ACS Sustainable Chemistry & Engineering

Research Article

pubs.acs.org/journal/ascecg

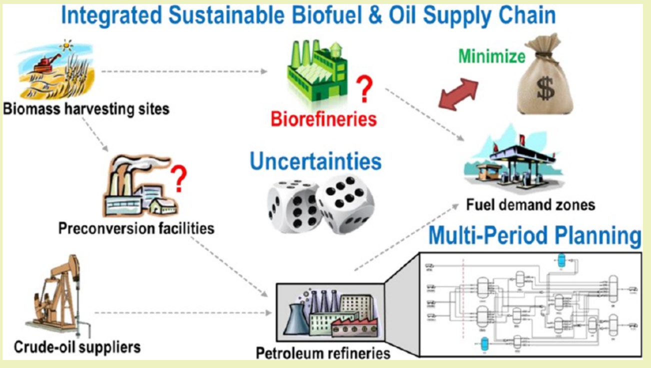
Stochastic Programming Approach to Optimal Design and Operations of Integrated Hydrocarbon Biofuel and Petroleum Supply Chains

Kailiang Tong,[†] Jian Gong,[†] Dajun Yue,[†] and Fengqi You*

Department of Chemical and Biological Engineering, Northwestern University, Evanston, Illinois 60208, United States

Supporting Information

ABSTRACT: This paper addresses the optimal design and strategic planning of the integrated biofuel and petroleum supply chain system in the presence of pricing and quantity uncertainties. The drop-in properties of advanced hydrocarbon biofuels pose considerable potential for biofuel supply chains to leverage the existing production and distribution infrastructures of petroleum supply chains, which may lead to significant capital savings. To achieve a higher modeling resolution and improve the overall economic performance, we explicitly model equipment units and material streams in the retrofitted petroleum processes and propose a multi-period planning model to coordinate the various activities in the petroleum refineries. Furthermore, in order to develop an integrated supply chain that is reliable in the dynamic marketplace, we employ a stochastic programming approach to optimize the expectation under a number of scenarios associated with biomass availability, fuel demand, crude oil prices, and technology evolution. The integrated model is formulated as a stochastic mixed-integer linear program, which is illustrated by a case study involving 21 harvesting sites, 7 potential preconversion facilities, 6 potential integrated biorefineries, 2 petroleum refineries, and 39 demand zones. Results show the market share of biofuels increases gradually due to the increasing crude oil price and biomass availability.



KEYWORDS: *Supply chain, Biofuel, Petroleum refinery, Stochastic programming, Uncertainty*

INTRODUCTION

Biomass-derived liquid transportation fuels have been proposed as part of the solution to climate change and our heavy dependence on fossil fuels because biomass feedstocks can be produced renewably from a variety of domestic sources, and the production and use of biomass have potentially lower environmental impacts than their petroleum counterparts.[1] Consequently, many countries have set national biofuels targets and provided incentives and supports to accelerate the growth of bioenergy industry. In the United States, the Renewable Fuels Standard (RFS), part of the Energy Independence and Security Act (EISA) of 2007, establishes an annual production target of 36 billion gallons of biofuels by 2022, of which 16 billion gallons should be advanced biofuels made from nonstarch feedstocks to avoid adverse impacts on the food market.[2] With the development of the third generation biofuel technologies, advanced biofuels can now be produced from cellulosic biomass such as crop residues, wood residues, or dedicated energy crops. Moreover, advanced hydrocarbon biofuel products (e.g., cellulosic–biomass-derived gasoline, diesel, and aviation fuel) are functionally identical to their petroleum counterpart. Hence, hydrocarbon biofuels are also named drop-in biofuels, which are essentially compatible with the existing distribution infrastructure and vehicle engines.[3] Considering all these appealing properties, it is foreseeable that the hydrocarbon biofuel industry will undergo a rapid expansion in the coming decades, thus requiring design and development of biomass-to-biofuel supply chains that are cost effective and economically viable.[3]

Many studies have been conducted on the design and planning of supply chains for the first and second generation of biofuels from diverse aspects including feedstock selection;[4,5] facility location and capacity design;[6−9] technology selection;[10,11] feedstock seasonality;[12,13] unit cost;[14] a multi-objective model considering economics, financial risk,[15] sustainability;[9,13,16] and social impact.[11] Also, these models were applied to various countries, such as the United States,[5,13] United Kingdom,[7,17] Italy,[8] etc. While most research works consider the design and development of biomass-to-biofuel supply chains independent of the existing petroleum supply chains, the U.S. Department of Energy (DOE)[3] has pointed out

Special Issue: Sustainable Chemical Product and Process Engineering

Received: August 1, 2013
Revised: October 31, 2013
Published: December 4, 2013

the opportunities for the integration of emerging hydrocarbon biofuel supply chains with existing petroleum production and distribution infrastructure. Although minimum retrofitting costs would be required on petroleum refinery units for compatibility reasons, the integration indicates considerable capital savings on the construction of biofuel production facilities, which would help the biofuel products to be cost competitive while bringing in extra profits and environmental benefits to the petroleum refineries.[3,18] However, the literature on the integration and synthesis of the biofuel and petroleum industry from a supply chain point of view is quite limited,[18,19] which is the focus of this work. The integrated supply chain system necessitates planning models to coordinate the additional biomass-related material streams with original crude oil-derived material streams in the petroleum refineries. Integration of supply chain design and strategic planning can provide a higher modeling resolution of the integrated supply chain system and help to improve the overall economic performance by taking advantage of the synergy.

Besides the aforementioned issues, the uncertainties potentially involved in the integrated biofuel and petroleum supply chains are also critical and should be taken into account. Major types of uncertainty include seasonal supply of biomass feedstocks, fluctuation of biofuel demands, volatility of crude oil prices, change in processing costs due to technology evolution, as well as future plan feasibility and potential economic risk.[20] Failure to consider these uncertainties may lead to nonoptimal designs and cause significant extra expenses to accommodate unexpected events. The widely used approaches for optimization under uncertainty[21] include robust programming,[22,23] chance-constraint programming,[24] stochastic inventory[25,26] and stochastic programming.[27−29] Robust optimization may be suitable for the case where the uncertain parameters are known only within certain bounds but not for those with certain probability distributions.[22] In the chance-constrained approach, uncertainties are represented through random variables with known probability distribution and are included in the constraints.[24] As an extension of the chance-constraint method, the stochastic inventory approach can effectively deal with demand and supply uncertainties in supply chain design and operations through simultaneous optimization of the safety stocks and supply chain design, with the expense of adding some nonlinear inventory terms.[25,26] Stochastic programming, which is the approach we will adopt in this work, is able to take advantage of our knowledge on the probability distribution into the optimization framework.[27] In practice, the space of uncertain parameters is discretized into scenarios, with each scenario representing a potential realization of uncertainty. By employing the typical two-stage stochastic programming method, we can explicitly incorporate all the scenarios and optimize the expectation in the objective function. Furthermore, stochastic programming is straightforward to formulate, thus making it the most widely used approach for optimization under uncertainty in both biofuel[15,30,31] and petroleum supply chain optimization.[28,32−35]

In this paper, we propose a two-stage stochastic MILP model for optimal design and strategic planning of the integrated hydrocarbon biofuel and petroleum supply chain considering uncertainties in biomass availability, fuel demand, crude oil prices, and technology evolution. Existing petroleum refineries are considered as potential facilities for the upgrading of biocrudes. In order to leverage the synergy and thus improve the overall economic performance, we explicitly model equipment units and material streams in the retrofitted petroleum processes and propose a multi-period planning model to coordinate the various activities (e.g., acquisition, production, and delivery) in the petroleum refineries on the backdrop of an integrated biofuel and petroleum supply chain system. The major novelties of this work are summarized as follows: (1) integration of biofuel supply chains with existing petroleum supply chains with detailed modeling of refinery operations and (2) two-stage stochastic programming approach to investigate the impacts of uncertainties (e.g., biomass availability, biofuel demand, crude oil prices, and technology evolution) on the multi-period design and planning of integrated biofuel and petroleum supply chains.

The rest of the paper is organized as follows. We first provide a background introduction to the opportunities and challenges for the integration of biofuel and petroleum supply chains, followed by a description of methodology proposed in the paper. This includes a general introduction of the stochastic programming approach, a formal problem statement, and a mathematical formulation. To illustrate the performance of the proposed model, we present a case study along with discussions of the results. The paper is concluded at the end.

BACKGROUND

Integrated Biofuel and Petroleum Supply Chain. A typical advanced hydrocarbon biofuel supply chain consists of harvesting sites, biorefineries, preconversion facilities, upgrading facilities, and demand zones.[1] The biomass is cultivated and harvested in harvesting sites. The harvested biomass feedstocks have two alternative destinies.

