46]. Algae derived biofuels do not directly displace or put market pressure on food crops, as do the production of biofuels derived from corn, soybean, or sugarcane. Furthermore, algae can be grown using different growth media including wastewater as well as brackish/saline water; the use of which has the capacity to substantially reduce the nutrient and water-footprint of microalgal fuels relative to traditional terrestrial biofeedstocks [47]. Algae can be grown in a semi-continuous to continuous manner, and thus do not require perennial harvesting such as other leading forms of biomass including poplar or perennial grasses. Brennan and Owende presented a comprehensive overview of the different technologies for microalgae cultivation, harvesting, conversion technologies, and the potential useful products including biofuels [48]. Furthermore, an emerging concept of using cyanobacteria to produce ethanol through intracellular photosynthetic process in cyanobacteria has shown promise due to its carbon footprint reduction potential [49].

Anaerobic digestion has gained interest as a process for producing renewable energy from biomass resources. Anaerobic digestion is a biological process in which microorganisms decompose biodegradable material, in the absence of oxygen, to produce biogas that is comprised primarily of carbon dioxide and methane. Biogas can be further upgraded via Fischer-Tropsh synthesis, or can be used for direct combustion for space heating or electricity production after further upgrading. Anaerobic digestion is often implemented in emerging microalgal biofuel systems [50], and has been cited as a crucial process for enhancing the environmental sustainability of microalgae to biodiesel systems as it can be used to recover biogas from micro-algal residue [51]. Another alternative to conventional biomass is use of a combination of perennial low input high diversity (LIHD) crops. These crops require very little input in terms of water, fertilizer and nutrients and have the ability to grow on degraded land; mitigating issues of food *vs.* fuel and boosting regional biodiversity. Additionally, these benefits enable LIHD based biofuel systems to produce higher net energy output per fossil fuel input compared to conventional biofuels [52]. However, due to lower biomass yields, LIHD biomass is often only used in decentralized, small-scale combustion and anaerobic digestion conversion systems [53–55]. The biofuel research landscape is rapidly evolving in regards to process multiplicity, complexity, and scope. A comprehensive review of historical trends in biofuel production and policy are beyond the scope of the current work but can be found in several notable studies [56–58]. Sustainable commercialization of biofuel production will require simultaneously addressing multiple technical, economic, social, and environmental challenges that occur throughout the supply chain, and thus inherently necessitates a collaborative approach.

## 3. Bibliometric Analysis of Biofuel Literature

Understanding the full range of potential environmental, social, and economic impacts of biofuel production prior to its widespread commercialization and use is pivotal for avoiding unintended consequences and for guiding the sustainable development of the biofuels industry [59]. Moreover, holistic assessment of the widespread direct and indirect impacts of biofuel production requires integrating data and information across multiple research domains and rigorous analysis of peer-reviewed literature. As such, collaboration and synthesis across multiple disciplines is necessary for environmentally conscious decision-making. However the degree to which interdisciplinary research is occurring between biofuel research domains is often not well-understood or studied, such information is critical for determining research gaps, fragmentation between research domains, and for guiding the future trajectory of research in biofuels.

We performed a bibliometric analysis to: (1) identify active topical areas of research in the biofuel literature; and (2) quantify the relative strength of connection between various biofuels research domains via analyzing the occurrence and co-occurrence frequency of author supplied and indexed keywords from over 20,000 biofuels articles published from 2000 to present. The resulting analysis provides useful insights regarding the strength of connection and coupling between various research domains in the biofuel literature, as well as potential research gaps, *i.e.*, research areas that may require further synthesis and integration. Keywords for over 20,700 articles were obtained using the search-term "Biofuels" from the SCOPUS database [60]. In absence of author-supplied keywords, indexed keywords were used. This approach was leveraged over using both author-supplied keywords and indexed keywords, so as to avoid potential double counting. Keywords were aggregated into 36 topic areas related to 7 broad themes; shown in Table 1. The analysis expands on the method of identifying and aggregating keywords provided in Ridley *et al.* [61], please see supporting information for a complete list of keywords and method of data aggregation. The analytic framework and bibliometric algorithm established in Van Eck and Waltman was used to detect the number of co-occurrences of select keywords [62]. The co-occurrence data was mapped via network software (ORA) [63] to visualize the dynamic interactions between select biofuel research domains. The strength of the linkage between research topics (nodes) indicates its relative co-occurrence and is proportional to the line width, while the size of the node indicates its relative occurrence.

