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Process modeling and supply chain design for advanced biofuel production based on bio-oil gasification

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Process modeling and supply chain design for advanced biofuel production

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by

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DEDICATION

In dedication to my father and mother for supporting me all the way!

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I would like to take this opportunity to express my thanks to many people who made this thesis possible and an unforgettable experience for me.

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ABSTRACT

As a potential substitute for petroleum-based fuel, second generation biofuels are playing an increasingly important role due to their economic, environmental, and social benefits. With the rapid development of biofuel industry, there has been an increasing literature on the techno-economic analysis and supply chain design for biofuel production based on a variety of production pathways. A recently proposed production pathway of advanced biofuel is to convert biomass to bio-oil at widely distributed small-scale fast pyrolysis plants, then gasify the bio-oil to syngas and upgrade the syngas to transportation fuels in centralized biorefinery.

This thesis aims to investigate two types of assessments on this bio-oil gasification pathway: techno-economic analysis based on process modeling and literature data; supply chain design with a focus on optimal decisions for number of facilities to build, facility capacities and logistic decisions considering uncertainties.

A detailed process modeling with corn stover as feedstock and liquid fuels as the final products is presented. Techno-economic analysis of the bio-oil gasification pathway is also discussed to assess the economic feasibility. Some preliminary results show a capital investment of 438 million dollar and minimum fuel selling price (MSP) of $5.6 per gallon of gasoline equivalent. The sensitivity analysis finds that MSP is most sensitive to internal rate of return (IRR), biomass feedstock cost, and fixed capital cost.

A two-stage stochastic programming is formulated to solve the supply chain design problem considering uncertainties in biomass availability, technology advancement, and biofuel price. The first-stage makes the capital investment decisions including the locations

and capacities of the decentralized fast pyrolysis plants and the centralized biorefinery while the second-stage determines the biomass and biofuel flows. The numerical results and case study illustrate that considering uncertainties can be pivotal in this supply chain design and optimization problem. Also, farmers' participation has a significant effect on the decision making process.

CHAPTER 1 GENERAL INTRODUCTION

As primary energy sources, petroleum products such as gasoline and diesel are widely used all around the world. The United States consumed 18.49 million barrels of refined petroleum products per day in 2012, which was about 20.7% of total world petroleum consumption according to the US Energy Information Administration (EIA) [1]. However, the use of petroleum has a negative impact on ecosystems and biosphere, releasing pollutants and greenhouse gases. Besides, 40% of the petroleum that the United States consumed in 2012 are relied on net imports [2]. Thus, the attentions on national energy security and independence as well as environmental impacts have brought rising interests in renewable energy in both public and private sectors.

Biofuels such as ethanol and biodiesel are transportation fuels that are made from biomass-based materials, which are recognized as a relatively clean and sustainable fuel source. The Renewable Fuel Standard (RFS) program was created by US Environmental Protection Agency (EPA) in 2005, and it's the first renewable fuel volume mandate established in the United States. Under the Energy Independence and Security Act (EISA) of 2007, the RFS program was revised. According to the revised Renewable Fuel Standard (RFS2), as shown in Figure 1.1, at least 36 billion gallons of renewable fuels will be produced every year by 2022, of which at least 16 billion gallons per year will be from cellulosic biofuels [3].

Biomass can be converted to transportation fuels through a variety of production pathways, including biochemical and thermochemical platforms. Recently, thermochemical conversion of biomass to produce transportation fuels has moved to the forefront of biofuel research and development. Fast pyrolysis and gasification are two of the most prominent technologies for the thermochemical conversion of cellulosic biomass. Fast pyrolysis thermally decomposes organic compounds in the absence of oxygen process, and the products include bio-oil, bio-char, and non-condensable gases [4]. The fast pyrolysis reactors typically run at temperature between 400 ºC and 600 ºC and can produce approximately 70% (by weight) bio-oil [5]. The other 30% splits between non-condensable gases (e.g., carbon dioxide or methane) and bio-char. On the other hand, biomass gasification runs at much higher temperature (800 ºC - 1300 ºC) and gasification a relatively mature technology. However, commercialization of biomass gasification has been hampered by its high capital and operating costs due to the challenges of transporting bulky solid biomass over a long distance, processing solid feedstock at high pressure, and removing contaminants from the product gas stream.

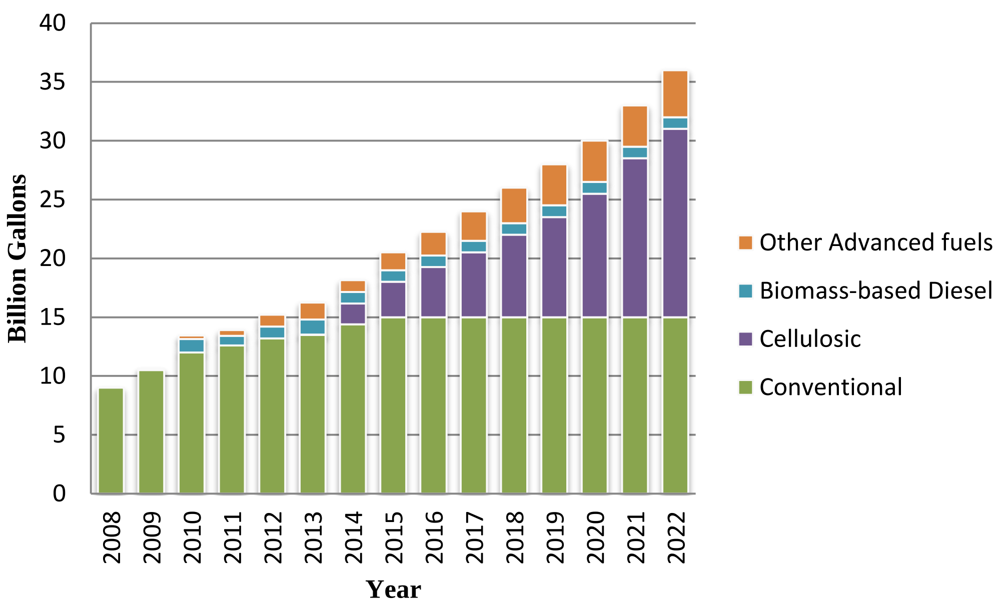

Figure 1.1 Revised Renewable Fuel Standard

With the rapid development of biofuel industry, there has been an increasing literature on the techno-economic analysis and supply chain design for biofuel production based on a variety of production pathways. The techno-economic analysis of biomass gasification by Swanson et al.

claims that the minimum fuel selling price is $4-5 per gallon of gasoline equivalent (GGE) and the capital investment requirement is $500-650 million for a 2000 metric ton per day facility [6]. Wright et al. reported that the capital cost of centralized gasification plant with a capacity of 550 million GGE per year is about 1.47 billion [7]. The capital cost of distributed fast pyrolysis facility with a capacity of 2,000 metric ton per day is $200 million [8]. To reduce system cost and improve supply chain efficiency, it has been suggested that biomass can be converted to bio-oil via fast pyrolysis near the harvest site, then the bio-oil can be transported to the upgrading plant for transportation fuels production [9]. On supply chain network design side of literature, Shah reviewed the previous studies in modeling, planning, and scheduling with a few real world examples to summarize the challenges and advantages of supply chain optimization [10]. An et al. compared the supply chain research on petroleum-based fuel with biofuel production [11]. Eksioglu et al. formulated a model to determine the numbers, locations, and capacities of the biorefineries, conducted a case study for the state of Mississippi to illustrate the optimization model [12]. Most of the literature on biofuel supply chain design assumes all the parameters in the system are deterministic.

Cellulosic biomass to liquid fuel technologies are not yet to be commercialized despite of the increasing research interests, mainly due to the lack of economic competitiveness of advanced biofuel production pathways. In this thesis, a hybrid production pathway that combined the two prominent thermochemical production pathways (fast pyrolysis and gasification) is considered. Its economic feasibility and supply chain design are investigated. The biofuel production process works as follows: cellulosic biomass such as corn stover is converted to bio-oil in relatively small fast pyrolysis processing plants at distributed locations; with mild-hydrotreating, the bio-oil is then transported to a centralized gasification facility to synthesize and produce the transportation fuels.

As a newly proposed pathway in the cellulosic biofuel technology, the process design, techno-economic analysis, and supply chain design of this pathway have not been studied extensively. To fulfill these gaps, this thesis aims to investigate the techno-economic feasibility at commercial scale and the optimal supply chain design decisions on the number and capacities of the facilities, as well as the logistic decisions. It should be noted that the techno-economic analysis is part of the ongoing project titled "Experiments, Technoeconomics, and Optimization of Bioenergy Systems Based on Bio-Oil Gasification" which is supported by Iowa Energy Center. Therefore, the preliminary results and analysis in CHAPTER 2 are subjected to update with additional experimental results. The conclusions and discussions can contribute to the system efficiency improvement of supply chain network and economic feasibility of the production pathway. The insights derived from this thesis can potentially facilitate the commercialization of this proposed advanced biofuel production technology.

The rest of the thesis is organized as follows. In CHAPTER 2, we present the process model and techno-economic analysis of bio-oil gasification pathway, with corn stover as feedstock and liquid transportation fuels as the final products. In CHAPTER 3, we provide a mathematical programming framework with a two-stage stochastic programming approach to design the supply chain network considering uncertainties along the supply chain such as biomass availability, technology advancement, and biofuel price. Besides, the effects of farmers' participation on decision making process are discussed in CHAPTER 3. CHAPTER 4 concludes the thesis with a summary of the research findings and conclusions. Some proposed future research directions are also provided in CHAPTER 4.

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CHAPTER 2 TECHNO-ECONOMIC ANALYSIS OF ADVANCED BIOFUEL PRODUCTION BASED ON BIO-OIL GASIFICATION

Modified from a paper to be submitted to *Fuel*

Qi Li[1], Yanan Zhang[2] and Guiping Hu[3]

Abstract

This chapter evaluates the economic feasibility of a hybrid production pathway combining fast pyrolysis and bio-oil gasification. In this pathway, cellulosic biomass such as corn stover is firstly converted to bio-oil through fast pyrolysis and then the bio-oil will go through gasification process to produce the syngas followed by catalytic Fischer-Tropsch synthesis and hydroprocessing to produce transportation fuels.

A detailed process modeling is presented using Aspen Plus® for a 2000 metric ton per day facility. Preliminary results of techno-economic analysis of this fast pyrolysis and bio-oil gasification pathway are discussed to assess the economic feasibility. The results of this analysis show a total capital investment of 438 million dollars and minimum fuel selling price (MSP) of $5.6 per gallon of gasoline equivalent. The sensitivity analysis shows that the MSP is most sensitive to internal rate of return (IRR) requirement, biomass feedstock cost, and fixed capital investment.

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2.1 Introduction

Biofuels are playing an increasingly important role as a cleaner substitute for fossil-based fuels. Second generation biofuels are made from nonedible plant residues or dedicated energy crop. The revised Renewable Fuel Standard (RFS2) has been enacted to accelerate the domestic biofuel production and consumption. By the year 2022, at least 36 billion gallons per year of renewable fuels will be produced and blended into the transportation fuel, of which at least 16 billion gallons per year should be produced from cellulosic biomass feedstock [1].

Biomass can be converted to transportation fuels through a variety of production pathways, including biochemical and thermochemical platforms. Recently, thermochemical conversion of biomass (e.g., fast pyrolysis and gasification) has attracted increasing attention. In this chapter, a hybrid production pathway combining fast pyrolysis and bio-oil gasification is considered. Cellulosic biomass such as corn stover is firstly converted to bio-oil through fast pyrolysis and then bio-oil will go through gasification process to produce the syngas followed by catalytic Fischer-Tropsch synthesis and hydroprocessing to produce transportation fuels.