(1) They can be sent to integrated biorefineries for direct biofuel. The state-of-the-art technologies for biomass conversion can be classified into two groups: biochemical conversion and thermochemical conversion. Biochemical conversion decomposes the biomass cell walls by enzymes or acids to extract sugars. Then these sugars are upgraded to biofuels using microorganisms. The biochemical conversion pathway benefits from sustainable and mild operating conditions but encounters the bottleneck of discovering efficient enzymes for hydrolysis and microorganisms for sugar conversion, as well as industrial scale-up. The thermochemical conversion pathway, on the other hand, applies heat, pressure, and catalyst to convert biomass to a variety of biofuels, including renewable gasoline, diesel, jet fuels, and chemicals, as well as heat and power. The most common pathways of thermochemical conversion involve gasification, fast pyrolysis, and hydrothermal liquefaction. In the gasification process, biomass from pretreatment facilities is broken down and oxidized into syngas, which constitutes mainly carbon monoxide and hydrogen. Then the syngas undergoes cleanup and conditioning processes to remove contaminants and adjust the hydrogen−carbon monoxide ratio for the following Fischer−Tropsch stage. In the pyrolysis process, biomass is decomposed in the absence of oxygen at a lower temperature, and this reaction results in liquid biocrude oil, which can be upgraded to hydrocarbon biofuels via hydrotreating and hydrocracking after a cleanup step. Unlike gasification and pyrolysis, other thermochemical conversion pathways are still in their infancy status, so we consider only gasification and pyrolysis as the potential technology alternatives for integrated biorefinery in our work.

(2) The feedstocks enter a two-stage conversion process:[13,36] preconversion and upgrading. The preconversion stage

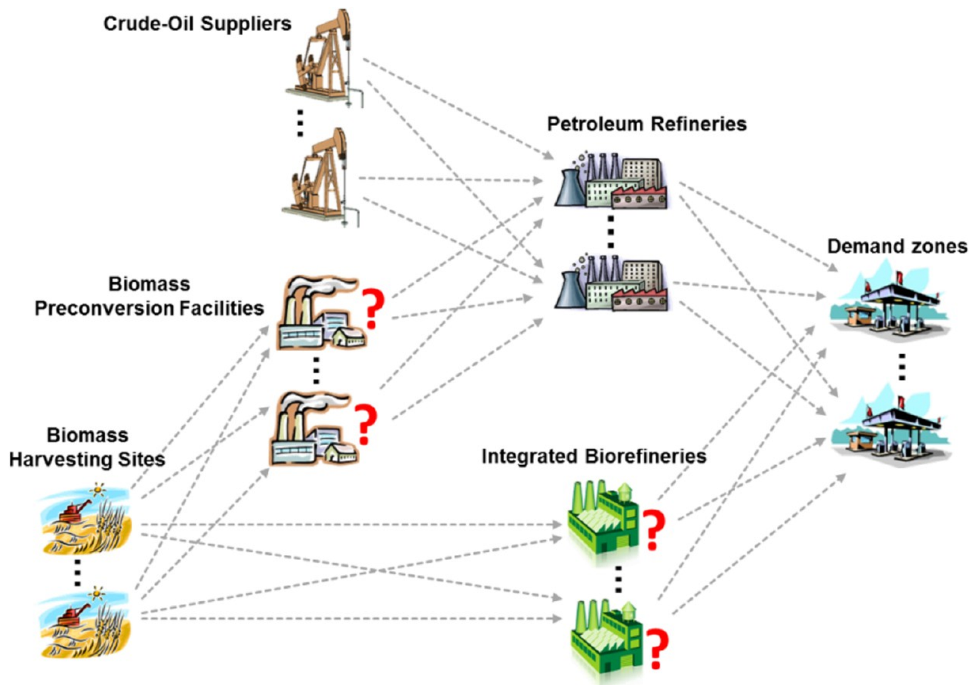


Figure 1. Superstructure of integrated biofuel and petroleum supply chain.

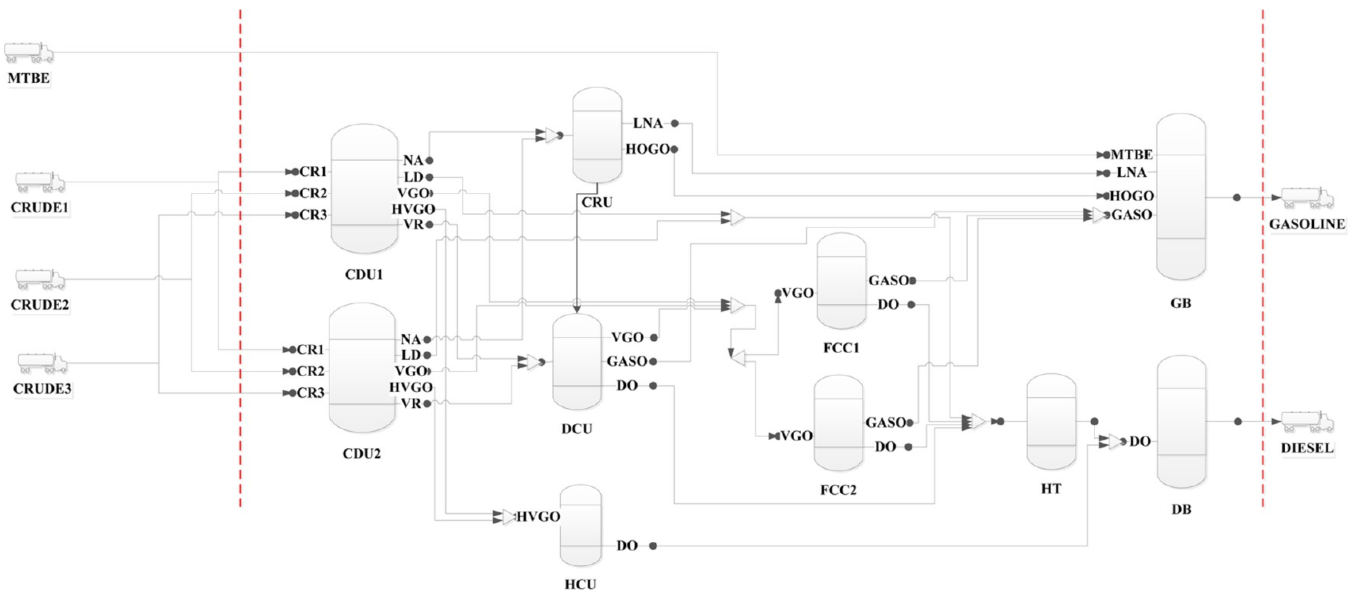


Figure 2. Flowchart of a typical refinery.

converts biomass into biocrude (e.g., pyrolysis oil) that is economical and efficient for transportation, whereas the upgrading stage upgrades the biocrude into final products (e.g., gasoline, diesel).[37,38] Because of the low energy density and high moisture content of the biomass, transporting biomass is much more expensive than transporting crude oil. In contrast, transporting biocrude is relatively easier and cheaper. Therefore, we can build the preconversion facilities and upgrading facilities in different locations in order to take advantage of the geographical benefits associated with each process. The resulting centralized distributed network[13,36] can improve the economic performance of the supply chain. All the fuel products are sent to the demand zones to meet customers' needs. By contrast, in a typical petroleum supply chain, crude oils are first purchased from suppliers and then processed in the petroleum refineries. The fuel products are usually delivered to demand zones using pipelines or trucks.

Both the DOE[3,17] and Universal Oil Product (UOP)[39] noted that advanced hydrocarbon biofuel can take advantage of the existing petroleum refinery infrastructure, which means that it is possible to use the upgrading unit in the existing refinery to upgrade biocrude into final products. Tong et al.[18] also quantitatively analyzed the three possible insertion points in petroleum refineries. In this work, we propose a novel superstructure of the integrated biofuel and petroleum supply chain in Figure 1. The strategic design and planning in both biofuel and petroleum supply chains are simultaneously optimized. Note that a well-designed supply chain will not choose to install additional upgrading facilities instead of using existing petroleum infrastructures.[18] Therefore, we do not consider an independent upgrading facility in the integrated supply chain. We assume that all the biomass processed in a preconversion facility is sent to a petroleum refinery immediately.

Planning of Petroleum Refinery. The integrated supply chain system necessitates planning models to coordinate the additional biomass-related material streams with original crude oil-derived material streams in the petroleum refineries. Moreover, integration of supply chain design and strategic planning can provide a higher modeling resolution of the integrated supply chain system and help to improve the overall economic performance by taking advantage of the synergy. In fact, units in refinery can have different product yield and different connectivity based on various crude oil supply and demand profiles. Therefore, the detailed planning of a refinery should be integrated in the oil supply chain model.[40] Figure 2 shows a typical flowchart of a petroleum refinery. Here, we give a brief description of the units in a typical refinery based on the work by Al-Qahtani et al.[41] Crude distillation units (CDU) are used to separate oil into fractions by distillation according to their boiling points. Catalytic reforming units (CRU) convert naphtha, which typically has low octane ratings, into high octane liquids. Delayed coking units (DCU) convert heavy feedstocks to more desirable and valuable products with higher quality. Fluid catalytic cracking units (FCC) break down and rearrange complex hydrocarbons into lighter molecules in order to increase the quality and quantity of desirable products. Hydrotreating units (HT) use hydrogen to upgrade feedstock to the desired products, e.g, remove sulfur in diesel. Hydrocracking units (HCU) combine catalytic cracking and hydrogenation where the feed is cracked in the presence of hydrogen to produce more desirable products. Gasoline blender (GB) and diesel blender (DB) are the virtual blending units that blend feedstocks into gasoline and diesel products.

The CDU fractionates crude oil into the following hydrocarbon streams: naphtha (NA), light diesel (LD), vacuum gas oil (VGO), heavy vacuum gas oil (HVGO), and vacuum residue (VR). Connections between different streams are defined as movement. The trucks denote the in-plant and out-plant points, which represent the supply of raw materials (e.g., crude oil, MTBE) going into the plant and fuel products (e.g., gasoline, diesel) going out of the plant. Methyl tertiary butyl ether (MTBE), which is a gasoline additive, is used as oxidant to increase the octane value in gasoline. In our model, MTBE is treated as a type of raw material. The strategic planning in petroleum refineries is to decide the optimal processing amount, product yield of each unit, flow rate of streams and movements, crude oil procurement, etc. This gives a high resolution of decisions in the integrated supply chain.