**Table 1.** Themes and topics for author supplied and indexed keywords. A detailed list of all keywords is in Table S1.

| Theme | Topic | Example Keywords |
|---|---|---|
| Environmental & Human Wellbeing | Food Security | Food Supply, Food Crop |
| | Human Health | Mortality, Asthma |
| | GHGs | Greenhouse Gases, Carbon Dioxide |
| | Air Quality (Non-GHGs) | Particulate Matter, Volatile Organic Compounds |
| | Soil Resources | Soil Organic Carbon, Soil Fertility |
| | Land Use Change | Indirect Land Use Change, Direct Land Use Change |
| | Water Resources | Groundwater, Water Footprint |
| | Biodiversity | Wildlife, Biodiversity |
| | Life Cycle Assessment | Life Cycle Analysis, Life Cycle Assessment |
| | Ecosystem Services | Ecosystem Services, Ecosystems |
| Economy | Cost of Production | Technoeconomic analysis, Infrastructure |
| | Market Forces | Supply and Demand, Cost Competitiveness |
| | Policy | RFS2, EISA, LCFS |
| | Trade | Import, Export, Tariff |
| Production Distribution, Technology & Infrastructure | Feedstock Production and Agronomics | Biomass Production, Agronomics |
| | Feedstock Logistics | Pretreatment, Biomass transportation |
| | Fuel Distribution and Infrastructure | Pipeline, Fuel Storage |
| Biofuels | Aviation Fuel | Aviation Fuel, Jet Fuel |
| | Biodiesel | Biodiesel, Biodiesel Blend |
| | Ethanol | Ethanol, Lignocellulosic Ethanol |
| | Hydrocarbon Biofuel | Drop in replacement biofuel, Renewable Diesel |
| | Butanol | Butanol, Biobutanol |
| | Biogas | Biogas, Biomethane |
| Conversion Platforms | Pyrolysis | Fast Pyrolysis, Pyrolysis oil |
| | Gasification | Gasification, BTL |
| | Transesterification | Esterification, FAME |
| | Hydrolysis | Hydrolysis, Fermentation |
| | Anaerobic Digestion | Anaerobic Digestion |
| Feedstocks | Woody Biomass | Willow, Poplar |
| | Perennial Grasses | Switchgrass, *Miscanthus* |
| | Oil Seeds | *Jatropha*, Soybean, Rapeseed |
| | Algae | Microaglae, Macroalgae |
| Feedstocks | Agricultural Residue | Sugarcane Bagasse, Corn Stover, Forest Residue |
| | Industrial & Municipal Waste | Waste Cooking Oil, Vegetable Oil |
| | Grains & Sugar Crops | Corn, Wheat, Rye |
| Thermodynamics | N/A | Exergy, Emergy |

Adapted from Ridley *et al.* [61].

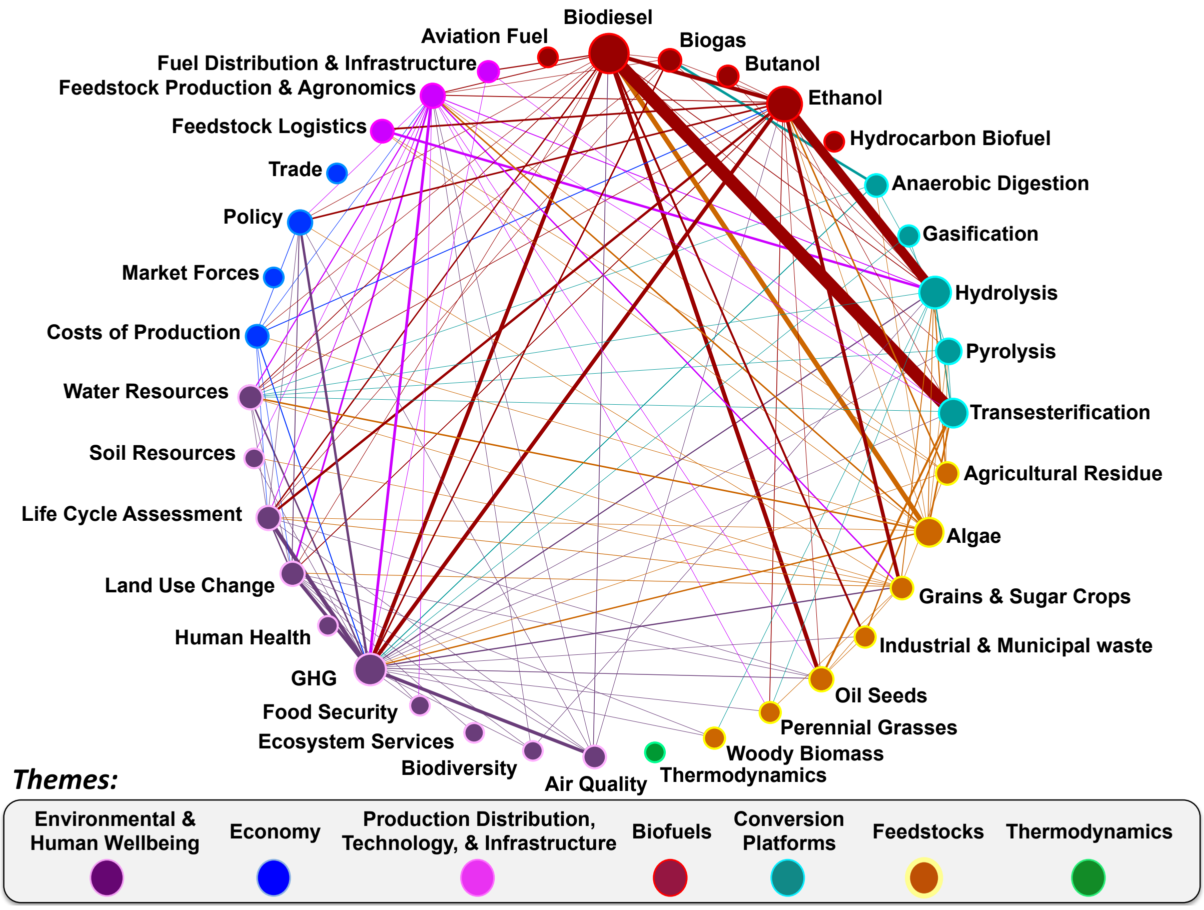

**Figure 2.** Bibliometric network analysis of biofuel research articles published between 2000 to present. The size of the nodes is scaled up as per the number of times each keyword occurs in the search. The width of the edges represents the co-occurrence of specific keywords. Colors of the nodes represent distinct research topic areas. Note: a co-occurrence cutoff value of 80 was chosen to identify significant connections between nodes in the network; as such some nodes appear to have no connections.

