

pubs.acs.org/journal/ascecg

# Poultry Waste Valorization via Pyrolysis Technologies: Economic and Environmental Life Cycle Optimization for Sustainable Bioenergy Systems

Ning Zhao, Johannes Lehmann, and Fengqi You\*

Cite This: ACS Sustainable Chem. Eng. 2020, 8, 4633–4646 Read Online					
ACCESS	III Metrics & More	E Artic	le Recommendations	(	s Supporting Information

**ABSTRACT:** This article addresses the life cycle optimization (LCO) of the poultry litter supply chain considering pyrolysis technologies that aim to sustainably convert poultry waste into biofuel and biochar. A multiobjective optimization framework integrated with a life cycle analysis methodology is developed. The economic objective is to maximize annualized profit per functional unit, and the environmental objective is to minimize the annual  $CO_2$ -equivalent greenhouse gas (GHG) emissions per functional unit. The formulated multiobjective mixed-integer fractional programming problems are solved using an  $\varepsilon$ -constraint method and parametric algorithm. To illustrate the applicability of the proposed framework, a case study on the State of Georgia is presented. The Pareto-optimal solutions illustrate a clear trade-off between the unit annualized profit and the unit annual  $CO_2$ -eq GHG emission. The most economically profitable solution has an annualized profit of \$91/ton poultry litter dry matter (DM) and an annual



sequestration of 0.04 kg  $CO_2$ -eq/ton DM. The most environmentally sustainable solution has a profit of -\$1.02/ton DM and annual emissions of -\$11 kg  $CO_2$ -eq/ton DM. Through spatial analysis, a clear correlation between pyrolysis facility locations and poultry litter production amount is revealed. Sensitivity analyses reveal biochar price and storage periods of unpyrolyzed poultry manure to be the greatest factors that influence the economics and environmental objectives, respectively.

**KEYWORDS**: waste-to-energy, life cycle optimization, biofuel, sustainable supply chain, pyrolysis

# INTRODUCTION

The United States is the largest producer and second largest exporter of poultry meat in the world and a major egg producer as well. Consumption of poultry meat, including broilers, other chicken, and turkey, is considerably higher than that of beef or pork in the United States.<sup>1</sup> The large scale of the poultry industry inevitably leads to vast production of poultry litter, which consists of manure, feathers, bedding, and spilled feed.<sup>2</sup> Traditionally, poultry litter has been land spread on soil as an amendment due to its high nutritional value from nutrients such as nitrogen, phosphorus, and potassium. However, overapplication of poultry litter can result in several environmental and health concerns that include, but are not limited to, eutrophication of water bodies, spread of pathogens, production of phytotoxic substances, air pollution, and emissions of greenhouse gases.<sup>3–6</sup>

If poultry litter is treated using thermochemical technologies, it has the potential to serve as a valuable source of renewable energy and sustainable value-added products that could mitigate the negative environmental impacts of poultry litter as well.<sup>7–9</sup> Pyrolysis is a thermochemical conversion technology that degrades organic matter in partial or total absence of an oxidizing agent, and it has been studied for years on poultry litter

applications.<sup>10</sup> Pyrolysis can be generally categorized as slow pyrolysis and fast pyrolysis based on reaction conditions, including heating rates, reaction temperature, and residence time.

Specifically, slow pyrolysis has low heating rates and occurs within a temperature range of 300–450 °C, and the reaction takes several hours to complete. The major product of slow pyrolysis is typically biochar, a carbon-rich residue, which has significant potential to improve soil fertility and reduce greenhouse gas concentrations by carbon dioxide sequestration.<sup>11,12</sup> On the other hand, fast pyrolysis has very high heating rates and takes place at a raised temperature, around 450–600 °C. Both types of pyrolysis technologies have been applied to poultry litter and show high-quality results for producing fuels and value-added products.<sup>13–15</sup> As for slow pyrolysis processes

Received:January 27, 2020Revised:February 24, 2020Published:March 4, 2020

Downloaded via CORNELL UNIV on March 26, 2020 at 13:35:59 (UTC).

of poultry litter, biochar is the major product with bio-oil as a byproduct.<sup>13</sup> Fast pyrolysis has also been applied to poultry litter using fluidized bed reactors, and the major product is bio-oil with biochar as a byproduct.<sup>2,10,15</sup> Bio-oil can be further upgraded into liquid fuels, e.g., gasoline and diesel, through upgrading technology of hydroprocessing.<sup>16,17</sup> The hydroprocessing step of bio-oil involves hydrotreating and hydrocracking. Hydrotreating removes undesired compounds such as oxygen in bio-oil through an exothermal process, and hydrocracking breaks down large carbon-chain compounds into liquid fuel products.

To design efficient sustainable systems for poultry litter valorization, life cycle optimization (LCO) of poultry litter supply chains that integrates techno-economic analysis (TEA),<sup>18</sup> life cycle assessment (LCA),<sup>19</sup> and multiobjective optimization, is an effective tool proposed in recent years.<sup>20-</sup> Generally, maximizing profit or minimizing costs is crucial to the economic viability of a supply chain, and minimizing the negative life cycle environmental impacts of a supply chain has gained more and more attention due to the increasing awareness of sustainability. LCO tools have been applied to several works on biofuel supply chains,<sup>23</sup> such as sustainable cellulosic biofuel supply chains.<sup>24</sup> Additionally, the supply chain can be optimized based on a functional unit, making the final product more costcompetitive and more environmentally friendly.<sup>25</sup> The multiobjective LCO framework for sustainable hydrocarbon biorefineries has been studied by integrating techno-economic analysis (TEA) and environmental impact analysis that follow LCA procedures.<sup>26–28</sup> In addition, biomass supply chain optimization, commodity chemical production, and biofuel production considering fast pyrolysis have been applied to several types of solid biomass, such as corn stover and woody biomass.

To the best of our knowledge, current pyrolysis studies on poultry waste are mainly conducted from experimental perspectives,<sup>2,13,32,33</sup> and there is no existing literature on LCO of the poultry waste supply chain that incorporates pyrolysis technologies on the scale of a region. Thus, there exists a knowledge gap in addressing the LCO and spatial analysis of the poultry litter supply chain considering pyrolysis technologies by combining TEA, LCA, spatial analysis, and optimization. To fill this knowledge gap, the objective of this work is to develop a multiobjective LCO modeling framework based on a functional unit, which is tailored to the poultry waste supply chain that involves pyrolysis and upgrading technologies.

Several research challenges are addressed in this work. The first challenge is to develop a novel and comprehensive LCO model that reflects the features of the poultry litter supply chain design from the perspectives of thermochemical conversion platforms, economics, and environmental impacts. The second challenge is to deal with the combinatorial nature and pseudoconvexity of the resulting functional-unit-based objective functions. The third challenge is to associate the optimal designs with existing spatial information and data, which could provide insights for the poultry waste supply chain system.

In this article, we address LCO of the poultry litter supply chain considering pyrolysis technologies and aim at promoting the sustainable conversion of poultry waste into liquid fuels and biochar. The goals are to assess the life-cycle economic and environmental impacts of poultry litter pyrolysis and to quantify scale effects depending on regional supplies of poultry litter and demand for biochar as a fertilizer. The LCO is formulated as a multiobjective mixed-integer linear fractional program (MILFP) for the poultry litter supply chain based on a functional unit of litter mass. Two objective functions are included in the MILFP: the economic objective function is to maximize the annualized profit per functional unit, and the environmental objective function is to minimize the environmental impact per functional unit. A parametric algorithm and an  $\varepsilon$ -constraint method are integrated and used to obtain Pareto-optimal solutions from the MILFP problems. To illustrate the applicability of the proposed modeling framework, its application to the poultry sector of Georgia is presented.

The major novelties of this work are summarized as follows:

- (1) A novel functional-unit-based LCO modeling framework for the design of the poultry litter supply chain considering slow and fast pyrolysis technologies.
- (2) A case study using optimization based on a region-scale poultry litter supply chain in Georgia to demonstrate the applicability of the proposed modeling framework.
- (3) Comprehensive spatial analysis of the LCO results for both the supply of the feedstock and the demand for biochar and liquid fuel products.