Processing Biocrude Oil in Petroleum Refinery. Nowadays, many researchers are investigating the feasibility and potential of producing biofuels in existing petroleum refineries.[3,39,42] Huber and Corma[43] summarized the techniques for converting biomass into biofuel in existing petroleum refineries. They noted that catalytic cracking, hydrotreating, and hydrocracking are the three main techniques for converting biomass to biofuels. It should be noted that biomass cannot be directly processed in petroleum refineries. Therefore, it must be first converted into biocrude in the preconversion facilities. The biocrude considered in our paper is pyrolysis oil, which is the product of the preconversion facility with fast pyrolysis technology. Researchers found that direct use of pyrolysis oil in a refinery requires complete deoxygenation and a low acid number to prevent corrosion.[39,42] Therefore, before its upgrading in the petroleum refinery, pyrolysis oil should be appropriately processed using 317 stainless cladding,[39] which is not a standard refinery unit, to lower the acid number. In this paper, we consider two technologies for upgrading pyrolysis oil into fuel products, which are studied by Marker et al.[39] and Jones et al,[42] respectively. One approach is that pyrolysis oil can be processed by hydrotreating units and then coprocessed with VGO in FCC units. The other is that pyrolysis oil is processed by hydrotreating units followed by HCU units. In this work, we denote them as FCC integration and HCU integration, respectively. Before being processed, pyrolysis oil should be pretreated in the 317 stainless steel system to reduce the acid number. Note that new hydrotreating units should be installed because the catalyst used in hydrotreating units is dedicated to specific processing purpose, thus not fungible. Figure 3 shows

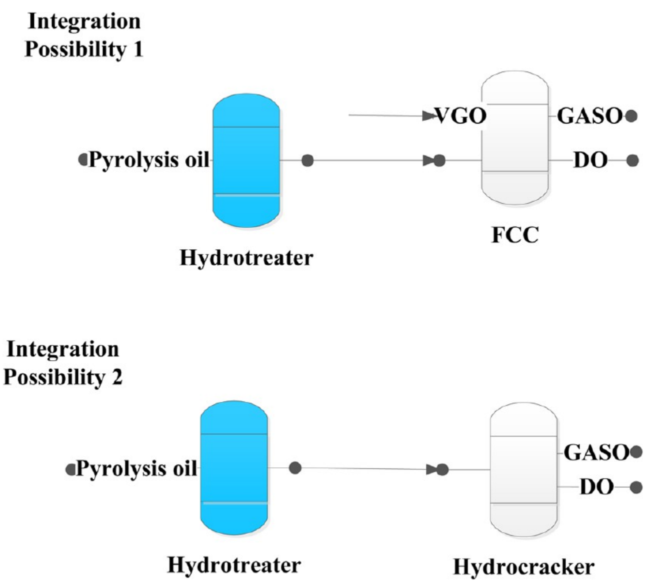


Figure 3. Two technologies for processing pyrolysis oil in petroleum refinery.

the two integration technologies for upgrading pyrolysis oil in the petroleum refinery. Note that the 317 stainless steel system is not depicted in the figure for clarity. It also should be noted that in order to maintain steady conversion, the processing amount of pyrolysis oil cannot exceed a certain ratio of capacity of integrating units.[42]

The whole flowchart of the refinery integrating pyrolysis oil processing is shown in Figure 4. The units in blue are the new ones required for processing pyrolysis oil. Note that in order to track the fuels converted from pyrolysis or crude oil, we add some virtual outlet streams (e.g., PDO and PGASO of FCC1 in Figure 4, denoting diesel and gasoline produced only from PO inlet stream).

■ METHODOLOGY

Stochastic Programming. As mentioned in previous sections, uncertainties considerably impact the economic performance of the integrated supply chains, among which seasonal supply of biomass feedstocks, fluctuation of biofuel demands, volatility of crude oil prices, and change in processing costs due to technology evolution are considered as the most

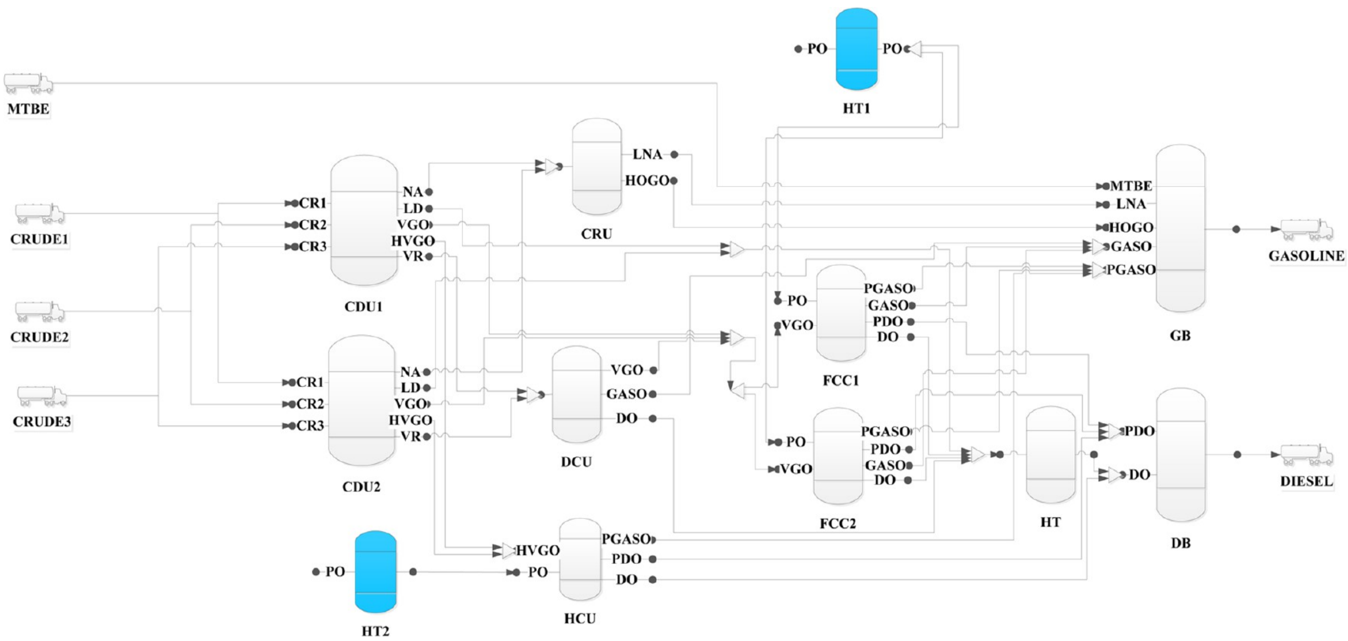


Figure 4. Flowchart of the refinery integrating pyrolysis oil processing.

critical ones.[1] The most widely employed approach for optimization under uncertainty is the stochastic programming method.[27] Two-stage stochastic programming with recourse is the most typical and classic stochastic programming model, where the first-stage variables represent "here and now" decisions, which must be made before the realization of uncertainties, while the second-stage variable are "wait and see" decisions, which can be made only after the realization of uncertainties. Typically, the objective of stochastic programming is to optimize the expected value of a performance function. Scenario-based stochastic programming is an approximation approach to transform the intractable stochastic problem into a tractable one. The main idea is to address only a finite number of selected realizations of uncertainty in the optimization. Each realization is regarded as one scenario and is assigned with a probability.[28] The scenario formulation retains the flexibility of choosing different second stage decisions according to different realization of uncertainty, and it often achieves a good estimation of the expected performance and return reasonable solutions.[44] Scenarios are usually defined according to one's insight and modeling experience or via advanced sampling methods (e.g., Monte Carlo sampling[45]). The typical formulation of scenario-based stochastic programming is given by eq 1

$$\begin{aligned} \min \quad & c^T x + \sum_s p_s q_s^T y_s \\ s.t. \quad & Ax \leq b \\ & T_s x + W_s y_s \leq h_s, \quad \forall\, s \end{aligned} \tag{1}$$

where the different realizations of uncertain parameters are characterized by scenario s and corresponding probability p_s. x and y_s are first-stage and second-stage variables, respectively. The objective function includes two parts. The first term indicates the cost related to first-stage variables, called first-stage cost; the second term, which is the summation of the cost for each scenario with predefined probability, is the expected second-stage cost. In a general supply chain optimization problem, design variables are usually regarded as first-stage variables, and operation variables are considered as second-stage variables.

Problem Statement. The superstructure of the integrated biofuel and petroleum supply chain is shown in Figure 1. We are given a set of biomass feedstock harvesting sites, potential preconversion facilities locations, potential integrated biorefineries locations, crude oil suppliers, existing petroleum refineries, and demand zones. We are given a planning horizon modeled as a number of time periods with identical duration. We are given a set of biomass feedstocks (namely, crop residues, wood residues, and energy crops) with their major properties, including moisture content, harvesting cost, and availability at each harvesting site specified. We are also given a set of crude oils with known purchasing cost and annual availability. The selling prices and demand of each type of fuel products (e.g., gasoline and diesel) at each demand zone are given as well. In preconversion facilities and biorefineries, we are given a set of conversion technologies, capacity levels and corresponding conversion rates, operation costs, and capital costs. The flowchart of each petroleum refinery is given. The capacity and conversion rate for each unit are also known. Two integration technologies are considered in our model. One is to coprocess the pyrolysis oil with VGO in the FCC (FCC integration). The other is to process the pyrolysis oil in the HCU (HCU integration). The capacity level, operating cost, and capital cost of installing new units for each integration technology are also given. The available transportation mode, transportation cost, and the government incentive for facility construction and biofuel sales are known.