This proposed hybrid pathway offers several advantages. Firstly, bio-oil can be produced in relatively small fast pyrolysis plants at distributed locations and shipped to centralized biorefinery such that high cost of shipping bulky solid biomass over long distance could be avoided. Secondly, liquids are relatively easy to pump to high pressure than solids, so high pressure gasification technology can be implemented to improve conversion efficiency. Thirdly, as most of nitrogen and potassium are left in biochar after the fast pyrolysis, bio-oil has reduced level of ash and other contaminants, which makes the syngas cleanup easier [2, 3].

Process modeling, which breaks down and simulate the entire production system with a series of processes, is an effective tool to assess the technical performance of a production facility. Also, the mass and energy balance data obtained from process modeling simulation could provide the basis for the estimation of capital and operational costs of the plant. Techno-economic analysis is a combination of process modeling and economic evaluation based on engineering economic principles.

There is an increasing literature on techno-economic analysis of a variety of advanced biofuel production pathways with a range of feedstock and products. The techno-economic analysis of biomass gasification using corn stover as the feedstock by Swanson et al. claimed that the MSP is $4-5 per gallon of gasoline equivalent and the capital investment requirement is $500-650 million for a 2000 metric ton per day facility [4]. Zhang et al. conducted a techno-economic analysis of biohydrogen production via bio-oil gasification and concluded that an IRR of 8.4% is realized with the prevailing market price [5]. Wright et al. reported that the capital cost of gasification plant with a capacity of 550 million GGE per year is about 1.47 billion [6]. The capital cost of fast pyrolysis facility with a capacity of 2,000 metric ton per day is $200 million and an MSP is $2.11 per gallon of gasoline equivalent under purchasing hydrogen scenario [7].

However, as a recent advancement in the cellulosic biofuel, the process design and techno-economic analysis of the proposed hybrid pathway have not been studied extensively. Motivated by this gap, this study aims to model the production process and evaluate the economic feasibility based on nth plant design. To be noted that this study is part of an ongoing project funded by Iowa Energy Center. Thus, the process model and techno-economic analysis are work-in-progress and modifications and updates for the results and analysis can be expected when more information becomes available.

The rest of the chapter is organized as follows: in Section 2, the methodology is presented with a focus on the process design. Then, some preliminary techno-economic analysis results are discussed in Section 3. Finally, we conclude the chapter in Section 4 with summary and potential research directions.

2.2 Methods

In this section, the methodology to perform this techno-economic study is presented. Materials and technologies are firstly selected according to some commonly used criteria. Then, Aspen Plus® process engineering software is employed to develop the detailed process model. After that, capital and operation costs of the plant are evaluated using the output of process models and literature data.

2.2.1 Material and Technologies

A variety of feedstock and operational design decisions are open for the bio-oil gasification pathway, e.g., gasification conditions, syngas cleanup techniques, and fuel synthesis methods. These options are selected by the following commonly used criteria in literatures: (i) the technology should be commercialized in the next 5-8 years; (ii) adequate feedstock should be provided by the current agricultural system; (iii) the final products are compatible with the present transportation fuels [4, 8].

Iowa possesses the largest quantity of corn stover, an important type of cellulosic biomass, in the United States [9]. Corn stover is therefore chosen as feedstock of this pathway. The ultimate and proximate analysis of corn stover can be found in Table 2.1 [7]. The plant capacity is set to be 2000 metric ton per day dry biomass for consistency and comparison with the literatures [4, 7, 8]. The fluidized bed gasifier operations in low temperature (870 ºC) for gasification and Fischer-Tropsch synthesis is employed for transportation fuel production.

Table 2.1 Ultimate and proximate analyses for corn stover feedstock and char (wt.%) [7]

Ultimate analysis (dry basis)			**Proximate analysis (wet basis)**		
Element	Corn Stover	Char	Element	Corn Stover	Char
Carbon	47.28	51.2	Moisture	25.0	0
Hydrogen	5.06	2.12	Fixed Content	17.7	51.21
Nitrogen	0.8	0.45	Volatile Matter	52.8	49.79
Chlorine	0	0.471	Ash	4.5	0
Sulfur	0.22	0.935			
Oxygen	40.63	11.5			
Ash	6	33.3			

2.2.2 Process Design

A thorough process model was established in Aspen Plus®. The model developed in this study is based on several previous models developed at Iowa State University [4, 5, 7]. A schematic of the generalized process model is shown in

Figure **2.1**, and the major components includes biomass preprocessing, bio-oil production (fast pyrolysis), bio-oil gasification, syngas cleanup, and fuel synthesis.

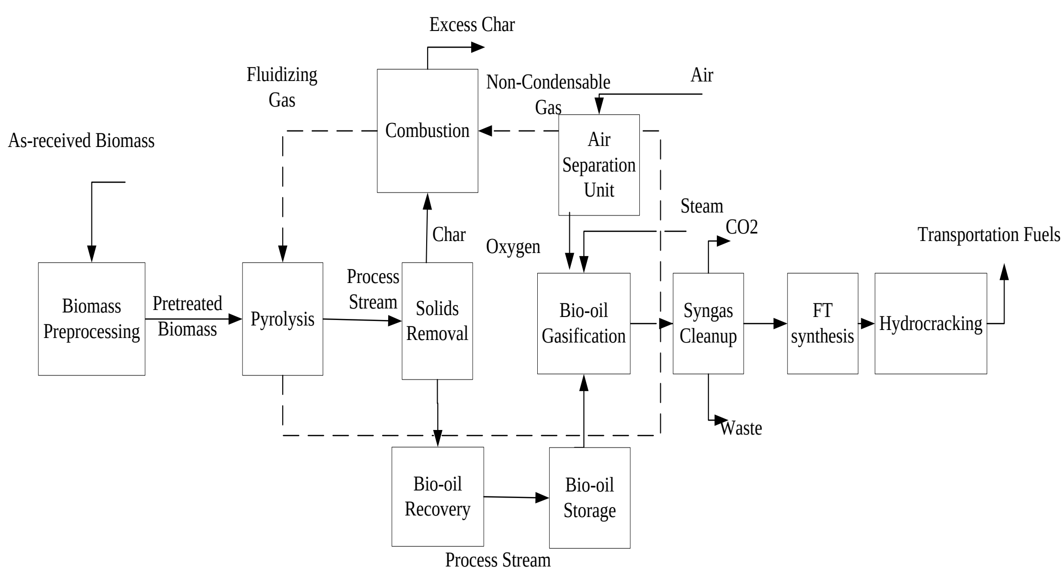

Figure 2.1 Generalized process flow diagram for bio-oil gasification pathway

Biomass preprocessing & fast pyrolysis process

Biomass preprocessing (chopping, drying, and grinding) are conducted before the pyrolysis process. Solids removal and bio-oil recovery are included to condense and collect the bio-oil. Table 2.2 provides detailed descriptions about these process sections and lists the key assumptions for the individual process.

Table 2.2 Process descriptions and assumptions [10]

Section name	Section descriptions	Key assumptions
Chopping	Particle size reduction to 10 mm	Incoming biomass average size of 10 to 25 mm
Drying	Biomass drying to 7% moisture	Steam drying at 200 ℃
Grinding	Particle size reduction to 3 mm	Incoming biomass maximum size of < 10 mm
Pyrolysis	Biomass conversion to pyrolysis Products	500 ℃ and 1 atm; Heat provided by char combustion
Solids Removal	Removal of entrained solid particles from vapor stream	90% particle removal

In the biomass pretreatment, biomass with 25% moisture is dried to 7% moisture and ground to 3 mm diameter size prior to feeding into a pyrolyzer. The fluidized bed pyrolyzer operates at 500 ℃ and atmospheric pressure. As shown in **Error! Not a valid bookmark self-reference.** [7, 11], data from previous techno-economic analysis of pyrolysis-based biofuels are employed to build RYield module in Aspen Plus®.

Table 2.3 Pyrolysis products distribution (wt.% of corn stover feedstock) [7]

Bio-oil composition		Gases	
Water	10.8	Nitrogen	0
Acetic acid	5.93	Carbon dioxide	5.42
Propionic acid	7.31	Carbon monoxide	6.56
Methoxyphenol	0.61	Methane	0.035
Ethylphenol	3.8	Ethane	0.142
Formic acid	3.41	Hydrogen	0.588
Propyl-benzoate	16.36	Propene	0.152
Phenol	0.46	Ammonia	0.0121

Table 2.3 continued

Toluene	2.27	Total	12.91
Furfural	18.98		
Benzene	0.77	Solids	
Total	70.7	Char/Ash	16.39

Standard cyclones remove solids consisting mostly of char particles entrained in the vapors exiting the pyrolyzer. It is assumed that the solid products and non-condensable gases are sent to a combustor to provide heat for the drying and pyrolysis process. The char composition analysis is shown in Table 2.1 [7]. Ash and char are removed from the raw bio-oil through the cyclones with 90% particle removal rate. The electrostatic precipitators (ESP) and condensers are used to collect liquid phase in bio-oil recovery process.

Bio-oil gasification process

In simulating the bio-oil gasification system (as shown in Figure 2.2), 95% purity oxygen and steam are employed as the gasifying agent. The bio-oil is a mixture of all fractions from the fast pyrolysis, so-called “whole bio-oil”. The gasifier operates at a pressure of 28 bar and a temperature of 870 °C. The mass ratios of oxygen to bio-oil are set to be 0.3 and the mass ratios of steam to bio-oil are set to be 0.2. After gasification, a separator is used to remove the slag. The syngas contains some particulate as well as all the ammonia, hydrogen sulfide, and other contaminants which need cleanup. A direct water quench is employed to reduce the syngas temperature to about 40 °C to condense tar and most of ammonia and ammonium chloride. Carbon dioxide and nitrogen hydrogen sulfide are removed in acid gas removal system based on monoethanolamine.

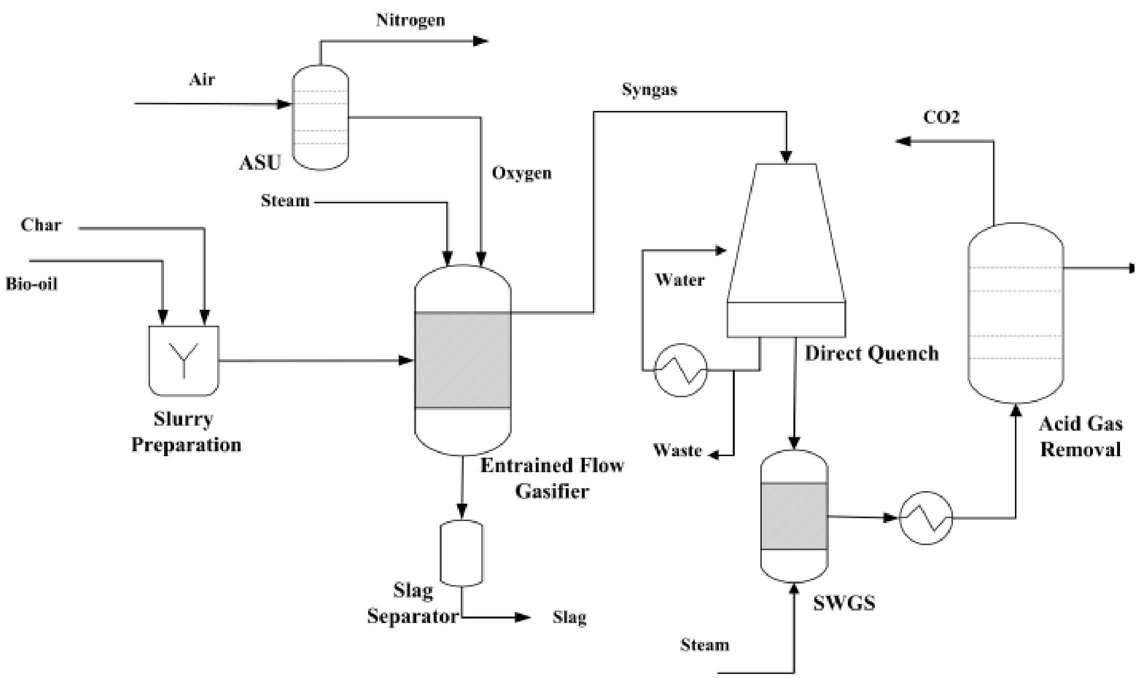

Figure 2.2 Schematic of the bio-oil gasification process

Fischer-Tropsch (FT) synthesis process

In the catalytic FT synthesis, one mole of CO reacts with two moles of H_2 to form mainly aliphatic straight-chain hydrocarbons (Equation (1)). Typical FT catalysts are based on iron or cobalt. The optimal ratio of H_2/CO is around 2.1 according to FT. When the feed gas H_2/CO ratio is lower, water-gas shift (WGS) reaction (Equation (2)) is used to adjust the ratio. Typical operation conditions for FT synthesis, when aiming for long-chain products, are under temperatures of 200-250 ºC and pressures of 25-60 bars [12].

$$CO + 2.1H_2 \Rightarrow -(CH_2)- + H_2O \quad (1)$$

$$CO + H_2O \Leftrightarrow CO_2 + H_2 \quad (2)$$

As shown in Figure 2.3, major operations in this area include zinc oxide/activated carbon gas polishing, syngas booster compression, steam methane reforming (SMR), WGS, pressure swing adsorption (PSA), FT synthesis, FT product separation, and unconverted syngas recycle [4].

