2014

Development of integrated assessment platform for biofuels production via fast pyrolysis and upgrading pathway

Yanan Zhang
Iowa State University

Recommended Citation

Zhang, Yanan, "Development of integrated assessment platform for biofuels production via fast pyrolysis and upgrading pathway" (2014). *Graduate Theses and Dissertations*. 13876.
http://lib.dr.iastate.edu/etd/13876

Development of integrated assessment platform for biofuels production via fast pyrolysis and upgrading pathway

by

Yanan Zhang

A dissertation submitted to the graduate faculty

In partial fulfillment of the requirements for the degree of

DOCTOR OF PHILLOSOPHY

Co-major: Mechanical Engineering; Biorenewable Resources Technology

Program of Study Committee:
Robert Brown, Major Professor
Guiping Hu
Terry Meyer
Song-Charng Kong
Laura Jarboe
Raj Raman

Iowa State University

Ames, Iowa

2014

DEDICATION

To my grandmother, my grandfather, and my parents.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS

First, I would like to thank my major professor Dr. Robert Brown, for his rigorous research attitude, innovation, and work ethic he always created. Thank you for supporting me for my Ph.D. study in Center for Suitable Energy Technologies (CSET), where I learned lots of knowledge across so many interesting disciplines, and had opportunity to know so many excellent researchers. Your enthusiasm and ethics for academic research set me a model and ignited my desires to be an outstanding researcher. Thank you for the generous help with my research. I was deeply touched by your efficient works, your careful review and edition work for my research papers, many of your help for the research, and your financial support for me to finish the PhD program. It encouraged me to know you are such a great mentor, not only in research. Your generosity and encouragement made these years the most valuable and productive period of my life.

I want to especially thank for my committee members: Dr. Guiping Hu, Dr. Terry Meyer, Dr. Song- Charng Kong, Dr Raj Raman, and Dr. Laura Jarboe. Thanks for your support, time, and insightful suggestions throughout my research. You are all supportive and resourceful advisors. Your valuable suggestions and directions are vital to my research process. Many thanks to Dr. Mark Wright, for all of your encouragement, patience, and supports especially when I just started up the research work.

As a member of CSET, I have enjoyed the companion of my colleagues. I gratefully appreciate all of your friendship and support over the many years, and for all the fun we have had. Special thanks to my colleagues, Patrick Woodcock, Dustin Dalluge, and Karl Broer. I am very thankful for all of the help, guidance, and discussions with staff at the CSET, in particular Ryan Smith, Patrick Johnston, Marjorie Rover, Xianglan

Bai. I would also like to thank Tristan Brown for the large contributions to my research papers and your help and guidance in the beginning of my research career.

Thanks a lot for all of the administration staffs in CSET and The Department of Mechanical Engineering. Special thanks to Jan, Becky, and Amy for many helps during my study in Iowa State University.

Thanks a lot for all my family and friends. Mum and Dad, thank you for supporting me to make the decision to pursue Ph.D. in United States. Especially thanks to my grandmother and grandfather. Thank you for always being there!

ABSTRACT

Growing concern over Greenhouse Gas (GHG) emissions from petroleum-based fuel consumption have prompted interest in the production of alternative transportation fuels from biorenewable sources. As required by the Energy Independence and Security Act of 2005, the U.S. Environmental Protection Agency (EPA) finalized the Renewable Fuel Standard (RFS) and mandated petroleum refineries and oil importers to increase the volume of renewable fuel that is blended into petroleum-based transportation fuels. Although biomass is a promising renewable energy for fuels and chemicals production, the technology, economics and environmental issues for bioenergy systems should be extensively evaluated.

Other researchers have analyzed bioenergy systems from a number of different perspectives but these perspectives have not been combined into an integrated analysis methodology because of the large number of disparate disciplinary fields that would have to be considered including bioenergy sciences and engineering, environmental sciences, economics, optimization, and numerical modeling. Nor is it a simple matter to integrate the different analytical methods used in economic assessment, environmental impact evaluation, supply chain management, and logistic planning.

This dissertation explores the development of integrated assessment platform for biofuels production, using separate modules to evaluate process engineering, economic feasibility, logistics of supply, and environmental impact within a general framework. Four modules are included: process simulation (module A), economics analysis (module B), life cycle assessment (module C), and supply chain & logistics optimization (module D). In this dissertation, the specific instance of production of drop-in biofuels using fast pyrolysis and upgrading is employed as the case study to examine this methodology. Two different bio-oil upgrading pathways are examined using this integrated assessment platform: 1. commodity chemicals production via forest residue fast pyrolysis and hydrotreating/fluidized catalytic cracking (FCC) pathway 2. Co-production of hydrogen and transportation fuels via corn stover fast pyrolysis and hydrotreating/hydrocracking pathway. The preliminary results prove that this developed integrated assessment methodology is a powerful tool to evaluate the biofuels production via fast pyrolysis pathway. This integrated assessment platform could also extended for other energy resource examination.

CHAPTER I

GENERAL INTRODUCTION

Biofuels

Biomass has the potential to become one of the major global primary energy sources during the next century and modernized bioenergy systems are suggested to contributing to future sustainable energy systems [1]. Growing concerns over Greenhouse Gas (GHG) emissions from petroleum-based fuel consumption have prompted interest in the production of biofuels from biorenewable sources. The biofuels produced from the renewable resources could help to minimize the fossil fuel consumption as well as mitigating the global warming [2]. In addition, production of biofuels and bioproducts could supply new employment opportunities and incomes in rural areas [2].

The first generation biofuels refer to the fuels that have been derived from sources like starch, sugar, animal fats and vegetable oil. Three main types of commercialized first generation biofuels are biodiesel, ethanol, and biogas. The production of first generation biofuels, such as sugarcane ethanol in Brazil, corn ethanol in U.S., oilseed grape biodiesel in Germany, and palm oil biodiesel in Malaysia is characterized by mature market and well understood technologies [3]. As 2007 U.S. Energy Independence and Security Act required, the total target volume increases to 36 billion US gallons by 2022, from 4.7 billion U.S. gallons mandated in 2007. This generated incentives for a massive investment in U.S. corn-based ethanol plants.

Although the first generation of biofuels is mature and commercialized, issues such as food competition and land displacement raised the doubts on the benefits of first generation biofuels promotion [3]. At the meanwhile, the U.S. 2007 Energy Independence and Security Act further specifies that 21 billion US gallons of the 2022 total must be derived from non-cornstarch products (e.g. sugar, biodiesel, or cellulose). The limitations of first generation biofuels produced from food crops have caused greater interest of developing the second generation biofuels. The second generation biofuels are typically made from lignocellulosic biomass or woody crops, agricultural residues or waste.

There are typically two platforms to convert lignocellulosic biomass to biofuels. One platform is biochemical route and the most common types of biochemical processes are fermentation and anaerobic digestion [4]. Fermentation uses microorganisms and/or enzymes to convert a fermentable substrate into recoverable products (usually alcohols or organic acids) [4]. The other platform is the thermochemical route, which typically include combustion, gasification, hydrothermal and pyrolysis [5]. Combustion of biomass is the most direct and technically easiest process but produces electricity instead of liquid transportation fuels [6]. A hydrothermal process is one that involves water at elevated temperatures and pressures and the advantage of hydrothermal processing for biomass is that hot water can serve as a solvent, a reactant, and even a catalyst or catalyst precursor [7]. The other thermochemical pathways are gasification and pyrolysis. For biomass gasification, biomass is converted into a combustible gas mixture by the partial oxidation of biomass at high temperature, in the range of 800-900^{o}C [8]. Gasification can use low-value feedstocks and convert them not only into electricity, but also into transportation fuels [6]. Usually, the Fischer–Tropsch (FT) process is integrated into gasification process to form a biomass-to-liquid (BTL) process where syngas from biomass gasification is synthesized to liquid fuels [9, 10]. Biomass pyrolysis is a process of thermal decomposition of biomass in the absence of oxygen. Typically there are three types of pyrolysis: slow pyrolysis, flash pyrolysis, and fast pyrolysis. For slow pyrolysis, biomass is pyrolyzed at slow heating rates (5-7K/min), which leads to less liquid and gaseous product and more of char production [8]. For biomass flash pyrolysis, the heating rate is very high and therefore the particle size should be fairly small [8, 11]. Besides, it requires special rector configuration in which the biomass residence times are only of few seconds [8].

Among the three types of pyrolysis, fast pyrolysis has gained more attention due to the higher yield of desirable liquid product. Fast pyrolysis is a high temperature process in which biomass is rapidly heated in the absence of oxygen and the products of biomass fast pyrolysis are vapors, aerosols, and some charcoal [12]. Fast pyrolysis product yields are typically reported between 60 –75 wt % bio-oil, 15 –25 wt % bio-char and 10 –20 wt % non-condensable gases [13]. Some research show that the maximum liquid yields are obtained with high heating, at reaction temperature of 500 ^{o}C and with short vapor residence time [12]. Czernik and Bridgwater [14] reviewed the application of biomass fast pyrolysis oil and pointed out that the liquid bio-oil product from fast pyrolysis has the considerable advantage of being a storable and transportable fuel as well a potential source of a number of valuable chemicals that offer the attraction of much higher added value than fuels.

Various reactors are designed for performing fast pyrolysis experiments, which include bubbling fluidized bed reactor, circulating fluidized bed reactor, rotating cone pyrolyzer, ablative pyrolyzer, vacuum pyrolysis, and auger reactor [15].The widely used fast pyrolysis reactor is the bubbling fluidized bed or simply the fluid bed reactor. Bubbling fluid beds have the advantages of a well understood technology that is simple in construction and operation, good temperature control and very efficient heat transfer to biomass particles arising from the high solids density [16]. Much research has been done on finding the optimal biomass feedstock and operating parameters for performing fast pyrolysis in fluidized bed reactors. Heo et al. [17] have investigated bio-oil production and found that the optimal pyrolysis temperature for increased yields of bio-oil was 450^{o}C. Wang et al. [18] conducted fast pyrolysis of algae remnant in a fluidized bed at 500^{o}C and the results show that yields of bio-oil, biochar, and gas were 53, 31, and 10 wt.%, respectively. A 2.5 kg/h biomass fast pyrolyzer has been developed at Agricultural Research Service (ARS) and tested for switchgrass conversion and it is found that bio-oil yields greater than 60% by mass have been demonstrated for switchgrass, with energy conversion efficiencies ranging from 52 to 81% [19]. Rice rusk has also been investigated by Zheng [20] and the experimental result shows that the highest bio-oil yield of 56wt% was obtained at 465 ^{o}C for rice husk. In addition, the results showed that bio-oil obtained from rice rusk can be directly used as a fuel oil for combustion in a boiler or a furnace without any upgrading according to the analyzed characteristics of heat value, stability, miscibility and corrosion [20].

Some researchers have conducted catalytic fast pyrolysis experiments to investigate the effects of catalysts on the final product yields and products qualities [21, 22]. It was found that the presence of the standard ZSM-5 catalyst increased the yields of non-condensable gas, water and coke, while decreased the liquid and char yields [21, 22]. Besides, the catalytically produced bio-oil contained less carbohydrate degradation products and more aromatic compounds [22]. Cheng et al. [23] tested bifunctional Ga/ZSM-5 catalysts for catalytic fast pyrolysis and show that Ga/ZSM-5 catalysts can be used to increase the yield of aromatics by catalytic fast pyrolysis by 40% compared to that with the standard ZSM-5 catalyst. In addition to standard ZSM-5 and Ga/ZSM-5 catalysts, LOSA-1, γ-Al2O3 and spent FCC catalysts are also studied for a novel reactor of Internally Interconnected Fluidized Bed (IIFB) and it is found that ZSM-5 shows the highest selectivity of naphthalene (12.1%), whereas spent FCC catalyst presents the highest selectivity of benzene (45.5%) [24].

Bioenergy Assessment

Although bioenergy systems are very promising, the full evaluations are needed before they are commercialized. Many issues must be examined for bioenergy utilization including economic feasibility, sustainability, logistics, politics, and social impacts.

Techno-economic Analysis

Techno-economic analysis is a tool for research and development (R&D) for biofuels production and can be used to evaluate the economic feasibility of the biofuels production. A number of studies focus on the techno-economic analysis of biofuels production via biochemical or thermochemical pathways. In these techno-economic analyses, usually the net present value (NPV), minimum selling price (MSP) or facility internal rate of return (IRR) is evaluated to examine the economic feasibility for various biofuels production. Lignocellulose ethanol is expected to be commercialized during the next decade as renewable energy for transportation [25]. Many techno-economic analyses have been conducted for biochemical ethanol [26-29]. The National Renewable Energy Laboratory (NREL) has published two detailed techno-economic analyses on the ethanol production via biochemical pathways [30, 31]. In the two studies, corn stover and poplar wood are studied as the feedstock and the two studies are both based on detailed process design, mass and energy balance using Aspen Plus and related economics evaluation. Using the same method, Kazi et al. [26] compared various pretreatment (dilute-acid, 2-stage dilute-acid, hot water, and ammonia fiber explosion); and downstream variations (pervaporation, separate 5-carbon and 6-carbon sugars fermentation, and on-site enzyme production) for the production of ethanol from corn stover.

In addition to the biochemical conversion pathway, the thermochemical pathway has also invested by the researchers. Gasification is one of the thermochemical conversion technologies. In these techno-economic analyses, ethanol is produced via indirect or direct gasification with mixed alcohol synthesis system [32-35]. In addition to ethanol, several techno-economic analysis studies related to liquid fuels production via gasification and FT synthesis process are reported [9]. Techno-economic analysis on bio-based products from fast pyrolysis and upgrading are reported by researchers recently due to the growing interest in fast pyrolysis technology. Wright et al. [36] designed the biomass-to-transportation fuels pathway using corn stover as the feedstock and conducted the techno-economic analysis. Johns et al. [37] also designed the process model for transportation fuels production via woody biomass fast pyrolysis and hydroprocessing. Islam and Ani [38] carried out a techno-economic analysis of the primary pyrolysis process and pyrolysis process with catalytic treatment converting rice husk waste to pyrolysis oil and solid char for three different scales and found that fluidized bed fast pyrolysis (FBFP) 1000 kg/h scale is most economically feasible with lowest production cost. In addition to the transportation fuels, the techno-economic analysis for chemicals and hydrogen production via biomass fast pyrolysis and upgrading are also examined. Annex et al. [39] compared the techno-economic analysis for six biomass-to-liquid fuels technology scenarios representing three conversion platforms: pyrolysis, gasification, and biochemical and found that the stand-alone biomass-to-liquid fuel plants are expected to produce fuels with a product value in the range of $2.00–5.50 per gallon ($0.53–1.45 per liter) gasoline equivalent, with pyrolysis the lowest and biochemical the highest.

Life Cycle Assessment

Use of biomass-based fuels could reduce the fossil fuel combustion thereby also reducing net greenhouse gas emissions. Life cycle assessment (LCA) is the process of evaluation the effects that a product has on the environment over the entire period of its operating life and is a tool that supports environmental decision making. Along with the growing interest of biofuels production, it is used to quantify the environmental impacts along with the biofuels production recently. In LCA, environmental issues such as GHG emissions, fossil fuels input, acidification, eutrophication, ecotoxicity are evaluated and assessed. A number of LCA studies for biofuels production have been reported and the majority of them focus on the net energy and GHG emissions.

Previous LCAs focused on the bioethanol production for transportation sector. In these studies, variable feedstocks have been investigated for bioethanol production including corn stover, sorghum, wheat straw, sugarcane , switch grass, cane molasses [40-45]. The life cycle assessment studies of biodiesel have been widely reported. Lardon et al. [46] conducted a comparative LCA study of a virtual facility has been undertaken to assess the energetic balance and the potential environmental impacts of the whole process chain, from the algae production to the biodiesel combustion. A pond-to-wheels life cycle assessment of algae biodiesel was conducted by Passell et al. [47] using current commercial data with two scenarios were examined: base case (using commercial data) and estimated future case. Stephenson et al. [48] conducted a lifecycle assessment comparison between hypothetical operations in either raceways or tubular photo-bioreactors for biodiesel production from algae. Dufour et al. [49] conducted a life cycle assessment of four biodiesel production systems including esterification-transesterification of waste vegetable oils (used cooking oil) and animal fats (beef tallow, poultry fat), and in situ transesterification of sewage sludge.

A number of life cycle assessments of biofuels production via fast pyrolysis have been reported [50-54]. A well-to-wheel (WTW) analysis of pyrolysis-based gasoline was conducted and compared with petroleum gasoline by Han et al. [55]. In this study, the probability distributions for key parameters were developed with data from literature for life cycle assessment uncertainty analysis of fast pyrolysis. Hsu et al. [52] has conducted the life cycle assessment for the gasoline and diesel produced via fast pyrolysis and hydroprocessing. It is found that the both gasoline and diesel basis have less GHG emissions and fewer net energy input compared to petroleum-based transportation fuels production. Fan et al. [56] compared Life cycle GHG emissions with power generated using fossil fuels and power generated using biomass direct combustion in a conventional Rankine power plant. It is found that life cycle GHG savings of 77%–99% were estimated for power generation from pyrolysis oil combustion relative to fossil fuels combustion. Fan et al. [57] also investigated the GHG emissions, criteria pollutants emissions, cumulative energy demand, fossil energy demand as well as other environmental impacts of using pyrolysis oil as produced in Eastern Quebec to replace heavy fuel oil in a heating application.

Supply Chain Optimization

Biomass is a promising energy that could mitigate the fossil energy utilization along with the GHG emissions reduction. However, one of the most important barriers in increased biomass utilization in energy supply is the cost of the respective supply chain and the technology to convert biomass into useful forms of energy [58]. Biomass has the character of high volume of low energy density which leads to the high transportation cost in the whole biofuels production supply chain design.

A number of research work focus on the design and optimization of biofuels production supply chain as a result of the unique nature of biomass feedstock [59, 60]. The general elements of the biofuels supply chain include biomass farms, storage facilities, preprocessing facilities, biorefinery facilities, transportation, and demand zones. So the decision makings in the biofuels supply chain usually consist of transportation modes, capabilities of preprocessing and biorefinery facilities, locations of preprocessing and biorefinery facilities. Concepts of economic and environmental impacts are usually incorporated into the biofuels supply chain infrastructure [61-63]. For economic analysis, the net present value (NPV), the production cost, and annual profitability are usually selected as the objective function for economic optimization of biofuels supply chain [64-66] while carbon or water footprint are incorporated to economic model to form a multi-objective function optimization model for optimal planning of biofuels supply chain [61, 63, 67-71]. In addition to economic and environmental considerations, social aspect such as job creation, quality of life or the number of consumer options is also incorporated in several biofuels supply chain design and optimization [72, 73]. Besides, impact on traffic is also considered in the social impacts of the biofuel supply chain. Bai et al. [74] presented the research that that traffic congestion impact are incorporated into the model to decide optimal locations of biofuel refineries.