Figure 2 presents a co-occurrence network graph, illustrating the connectivity between various research topics in the biofuels literature. Figure 2 reveals that greenhouse gases, biodiesel, ethanol, transesterification, and hydrolysis had the highest frequency of co-occurrence in the literature, while market forces, trade, biodiversity, ecosystems goods and services (EGS), thermodynamics, aviation fuel, and hydrocarbon biofuels were not well represented. Nodes with no connections represent research fields that lack significant collaborations with other research areas in the biofuel literature, and may be emerging or nascent topics. Figure 2 reveals that substantial research has been invested in evaluating GHG emissions related to biofuel production, while little effort has been made to evaluate impacts on soil resources, human health, food security, biodiversity, and ecological goods and services. While GHG emissions represent an important sustainability aspect for biofuel production, other categories must also be considered so that biofuels do not inadvertently shift their impacts to other domains.

Furthermore, the lack of research (represented by lack of connecting links) on ecological goods and services, biodiversity, soil resources, and water resources is alarming, as prior research has suggested that the adoption of first generation biofuels have resulted in higher rates of deforestation and soil erosion, loss of biodiversity, and increased stress on water resources [64,65]. Hydrocarbon biofuels as well as aviation fuels were found to have marginal to no connectivity with other research domains, as these biofuels represent emerging topics and have only recently received widespread scientific inquiry. As such, further collaborative research is needed in all aspects of these emerging fuel platforms. The network diagram shows sparse scientific coverage on the market forces and/or trade aspects of biofuel production, despite consistent growth in the international trade of biomass/biofuels over the past decade. Failure to consider the broader trade and market implications of biofuel production could have significant global economic and social repercussions. This is particularly important for developing countries that are increasing biofuel exports to meet international policy mandated volumetric biofuel production and renewable energy targets, as developing nations are often highly sensitive to the potential adverse impacts of biofuel production including accelerated destruction of natural ecosystems, agricultural runoff and soil erosion, increased food insecurity and malnutrition, and global climate change. The results of the bibliographic analysis highlight the need for further interdisciplinary research so to assess any potential dynamic interactions, feedbacks, trade-offs, and mitigate any unintended consequences of biofuel production.

## 4. Designing Sustainable Biofuel Supply Chains

The process of introducing and implementing environmentally benign strategies in chemical process design started with the introduction of heat integration strategies. These schemes were primarily introduced in response to the energy crisis at that time and not only led to reduction in the overall energy consumption in production plants but also increased revenues by minimizing the plant operating costs. Although these strategies introduced the concept of environmentally conscious design, they generally had a narrow scope and boundary. Traditionally, the chemical process industry has responded to the environmental challenge by resorting to end-of-pipe solutions or pollution remediation such as recycling, waste treatment, and disposal. Although these practices are valuable, they may require vast capital and operating expenditures and can often shift the domain of pollution by moving it outside the analysis boundary. It is for this reason that in the last decade strategies and concepts such as green chemistry, life cycle assessment, environmentally conscious process design, and design for environment have come into prominence [66,67]. These concepts are attractive with their primary focus on avoiding waste generation rather than waste minimization. The unifying theme behind these approaches is to look at systems holistically by expanding the system boundary in traditional process design. Although, expanding the system boundary for a more holistic analysis is appealing, it presents a new challenge associated with the need for increased amount of data and computational time. With appreciation of such challenges and to address the shortcomings of some of these earlier approaches, process systems engineering has gradually expanded its analysis boundary from the narrowly focused process scale to the life cycle or supply chain scale and more recently to the ecosystem scale [68–72]. These approaches take a more holistic view by focusing on the entire life cycle or supply and demand webs of the selected products or processes. Zhuang *et al.* reviewed several existing modeling approaches for sustainable chemical production and their applications at multiple scales ranging from metabolism, to the life cycle, to ecosystems, and proposed a multi-scale approach integrating these models into a single cohesive framework [73].