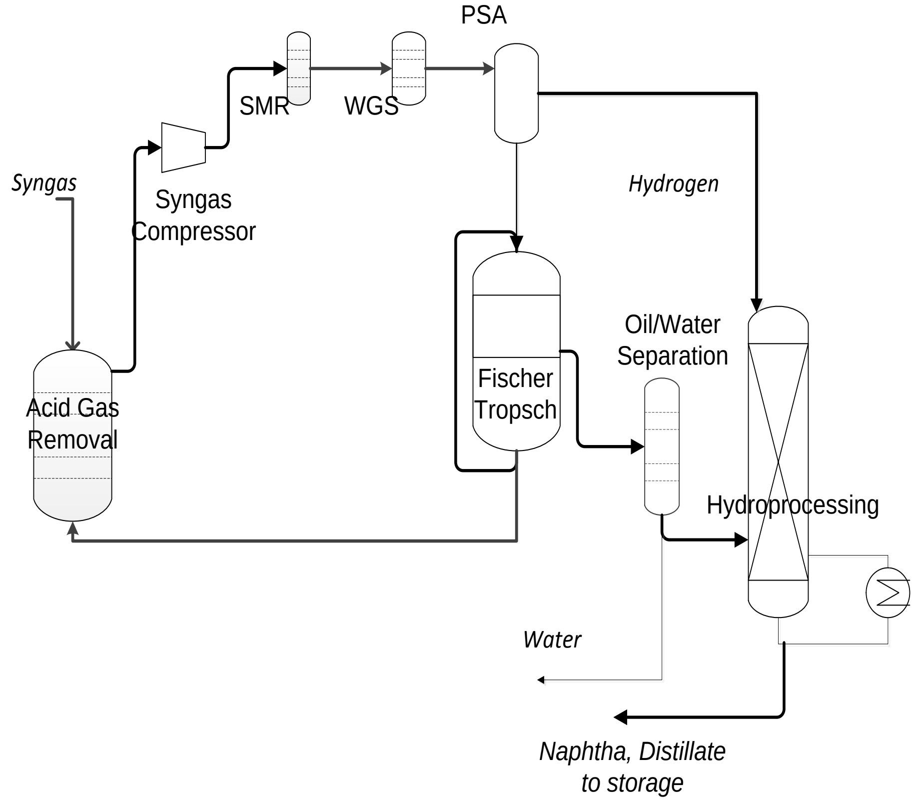

Figure 2.3 Process flow diagram for Fischer-Tropsch synthesis

Appropriate pretreatment must be taken so that the syngas entering FT synthesis contaminants below 200 ppb sulfur and 10 ppm ammonia at a pressure of 25 bar [13]. First, a zinc oxide and activated carbon gas polishing is used to polish sulfur and trace contaminants. Next, the syngas stream is compressed to 25 bar in syngas booster compression unit. Experimental data indicate that there is a significant amount of methane and ethane in the syngas stream in the low temperature bio-oil gasification scenario. Thus, a SMR is utilized to reduce those components. As mentioned, a WGS unit is included to adjust syngas H_2/CO ratio to just above the optimal value for FT synthesis. After that, pressure swing adsorption (PSA) is used to provide hydrogen for the hydroprocessing section. Next, the syngas reacts over a cobalt-based catalyst in a fixed-bed FT reactor at 200 ºC. The Anderson-Schulz-Flory alpha chain growth model described by Song et al. is used to predict the FT product distribution [14]. After the gas is cooled, the liquid hydrocarbons and water are separated before the hydroprocessing section. The unconverted syngas is partially recycled back into the FT reactor while the other portions go back to the acid gas removal system in syngas cleanup section.

2.2.3 Economic Analysis

Literature data and Aspen Economic Evaluation® software are employed to estimate the facility cost for this pathway. Unit costs for equipment are scaled from base equipment costs by using Equation (3). $Cost_{new}$ is the scaled new equipment cost and $Cost_0$ is the base equipment cost; $size_{new}$ is the size of new equipment and $size_0$ is the size of base equipment; I is the index of calculated year and I_0 is the index of the base year. n is the particular scaling factor for a particular type of equipment with a range from 0.6 to 0.8. The scaling factor and some base equipment cost come from literature [4, 5, 7]. The estimated costs have been adjusted to the 2013 US dollars.

$$Cost_{new} = \left(\frac{I}{I_0}\right) * Cost_0 * \left[\frac{size_{new}}{size_0}\right]^n \qquad (3)$$

Aspen Economic Evaluation software is employed to estimate equipment size and cost and calculate project capital expenditures. The methodology developed by Peters et al. is used for calculating installation costs [15]. A total installation factor of 3.02 is used to estimate the installed equipment costs [5]. A Lang Factor of 5.46 is chosen to estimate the total capital investment (TCI) [5, 7, 16]. Table 2.4 provides a summary of methodology for capital cost estimation.

Table 2.4 Summary of methodology for capital cost estimation

Parameter	Assumption
Total Purchased Equipment Cost (TPEC)	100%
Purchased Equipment Installation	39%
Instrumentation and Controls	26%
Piping	10%
Electrical Systems	31%
Buildings (including services)	29%
Yard Improvements	12%
Service Facilities	55%
Total Installed Cost (TIC)	3.02*TPEC
Indirect Cost (IC)	0.89*TPEC
Engineering	32%
Construction	34%
Legal and Contractors Fees	23%
Total Direct and Indirect Costs(TDIC)	TIC + IC
Contingency	20% of TDIC
Fixed Capital Investment (FCI)	TDIC + Contingency
Working capital (WC)	15% of FCI
Land Use	6% of TPEC
Total Capital Investment (with land)	FCI + WC + Land

Table 2.5 provides the assumptions for the material and operating cost estimation. The electricity price are based on the average 20-year forecast from Energy Information Administration [17]. The facility-gate corn stover feedstock price is assumed to be 83 $ t^{-1} [18]. The solid and waste water disposal costs are based on biomass gasification design [4].

Table 2.5 Assumptions for material and operating parameters

Parameters	Values
Electricity	6.6 cents/kWh
Process Water	0.032 $ t^{-1}
Delivered Feedstock Cost	83 $ t^{-1}
Fuel Gas	1.06 $ GJ^{-1}
Steam	9.05 $ t^{-1}
Solids Disposal Cost	19.84 $ t^{-1}
Waste Water Disposal Cost	1.16 $ t^{-1}
Operating Hours per Year	7884(90%)
Balance of Plant	12%

A modified National Renewable Energy Laboratory (NREL) discounted cash flow rate of return (DCFROR) analysis spreadsheet is employed in this study to evaluate the economic feasibility with the IRR under the prevailing market conditions. Assumptions in DCFROR analysis are listed in Table 2.6 [5]. The process design is assumed to be the nth plant with a life cycle of 20 years based on the current state of technology.

Table 2.6 Assumptions for DCFROR analysis [5]

Parameter	**Assumption**
Working Capital (% of FCI)	15%
Salvage Value	0
Type of Depreciation	DDB
General Plant	200
Steam Plant	150
Depreciation Period (Years)	
General Plant	7
Steam/Electricity System	20
Construction Period (Years)	2.5
% Spent in Year -3	8%
% Spent in Year -2	60%
% Spent in Year -1	32%
Start-up Time (Years)	0.5
Revenues (% of Normal)	50%
Variable Costs (% of Normal)	75%
Fixed Cost (% of Normal)	100%
Income Tax Rate	39%
Facility Type	nth facility

2.3 Preliminary Results and Analysis

2.3.1 Process Modeling

The corn stover with 25% moisture is as the biomass feedstock, and the moisture level is reduced to 7% with pretreatment. The fast pyrolysis process has a capacity of 2000 metric ton per day (t d^{-1}) dry corn stover and the yield of wet bio-oil (with a moisture content of 15%) is 63%, which means it will yield 1260 t d^{-1} of wet bio-oil. The transportation fuel yield for gasoline and diesel are 170 t d^{-1} and 69 t d^{-1}, representing 13.5% and 5.5% of the wet bio-oil, respectively. The comparisons of fuel yield for different pathways are included in Table 2.7.

Table 2.7 Comparison of fuel yield for a variety of pathways (t d^{-1})

Pathway	**Biomass gasification [4]**	**Fast pyrolysis and hydroprocessing [7]**	**Fast pyrolysis and Bio-oil gasification**
Biomass input	2000	2000	2000
Bio-oil yield	NA	1260	1260
FT liquids yield	331	NA	270
Fuel yield	293	192	239

Gasification experiments have been conducted with whole red oak bio-oil at Iowa State University. The gasification reactor runs at 850 °C. Pure oxygen was maintained at an equivalence ratio of 25% for full combustion. The results show that about 88% of reactants react into products by weight, of which 71% are syngas and 29% are water and tar. The bio-oil gasification yields are estimated based on the preliminary experimental and literature data [4, 5]. Table 2.8 shows the comparison of gasification conditions and syngas composition.

Table 2.8 Comparison of gasification conditions and syngas composition

	Biomass gasification[4]	**Bio-oil gasification [5]**	**Bio-oil gasification (experiments)**	**Assumptions in this study**
Gasification conditions				
Temperature	870 ºC	1200 ºC	850 ºC	870 ºC
Pressure	28 bar	20 bar	1.01 bar	28 bar
mass ratios of oxygen to bio-oil/biomass	0.26	0.42	0.37	0.3
mass ratios of steam to bio-oil/biomass	0.17	0.2	0	0.2
Gas Composition (mole basis)				
Water (H_2O)	19.39%	21.49%	20.20%	20.00%
Carbon monoxide (CO)	24.08%	36.15%	32.50%	32.00%
Hydrogen (H^2)	20.02%	32.71%	16.40%	17.00%
Carbon dioxide (CO^2)	27.24%	9.63%	20.80%	20.00%
Methane (CH_4)	5.48%	0.02%	5.60%	6.00%
Other	3.79%	0.01%	4.50%	5.00%

2.3.2 Economics Results

Estimated total installed equipment cost (TIEC) for 2000 t d^{-1} facility is 273 million dollars for this bio-oil gasification pathway. As mentioned in Table 2.4, total capital investment (TCI) is the summation of total installed equipment cost, working capital cost, total indirect cost, land use and project contingency. Detailed capital costs are shown in Table 2.9.