The objective is to minimize the systems-wide cost of the integrated biofuel and petroleum supply chain system over the planning horizon by optimizing the following decision variables: (1) supply network structure, including (1a) number, size, locations, technology selection, and year of installation of the preconversion facilities and the integrated biorefineries and (1b) retrofitting petroleum refinery, including selecting integrating technology, corresponding unit size and installation time; (2) purchase amount of each type of biomass feedstock and crude oil from each supplier in each year; (3) amount of feedstock consumption, material processing, and product yield in preconversion facilities, integrated biorefineries, and petroleum refineries, as well as the material flow rates associated with each unit in the petroleum refinery; and (4) selection of transportation mode and the transportation amount for each link.

We assume the crude oil availability, crude oil price, biomass availability, harvesting cost, government incentive, and product demand are considered uncertain. Production cost and investment cost for biofuel production facilities are also considered uncertain. A number of possible scenarios regarding the uncertain parameters are given. In our stochastic programming model, all the decisions related to supply chain design are regarded as first-stage variables. These variables include the number, size, locations, technology selection, and the installation time for preconversion facilities, biorefineries, and hydrotreating units in petroleum refinery. All the other variables related to operation are regarded as second-stage variables that can be made after the uncertainties are realized. These variables include the purchase amount of biomass and crude oil, processing amount of raw materials and product yield of fuels in any production facilities, transportation amount, material flow in refineries, etc.

Mathematical Formulation. We develop a multi-period stochastic MILP model addressing the optimization of design and planning for integrated hydrocarbon biofuel and petroleum supply chain under uncertainty. The model for petroleum refinery planning is based on the work of Tong et al.[34] and Neiro et al.[40] The model for biofuel supply chain is based on the work of Tong et al.[18] Considering the length of the article, we present a brief introduction of the proposed model in this section. For concise reasons, the detailed mathematical formulation and nomenclature are provided in the Supporting Information.

The objective in eq 2 is to minimize the expected overall cost over the entire planning horizon. This cost involves the capital costs for facility/unit installation, operation costs for fuel production, penalties for failure to meet the demands, and government incentives. IR is the interest rate used for the computation of present value in multi-year planning. In our model, all the design decisions are considered first-stage variables, while the others are second-stage variables. Therefore, in the objective function (1), the first term represents the first-stage cost, and the second term stands for the expected second-stage cost, which is the summation of the cost in each scenario with the predefined probability π_s. The variables x in the first term of the objective function is independent of the realization of uncertainty. However, the variables y_s in the second term of the objective function can be executed only after the realization of uncertainty. Therefore, the subscript s indicates decisions under different scenarios.

$$\min C^{\text{total}} = \sum_{t,s} \pi_s \times \frac{1}{(1+IR)^{t-1}} \times C_{t,s}^{\text{capital}} + \sum_{t,s} \pi_s \times \frac{1}{(1+IR)^{t-1}} \times \{C_{t,s}^{\text{operation}} - C_{t,s}^{\text{incentive}} + C_{t,s}^{\text{penalty}}\} \quad (2)$$

The capital cost consists of the installation costs of the preconversion facilities $tcapk_{k,t,s}$, biorefineries $tcapl_{l,t,s}$, and retrofitting of the petroleum refineries $tcapsr_{sr,un,t,s}$.

$$C_{t,s}^{\text{capital}} = \sum_k tcapk_{k,t,s} + \sum_l tcapl_{l,t,s} + \sum_{sr,un} tcapsr_{sr,un,t,s} \quad \forall\, t, s \quad (3)$$

The operation cost consists of purchase cost, operation and maintenance (O&M) cost, production cost, and transportation cost. All the costs are evaluated by linear relationships of the real flow rates. One can refer to the Supporting Information for more details.

$$C_{t,s}^{\text{operation}} = C_{t,s}^{\text{purchase}} + C_{t,s}^{\text{O\&M}} + C_{t,s}^{\text{production}} + C_{t,s}^{\text{transportation}} \quad \forall\, t, s \quad (4)$$

The government incentive includes construction incentive and volumetric incentive for biofuel production and usage.

$$C_{t,s}^{\text{incentive}} = \sum_k inck_{k,t,s} + \sum_l incl_{l,t,s} + \sum_{sr} incsr_{sr,t,s} + \sum_{p,t} INCVO_{p,t,s} \times \phi_p \times pw_{p,t,s} \quad \forall\, t, s \quad (5)$$

The model satisfies mass balance constraints, production constraints, capacity constraints, and logical constraints. The mass balance constraints define the mass conservation of materials at each node of the supply chain. The production constraints describe the input−output relationship at the material processing facilities for the production of both biofuel and petroleum. Capacity constraints limit the raw material purchases, production amounts, and transportation flows. Logical constraints, usually related to first-stage binary 0−1 variables, regard the existence of a processing facility, equipment unit, or transportation link.

The demands for gasoline and diesel at demand zones can be fulfilled by fuel products either derived from biomass or crude oil with no bias. Pyrolysis oil produced from preconversion facilities can be upgraded into fuel products in retrofitted petroleum refineries by adding integrating units. Therefore, we introduce binary 0−1 variable $inu_{sr,un,u,t}$ to indicate whether the integrating unit (e.g., hydrotreating unit for pretreating before FCC integration or HCU integration) un in refinery sr with capacity level u is built at time period t. The continuous variable $ucap_{sr,un,t}$, indicates the capacity level of integrating unit un in refinery sr at time period t. $ucap_{sr,un,t}$ specifies an upper bound for the processing amount of each unit in the petroleum refinery. In this way, we establish the link between the hydrocarbon biofuel supply chain and petroleum supply chain as shown in (S39−S48, Supporting Information).

■ CASE STUDY

Input Data. To illustrate the application of the proposed model, we present a case study on a potential integrated biofuel and petroleum supply chain involving 21 biomass harvesting sites, 4 petroleum crude oil suppliers, 7 potential preconversion facilities, 6 integrated biorefineries, 2 existing petroleum refineries, and 39 fuel demand zones. The planning horizon considered in our case is 20 years with each year as one time period. Please note that the planning horizon is a fundamental subjective decision that is not influenced by objective market conditions, so it is not included in the uncertain parameters. All the data used in this case study is adopted and customized from existing literature and reports.[3,13,18,34,46,47] Three major types of biomass are considered in our case, namely, crop residues (e.g., corn stover), energy crops (e.g., switchgrass), and wood

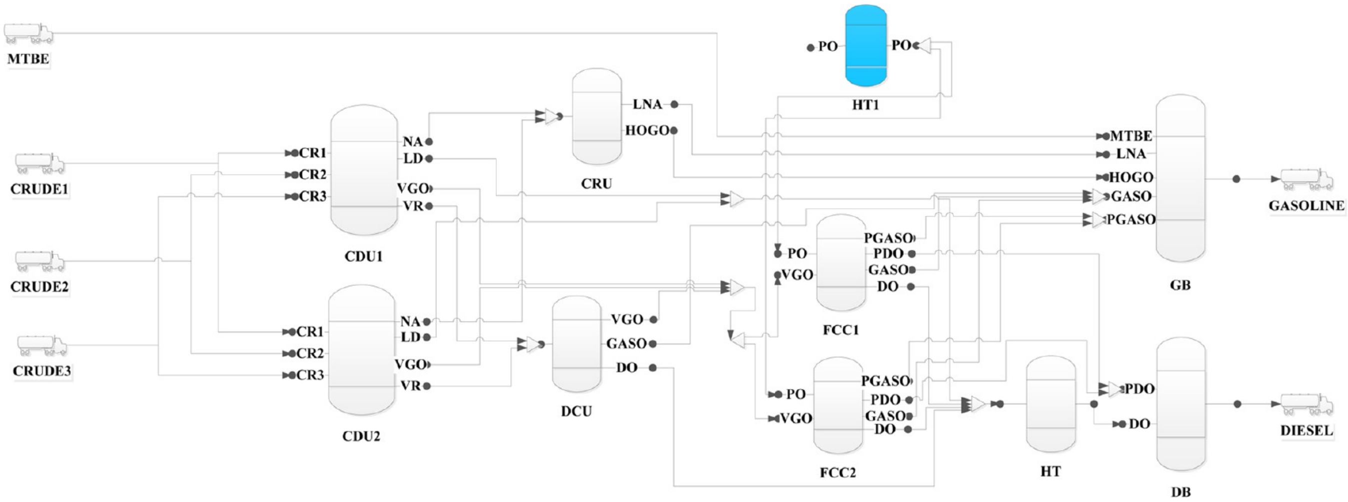


Figure 5. Flowchart for second refinery.

residues (e.g., forest residues). The annual yields of each type of biomass resources in each harvesting site are given in the Supporting Information. The harvesting loss is assumed to be 5%. We consider two major types of liquid fuel products, namely, gasoline and diesel. The demands of each type of fuel product in each demand zone in the first time period are also specified in the information.