The remainder of this article is organized as follows. The next section provides information and knowledge on the method of life cycle optimization. The Problem Statement section formally states the modeling framework for the LCO for the poultry sector. The resulting mathematical model formulation and corresponding solution algorithm are given in the General Model Formulation and Solution Algorithm section. Application to the State of Georgia is shown in the next section. Conclusions are drawn in the last section.

## METHODS: LIFE CYCLE OPTIMIZATION FRAMEWORK FOR THE POULTRY WASTE SUPPLY CHAIN

It requires significant efforts for LCA approaches to compare between alternative systems designs, and LCA is less focused on the economic aspect of a system. To overcome these disadvantages of LCA, an LCO framework is used to improve both the economic and environmental performances of a poultry litter supply chain. The LCO framework integrates a multiobjective optimization scheme, TEA, and the fourphase process-based LCA method, namely, (a) goal and scope definition, (b) inventory analysis, (c) impact assessment, and (d) interpretation, <sup>20,25,34,35</sup> and the LCO framework has the same fourphase structure. Considering life-cycle impacts is crucial for measuring environmental effects of introducing thermochemical conversion of poultry waste, and the consequences from the lack of life cycle impacts have been demonstrated by previous work.<sup>36,37</sup> The LCA approach provided data on the environmental impact of each process or activity included in the poultry waste supply chain network, which is necessary for the calculation of the environmental impact for the supply chain in the impact analysis phase. LCA and TEA data are passed to the optimization program as parameters that are used to determine the economic and environmental performance of any supply chain alternative during computational optimization.<sup>20,25</sup> In other words, the calculations for LCA and TEA methods have been integrated in the developed optimization model. For the compactness of the article, details on the TEA and multiobjective optimization methods are discussed in the Supporting Information.

**Goal and Scope Definition.** The first and most critical phase is goal and scope definition where the major features of the poultry litter supply chain LCO framework are defined. These include, but are not limited to, the goal of the study, system boundary, functional unit, and key assumptions.

Specifically, the goal of this study is to improve the environmental sustainability and economic performance of the poultry litter supply chain by considering various designs and operating options. Both the

pubs.acs.org/journal/ascecg

**Research Article** 



Figure 1. Illustrative material flow diagram of the poultry waste supply chain system using slow and fast pyrolysis technologies.



Figure 2. Supply chain network for poultry litter valorization.

environmental and the economic objectives are measured per functional unit, which enables direct and intuitive comparison between multiple alternative supply chain networks.<sup>38–40</sup> The material flow of the poultry waste supply chain system is shown in Figure 1, which consists of processes and activities in this system, and thus a system boundary can be defined.

The functional unit is a measure of the function of interest, and it serves as a reference for the relationship between inputs and outputs.<sup>41</sup> Typically, a functional unit is proportional to the amount of feedstock input or product output.<sup>42</sup> In this study, since both liquid fuel and biochar are produced from the system, using the feedstock amount as a functional unit is a more reasonable option. While the exact elemental composition of poultry litter may vary based on the type of poultry and management style,<sup>43</sup> the proportion of organic carbon, which is the most effective element for pyrolysis processes, lies in a short range across different poultry types.<sup>44</sup> Thus, a unit weight of poultry litter feedstock is chosen as the functional unit in this study, which has been applied to other works in this field as well.<sup>45</sup>

**Inventory Analysis.** The second phase is inventory analysis where the life cycle inventory associated with each process or activity within the system boundary is analyzed. Specifically, the mass balance and energy balance for all processes shown in Figure 1 within the system boundary should be determined, and such processes include a slow pyrolysis process, fast pyrolysis process, upgrading process, material transportation, etc. In addition, since multiple time periods are considered in this study, the flow and stock of poultry litter feedstock, bio-oil intermediates, and liquid fuel products should be derived considering the inputs, outputs, and previous inventory levels. These lead to a time-dependent high-fidelity inventory analysis for the poultry litter supply chain life cycle optimization.

**Impact Assessment.** The third phase is impact assessment where the inventory information from the previous phase is translated into environmental impacts using impact factors, and the impacts are subsequently aggregated into a single environmental metric. In this study, global warming potential (GWP) is applied as the impact assessment indicator, which measures how much heat greenhouse gases

trap in the atmosphere up to a specific time horizon, relative to carbon dioxide. The GWP time horizon is selected as 100 years in this study. The environmental impact for the poultry litter supply chain is converted into a functional-unit-based metric, which is carbon dioxide equivalent ( $CO_2$ -eq) emissions per year per ton of poultry waste dry matter (DM) feedstock.

**Interpretation.** The fourth and last phase is interpretation where a multiobjective poultry litter supply chain LCO model is formulated to optimize the economic and environmental metrics subject to constraints on material transportation, slow pyrolysis processes, fast pyrolysis processes, upgrading processes, logic relationships, economics, and environmental impact assessment. The LCA and TEA data from the previous phases are integrated in the optimization program so that the economic and environmental performance of any supply chain alternative can be calculated and compared automatically during optimization. Through the optimization process, a set of Pareto-optimal solutions can be obtained based on the environmental and economic indicators, and trade-offs between the two objectives can be revealed from the Pareto-optimal solutions, which facilitate the sustainable design of poultry litter supply chain by providing insights and strategic recommendations.

### PROBLEM STATEMENT

The problem of the poultry litter supply chain optimization considering pyrolysis technologies is formally defined in this section. The objective of this study is to address the optimal design of the poultry litter supply chain considering pyrolysis technologies using life cycle optimization.

The process overview of the supply chain network is shown in Figure 2. Different types of poultry litter feedstock are first collected from poultry farms and then transported to pyrolysis facilities, which are shown in purple and deep blue in the figure. Two types of pyrolysis technologies are considered in this work, namely, slow pyrolysis and fast pyrolysis. All types of poultry waste feedstock would be processed by either slow pyrolysis or fast pyrolysis. It is reasonable to assume that there are no differences in the pyrolysis process for different types of poultry waste because of their highly similar chemical composition.<sup>10</sup>

Slow pyrolysis has low heating rates, low reaction temperature, and long residence time, while fast pyrolysis has very high heating rates, high reaction temperature, and short residence time. Through both types of pyrolysis processes, poultry waste feedstock is converted into biochar, syngas, and bio-oil. Slow pyrolysis produces biochar, bio-oil, and syngas from poultry litter feedstock, and bio-oil is the major product from fast pyrolysis processes with biochar as a byproduct. The produced biochar is transported to demand zones and distributed as soil amendment for cropland. Notably, the carbon sequestration feature of biochar is considered in this work considering that the environmental objective is based on greenhouse gas (GHG) emission.

The byproduct syngas is combusted on-site at the pyrolysis facilities, and the tail gas is subsequently treated through a  $NO_x$  removal process before being emitted to the atmosphere. Syngas combustion can provide energy for the pyrolysis plants, and the equivalent revenue from such energy production is considered to offset the operation cost in this study. Consequently, there are no energy revenues that are explicitly shown in the modeling framework.

The intermediate bio-oil is collected at the pyrolysis facilities and transported to upgrading facilities where the bio-oil can be upgraded to liquid fuels, such as gasoline and diesel. Lastly, the produced liquid fuels are transported from upgrading facilities to demand zones to serve the need of transportation, heating, etc. In this problem, we are given a set of poultry waste feedstock, including broiler litter, layer litter, and turkey litter. A number of conversion technologies can be selected to convert organic waste feedstock into a set of products (i.e., biochar, bio-oil, and syngas), including slow pyrolysis and fast pyrolysis. Additionally, syngas combustion and the NO<sub>x</sub> removal process are integrated in all pyrolysis facilities. The corresponding upgrading technology for bio-oil is hydroprocessing in this study.

In the design of poultry litter supply chain, we are given the following parameters:

- (1) A set of locations, including poultry farms, candidate locations for pyrolysis facilities, candidate locations for upgrading facilities, and demand zones;
- (2) Technology and logistic options regarding pyrolysis and upgrading technologies, including alternative technology options, processing capacity of pyrolysis facilities, production capacity of upgrading facilities, conversion rate for each product, storage, and degradation rate.
- (3) Transportation parameters, including transportation modes, transportation distance between locations, and maximum allowable transportation distance.
- (4) Capacity limitations, including poultry waste availability, upper and lower bounds of product demands, and transportation capacity for feedstock and product.
- (5) Time-related parameters, including planning horizon and product demand data for different time periods.
- (6) Economic data, including cost for poultry litter acquisition, transportation, capital investment, operations and maintenance (O&M), storage and product distribution, government incentive rate, discount rate, and market price of products.
- (7) Environmental impact data, including environmental impacts for organic waste feedstock acquisition, transportation, pyrolysis and upgrading processes, storage, product distribution, and carbon dioxide sequestration.