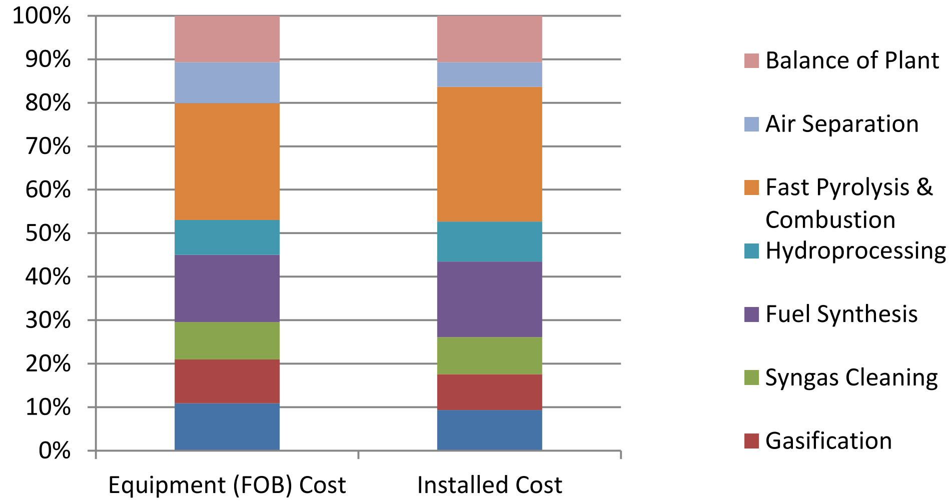

Figure 2.4 Equipment cost and installed cost for each area

The free on board (FOB) equipment cost and installed equipment cost are breakdown to model area. Figure 1.1Figure 2.4 shows the percentage of equipment cost and installed cost for each model area. Fast pyrolysis, combustion and fuel synthesis contribute 48% of equipment cost and 42% of installed cost.

Table 2.9 Capital costs for bio-oil gasification pathway (million dollars)

Item	Costs
Total Installed Equipment Cost	273
Total Indirect Cost	92
Project Contingency	73
Working Capital	66
Land Use	6
Total Capital Investment	510

Stream mass flows in the Aspen Plus model and current market prices of the products are used to calculate the total annual operating costs. The fixed operating costs include salaries, maintenance cost, and insurance. The costs of cooling water, steam, waste disposal etc. are included in other variable operating costs category. As show in Figure 2.5, the biomass feedstock cost, about 54.3 million dollars, is the largest contributor to annual operating costs.

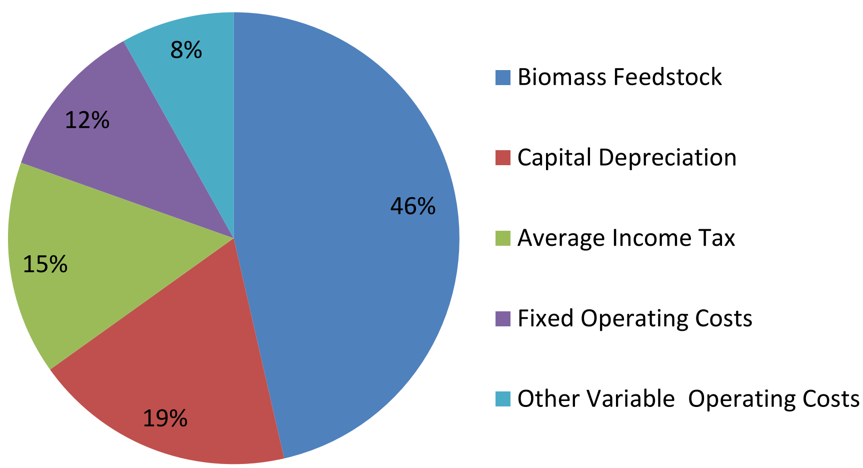

Figure 2.5 Annual itemized operating costs

Based on the estimated capital costs, operating costs and IRR of 10%, an MSP of $5.6 per gallon of gasoline equivalent is calculated for the bio-oil gasification pathway.

2.3.3 Sensitivity Analysis

The results of sensitivity analysis for bio-oil gasification are presented in Figure 2.6 to demonstrate the sensitivity of MSP to changes in the parameters. The parameters under investigation are IRR, feedstock cost, fixed capital cost, catalyst cost, catalyst life, balance of plant (BOP), and availability operating hours. The analysis finds that MSP is most sensitive to IRR, feedstock cost, and fixed capital cost. IRR is influential because it affects the entire cash flow. As a significant portion of operating costs, feedstock price is a highly sensitive parameter. The fixed capital cost affects the capital depreciation and average income tax, a ±20% range in fixed capital cost results an MSP in a range of \$5.02 to \$6.17 per gallon.

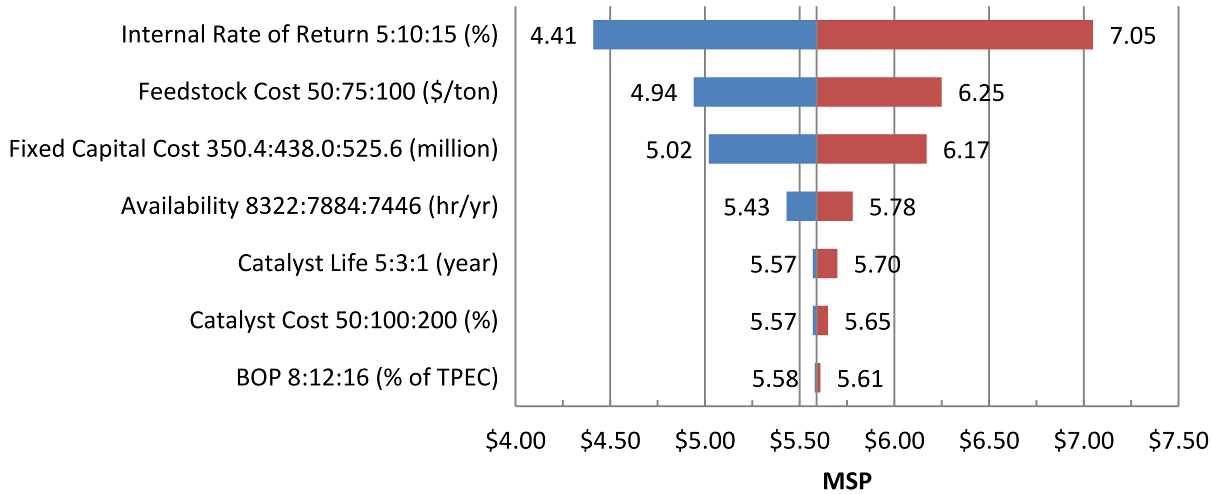

Figure 2.6 Sensitivity analysis for MSP in 2013 \$ per GGE

The results of this study show higher capital investment and MSP compared to the previous techno-economic studies on thermochemical production pathways. This is mainly due to the conservative assumptions on fuel yields and installation factor. Additionally, capital and operational costs are all adjusted to cost year 2013, therefore, the economic feasibility is affected by the rapid escalation in construction and equipment costs in recent years.

2.4 Conclusion

In this chapter, a detailed process modeling is presented and some preliminary results of techno-economic analysis of this fast pyrolysis and bio-oil gasification pathway are also discussed to assess the economic feasibility. The results of this study show a capital investment of 438 million dollar and MSP of \$5.6 per gallon of gasoline equivalent. The sensitivity analysis illustrates that MSP is most sensitive to IRR, feedstock cost, and fixed capital cost. As an ongoing work, the techno-economic analysis will continue to be updated and improved with additional experimental data.

There are numerous aspects that could be improved in the techno-economic analysis. First, the levels of the details of the Aspen model will continue to be refined in order to obtain accurate predictions. Experimental data have been, and will be, used to adjust the model parameters to improve the model accuracy. Second, we could increase the complexity of the techno-economic analysis of commercial biorefinery by considering the practical logistic settings and constraints. For example, a supply chain including various 2000-metric-ton-per-day decentralized pyrolysis facilities coupled with a central bio-oil gasification facility for the entire state of Iowa could be considered. Moreover, comparative study of similar pathway could be conducted to assess the economic superiority. Finally, other uncertainty analysis such as Monte-Carlo simulation could be performed to test the uncertainty in technical data (e.g., reactor performance, product yields), facility size, and capital costs.

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CHAPTER 3 SUPPLY CHAIN DESIGN UNDER UNCERTAINTY FOR ADVANCED BIOFUEL PRODUCTION BASED ON BIO-OIL GASIFICATION

Modified from a paper submitted to *Energy*

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Abstract

To reduce biomass transportation costs and take advantage of the economics of scales for gasification facility, a proposed production pathway of advanced biofuel is to convert biomass to bio-oil at widely distributed small-scale fast pyrolysis plants, then gasify the bio-oil to syngas and upgrade the syngas to transportation fuels in centralized biorefinery.

This chapter aims to provide an optimal supply chain design for this advanced biofuel production pathway considering uncertainties in biomass availability, technology advancement, and biofuel price. A two-stage stochastic programming is formulated to solve this supply chain design problem. The first-stage makes the capital investment decisions including the locations and capacities of the decentralized fast pyrolysis plants and the centralized biorefinery while the second-stage determines the biomass and biofuel flows. The numerical results and case study illustrate that considering uncertainties can be pivotal in this supply chain design and optimization problem. Also, farmers' participation has a significant effect on the decision making process.

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3.1 Introduction

As a potential substitute for petroleum-based fuel, second generation biofuels are playing an increasingly important role due to their economic, environmental, and social benefits. Second generation biofuels are made from nonedible plant residues or dedicated energy crop, such as corn cobs, corn stover, switchgrass, miscanthus, and woody residues. As a result, the biomass feedstock for second generation biofuels are less land and water intensive, which will not have significant negative impact on the food market [1]. According to the revised Renewable Fuel Standard (RFS2) established in 2007, at least 36 billion gallons per year of renewable fuels will be produced by 2022, of which at least 16 billion gallons per year will be from cellulosic biofuels [2]. However, the targeted cellulosic biofuel volume requirement for 2013 was revised to be only 14 million gallons, which is significantly lower than the original target. This is mainly due to the high capital investment and logistic challenges in cellulosic biofuel. The supply system activities of harvest, collection, storage, preprocessing, handling, and transportation, represent one of the biggest challenges to the cellulosic biofuel industry. It becomes necessary to consider the supply chain design of a biofuel production system. Thus, it is timely and meaningful to study the economic feasibility of the commercialization of cellulosic biofuel considering the supply chain design and logistic analysis.

Biomass can be converted to transportation fuels through a variety of production pathways, including biochemical and thermochemical platforms. One example of biochemical pathways is the corn ethanol production from fermentation. On the other hand, thermochemical conversion of biomass to produce transportation fuels has recently moved to the forefront of biofuel research and development. Fast pyrolysis and gasification are two of the most prominent technologies for thermochemical conversion of cellulosic biomass.

Fast pyrolysis thermally decomposes organic compounds in the absence of oxygen process, and the products include bio-oil, bio-char, and non-condensable gases[3]. The fast pyrolysis reactors typically run at temperature between 400 ºC and 600 ºC and can produce approximately 70% (by weight) bio-oil [4]. The other 30% is split between non-condensable gases (e.g., carbon dioxide or methane) and bio-char. The non-condensable gases and bio-char could be combusted to provide heat for the facility. In addition, bio-char is mostly organic carbon which can be sequestered or gasified to produce syngas [5]. Bio-oil has three to five times the energy density compared to raw biomass [6]. However, due to the high viscosity and acidity, bio-oil needs to be upgraded to be used as transportation fuels. The bio-oil upgrading has proven to be a challenging process due to the low conversion efficiency and fuel quality. On the other hand, biomass gasification runs at much higher temperature (800 ºC - 1300 ºC) and it is a relatively mature technology. The syngas produced from the biomass gasification process will typically go through the Fischer-Tropsch synthesis to produce liquid transportation fuels [7]. However, commercialization of biomass gasification has been hampered by its high capital and operating costs due to the challenges of transporting bulky solid biomass over a long distance, processing solid feedstock at high pressure, and removing contaminants from the product gas stream. The techno-economic analysis of biomass gasification by Swanson et al. claims that the minimum fuel selling price is $4-5 per gallon of gasoline equivalent and the capital investment requirement is $500-650 million for a 2000 metric ton per day facility [7].