Uncertainties may impact the performance of biofuels supply chain infrastructure so many researchers incorporate various uncertainties in decision making for biofuel supply chain design and optimization. The uncertainties considered in biofuels supply chain usually include the market demands, biomass supply, price uncertainty, conversion technologies and other related uncertainties [75-79]. Stochastic models are usually developed to design biofuels supply chain with uncertainties. Gebreslassie et al. [80] presented a bicriterion, multiperiod, stochastic mixed-integer linear programming model to address the optimal design of hydrocarbon biorefinery supply chains under supply and demand uncertainties. This model implemented multicut L-shaped method to circumvent the computational burden of solving large scale problems burden of solving large scale problems and simultaneously determines the optimal network design, technology selection, capital investment, production planning, and logistics management decisions. Osmani and Zhang [81] presented one two-stage stochastic model for maximizing profit of a multi-feedstock lignocellulosic-based bioethanol supply chain with multiple uncertainties in switchgrass yield, crop residue purchase price, bioethanol demand, and bioethanol sale price. They found that stochastic parameters significantly affect marginal land allocation for switchgrass cultivation and bioethanol production but location of biorefineries is found to be insensitive to the stochastic environment [81]. Kazemzadeh and Hu [82] developed a two-stage stochastic programming models in which Conditional

Value at Risk (CVaR) is utilized as a risk measure to control the amount of shortage in demand zones for biofuels supply chain. Using this model, they determined the optimal design of supply chain for biofuel refineries in order to maximize annual profit considering uncertainties in fuel market price, feedstock yield, and logistic costs [82].

Dissertation Organization

This dissertation is to develop an integrated assessment platform for biofuels production via fast pyrolysis. It is composed of five chapters in addition to the introduction and conclusions. Chapter 3 describes the integrated assessment platform for biofuels production using fast pyrolysis with two bio-oil upgrading pathways as the case study. Chapter 4 provides a comparative techno-economic analysis based on the two bio-oil upgrading pathway. Chapter 5 and Chapter 6 present the life cycle assessments for the two upgrading pathways, respectively. Chapter 7 develops a multi-objective optimization model to design and optimize the supply chain of commodity chemicals production pathway including environmental and economic considerations.

References

[1] G. Berndes, M. Hoogwijk, R. van den Broek, The contribution of biomass in the future global energy supply: a review of 17 studies, Biomass and Bioenergy, 25 (2003) 1-28.

[2] S.N. Naik, V.V. Goud, P.K. Rout, A.K. Dalai, Production of first and second generation biofuels: A comprehensive review, Renewable and Sustainable Energy Reviews, 14 (2010) 578-597.

[3] IEA Bioenergy, From 1st to 2nd generation biofuel technologies -An review of current industry and R&D activities, 2008. (Available at: http://www.iea.org/publications/freepublications/publication/2nd_Biofuel_Gen.pdf)

[4] F. Cherubini, The biorefinery concept: Using biomass instead of oil for producing energy and chemicals, Energy Conversion and Management, 51 (2010) 1412-1421.

[5] R.L. Bain, An Introduction to Biomass Thermochemical Conversion, 2004. (Available at: http://www.nrel.gov/docs/gen/fy04/36831e.pdf)

[6] A. Kumar, D. Jones, M. Hanna, Thermochemical Biomass Gasification: A Review of the Current Status of the Technology, Energies, 2 (2009) 556-581.

[7] P.E. Savage, R.B. Levine, C.M. Huelsman, Chapter 8 Hydrothermal Processing of Biomass, in: Thermochemical Conversion of Biomass to Liquid Fuels and Chemicals, The Royal Society of Chemistry, (2010) 192-221.

[8] H.B. Goyal, D. Seal, R.C. Saxena, Bio-fuels from thermochemical conversion of renewable resources: A review, Renewable and Sustainable Energy Reviews, 12 (2008) 504-517.

[9] R.M. Swanson, A. Platon, J.A. Satrio, R.C. Brown, Techno-economic analysis of biomass-to-liquids production based on gasification, Fuel, 89 S11-S19.

[10] F. Trippe, M. Fröhling, F. Schultmann, R. Stahl, E. Henrich, Techno-economic assessment of gasification as a process step within biomass-to-liquid (BtL) fuel and chemicals production, Fuel Processing Technology, 92 (2011) 2169-2184.

[11] H.F. Gerçel, Production and characterization of pyrolysis liquids from sunflower-pressed bagasse, Bioresource Technology, 85 (2002) 113-117.

[12] A.V. Bridgwater, D. Meier, D. Radlein, An overview of fast pyrolysis of biomass, Organic Geochemistry, 30 (1999) 1479-1493.

[13] D. Mohan, C.U. Pittman, P.H. Steele, Pyrolysis of Wood/Biomass for Bio-oil: A Critical Review, Energy & Fuels, 20 (2006) 848-889.

[14] S. Czernik, A.V. Bridgwater, Overview of Applications of Biomass Fast Pyrolysis Oil, Energy & Fuels, 18 (2004) 590-598.

[15] R.C. Brown, J. Holmgren, Fast Pyrolysis and Bio-Oil Upgrading, 2009. (Avaialble at: http://www.ars.usda.gov/sp2UserFiles/Program/307/biomasstoDiesel/RobertBrown&JeniferHolmgrenpresentationslides.pdf)

[16] A.V. Bridgwater, Review of fast pyrolysis of biomass and product upgrading, Biomass and Bioenergy, 38 (2012) 68-94.

[17] H.S. Heo, H.J. Park, Y.-K. Park, C. Ryu, D.J. Suh, Y.-W. Suh, J.-H. Yim, S.-S. Kim, Bio-oil production from fast pyrolysis of waste furniture sawdust in a fluidized bed, Bioresource Technology, 101 (2010) S91-S96.

[18] K. Wang, R.C. Brown, S. Homsy, L. Martinez, S.S. Sidhu, Fast pyrolysis of microalgae remnants in a fluidized bed reactor for bio-oil and biochar production, Bioresource Technology, 127 (2013) 494-499.

[19] A.A. Boateng, D.E. Daugaard, N.M. Goldberg, K.B. Hicks, Bench-Scale Fluidized-Bed Pyrolysis of Switchgrass for Bio-Oil Production†, Industrial & Engineering Chemistry Research, 46 (2007) 1891-1897.

[20] J. Zheng, Bio-oil from fast pyrolysis of rice husk: Yields and related properties and improvement of the pyrolysis system, Journal of Analytical and Applied Pyrolysis, 80 (2007) 30-35.

[21] H. Zhang, R. Xiao, H. Huang, G. Xiao, Comparison of non-catalytic and catalytic fast pyrolysis of corncob in a fluidized bed reactor, Bioresource Technology, 100 (2009) 1428-1434.

[22] V. Paasikallio, F. Agblevor, A. Oasmaa, J. Lehto, J. Lehtonen, Catalytic Pyrolysis of Forest Thinnings with ZSM-5 Catalysts: Effect of Reaction Temperature on Bio-oil Physical Properties and Chemical Composition, Energy & Fuels, 27 (2013) 7587-7601.

[23] Y.-T. Cheng, J. Jae, J. Shi, W. Fan, G.W. Huber, Production of Renewable Aromatic Compounds by Catalytic Fast Pyrolysis of Lignocellulosic Biomass with Bifunctional Ga/ZSM-5 Catalysts, Angewandte Chemie International Edition, 51 (2012) 1387-1390.

[24] H. Zhang, R. Xiao, B. Jin, D. Shen, R. Chen, G. Xiao, Catalytic fast pyrolysis of straw biomass in an internally interconnected fluidized bed to produce aromatics and olefins: Effect of different catalysts, Bioresource Technology, 137 (2013) 82-87.

[25] E. Gnansounou, A. Dauriat, Techno-economic analysis of lignocellulosic ethanol: A review, Bioresource Technology, 101 (2010) 4980-4991.

[26] F.K. Kazi, J.A. Fortman, R.P. Anex, D.D. Hsu, A. Aden, A. Dutta, G. Kothandaraman, Techno-economic comparison of process technologies for biochemical ethanol production from corn stover, Fuel, 89, Supplement 1 (2010) S20-S28.

[27] C.N. Hamelinck, G.v. Hooijdonk, A.P.C. Faaij, Ethanol from lignocellulosic biomass: techno-economic performance in short-, middle- and long-term, Biomass and Bioenergy, 28 (2005) 384-410.

[28] P. Sassner, M. Galbe, G. Zacchi, Techno-economic evaluation of bioethanol production from three different lignocellulosic materials, Biomass and Bioenergy, 32 (2008) 422-430.

[29] C. Piccolo, F. Bezzo, A techno-economic comparison between two technologies for bioethanol production from lignocellulose, Biomass and Bioenergy, 33 (2009) 478-491.

[30] D. Humbird, R. Davis, L. Tao, C. Kinchin, D. Hsu, A. Aden, P. Schoen, J. Lukas, B. Olthof, M. Worley, D. Sexton, D. Dudgeon, Process Design and Economics for Biochemical Conversion of Lignocellulosic Biomass to Ethanol: Dilute-Acid Pretreatment and Enzymatic Hydrolysis of Corn Stover, 2011. NREL/TP-5100-47764 (Available at: http://www.nrel.gov/biomass/pdfs/47764.pdf)

[31] R. Wooley, M. Ruth, J. Sheehan, K. Ibsen, H. Majdeski, A. Galvez, Lignocellulosic Biomass to Ethanol Process Design and Economics Utilizing Co-Current Dilute Acid Prehydrolysis and Enzymatic Hydrolysis Current and Futuristic Scenarios, 2009. NREL/TP-580-26157 (Available at: http://www.nrel.gov/docs/fy99osti/26157.pdf)

[32] A. Dutta, M. Talmadge, J. Hensley, M. Worley, D. Dudgeon, D. Barton, P. Groendijk, D. Ferrari, B. Stears, E.M. Searcy, C.T. Wright, J. Hess, Process Design and Economics for Conversion of Lignocellulosic Biomass to Ethanol: Thermochemical Pathway by Indirect Gasification and Mixed Alcohol Synthesis, 2011. NREL/TP-5100-51400 (Available at: http://www.nrel.gov/biomass/pdfs/51400.pdf)

[33] A. Dutta, S.D. Phillips, Thermochemical Ethanol via Direct Gasification and Mixed Alcohol Synthesis of Lignocellulosic Biomass, 2009. NREL/TP-510-45913 (Available at: http://www.cfr.washington.edu/classes.pse.487/Thermochemical Ethanol via Direct Gasification and Mixed Alcohol Synthesis of Lignocellulosic Biomass.pdf)

[34] S.D. Phillips, Technoeconomic Analysis of a Lignocellulosic Biomass Indirect Gasification Process To Make Ethanol via Mixed Alcohols Synthesis, Industrial & Engineering Chemistry Research, 46 (2007) 8887-8897.

[35] J. He, W. Zhang, Techno-economic evaluation of thermo-chemical biomass-to-ethanol, Applied Energy, 88 (2011) 1224-1232.

[36] M.M. Wright, D.E. Daugaard, J.A. Satrio, R.C. Brown, Techno-economic analysis of biomass fast pyrolysis to transportation fuels, Fuel, 89 (2010) S2-S10.
[37] S.B. Jones, C. Valkenburg, C.W. Walton, D.C. Elliott, J.E. Holladay, D.J. Stevens, C. Kinchin, S. Czernik, Production of Gasoline and Diesel from Biomass via Fast Pyrolysis, Hydrotreating and Hydrocracking: A Design Case, 2009.(Available at: http://www.pnl.gov/main/publications/external/technical_reports/pnnl-18284.pdf)

[38] M.N. Islam, F.N. Ani, Techno-economics of rice husk pyrolysis, conversion with catalytic treatment to produce liquid fuel, Bioresource Technology, 73 (2000) 67-75.

[39] R.P. Anex, A. Aden, F.K. Kazi, J. Fortman, R.M. Swanson, M.M. Wright, J.A. Satrio, R.C. Brown, D.E. Daugaard, A. Platon, G. Kothandaraman, D.D. Hsu, A. Dutta, Techno-economic comparison of biomass-to-transportation fuels via pyrolysis, gasification, and biochemical pathways, Fuel, 89, Supplement 1 (2010) S29-S35.

[40] A.L. Borrion, M.C. McManus, G.P. Hammond, Environmental life cycle assessment of bioethanol production from wheat straw, Biomass and Bioenergy, 47 (2012) 9-19.

[41] H. Cai, J. Dunn, Z. Wang, J. Han, M. Wang, Life-cycle energy use and greenhouse gas emissions of production of bioethanol from sorghum in the United States, Biotechnol Biofuels, 6 (2013) 141.

[42] M. Amores, F. Mele, L. Jiménez, F. Castells, Life cycle assessment of fuel ethanol from sugarcane in Argentina, Int J Life Cycle Assess, 18 (2013) 1344-1357.

[43] S. Spatari, Y. Zhang, H.L. MacLean, Life Cycle Assessment of Switchgrass- and Corn Stover-Derived Ethanol-Fueled Automobiles, Environmental Science & Technology, 39 (2005) 9750-9758.

[44] T. Nguyen, S. Gheewala, Life cycle assessment of fuel ethanol from cane molasses in Thailand, Int J Life Cycle Assess, 13 (2008) 301-311.

[45] L. Luo, E. Voet, G. Huppes, H. Udo de Haes, Allocation issues in LCA methodology: a case study of corn stover-based fuel ethanol, Int J Life Cycle Assess, 14 (2009) 529-539.

[46] L. Lardon, A. Hélias, B. Sialve, J.-P. Steyer, O. Bernard, Life-Cycle Assessment of Biodiesel Production from Microalgae, Environmental Science & Technology, 43 (2009) 6475-6481.

[47] H. Passell, H. Dhaliwal, M. Reno, B. Wu, A. Ben Amotz, E. Ivry, M. Gay, T. Czartoski, L. Laurin, N. Ayer, Algae biodiesel life cycle assessment using current commercial data, Journal of Environmental Management, 129 (2013) 103-111.

[48] A.L. Stephenson, E. Kazamia, J.S. Dennis, C.J. Howe, S.A. Scott, A.G. Smith, Life-Cycle Assessment of Potential Algal Biodiesel Production in the United Kingdom: A Comparison of Raceways and Air-Lift Tubular Bioreactors, Energy & Fuels, 24 (2010) 4062-4077.

[49] J. Dufour, D. Iribarren, Life cycle assessment of biodiesel production from free fatty acid-rich wastes, Renewable Energy, 38 (2012) 155-162.

[50] Z. Wang, J.B. Dunn, J. Han, M.Q. Wang, Effects of co-produced biochar on life cycle greenhouse gas emissions of pyrolysis-derived renewable fuels, Biofuels, Bioproducts and Biorefining, (2013). DOI: 10.1002/bbb.1447

[51] D. Iribarren, J.F. Peters, J. Dufour, Life cycle assessment of transportation fuels from biomass pyrolysis, Fuel, 97 (2012) 812-821.

[52] D.D. Hsu, Life cycle assessment of gasoline and diesel produced via fast pyrolysis and hydroprocessing, Biomass and Bioenergy, 45 (2012) 41-47.

[53] Z.W. Zhong, B. Song, M.B.M. Zaki, Life-cycle assessment of flash pyrolysis of wood waste, Journal of Cleaner Production, 18 (2010) 1177-1183.

[54] N. Kauffman, D. Hayes, R. Brown, A life cycle assessment of advanced biofuel production from a hectare of corn, Fuel, 90 (2011) 3306-3314.

[55] J. Han, A. Elgowainy, J.B. Dunn, M.Q. Wang, Life cycle analysis of fuel production from fast pyrolysis of biomass, Bioresource Technology, 133 (2013) 421-428.

[56] J. Fan, T.N. Kalnes, M. Alward, J. Klinger, A. Sadehvandi, D.R. Shonnard, Life cycle assessment of electricity generation using fast pyrolysis bio-oil, Renewable Energy, 36 (2011) 632-641.

[57] J. Fan, D. Shonnard, T. Kalnes, M. Streff, G. Hopkins, Emission Reduction Using RTP Green Fuel in Industry Facilities: A Life Cycle Study, Energy & Fuels, 27 (2013) 5260-5267.

[58] A.A. Rentizelas, A.J. Tolis, I.P. Tatsiopoulos, Logistics issues of biomass: The storage problem and the multi-biomass supply chain, Renewable and Sustainable Energy Reviews, 13 (2009) 887-894.

[59] S. Sokhansanj, A. Kumar, A.F. Turhollow, Development and implementation of integrated biomass supply analysis and logistics model (IBSAL), Biomass and Bioenergy, 30 (2006) 838-847.

[60] A. Kumar, S. Sokhansanj, Switchgrass (Panicum vigratum, L.) delivery to a biorefinery using integrated biomass supply analysis and logistics (IBSAL) model, Bioresource Technology, 98 (2007) 1033-1044.

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

[62] A. Zamboni, R.J. Murphy, J. Woods, F. Bezzo, N. Shah, Biofuels carbon footprints: Whole-systems optimisation for GHG emissions reduction, Bioresource Technology, 102 (2011) 7457-7465.

[63] A. Bernardi, S. Giarola, F. Bezzo, Optimizing the economics and the carbon and water footprints of bioethanol supply chains, Biofuels, Bioproducts and Biorefining, 6 (2012) 656-672.

[64] W. Alex Marvin, L.D. Schmidt, S. Benjaafar, D.G. Tiffany, P. Daoutidis, Economic Optimization of a Lignocellulosic Biomass-to-Ethanol Supply Chain, Chemical Engineering Science, 67 (2012) 68-79.

[65] I.M. Bowling, J.M.a. Ponce-Ortega, M.M. El-Halwagi, Facility Location and Supply Chain Optimization for a Biorefinery, Industrial & Engineering Chemistry Research, 50 (2011) 6276-6286.

[66] Y. Huang, C.-W. Chen, Y. Fan, Multistage optimization of the supply chains of biofuels, Transportation Research Part E: Logistics and Transportation Review, 46 (2010) 820-830.

[67] F. You, B. Wang, Life Cycle Optimization of Biomass-to-Liquid Supply Chains with Distributed–Centralized Processing Networks, Industrial & Engineering Chemistry Research, 50 (2011) 10102-10127.

[68] D. Yue, M.A. Kim, F. You, 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 & Engineering, 1 (2013) 1003-1014.

[69] A. Zamboni, F. Bezzo, N. Shah, Spatially Explicit Static Model for the Strategic Design of Future Bioethanol Production Systems. 2. Multi-Objective Environmental Optimization, Energy & Fuels, 23 (2009) 5134-5143.

[70] L. Čuček, P.S. Varbanov, J.J. Klemeš, Z. Kravanja, Total footprints-based multi-criteria optimisation of regional biomass energy supply chains, Energy, 44 (2012) 135-145.

[71] K.B. Aviso, R.R. Tan, A.B. Culaba, J.B. Cruz Jr, Fuzzy input–output model for optimizing eco-industrial supply chains under water footprint constraints, Journal of Cleaner Production, 19 (2011) 187-196.

[72] A. Kumar, S. Sokhansanj, P. Flynn, Development of a multicriteria assessment model for ranking biomass feedstock collection and transportation systems, Appl Biochem Biotechnol, 129 (2006) 71-87.

[73] H. Safaei Mohamadabadi, G. Tichkowsky, A. Kumar, Development of a multi-criteria assessment model for ranking of renewable and non-renewable transportation fuel vehicles, Energy, 34 (2009) 112-125.

[74] Y. Bai, T. Hwang, S. Kang, Y. Ouyang, Biofuel refinery location and supply chain planning under traffic congestion, Transportation Research Part B: Methodological, 45 (2011) 162-175.

[75] M. Dal-Mas, S. Giarola, A. Zamboni, F. Bezzo, Strategic design and investment capacity planning of the ethanol supply chain under price uncertainty, Biomass and Bioenergy, 35 (2011) 2059-2071.

[76] J. Kim, M.J. Realff, J.H. Lee, Optimal design and global sensitivity analysis of biomass supply chain networks for biofuels under uncertainty, Computers & Chemical Engineering, 35 (2011) 1738-1751.

[77] C.-W. Chen, Y. Fan, Bioethanol supply chain system planning under supply and demand uncertainties, Transportation Research Part E: Logistics and Transportation Review, 48 (2012) 150-164.