Major decision variables for the LCO of the poultry litter supply chain are listed below:

- (1) Selection of poultry litter suppliers and feedstock acquisition schedule.
- (2) Number, location, capacity, and technology selection of each pyrolysis facility and upgrading facility.
- (3) Production planning for pyrolysis facilities in each time period, including feedstock consumption rates, intermediate and product yields, production profiles, and inventory level of feedstock and products.
- (4) Production planning for upgrading facilities in each time period, including intermediate consumption rates, liquid fuel product yields, and inventory level of intermediate and products.
- (5) Transportation level of each transportation link.
- (6) Product distribution planning.

The LCO of the poultry litter supply chain has two objectives: the economic objective is to maximize the annualized profit per functional unit, and the environmental objective is to minimize the environmental impact per functional unit. Following the section Methods: Life-Cycle Optimization Framework for the Poultry Waste Supply Chain, the functional unit is defined as a unit weight of poultry litter DM because the carbon contents (that energetically drive the pyrolysis processes) lie in a narrow range for different types of poultry litter. Specifically, the economic performance is represented by the total annualized profit (calculated from annualized costs and annualized product

sales revenues using a cash basis accounting method) associated with the unit weight of processed poultry waste DM. It is worth noting that the annualized cost calculation considers the time value of money using the equivalent cost method based on discount rates and facility lifetime.<sup>46</sup> The environmental performance refers to the annual environmental impact based on the unit weight of poultry litter DM. Notably, the environmental metric used in this study focuses on GHG emissions because it is the most important sustainability criteria for bioenergy systems,<sup>47</sup> and it has been widely applied in bioenergy life cycle studies of other systems.<sup>48–52</sup>

# GENERAL MODEL FORMULATION AND SOLUTION ALGORITHM

Following the problem statement, the general LCO model for the poultry litter supply chain considering pyrolysis technologies is presented in this section as well as the solution strategy for the resulting multiobjective MILFP model. Detailed equations and notation are presented in the Supporting Information.

**Multiobjective MILFP Model.** The multiperiod poultry waste supply chain optimization problem can be formulated as a multiobjective MILFP model denoted as (P0). The two conflicting objective functions are introduced, namely, maximizing the unit annualize profit of the supply chain and minimizing the unit annual GHG emission. The objective functions are subject to poultry litter feedstock supply system constraints, pyrolysis facility constraints, upgrading facility constraints, economic constraints, and environmental constraints. The outline of (P0) is shown as follows:

max Unit Annualized Profit

```
min Unit Annual CO<sub>2</sub>-eq GHG Emissions
```

s.t. poultry litter feedstock supply system constraints pyrolysis facility constraints upgrading facility constraints product distribution system constraints economic constraints environmental constraints

The model (P0) is a multiobjective MILFP model where two fractional objective functions are involved. The denominators and numerators of both objective functions are linear, and all constraints are in linear forms.

**Solution Strategy.** The resulting problem is formulated into a multiobjective MILFP problem. We integrate an  $\varepsilon$ -constraint method and a parametric algorithm<sup>53</sup> to deal with the problem's multiobjective feature and fractional feature, respectively.

The  $\varepsilon$ -constraint method is widely used to handle multiobjective optimization problems to obtain Pareto-optimal solutions owing to its simplicity. Since there are two objective functions, the Pareto-optimal frontier will be in the form of a curve. To obtain the Pareto-optimal curve, one of the objective functions should be converted into an  $\varepsilon$ -constraint, and the economic constraint (eq S49) in the Supporting Information is selected to be converted. The additional  $\varepsilon$ -constraint is shown as a constraint (eq 1).

$$REV - C_{capital} - C_{acquisition} - C_{distribution} - C_{production} - C_{transportation} - C_{storage} + C_{incentive} \geq \epsilon \cdot \sum_{b} \sum_{i} \sum_{t} \rho_{b} bm p_{b,i,t}$$
(1)

After transforming the economic objective function into a corresponding  $\varepsilon$ -constraint, the multiobjective MILFP model (P0) is reformulated into a single-objective MILFP model (P1) of which the outline is given as follows:

- min Unit Annual CO<sub>2</sub>-eq GHG Emissions
- s.t. *e*-constraint on the economic objective function poultry litter feedstock supply system constraints pyrolysis facility constraints upgrading facility constraints product distribution system constraints economic constraints environmental constraints

(P1) is a single-objective MILFP model consisting of a fractional objective function and linear constraints. Although single-objective MILFP problems can be solved using generalpurpose mixed-integer non-linear programming (MINLP) solvers, it may become computationally intractable to use general-purpose MINLP solvers on large-scale MILFP problems due to the combinatorial nature and pseudo-convexity of the MILFP. To tackle this computational challenge, the parametric algorithm based on Newton's method is adopted to efficiently solve the MILFP problem.<sup>53</sup> Using the parametric algorithm, the fractional objective function is reformulated into a linear function F(q), which represents the difference between the numerator and denominator multiplied by a parameter q. After iteratively solving a series of mixed-integer linear programming (MILP) programs, the optimal solution of the MILFP problem can be obtained as the reformulated objective function reaches zero, i.e., F(q) = 0.54 In addition, the global optimal solution is guaranteed to be found using the parametric algorithm as long as the relatively optimality gap is less than 100%.53 The pseudocode for detailed steps of the parametric algorithm is presented in Figure 3. In the pseudocode, k is the number of outer iterations and  $\xi$  is the optimality gap for the parametric algorithm;

1	1 <b>Reformulation:</b>				
	$\rightarrow \min F(ue) = TotalAnnualEmission - ue \cdot PoultryLitterAmount$				
2 <b>Initialization:</b> Set $k = 0$ , $ue^1 = 0$ , $F(ue^0) = \xi + 1$					
3 while $(F(ue^k) \ge \xi)$ Do					
4	k = k + 1				
5	Solve the MILP problem minimizing $F(ue^k)$				
6	Denote the optimal solution as $(x^k, y^k)$ , TotalAnnualEmission*				
-	and PoultryLitterAmount*				
/	$ue^{1} = \frac{10tutAtututEtutSston}{PoultryLitterAmount^{*}}$				
8 end while					
9	9 Output $(x^k, y^k)$ as the optimal solution				
10	10 Output $ue^k$ as the optimal value of unit annual CO <sub>2</sub> -equivalent GHG emission				

**Figure 3.** Pseudocode of the parametric algorithm, which solves the mixed-integer linear fractional programming problem on poultry litter supply chain systems.

## APPLICATION TO THE STATE OF GEORGIA

To illustrate the applicability of the proposed modeling framework for an entire region, we present a case study on the optimal designs of a poultry litter supply chain in Georgia. Georgia is one of the largest states in terms of poultry industry,<sup>55</sup> and poultry is the largest segment of agriculture in Georgia. Since the number of broilers in Georgia is significantly larger (around 100 times higher) compared to the number of other poultry animals,<sup>57</sup> broiler litter is selected as the poultry litter feedstock in this case study.

pubs.acs.org/journal/ascecg

**Research Article** 



**Figure 4.** County-level biochar demand, poultry litter supply, population distribution, and candidate locations for pyrolysis and upgrading facilities in Georgia: (a) biochar demand distribution in Georgia; (b) broiler litter production distribution in Georgia; (c) population distribution of Georgia; and (d) candidate locations of pyrolysis and upgrading facilities in Georgia.