It is thus necessary to reduce system cost and improve supply chain efficiency to improve the economic feasibility and competitiveness of the advanced biofuel production pathways. Feedstock production and logistics constitute more than 35% of the total production cost of advanced biofuel [8] and logistics associated with moving biomass from farmland to biorefinery can make up 50–75% of the feedstock cost [9]. To reduce feedstock transportation cost, it has been suggested that biomass can be converted to bio-oil via fast pyrolysis near the harvest site, then the bio-oil can be transported to the upgrading plant for transportation fuels production [10]. In this chapter, the proposed hybrid production pathway is to combine the two prominent thermochemical production pathways. Biomass fast pyrolysis produces bio-oil in relatively small processing plants at distributed locations so that the transportation of bulky biomass over a long distance can be avoided. After mild hydrotreating, the bio-oil is then transported to a centralized gasification facility to produce transportation fuels. It should be recognized that centralized plant has advantages such as economies of scale, the inventory buffer storage reduction, and administration overhead cost savings [11].

One of the biggest challenges of advanced biofuel production industry is the design of supply chain networks under uncertainty. There is a rich literature on supply chain network design. Shah reviewed the previous studies in modeling, planning, and scheduling with some real world examples to summarize the challenges and advantages of supply chain optimization [12]. An et al. compared the supply chain research on petroleum-based fuel and biofuel [13]. Eksioglu et al. formulated a model to determine the numbers, locations, and capacities of the biorefineries, conducted a case study for the state of Mississippi to illustrate, and verified the optimization model [14]. Most of the literature on biofuel supply chain design assumes all the parameters in the system are deterministic. However, the biofuel industry is highly affected by the uncertainties along the supply chain such as biomass supply availability, technology advancement and biofuel price. For example, the biomass feedstock supply is highly dependent on biomass yield and farmers' participation. As a result, it is of vital importance to design the biofuel supply chain considering the uncertainties along the supply chain. Kim et al. considered a two-stage stochastic model using bounds of the parameters to determine the capacities and locations of the biorefineries [15]. Marvin et al. formulated a mixed integer linear programming model to determine optimal locations and capacities of biorefineries [16]. As a recent advancement in the cellulosic biofuel technology, decentralized supply chain design for thermochemical pathways have not been studied extensively, especially the planning scenario under uncertainty. This chapter aims to provide a mathematical programming framework with a two-stage stochastic programming approach to design the supply chain network considering uncertainties along the supply chain. The production pathway under consideration is the bio-oil gasification, with bio-oil production from biomass fast pyrolysis at decentralized facilities and syngas production and fuel synthesis in the centralized gasification facility. This model provides methodological insights for the decision makers on the capital investment decisions and logistic decisions for the thermochemical pathway of bio-oil gasification.

The rest of the chapter is organized as follows: in Section 2, the problem statement for this biofuel supply chain design is presented. Then, we discuss the deterministic mixed integer linear programming model and the two-stage stochastic programming models in Section 3. A case study of Iowa is conducted to illustrate and validate this optimization model in Section 4. Finally, we conclude the chapter in Section 5 with brief summary and potential research directions.

3.2 Problem Statement

As mentioned, one of the most important decisions faced by the biofuel industry is the design of the supply chain networks, especially under the system uncertainties. This provides the major motivation for this study.

The supply chain system schematics for the bio-oil gasification pathway are shown in Figure 3.1. Biomass is collected and consolidated at the county level. Biomass is then transported to the decentralized fast pyrolysis facilities to be converted to bio-oil. Mild-hydrotreated bio-oil is transported to the centralized gasification facility to produce the transportation fuels. It is assumed that each biomass feedstock supply location/county can serve multiple fast pyrolysis facilities; each fast pyrolysis facility can acquire feedstock from multiple biomass supply locations. The locations for the decentralized fast pyrolysis facilities and centralized gasification facility are assumed to be the centroids of counties.

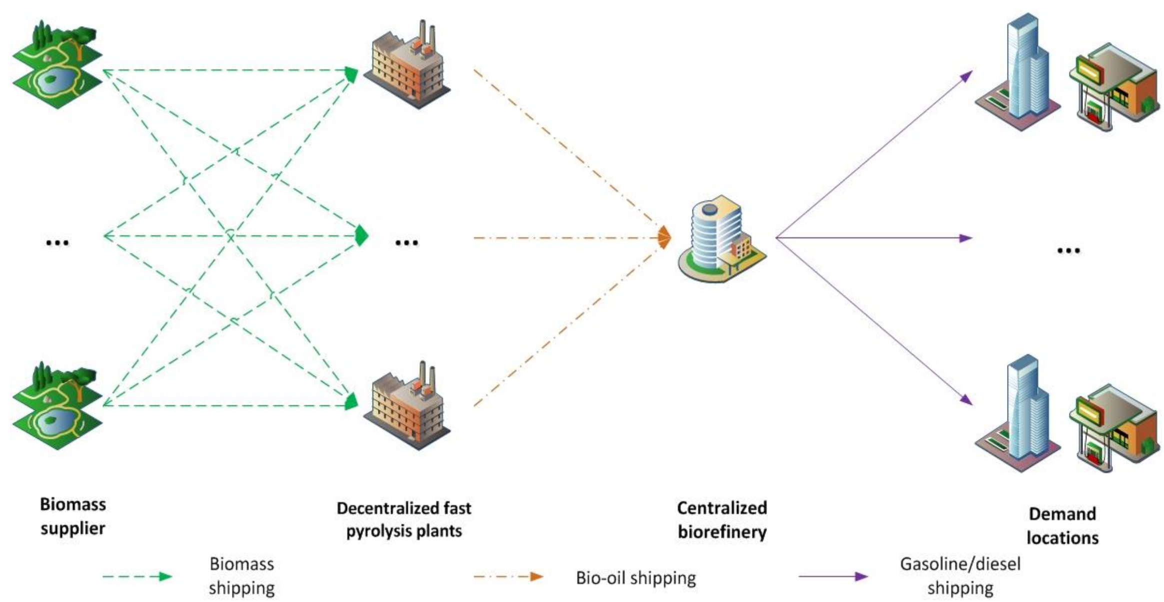

Figure 3.1 System schematics of supply chain

The supply chain network design of biofuel production is highly affected by the uncertainties along the supply chain such as biomass supply availability, technology advancement and biofuel price. The biomass supply availability is highly dependent on crop yields and farmers' participation; the conversion rates are affected by technology advancement and operating conditions; the biofuel price would change based on market conditions and enacted policies. Thus, it is of vital importance to make the supply network design decisions with the system uncertainties taken into consideration. Stochastic programming is one of the most widely used modeling frameworks to study the decision making under uncertainties.

The goal of this chapter is to provide a mathematical framework for the biofuel supply chain design and optimization under uncertainty. A two-stage stochastic programming approach is employed for the supply chain decision making. The comparison and analysis of the results provide methodological suggestions for the decision makers on the capital investment and logistic decisions. The insights derived from this study can contribute to the system efficiency improvement of the supply chain network and thus improve the economic feasibility of the production pathway.

3.3 Model Formulation

In this section, we introduce the deterministic and stochastic models for this biofuel supply chain design problem. The objective is to maximize the annual profit for biofuel producer based on the hybrid production pathway of bio-oil gasification. The deterministic mixed integer linear programming model is firstly introduced as a baseline model and then the two-stage stochastic model is presented to address the uncertainties in the supply chain design problem. The stochastic programming framework bears the concept of recourse, which means some decisions (recourse actions) are taken after uncertainties have been realized. In other words, first-stage decisions are made by taking some factors' future effects into account. In the second stage, the actual value of the variables becomes known and some corrective actions can be taken [17].

3.3.1 Mathematical Notations

The mathematical notations are summarized in Table 3.1.

Table 3.1 Notations for deterministic model

Subscripts		
$\boldsymbol{i}$	$1,2,\dots,I$	Biomass supply locations
$\boldsymbol{j}$	$1,2,\dots,J$	Candidate fast pyrolysis facility locations
$\boldsymbol{k}$	$1,2,\dots,K$	Biofuel demand locations
$\boldsymbol{l}$	$1,2,\dots,L$	Allowed fast pyrolysis capacity levels
$\boldsymbol{m}$	$1,2,\dots,M$	Candidate refining facility locations
Decision variables		
x_{ij}	Amount of biomass transported from supply location i to candidate fast pyrolysis facility location j	
y_{jm}	Amount of bio-oil transported from candidate fast pyrolysis facility location j to candidate refining facility location m	
z_{mk}	Amount of biofuel transported from refining facility location m to demand location k	
a_{jl}	Whether a fast pyrolysis facility of capacity level l is planned at candidate location j (binary variable)	
g_m	Whether a refining facility is planned at candidate location m (binary variable)	
Parameters		
B	Total budget	
C^{UP}	Capital cost of the centralized refining facility	
C_l^{Cap}	Capital cost of the decentralized fast pyrolysis facility at level l	
P_k	Biofuel price at demand location k	
D_k	Biofuel demand at demand location k	
Pe_k	Penalty for not meeting the demand at demand location k	
$Pe_k{}'$	Penalty for exceeding the demand at demand location k	
C_i^{Col}	Unit biomass collecting cost at supply location i	
C^{MO}	Unit conversion cost from dry biomass to bio-oil	
C^{OF}	Unit conversion cost from bio-oil to biofuel	
C_{ij}^{BM}	Unit biomass shipping cost from supply location i to fast pyrolysis facility location j	
C_{jm}^{BO}	Unit bio-oil shipping cost from fast pyrolysis facility location j to refining facility location m	
C_{mk}^{BF}	Unit biofuel shipping cost from refining facility location m to demand location k	
U_l	Capacity of fast pyrolysis facility at level l	

Table 3.1 continued

V	Capacity of refining facility
A_i	Available biomass feedstock at location i
α	Sustainability factor
β	Conversion factor from wet biomass to dry biomass
γ	The loss factor of biomass during collection and transportation
θ_1	Conversion ratio, metric ton of bio-oil per metric ton of dry biomass
θ_2	Conversion ratio, metric ton of biofuel per metric ton of bio-oil
δ	Availability factor
n	Operation life for facilities in year
q	Interest rate in percentage

3.3.2 Deterministic Model

In the deterministic mixed integer linear programming model, all the system parameters are assumed to be known with certainty.

Objective function

The objective function is to maximize the annual profit for biofuel producer, which can be defined as the revenue from selling the biofuel subtracted by the total system costs along the supply chain including the potential penalties. Penalties are imposed on the unmet demand which is based on the assumption that the producers have to purchase fuels from other sources to satisfy unmet demand. Penalties are also imposed for the surplus production due to additional inventory holding and storage costs. A variety of system costs have been considered in the model including facility capital investment cost, biomass collection cost, biofuel conversion cost, and logistics cost.

Firstly, the total capital cost for the decentralized fast pyrolysis facility at level l is $\sum_{j=1}^{J}\sum_{l=1}^{L} C_l^{Cap} a_{jl}$. With the assumption that the facilities have an n-year operation life and an interest rate of i, the annual amortized capital costs are $\frac{i(i+1)^n}{(i+1)^n-1}(\sum_{j=1}^{J}\sum_{l=1}^{L} C_l^{Cap} a_{jl} + C^{UP})$. Secondly, the cost of collection biomass from different feedstock location is $\sum_{i=1}^{I}\sum_{j=1}^{J} C_i^{Col} x_{ij}$. Thirdly, $C^{MO}(1-\gamma)\beta\sum_{i=1}^{I} x_{ij}$ is the fast pyrolysis conversion cost from biomass to bio-oil and $C^{OF}\sum_{j=1}^{J}\sum_{m=1}^{M}y_{jm}$ is the conversion cost from bio-oil to biofuel at the gasification and upgrading biorefinery. Lastly, the logistics costs include the biomass shipping cost from biomass feedstock locations to fast pyrolysis facility locations, the bio-oil shipping cost from fast pyrolysis facility locations to gasification and upgrading biorefinery location, and the biofuel shipping cost from gasification and upgrading biorefinery location to demand locations.