[78] B.H. Gebreslassie, Y. Yuan, Y. Fengqi, Multiobjective optimization of hydrocarbon biorefinery supply chain designs under uncertainty, in: Decision and Control (CDC), 2012 IEEE 51st Annual Conference on, 2012, pp. 5560-5565.

[79] A. Osmani, J. Zhang, Economic and environmental optimization of a large scale sustainable dual feedstock lignocellulosic-based bioethanol supply chain in a stochastic environment, Applied Energy, 114 (2014) 572-587.

[80] B.H. Gebreslassie, Y. Yao, F. You, Design under uncertainty of hydrocarbon biorefinery supply chains: Multiobjective stochastic programming models, decomposition algorithm, and a Comparison between CVaR and downside risk, AIChE Journal, 58 (2012) 2155-2179.

[81] A. Osmani, J. Zhang, Stochastic optimization of a multi-feedstock lignocellulosic-based bioethanol supply chain under multiple uncertainties, Energy, 59 (2013) 157-172.

[82] N. Kazemzadeh, G. Hu, Optimization models for biorefinery supply chain network design under uncertainty, Journal of Renewable and Sustainable Energy, 5 (2013). (Available at: http://dx.doi.org/10.1063/1.4822255)

CHAPTER II

BACKGROUND

Methodology

This dissertation involves the development of a generalized methodology for the integrated assessment of bioenergy systems using separate modules to evaluate process engineering, economic feasibility, logistics of supply, and environmental impact within a general framework. Specific emphasis on process design and simulation, techno-economic analysis, life-cycle assessment, and logistic optimization for bioenergy systems are investigated in the integrated assessment platform. An integrated assessment methodology serves as a decision making tool for assessing the commercialization prospects of bioenergy systems, enabling more rational and efficient resource utilization and accelerating the diffusion of bioenergy technologies in the U.S. The integrated assessment of bioenergy systems is presented in Figure 1.

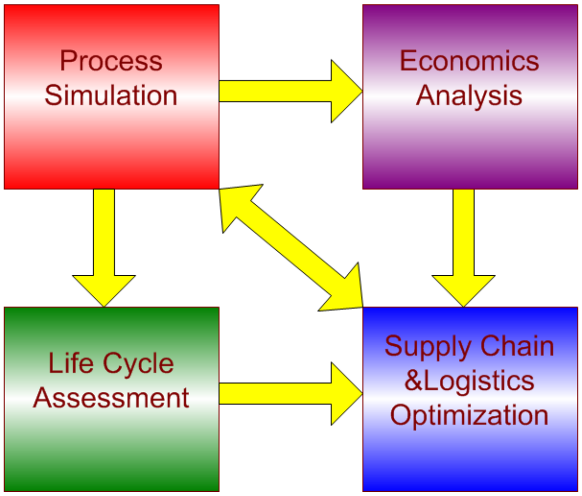


Figure 1. Modular components for the biofuels integrated assessment platform.

The basic modules are incorporated in the integrated assessment platform, which included four modules: process simulation (module A), economics analysis (module B), life cycle assessment (module C), and supply chain &logistics optimization (module D). The four modules are depending on each other which make a general system.

To better illustrate the methodology, Figure 2 is employed to describe the detailed flows for the biofuel integrated assessment platform. The four modules are presented in different dashed boxes.

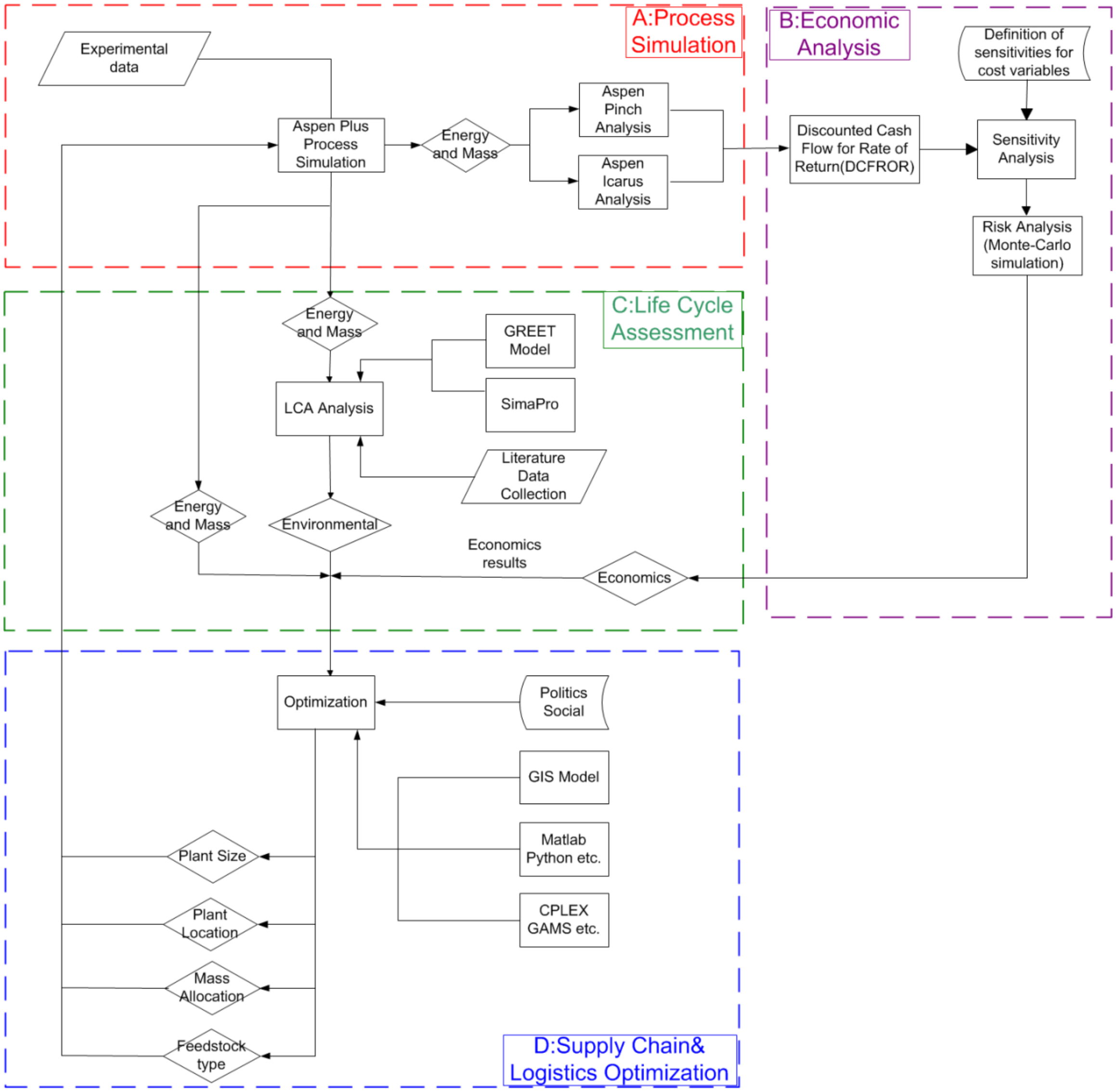


Figure 2. Flow chart of biofuels integrated assessment platform.

Process Simulation

Module A is a chemicals process model used to help design, test, optimize, and integrate concepts for processing of biomass. The proposed chemical process is presented as a process flow diagram (PFD), drawing with boxes representing process units and lines representing process streams. After the PFD is drawn, the process simulation software (e.g., Aspen Plus, ChemCAD) is employed to configure the simulation model. Based on the number of components (the chemicals and other materials used in the process), process equipment, input and output streams, the mass and energy balance is calculated. The operating parameters (e.g., temperature, pressure) based on results from engineering studies, experiment, and estimates for commercial technologies. Also the experimental data could be cooperated into the process models to validate the reactor data such as pyrolysis yield data. After the mass and energy balance calculations are converged in the process modeling software, the mass and energy data for the biofuels production pathway could be derived from the process modeling. These mass and energy data are the essential data for the whole integrated assessment platform. They could be further used to estimate the process utilities through other software (e.g., Aspen Pinch). Usually the utilities such as process water for cooling down the streams and the required heat for heating the stream to specific temperatures are calculated for economic analysis. Using the PFDs and the mass and energy balance information, equipment costs are estimated based on a combination of sources such as vendor quotations, cost scaling, and cost estimation software (e.g., Aspen Icarus). Vendor quotations are the most accurate cost estimation the vendor quotations. Equipment cost could be estimated by cost estimation software once the related information is specified such as size, operating parameters, and equipment materials. Cost scaling method could be used if the same processes with different plant sizes have been examined before. For each specific equipment type, there is a scaling factor based on the mass flow. Details about cost scaling are presented in Chapter 3.

Economic Analysis

In module B, the economics analysis is conducted for biofuels production. This economic analysis is a typical engineering economics analysis, which applies economic techniques to evaluate the design and engineering alternatives [1]. The role of engineering economics is to assess the appropriateness of a given project, estimate its value, and justify it from an engineering standpoint [2]. Discounted Cash Flow Rate of Return (DCFROR) method is employed to conduct the engineering economics analysis. The mass, energy, utilities, and equipment cost data from process simulation (model A) could be used as the inputs for DCFROR model, where the production cost or facility IRR could be estimated. The costs considered in the engineering economic estimation include the capital costs, revenues, fixed operating costs and variable operating costs. The capital costs include the direct and indirect capital cost. The fixed operating costs usually include the salaries, overheads, and maintenance fees etc. The viable operating costs usually contain the utilities costs (e.g., electricity, steam, process water), raw materials (e.g. biomass), and operating materials costs (e.g. catalysts, chemicals, waste disposal). A detailed economic analysis method description is presented in Chapter 3. From the discounted cash flow analysis, net present value could be obtained for the project. Then the production cost could be obtained (which is also known as the minimum selling price) to set the zero net present value. The minimum selling price (MSP) is usually calculated based on a fixed interest rate (e.g., 10%). In addition to MSP, facility IRR also could be examined based on the fixed value of the products with zero net present value. After baseline results are obtained, several sensitive parameters could be selected for the sensitivity analysis of the biofuels production pathway. The selections of the parameters are based on the empirical observations or the data in the literatures.

The risk analysis could also be conducted using Monte-Carlo simulation based on the sensitivity analysis results. For sensitivity analysis, there is only one change parameter each time. But Monte-Carlo simulation relies on repeated random sampling to obtain numerical results. A large quantity of scenarios could be generated due to the changing of these parameters. Here Crystal Ball software could be used to build on existing Monte Carlo and predictive modeling tools. Also statistic software (e.g., R, JMP, and SAS) could be used to interpret the Monte-Carlo simulation results such as data distribution or cumulative probability. This will illustrate the significance of project investment risk in current technologies.

Life Cycle Assessment

A life cycle assessment (LCA) is the assessment of the environmental impact of a given product throughout its lifespan [3]. There are four phases for life cycle assessment: definition of the goal and scope of the LCA, life cycle inventory analysis, life cycle impact assessment, and life cycle interpretation [3]. In the phase of definition of the goal and scope, the definition of functional unit could provide a suitable comparison criterion for alternative products or services. Based on the functional unit, alternatives products could be compared in quantities. The scope of a LCA is related to the level of sophistication for the goal of the study. In the phase of life cycle inventory, each process for a product system requires an input and produces an output, creating inventory flows. Inputs of water, energy, and raw materials, and releases to air, soil, and water are considered in inventory flows of LCA. Also the system boundary and allocation method should be selected accurately based on the goal and scope of particular LCA study. After the first two phases, life cycle impact assessment and life cycle interpretation could be conducted. The phase of life cycle impact assessment is conducted to evaluate the potential environmental impacts based on the life cycle inventory results. Three steps are included in the life cycle assessment: classification, characterization, and valuation. In the classification, all environmental impacts are classified according to their contributions to the categories of environmental problems (e.g., global warming, human toxicity, ozone depletion, resources depletion). In the characterization, the contributions to the environmental problem are quantified. It is not easy to compare the contributions to different categories of environmental problems since they have different quantity units. Therefore a normalization step is usually included in the characterization, from which all environmental problems are normalized to the standard unit for convenient comparison. The last step of valuation involves the overall comparison of the environmental problems. The single environmental index is used to weight each environmental problem. The scores of each environmental problems are multiplied by their weighting factor and can be added together to provide an overall environmental index. In the life cycle interpretation, all the results from life cycle inventory and life cycle impact assessment are summarized to draw conclusions and make recommendations to the sustainable development. This phase is the basis process for the decision makers considering the environmental aspects for products.

Module C is a life cycle assessment module, where the environmental impacts such as carbon footprint or fossil energy demand are estimated for the selected biofuels production pathway. Life cycle assessment software such as SimaPro could be used to develop and link primary unit processes related to the current chemicals production pathway. Materials and energy associated with the unit processes are collected as the inventory data which is set as primary materials and energy in SimaPro. Then the built-in databases in SimaPro provide life cycle inventories for secondary materials and energy required in those primary unit processes. The required primary materials and energy inputs associated with the unit processes of the LCA is a combination of the energy and mass data derived from the process modeling, GREET (Greenhouse gases, Regulated Emissions, and Energy use in Transportation) [4] model and related literatures.

Supply Chain & Logistics Optimization

A supply chain is an integrated manufacturing process wherein raw materials are converted into final products, then delivered to customers [5]. A supply chain at its highest level is consists of two integrated processes: (1) the production planning and inventory control process, and (2) the distribution and logistics process[5]. Supply chain optimization is an important component in supply chain design since it will determine how an effective supply chain design is achieved based on performance measures [5]. Biomass energy is complicated due to the bulky, distributed nature of biomass feedstocks and the high volumes of the relatively low energy density materials that have to be moved to the conversion equipment [6]. So the supply chain and logistic activities related to biorefinery processes play an important role in the infrastructure of biofuels industry. The unique natural of biomass leads to the development of sustainable biofuels and biomass supply chain system. Thus, supply chain and logistics activities (e.g., biomass collection, delivery planning, and freight forwarder and delivery mode) selection should be optimized to achieve a profitable and sustainable supply chain of biofuels. For supply chain& logistics optimization, the performance measures should be clearly defined, expressed as the objective function. In biofuels supply chain modeling, the objective function is expressed as functions of one or more decision variables. The decision variables usually contain the feedstocks types, mass allocation, plant size, delivery modes etc. The objective of the biofuels supply chain is usually to minimize the total cost or maximize the profitability along with the whole supply chain of biofuels industry. Some environmental or social considerations may also be incorporated into the biofuels supply chain design such as minimizing the total carbon footprint or maximize the created jobs [7]. The constrains for biofuel supply chain design and optimization usually include the mass and energy balances, capacity allowance, budget constraints , supply and demand constrains and so on.

Module D is logistic optimization, where the supply chain of the biofuels production is optimized. In this module, the input data are from module A, B, and C, which combine the mass, energy, economic, and environmental data together for multi objective optimization. The politics considerations can be also added to the constraints of the optimization problem such as carbon tax or RFS2 issues. In module D, mathematical programming software is used to process the data (e.g., Matlab, Python) and the GIS software is used for data availability exploration for the feedstocks. The optimization software (e.g., CPLEX or Gurobi) could be employed to solve this logistic problem. Through module D, the plant size, plant location, mass allocation or feedstock type can be optimized. This could be used as a feedback for the module A which designs and simulates the proposed biofuels production pathways. For logistic optimization, variable mathematical models could be used to optimize the logistic problem such as linear programing, non-linear programing, stochastic programming, multi-objective programming etc. The mathematical model selections should be based on the characters of the optimization problems.

Case Study

The methodology is generalizable and can be extended to the integrated assessment of other bio-fuel production pathways. In this dissertation, the specific instance of production of drop-in biofuels or chemicals using fast pyrolysis and upgrading is employed as the case study to examine this methodology. Recently, fast pyrolysis has attracted considerable interest as a means for converting biomass into valuable fuels or energy. At this time fast pyrolysis appears to be more economically viable than gasification and fermentation processes [8]. Fast pyrolysis can generate up to 75 wt.% of liquid bio-oil, which can then be used in various applications such as transportation, heating, and electricity generation [9]. A variety of products can be produced through bio-oil upgrading, including hydrogen, transportation fuels, and sugars [10-15]. While researchers work to incorporate fast pyrolysis into their development of biorefinery concepts, they are simultaneously investigating the conversion of bio-oil into chemicals through versatile upgrading processes. With the addition of water to the pyrolysis oil, the pyrolysis oil can be separated into an aqueous phase and a water-insoluble phase. Technologies such as aqueous phase processing and catalytic pyrolysis processing are used to convert the bio-oil or its fraction into valuable chemicals [16-18]. Researchers have also found that olefins and aromatics (i.e., benzene, toluene, xylene) can be generated through FCC of hydrotreated bio-oil over zeolite catalysts [10, 19-25]. Through hydrotreating, the bio-oil is deoxygenated to produce a partially-upgraded oil with reduced oxygen content and improved stability [26]. Vispute et al. [27] combined a two-stage hydrotreating process with FCC to form an integrated catalytic process for the high-yield production of green commodity chemicals (i.e., olefins and aromatics). The team found that integrated catalytic processing of aqueous-phase bio-oil has higher carbon selectivity for commodity chemicals production when compared to simple FCC of the whole bio-oil or FCC of one-stage hydrotreated bio-oil [27].

So two different bio-oil upgrading pathways are examined using this integrated assessment platform. One is the FCC of hydrotreated water-soluble bio-oil to produce commodity chemicals as stated by Vispute et al. [27] and the other is hydrotreating/hydrocracking the bio-oil to produce hydrogen and transportation fuels. The technology details related to the two upgrading pathways are presented in Chapter 3-6. In Chapter 3, techno-economic analysis has been done for the two different upgrading pathways. Chapter 4 evaluated the environment impacts of co-generation of hydrogen and transportation fuels via corn stover fast pyrolysis with hydrotreating/hydrocracking pathways. Chapter 5 evaluated the environment impacts of commodity chemicals production from forest residue fast pyrolysis and hydrotreating/FCC pathway. Finally, Chapter 6 combines the results from Chapter3-5 and developed a multi-objective optimization model to design and optimize the supply chain of commodity chemicals production.

References

[1] ASTM E833, Definitions of Terms Relating to Building Economics, American Society for Testing and Materials, West Conshohocken,PA (1999).

[2] J.M. Watts, R.E. Chapman, Engineering Economics. (Available at: http://fire.nist.gov/bfrlpubs/build02/PDF/b02155.pdf)

[3] ISO, Environmental management -- Life cycle assessment -- Principles and framework, (2006).

[4] Argone National Laboratory, The greenhouse gases, regulated emissions, and energy use in tranportation (GREET) model, 2011. (Available at: http://greet.es.anl.gov/)

[5] B.M. Beamon, Supply chain design and analysis:: Models and methods, International Journal of Production Economics, 55 (1998) 281-294.

[6] J. Tallaksen, Biomass Gasification: A Comprehensive Demonstration of a Community Scale Biomass Energy System -Chapter 6: Guidelines for Developing a Sustainable Biomass, 2011.(Available at: http://renewables.morris.umn.edu/biomass/documents/USDA_Report/SII_SupplyChain.pdf)

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

[8] R.P. Anex, A. Aden, F.K. Kazi, J. Fortman, R.M. Swanson, M.M. Wright, J.A. Satrio, R.C. Brown, D.E. Daugaard, A. Platon, G. Kothandaraman, D.D. Hsu, A. Dutta, Techno-economic comparison of biomass-to-transportation fuels via pyrolysis, gasification, and biochemical pathways, Fuel, 89, Supplement 1 (2010) S29-S35.

[9] S. Czernik, A.V. Bridgwater, Overview of Applications of Biomass Fast Pyrolysis Oil, Energy & Fuels, 18 (2004) 590-598.