In this model, we consider two available conversion pathways in the integrated biorefinery, namely, "gasification + FT synthesis" and "pyrolysis + hydroprocessing". Three capacity levels are considered for each biorefinery in the ranges of 20−50, 50−100, and 100−200 MM GGE/y. We assume rotating cone reactor pyrolysis is used in all preconversion facilities. The capacity levels considered for preconversion facilities are 200−500, 500−1000, and 1000−2000 kton/y. We take into account the economy of scale by using a scale factor of 0.6 to calculate the capital cost of conversion facilities.[36] In order to preserve the advantage of linear formulation, the original six-tenths power functions are approximated by continuous piecewise linear functions with three partition points 50,100 and 200 MM GGE/y. Further information regarding the capacities, total capital investment, and yield is provided in the Supporting Information.

We consider two existing petroleum refineries in our model, whose flowcharts are shown in Figures 2 and 5, respectively. The only difference between refinery 1 and 2 is that we do not have HCU units in refinery 2. Therefore, only FCC integrating technology can be applied in refinery 2. We also consider three capacity levels for the hydrotreating unit in the petroleum refinery in the range of 50−125, 125−250, and 250−500 M gal/y. We consider the octane number as the quality indicator of gasoline blending. We assume the octane value of inlet streams of the GB unit is constant. The requirement of the octane number for gasoline is provided in the Supporting Information. The maximum mixing ratio of pyrolysis oil into the FCC or HCU is set to 20% in the first 5 years and is increased to 30% in the later 15 years due to technology evolution.

The interest rate is assumed to be 10%. The construction incentive for each facility installation cannot exceed $4,000,000 and cannot be above 10% of the total capital investment.[48] The volume incentive is set to $1/gallon for all fuel products derived from biomass feedstocks.[48]

Scenario Generation. Uncertainties must be considered in the design and strategic planning to guarantee the development of a reliable integrated supply chain in dynamic marketplace.[1] In our model, we consider biomass availability, product demand, crude oil price and availability, biomass harvesting cost, operation cost, capital cost, and government incentive as uncertain parameters. All the data for scenario generation is estimated and customized based on historical data.[3,46,47,49] Considering the correlation between these uncertain parameters, we further categorize them into four groups: biomass availability, fuel demand, crude oil price and availability, and biofuel technology evolution. For each group, we define a series of scenarios as follows.[50]

Spurred by RFS,[2] the availability of cellulosic biomass resources is foreseeable to increase in the future. We assume two scenarios for biomass availability, namely, LOW and HIGH. The probability of each scenario is assumed to be 50%. In the LOW scenario, biomass availability is assumed to increase by 5% every year, while in the HIGH scenario 7%. For the demand uncertainty, we consider two scenarios: LOW (50%) and HIGH (50%). In the LOW scenario, the fuel demand increases by 1% every year, while in the HIGH scenario 2.5%. For the crude oil uncertainty, we consider two scenarios: LOW (50%) and HIGH (50%). In the LOW scenario, we assume the crude oil price increases by 7% every year and the availability of crude oil decreases by 1% every year, while in the HIGH scenarios crude oil price increases by 10% every year and the availability of crude oil decreases by 1.5% every year. In both scenarios, we assume the percentage of increase in crude oil price is higher than 5%, which equals to the rate of inflation, because the price of the crude oil is foreseeable to soar due to its shortage.[3] The last type of uncertainty considered is related to the evolution in biofuel technologies. In general, with the improvement in biofuel technologies, the costs of biomass acquisition, biofuel production, and facility construction will gradually decrease. Therefore, we consider three scenarios for technology evolution: LOW (25%), BASE (50%), and HIGH (25%). In the LOW scenario, all the aforementioned costs increase by 2% every year. In the BASE scenario, the costs increase by 3% per year, and in the HIGH scenario, they increase by 5% per year. Note that the higher the percentage of increase in costs, the less improvement in the biofuel technologies. The costs in the

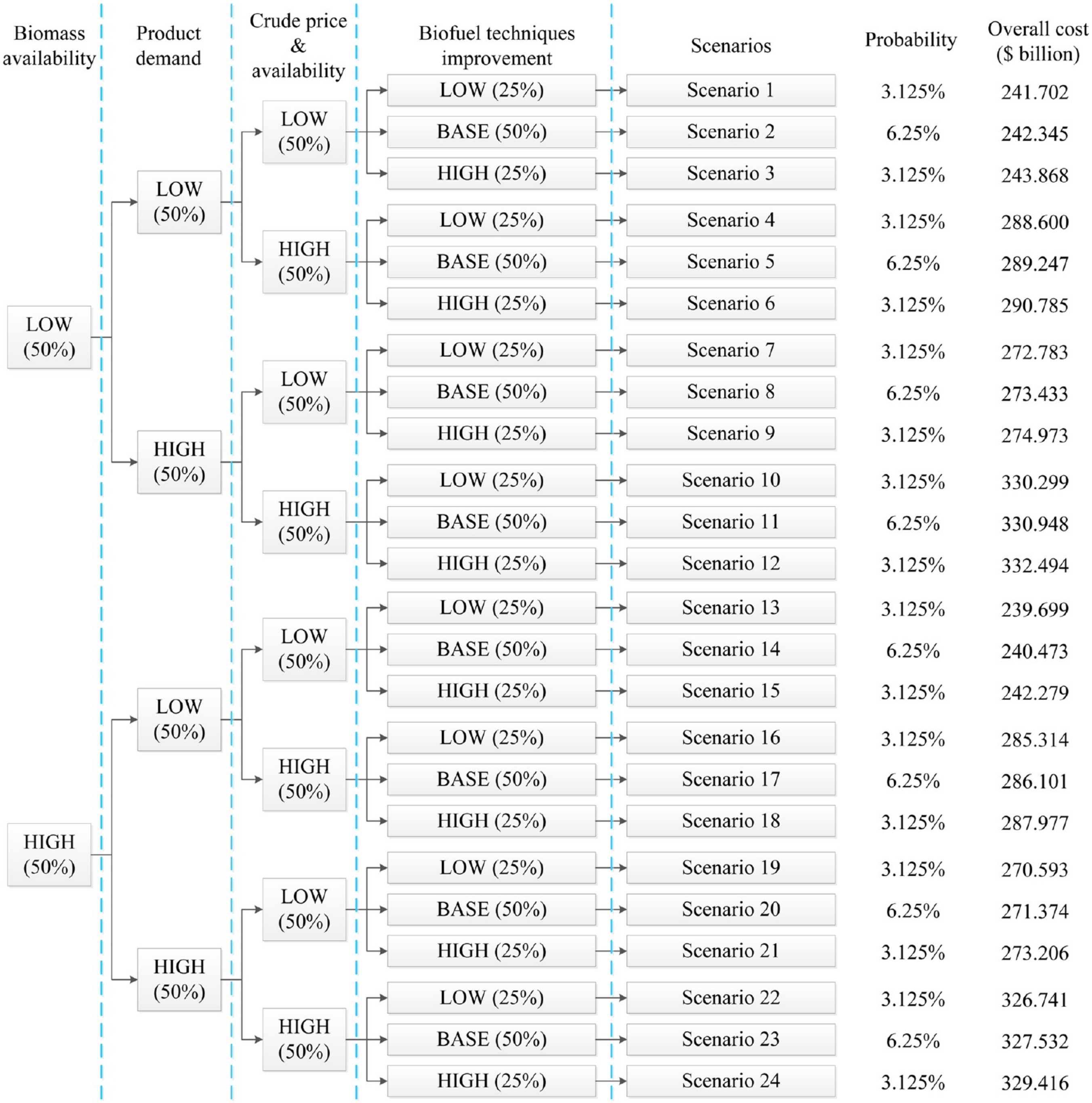


Figure 6. Scenario generation for the integrated supply chain model.

HIGH scenario actually remain constant as the percentage of increase in costs is equal to the rate of inflation. On the basis of these assumptions, we can generate a total of $2 \times 2 \times 2 \times 3 = 24$ scenarios, as shown in Figure 6.

Results. The optimization is performed on a Dell computer with an Intel Core i5-2400 3.10 GHz CPU and 8 GB RAM. The MILP model is coded in GAMS 24.0.1[51] and is solved using CPLEX 12.5 with three processing cores under parallel mode. The optimality tolerance is set to 1%. The stochastic model consists of 1320 binary variables, 186,245 continuous variables, and 625,902 constraints.