In sum, the objective function can be formulated as follows:

$$max\,\zeta = income - penalty - cost$$

$$= \sum_{k=1}^{K}\{(P_k\sum_{m=1}^{M}z_{mk}) - \left(D_k - \sum_{m=1}^{M}z_{mk}\right)_+ Pe_k - \left(\sum_{m=1}^{M}z_{mk} - D_k\right)_+ Pe'_k\}$$

$$- \{\frac{q(q+1)^n}{(q+1)^n-1}(\sum_{j=1}^{J}\sum_{l=1}^{L}C_l^{Cap}a_{jl} + C^{UP}) + \sum_{i=1}^{I}\sum_{j=1}^{J}C_i^{Col}x_{ij}$$

$$+ C^{MO}(1-\gamma)\beta\sum_{i=1}^{I}x_{ij} + C^{OF}\sum_{j=1}^{J}\sum_{m=1}^{M}y_{jm} + \sum_{i=1}^{I}\sum_{j=1}^{J}C_{ij}^{BM}x_{ij}$$

$$+ \sum_{j=1}^{J}\sum_{m=1}^{M}C_{jm}^{BO}y_{jm} + \sum_{m=1}^{M}\sum_{k=1}^{K}C_{mk}^{BF}z_{mk}\}$$

<u>Constraints</u>

The constraint (1) is included to ensure that the sum of capital cost of decentralized fast pyrolysis facilities and centralized biorefinery does not exceed the total budget.

$$B \geq C^{UP} + \sum_{j=1}^{J}\sum_{l=1}^{L}C_l^{Cap}a_{jl} \qquad (1)$$

The total amount of biomass transported from supply location i to all the candidate fast pyrolysis facility locations should not exceed the available feedstock at that supply location as denoted in constraint (2). α is the sustainability factor which is the percentage of biomass that has to be left in the field to sustain the soil nutrients. δ is the availability factor which is defined as the ratio of the available biomass to collectable biomass. This factor represents the social factors that could impact the biomass availability for biofuel production such as farmers' willingness to participate [18].

$$\sum_{j=1}^{J} x_{ij} \leq (1-\alpha)\delta A_i, \ \forall i \tag{2}$$

The facility capacity limits are included in the model in constraint (3) and constraint (4). The loss factor $\gamma \in [0,1)$ is the fraction weight loss of biomass during the collection, transportation, and unloading process and β is the conversion ratio from wet biomass to dry biomass on the weight basis.

$$\sum_{l=1}^{L} U_l a_{jl} \geq (1-\gamma)\beta \sum_{i=1}^{I} x_{ij}, \forall j \tag{3}$$

$$V g_m \geq \sum_{j=1}^{J} y_{jm}, \ \forall m \tag{4}$$

There should be no more than one fast pyrolysis facility planned in each candidate facility location as shown in constraint (5). In addition, only one centralized refining facility will be constructed in one region of interest (typically one state) as denoted in constraint (6).

$$\sum_{l=1}^{L} a_{jl} \leq 1, \forall j \tag{5}$$

$$\sum_{m=1}^{M} g_m = 1 \tag{6}$$

We assume that biomass is converted to bio-oil with conversion efficiency θ_1 and bio-oil is converted to biofuel with conversion efficiency θ_2 on the weight basis. Thus, we have the following conversion balance constraints (7) and (8):

$$(1-\gamma)\beta\theta_1 \sum_{i=1}^{I} x_{ij} = \sum_{m=1}^{M} y_{jm}, \forall j \tag{7}$$

$$\theta_2 \sum_{j=1}^{J} \sum_{m=1}^{M} y_{jm} = \sum_{m=1}^{M} \sum_{k=1}^{K} z_{mk} \tag{8}$$

In summary, this mixed integer linear programming model aims to maximize the annual profit considering the capital investments and logistics decisions. This deterministic model provides the baseline for the stochastic programming model in the next sections.

3.3.3 Two-stage Stochastic Programming Model

In this section, the two-stage stochastic programming model is discussed considering the uncertainties of the biomass availability, technology advancement, and biofuel prices. The stochastic parameters in this model are assumed to be discretely distributed. We use subscript s to represent scenario with corresponding probability Pr_s and this subscript is also incorporated into the decision variables and parameters.

The two-stage stochastic programming model is formulated as follows:

$$max\, \zeta = -\frac{q(q+1)^n}{(q+1)^n-1}\left(\sum_{j=1}^{J}\sum_{l=1}^{L} C_l^{Cap} a_{jl} + C^{UP}\right) + \sum_{s=1}^{S} Pr_s\{\sum_{k=1}^{K}\sum_{m=1}^{M}(P_{ks} z_{mks})$$

$$-\sum_{k=1}^{K}\{\left(D_k - \sum_{m=1}^{M} z_{mks}\right)_+ Pe_k + \left(\sum_{m=1}^{M} z_{mks} - D_k\right)_+ Pe'_k\}$$

$$-\left(\sum_{i=1}^{I}\sum_{j=1}^{J} C_i^{Col} x_{ijs} + C^{MO}(1-\gamma)\beta\sum_{i=1}^{I} x_{ijs} + C^{OF}\sum_{j=1}^{J}\sum_{m=1}^{M} y_{jms}\right.$$

$$\left.+\left(\sum_{i=1}^{I}\sum_{j=1}^{J} C_{ij}^{BM} x_{ijs} + \sum_{j=1}^{J}\sum_{m=1}^{M} C_{jm}^{BO} y_{jms} \sum_{m=1}^{M}\sum_{k=1}^{K} C_{mk}^{BF} z_{mks}\right)\right)\}$$

$s.t.\quad Constraints\ (1), (5), (6).$

$$\textstyle\sum_{j=1}^{J} x_{ijs} \leq (1-\alpha)\delta A_{is}, \forall i, \forall s \qquad (9)$$

$$\textstyle\sum_{l=1}^{L} U_l a_{jl} \geq (1-\gamma)\beta \sum_{i=1}^{I} x_{ijs}, \forall j, \forall s \qquad (10)$$

$$V g_m \geq \textstyle\sum_{j=1}^{J} y_{jms}, \forall m, \forall s \qquad (11)$$

$$(1-\gamma)\beta\theta_{1,s}\sum_{i=1}^{I}x_{ijs} = \sum_{m=1}^{M}y_{jms}\,,\ \forall j, \forall s \tag{12}$$

$$\theta_{2,s}\sum_{j=1}^{J}\sum_{m=1}^{M}y_{jms} = \sum_{m=1}^{M}z_{mks}\,,\ \forall s \tag{13}$$

$$x_{ijs}, y_{jms}, z_{mks} \geq 0, a_{jl}, g_m \in \{0,1\}, \forall i, j, k, m, l, s$$

The first-stage decisions involve variables which have to be decided before the uncertainties are realized. After the uncertainties are realized, the second-stage decisions are made. In this supply chain network design model, the first-stage decision variables include the binary variables a_{jl} and g_m, which make the capital investment decisions including the facility locations (decentralized fast pyrolysis and centralized refining facilities) and capacities of the decentralized fast pyrolysis facilities. The second-stage decision variables x_{ijs}, y_{jms}, and z_{mks} determine the biomass and biofuel flows.

Constraints (1), (5), and (6) are the first-stage constraints, these constraints remain the same in all scenarios and they are same as in the deterministic linear program model. The rest of the constraints change based on the stochastic scenario.

One of the most commonly used methods for scenario generation is moment matching method. To implement this method, let S be the set of all selected statistical properties, and S_{VALs} be the value of the selected statistical property $s \in S$; let $f_s(x;\ p)$ be the mathematical expression for statistical property $s \in S$ and p is the probability vector; let H be a constant matrix of zeroes and ones; let w_s be the weight for statistical property $s \in S$ [41]. Then, the following nonlinear programming problem can be solved for the probabilistic scenario.

$$\min_{x,p}\sum_{s\in S}\omega_i\left(f_s(x;\ p) - S_{VALs}\right)^2$$

$$s.t.\ \ \sum pH = 1;\, p \geq 0.$$

3.4 Case Study

We apply the supply chain design model for a case study in Iowa State, USA to illustrate and validate the optimization model. Iowa possesses the largest quantity of corn stover in the United States and has been one of the leading states of corn ethanol and soybean biodiesel production [19]. With the abundance of cellulosic biomass, Iowa has the potential in the cellulosic biofuel production via thermochemical conversion processes. The objective for the supply chain design is to maximize the yearly profit for biofuel producer by choosing the locations and capacity levels for the distributed fast pyrolysis facilities, and the location of the centralized gasification biorefinery. Meanwhile, the logistic flow decisions of the biomass and biofuel will also be investigated.

3.4.1 Data Sources

The centroids of 99 counties of Iowa are chosen as candidate biomass (corn stover in this case study) supply locations, the potential sites for distributed fast pyrolysis facilities, and the candidate location for the centralized gasification facility. The annual corn stover yield is estimated based on corn grain yield with the residue harvest index of 0.5 meaning 50% of the above ground biomass is grain and consequently stover is generated in the same amount as grain [20]. The weight of #2 corn at 15.5% moisture is applied to calculate the corn grain yields [21]. The county level corn production and yield data from 2003-2012 are collected from the National Agricultural Statistics Service (NASS), United States Department of Agriculture (USDA) [22]. The average county level corn stover yield in Iowa for 2003-2012 is shown in Figure 3.2 with the darkness of the shade corresponding to the corn stove yield.

In addition, the collectable corn stover is limited by growing conditions, soil nutrient levels, and method of harvest. Montross et al. reported the collection efficiencies of using three strategies in Kentucky: bale only to be 38%; rake and bale to be 55%; and mow, rake, and bale to be 64% [23]. Schechinger and Hettenhaus reported collection efficiencies of 40% to 50% without raking and 70% with raking in large-scale stover collection operations in Nebraska and Wisconsin [24]. Lindstrom suggested that a 30% removal rate would not significantly increase soil loss [25]. Later, Papendick et al. shows that a 30% removal rate results in 93% soil cover after residue harvest [26]. The National Resource Conservation Service (NRCS) suggests that a minimum of 30% of stover cover must remain in the field to prevent soil erosion [27]. In this analysis, we assume the sustainability factor to be 0.3, which means at least 30% of the stover must be left in the field to promote soil health.