[10] A.V. Bridgwater, Review of fast pyrolysis of biomass and product upgrading, Biomass and Bioenergy, 38 (2012) 68-94.

[11] S. Czernik, R. Evans, R. French, Hydrogen from biomass-production by steam reforming of biomass pyrolysis oil, Catalysis Today, 129 (2007) 265-268.

[12] N. Kuzhiyil, D. Dalluge, X. Bai, K.H. Kim, R.C. Brown, Pyrolytic Sugars from Cellulosic Biomass, ChemSusChem, 5 (2012) 2228-2236.

[13] Z. Luo, S. Wang, Y. Liao, J. Zhou, Y. Gu, K. Cen, Research on biomass fast pyrolysis for liquid fuel, Biomass and Bioenergy, 26 (2004) 455-462.

[14] Y. Zhang, T.R. Brown, G. Hu, R.C. Brown, Techno-economic analysis of monosaccharide production via fast pyrolysis of lignocellulose, Bioresource Technology, 127 (2013) 358-365.

[15] Y. Zhang, T.R. Brown, G. Hu, R.C. Brown, Comparative techno-economic analysis of biohydrogen production via bio-oil gasification and bio-oil reforming, Biomass and Bioenergy, 51 (2013) 99-108.

[16] T.P. Vispute, G.W. Huber, Production of hydrogen, alkanes and polyols by aqueous phase processing of wood-derived pyrolysis oils, Green Chemistry, 11 (2009) 1433-1445.

[17] J. Fu, S. Hakim, B. Shanks, Aqueous-Phase Processing of Bio-oil Model Compounds Over Pt–Re Supported on Carbon, Top Catal, 55 (2012) 140-147.

[18] Y. Zhao, L. Deng, B. Liao, Y. Fu, Q.-X. Guo, Aromatics Production via Catalytic Pyrolysis of Pyrolytic Lignins from Bio-Oil, Energy & Fuels, 24 (2010) 5735-5740.

[19] T.R. Carlson, T.P. Vispute, G.W. Huber, Green Gasoline by Catalytic Fast Pyrolysis of Solid Biomass Derived Compounds, ChemSusChem, 1 (2008) 397-400.

[20] T.R. Carlson, Y.-T. Cheng, J. Jae, G.W. Huber, Production of green aromatics and olefins by catalytic fast pyrolysis of wood sawdust, Energy & Environmental Science, 4 (2011) 145-161.

[21] K. Giannakopoulou, M. Lukas, A. Vasiliev, C. Brunner, H. Schnitzer, Conversion of rapeseed cake into bio-fuel in a batch reactor: Effect of catalytic vapor upgrading, Microporous and Mesoporous Materials, 128 (2010) 126-135.

[22] H. Zhang, Y.-T. Cheng, T.P. Vispute, R. Xiao, G.W. Huber, Catalytic conversion of biomass-derived feedstocks into olefins and aromatics with ZSM-5: the hydrogen to carbon effective ratio, Energy & Environmental Science, 4 (2011) 2297-2307.

[23] S. Vitolo, M. Seggiani, P. Frediani, G. Ambrosini, L. Politi, Catalytic upgrading of pyrolytic oils to fuel over different zeolites, Fuel, 78 (1999) 1147-1159.

[24] S. Vitolo, B. Bresci, M. Seggiani, M.G. Gallo, Catalytic upgrading of pyrolytic oils over HZSM-5 zeolite: behaviour of the catalyst when used in repeated upgrading–regenerating cycles, Fuel, 80 (2001) 17-26.

[25] L. Qiang, L. Wen-zhi, Z. Dong, Z. Xi-feng, Analytical pyrolysis–gas chromatography/mass spectrometry (Py–GC/MS) of sawdust with Al/SBA-15 catalysts, Journal of Analytical and Applied Pyrolysis, 84 (2009) 131-138.

[26] D.C. Elliott, T.R. Hart, G.G. Neuenschwander, L.J. Rotness, A.H. Zacher, Catalytic hydroprocessing of biomass fast pyrolysis bio-oil to produce hydrocarbon products, Environmental Progress & Sustainable Energy, 28 (2009) 441-449.

[27] T.P. Vispute, H. Zhang, A. Sanna, R. Xiao, G.W. Huber, Renewable Chemical Commodity Feedstocks from Integrated Catalytic Processing of Pyrolysis Oils, Science, 330 (2010) 1222-1227.

CHAPTER III

TECHNO-ECONOMIC ANALYSIS OF BIOMASS FAST PYROLYSIS WITH TWO UPGRADING PATHWAYS

A paper published in Chemical Engineering Journal

Yanan Zhang, Tristan R. Brown, Guiping Hu and Robert C. Brown

Abstract

We evaluate the economic feasibility of fast pyrolysis and upgrading facilities employing either of two upgrading pathways: two-stage hydrotreating followed by a fluid catalytic cracking (FCC) stage or single-stage hydrotreating followed by a hydrocracking stage. In the hydrotreating/FCC pathway, two options are available as the hydrogen source for hydrotreating: merchant hydrogen or hydrogen from natural gas reforming. The primary products of the hydrotreating/FCC pathway are commodity chemicals whereas the primary products for the hydrotreating/hydrocracking pathway are transportation fuels and hydrogen. The two pathways are modeled using Aspen Plus® for a 2000 metric tons/day facility. Equipment sizing and cost calculations are based on Aspen Economic Evaluation® software.

The fast pyrolysis bio-oil yield is assumed to be 65% of biomass. We calculate the internal rate of return (IRR) for each pathway as a function of feedstock cost, Fixed Capital Investment (FCI), hydrogen and catalyst costs, and facility revenues. The results show that a facility employing the hydrotreating/FCC pathway with hydrogen production via natural gas reforming option generates the highest IRR of 13.3%. Sensitivity analysis demonstrates that product yield, FCI, and biomass cost have the greatest impacts on facility IRR. Monte-Carlo analysis shows that two-stage hydrotreating and FCC of the

aqueous phase bio-oil with hydrogen produced via natural gas reforming has a relatively low risk for project investment.

Introduction

Thermochemical conversion has attracted recent attention as a biorenewable pathway for its ability to produce hydrocarbons [1]. Pyrolysis, liquefaction, gasification, and combustion are frequently investigated as thermochemical pathways, and each generates a different range of products [2]. This paper investigates fast pyrolysis as a route for the production of hydrocarbon-based fuels and hydrocarbon-based commodity chemicals. A primary benefit of fast pyrolysis over other thermochemical pathways (i.e., liquefaction, gasification, combustion) is its conversion of solid biomass feedstocks to bio-oil, which is a more convenient and thus more readily marketable liquid product [3]. Bio-oil is attracting attention due to its lower sulfur and nitrogen content compared with fossil fuels [4]. Fast pyrolysis rapidly heats biomass feedstock in a high-temperature and oxygen-free environment, yielding a mix of a liquid (bio-oil, combustible gases, and solid char) [3].

Bio-oil has been considered as an alternative fuel in turbines and diesel engines or a co-firing feedstock with fossil fuels in heat and power generation plants [5], but bio-oil may also be upgraded to produce a variety of energy products, including hydrogen [6] and transportation fuels [7]. Bio-oil is a viscous and oxygenated mixture of compounds with a wide range of molecular weights. Polymeric and oligomeric bio-oil compounds must be depolymerized to yield hydrocarbons in the gasoline and diesel fuel ranges. Fast pyrolysis and upgrading facilities can utilize one of two upgrading pathways for this purpose: fluid catalytic cracking with a zeolite catalyst [8] or hydrocracking [7]. Both upgrading methods usually employ one or more hydrotreating steps to stabilize and deoxygenate the bio-oil prior to cracking.

Elliott et al. [7] found that hydrotreating to deoxygenate bio-oil greatly improves yields of hydrocarbons from hydrocracking. Hydrocracking of hydrotreated bio-oil produces alkenes (i.e., napthene) and aromatics, which are valuable molecules for transportation applications [7, 9, 10]. Vispute et al. [11] found that increasing bio-oil's hydrogen content via hydrotreating also greatly improves yields of hydrocarbons from fluid catalytic cracking (FCC). FCC of hydrotreated bio-oil produces olefins and aromatics (i.e., BTX) [12-19]. In Vispute's study, five scenarios are investigated: FCC of whole bio-oil; one-stage hydrotreating and FCC of whole bio-oil; FCC of the aqueous phase of bio-oil; one-stage hydrotreating and FCC of the aqueous phase; and two-stage hydrotreating followed by FCC of the aqueous phase. The results found that initial hydrotreating with a Ru/C catalyst at 398 K and 52 bar pressure, followed by a second, higher-temperature stage of hydrotreating with a Pt/C catalyst at 523 K and 100 bar pressure, followed finally by FCC resulted in the highest carbon selectivity for the final products. The final products of FCC of hydrotreated bio-oil include olefins and aromatics (i.e., BTX), which have high market values [20].

High carbon utilization during the conversion of bio-oil to hydrocarbons is desirable as it results in greater hydrocarbon yields. However, high utilization is generally only achieved via the consumption of large quantities of hydrogen during upgrading. Hydrogen can be produced from a number of sources: steam reforming of natural gas; coal gasification; and partial oxidation of hydrocarbons, to name a few. Steam reforming of natural gas (mainly methane) is a well-developed and important technology for large-scale hydrogen production. It typically includes natural gas desulfurization, steam methane reforming, and water gas shift processes [21]. However, the utilization of fossil fuels by a biofuel pathway increases its lifecycle Greenhouse Gas (GHG) emissions. In the U.S., which defines biofuel pathways under the revised Renewable Fuel Standard (RFS2) according to their lifecycle GHG emission reductions relative to gasoline [22], such an increase in emissions can prevent a pathway from qualifying for high-value Renewable Identification Numbers (RIN) under the RFS2.To reduce CO_2 emissions associated with hydroprocessing, production of hydrogen from biorenewable sources is of interest. Bio-oil derived from biomass fast pyrolysis consists of an aqueous phase and a water-insoluble phase. Following phase-separation, the aqueous phase can be reformed to produce the hydrogen while heavy molecules in the water-insoluble phase can be hydrocracked to lighter hydrocarbons. The aqueous phase, mostly derived from the carbohydrate in biomass, often contains highly-decomposed light compounds that are not only highly oxygenated, but often contain too few carbon atoms to permit efficient conversion to gasoline-range fuels. Thus, the aqueous phase is attractive as a source of hydrogen for upgrading through steam reforming [23]. The water-insoluble phase, mostly derived from the lignin in biomass, is attractive for upgrading because of its low oxygen-to-carbohydrate ratio [24].

Previous techno-economic analyses (TEA) have attempted to quantify the economic feasibility of each upgrading pathway [25-27]. Brown et al. [27] calculated the 20-year internal rate of return (IRR) for a facility employing two-stage hydrotreating and FCC to be as high as 14% (assuming a high bio-oil yield of 70 wt% of dry biomass).

Wright et al. [25] analyzed transportation fuels production from hydrocracking of hydrotreated bio-oil derived from biomass fast pyrolysis and estimated the minimum selling price of the transportation fuels based on that analysis. These TEAs found both the two-stage hydrotreating followed by FCC pathway and the hydrotreating followed by hydrocracking pathway to generate positive returns on investment. However, there are no TEAs in the open literature on the production of multiple products (i.e., hydrogen and transportation fuels) via upgrading of both bio-oil phases (the aqueous phase and the water-insoluble phase). Moreover, previous TEAs on fast pyrolysis and upgrading have quantified economic feasibility by calculating a minimum fuel selling price [25, 26, 28], which is less suitable than calculation of IRR for multi-year analyses due to the volatile nature of energy prices.

The objective of this paper is to provide a detailed evaluation of the economic feasibility of fast pyrolysis and upgrading facilities by analyzing two upgrading pathways: hydrotreating/FCC and hydrotreating/hydrocracking. For the hydrotreating/FCC pathway, the aqueous phase undergoes two-stage hydrotreating followed by FCC process. There is a large demand for hydrogen during the two-stage hydrotreating process for this pathway. To investigate the impact of hydrogen, two options are explored for meeting this demand: purchasing hydrogen from the market; and producing onsite hydrogen via natural gas reforming. For the hydrotreating/hydrocracking pathway, the water-insoluble phase of bio-oil undergoes one-stage hydrotreating followed by one-stage hydrocracking and the aqueous phase bio-oil is reformed to hydrogen. Both of the upgrading pathways are modeled for facilities with a capacity of 2000 metric tons per day (MTPD) of biomass feedstock. The projected prices of commodity chemicals, gasoline, and diesel fuel over a

20 year period (2011-2030) are calculated using a Discounted Cash Flow Rate of Return (DCFROR) model for both pathways. Facility capital costs and operating costs are estimated and used to calculate a 20-year IRR as a measure of pathway economic feasibility.

Process Model Description

The two bio-oil upgrading pathways are divided into six technical areas (see Figure 1) including: biomass pretreatment (A100) where the biomass is chopped, dried, and finely ground to particles 3 mm in diameter with 5% moisture; biomass pyrolysis (A200) where biomass is converted into bio-oil using a fluidized bed reactor operating in an oxygen-free environment at around 500^{o}C and ambient pressure; solids removal (A300) where ash and char are removed from the pyrolysis gas stream before it is condensed to liquid; bio-oil recovery (A400) where bio-oil is condensed and stored to preserve the oil compounds and obtain high yield of good quality bio-oil; heat generation (A500) where non-condensable pyrolysis gases and part of the char generated from pyrolysis are combusted to provide heat for pyrolysis; and bio-oil upgrading (A600) where bio-oil is upgraded into various final products including hydrogen, gasoline, diesel fuel, and commodity chemicals (i.e., aromatics and olefins).

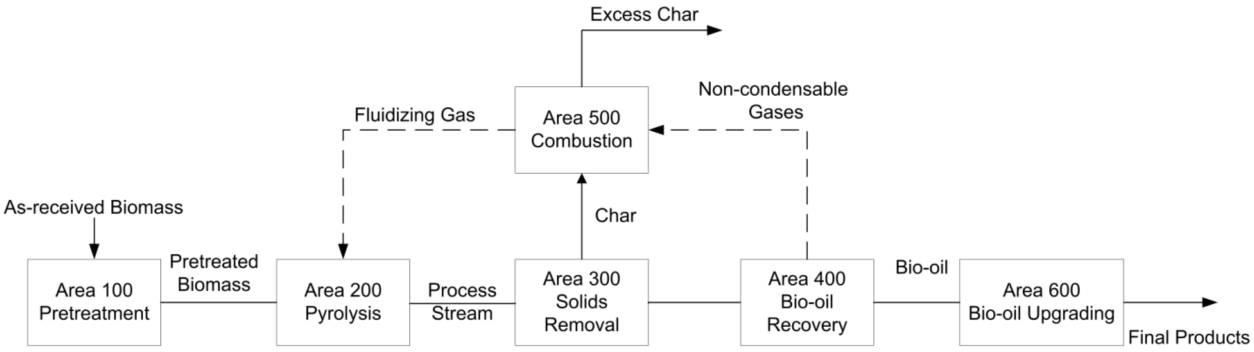


Figure 1. Generalized process diagram for the two pathways

The analysis of the bio-oil production through biomass fast pyrolysis (Areas 100 to 500) is similar to previous TEAs conducted at Iowa State University [25, 27, 29]. Two bio-oil upgrading pathways are analyzed in Area 600 in this study. For the first pathway, two-stage hydrotreating and FCC processing is employed to upgrade the aqueous phase bio-oil to commodity chemicals (olefins and aromatics). In the second pathway, single-stage hydrotreating and hydrocracking is employed to upgrade water-insoluble bio-oil to biobased transportation fuels (synthetic gasoline and diesel fuel).

In the hydrotreating/FCC pathway, two-stage hydrotreating followed by FCC of the aqueous phase scenario presented in Vispute et al. [11] is adopted. The aqueous phase is separated from the bio-oil through a Liquid-Liquid (L-L) extractor before being hydrotreated and catalytically cracked. The first stage of hydrotreating is carried out at 125 ℃ and 100 bar hydrogen pressure over a Ru/C catalyst in a low-temperature hydrotreater while the second stage occurs at 250 ℃ and 100 bar hydrogen pressure over a Pt/C catalyst [11]. Following the two-stage hydrotreating process, the hydrotreated aqueous phase undergoes fluidized catalytic cracking in an FCC reactor over HZSM-5 catalyst at 600 ℃. This converts the hydrotreated aqueous phase to aromatics and olefins.

The separated water-insoluble fraction, which has high phenolic oligomer content, is sold as boiler fuel.

The difference between Options 1 and 2 is the source of hydrogen (See Figure 2 and Figure 3). In Option 1, hydrogen is purchased from the market while Option 2 employs natural gas as the hydrogen feedstock via a two-stage steam-reforming process. The natural gas is first scrubbed of sulfur in a desulfurizer, and then sent on to the two-stage steam reforming process. The first stage is a steam methane reformer (SMR) operated at 700–1100 ℃, where steam reacts with the natural gas to yield syngas. In the second stage, further hydrogen is generated through a lower-temperature water gas shift (WGS) reaction occurring at about 130 ℃. A pressure swing adsorption (PSA) unit is employed to separate hydrogen from the syngas, and the remaining syngas is treated as a fuels gas with commercial value of $5/MMBTU.

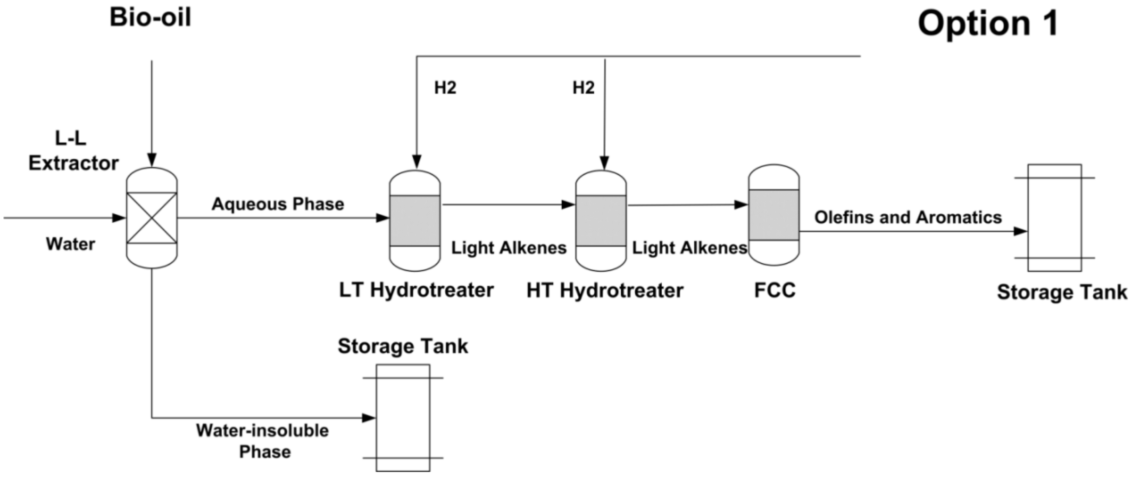


Figure 2. Bio-oil upgrading process for hydrotreating/FCC pathway under Option 1.