To gain insights of the supply distribution and demand distribution of the system from a spatial perspective, the distribution of biochar demand, broiler litter production, population, and candidate locations for facilities are shown in Figure 4. The demand of biochar, shown in Figure 4a, is calculated based on soil phosphorus contents,<sup>58</sup> recommended phosphorus application rates for different crops,<sup>59</sup> phosphorus contents in poultry litter biochar,<sup>60</sup> and county-level cropland areas for different crops.<sup>57</sup> The production of broiler litter (Figure 4b) directly depends on the number of broilers. Since broilers are raised by six turns per year,<sup>61</sup> it is more straightforward and accurate to estimate the broiler litter production using the sales amount of broilers instead of the inventory level. The data of the broiler sales amount can be acquired from the United States Department of Agriculture (USDA) census data,<sup>57</sup> and the broiler litter production rate is assumed to be 1.2 kg/broiler.<sup>62</sup> The demands of liquid fuels are assumed to be proportional to the population;<sup>63</sup> thus, the spatial distribution of liquid fuel demands should be similar to the distribution of the population in Figure 4c. The candidate locations in Figure 4d are set to be the geological centers of regions partitioned by the Georgia Department of Transportation (GDOT).<sup>64</sup>

USDA census data are used for determining the sales amount of broilers, poultry waste feedstock supply capacity, and cropland area for different crops in each region.<sup>57</sup> The minimum biochar supply amount as a proportion of the maximum supply is estimated based on the utilization of cover crop management, which serves as an indicator for the proportion of agricultural innovators.<sup>57,65</sup> Data related to the pyrolysis process and characteristics of feedstock and products are acquired from the literature, government websites, and advice from industrial experts; the details of which are shown in the Supporting Information.<sup>2,10,11,13,20,66–73</sup> Data on environmental impacts of each activity are obtained from the ecoinvent database version 3.5 and in-house high-fidelity rigorous process simulations based on experimental results.<sup>10,13,74</sup> These data are subsequently used to determine the total GHG emissions for any alternative

pubs.acs.org/journal/ascecg

Research Article

poultry litter supply chain in the optimization process, which represent values for the numerator of the environmental objective function.

Aspen Plus is used for LCI data,<sup>75</sup> Excel-based in-house calculation tools is used for LCA, and GAMS was used for optimization.<sup>76</sup> The specific production planning for each plant in each time period and the material transportations are obtained from optimization; based on which, the economic and environmental evaluation as well as the spatial analysis are subsequently conducted for each Pareto-optimal solution.

It is worth noting that both the environmental and economic objectives are measured for one functional unit. Since the emissions and costs related to the upstream processes (including chicken food production and animal feeding) are too complex to be accurately measured and such cost and emissions are constant for one functional unit across all supply chain designs, their involvement or absence would not affect the Paretooptimal designs of the supply chain network. In this case study, the cost and emissions from upstream processes are not included. Additionally, they can be conveniently included by directly adding the numerical values per unit cost and unit emission from upstream processes to the current economic and environmental objective values for this case study as long as such data are available.

**Computational Results.** The model and solution algorithm are coded in GAMS  $27.3^{76}$  on a PC with an Intel Core i7-8700 at 3.20 GHz and 32.00 GB RAM, running on a Windows 10 Enterprise, 64-bit operating system. The reformulated MILPs are solved using CPLEX 12.9.0.0. The absolute optimality tolerance is set to be  $10^{-2}$ . The optimality tolerance for CPLEX is set as  $10^{-6}$ .

The reformulated MILFP model (P1) has 174 discrete variables, 20,773 continuous variables, and 13,785 constraints. Generally, the MILFP algorithm converges within a reasonable range of computational time and number of iterations. The computational times range from 14.593 to 627.203 CPU seconds, and the parametric algorithm converges within four iterations for all solutions.

Pareto-Optimal Solutions. The Pareto-optimal solutions for LCO of the poultry litter supply chain are shown as the green curve in Figure 5, illustrating the trade-off between the economic and environmental objectives. The x axis represents the annual CO<sub>2</sub>-eq GHG emission per unit weight DM of the feedstock (unit emission), which stands for the environmental objective. The  $\gamma$  axis represents the economic objective value, the unit annualized profit (unit profit), which equals the total annualized profit for unit weight of poultry litter DM conversion. Notably, a negative value of the unit profit indicates that the system is unprofitable, and a negative value of unit emissions indicates that the amount of carbon dioxide sequestration is higher than the amount of CO2-eq GHG emission. Since lower unit emission and higher unit profit are preferred, the region above the Pareto-optimal curve is infeasible, and the region below is suboptimal. In addition, the solutions for complete and zero processes of poultry litter are shown in purple (point D) and orange (point E), respectively. Solutions under these two scenarios are located in the region below the Pareto curve, and thus they are suboptimal solutions.

A clear trade-off trend between the economic and environmental objectives can be observed from the Pareto-optimal curve in Figure 5. The Pareto-optimal curve has a sheer increase near the extreme point A with minimum unit emissions. The trade-off solution B has significantly higher unit profit and



**Figure 5.** Pareto-optimal curve illustrating trade-offs between annualized profit and greenhouse gas emissions with the extent of poultry litter processing (pie charts), number of pyrolysis facilities (bar charts), and solution points for the complete process (point D) and zero process (point E) of poultry litter.

slightly higher unit emissions compared to solution A. In contrast, the unit profit for Pareto-optimal solutions between points B and C becomes less sensitive to the value of unit emission, compared to the solutions between A and B when their unit emissions are close to the minimum value.

In Figure 5, points close to the lower left corner have a worse economic performance and better environmental performance, while points close to the upper right corner have better economic performance and a worse environmental performance. For example, point A represents the optimal solution minimizing unit emissions with unit emissions of  $-511 \text{ kg CO}_2$ eq/ton poultry litter DM and a loss of \$1.02/ton DM feedstock; point C stands for the optimal solution maximizing the unit profit with a unit profit of \$91/ton poultry litter DM and unit sequestration of 0.04 kg CO<sub>2</sub>-eq/ton poultry litter DM; and points on the Pareto-optimal curve and between point A and point C are Pareto-optimal solutions as well. For instance, point B has a unit annualized loss of \$40/ton DM feedstock and unit emission of  $-510 \text{ kg CO}_2$ -eq/ton DM waste, indicating that it has better economic performance than point A and better environmental performance than point C. It is worth noting that all solutions on the green curve are Pareto optimal, and the selection of which depends on the preference between the two objectives. Solutions to the left emphasize to a greater extent reducing negative environmental impacts, while solutions on the right are seeking more profitable supply chain systems.

In addition to the Pareto-optimal curve, details of the poultry litter treatment and technology selections corresponding to points A, B, and C are shown as pie charts and bar charts in Figure 5. In terms of poultry litter treatment, less than half of the produced poultry litter is processed through pyrolysis facilities for the environmentally optimal solution A and the trade-off solution B, while the economically optimal solution C has 63% poultry litter processed through fast and slow pyrolysis facilities. In terms of the number of pyrolysis facilities, only slow pyrolysis facilities are built for point A and point B, and both slow and fast pyrolysis technologies are selected for point C. Since points A and B are more environmentally sustainable compared to point C, it can be inferred that slow pyrolysis technology may lead to

pubs.acs.org/journal/ascecg



Figure 6. Economic breakdowns of Pareto-optimal solutions A, B, and C as well as related total annualized loss and total annualized profit.

lower GHG emissions than those of fast pyrolysis technology. On the other hand, point C has higher profits than points A and B, which indicates that the fast pyrolysis technology may have better economic performance compared to slow pyrolysis under baseline assumptions. Additionally, the production planning of the pyrolysis plants for the economically optimal solution (point C) is shown in Figure S2 in the Supporting Information.

The economic breakdowns of Pareto-optimal solutions A, B, and C are shown in Figure 6. The total annualized cost breakdowns are shown on the left side of each cluster of columns, and the total annualized revenue breakdowns are shown on the right side. It is noteworthy that the cost and revenue shown in this figure refer to the total amount instead of the amount based on a functional unit. From the stacked columns of cost, one can observe that the storage costs shown in blue are the minimum compared to other categories of cost among all three Pareto-optimal solutions. The transportation costs shown in red are one of the major sources of cost for all three representative solutions, and their trend is consistent with the processed amount of poultry litter shown by the pie charts in Figure 5. This is due to the fact that more transportation is needed for both feedstock and products when more poultry litter is processed. The acquisition costs for the three representative solutions share a small portion of the total cost for the supply chain network, and the acquisition costs are proportional to the processed amount of poultry waste. The capital and production costs are major sources of costs across all representative Pareto-optimal solutions (A, B, and C). The capital cost follows a similar trend of the processed poultry litter amount, while the production cost for solution C is significantly higher than that of points A and B due to higher unit production costs for fast pyrolysis plants compared to slow pyrolysis plants. In terms of revenue breakdowns, over half of the revenue comes from the sale of liquid fuel products, namely, gasoline and diesel, for all three representative solutions. Biochar sales share a large proportion of revenue for points A and B where only slow pyrolysis facilities are built. In comparison, liquid fuel sales are major sources of revenue for solution C in which both fast and slow pyrolysis technologies are chosen. The total annualized loss and profit are shown in black and blue arrows, respectively. The total loss for point A is \$0.4 million/year; the total annualized profit for point B is \$24.9 million; and the total profit for point C is \$93.2 million/year.