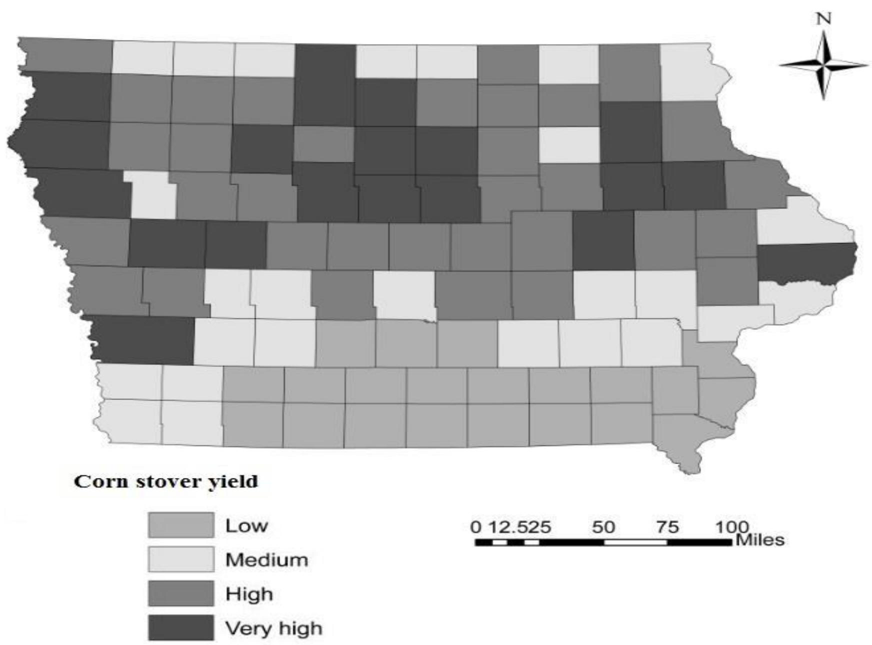

Figure 3.2 Average corn stover yield in Iowa (2003-2012)

Although significant literature has investigated the environmental consequences of biomass collection from the field, limited studies have taken the social factors such as farmers' willingness to participate into consideration. However, the farmers' willingness to participate makes a direct impact on the biomass feedstock availability. Recently, an Iowa farmer survey conducted by Tyndall et al. shows that only 17% of farmers in Iowa show interest in harvesting their stover and about 37% are undecided [19]. These results suggest that about half of the farmers will not collect the corn stover in the near future. In the base case scenario, the availability factor is assumed to be 0.4, and the influence of this availability factor on the supply chain design is also investigated in this study.

The collection cost for corn stover is different for each county due to the differences in collection quantities and collection methods. The collection cost utilized in this case study is based on the regression analysis from Graham et al. [28]. Biomass loss factor, which accounts for possible mass loss during loading, transportation, and unloading of the biomass, is assumed to be 0.05 in this analysis [29].

The total gasoline demand of Iowa is based on the state-level gasoline consumption data from the Energy Information Administration (EIA) [30]. Weekly retail gasoline prices for the Midwest area from 2003 to 2012 are also from EIA [31]. Gasoline demand of each demand area is assumed to be proportional to the population of metropolitan statistical areas (MSAs). The partitions and population information of Iowa MSAs are based on U.S. Census Bureau [32].

All the biomass suppliers, biorefineries, and demand locations are assumed to be at the county centroids. Transportation distances for biomass, bio-oil and biofuel are calculated using the great circle distance, which is defined as the shortest distance between the two locations on a sphere. In addition, the actual distances have been adjusted to account for the difference in the transportation methods by the circuit factors from the Congressional Budget Office [33].

The fixed transportation cost of corn stover via truck is $5.34/metric ton-mile and the variable cost of $0.23/metric ton-mile [34]. The transportation cost of bio-oil via truck is assumed to be equal to the national average truck shipping cost of $0.312/metric ton-mile based on Bureau of Transportation Statistics (BTS). The transportation cost of biofuel via pipeline is assumed to be equal to the national average oil pipeline cost, which is $0.032/metric ton-mile [35]. The cost data have been adjusted to the 2012 US dollars.

In the fast pyrolysis process, the biomass is converted into bio-oil (53-78%), char (12-34%), and gas (8-20%) [36]. The bio-oil yield is assumed to follow the normal distribution based on the experimental results from Iowa State University. In this study, the fluidized bed reactor is employed in the fast pyrolysis which has an average conversion ratio of 0.63 from biomass to bio-oil on weight basis [37]. The conversion ratio from bio-oil to biofuel is not available due to lack of experimental data. Limited experiment shows high carbon conversion of gasification but low efficiency from syngas to fuel (due to the diverse H_2/CO ratio). Raffelt et al. reported a conversion ratio of 0.156 on weight basis for slurry (80% bio-oil and 20% char) gasification [36]. We assume that the conversion ratio from bio-oil to biofuel follows a normal distribution with an average of 0.20 on weight basis. With these assumptions, the average fuel yield for the pathway under analysis would be 31.2 million gasoline gallon equivalent (GGE) per year for the plant size to of 2000 metric ton biomass per day facility. This is consistent with reported fuel yield of 29.3-58.2 million GGE per year for 2000 metric ton per day facility [38].

Wright et al. reported that the capital cost of centralized gasification plant with a capacity of 550 million GGE per year is about 1.47 billion [39]. The capital cost of distributed fast pyrolysis facility with a capacity of 2,000 metric ton per day is $200 million [37]. The commonly used scaling factor of 0.6 (the “sixth-tenth rule” [40]) is applied to estimate capital cost for facilities with other capacity levels. In this study, we consider three capacity levels of distributed fast pyrolysis facilities: 500, 1000, and 2000 metric ton per day. According to RFS2, at least 36 billion gallons per year of renewable fuels will be produced by 2022, which is about 28% of the national gasoline consumption. In this study, we assume the centralized gasification and upgrading plant has a capacity of 550 million GGE per year, which could satisfy more than 30% of the gasoline consumption in Iowa. Thus, we only need to consider one centralized bio-oil gasification and upgrading facility in this case study.

It is assumed that all the facilities have a 20-year operation life and an interest rate of 10%; the online time of all the facilities is 328 days per year (equivalent capacity factor of 90%). In the following two sections, the computational results of the biofuel supply chain design for both deterministic case and stochastic case are presented.

3.4.2 Analysis for Deterministic Case

In the deterministic case, 17 distributed fast pyrolysis plants will be built, and all of them are at the highest capacity level (2000 metric ton per day). This is mainly due to the budget limit and economies of scale. The centralized gasification plant is planned to be located in Hamilton County. The optimal locations for these facilities are shown in Figure 3.3. The shaded areas are biomass feedstock suppliers (71 counties) in this case. These counties are mainly located at the central and northern part of Iowa, which have a higher yield of corn and thus have better availability for corn stover.

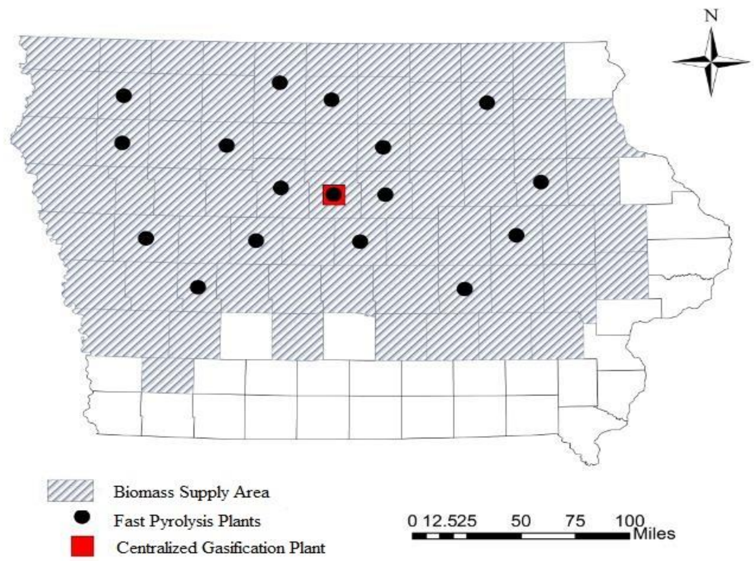

Figure 3.3 Optimal facilities locations in deterministic case

Table 3.2 includes the annual itemized costs in deterministic case. Total shipping cost accounts for 14% of the total cost; biomass collecting cost accounts for 18% of the total cost; total capital cost accounts for about 25% of the total cost; conversion cost accounts for 43% of the total cost. In the category of shipping cost, biomass shipping cost is the most significant (54%).

Table 3.2 Annual itemized costs in deterministic case (million dollars)

Biomass collecting cost	**416.93**
Total capital cost	**604.33**
Capital cost of the centralized refining facility	184.06
Capital cost of the fast pyrolysis facility	420.27
Total shipping cost	**334.04**
Biomass shipping cost	181.99
Bio-oil shipping cost	146.80
Biofuel shipping cost	5.25
Conversion cost	**1020.20**
Total	**2375.51**

3.4.3 Analysis for Stochastic Case

In the stochastic case, uncertainties along the supply chain are incorporated into the modeling framework. The uncertainties under considerations include biomass availability, technology advancements and biofuel price. Technology advancements uncertainty is represented by the probabilistic distribution of two conversion ratios. Historical data for corn stover yield and retail gasoline prices are available to estimate the probabilistic scenarios. In this case study, moment matching method has been employed to generate the probabilistic scenarios. Data statistics such as mean, variance, skewness, and kurtosis are calculated for moment matching based on the historical data.

Table 3.3 Scenario summary

No.	Statistics	Corn stover yield (metric ton/acre)	Gasoline prices ($/Gallon)	Conversion ratio θ_1	Conversion ratio θ_2
1	Mean	2.8848	2.6473	0.63	0.2
2	Variance	0.0497	0.4684	0.0049	0.0001
3	Skewness	-1.5047	-0.0838	0	0
4	Kurtosis	3.0143	-0.8540	3	3
Scenario	**Probability**				
1	0.0128	2.2066	2.2035	0.4961	0.1825
2	0.0114	2.1568	2.5758	0.4476	0.1810
3	0.1269	2.9174	2.4271	0.7770	0.2197
4	0.1130	3.1437	4.5391	0.6242	0.1993
5	0.1116	2.9115	4.4923	0.6243	0.1984
6	0.1078	2.9048	3.4381	0.6253	0.1959
7	0.1092	2.6570	3.5253	0.6229	0.2097
8	0.1255	2.9986	3.2187	0.6206	0.1963
9	0.0531	2.7582	3.3948	0.6198	0.1961
10	0.0100	2.1041	2.5689	0.3952	0.1875
11	0.0288	2.7502	3.3767	0.5742	0.1917
12	0.0164	2.6637	3.2652	0.5465	0.1925
13	0.0259	2.7056	3.3314	0.5897	0.1944
14	0.0143	2.6095	3.1129	0.5376	0.1945
15	0.1231	3.1086	4.0164	0.6265	0.1950
16	0.0100	2.0942	2.8036	0.3858	0.1562

The non-linear optimization problem is solved by applying a heuristic of changing initiating value until a satisfactory solution is obtained. The General Algebraic Modeling System (GAMS) is utilized to solve the moment matching problem and a scenario tree with a size of 16 is generated. A summary of scenarios in the stochastic model are included in Table 3.3.

17 distributed fast pyrolysis plants are proposed in the stochastic case, and all of them are at the highest capacity level. This is same as the deterministic case. The numbers of biomass feedstock sites (counties) involved in stochastic case are various based on scenarios with a maximum of 79 counties. Nine scenarios (with a total probability of 0.6) need biomass supply from more than 71 counties. The optimal locations for these facilities are represented in Figure 3.4. The shaded areas are additive biomass feedstock sites involved in all the stochastic scenarios (81 counties).

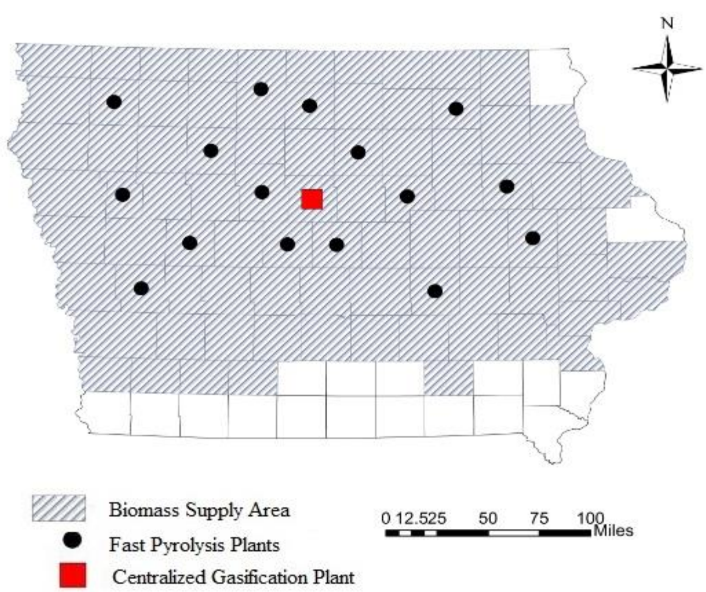

Figure 3.4 Optimal facilities locations in stochastic case

In both deterministic and stochastic cases, 17 distributed fast pyrolysis plants are proposed but they are not at the same locations. The plants are all proposed to be built at the highest capacity level to reduce the capital cost due to the economies of scale. The centralized gasification plant will be constructed at Hamilton County in both cases, which is at the center of high corn yield counties.