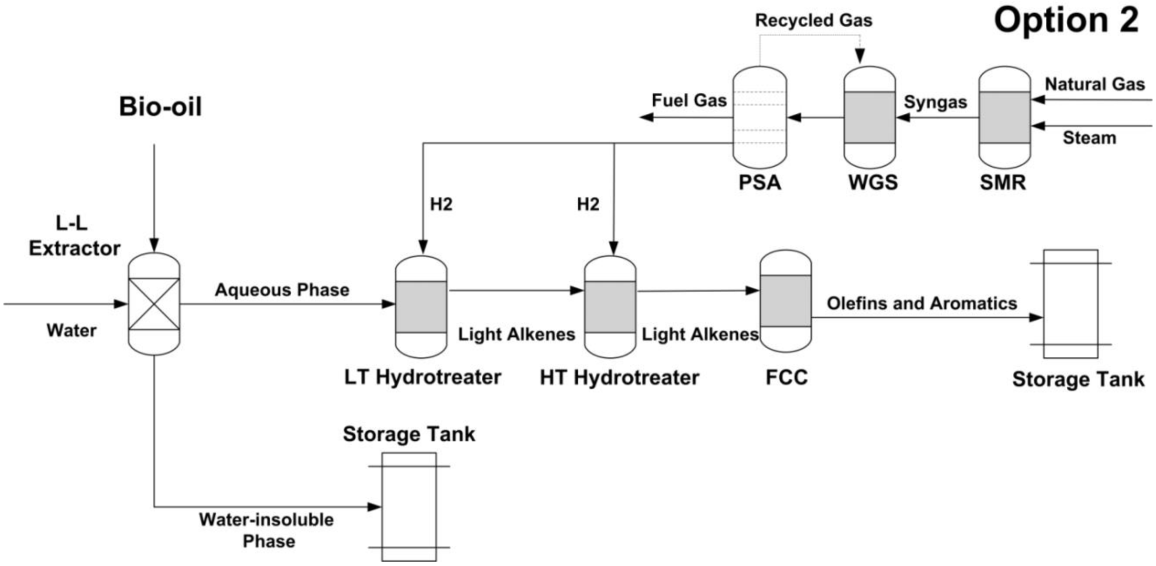


Figure 3. Bio-oil upgrading process for hydrotreating/FCC pathway under Option 2.

Figure 4 describes the bio-oil upgrading process for the hydrocracking pathway. The previous TEA study shows that purchasing hydrogen for hydrotreating process is not as profitable as producing hydrogen via reforming part of bio-oil [25]. In this pathway, the bio-oil is first phase-separated into water-insoluble and aqueous phases through the liquid-liquid (L-L) extractor. The aqueous phase undergoes two-stage catalytic reforming. First, the aqueous phase is sent to the pre-reformer, where water-gas-shift and steam-reforming reactions generate syngas. Then the aqueous phase bio-oil is sent to the reformer to produce hydrogen through catalytic steam reforming. The steam-reforming reaction mechanism used in the reformer is based on Marquevich et al. (see Table 1) [30]. It is assumed that all the hydrogen is separated by the PSA and then compressed in a two-stage process (compressors 1 and 2) for further use. A portion of the hydrogen is employed in the hydrotreating/hydrocracking process and the rest is sold to the market. The water-insoluble phase with its lower oxygen content is hydrotreated and hydrocracked to produce liquid fuels such as synthetic gasoline and diesel fuel.

Table 1. Main reactions for water soluble phase reforming.

Number	Equilibrium Reactions
1	$C_2H_4O_2 \rightarrow 2H_2+2CO$
2	$CH_2O_2 \rightarrow H_2O + CO$
3	$C_5H_4O_2+8H_2O \rightarrow 10H_2+5CO_2$
4	$C_3H_6O_2+4H_2O \rightarrow 7H_2+3CO_2$
5	$C_6H_6O+11H_2O \rightarrow 14H_2+6CO_2$
6	$C_7H_8O_2+12H_2O \rightarrow 16H_2+7CO_2$
7	$C_8H_{10}O+15H_2O \rightarrow 20H_2+8CO_2$
8	$C_7H_8+14H_2O \rightarrow 18H_2+7CO_2$
9	$C_{10}H_{12}O_2+18H_2O \rightarrow 24H_2+10CO_2$
10	$CH_2O_2 \rightarrow H_2 + CO_2$
11	$CO + H_2O \rightarrow CO_2 + H_2$
12	$CO + 3 H_2 \rightarrow CH_4 + H_2O$
13	$CH_4 + H_2O \rightarrow CO + 3 H_2$

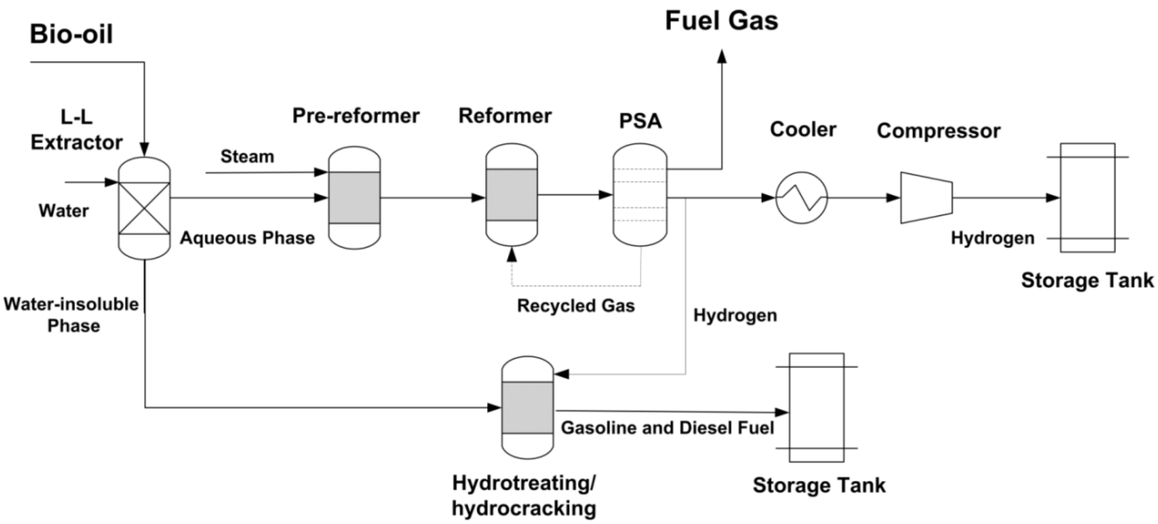


Figure 4.Bio-oil upgrading process for the hydrotreating/hydrocracking pathway.

The Pacific Northwest National Laboratory (PNNL) has conducted several experiments on hydrotreating and hydrocracking of bio-oil derived from various biomass feedstocks. The pyrolysis products are categorized as solids, gases, and liquid fractions. PNNL researchers found that hydrotreating and hydrocracking bio-oil from the pyrolysis of corn stover produces a higher yield of stable oil layer products than other biomass feedstocks (mixed wood, poplar, etc.) [7]. As a result, corn stover is employed in this paper as the biomass feedstock for synthetic gasoline and diesel fuel production through the hydrotreating/hydrocracking pathway.

Mixed wood usually has a lower ash content, which results in bio-oil with a lower level of metals compared to corn stover bio-oil [7]. Fast pyrolysis produces 60-75wt% of liquid bio-oil depending on the feedstock used [4]. For woody biomass, 75 wt% of liquid bio-oil can be generated through fast pyrolysis [19], which is higher than for bio-oils derived from other kinds of biomass. To achieve the highest yields of aromatic hydrocarbons, mixed wood is employed as the biomass feedstock for commodity chemicals production through the hydrotreating/FCC pathway. Table 2 details the properties of mixed wood [31] and corn stover [25].

Table 2. Properties of mixed wood and corn stover

Ultimate Analysis (dry basis)		
Element	Mixed Wood (wt%)	Corn Stover (wt%)
Carbon	47.51	47.28
Hydrogen	5.24	5.06
Nitrogen	0.28	0.8
Chlorine	0.01	0
Sulfur	0.21	0.22
Oxygen	43.07	40.63
Proximate Analysis (wet basis)		
Element	Mixed Wood (wt%)	Corn Stover (wt%)
Moisture	5.23	25
Fixed Content	12.91	17.7
Volatile Matter	81.39	52.8
Ash	0.48	4.5

Equipment sizing and cost estimation are calculated with Aspen Economic Evaluation software. The methodology developed by Peters and Timmerhaus [32] for installation costs and rate of return analysis is employed for the capital cost analysis (see Table 3). A Lang factor of 5.46, which has been employed in previous analyses of pyrolysis-based biofuels production, is employed to calculate the total investment cost based on the total purchased equipment cost [25, 27, 29]. A modified Discounted Cash Flow Rate of Return (DCFROR) analysis spreadsheet is employed to calculate IRRs for the facilities analyzed in this study.

Table 3. Methodology for capital cost estimation for an nth plant.

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 4 details the major assumptions employed in the DCFROR analysis. The process design is based on the current state of technology and is assumed to be an nth plant of its kind with a 20 year facility life. All costs are provided in 2010 dollars.

Table 4. Assumptions for DCFROR analysis.

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

Analysis and Results

For Options 1 and 2 of the hydrotreating/FCC pathway, the total olefins and aromatics yields are 223 metric tons per day and 88.9 metric tons per day, respectively. In addition to the commodity chemicals, char and pyrolytic lignin are also produced regardless of the source of hydrogen. The yields of char and pyrolytic lignin are 174 MTPD and 166 MTPD, respectively. Detailed commodity chemicals yields are shown in Table 5. The chemical yields data is calculated based on carbon selectivity and final products yields presented in Vispute et al. [11]. For the hydrotreating/hydrocracking pathway, hydrogen yield is 63.2 MTPD, total synthetic gasoline and diesel fuel yields are 165 MTPD, and the yield of the by-product char is 206 MTPD.

Table 5. Commodity chemical yield distributions for Option 1 and Option 2 of hydrotreating/FCC pathway.

Chemicals	**Yield (MTPD)**
Ethylene	71.4
Propylene	120
Butylene	31.7
Benzene	23.8
Toluene	43.9
Xylenes	17.0
Ethylbenzene	2.1
Styrene	1.2
Indene	0.4
Naphthalene	0.4

Installed equipment costs for the two pathways are summarized in Figure 5. The total installed equipment costs for the two hydrogen source options under the hydrotreating/FCC pathway are $130 million and $155 million, respectively, and is $190 million for the hydrotreating/hydrocracking pathway. Differences in installed equipment costs result primarily from differences in the costs of the bio-oil upgrading process: upgrading costs are $35 million for a facility employing the hydrotreating/FCC pathway under Option 1; $58 million for a facility employing the hydrotreating/FCC pathway under Option 2; and $69 million for a facility employing the hydrotreating/hydrocracking pathway. For the hydrotreating/FCC pathway, Options 1 and 2 share some installed equipment costs, including those attributed to pretreatment, pyrolysis and oil recovery, combustion, and storage. Differences in bio-oil upgrading installed equipment costs for Options 1 and 2 are the result of the $23 million equipment incurred by the natural gas reforming process.

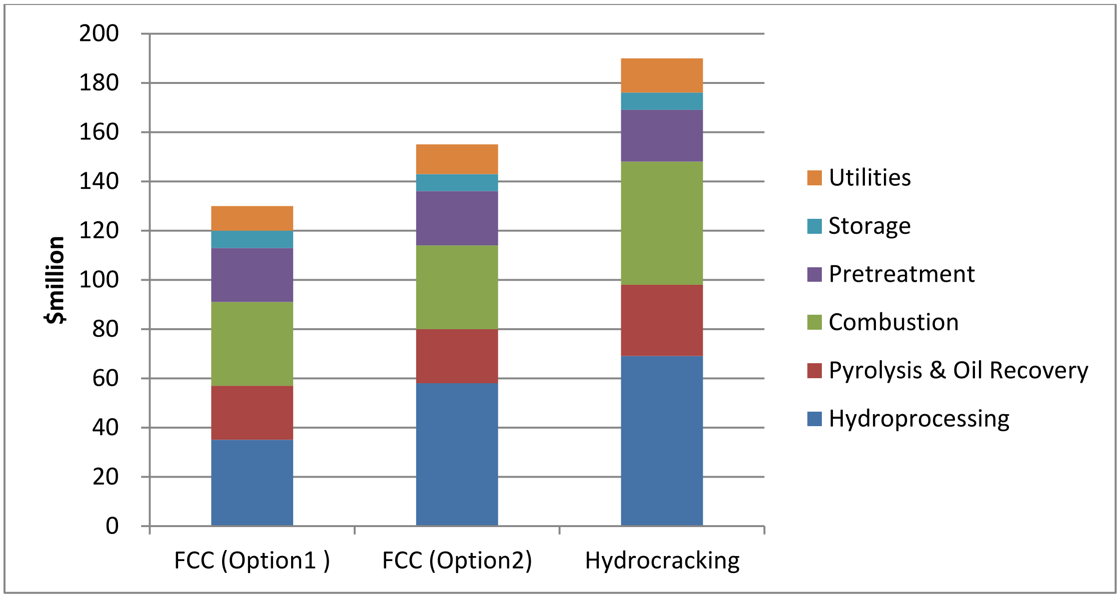


Figure 5. Installed equipment costs for the two pathways.

Table 6 details the operating parameters employed in the analysis. The biomass feedstock purchase price is assumed to be $83/metric ton. The prices for electricity, natural gas, hydrogen, and char are based on the averages from the U.S. Energy Information Administration's (EIA) Annual Energy Outlook's 20-year price forecasts [33]. The price of merchant hydrogen is calculated as a function of natural gas prices under the assumption that it is produced via steam reforming [34]. It is assumed that the char is sold as a low-value coal substitute with a price of $18.21 per metric ton, which is equal to one-half the predicted 20-year average price of U.S. coal. Catalyst costs are based on a previous TEA study that calculated the 20-year internal rate of return for an integrated catalytic pyrolysis (i.e., hydrotreating/FCC) facility [27].

Table 6. Material and operating parameters employed in the evaluation.

Commodity	**Price**
Feedstock	$0.83/kg
Hydrogen	$3.33/kg
Pt	$56.29/kg
Ru	$5.60/kg
Zeolite	$1.60/kg
Natural Gas	$5MMBTU
Electricity	$0.061/kwh
Process Water	$0.032/MT
Solids Disposal Cost	$19.84/MT
Char	$18.21/MT

Total annual facility operating costs are calculated based on assumed input costs (see Figure 6). Feedstock costs represent the majority of the operating costs at $54.4 million annually. For Option 1, hydrogen consumption is the second largest operating cost at $30.2 million on the basis of a $3.33/kg market price. This additional operating cost results in a much higher total operating cost for Option 1 compared to Option 2 under the hydrotreating/hydrocracking pathway. Option 2 has the highest catalyst cost ($4.9 million), which includes the costs of Pt, Ru, and zeolite catalysts for two-stage hydrotreating and hydrocracking and WGS catalyst. Compared with Option 1 under the hydrotreating/hydrocracking pathway, Option 2 has a higher natural gas cost, although this contributes little to the total operating cost because of natural gas's low market price.

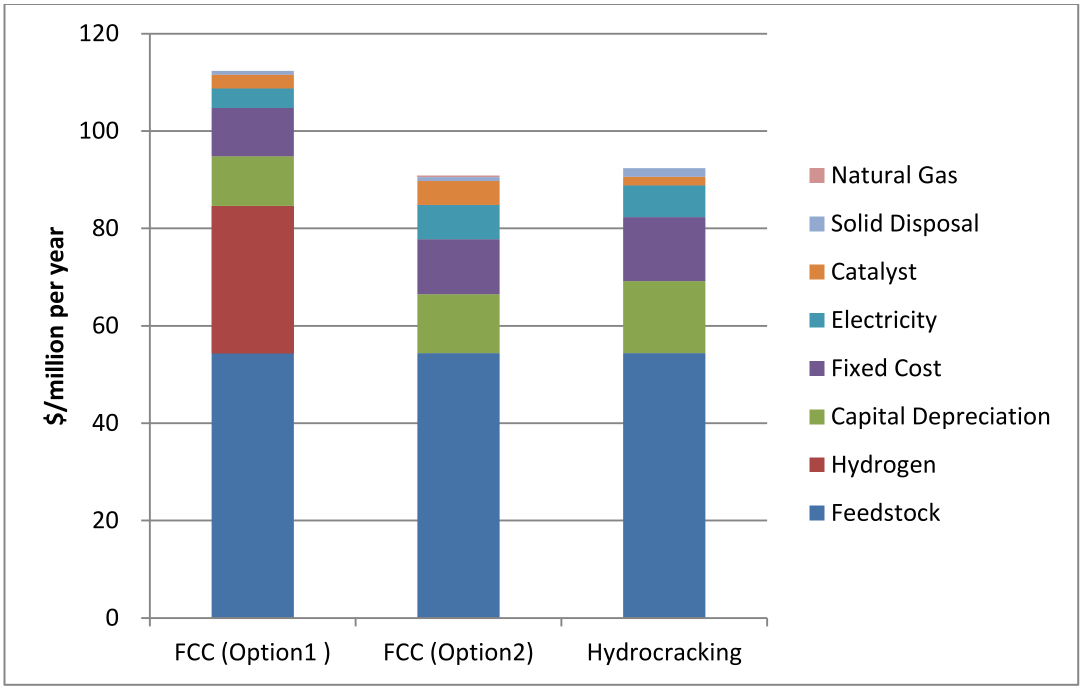


Figure 6. Annual operating costs for the two pathways.

Previous TEAs have assumed a fixed product price. In reality the market prices of commodity products (particularly energy products) are volatile, fluctuating due to changing market conditions or government policies. To account for these fluctuations, the projected prices for commodity chemicals, gasoline, and diesel fuel over the next 20 years (2011-2030) are incorporated into the DCFROR model for both upgrading pathways. An annual petroleum price trend (1995-2035) is detailed based on historical petroleum prices and annual price projections provided by EIA [35, 36] (see Figure 7). The price trend shows that petroleum has a history of volatility and achieved a recent low in 2010. The EIA also forecasts a steady increase in the petroleum price after 2015 due to greatly increased petroleum demand in countries such as China and India.

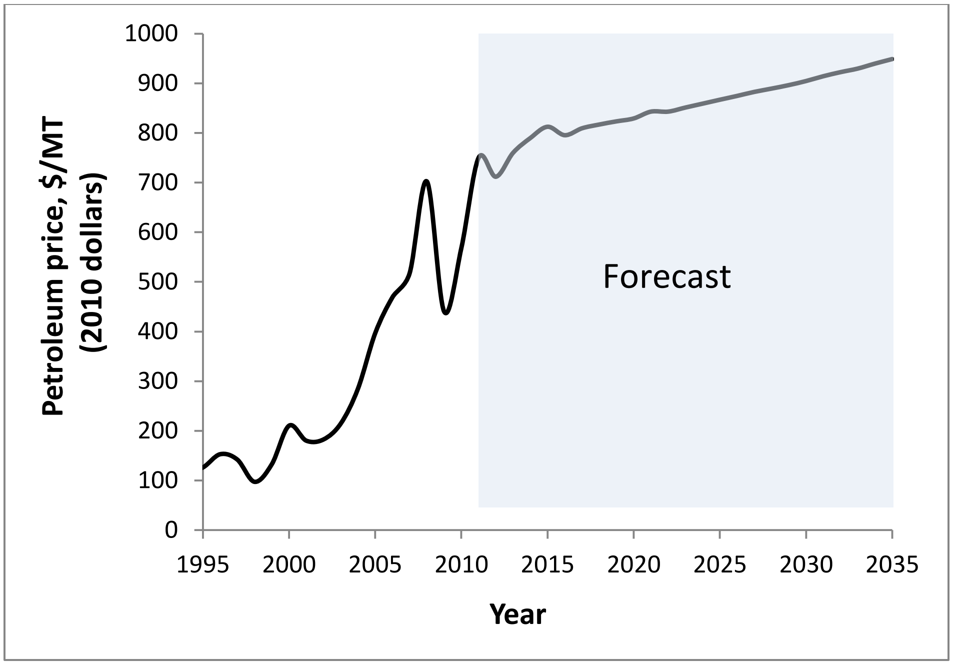


Figure 7. Historical and forecasted petroleum prices (2010 dollars) [35, 36].