The attributions of the life-cycle GHG emissions for the state of Georgia of Pareto-optimal solutions A, B, and C are shown in Figure 7. The emissions are shown on the left side of each cluster



**Figure 7.** GHG emissions and carbon dioxide sequestration from biochar application to soil of Pareto-optimal solutions A, B, and C as well as the resulting total net carbon dioxide sequestration for the state of Georgia.

of bars, and the carbon dioxide sequestration is shown on the right side. Notably, this figure presents the total amount of GHG emissions and sequestration for the investigated region, instead of the amount based on the functional unit. Emissions from feedstock acquisition and storage are negligible compared with other types of emissions for all three solutions (Figure 7). The emissions introduced by transportation are 34 and 57% higher compared to emissions related to feedstock acquisition and storage, respectively. The emissions from these three categories share a small proportion of total CO<sub>2</sub>-eq emissions. Most GHG emissions for the three representative solutions come from the production processes, which refer to the slow and fast pyrolysis processes of poultry litter feedstock, and the upgrading process of bio-oil. Since the emissions introduced by production processes from point C are 185% higher than those from point B and considering that the conversion level of poultry waste for point C is only 65% higher than that of point B, it can be inferred that fast pyrolysis may lead to more emissions during the production process, compared to slow pyrolysis. This is



Figure 8. Facility location, technology selection, and capacity from optimal solution A in the Pareto-optimal curve as well as corresponding transportation of feedstocks, intermediates, and products.

partially due to the higher GHG emissions from fast pyrolysis and upgrading processes since more bio-oil is produced from fast pyrolysis than from slow pyrolysis. Because of the wide application of slow pyrolysis for solutions A and B, the amount of carbon dioxide sequestration shown in green columns is significant, considering that much less poultry litter is pyrolyzed for points A and B than for solution C. The net amounts of  $CO_2$ eq sequestration are shown in deep green arrows and numbers on the top of each bar to the left. Because of the significant performance offsetting  $CO_2$ -eq emissions for solutions A and B, their net  $CO_2$ -eq sequestration is considerable. In comparison, the  $CO_2$ -eq sequestration from biochar for solution C is just enough to offset the  $CO_2$ -eq emissions from the supply chain network, which results in a positive but small amount of net carbon dioxide sequestration.

Spatial Analysis. The spatial information for the supply chain design corresponding to the most environmentally sustainable solution (point A) is illustrated in Figure 8. Slow pyrolysis and upgrading facilities are built for this solution, and the corresponding locations and capacities are presented in the figure using orange dots and red stars with different sizes. The orange arrows represent the transportation of biochar between different regions, and their widths indicate the amount being transported. Similarly, the purple arrows stand for the crossregion transportation of bio-oil. It can be observed from the figure that slow pyrolysis facilities are widely adopted across the state under the baseline assumptions. For regions with little or no poultry litter production, given by the white areas in Figure 4b, slow pyrolysis facilities are less likely to be built, such as regions around Atlanta and east Georgia. On the contrary, in regions with a great amount of poultry litter feedstock

production, such as regions to the North, slow pyrolysis facilities tend to have large capacities, presented by large orange dots at the top of Figure 8. No cross-region transportation of poultry waste feedstock was predicted, which suggests that the poultry litter feedstocks of all slow pyrolysis facilities are acquired from the regions where the facilities are located (the region being a unit of 3000–9300 km<sup>2</sup>). In terms of biochar transportation, all destinations are regions without a slow pyrolysis facility that cannot produce the biochar needed in this region, indicating that the cost of transporting biochar into these regions is less than the cost to build pyrolysis plants and produce biochar locally. On the other hand, regions with a slow pyrolysis facility would be able to satisfy the local biochar demands by themselves.

The Pareto-optimal supply chain design corresponding to the trade-off solution (point B) is illustrated in Figure 9. Similar to point A, slow pyrolysis facilities are less likely to be located in regions with little poultry litter production, for instance, several regions in east Georgia and Atlanta. Since more poultry litter is processed through the supply chain network for point B compared to point A, more slow pyrolysis facilities with large capacities are built, presented by large orange dots in Figure 9. These large-capacity slow pyrolysis facilities are mainly located in the North with regions with considerable production levels of poultry litter shown in deep blue in Figure 4b. Notably, the profit for solution B is significantly higher than that of solution A in Figure 5, and this may partially be due to the economic scaling effect in that larger pyrolysis or upgrading plants have lower capital costs. Additionally, there is no cross-region transportation of poultry litter feedstock, which indicates that litter feedstocks of the slow pyrolysis facilities are acquired locally in each region. As in Figure 8, all destinations of biochar



Figure 9. Facility location, technology selection, and capacity from optimal solution B in the Pareto-optimal curve as well as corresponding transportation of feedstock, intermediates, and products.



Figure 10. Facility location, technology selection, and capacity from optimal solution C in the Pareto-optimal curve as well as corresponding transportation of feedstocks, intermediates, and products.



Figure 11. Sensitivity analysis of life cycle optimization of the poultry litter supply chain: (a) sensitivity analysis on the economic objective of maximizing unit profit with economic breakdowns for scenarios with different biochar prices; (b) sensitivity analysis on the environmental objective of minimizing unit emission.

transportation are regions without local biochar production. There are 18 upgrading facilities for solution A in Figure 8, while there are only 5 upgrading facilities for this trade-off solution, accounting for upgrading bio-oil from 24 slow pyrolysis plants.

The spatial information for the supply chain network corresponding to the most economically optimal solution (point C) is illustrated in Figure 10. The location of slow pyrolysis facilities, fast pyrolysis facilities, and upgrading facilities are shown in orange dots, blue dots, and red stars, respectively. The sizes of the symbols reflect the capacities of pyrolysis and upgrading facilities. The fast pyrolysis facilities are located in regions with vast amounts of poultry litter production, namely, northwest and northeast Georgia, which may help reduce the cost of organic waste feedstock transportation. Nonetheless, cross-region transportation of poultry litter feedstock exists. The destinations of all cross-region poultry litter feedstock transportations are fast pyrolysis facilities because the comparatively high revenue from poultry waste valorization through fast pyrolysis could offset the transportation cost of the feedstock. In addition, the capacities of fast pyrolysis facilities are much higher than those of the slow pyrolysis facilities. This is possibly due to an economic scaling effect of larger facility capacities for fast pyrolysis compared to slow pyrolysis and the fact that the material flow rates for slow pyrolysis facilities are typically limited compared to fast pyrolysis because of heat transfer limitations. Thus, a higher facility capacity would lead to lower capital costs per unit of poultry waste feedstock, and fast pyrolysis facilities could take a larger advantage of this economic scaling effect, which may result in higher profits. All slow pyrolysis facilities are spread in south and middle Georgia and supply biochar for the southern regions of Georgia since these regions have large distances from the fast pyrolysis facilities in the North. In addition, their feedstock supply is not as large as that in the northern regions, and it can be difficult for fast pyrolysis plants to take advantage of the economic scaling effect; thus, slow pyrolysis tends to be a more economically favorable option for these southern regions. There are two upgrading

facilities for this solution: one with a larger capacity located between the fast pyrolysis plants and the other with a smaller capacity located at the center of the slow pyrolysis plants. All biooil produced from the two fast pyrolysis facilities and slow pyrolysis plant in the middle is transported to the upgrading facility in the North, while bio-oil produced from pyrolysis facilities in southern regions is transported to the upgrading facility in the South. We note that there is no transportation of liquid fuels shown in Figure 10, suggesting that all liquid fuel products from the upgrading facility are sold locally.