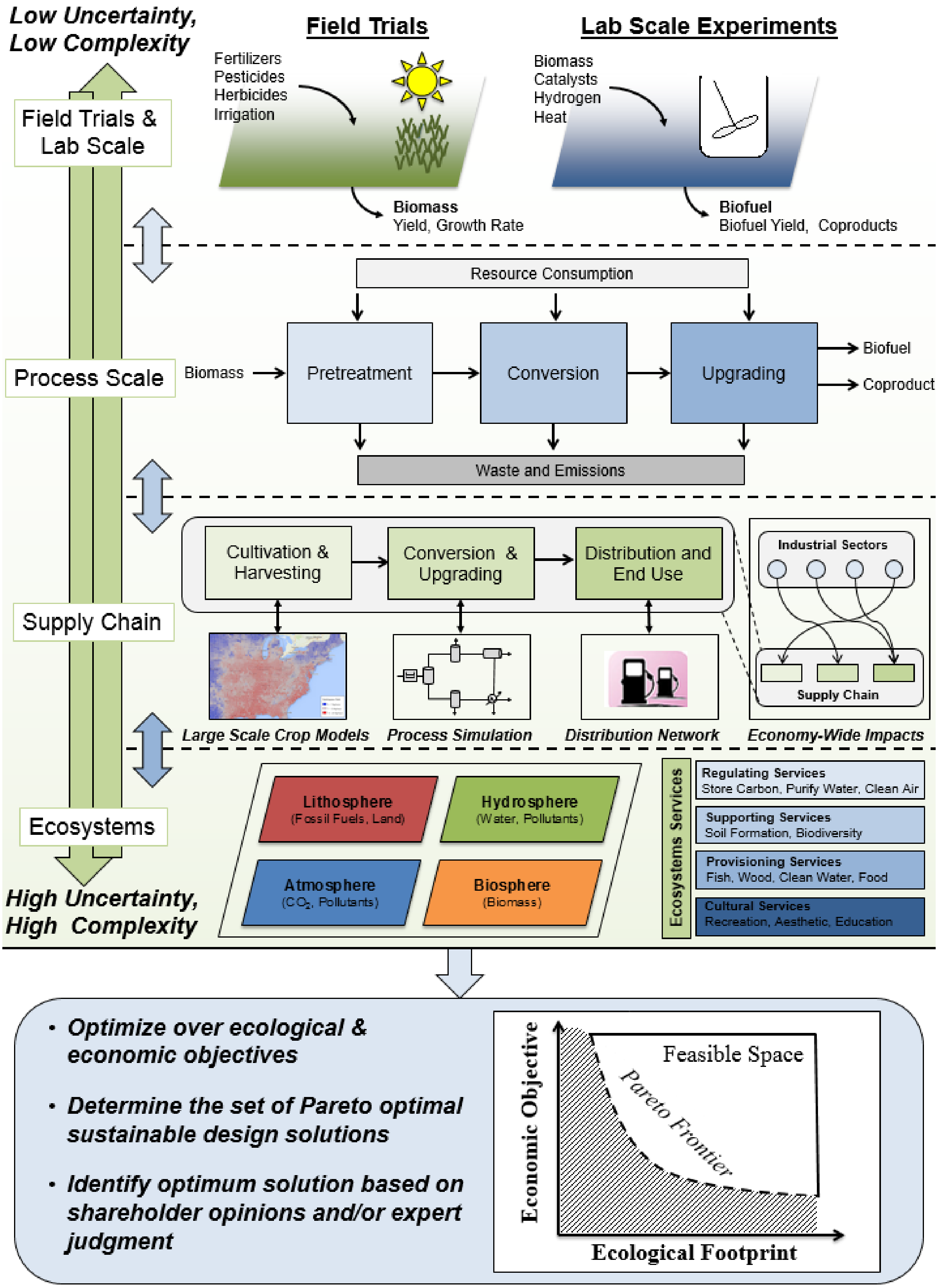

**Figure 3.** Modular Multi-scale, Multi-objective, Biofuel Supply Chain Optimization Framework.

Recent interest in biofuels has led to the development and use of models and computational tools at multiple scales including large-scale crop models, detailed chemical process design simulations, life cycle assessment models, and mathematical optimization tools. While these computational methods each provide unique and novel insights into the sustainability of emerging biofuels, these tools are often used in isolation and thus are limited in their ability for guiding decision-making. Synthesis of these models and tools into a unified framework, via collaboration between researchers across disciplines and modeling scales is required to provide a broader understanding of the sustainability of emerging biomass-to-fuel supply chains. Accordingly, this work discusses a modular multi-scale and multi-objective framework spanning from the field/lab scale, to the detailed process scale, the life cycle scale, and finally the ecosystems scale for holistic sustainability assessment of biofuel production; see Figure 3. The envisioned multi-scale approach evaluates the process in a hierarchical fashion, starting from the field/lab scale and expanding the system boundaries as successive scales are added. Information from lab/field trials such as reactor kinetic studies, pilot-scale biomass growth trials, and experimental trials on biofuel yields are used to parameterize design blocks and crop models used at the process level. Information such as liquid product distribution and operating plant utility requirements obtained via the process level is subsequently utilized to model unit processes in the supply chain. Information at the supply chain is coupled with the larger economy and ecosystems via the use of environmentally extended economic models. The proposed framework synthesizes results obtained from models/methods across disciplines and scales (*i.e.*, the lab/field scale, process scale, supply chain, and ecosystem scale) to inform process design and decision-making. Insights obtained from models/methods at differing scales (as well as their limitations) are disseminated between researchers working at different modeling tiers. This multi-scale interdisciplinary approach provides stakeholders different tiers of decision-making criteria (*i.e.*, capital and operating costs, environmental damages, or ecological impacts), and thus a holistic understanding of the broader consequences of emerging fuel pathways. Further, such an approach is conceptually attractive since it facilitates the evaluation procedure starting with simple systems and increasing complexity gradually as successive information layers are added. This approach can allow for screening out bad alternatives, for example, those with a negative economic potential early in the design stage thus saving computational time and providing a range of alternatives to the decision maker while avoiding arbitrary combinations. Further, the proposed framework considers multi-objective optimization over the broader superstructure to identify supply chain configurations that optimize ecological and economic performance while simultaneous achieving minimum threshold sustainability criteria. Design opportunities and challenges for each scale of analysis are discussed in the following sections.

### *4.1. Field Trials and Laboratory Scale Experiments*

The first level of analysis involves field trials and laboratory scale experiments such as model compound studies [74,75], effects of catalysts and reactor conditions on product streams [76], estimation of fuel properties [77], reactor kinetic studies [78,79], pilot-scale biomass growth trials [80], and the effect of varying fertilizer and management practice on biomass yield [81,82]. This research is often focused on understanding the mechanism or principles underlying experimental observation, or determining the technically feasibility of an emerging technology. Factorial designs are often implemented to study the effect of each effect factor on the response variable (*i.e.*, biofuel yield), as well as the effect of interactions between factors on the response variable [83]. Further, data at the field/lab scale typically has low uncertainty, and is often used for calibration and parameterization in process models.