In the hydrotreating/FCC pathway, commodity chemicals, especially olefins and aromatics, are the main products. Among all the commodity chemicals, propylene represents the largest yield (see Table 5). An analysis of historical monthly spot prices of petroleum (average of Brent and West Texas Intermediate [WTI] crude) [35] and propylene from April 1993 to July 2011 [37] shows a strong correlation (R^2=0.89) between the two (see Figure 8). Similarly, the prices of other commodity chemicals (benzene, toluene, xylenes, ethylene, etc.) also have strong positive correlations with petroleum prices. The detailed correlations between the commodity chemicals and the petroleum prices are shown in Table 7. For the hydrotreating/hydrocracking pathway, the main products are gasoline and diesel fuel and the same analysis shows a strong exponential correlation (R^2=0.96) between the historical monthly spot prices of gasoline and diesel fuel from April 1993 to July 2011 [38] and the prices of petroleum over same period [35] (see Figure 9).

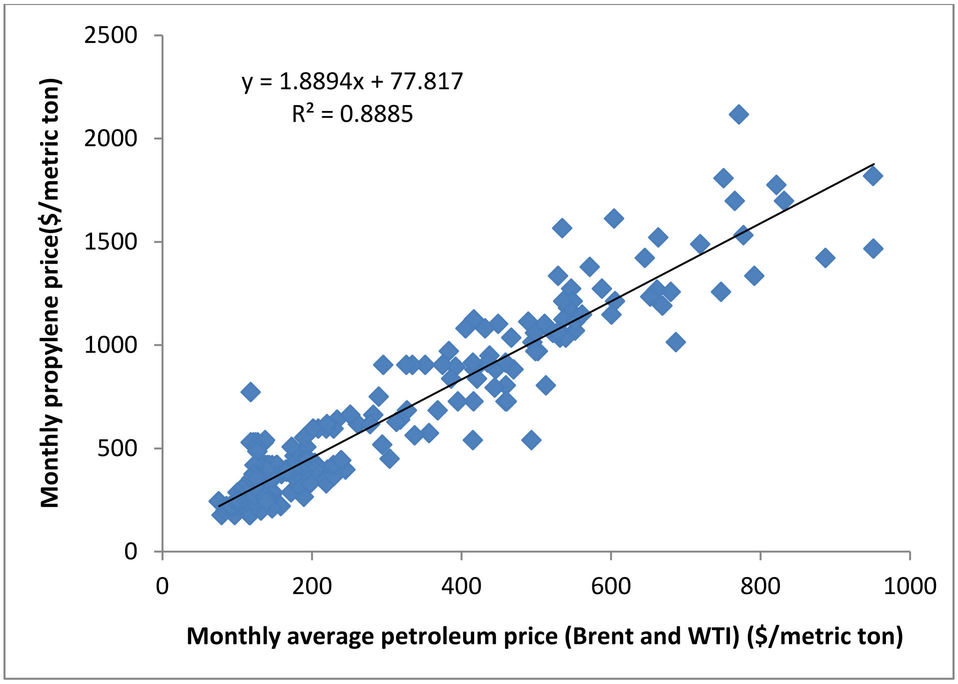


Figure 8. Correlation between the monthly prices of petroleum and propylene [35, 37].

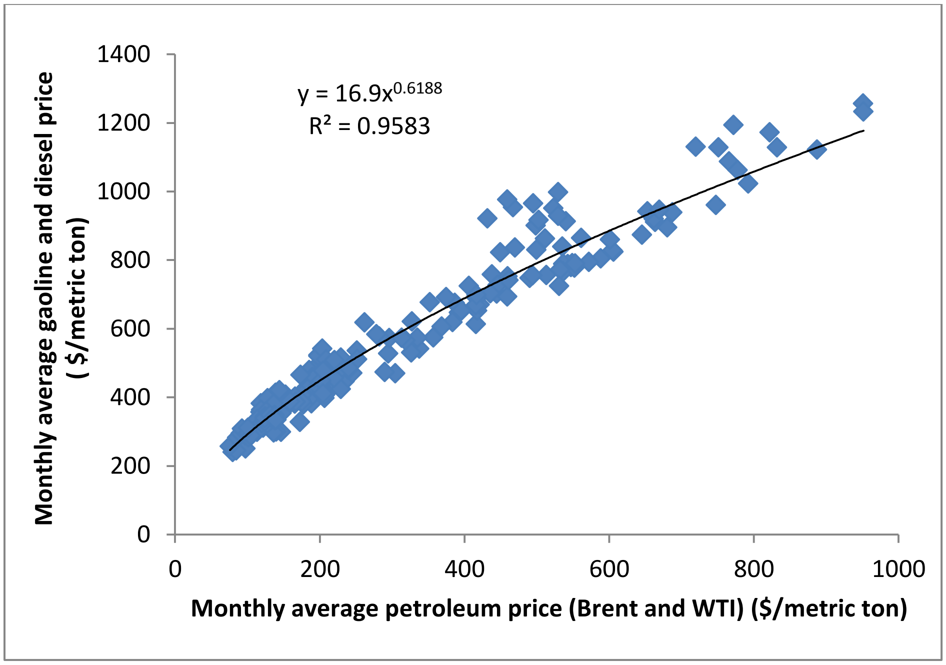


Figure 9.Correlation between the monthly price of petroleum and average price of gasoline and diesel fuel [35, 38].

Table 7. Correlations between the commodity chemicals and petroleum prices.

Chemicals	**Correlations with petroleum**	**R^2**
Benzene	$y = 4.5522x^{0.8501}$	0.8447
Toluene	$y = 4.6562x^{0.8194}$	0.9365
Xylenes	$y = 6.5132x^{0.774}$	0.9107
Ethylene	$y= 1.3326x + 284.18$	0.7063
Propylene	$y= 1.8894x + 77.817$	0.8885

The EIA projects petroleum to have a steadily increasing price over the next 20 years. As a result of these strong positive correlations, the prices of commodity chemicals and transportation fuels are expected to also increase over the same time period. The projected prices of commodity chemicals and transportations fuels for the next 20 years are calculated through these correlations and incorporated into the DCFROR analysis.

Based on the calculated capital costs, operating costs, and assumptions, facility IRRs of 7.6%, 13.3%, and 9.8% are obtained for Options 1 and 2 of the hydrotreating/FCC pathway and the hydrotreating/hydrocracking pathway, respectively, via a DCFROR analysis setting a goal of zero net present value (NPV) at the end of the 20-year project.

Uncertainty Analysis

The results of the sensitivity analysis for the two pathways demonstrate the sensitivity of facility IRR to parameter values (see Figure 10, Figure 11, and Figure 12). The parameters investigated are biomass cost, fixed capital cost, product yield, hydrogen price, catalyst cost, char credit value, gas credit value, income tax rate, and working capital amount. The uncertainty analysis finds that facility IRRs for the two pathways are most sensitive to hydrogen price, product yield, fixed capital cost, and biomass cost.

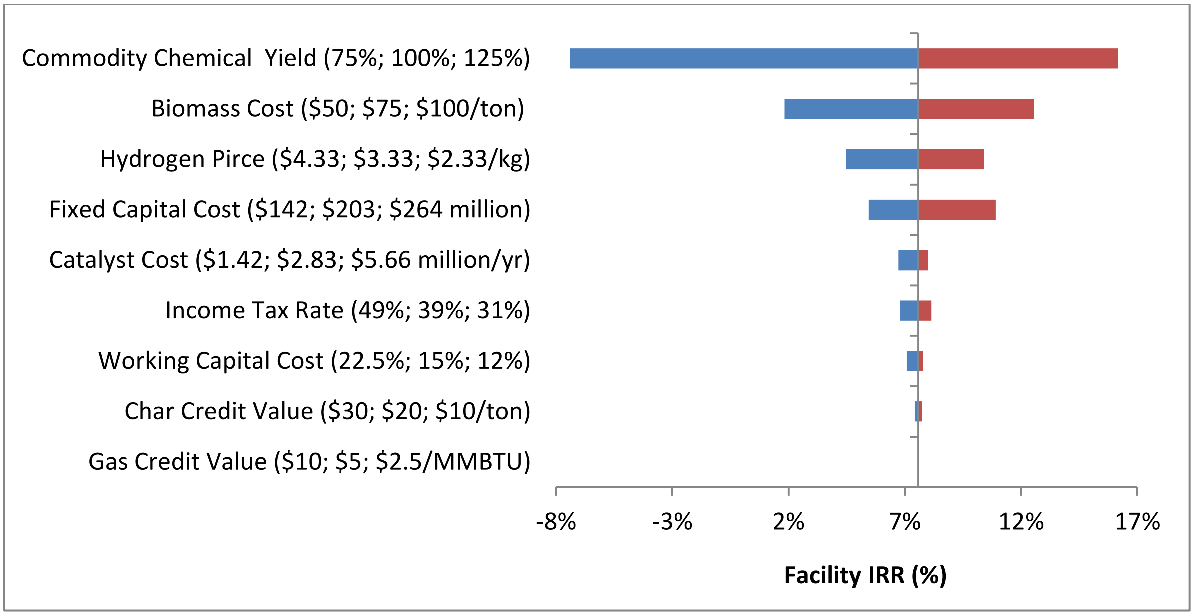


Figure 10. Sensitivity analysis for Option 1 of the hydrotreating/FCC pathway.

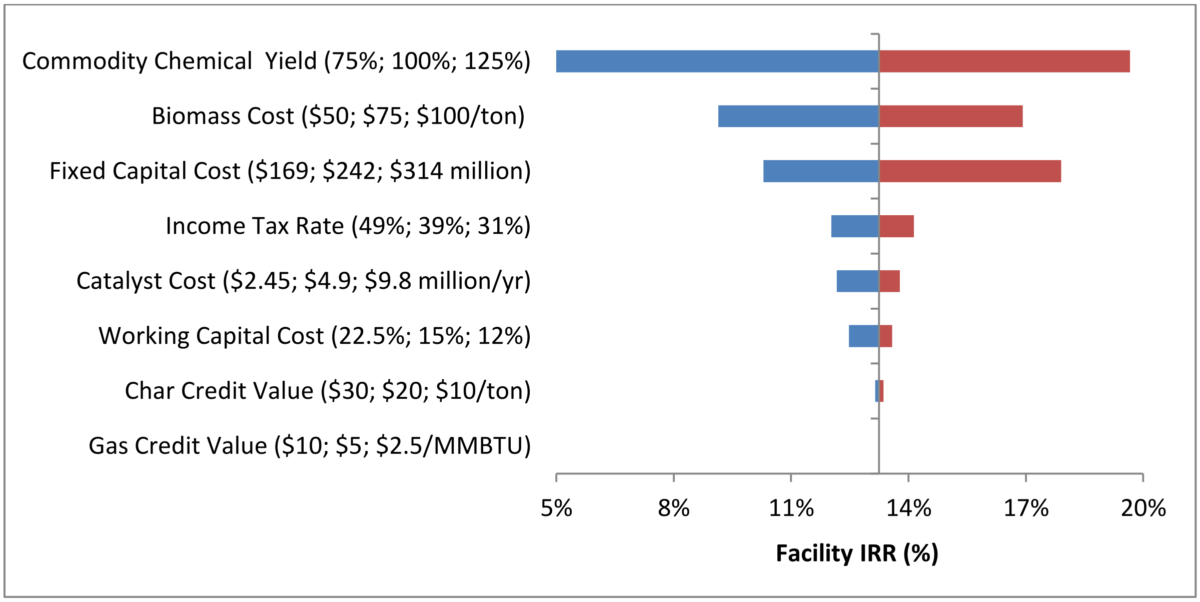


Figure 11. Sensitivity analysis for Option 2 of the hydrotreating/FCC pathway.

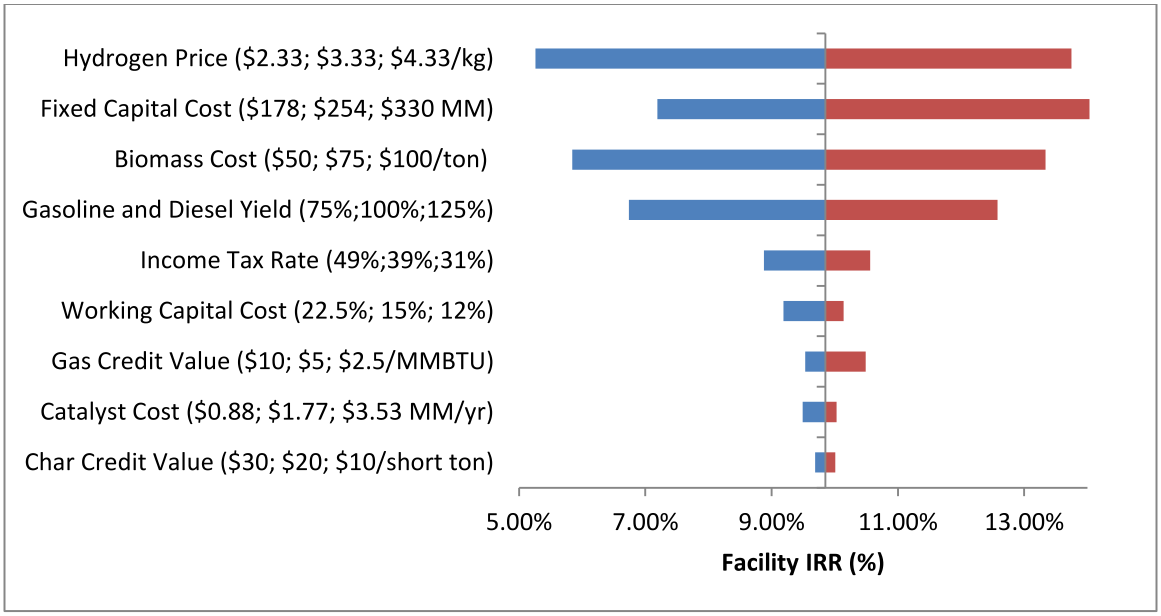


Figure 12. Sensitivity analysis for the hydrotreating/hydrocracking pathway.

Commodity chemicals are the main products for both options of the hydrotreating/FCC pathway, so the yield of commodity chemicals has a significant impact on facility IRR. Increasing the commodity chemicals yield from 75% to 125% of the base case increases facility IRR from -7.4% to 16.2% for Option 1 and from 5% to 19.6% for Option 2. A variation of biomass cost from $50/ton to $100/ton results in a facility IRR range of 1.8 - 12.6% for Option 1 and 9 - 16.9% for Option 2. A ±30% range in fixed capital cost results in a facility IRR range of 5.4 - 10.9% for Option 1 and 10.3 - 17.9% for Option 2.

For the hydrotreating/hydrocracking pathway, hydrogen price, fixed capital cost, biomass cost, gasoline yield, and diesel fuel yield have the greatest impact on facility IRR. For Option 1 of the hydrotreating/FCC pathway and the hydrotreating/hydrocracking pathway, the facility IRRs are sensitive to hydrogen price. For the hydrotreating/hydrocracking pathway, however, the hydrogen price is the most important factor. Figure 13 describes the facility IRR variation and the hydrogen market price for the two pathways. The figure shows that the hydrotreating/FCC pathway under Option 1 and the hydrotreating/hydrocracking pathway both have facility IRR of 8.5% when the hydrogen price reaches $3.02/kg. The hydrotreating/hydrocracking pathway will have a higher facility IRR if the hydrogen price exceeds $3.02/kg. When the hydrogen price is $4.20/kg, the facility IRR for the hydrotreating/hydrocracking pathway reaches 13.3%, which is equal to the IRR of a facility employing Option 2 of the hydrotreating/FCC pathway. The IRR of a facility employing Option 1 is 13.3% at a hydrogen price of $1.04/kg. The correlation between the IRRs of facilities employing Option 1 of the hydrotreating/FCC pathway and the hydrotreating/hydrocracking pathway and the hydrogen price are almost linear, suggesting that they will attain equal IRR values only when the hydrogen price is either very low ($1/kg) or very high ($4.50/kg).

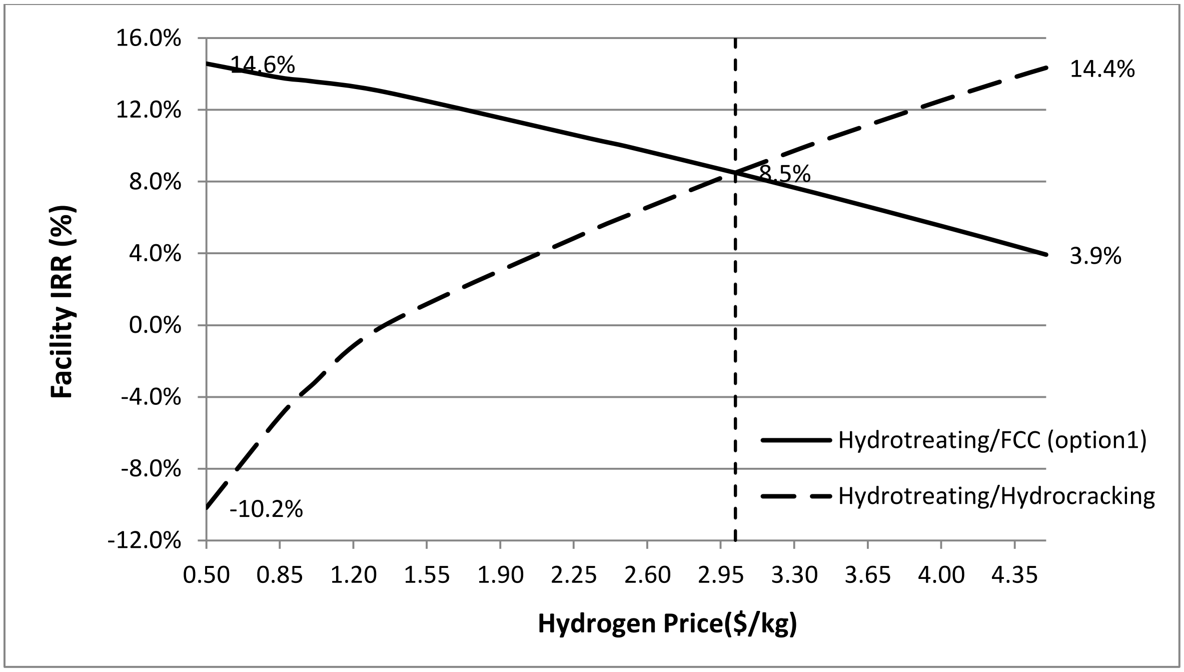


Figure 13. Facility IRR distribution from Monte-Carlo simulation.

Option 2 of the hydrotreating/FCC pathway is found to be the most favorable pathway in the initial sensitivity analysis, with a base case facility IRR of 13.3%, an upper bound facility

IRR of 19.6%, and a comparatively low investment risk. However, the hydrogen for Option 2 is produced via natural gas steam reforming, and this reliance on a volatile fossil fuel source may pose a future challenge to the pathway's economic feasibility. Among all the fossil fuels, natural gas has the advantages of clean burning, lower greenhouse gas emissions, and very low cost. However, increased utilization resulting from its current low value in the North American market would spur demand and cause natural gas prices to rise, hindering the economic feasibility of the hydrotreating/FCC pathway under Option 2.