Sensitivity Analysis. In order to further quantify the impacts from the deviation of input parameters, sensitivity analyses were conducted. Specifically, the factors with the greatest effect for economic and environmental outcomes are shown in Figure 11a,b, respectively. The horizontal bars describe the changes in economic or environmental objective values due to changes in the input parameters. A blue bar indicates a higher input parameter than the baseline scenario, and a red bar represents a lower input value of the factor. For the sensitivity to biochar sales prices, attributions to different input factors are shown (other attributions to the sensitivity are shown in Figure S1 of the Supporting Information). It is worth noting that while investigating the effects of varying one factor on the economic and environmental outcomes, the optimal supply chains under different values of the factors are being compared for the entire network. Consequently, the value of variables in the two optimal solutions may be different, such as the number of pyrolysis plants, capacities of the plants, transportation planning, and storage decisions.

Biochar prices, maximum fast pyrolysis facility capacities, and minimum region-level biochar supply amounts have significant impacts on the optimal profit, while maximum transportation distances, storage periods of unpyrolyzed poultry litter, and maximum slow pyrolysis facility capacities affect the economic outcome to a lesser extent. Notably, the market price of biochar is the most sensitive factor that influences the profit of the network. The biochar price of \$100/ton used for the baseline scenarios is estimated mainly based on the value of phosphorus in poultry litter biochar. The lower value of the biochar price is \$50/ton, and two alternative higher values are chosen, \$200 and \$1900/ton. From the corresponding pie charts in Figure 11a (for all factors, see Figure S1 in the Supporting Information), the biochar sales revenue increases with an increase of the biochar price, and the revenue from biochar dominates the product sales revenue when biochar price reaches \$1900/ton.<sup>77</sup> Additionally, the increased proportion of capital costs and decreased proportion of production costs under the biochar price of \$1900/ton indicate that more slow pyrolysis facilities would be built compared to a scenario of lower biochar prices, which can be inferred from the cost breakdowns in Figure 6. It is worth noting that the value of biochar may be underestimated since its market price for the baseline scenario in this study does not reflect all of its benefits, such as the ability to increase fertilizer efficiency or other growth-promoting properties, which are difficult to be monetized.

In addition, a decrease of the maximum fast pyrolysis facility capacity could significantly reduce the profit, and an increase of the maximum fast pyrolysis capacity could increase optimal profit, which is due to the economic scaling effect mentioned in the previous subsection. From the cost breakdowns in Figure S1 of the Supporting Information, it can be found that the proportions of capital cost and production cost increased under both lower and higher maximum fast pyrolysis capacity compared to the baseline scenarios. Notably, while the minimum region-level biochar supply amount is zero, the proportion of transportation cost decreased (Figure S1), possibly because less cross-region product transportation is needed when the required biochar supply amount is zero for each region. Under this circumstance, biochar produced from pyrolysis plants would satisfy the local needs first before being transported and sold to a nearby region since the costs of crossregion transportation are higher than that of transportation within the region. For the changes of other factors, there are no notable changes with respect to revenue and cost breakdowns shown in Figure S1.

In Figure 11b, changes of the storage period of unpyrolyzed poultry litter, minimum region-level biochar supply amount, and maximum slow pyrolysis facility capacity influence the environmental outcome, while other factors have negligible effects on GHG emissions compared to the baseline scenario. It is noteworthy that the storage period of poultry litter has the most significant effects on GHG emissions among all factors, although the storage emissions share a small proportion of total emissions as shown in Figure 7. When the minimum region-level biochar supply amount is 0, the environmentally optimal supply chain has lower GHG emissions, and this is possibly due to the decrease of emissions associated with decreased cross-region biochar transportation.

There are limitations that should be noted for this work. Several uncertainties in the poultry litter supply chain are not included in the optimization modeling framework, such as the fluctuation of poultry litter feedstock production and potential changes on transportation cost of materials. Thus, a future research direction is to consider several types of uncertainties in the LCO framework.

## CONCLUSIONS

In this paper, we proposed an LCO framework for a poultry waste supply chain considering fast and slow pyrolysis technologies under economic and environmental criteria. A multiobjective MILFP model was formulated to find optimal designs of the poultry litter supply chain. LCA and TEA were integrated into the multiobjective optimization framework, which provided environmental impact assessment for solution alternatives automatically from a life cycle perspective during an optimization process. The multiobjective optimization problem was solved with an  $\varepsilon$ -constraint method and parametric algorithm.

A case study for the poultry litter supply chain in the State of Georgia was presented to illustrate the applicability of the proposed modeling framework. The following insights were gained from the results. First, a Pareto-optimal curve revealed a clear trade-off between the economic objective function of maximizing unit annualized profit and environmental objective function of minimizing the unit annual GHG emissions. Besides, the most economically optimal design could achieve a unit profit of \$91/ton DM feedstock and net unit sequestration of 0.04 kg CO<sub>2</sub>-eq/ton poultry litter DM, while the most environmentally sustainable design led to unit emissions of  $-511 \text{ kg CO}_2$ -eq/ton DM and a unit loss of \$1.02/ton DM feedstock. Furthermore, spatial analysis showed a clear correlation between the production amount of poultry litter feedstock and the location of pyrolysis facilities. Last but not least, biochar price, maximum fast pyrolysis facility capacity, and the amount of minimum region-level biochar supply were the most influential factors for the economic objective function, while the length of the storage period of unpyrolyzed poultry litter, minimum region-level biochar supply amount, and maximum slow pyrolysis facility capacity had impacts on the environmental outcomes.

A potential future research direction is to consider multiple types of uncertainties in the poultry litter supply chain network, such as fluctuation of poultry litter feedstock production and the potential cost changes of material transportation.

## ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.0c00704.

Detailed life cycle optimization model formulation, nomenclature, and tables on parameters used for the Georgia case study (PDF)

## AUTHOR INFORMATION

#### **Corresponding Author**

Fengqi You – Systems Engineering, Atkinson Center for a Sustainable Future, and Robert Frederick Smith School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, New York 14853, United States; oorcid.org/0000-0001-9609-4299; Phone: (607) 255-1162; Email: fengqi.you@cornell.edu; Fax: (607) 255-9166

#### Authors

- Ning Zhao Systems Engineering, Cornell University, Ithaca, New York 14853, United States
- Johannes Lehmann Soil and Crop Sciences, School of Integrated Plant Sciences, College of Agriculture and Life Sciences and Atkinson Center for a Sustainable Future, Cornell University, Ithaca, New York 14853, United States; oricid.org/0000-0002-4701-2936

Complete contact information is available at: https://pubs.acs.org/10.1021/acssuschemeng.0c00704

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

The authors acknowledge financial support from the Cornell Initiative for Digital Agriculture, Cornell University David R. Atkinson Center for a Sustainable Future, and the National Science Foundation (NSF) CAREER award (no. CBET-1643244).

## REFERENCES

(1) USDA *Poultry* & *Eggs Overview*. https://www.ers.usda.gov/ topics/animal-products/poultry-eggs/(accessed Aug 12, 2019).

(2) Agblevor, F. A.; Beis, S.; Kim, S. S.; Tarrant, R.; Mante, N. O. Biocrude oils from the fast pyrolysis of poultry litter and hardwood. *Waste Manage*. **2010**, *30*, 298–307.

(3) Kelleher, B. P.; Leahy, J. J.; Henihan, A. M.; O'Dwyer, T. F.; Sutton, D.; Leahy, M. J. Advances in poultry litter disposal technology – a review. *Bioresour. Technol.* **2002**, *83*, 27–36.

(4) Font-Palma, C. Characterisation, kinetics and modelling of gasification of poultry manure and litter: An overview. *Energy Convers. Manage.* **2012**, *53*, 92–98.

(5) Gerba, C. P.; Smith, J. E., Jr. Sources of pathogenic microorganisms and their fate during land application of wastes. *J. Environ. Qual.* **2005**, *34*, 42–48.

(6) Garcia, D. J.; You, F. The water-energy-food nexus and process systems engineering: A new focus. *Comput. Chem. Eng.* **2016**, *91*, 49–67.

(7) Garcia, D.; You, F. Systems engineering opportunities for agricultural and organic waste management in the food-water-energy nexus. *Curr. Opin. Chem. Eng.* **2017**, *18*, 23-31.

(8) Dalólio, F. S.; da Silva, J. N.; de Oliveira, A. C. C.; de Fátima Ferreira Tinôco, I.; Barbosa, R. C.; de Oliveira Resende, M.; Albino, L. F. T.; Coelho, S. T. Poultry litter as biomass energy: A review and future perspectives. *Renewable Sustainable Energy Rev.* **201**7, *76*, 941–949.