The minimum total cost is \$282.926 billion. The solution time is 31,996 CPUs (around 9 h). The optimal design of the integrated supply chain is shown in Figure 7. In the optimal solution, six preconversion facilities are built, with capacity levels ranging from 500 to 2000 kton/y. Three (PR2, PR4, and PR5) are built in the first year, while two (PR1 and PR6) are built in the second year. PR7 is built in the ninth year due to the increasing biomass availability and product demand. Six integrated biorefineries are built with capacity levels ranging from 50 to 200 M GGE/y. Three of the integrated biorefineries (BI2, BI3, and BI5) use the technology of "gasification + FT synthesis", while the others use the technology of "fast pyrolysis + hydroprocessing". Unlike the case of preconversion facilities, only three biorefineries (BI2, BI3, and BI5) are built in the first two years, while the others are built in the last 10 years. All the

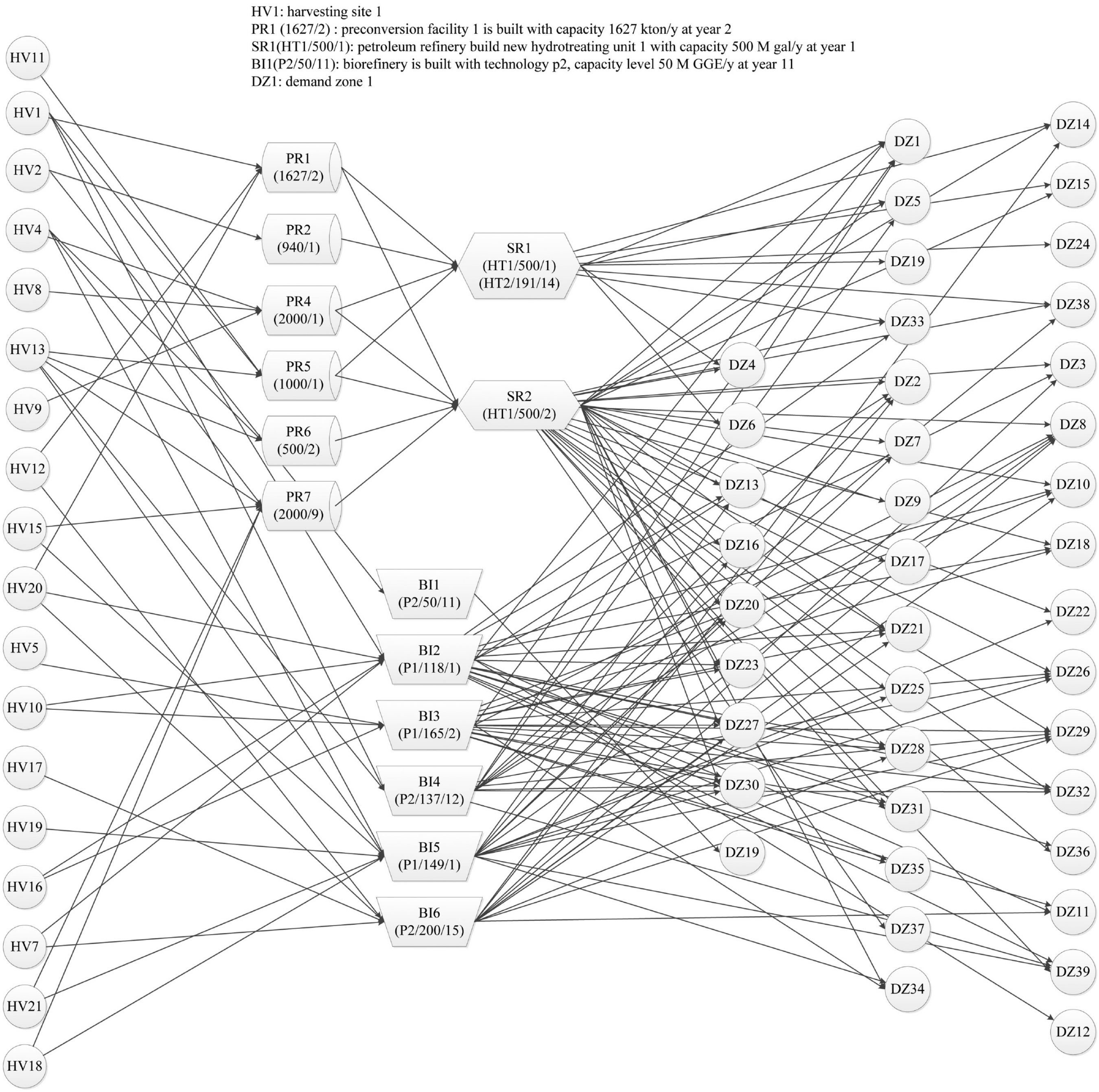


Figure 7. Optimal results for supply chain design and transportation links for scenario 16.

existing petroleum refineries are utilized and retrofitted for biofuel production, which indicates that the integration of biofuel supply chains with petroleum refineries indeed helps to reduce the overall cost while satisfying the demands for hydrocarbon transportation fuels. The hydrotreating units using FCC integration are built with full capacity in both refinery SR1 and SR2 in year 1 and 2, respectively. In contrast, the hydrotreating unit using HCU integration is built with a capacity of 191 M gal/y in year 14. This indicates that FCC integration may present better economic performance than HCU integration. The transportation connection profile for delivering materials between the nodes in scenario 16 is also depicted in Figure 7. We choose scenario 16 as the example because its overall cost is the closest to the optimal expected cost among all the scenarios. We show part of the results on strategic planning by depicting the processing amount of CDU in retrofitted petroleum refineries (Figure 8). Although the annual processing amount of CDUs fluctuates due to the demand and supply uncertainties, the total processing amount of CDUs in SR1 increases gradually from 1400 to 1900 M gal/y. In contrast, the total processing amount of CDUs in SR2 decreases from 5200 to 4600 M gal/y from year 1 to year 20. However, the total processing amount for all four CDUs decreases over the planning horizon indicating that we are producing more hydrocarbon biofuels as replacement of petroleum fuel products.[3]

The total costs corresponding to all the scenarios are shown on the right in Figure 6. Although each scenario is solved to optimality, the production scale considered in this supply chain is very large. Moreover, we define the objective function by

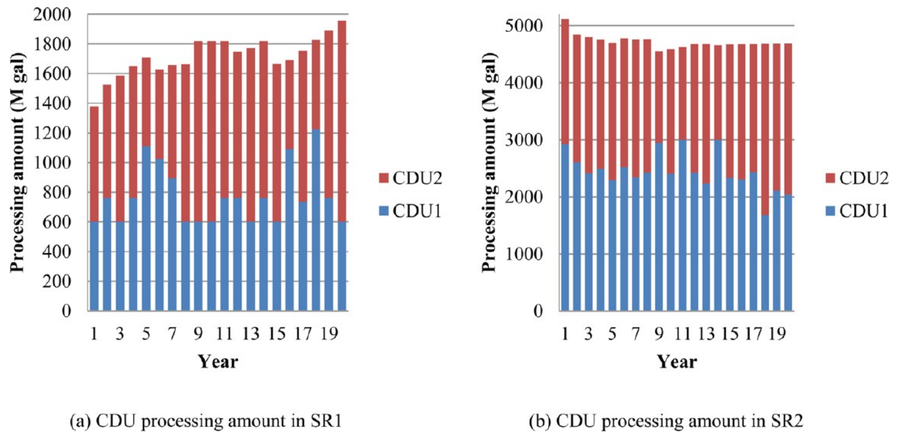


Figure 8. CDU processing amount in each year.

converting the costs emerging during the 20 years to their present values, which further enlarges the absolute value of the total cost. Therefore, given the optimal result from similar work,[52] the large costs are reasonable. Scenario 12 leads to the highest cost of $332.494 billion, which is 17.5% higher than the expected cost. It corresponds to the scenario of LOW biomass availability, HIGH demand, HIGH crude oil price, and HIGH operation cost with no technology improvement. Scenario 13 leads to the lowest cost of $239.699 billion, which is 15.3% lower than the expected cost. It corresponds to the scenario of HIGH biomass availability, LOW demand, LOW crude oil price, and LOW production cost with significant technology improvement.

Next, we perform a comparative analysis to develop more insights into the scenario results. Again, we take scenario 16 as the reference scenario, whose cost is the closest to the expected total cost among all 24 scenarios. Scenario 16 corresponds to HIGH biomass availability, LOW demand, HIGH crude oil price, and LOW production cost indicating significant technology improvement. We compare four selected scenarios (scenario 4, 13, 18, and 22) with the reference scenario to see how different types of uncertainty would influence the optimal decisions. The reason for choosing the four scenarios is that each of these scenarios only differs from the reference scenario in one uncertain parameter. Figure 9 shows the total cost of the four selected scenarios and the reference scenario. Scenario 22 has a much higher cost than the other four scenarios, indicating that the total cost is very sensitive to the changes in fuel demands. When demands increase, there will be more raw materials consumed and more hydrocarbon fuels produced, thus leading to significant increase in the total cost. Scenario 13 has the lowest cost because it corresponds to a lower crude oil price and higher crude oil availability. When crude oil price increases and its availability decreases, the integrated supply chain will intend to produce more hydrocarbon fuels from biomass so as to reduce the total cost. Comparing scenario 4 with scenario 16, we can see that when the biomass availability increases, we also tend to produce more hydrocarbon fuels from biomass. However, the impact of biomass availability on the total cost is relatively small compared with the uncertainty in crude oil price and fuel demand. With the improvement in biofuel technologies, the total cost will decrease as we can see from the comparison between scenario 16 and scenario 18. However, the impact of technology evolution is not very significant. This is because at the current stage of the integrated supply chain, most of the fuel demands are still fulfilled by petroleum fuels. In other words, petroleum products have the major market share. However, the improvement in biofuel technology only influences the biofuel part of the integrated supply chain rather than the whole one.

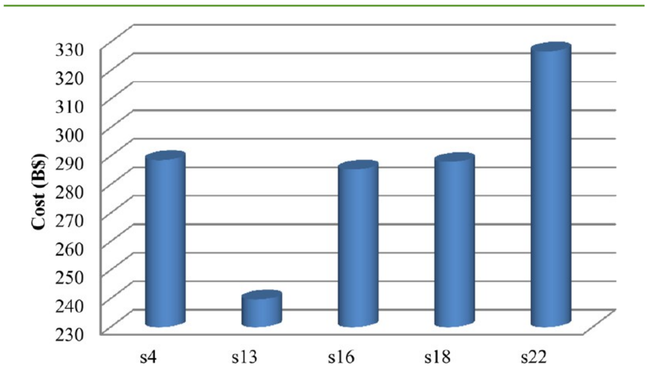


Figure 9. Total cost for selected scenarios.