### *4.2. Process Scale*

The next tier of analysis involves the use of agricultural crop models as well as traditional process design analysis. A variety of large-scale crop models have been developed to simulate bioenergy crop production including herbaceous crops (e.g., EPIC, ALMANAC, MISCANMOD, MISCANFOR, WIMOVAC, Agro-IBIS, Agro-BGC, APSIM, AUSCANE, LPJmL, CANEGRO), woody bioenergy crops (e.g., 3PG, SECRETS), and crassulacean acid metabolism crops (e.g., EPI) [84]. These models simulate biomass yield, nutrient cycling, water requirements, carbon flux, and other key parameters under different crop management practices. Recent efforts have been made to integrate these models with Geographic Information System (GIS) to create spatially explicit large-scale crop models [85]. Conversion of biomass to fuel can be modeled using conventional process simulators such as Aspen Plus, ChemCAD, or SuperPro [86]. Inputs to the biorefinery generally include raw materials and utilities such as biomass, steam, electricity, and cooling water. Similarly, final products typically include biofuel, coproducts, waste, and emissions. Process simulators provide a scientifically rigorous method for determining the utility requirements as well as material and energy flows for conversion of biomass to renewable transportation fuel. Information at this scale of analysis is often used for developing technoeconomic models [30,87], with the primary objective of maximizing material and energy efficiency while concurrently minimizing operating costs. Life cycle considerations such as the embodied impacts of material and energy inputs are not considered within the scope of analysis at this scale, thus decision-making based solely on information at the process scale could result in unsustainable design choices. For example, analysis based solely on the process scale could result in selection of high quality resources (*i.e.*, fossil fuels) for maximizing plant performance and economics; however, these resources often have high upstream environmental or human health impacts.

### *4.3. Modeling the Supply Chain and Life Cycle*

The third level of analysis extends the analytic boundary to consider the material, energy, and emissions flows throughout the entire supply chain. This holistic systems approach captures environmental impacts that are outside the purview of the traditional process design boundary. Life Cycle Assessment (LCA) is one of the most common approaches for evaluating the environmental impact of a product or a process over its entire life cycle, and in recent years has emerged as the predominant method for analyzing the environmental sustainability of emerging biofuel platforms [88–95]. LCA considers impacts throughout all stages of the fuel life cycle—from raw material acquisition, to fuel conversion, and final use. LCA allows for a comprehensive understanding of the environmental impacts that occur at each stage of the supply chain, enabling the LCA practitioner to identify processes responsible for highest environmental burden and thus target these areas for process improvement. LCA can be used to quantify the anticipated impacts of a product or service prior to its widespread adoption, thus identifying and avoiding potential environmental pollutants, wastes, and environmental damages before they become embedded within the supply chain. Further, LCA can be used to compare the environmental performance between two products with the same functionality and can inform environmentally conscious decision-making. Garcia and You reviewed major challenges and opportunities in supply chain design and optimization—identifying several key technical challenges including: (i) multiscale challenges; (ii) multiobjective and sustainability challenges; and (iii) multi-player challenges [96].

### 4.3.1. Process LCA

LCA is a data intensive approach and has been extensively applied to study biofuel systems over the past decade. Several different LCA modeling methods have been developed; the most widely used LCA approach (*i.e.*, Process-LCA) defines a finite boundary by selecting the most important processes in a life cycle [97]. Data concerning the resource consumption and emissions for these processes are developed and compiled to generate a life cycle inventory (LCI). The life cycle impact assessment (LCIA) phase translates the energy, resource, and emissions flows identified in the LCI into their potential consequences for human health and the environment, and consists of a two-step process of impact classification and quantitative characterization. The classification step links each LCI flow with its related impacts on resource use, human health, and the environment. The characterization step calculates the magnitude of the associated impacts in terms of a reference unit for each category via multiplying the related resource, material, or energy flows with their respective impact factors. Translating the environmental impacts to a reference unit provides a common basis or measure for the generated impact, so that different emissions and resources can be compared and aggregated using a common unit. Data required for LCA can be obtained via commercial life cycle databases (e.g., ecoinvent [98]), publicly available life cycle data (e.g., OpenLCA [99], USLCI [100], GREET [101]), information from the open literature, or proprietary information.

Although widely used, process LCA suffers from many limitations including the use of an arbitrary life cycle boundary, combining data in disparate units and at multiple spatial and temporal scales, dealing with high dimensionality data involving varying degrees of uncertainty, and dealing with processes having a range of emissions [11]. Furthermore, for a system that simultaneously produces multiple products and coproducts these is no universally accepted method as to how to apportion the environmental impacts amongst said products. This is particularly important for biofuel systems in which non-fuel coproducts represent a significant fraction of total market value, mass, or energy flow as the choice of allocation procedure can often yield divergent results concerning the sustainability of these systems [102,103]. Additionally, biofuel LCAs often utilize differing functional units, system boundaries, allocation schemes, impact assessment methods, and report different sustainability metrics. Consequently, it is not unusual for LCA practitioners to obtain contradictory LCA results for the same system; this discrepancy has led to several harmonization and meta-analysis studies in the biofuels literature [104,105]. Data used in process LCA is at an intermediate scale since it is typically averaged to represent manufacturing processes, thus making it of limited use for making environmentally conscious engineering decisions about an individual process or equipment, which are at a finer scale, or for evaluating the effect on the macro economy, which is at a coarser scale.