For further risk analysis, Crystal Ball® is employed to conduct a Monte-Carlo simulation to generate a facility IRR distribution to quantify the uncertainty of the hydrotreating/hydrocracking pathway under Option 2. Commodity chemical yield, fixed capital cost, and biomass cost are treated as changing variables since these parameters were shown by the sensitivity analysis to have the great impact on facility IRR. All of these variables are assumed to follow triangular distributions with the same variation ranges used in the sensitivity analysis (see Figure 11). Two thousand random facility IRRs are generated during the Monte-Carlo simulation and JMP® software is employed to analyze the resulting data.

Figure 14 details the facility IRR distribution from the Monte-Carlo simulation. The expected value of the mean facility IRR is 13.1% and the standard deviation is 3.8%. The minimum IRR is 0% and the maximum IRR is 26.2%. The median, 25% quartile, and 75% quartile facility IRRs are 13.1%, 10.6%, and 15.7%, respectively. For the cumulative probability distribution of the facility IRR, about 80% of facilities in the analysis have IRRs exceeding 10%, and 30% of facilities have IRRs exceeding 15% (see Figure 15). This result shows that the hydrotreating/FCC pathway under Option 2 is likely to present a relatively low risk in the future, even if some economic parameters are pessimistic.

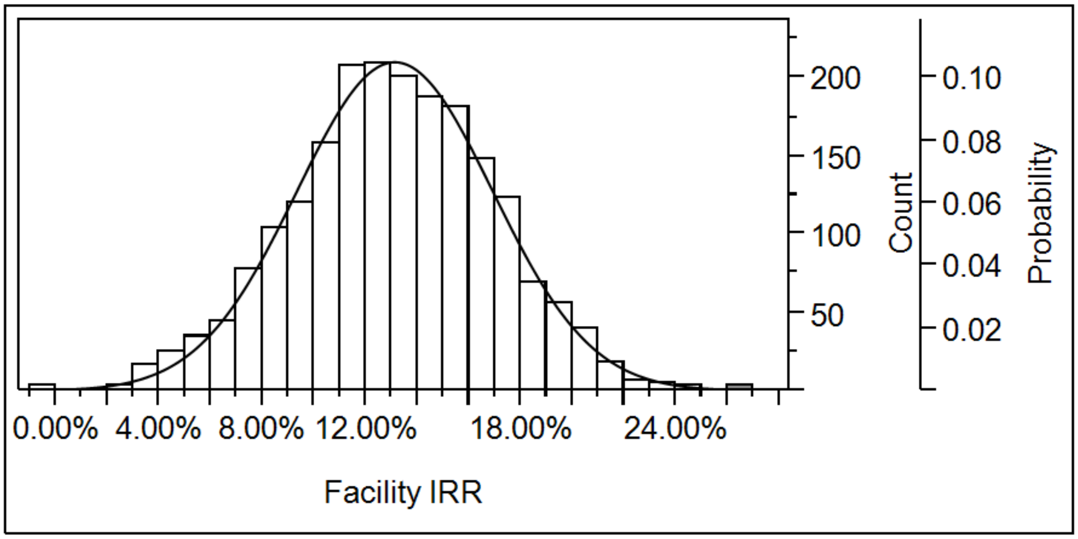


Figure 14.Facility IRR distribution from Monte-Carlo simulation.

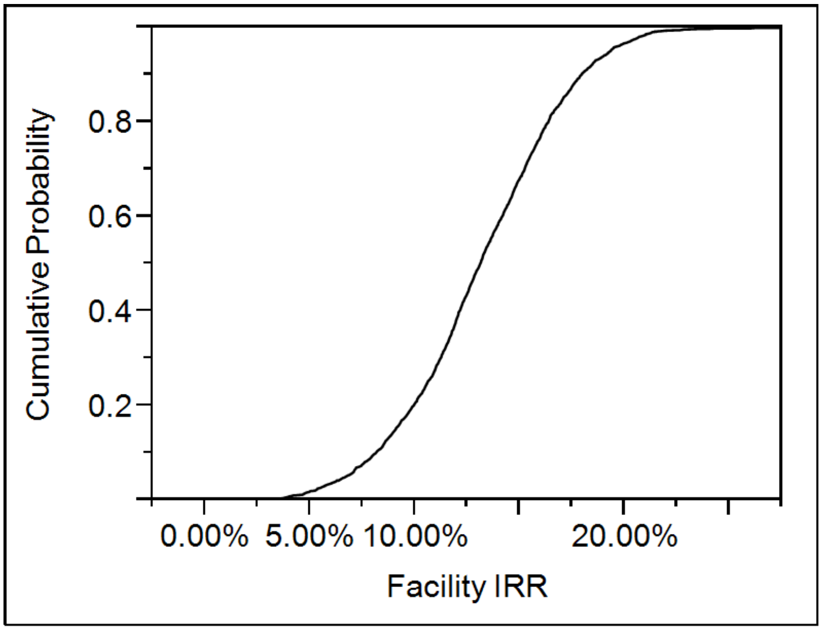


Figure 15.Cumulative probability distribution of facility IRR from Monte-Carlo simulation.

Conclusions

This techno-economic analysis evaluates the economic feasibility of biomass fast pyrolysis and two bio-oil upgrading pathways. The two bio-oil upgrading pathways are: hydrotreating/FCC and hydrotreating/hydrocracking. Both upgrading methods require one or more hydrotreating steps to stabilize the bio-oil prior to cracking. For the hydrotreating/FCC pathway, the aqueous phase of the bio-oil is upgraded to commodity chemicals via a two-stage hydrotreating and FCC process. In this pathway, two options are developed regarding the hydrogen source (Options 1 and 2). Option 1 uses merchant hydrogen purchased from the market, and Option 2 uses hydrogen produced via on-site reforming of natural gas. For the hydrotreating/hydrocracking pathway, the water-insoluble phase is upgraded to transportation fuels (synthetic gasoline and diesel fuel) via a one-stage hydrotreating and hydrocracking process and the aqueous phase is reformed to hydrogen. Facility IRR is calculated as a function of annual revenues, fixed capital investment, and annual operating costs. The technology is assumed to be mature enough from the perspectives of reliability and performance to ensure that the facility operates as an nth plant rather than as a pioneer plant.

Based on a 2000 MTPD facility, the total olefins and aromatics yields are 223.3 MTPD and 88.9 MTPD for the hydrotreating/FCC pathway under Options 1 and 2, respectively. In addition to the commodity chemicals, char and pyrolytic lignin are also produced via this pathway. The yield of char and pyrolytic lignin is 174 MTPD and 166 MTPD, respectively. For the hydrotreating/hydrocracking pathway, the hydrogen yield is 63.2 MTPD, total synthetic gasoline and diesel fuel yield is 165 MTPD, and the yield of the by-product char is 206 MTPD. The estimated installed equipment costs for the hydrotreating/FCC pathway under Options 1 and 2, and the hydrotreating/hydrocracking pathway are \$130 million, \$155 million, and \$190 million, respectively. The fixed capital costs for the two options of the hydrotreating/FCC pathway and the hydrotreating/hydrocracking pathway are \$203 million, \$242 million, and \$296 million, respectively. The 20-year IRR is calculated to be 7.6%, 13.3%, and 9.8% for the two options of the hydrotreating/FCC pathway and the hydrotreating/hydrocracking pathway, respectively.

Sensitivity analysis is performed to determine the sensitivity of the facility's economic feasibility to the model parameter values for the two pathways. Sensitivity analysis results show that hydrogen price, fixed capital cost, feedstock cost, and product yield are key factors in the economic feasibility of the two bio-oil upgrading pathways. Facility IRR ranges from -7.4% to 16.2% and 5% to 19.7% for Options 1 and 2 of the hydrotreating/FCC pathway, respectively. For the hydrotreating/hydrocracking pathway, facility IRR ranges from 5.3% to 14.1%.

A Monte-Carlo simulation analysis of Option 2 of the hydrotreating/FCC pathway predicts that more than 80% of facilities will have IRRs exceeding 10%, and 30% of facilities will have IRRs exceeding 15%, based on 2000 random runs of the simulation. This indicates that an investment in Option 2 of the hydrotreating/FCC pathway would present a relatively low risk.

Acknowledgements

The authors would like to thank the Bioeconomy Institute of Iowa State University for funding and logistical support.

References

[1] J.R. Regalbuto, The sea change in US biofuels' funding: from cellulosic ethanol to green gasoline, Biofuels, Bioproducts and Biorefining, 5 (2011) 495-504.

[2] M.M. Wright, R.C. Brown, Comparative economics of biorefineries based on the biochemical and thermochemical platforms, Biofuels, Bioproducts and Biorefining, 1 (2007) 49-56.

[3] P.E. James L. Easterly, Assessment of Bio-Oil as a Replacement for Heating Oil (2002) 1-18. (Available at: http://www.nrbp.org/pdfs/pub34.pdf)

[4] D. Mohan, C.U. Pittman, P.H. Steele, Pyrolysis of Wood/Biomass for Bio-oil:A Critical Review, Energy & Fuels, 20 (2006) 848-889.

[5] S. Czernik, A.V. Bridgwater, Overview of Applications of Biomass Fast Pyrolysis Oil, Energy & Fuels, 18 (2004) 590-598.

[6] K. Takanabe, K.-i. Aika, K. Seshan, L. Lefferts, Sustainable hydrogen from bio-oil—Steam reforming of acetic acid as a model oxygenate, J. Catal., 227 (2004) 101-108.

[7] D.C. Elliott, T.R. Hart, G.G. Neuenschwander, L.J. Rotness, A.H. Zacher, Catalytic hydroprocessing of biomass fast pyrolysis bio-oil to produce hydrocarbon products, Environmental Progress & Sustainable Energy, 28 (2009) 441-449.

[8] P.M. Mortensen, J.D. Grunwaldt, P.A. Jensen, K.G. Knudsen, A.D. Jensen, A review of catalytic upgrading of bio-oil to engine fuels, Applied Catalysis A: General, 407 (2011) 1-19.

[9] D.C. Elliott, Historical Developments in Hydroprocessing Bio-oils, Energy & Fuels, 21 (2007) 1792-1815.

[10] J. Wildschut, F.H. Mahfud, R.H. Venderbosch, H.J. Heeres, Hydrotreatment of fast pyrolysis oil using heterogeneous noble-metal catalysts, Industrial and Engineering Chemistry Research, 48 (2009) 10324-10334.

[11] T.P. Vispute, H. Zhang, A. Sanna, R. Xiao, G.W. Huber, Renewable Chemical Commodity Feedstocks from Integrated Catalytic Processing of Pyrolysis Oils, Science, 330 (2010) 1222-1227.

[12] T.R. Carlson, T.P. Vispute, G.W. Huber, Green Gasoline by Catalytic Fast Pyrolysis of Solid Biomass Derived Compounds, ChemSusChem, 1 (2008) 397-400.

[13] T.R. Carlson, Y.-T. Cheng, J. Jae, G.W. Huber, Production of green aromatics and olefins by catalytic fast pyrolysis of wood sawdust, Energy & Environmental Science, 4 (2011) 145-161.

[14] K. Giannakopoulou, M. Lukas, A. Vasiliev, C. Brunner, H. Schnitzer, Conversion of rapeseed cake into bio-fuel in a batch reactor: Effect of catalytic vapor upgrading, Microporous and Mesoporous Materials, 128 (2010) 126-135.

[15] H. Zhang, Y.-T. Cheng, T.P. Vispute, R. Xiao, G.W. Huber, Catalytic conversion of biomass-derived feedstocks into olefins and aromatics with ZSM-5: the hydrogen to carbon effective ratio, Energy & Environmental Science, 4 (2011) 2297-2307.

[16] S. Vitolo, M. Seggiani, P. Frediani, G. Ambrosini, L. Politi, Catalytic upgrading of pyrolytic oils to fuel over different zeolites, Fuel, 78 (1999) 1147-1159.

[17] S. Vitolo, B. Bresci, M. Seggiani, M.G. Gallo, Catalytic upgrading of pyrolytic oils over HZSM-5 zeolite: behaviour of the catalyst when used in repeated upgrading–regenerating cycles, Fuel, 80 (2001) 17-26.

[18] L. Qiang, L. Wen-zhi, Z. Dong, Z. Xi-feng, Analytical pyrolysis–gas chromatography/mass spectrometry (Py–GC/MS) of sawdust with Al/SBA-15 catalysts, Journal of Analytical and Applied Pyrolysis, 84 (2009) 131-138.

[19] A.V. Bridgwater, Review of fast pyrolysis of biomass and product upgrading, Biomass and Bioenergy, 38 (2012) 68-94.

[20] T.R. Brown, Y. Zhang, G. Hu, R.C. Brown, Techno-economic Analysis of Biobased Chemicals Production via Integrated Catalytic Processing, Biofuels, Bioproducts and Biorefineries, 6 (2012) 73-87.

[21] R. Kothari, D. Buddhi, R.L. Sawhney, Comparison of environmental and economic aspects of various hydrogen production methods, Renewable and Sustainable Energy Reviews, 12 (2008) 553-563.

[22] EPA, Regulation of Fuels and Fuel Additive Changes to Renewable Fuel Standard Program; Final Rule, Fed. Regist., 75 (2010) 14790.

[23] D. Chen, L. He, Towards an Efficient Hydrogen Production from Biomass: A Review of Processes and Materials, ChemCatChem, 3 490-511.

[24] R.C. Brown, Generation of Thermochemical Intermediates Suitable for Catalytic Upgrading, 2011. (Available at: http://www.usbiomassboard.gov/pdfs/brown_tac_may_2011.pdf)

[25] M.M. Wright, Daugaard, Daren E., Satrio, Justinus A., Brown, Robert C., Techno-economic analysis of biomass fast pyrolysis to transportation fuels, Fuel, 89 S2-S10.

[26] S.B.V. Jones, Corinne Walton, Christie W. Elliott, Douglas C. Holladay, Johnathan E. Stevens, Don J. Kinchin, Christopher Czernik, Stefan, Production of Gasoline and Diesel from Biomass via Fast Pyrolysis, Hydrotreating and Hydrocracking: A Design Case, in, 2009.

[27] T.R. Brown, Y. Zhang, G. Hu, R.C. Brown, Techno-economic analysis of biobased chemicals production via integrated catalytic processing, Biofuels, Bioproducts and Biorefining, 6 (2012) 73-87.

[28] M.M. Wright, Y. Román-Leshkov, W.H. Green, Investigating the techno-economic trade-offs of hydrogen source using a response surface model of drop-in biofuel production via bio-oil upgrading, Biofuels, Bioproducts and Biorefining, 6 (2012) 503-520.

[29] Y. Zhang, T.R. Brown, G. Hu, R.C. Brown, Techno-economic Analysis of Monosaccharide Production via Fast Pyrolysis of Lignocellulose, Bioresource Technology.

[30] M. Marquevich, S. Czernik, E. Chornet, D. Montané, Hydrogen from Biomass: Steam Reforming of Model Compounds of Fast-Pyrolysis Oil, Energy & Fuels, 13 (1999) 1160-1166.

[31] S. Czernik, Electronic communication re: Bio-oil feedstock, in: R.C. Brown (Ed.), Ames, 2011.

[32] M. Peters, K. Timmerhaus, R. West, Plant Design and Economics for Chemical Engineers, 5 ed., McGraw Hill, 2003.

[33] EIA, Annual Energy Outlook 2011, in, EIA, Washington, DC, 2011. (Available at: http://www.eia.gov/dnav/pet/pet_pri_spt_s1_d.htm)

[34] NREL, Distributed Hydrogen Production from Natural Gas, in, National Renewable Energy Laboratory, Golden, CO, 2006, pp. 10.

[35] EIA, Petroleum & Other Liquids - Spot Prices, in, U.S. Energy Information Administration, 2011.

[36] EIA, Annual Energy Outlook 2012, in, 2012. (Available at: http://www.eia.gov/oiaf/aeo/tablebrowser/)

[37] Anon, CHEMICAL PRICES, ICIS Chemical Business, 279 (2011) 15.

[38] EIA, Retail Gasoline Historical Prices, 2011. (Available at :http://www.eia.gov/oil_gas/petroleum/data_publications/wrgp/mogas_history.html)

CHAPTER IV

LIFE CYCLE ASSESSMENT LIFE CYCLE ASSESSMENT OF THE PRODUCTION OF HYDROGEN AND TRANSPORTATION FUELS FROM CORN STOVER VIA FAST PYROLYSIS

A paper published in Environmental Research Letters Journal

Yanan Zhang, Guiping Hu and Robert C. Brown

Abstract

This Life Cycle Assessment (LCA) evaluates and quantifies the environmental impacts of the production of hydrogen and transportation fuels from the fast pyrolysis and upgrading of corn stover. Input data for this analysis come from Aspen Plus modeling, a GREET model database and a U.S Life Cycle Inventory Database. SimaPro 7.3 software is employed to estimate the environmental impacts. The results indicate that the net fossil energy input is 0.25 MJ and 0.23 MJ per km traveled for a light-duty vehicle fueled by gasoline and diesel fuel, respectively. Bio-oil production requires the largest fossil energy input. The net Global Warming Potential (GWP) is 0.037 kg CO_2eq and 0.015 kg CO_2eq per km traveled for a vehicle fueled by gasoline and diesel fuel, respectively. Vehicle operations contribute up to 33% of the total positive GWP, which is the largest GHG footprint of all the unit processes. The net GWPs in this study are 88% and 94% lower than for petroleum-based gasoline and diesel fuel (2005), respectively. Biomass transportation has the largest impact on ozone depletion among all of the unit processes. Sensitivity analysis shows that fuel economy, transportation fuel yield, bio-oil yield, and electricity consumption are the key factors that influence GHG emissions.

Introduction

Growing concerns over Greenhouse Gas (GHG) emissions from petroleum-based fuel consumption have prompted interest in the production of alternative transportation fuels from biorenewable sources. As required by the Energy Independence and Security Act of 2005, the U.S. Environmental Protection Agency (EPA) finalized the Renewable Fuel Standard (RFS) and mandated petroleum refineries and oil importers to increase the volume of renewable fuel that is blended into petroleum-based transportation fuels. Life cycle assessment (LCA), a standard evaluation method of environmental impact, is increasingly being used to evaluate biofuel production systems. In previous life cycle assessments, evaluations have emphasized the environmental impacts of ethanol-based transportation fuels [1-10]. The majority of these studies found that bioethanol has fewer GHG emissions than petroleum-based gasoline and diesel, which can potentially improve the environmental performance of the transportation and energy sectors. In these studies, both first generation (such as corn grain) and second generation feedstocks, (for example, corn stover, forest residues, and switchgrass) were analyzed for bioethanol production using both biochemical and thermochemical pathways.

The Energy Independence and Security Act of 2007 amended RFS to RFS2, which expanded the mandate for the utilization of 36 billion gallons of biofuel annually in 2022, of which no more than 15 billion gallons can be ethanol from corn starch, and no less than 16 billion must be from cellulosic biofuels [11]. RFS2 also mandates the inclusion of other biofuels such as biodiesel into the petroleum-based fuel supply and requires renewable fuels other than corn-based ethanol with at least a 50% reduction of GHG emissions (60% for cellulosic biofuels) compared to petroleum-based gasoline and diesel [11]. The issue of RFS2 drives a growing interest in advanced biofuels production such as renewable gasoline and diesel fuels from second generation feedstocks.

Fast pyrolysis, which is carried out at a moderate temperature (around 500^{o}C) and short reaction time (about two seconds), has attracted considerable interest as a means for converting biomass fuels and residues into biofuels [12]. Fast pyrolysis can generate up to 75wt.% of liquid bio-oil, which can then be used in various applications such as supplying energy for transportation, heating, and electricity generation [13]. With the growing interest in fast pyrolysis of biomass and catalytic upgrading of the resulting bio-oil into hydrocarbon fuels, a number of LCA studies have been recently conducted to explore the environmental impacts of this pathway to biofuels [10, 14-18]. In these studies, different types of biomass feedstocks (willow, poplar, wood logging residue, corn stover etc.) were investigated and various applications of the bio-oil were examined, such as power generation from bio-oil combustion and hydrogen production from steam reforming of bio-oil.