(9) Garcia, D. J.; Lovett, B. M.; You, F. Considering agricultural wastes and ecosystem services in Food-Energy-Water-Waste Nexus system design. *J. Cleaner Prod.* **2019**, *228*, 941–955.

(10) Kim, S.-S.; Agblevor, F. A.; Lim, J. Fast pyrolysis of chicken litter and turkey litter in a fluidized bed reactor. *J. Ind. Eng. Chem.* **2009**, *15*, 247–252.

(11) Shabangu, S.; Woolf, D.; Fisher, E. M.; Angenent, L. T.; Lehmann, J. Techno-economic assessment of biomass slow pyrolysis into different biochar and methanol concepts. *Fuel* **2014**, *117*, 742–748.

(12) Gaunt, J. L.; Lehmann, J. Energy Balance and Emissions Associated with Biochar Sequestration and Pyrolysis Bioenergy Production. *Environ. Sci. Technol.* **2008**, *42*, 4152–4158.

(13) Baniasadi, M.; Tugnoli, A.; Conti, R.; Torri, C.; Fabbri, D.; Cozzani, V. Waste to energy valorization of poultry litter by slow pyrolysis. *Renewable Energy* **2016**, *90*, 458–468.

(14) Song, W.; Guo, M. Quality variations of poultry litter biochar generated at different pyrolysis temperatures. *J. Anal. Appl. Pyrolysis* **2012**, *94*, 138–145.

(15) Kantarli, I. C.; Stefanidis, S. D.; Kalogiannis, K. G.; Lappas, A. A. Utilisation of poultry industry wastes for liquid biofuel production via thermal and catalytic fast pyrolysis. *Waste Manage. Res.* **2018**, *37*, 157–167.

(16) Wright, M. M.; Daugaard, D. E.; Satrio, J. A.; Brown, R. C. Techno-economic analysis of biomass fast pyrolysis to transportation fuels. *Fuel* **2010**, *89*, S2–S10.

(17) Jones, S. B.; Valkenburt, C.; Walton, C. W.; Elliott, D. C.; Holladay, J. E.; Stevens, D. J.; Kinchin, C.; Czernik, S. *Production of Gasoline and Diesel from Biomass via Fast Pyrolysis, Hydrotreating and Hydrocracking: A Design Case*; Office of ScienceOffice of Scientific and Technical Information, 2009.

(18) Winjobi, O.; Shonnard, D. R.; Zhou, W. Production of Hydrocarbon Fuel Using Two-Step Torrefaction and Fast Pyrolysis of Pine. Part 1: Techno-economic Analysis. ACS Sustainable Chem. Eng. 2017. 5, 4529–4540.

pubs.acs.org/journal/ascecg

(19) Heng, L.; Zhang, H.; Xiao, J.; Xiao, R. Life Cycle Assessment of Polyol Fuel from Corn Stover via Fast Pyrolysis and Upgrading. ACS Sustainable Chem. Eng. 2018, 6, 2733–2740.

(20) You, F.; Wang, B. Life Cycle Optimization of Biomass-to-Liquid Supply Chains with Distributed–Centralized Processing Networks. *Ind. Eng. Chem. Res.* **2011**, *50*, 10102–10127.

(21) Yue, D.; You, F.; Snyder, S. W. Biomass-to-bioenergy and biofuel supply chain optimization: Overview, key issues and challenges. *Comput. Chem. Eng.* **2014**, *66*, 36–56.

(22) Garcia, D. J.; You, F. Supply chain design and optimization: Challenges and opportunities. *Comput. Chem. Eng.* **2015**, *81*, 153–170.

(23) Garcia, D. J.; You, F. Network-Based Life Cycle Optimization of the Net Atmospheric CO2-eq Ratio (NACR) of Fuels and Chemicals Production from Biomass. *ACS Sustainable Chem. Eng.* **2015**, *3*, 1732– 1744.

(24) You, F.; Tao, L.; Graziano, D. J.; Snyder, S. W. Optimal design of sustainable cellulosic biofuel supply chains: Multiobjective optimization coupled with life cycle assessment and input–output analysis. *AIChE J.* **2012**, *58*, 1157–1180.

(25) Yue, D.; Kim, M. A.; You, F. Design of Sustainable Product Systems and Supply Chains with Life Cycle Optimization Based on Functional Unit: General Modeling Framework, Mixed-Integer Nonlinear Programming Algorithms and Case Study on Hydrocarbon Biofuels. ACS Sustainable Chem. Eng. 2013, 1, 1003–1014.

(26) Gebreslassie, B. H.; Slivinsky, M.; Wang, B.; You, F. Life cycle optimization for sustainable design and operations of hydrocarbon biorefinery via fast pyrolysis, hydrotreating and hydrocracking. *Comput. Chem. Eng.* **2013**, *50*, 71–91.

(27) Wang, B.; Gebreslassie, B. H.; You, F. Sustainable design and synthesis of hydrocarbon biorefinery via gasification pathway: Integrated life cycle assessment and technoeconomic analysis with multiobjective superstructure optimization. *Comput. Chem. Eng.* 2013, 52, 55–76.

(28) Gebreslassie, B. H.; Waymire, R.; You, F. Sustainable Design and Synthesis of Algae-Based Biorefinery for Simultaneous Hydrocarbon Biofuel Production and Carbon Sequestration. *AIChE J.* **2013**, *59*, 1599–1621.

(29) Li, Y.; Hu, G.; Wright, M. M. An optimization model for sequential fast pyrolysis facility location-allocation under renewable fuel standard. *Energy* **2015**, *93*, 1165–1172.

(30) Zhang, Y.; Hu, G.; Brown, R. C. Integrated supply chain design for commodity chemicals production via woody biomass fast pyrolysis and upgrading. *Bioresour. Technol.* **2014**, *157*, 28–36.

(31) De Meyer, A.; Almeida, J.; Achten, W.; Muys, B.; Cattrysse, D.; Van Orshoven, J., *Incorporating life cycle impact assessment in mathematical model to optimize strategic decisions in biomass-for-bioenergy supply chains*; American Center for Life Cycle Assessment; United States 2013.

(32) Kantarli, I. C.; Kabadayi, A.; Ucar, S.; Yanik, J. Conversion of poultry wastes into energy feedstocks. *Waste Manage*. **2016**, *56*, 530–539.

(33) Mante, N. O. D.; Agblevor, F. F.; Frazier, C. E.; Wen, Z. Influence of Wood on the Pyrolysis of Poultry Litter; Virginia Polytechnic Institute and State University, 2008.

(34) Kim, H. C.; Keoleian, G. A.; Grande, D. E.; Bean, J. C. Life Cycle Optimization of Automobile Replacement: Model and Application. *Environ. Sci. Technol.* **2003**, *37*, 5407–5413.

(35) Bloemhof-Ruwaard, J. M.; Van Wassenhove, L. N.; Gabel, H. L.; Weaver, P. M. An environmental life cycle optimization model for the European pulp and paper industry. *Omega* **1996**, *24*, 615–629.

(36) Azapagic, A. Life cycle assessment and its application to process selection, design and optimisation. *Chem. Eng. J.* **1999**, *73*, 1–21.

(37) Fava, J. Technical Framework for Life-Cycle Assessment, SETAC, 1994.

(38) Thomassen, G.; Van Dael, M.; Van Passel, S.; You, F. How to assess the potential of emerging green technologies? Towards a

prospective environmental and techno-economic assessment framework. *Green Chem.* **2019**, *21*, 4868–4886.

(39) Gao, J.; You, F. Dynamic Material Flow Analysis-Based Life Cycle Optimization Framework and Application to Sustainable Design of Shale Gas Energy Systems. *ACS Sustainable Chem. Eng.* **2018**, *6*, 11734–11752.

(40) Yue, D.; Pandya, S.; You, F. Integrating Hybrid Life Cycle Assessment with Multiobjective Optimization: A Modeling Framework. *Environ. Sci. Technol.* **2016**, *50*, 1501–1509.

(41) Gao, J.; You, F. Economic and Environmental Life Cycle Optimization of Noncooperative Supply Chains and Product Systems: Modeling Framework, Mixed-Integer Bilevel Fractional Programming Algorithm, and Shale Gas Application. *ACS Sustainable Chem. Eng.* **2017**, *5*, 3362–3381.