### 4.3.2. EIO-LCA and Hybrid LCA

Input-output (IO) models, first developed by Nobel Prize winning economist Wassily Leontief, provide a mathematical framework for quantifying the inter-industrial connections and economic flows between different industrial sectors in the economy [106]. The traditional IO framework can be extended to consider the environmental impacts, emissions, and resource use for industrial sectors in the economy; and thus be utilized to perform LCA at the economy scale. This approach, known as Economic

Input-Output LCA (EIO-LCA) [107], does not suffer from the challenge of defining a finite life cycle boundary as does Process LCA. Further, EIO-LCA uses a relatively complete network, but at a coarse scale of resolution. Data at this scale often do not include the use phase of the life cycle. Recently, Bakshi and colleagues have developed Ecologically-based Life Cycle Assessment (EcoLCA), an environmentally extended input-output life cycle model capable of accounting for the consumption/role of ecosystem goods and services in a life cycle framework [108,109]. The EcoLCA model extends the traditional I-O framework to consider the direct and indirect environmental impacts that result from economic activities; including ecological and natural resource consumption, emissions, land-use, and other environmental impact categories [110–112]. EcoLCA quantifies ecological resource consumption using a hierarchy of thermodynamic metrics including energy, industrial cumulative exergy consumption (ICEC), and ecological cumulative exergy consumption (ECEC), as well as mass flow. However, while exergy-based methods for thermodynamic aggregation of natural resource consumption may provide useful insights, these methods have their own limitations and are debated in the literature [113–120]. Research on combining the best advantages of Process LCA and EIO-LCA has also resulted in Hybrid LCA approaches, which combine the details of Process LCA with the greater completeness of EIOLCA [121,122]. Hybrid LCA attempts to balance computational tractability, completeness, and the use of detailed information.

### 4.3.3. Attributional *vs.* Consequential LCA

LCA models may also differ in the approach employed to address the material and energy flows in the system under investigation. The attributional LCA (ALCA) methodology, which has been utilized for a vast majority of the LCA studies, attempts to quantify the flow of resources and emissions from a product system and its subsystems. Emissions and their impact are attributed to the final product by one of the several available methods (allocation or system expansion). However, researchers have argued that it is not fully possible to draw conclusions on future changes by using only ALCA [123,124]. In contrast, consequential LCA (CLCA) methodology, aims to explain how the physical flows to and from the technosphere may change in response to a change in the life cycle of the product or service [125]. CLCAs attempt to consider a much broader system boundary. The most commonly employed form of a CLCA considers the use of economic models that track monetary, material, and energy flows across economic systems. This is generally accomplished using marginal data and is accounted for on the basis of price elasticity of supply and demand [126–128].

The US Environmental Protection Agency (US EPA) has used a multi-market multi-region partial equilibrium model to determine land use change emissions in biofuel lifecycles. Several dynamic general/partial equilibrium models have been used to predict the implications of biofuel policy and commercialization on land use, international/domestic trade, and GHG fluxes and commodity markets within the agricultural sector including the Global Trade Analysis Project (GTAP), the Market Allocation Model, the Forestry and Agricultural Sector Optimization Model (FASOM), and the Food and Agricultural Policy Research Institute model, LEI-TAP model, and Modular Applied General Equilibrium Tool, Center for Agricultural and Rural Development model, International Model for Policy Analysis of Agricultural Commodities and Trade model, Common Agricultural Policy Regional Impact Analysis model, the Worldwide Agribusiness Linkage Program and Commodity Simulation Model, and the Modeling International Relationships in Applied General Equilibrium model [129–134]. However, lack of model transparency and high complexity often limit the utility of these approaches. Furthermore, these models often vary in regards to data requirements, scope, and model resolution. For example, models such as FASOM have high resolution for the United States but lack information regarding international trade; while models such as GTAP can provide estimates for domestic and international land-use change but at a low level resolution. Synthesis and coupling these dynamic economic models with biophysical land-use models such as the Integrated Model to Assess the Greenhouse Effect, Conversion of Land Use and its Effects as well as energy models such as the PRIMES Energy System Model can help support informed decision making [135,136]. However, it is important to note that that economic systems exhibit structural inconstancy (*i.e.*, change in individual behavior in response to a policy change), and coupling economic and biophysical models will increase overall model uncertainty [137]. Plevin *et al.* pair an economic-computable general equilibrium model with a $CO_2$ emissions estimation model and conclude that due to parametric uncertainties, the results obtained should be used for developing a range of possible results for comparison purposes rather than as deterministic estimates of land use change emissions [138].

LCAs of emerging technologies are difficult to conduct due to lack of technology specific data, dynamic and rapidly evolving systems, and isolation of environmental research from technical developments [139]. Prospective LCAs involve estimating environmental impacts of possible future scenarios and are affected by the choice of time horizon, complexity of the system, and extent of stakeholder engagement. Studies have used approaches such as scenario analysis [140,141], participatory methods involving expert elicitations and stakeholder opinions [139] and modeling of economic transactions to understand market-mediated effects [142]. Many of the challenges associated with prospective LCA can be overcome with inclusion of life cycle thinking at an early stage in research and development (R&D) via a collaborative dialogue between industry experts, stakeholders, and LCA practitioners.

Analysis at the supply chain or life cycle scale is often focused on improving efficiency and reducing environmental impacts across the life cycle, utilizing methods and metrics such as eco-efficiency, life cycle GHG emissions, net energy analysis, water footprint, and others. However, these methods fail to capture the impact of biofuel life cycles on ecological goods and services, *i.e.*, the fundamental goods and services provided by nature that sustain human life and are the fodder for all man-made capital and industrial activity [143]. Consequently, decisions based on these methods could result in unsustainable choices including heightened depletion and degradation of natural capital and ecosystems [111,144,145].

### *4.4. Ecosystems Scale*

The final tier of analysis extends the analytic scope to consider the role of ecological goods and services throughout the supply chain. As ecological goods and services play a fundamental role in sustaining industrial activity, it is paramount to account for their role in evaluating the impact and sustainability of emerging biofuel platforms. Examples of ecological goods and services include: timber, food, water, energy resources, clean air, minerals and ores, purification of air and water resources, flood and drought mitigation, pollination of crops and vegetation, maintenance of global biodiversity, as well as climate and disease regulation [146–148]. Since it is computationally intractable to model the complete supply chain by including each process as done at the life cycle level of analysis, the approach leveraged at this scale of analysis is closely related to existing hybrid (*i.e.*, tiered) LCA methods in which a process level model is used to determine process level consumption of ecological goods and services while economy wide-impacts are incorporated using EcoLCA [108,109,112,116,149].