From the analysis above, we can conclude that the uncertainties in fuel demand and the price and availability of crude oil have the most significant impacts on the total cost, whereas the uncertainties in technology improvement and biomass availability are less critical.

Figure 10 shows the evolution of the share of biofuels in the fuel product marketplace over the planning horizon. The market share of hydrocarbon biofuels increases from 9% to around 18% from year 1 to year 20. As the crude oil price increases and its availability decreases, biomass availability increases, and as the biofuel technology improves, biofuels will gain more and more market share. The curve of scenario 18 is quite similar to the one of scenario 16, this demonstrates again that the impact of technology evolution is not significant compared with other type of uncertainties. When comparing scenario 16 with scenario 13, we can see that increasing the crude oil price and decreasing its availability do not expand the market share of biofuels significantly. This is because in both the two scenarios, the consumption of biomass is close to its maximum availability, thus increasing the crude oil price does not increase the biofuel production significantly. In scenario 4, where the biomass availability is low, the market share of biofuels increase from 7% to 18% over the planning horizon, of which the expansion speed is much slower than the other three scenarios discussed. This again suggests that biomass availability is the most critical factor influencing the market share.

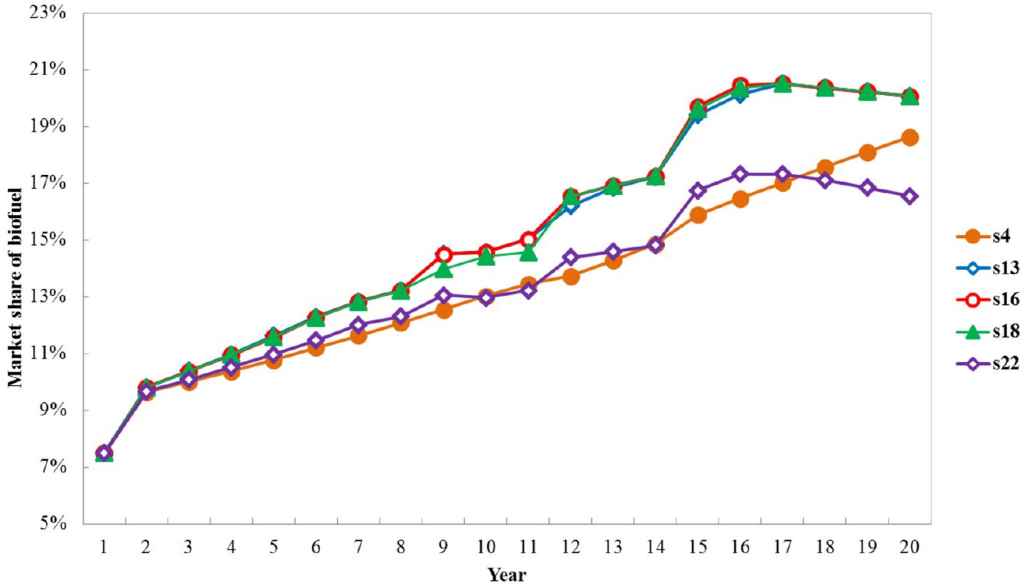


Figure 10. Product demand fulfilled by biofuels in each time period.

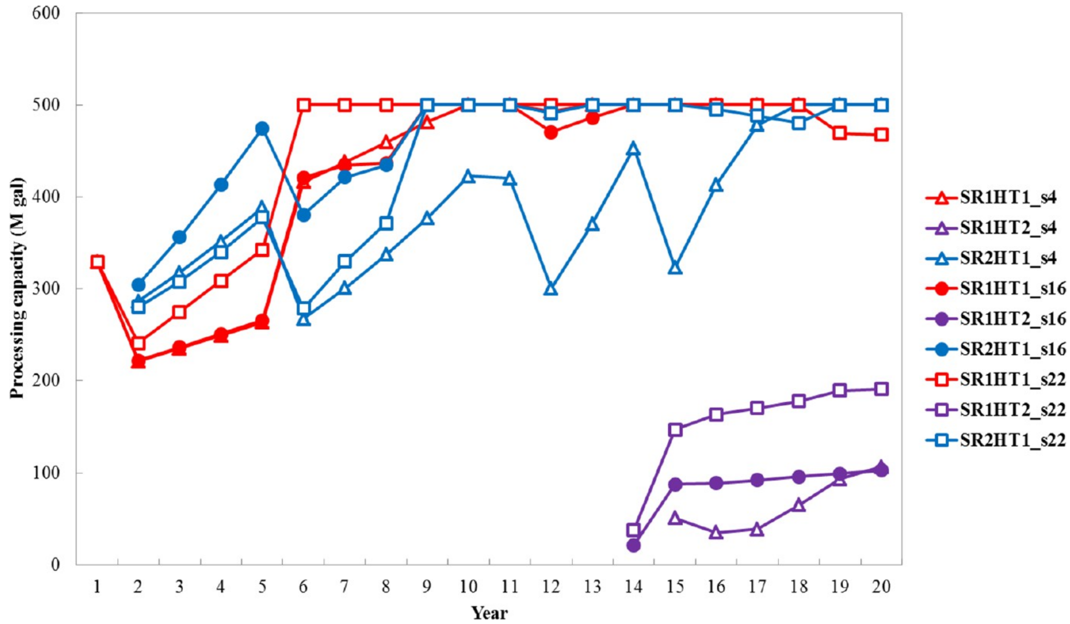


Figure 11. Planning of new hydrotreating units over 20 years.

Surprisingly, the ratio in scenario 22, where the demand is high, is lower than the reference scenario. This is also due to the biomass availability. As the demand increases, the biofuel production amount, which is limited by the biomass availability, is not likely to increase. Therefore, its market share will decrease. This can also explain why there is a minor drop at the last three time periods in most scenarios.

Figure 11 shows the planning results of the new hydrotreating units built for both FCC integration and HCU integration. We compare the result of the reference scenario with that of scenario 4 (change in biomass availability) and 22 (change in fuel demand). The triangle marker, circle marker, and rectangle marker indicates scenario 4, 16, and 22, respectively. The line in red, purple, and blue represents the hydrotreating unit 1 (HT1) in refinery 1 (SR1) using FCC integration, HT2 in SR1 using HCU integration, and HT1 in SR2 using FCC integration, respectively. As shown, the processing amount of all the units in all scenarios increases gradually over the planning horizon. The processing amount for HT2 is relatively smaller than the other two hydrotreating units. This is due to the smaller capacity of HT2, which is determined by the first-stage design decisions. Moreover, in scenario 4, the processing amount of all the units is smaller than that in other scenarios. This is because scenario 4 has the LOW biomass availability, which leads to less biofuel production. In scenario 22, where fuel demand is high, the processing amount either rapidly increases to the maximum capacity level (HT1 using FCC integration in both SR1 and SR2) or is much higher than that in other scenarios (HT2 using HCU integration in SR2). Therefore, high fuel demand leads to high processing amount.

■ CONCLUSIONS

This paper addresses the optimal design and strategic planning of the integrated hydrocarbon biofuel and petroleum supply chain system under quantity uncertainty. We analyzed the performance and benefit for supply chain integration. Distinct from most works in this field, we explicitly considered the equipment units and material flows in the petroleum process, thus seamlessly connecting the supply chain design and process operation. More importantly, we took into account the various uncertainties inherent in the integrated supply chain system, thus deriving an optimal solution that would be viable in the dynamic marketplace. A two-stage stochastic MILP model was developed in this work to optimize the design and planning of the integrated supply chain network. The proposed model was illustrated by a case study involving 39 geographically explicit locations. The planning decisions spanned over 20 years in the presence of four groups of uncertainty. Results indicated the gradual expansion of biofuel market shares from 7% to 20% over the project lifetime. Our analysis of the 24 scenarios suggested that the total cost of the integrated supply chain was quite sensitive to changes in fuel demand, crude oil price, and availability, while biomass availability had a great impact on the biofuel market share.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed mathematical model formulation and notations for the case study. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: 1 (847) 467-2943. Fax: 1 (847) 491-3728. E-mail: you@northwestern.edu.

Author Contributions

†These authors contributed equally.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank Initiative for Sustainability and Energy at Northwestern University (ISEN) and Chinese Scholarship Council for financial support.

■ REFERENCES

(1) Yue, D.; You, F.; Snyder, S. W. Biomass-to-bioenergy and biofuel supply chain optimization: Overview, key issues and challenges. *Comput. Chem. Eng.* **2013**, Accepted. DOI: 10.1016/j.compchemeng.2013.11.016.

(2) Energy Independence and Security Act of 2007. Public Law 110-140, 110th Congress, December 19, 2007.

(3) U.S. Department of Energy. Replacing the Whole Barrel To Reduce U.S. Dependence on Oil, 2012. http://www1.eere.energy.gov/biomass/pdfs/replacing_barrel_overview.pdf (accessed October 1, 2012).

(4) Sokhansanj, S.; Kumar, A.; Turhollow, A. F. Development and implementation of integrated biomass supply analysis and logistics model (IBSAL). *Biomass Bioenergy* **2006**, *30* (10), 838−847.