Despite of the similarities of the both cases, differences exist for the supply chain network configurations. In the stochastic case, it is preferred to build the fast pyrolysis plants farther away from the centralized gasification and upgrading plant because biomass collection sites are more distributed due to the uncertainties in biomass feedstock supply availability.

The yearly profit in the deterministic case is 154.53 million dollars. For comparison, the numerical value of parameters used in deterministic case are the expected value of those parameters from the stochastic scenarios, thus this deterministic solution is also called the expected value solution (EV). The solution in the stochastic case is known as recourse problem solution (RP). In this case study, the yearly profit from the recourse problem is 129.57 million dollars. If we apply the decisions in deterministic case to the stochastic environment, we will get the expected yearly profit with the EV solution. This is called expected results of EV solution (EEV), which is 129.11 million dollars in this case study. The value of the stochastic solution (VSS) could be defined as $VSS = EEV - RP$. The VSS is about 0.46 million dollars, which is the benefit of considering uncertainties in the decision making process.

3.4.4 Discussion on the Impact of Farmers' Participation

In this section, we discuss the impact of farmers' participation, which is represented as the availability factor δ in the model, on the decisions in both the deterministic case and stochastic case.

For the deterministic case, if the availability factor δ is less than 0.23, which means no more than 23% of the farmers would participate in corn stover collection in each county, the objective function value is equal to zero. In this case, this biofuel supply chain system is not profitable and it is optimal not to construct any facilities. When the availability factor δ is in the range of 0.23 to 0.36, the system is profitable but it could not satisfy the biofuel target of the entire state. Recall that the goal is to satisfy at least 30% of the gasoline consumption in Iowa, which is about 517 million GGE per year. Thus, at least 33000 metric ton dry biomass per day is needed at distributed fast pyrolysis plants. The biofuel supply target will be met if the availability factor δ is larger than 0.36.

Table 3.4 provides the annual itemized costs and profit for a variety of availability factor $\delta's$. The total capital cost, biomass collection cost and total shipping cost increase when availability factor δ increases from 0.3 to 0.4. This is because of the increase of the facilities production and capacities. It should be noted that when the biofuel production capacity can meet the target biofuel demand, the total shipping cost and biomass collection cost will decrease as the availability factor increase. After that, the total capital cost will not change since the same number and capacities of facilities are planned. As a result, the yearly profit will increase as the availability factor increase. In sum, the system cost will decrease and yearly profit will increase with increase in the farmers' participation.

Table 3.4 Annual itemized costs and profit for different δ (million dollars)

δ	**0.3**	**0.4**	**0.5**	**0.6**	**0.7**
Profit	69.246	154.53	200.92	232.09	256.43
Total capital cost	530.21	604.39	604.39	604.39	604.39
Biomass collecting cost	347.72	416.93	409.46	402.17	398.69
Total shipping cost	296.27	334.04	295.13	271.24	250.38
Conversion cost	840.14	1020.20	1020.20	1020.20	1020.20

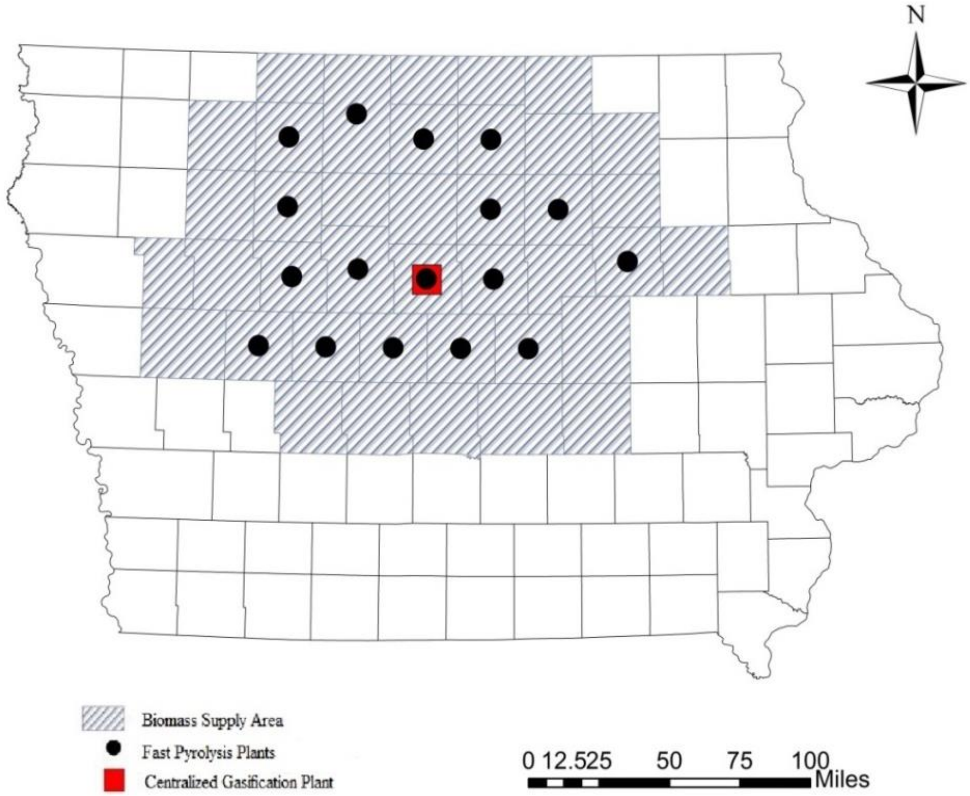

Figure 3.5 Optimal facilities locations in deterministic case (δ=0.7)

If we compare Figure 3.5 to Figure 3.3, it is observed that the locations of fast pyrolysis plants are more centralized when availability factor δ is equal to 0.7 and we only need 40 counties (rather than 71 when δ is equal to 0.4) to supply the biomass. The main reason for these phenomena is the biomass availibility for each county increases as the availability factor δ increases. As a result, optimal decisions will be improved due to the additional flexilities in choosing the biomass harvesting sites.

Table 3.5 shows the value of the stochastic solution (VSS) will decrease as the availability factor increase. The VSS will reduce to zero when the availability factor is larger than 0.5. It can be observed from the model that as farmers' participation increase in Iowa, the supply chain design and optimization model will become more robust. On the other hand, since the advanced biofuel industry is still at its infancy, the farmers' participation is currently at a relatively low level. Therefore, it is beneficial to apply stochastic programming framework to deal with the uncertainties and improve the decision making. This analysis provides the decision makers another insight to improve system resiliency by increasing farmers' participation.

Table 3.5 Stochastic programming results for different δ

δ	EV	RP	EEV	VSS
0.3	69.25	56.25	55.74	0.51
0.4	154.53	129.57	129.11	0.46
0.5	200.92	171.82	171.76	0.06
0.6	232.09	200.93	200.93	0
0.7	256.43	222.74	222.74	0

3.5 Conclusion

Cellulosic biofuels play an increasingly important role in RFS2 and renewable energy. The hybrid thermochemical production pathway of bio-oil gasification which combines fast pyrolysis and gasification is one of the promising production pathways of advanced biofuel. In this production pathway, the widely distributed small-scale fast pyrolysis processing plants could avoid transporting bulky solid biomass over a long distance and the centralized gasification and fuel synthesis facility can take advantage of the economies of scales. Due to the significance of supply chain related system costs, the design of biofuel supply chain networks is playing an essential role in the commercialization process.

This chapter provides a mathematical programming framework with a two-stage stochastic programming approach to deal with the uncertainties in the biofuel industry. The first-stage makes the capital investment decisions including the locations and capacities of facilities while the second-stage determines the biomass and biofuel flows. The optimization model could provide methodological suggestions for the decision makers on the capital investment decisions and logistic decisions of this thermochemical conversion pathway based on bio-oil gasification.

A case study of Iowa is presented to illustrate and validate this supply chain design and optimization model. The results show that uncertain factors such as biomass availability, technology advancement and biofuel price can be pivotal in this supply chain design and optimization. In addition, farmers' participation has a significant effect on the decision making process. It is appropriate and necessary to apply stochastic programming framework to deal with the uncertainties, especially at a low farmers' participation level. As farmers' participation increase in Iowa, the supply chain design and optimization model will become more robust against the uncertainties along the supply chain.

In summary, this chapter provides a modeling framework to study the advanced biofuel production pathway under uncertainty. Our study is subject to a number of limitations. Firstly, we assume the sustainability factor and farmers' participation are the same for each county. However, these factors may vary based on the land characteristics and agricultural management practices; we could include additional constraints and assumptions to better describe the biomass availability. Secondly, we assume the transportation cost within counties is negligible, which could impact the supply chain design and decision making. Thirdly, we consider three sources of uncertainties and more uncertainty factors can be considered. Last but not least, only one set of scenarios is generated in this chapter, more scenarios could be generated to test the results' stability. We shall address these limitations in our future research.

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CHAPTER 4 CONCLUSION

With the growing concerns of renewable energy and the mandates of the Revised Renewable Fuel Standard (RFS2), cellulosic biofuels have been moved to the frontier of bioenergy research and development. With this motivation, this thesis is dedicated to investigate the economic assessment and supply chain design of a hybrid production pathway. This hybrid thermochemical production pathway based on bio-oil gasification which combines fast pyrolysis and gasification is one of the promising production pathways of advanced biofuel.

In Chapter 2, a detailed process modeling with corn stover as feedstock and transportation fuels as the final products are presented. Techno-economic analysis of this fast pyrolysis and bio-oil gasification pathway is also discussed to assess the economic feasibility. The preliminary results of this study show a capital investment of 438 million dollar and MSP of $5.6 per gallon of gasoline equivalent. The sensitivity analysis finds that MSP is most sensitive to IRR, feedstock cost, and fixed capital cost.

As one of the superiority of bio-oil gasification, a supply chain design with various widely distributed small-scale fast pyrolysis processing plants coupled with a central bio-oil gasification facility could be considered. In Chapter 3, a two-stage stochastic programming is formulated to solve this supply chain design problem considering uncertainties in biomass availability, technology advancement, and biofuel price. The numerical results and case study of Iowa illustrate that considering uncertainties can be pivotal in this supply chain design and optimization problem. Also, farmers' participation has a significant effect on the decision making process.

In summary, this thesis provides a techno-economic analysis and supply chain design for advanced biofuel production based on bio-oil gasification. This study is subject to a number of limitations which could also serve as future research directions.

For Chapter 2, the techno-economic analysis will continue to be updated and improved with additional experimental data as they become available. Practical logistics settings and constraints could be considered at commercial scale. Other uncertainty analysis such as Monte-Carlo simulation could be performed to test the uncertainty in technical data, facility size, and capital costs. Comprehensive comparisons should be conducted to evaluate the difference between bio-oil gasification pathway and direct solid biomass gasification pathway for fuel production. Optimization models can also be formulated for a facility design and operational improvement such as production scheduling and inventory control.

For the supply chain design model detailed in Chapter 3, additional constraints and assumptions should be incorporated to better describe the practical supply chain, e.g., transportation cost within counties and diversification of the sustainability factor and farmers' participation in different areas. Moreover, more uncertainty factors could be considered and more scenarios could be generated to test the results' stability.