Process level flows of ecological goods and services can be modeled using a host of computational models. Detailed models such as Century, EPIC, APEX, and SWAT can be used to simulate the effects of land management decisions on soil, water, nutrients and watersheds; however, these tools are data intensive and suffer from high model complexity [150–152]. The Integrated Valuation of Ecosystems Services and Tradeoffs (InVEST) modeling suite can be used to quantify and map a variety of regional ecosystems goods services as well as biodiversity for both terrestrial and marine environments including crop pollination, habitat quality, habitat risk assessment, managed timber production, managed fish aquaculture, marine water quality, sediment retention, water purification, carbon sequestration, and others [153]. Further, InVEST model(s) are open-source, generally simpler, more transparent, and user friendly as compared to the aforementioned approaches. Synthesizing these computational models with EcoLCA can provide a holistic understanding of the potential impacts and tradeoffs of biofuel production on ecological resources and biodiversity. Although this tier of analysis is the most comprehensive it often has high uncertainty due to (i) variability that is propagated and compounded at each preceding level of analysis (*i.e.*, from lab/field scale, to process scale, to supply chain); and (ii) high uncertainty in the modeling approaches used to quantify ecological goods and services.

Bakshi and colleagues have developed and applied a hybrid EcoLCA framework to investigate the sustainability of petroleum transportation fuels as well as select first and second-generation biofuels [110,111]. More recently, this framework has been applied to study emerging microalgal biofuel systems [145]. The results of these studies reveal that biofuels have high renewability but typically have low thermodynamic return on investment relative to baseline petroleum fuels. The low energy return on investment for biofuels is concerning as prior studies have suggested that a liquid technical fuel must achieve minimum threshold energy return on investment (EROI) values to sustain society. Failure to meet this minimum EROI criterion could result in widespread economic and social ramifications as more useful work must be expended by society for fuel production and thus cannot sustain other economic activities [154,155]. Recently, Bakshi and colleagues have developed a conceptual framework for designing technological and ecological systems that encourages synergy between human activity and nature [70,156]. The proposed techno-ecological synergy (TES) framework considers the demand of ecological goods and services from technological systems at multiple spatial scales ranging from the individual process scale, to supply chains and life cycles, as well as the supply of ecological good and services from ecological systems ranging from regional, to watershed, to global. The TES framework aims to reduce overconsumption of natural capital, and promotes technological systems to operate within safe ecological boundaries at multiple analytic scales. Application of the TES framework can provide unique insights into the sustainability of emerging biofuel supply chains.

### *4.5. Accounting for Multiple Objectives and Scales in Designing Sustainable Biofuel Processes/Supply Chains*

Environmentally conscious development of emerging biofuel pathways requires addressing alternatives that exist at each step along the life cycle with the possibility of a multitude of useful coproducts and waste streams. As such, decisions based on optimizing a single criterion (such as carbon footprint, EROI, or economic potential) can lead to the unintended consequence of trading one environmental problem for another. Many studies have focused on evaluating bioenergy potential encompassing several criteria—economic performance, environmental and social impact and have developed several tools that quantify these indicators [157]. For example, the SCORE Model developed by Krajnc and Domac uses a mix of qualitative and quantitative indicators such as contribution to forest management, impact of regional unemployment, $CO_2$ emissions, and percentage of self-sufficiency in electricity production, to analyze the sustainability of woody biomass production [158].

Studies often employ various optimization techniques to design an optimal biomass supply chain based on multiple criteria [159,160]. Formulating the design problem as a mathematical optimization task has been a common approach for analyzing technological systems. The design problem is generally formulated as either a mixed integer linear or non-linear optimization problem [161,162]. Research efforts have also resulted in coupling the design problem with LCA by quantifying the life cycle impacts of process alternatives. This could be accomplished using either single objective or multi-objective optimization (MOP) resulting in designs or options that represent the best compromise between the selected design criteria [163,164] Several studies have utilized MOP for the strategic design and implementation of biofuel systems. Zamboni *et al.* developed a spatially explicitly mixed integer linear program (MILP) optimization model for bioethanol production systems that simultaneously considers supply chain costs and life cycle GHG emissions [165,166]. De Meyer *et al.* developed a generalized mathematical model, OPTIMASS, that optimizes over strategic and tactical decisions, and can be used to investigate the potential effect of policy changes, emerging biofeedstocks, technological adoption/evolution, and logistics on the environmental sustainability of biofuel supply chains [167]. Čuček *et al.* coupled MOP with a regional biomass supply chain model [168]. Mele *et al.* developed a MILP optimization model to optimize economic and environmental objectives of the biofuel production chain, and applied the model to the sugarcane industry in Argentina [169]. More recently, Yue *et al.* developed a multi-objective life cycle optimization framework and applied it to study emerging hydrocarbon biofuel production [170]. MOP can be used to identify design solutions that optimize economic, environmental, and ecological dimensions of biofuel production; this set of optimal points constitutes a Pareto frontier in the design-solution space. Moreover, solutions that do not lie on the Pareto frontier are either infeasible or are sub-optimal. The Pareto frontier is particularly useful in MOP problems since by restricting attention to the set of choices that are Pareto efficient, a designer can evaluate tradeoffs within this set, rather than considering the full range of every parameter. Further, MOP can be used to identify the optimal mix of useful coproducts satisfying the selected set of life cycle environmental constraints. An alternative to mathematical programing is a heuristic approach that employs algorithms based on artificial intelligence to obtain a satisfactory local optimal solution, when a global optimal solution is not possible. Studies have employed various algorithms such as particle swarm optimization, genetic algorithms or honeybee foraging algorithms to identify a range of optimal solutions for various aspects of the biomass supply chain [171–173]. These approaches are expected to lead to the identification of synergies between feedstock production, processing methods, and the final mix of fuels and coproducts for the sustainable design of biorefineries [170,174,175].