(5) Elia, J. A.; Baliban, R. C.; Xiao, X.; Floudas, C. A. Optimal energy supply network determination and life cycle analysis for hybrid coal, biomass, and natural gas to liquid (CBGTL) plants using carbon-based hydrogen production. *Comput. Chem. Eng.* **2011**, *35* (8), 1399−1430.

(6) Bowling, I. M.; Ponce-Ortega, J. M.; El-Halwagi, M. M. Facility location and supply chain optimization for a biorefinery. *Ind. Eng. Chem. Res.* **2011**, *50* (10), 6276−6286.

(7) Dunnett, A.; Adjiman, C.; Shah, N. A spatially explicit whole-system model of the lignocellulosic bioethanol supply chain: An assessment of decentralised processing potential. *Biotechnol. Biofuels* **2008**, *1* (1), 1−17.

(8) Zamboni, A.; Shah, N.; Bezzo, F. Spatially explicit static model for the strategic design of future bioethanol production systems. 1. Cost minimization. *Energy Fuels* **2009**, *23* (10), 5121−5133.

(9) Lira-Barragán, L. F.; Ponce-Ortega, J. M.; Serna-González, M.; El-Halwagi, M. M. An MINLP model for the optimal location of a new industrial plant with simultaneous consideration of economic and environmental criteria. *Ind. Eng. Chem. Res.* **2010**, *50* (2), 953−964.

(10) Kim, J.; Realff, M. J.; Lee, J. H.; Whittaker, C.; Furtner, L. Design of biomass processing network for biofuel production using an MILP model. *Biomass Bioenergy* **2011**, *35* (2), 853−871.

(11) 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. *AlChE J.* **2012**, *58* (4), 1157−1180.

(12) Giarola, S.; Zamboni, A.; Bezzo, F. Spatially explicit multi-objective optimization for design and planning of hybrid first and second generation biorefineries. *Comput. Chem. Eng.* **2011**, *35* (9), 1782−1797.

(13) You, F.; Wang, B. Life cycle optimization of biomass-to-liquid supply chains with distributed−centralized processing networks. *Ind. Eng. Chem. Res.* **2011**, *50* (17), 10102−10127.

(14) 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 Chemistry Eng.* **2013**, *1* (8), 1003−1014.

(15) Gebreslassie, B. H.; Yao, Y.; You, F. Design under uncertainty of hydrocarbon biorefinery supply chains: Multiobjective stochastic programming models, decomposition algorithm, and a comparison between CVaR and downside risk. *AlChE J.* **2012**, *58* (7), 2155−2179.

(16) Corsano, G.; Vecchietti, A. R.; Montagna, J. M. Optimal design for sustainable bioethanol supply chain considering detailed plant performance model. *Comput. Chem. Eng.* **2011**, *35* (8), 1384−1398.

(17) Akgul, O.; Shah, N.; Papageorgiou, L. G. Economic optimization of a UK advanced biofuel supply chain. *Biomass Bioenergy* **2012**, *41* (0), 57−72.

(18) Tong, K.; Gleeson, M.; Rong, G.; You, F. Optimal design of advanced 'drop-in' hydrocarbon biofuel supply chain integrating with existing petroleum refineries under uncertainty. **2013**, submitted.

(19) Andersen, F.; Díaz, M.; Grossmann, I. Multiscale Strategic Planning Model for the Design of Integrated Ethanol and Gasoline Supply Chain. http://egon.cheme.cmu.edu/Papers/Andersen_Diaz_Grossmann_Ethanol-Gasoline.pdf (accessed November 13, 2013).

(20) Ierapetritou, M. G.; Pistikopoulos, E. N.; Floudas, C. A. Operational planning under uncertainty. *Comput. Chem. Eng.* **1994**, *18*, S553−S557.

(21) Sahinidis, N. V. Optimization under uncertainty: State-of-the-art and opportunities. *Comput. Chem. Eng.* **2004**, *28* (6−7), 971−983.

(22) Ben-Tal, A.; Nemirovski, A. Robust optimization−methodology and applications. *Mathematical Programming* **2002**, *92* (3), 453−480.

(23) Verderame, P. M.; Floudas, C. A. Operational planning of large-scale industrial batch plants under demand due date and amount uncertainty. I. Robust optimization framework. *Ind. Eng. Chem. Res.* **2009**, *48* (15), 7214−7231.

(24) Charnes, A.; Cooper, W. W. Chance-constrained programming. *Manage Sci.* **1959**, *6* (1), 73−79.

(25) You, F.; Grossmann, I. E. Mixed-integer nonlinear programming models and algorithms for large-scale supply chain design with stochastic inventory management. *Ind. Eng. Chem. Res.* **2008**, *47* (20), 7802−7817.

(26) You, F.; Grossmann, I. E. Stochastic inventory management for tactical process planning under uncertainties: MINLP models and algorithms. *AIChE J.* **2011**, *57* (5), 1250−1277.
(27) Birge, J. R., Louveaux, F. V. *Introduction to Stochastic Programming*; Springer: New York, 1997.
(28) You, F.; Wassick, J. M.; Grossmann, I. E. Risk management for a global supply chain planning under uncertainty: Models and algorithms. *AIChE J.* **2009**, *55* (4), 931−946.
(29) Liu, P.; Pistikopoulos, E. N.; Li, Z. Decomposition based stochastic programming approach for polygeneration energy systems design under uncertainty. *Ind. Eng. Chem. Res.* **Apr 7 2010**, *49* (7), 3295−3305.
(30) Kim, J.; Realff, M. J.; Lee, J. H. Optimal design and global sensitivity analysis of biomass supply chain networks for biofuels under uncertainty. *Comput. Chem. Eng.* **2011**, *35* (9), 1738−1751.
(31) Dal-Mas, M.; Giarola, S.; Zamboni, A.; Bezzo, F. Strategic design and investment capacity planning of the ethanol supply chain under price uncertainty. *Biomass Bioenergy* **2011**, *35* (5), 2059−2071.
(32) Li, W.; Hui, C-W; Li, P.; Li, A.-X. Refinery planning under uncertainty. *Ind. Eng. Chem. Res.* **2004**, *43* (21), 6742−6755.
(33) Khor, C. S.; Elkamel, A.; Douglas, P. L. Stochastic refinery planning with risk management. *Pet. Sci. Technol.* **2008**, *26* (14), 1726−1740.
(34) Tong, K.; Feng, Y.; Rong, G. Planning under demand and yield uncertainties in an oil supply chain. *Ind. Eng. Chem. Res.* **2011**, *51* (2), 814−834.
(35) Khor, C. S.; Elkamel, A.; Ponnambalam, K.; Douglas, P. L. Two-stage stochastic programming with fixed recourse via scenario planning with economic and operational risk management for petroleum refinery planning under uncertainty. *Chem. Eng. Process.* **2008**, *47* (9−10), 1744−1764.
(36) Wright, M. M.; Brown, R. C.; Boateng, A. A. Distributed processing of biomass to bio-oil for subsequent production of Fischer−Tropsch liquids. *Biofuels, Bioprod Biorefin.* **2008**, *2* (3), 229−238.
(37) 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* (0), 71−91.
(38) 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* (0), 55−76.
(39) Marker, T. *Opportunities for Biorenewables in Oil Refineries*; UOP LLC: Des Plaines, IL, 2005.
(40) Neiro, S. M. S.; Pinto, J. M. A general modeling framework for the operational planning of petroleum supply chains. *Comput. Chem. Eng.* **2004**, *28* (6−7), 871−896.
(41) Al-Qahtani, K. Y., Elkamel, A. *Planning and Integration of Refinery and Petrochemical Operations*; Wiley-VCH: Weinheim, Germany, 2011.
(42) Jones, S. B., Valkenburg, C, Walton, C. W., et al. *Production of Gasoline and Diesel from Biomass via Fast Pyrolysis, Hydrotreating and Hydrocracking: A Design Case*; Pacific Northwest National Laboratory: Richland, WA, 2009.
(43) Huber, G. W.; Corma, A. Synergies between bio- and oil refineries for the production of fuels from biomass. *Angew. Chem., Int. Ed.* **2007**, *46* (38), 7184−7201.
(44) McLean, K.; Li, X. Robust scenario formulations for strategic supply chain optimization under uncertainty. *Ind. Eng. Chem. Res.* **2013**, *52* (16), 5721−5734.
(45) Shapiro, A.; Homem-de-Mello, T. A simulation-based approach to two-stage stochastic programming with recourse. *Math. Program.* **1998**, *81* (3), 301−325.
(46) Biomass Multi-Year Program Plan. U.S. Department of Energy, 2012. http://www1.eere.energy.gov/biomass/pdfs/mypp_november_2012.pdf (accessed December 1, 2012).
(47) U.S. Energy Information Administration. http://www.eia.gov/ (accessed October 1, 2012).
(48) Alternative Fuels Data Center. U.S. Department of Energy. http://www.afdc.energy.gov/laws/ (accessed October 1, 2012).
(49) National Agricultural Statistics Service. U.S. Department of Agriculture. http://www.nass.usda.gov/ (accessed October 1, 2012).
(50) Carneiro, M. C.; Ribas, G. P.; Hamacher, S. Risk management in the oil supply chain: A CVaR approach. *Ind. Eng. Chem. Res.* **2010**, *49* (7), 3286−3294.
(51) Rosenthal, R. *GAMS: A User's Manual*; GAMS Development Corporation: Washington, DC, 2012.
(52) You, F. Q.; 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* (4), 1157−1180.