(42) Han, J.; Elgowainy, A.; Palou-Rivera, I. B.; Dunn, J.; Wang, M. *Well-to-wheels analysis of fast pyrolysis pathways with the GREET model*; Office of Scientific and Technical Information, 2011.

(43) Bernhart, M.; Fasina, O.; Fulton, J. In Characterization of Poultry Litter for Storage and Process Design. 2007 ASAE Annual Meeting; St. Joseph, MI, ASABE: St. Joseph, MI, 2007.

(44) Nicholson, F. A.; Chambers, B. J.; Smith, K. A. Nutrient composition of poultry manures in England and Wales. *Bioresour. Technol.* **1996**, *58*, 279–284.

(45) Roberts, K. G.; Gloy, B. A.; Joseph, S.; Scott, N. R.; Lehmann, J. Life Cycle Assessment of Biochar Systems: Estimating the Energetic, Economic, and Climate Change Potential. *Environ. Sci. Technol.* **2010**, *44*, 827–833.

(46) Sinclair, D. R. Equivalent annual cost: a method for comparing the cost of multi-use medical devices. *Can. J. Anesth.* **2010**, *57*, 521–522.

(47) Buchholz, T.; Luzadis, V. A.; Volk, T. A. Sustainability criteria for bioenergy systems: results from an expert survey. *J. Cleaner Prod.* **2009**, *17*, S86–S98.

(48) Bello, M.; Ranganathan, P.; Brennan, F. Life Cycle Optimization for Sustainable Algal Biofuel Production Using Integrated Nutrient Recycling Technology. ACS Sustainable Chem. Eng. 2017, 5, 9869– 9880.

(49) Calvo-Serrano, R.; Guo, M.; Pozo, C.; Galán-Martín, Á.; Guillén-Gosálbez, G. Biomass Conversion into Fuels, Chemicals, or Electricity? A Network-Based Life Cycle Optimization Approach Applied to the European Union. ACS Sustainable Chem. Eng. **2019**, *7*, 10570–10582.

(50) Murphy, F.; Sosa, A.; McDonnell, K.; Devlin, G. Life cycle assessment of biomass-to-energy systems in Ireland modelled with biomass supply chain optimisation based on greenhouse gas emission reduction. *Energy* **2016**, *109*, 1040–1055.

(51) Sorunmu, Y.; Billen, P.; Elangovan, S. E.; Santosa, D.; Spatari, S. Life-Cycle Assessment of Alternative Pyrolysis-Based Transport Fuels: Implications of Upgrading Technology, Scale, and Hydrogen Requirement. *ACS Sustainable Chem. Eng.* **2018**, *6*, 10001–10010.

(52) Gong, J.; You, F. Sustainable design and synthesis of energy systems. *Curr. Opin. Chem. Eng.* **2015**, *10*, 77–86.

(53) Zhong, Z.; You, F. Globally convergent exact and inexact parametric algorithms for solving large-scale mixed-integer fractional programs and applications in process systems engineering. *Comput. Chem. Eng.* **2014**, *61*, 90–101.

(54) Wang, B.; Han, Z.; Liu, K. J. R. Distributed Relay Selection and Power Control for Multiuser Cooperative Communication Networks Using Stackelberg Game. *IEEE Trans. Mobile Comput.* **2009**, *8*, 975– 990.

(55) Hudson, P. Georgia No. 1 producer of chicken; https://www. bizjournals.com/atlanta/news/2014/09/19/georgia-no-1-producerof-chicken.html (accessed Mar 03, 2020).

(56) Bishop, S. D., Jr.; Tablante, N. L.; Reed, M.; Kolla, N.; Gigle, M. Georgia's Poultry Industry and Its Impact on the Local Economy and Global Trade; https://bishop.house.gov/media-center/op-eds/georgia-s-poultry-industry-and-its-impact-on-the-local-economy-and-global-trade (accessed Mar 03, 2020).

(57) USDA Census of Agriculture 2017; https://www.nass.usda.gov/ Publications/AgCensus/2017/index.php(accessed Mar 03, 2020). (58) Kissel, D. E.; Sonon, L. Soil Test Handbook for Georgia; http://aesl.ces.uga.edu/publications/soil/STHandbook.pdf (accessed Mar. 03, 2020).

(59) Kissel, D. E.; Harris, G. Fertilizer Recommendations by Crops; http://aesl.ces.uga.edu/publications/soil/CropSheets.pdf (accessed Mar 03, 2020).

(60) Enders, A.; Hanley, K.; Whitman, T.; Joseph, S.; Lehmann, J. Characterization of biochars to evaluate recalcitrance and agronomic performance. *Bioresour. Technol.* **2012**, *114*, 644–653.

(61) Andersen, D. S.; Pepple, L. M. A County-Level Assessment of Manure Nutrient Availability Relative to Crop Nutrient Capacity in Iowa: Spatial and Temporal Trends. *Transactions of the ASABE*; American Society of Agricultural and Biological Engineers, 2017, 60 (5), 1669–1680.

(62) Vest, L.; Merka, B.; Segars, W. *Poultry Waste: Georgia's 50 Million Dollar Forgotten Crop*; Food and Agriculture Organization of the United Nations, 1998.

(63) Yue, D.; You, F. Fair Profit Allocation in Supply Chain Optimization with Transfer Price and Revenue Sharing: MINLP Model and Algorithm for Cellulosic Biofuel Supply Chains. *AIChE J.* **2014**, *60*, 3211–3229.

(64) GDOT Georgia DOT regional district; http://www.dot.ga.gov/ AboutGDOT/Districts (accessed Mar 03, 2020).

(65) USDA Census of Agriculture 2012; https://www.nass.usda.gov/ Publications/AgCensus/2012/ (accessed Mar 03, 2020).

(66) Georgia Transportation Data for Alternative Fuels and Vehicles; https://afdc.energy.gov/states/ga (accessed Mar 03, 2020).

(67) BART Determination Review of NV Energy's Tracy Generating Station Units 1, 2 and 3; https://ndep.nv.gov/air/planning-and-modeling/regional-haze-and-bart (accessed Mar 03, 2020).

(68) Collins, A. R.; Basden, T. A Policy Evaluation of Transport Subsidies for Poultry Litter in West Virginia. *Rev. Agric. Econ.* 2006, *28*, 72–88.

(69) *Biodiesel Laws and Incentives in Georgia*; https://afdc.energy.gov/fuels/laws/BIOD?state=GA (accessed Mar 03, 2020).

(70) DoE Fuel Conversion Factors to Gasoline Gallon Equivalents; https://epact.energy.gov/fuel-conversion-factors (accessed Mar 03, 2020).

(71) Tiquia, S. M.; Tam, N. F. Y. Fate of nitrogen during composting of chicken litter. *Environ. Pollut.* **2000**, *110*, 535–541.

(72) Aksoy, B.; Cullinan, H. T.; Sammons, N. E., Jr.; Eden, M. R. Identification of optimal poultry litter biorefinery location in Alabama through minimization of feedstock transportation cost. *Environ. Prog.* **2008**, *27*, 515–523.

(73) Whittington, A. Availability of Poultry Litter as an Alternative Energy Feedstock: the Case of Mississippi; http://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.488.9141&rep=rep1&type=pdf (accessed Mar 03, 2020).

(74) Ecoinvent database https://www.ecoinvent.org/home.html (accessed Mar 03, 2020).

(75) Aspen Plus User Guide; https://web.ist.utl.pt/ist11038/acad/ Aspen/AspUserGuide10.pdf (accessed Mar 03, 2020).

(76) Brooke, A.; Kendrick, D. A.; Meeraus, A.; Rosenthal, R. E. *GAMS, a user's guide*; http://www2.imm.dtu.dk/courses/02724/general\_information/GAMS\_userguide/GAMSUsersGuide.pdf (accessed Mar 03, 2020).

(77) Enders, A.; Gaunt, J.; Stone, J.; Krounbi, L.; Lehmann, J.; Chintala, R. Feasibility Assessment of Dairy Biochar as a Value-Added Potting Mix in Horticulture and Ornamental Gardening; http://blogs. cornell.edu/whatscroppingup/2018/11/29/feasibility-assessment-ofdairy-biochar-as-a-value%E2%80%90added-potting-mix-inhorticulture-and-ornamental-gardening/ (accessed Mar. 03, 2020).