### *4.6. Uncertainty and Variability*

Emerging hydrocarbon biofuel platforms have a high degree of uncertainty [176], due to lack of commercialization, climatic variability, technological evolution, material and energy price volatility, variability in supply and demand dynamics, dynamic effects in ecosystems, and changes in biofuel incentives and legislation over time. Further, sources of modeling uncertainty generally include: (i) parameter uncertainty; (ii) technological uncertainty; (iii) random error; (iv) systematic uncertainty; (v) methodological uncertainty; (vi) parametric variability; (vii) structural uncertainty; (viii) algorithmic/interpolation uncertainty; and (ix) policy uncertainty. These sources of uncertainty introduce variability at each stage of the analysis, which are compounded and propagated with subsequent modeling scales and the use of higher complexity models. Several commons approaches are often utilized to quantify uncertainty in environmental sustainability analysis including stochastic modeling and one-at-a-time (OAT) sensitivity analysis [177–179]. It is important to note that the primary utility of environmental sustainability analysis is to identify potential environmental impacts or damages of emerging technologies at early stages of R&D. However, recommendations at the design/conceptual phase typically have high uncertainty, which is often only reduced after large investments and progress in R&D have been made. As such, environmental sustainability analysis of emerging technologies inherently faces a tradeoff between utility and uncertainty. Additionally, for biofuel production uncertainty in upstream processes can translate into heightened risk downstream. For example, farmers are often reluctant to grow second generation biofeedstocks due to their high fixed cost of production, long establishment period, and uncertainty regarding the demand for these crops. However, the lack of large-scale agricultural production of second generation biofeedstocks generates heightened risk for developing next generation biorefineries, thus potentially limiting the demand for second-generation biofeedstocks.

## 5. Conclusions and Outlook

The framework outlined in this study has multiple features that make it conceptually attractive; however, the approach faces several challenges: (I) Interdisciplinary research requires effective communication, transfer, and synthesis of domain specific knowledge and data across research fields. This requires that collaborators become proficient in the colloquial terminology commonly used in said research fields, so that domain specific modeling results and technical information can be exchanged efficiently and information is not lost at the interface of research fields. (II) The long timeframe required for laboratory/field trials as well as the development and implementation of modeling tools may limit the effectiveness of this approach, as the "state of the art" may have changed or the technical system evolved from its prior conception at the start of the analysis. However, this issue can be addressed via several means. Streamlined models and methods can help reduce the computation time necessary for model development and implementation. Further, open source databases and the use of "big data" may help reduce the time required for data acquisition. Additionally, the modeling approach should be iterative; models should be configured to use the most robust, accurate and up-to-date data, with modeling tiers providing feedback-loops to inform the strategic design and development of biofuel processes and supply chains. (III) Differing models/tools may have contrasting assumptions, conflicting theoretical premises, and may report the results using disparate metrics. Additionally, the results may be subjective and have high degree of uncertainty. For these reasons, results should not be considered deterministic outcomes, but probabilistic measures to be used for comparative purposes [180].

In its inception, first generation biofuels were touted as a revolutionary new renewable and sustainable fuel source. Technological exuberance and naivety lead to their large-scale commercialization without proper consideration of the potential consequences for industry and the environment. Since then, a multitude of studies have shown that the production and use first generation biofuels has resulted in detrimental impacts on the ecosphere, environment, economy, and social welfare [64,181]. As biofuel production is inherently interconnected with various critical sectors of the economy (*i.e.*, agriculture, transportation, *etc.*), it is crucial to understand the potential widespread impact of biofuels on economics, environment, and human welfare before their widespread adoption and commercialization. Accordingly, a new paradigm is needed for the design of sustainable biofuel processes supply chains, and is contingent on collaboration across research domains and evaluation of potential impacts over multiple spatial and temporal scales. This work discussed a novel modular multiscale and multiobjective framework for analyzing emerging biofuel supply chains. While process-scale analysis is the most reductionist and is commonly employed in engineering analysis and traditional process design, this narrowly focused approach fails to capture broader environmental externalities; such shortsightedness could jeopardize the sustainability of emerging biofuel systems. The conceptual multiscale and multiobjective framework presented in this work addresses these limitations by optimizing economic and environmental objectives over the field/lab scale, process scale, supply chain, and ecosystems scale. This broad-based interdisciplinary approach is critical for guiding the sustainable development of the biofuels industry and for mitigating and avoiding any unintended consequences. Further, the results of the bibliographic analysis support the need for such a collaborative framework. Next generation biofuels represent a promising opportunity for the chemical industry and sustainability engineers to work hand in hand, and transform the traditional paradigm from “end of pipe” solutions to innovative, state of the art, and sustainable design solutions.

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## Author Contributions

GGZ and NV wrote the manuscript and conducted the bibliometric analysis. SSC performed the network analysis and constructed the bibliometric network figure. VK coordinated the study, and assisted/guided in the development and analysis of the network figure. VK and AEL reviewed the manuscript. All authors read and approved the final manuscript.

## Conflicts of Interest

The authors declare no conflict of interest related to the work.

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