Catalytic upgrading methods can be employed to upgrade bio-oil to a variety of gaseous and liquid fuels including diesel fuel, gasoline, kerosene, and methane [12]. However, only a small number of LCAs have been conducted on the production of renewable gasoline and diesel fuel from biomass fast pyrolysis and upgrading. Hsu [16] conducted a well-to-wheel analysis of transportation fuel from the fast pyrolysis and upgrading of forest residues, based on data from a Pacific Northwest National Laboratory (PNNL) process design report [19]. An uncertainty analysis for GHG emissions was also conducted in this study and found that all scenarios considered had lower GHG emissions than petroleum-based gasoline. Iribarren et al. [18] performed an LCA for fast pyrolysis and upgrading of woody biomass using a cradle-to-gate approach. Kauffman et al. [10] conducted an LCA for combined ethanol and drop-in fuels production from corn grain and corn stover, respectively, on the basis of an hectare farmland and found that a 52% reduction in GHG emissions was possible.

In all of these studies, hydrotreating is employed to deoxygenate bio-oil to hydrocarbons. Hydrotreating, done either in a single stage or two stages, is a common pretreatment in the oil refinery process, but it requires a large amount of hydrogen. Currently, the majority of industrial hydrogen is obtained from steam reforming of natural gas [20]. However, hydrogen can be produced from other sources. The aqueous phase of bio-oil contains carbohydrate-derived compounds that can be catalytically steam reformed to renewable hydrogen [21]. Catalytic steam reforming of bio-oil compounds has been investigated in previous studies [21-35]. In these studies, various metal-supported catalysts, bio-oil modeling components, pyrolysis reactor designs, and biomass-feedstock selections have been tested and compared for their efficiency in biohydrogen production. Through hydrogen production via a bio-oil reforming pathway, natural gas consumption could be reduced. In this study, the environmental impacts of the production of hydrogen and transportation fuels from corn stover fast pyrolysis and upgrading are evaluated.

The objective of this study is to perform a life cycle assessment of the environmental impacts of the production of hydrogen and transportation fuels from the fast pyrolysis and upgrading of corn stover. An Aspen Plus model of the pyrolysis and upgrading processes in combination with a GREET model database and a U.S Life Cycle Inventory Database provide data to support the LCA using SimaPro 7.3.

Description for the Biofuel Production Pathway

The plant capacity for the fast pyrolysis and bio-oil upgrading facility is assumed to be 2000 metric tons per day of dry biomass feedstock and the bio-oil yield is assumed to be 65% of the dry biomass, based on a previous techno-economic analysis we have performed [36]. Corn stover is selected as the feedstock for the production of hydrogen and transportation fuels. Bio-oil production from raw feedstock includes biomass preprocessing, biomass fast pyrolysis, bio-oil recovery, solids removal, and heat generation. All of the five steps are identical to those of previous techno-economic analyses [37-40]. In the biomass preprocessing step, biomass containing 25 wt.% moisture is chopped to 10 mm particle diameter, dried to 7 wt.% moisture content, and ground to 3 mm particle diameter. In the fast pyrolysis step, biomass is converted into non-condensable gases, bio-oil vapors, and solid char phases in a fluidized bed reactor operating at 500^{o}C and ambient pressure. The bio-oil vapors are recovered using a condenser and an electrostatic precipitator. In the solids removal step, 90% of the entrained char and ash particles are removed from the pyrolysis products through cyclones. Finally, in the combustion step, the non-condensable gases and a portion of the solid char are burned to generate heat for operating the pyrolyzer. The remainder of the char is treated as coal substitute locally consumed. The complete process diagram is illustrated in Figure 1.

The bio-oil is phase-separated into a water insoluble phase and an aqueous phase using a liquid-liquid (L-L) extractor. The insoluble phase is upgraded to gasoline and diesel fuel through hydrotreating and hydrocracking. Although some studies assume hydrogen for upgrading is obtained from steam reforming of natural gas, this study assumes that hydrogen is produced from steam reforming of the aqueous phase of bio-oil [41], which has advantages in decreasing GHG emissions, but at the cost of lower carbon yields of gasoline and diesel fuel from bio-oil. The water-insoluble phase is first hydrotreated followed by hydrocracking under zeolite catalysts to produce gasoline and diesel fuel. The aqueous phase is reformed to hydrogen through a two-stage catalytic process. A pressure swing adsorption (PSA) unit is employed to separate hydrogen from the reformed gas. A portion of the hydrogen is used to hydrocrack the water-insoluble phase of the bio-oil, and the rest of the hydrogen is treated as a co-product.

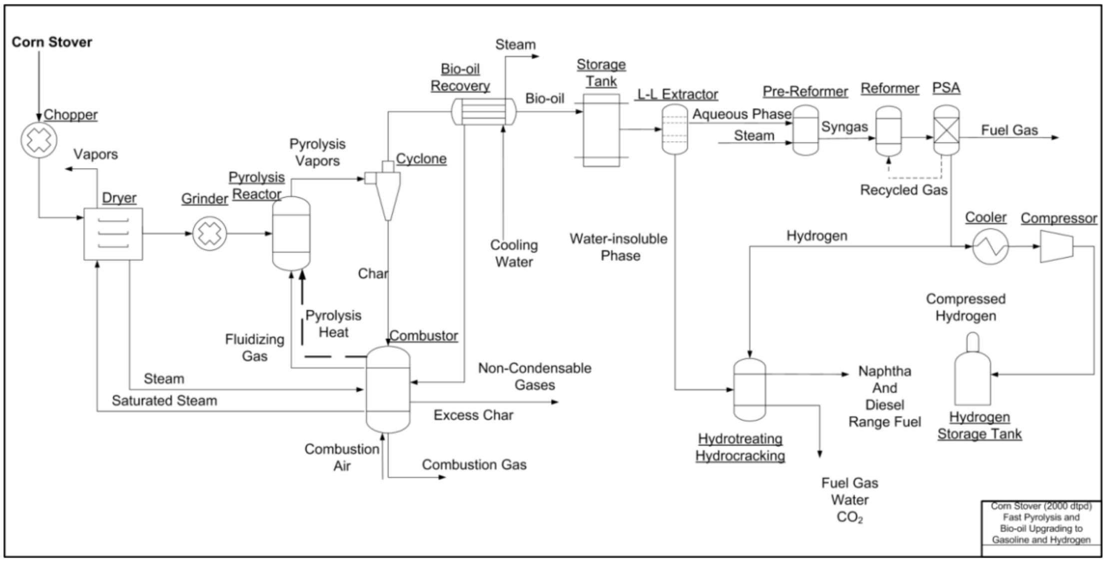


Figure 1. Process diagram for fast pyrolysis of corn stover and upgrading of the resulting bio-oil to hydrogen, gasoline and diesel fuel (adapted from [40, 47]).

LCA Goal and Scope Definition

The goal of this LCA study is to identify the environmental impacts of the production of hydrogen and transportation fuels from corn stover fast pyrolysis with upgrading. This well-to-wheel analysis is divided into seven unit processes, which include biomass production, biomass transportation, biomass preprocessing, bio-oil production, bio-oil upgrading, product distribution, and vehicle operations. It includes all resource consumption from biomass production to vehicle operations. Figure 2 illustrates the system boundary for the LCA. The bio-oil production unit is a combination of the steps of biomass fast pyrolysis, bio-oil recovery, solids removal, and heat generation. The bio-oil production unit is shown as a sub-block within the system boundary. Initially, corn stover is produced on farms and transported to an integrated biomass fast pyrolysis and upgrading facility. In the integrated facility, the biomass is preprocessed and converted to intermediate bio-oil that is upgraded to transportation fuels. The transportation fuels are then transported and distributed to the customer zones, where the fuel is used for vehicle operations. Electricity needed for processing is assumed to be generated from the same fuel mix in the Midwest region of the U.S. [42]. Indirect effects such as Indirect Land Use Change (ILUC) are not included in this study. The effects of indirect land use change are potentially large [43-45] but also highly controversial. ILUC is thought to be too diffuse and subject to too many arbitrary assumptions to be useful for rule-making [46]. In addition, severe qualifications are required for measurement of GHG emissions associated with ILUC [46]. So the indirect land use change effects are not considered in this LCA study.

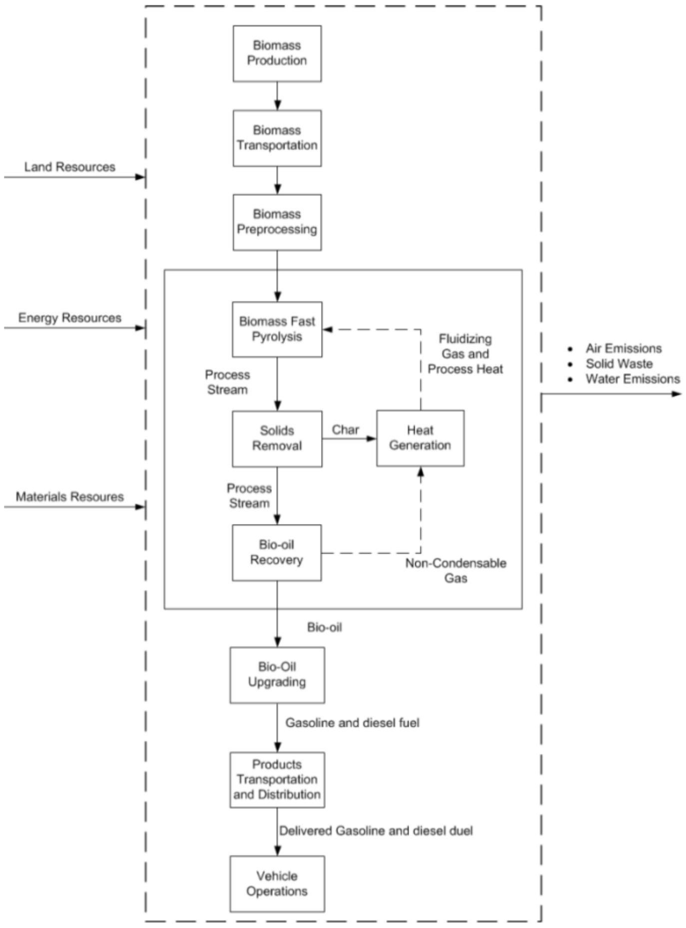


Figure 2. Life cycle system boundary for the production of hydrogen and transportation fuels from corn stover via fast pyrolysis and upgrading.

The Aspen Plus process model for the production of hydrogen and transportation fuels from fast pyrolysis of corn stover is adapted from a previous model developed as part of a joint study by Iowa State University, the National Renewable Energy Laboratory, and ConocoPhillips Company [47]. This Aspen Plus model has been adapted for subsequent techno-economic analysis of the production of hydrogen and transportation fuels from corn stover [48]. In the present study, the model assumes an n^{th} plant facility with mature technology processing 2000 metric tons per day of dry biomass. The functional unit for interpreting the LCA results is 1 km traveled by a light-duty passenger vehicle operated on fuels generated via fast pyrolysis. The required materials and energy inputs associated with the unit processes of the LCA are derived from an Aspen Plus model [48] along with GREET model [49] and U.S. Life Cycle Inventory Database [50]. SimaPro 7.3 software with an Eco-invent 2.2 database is employed to estimate environmental aspects such as climate change, fossil energy input, land use, and ozone layer impacts for the primary unit processes. IPCC 2007 GWP 100a, Cumulative Energy Demand (CED), and TRACI 2 methods developed by the US Environmental Protection Agency (EPA) are used to calculate life cycle impacts. The IPCC 2007 GWP 100a method is employed to evaluate life cycle GHG emissions for the production of hydrogen and transportation fuels from corn stover [51]. The Cumulative Energy Demand (CED) method [52] is used to estimate the energy demand for the production of hydrogen and transportation fuels. The TRACI 2 method [53] is employed to evaluate other potential environmental impacts (acidification, eutrophication, ecotoxicity, etc.).

Inventory Analysis

Biomass Production

Biomass production is based on the cultivation and collection of corn stover residue. The input energy and GHG emissions associated with corn stover cultivation and collection are included in the overall inventory analysis. Inventory data for corn stover collection is compiled from a U.S. Life Cycle Inventory Database [50] and a GREET model [49]. The Low Heating Value (LHV) for corn stover is assumed to be 15.4 MJ/kg [50]. The yield of corn stover is assumed to be 2.1 dry tons/acre [54]. The mass ratio and energy content ratio of stover to corn produced in agriculture are roughly 1:1 [55, 56]. We assume a corn stover removal rate of 62% from a previous LCA [5]. The ratio of energy and emissions allocation between corn and stover for partitioning is assumed to be 1:0.62 [5]. Diesel fuel input data for the corn stover production is adopted from the GREET model [49].

Traditionally, the bulk of corn stover has been left in the field to replenish the soil with nitrogen (N), phosphorus (P), and potassium (K) [54]. If the corn stover is used for biofuels production, it will require farmers to replenish lost nutrients through supplementary fertilization [54]. Based on the GREET model analysis, the replacement rates for N, P, and K-fertilizer sources are 7700 g N, 2000 g P_2O_5 (873 g P) and 12000 g K_2O (9957 g K) for 1 ton of removed corn stover [49]. Direct N_2O and NO emissions from agricultural soil due to N fertilizer application are assumed to be 1.325% and 0.65% [49]. Diesel fuel is consumed during biomass production. All of the input data for biomass production are detailed in Table 1.

Table 1. Inventory data for biomass production

Item	Amount	Unit
Outputs		
Collected corn stover	1	kg
Resources		
Biomass energy	15.4	MJ
Materials and fuels		
N fertilizer	8.5	g
P_2O_5	2.2	g
K_2O	13.2	g
Diesel fuel for corn stover loader	0.12	g
Diesel fuel for corn stover	5.15	g
Emission to air		
N_2O	0.085	g
NO	0.12	g

Biomass Transportation

For biomass transportation, it is assumed that the wet feedstock, which contains 25 wt.% moisture, is transported by 40 ton trucks (one-way). The transportation distance of feedstock is 60 miles one way for corn stover, based on analysis of the GREET model [49]. The delivered wet biomass is 2670 metric tons with 25 wt.% moisture. Detailed input data for the biomass transportation are summarized in Table 2.

Table 2. Inventory data for biomass transportation.

Item	Amount	Unit
Outputs		
Delivered corn stover	2670	metric ton
Input from material		
Truck 40t	284000	tkm
Collected corn stover	2670	metric ton

Biomass Preprocessing

In the drying step, steam is employed to remove water from the biomass. For the inventory analysis of biomass preprocessing, the electricity and steam usages are considered as material inputs and the ejected water vapor from the drying step is considered an emission to the air (see Table 3). The electricity requirement for reducing biomass particle size is calculated from the correlation developed by Mani et al. [57].

Table 3. Inventory data for biomass preprocessing

Item	Amount	Unit
Outputs		
Pretreated corn stover	2150	metric ton
Materials and fuels		
Delivered corn stover	2670	metric ton
Steam	184	metric ton
Electricity for chopping	44600	kwh
Electricity for grinding	109000	kwh
Electricity for compressor	124000	kwh
Emission to air		
Water	519	metric ton

Bio-oil Production

The inventory analysis of bio-oil production includes the inventory for biomass fast pyrolysis, bio-oil recovery, solids removal, and heat generation (see Table 4). In the biomass fast pyrolysis and recovery processes, a portion of the generated char is sent to a combustor to supply heat for pyrolysis. The heating value of the char is assumed to be 27.5 MJ/kg [47]. The non-condensable gases and part of the char generated during pyrolysis provide sufficient heat to operate the pyrolyzer. . The excess char is treated as a product that displaces coal with an assumed heating value that is half that of the coal it displaces. Local consumption of excess char is assumed, so char transport is not considered for local consumption.

The electricity, air, and process water are considered to be the inputs while the bio-oil is considered to be the output. The electricity inputs include electricity for biomass pyrolysis, bio-oil recovery, and char combustion, which are collected from the Aspen Plus model [36]. The process water is mainly used in bio-oil recovery, and air provides oxygen for combustion of non-condensable gases and char. The emissions from the bio-oil production unit are gases and solids, including carbon oxides, hydrocarbons, nitrogen oxides, sulfide, PM10, and ash. Combustion accounts for virtually all of the PM10 particulate emissions from processing-related activities. Studies of the emission behavior and characteristics of PM10 from combustion of biochar or coal show that there is a correlation between the inherent ash content and the amount of PM10 emitted [58, 59]. For PM10 emission calculations, linear regression was used to identify the correlation between ash content and the wt.% of coal ash transferred into PM10, as reported in the literature [59]. The ash separated in cyclones is disposed to sanitary landfills for waste treatment.

Table 4.. Inventory data for bio-oil production.

Item	**Amount**	**Unit**
Outputs		
Corn stover bio-oil	1300	metric ton
Char	216	metric ton
Avoided Products		
Coal	216	metric ton
Resources		
Air	4300	metric ton
Process water	8010	metric ton
Materials and fuels		
Pretreated corn stover	2150	metric ton
Electricity for pyrolysis	543000	kwh
Emission to air		
N_2	1330	metric ton
O_2	20.0	metric ton
H_2	1.5	metric ton
CO	113	metric ton
CO_2	754	metric ton
Water	114	metric ton

Table 4 continued		
NH_3	0.000024	metric ton
NO	2.4	metric ton
NO_2	0.00017	metric ton
Sulfur	0.059	metric ton
SO_2	0.16	metric ton
COS	0.00038	metric ton
H_2S	0.00084	metric ton
N_2O	0.00014	metric ton
HCN	0.000048	metric ton
PM10	2.7	metric ton
Waste or emissions to treatment		
Ash	84.9	metric ton

Bio-oil Upgrading

The final products are gasoline, diesel fuel and hydrogen from bio-oil upgrading. The total gasoline and diesel fuel yield is 164.6 metric ton/day (50% share of gasoline and 50% share of diesel), and the hydrogen yield is 63 metric ton/day. Hydrogen is assumed to be a co-product with product displacement based on the displaced usage of natural gas. Based on a previous study, 3.53 kg of natural gas is required for 1 kg of hydrogen production [60]. The environmental impacts allocation is based on the mass allocation between gasoline and diesel, which is 50% of the total environmental burden. The inventory inputs include air, catalysts, process water, electricity, and bio-oil. The process water includes water used for gas cooling and separation. The waste water from bio-oil upgrading step is assumed to be sent to a waste water treatment plant. The catalysts employed in bio-oil upgrading are zeolite powders (0.45 metric ton) for hydrocracking and Ni-based catalysts (0.73 metric ton) for hydrotreating, with consumption based on gas hourly space velocities (GHSV). Details of the inventory data are shown in Table 5.

Table 5..Inventory data for bio-oil upgrading.

Item	Amount	Unit
Outputs		
Gasoline	82.3	metric ton
Diesel fuel	82.3	
Hydrogen	63.2	metric ton
Avoided Products		
Natural Gas (in ground)	223	metric
Resources		
Air	1500	metric ton
Process water	12300	metric ton
Materials and fuels		
Corn stover bio-oil	1250	metric ton
Electricity for upgrading	291000	kwh
Zeolite powder	0.45	metric ton
Ni-based catalyst	0.73	metric ton
Emission to air		
N_2	1160	metric ton
O_2	234	metric ton
CO	0.0015	metric ton
CO_2	1070	metric ton
Water	906	metric ton
CH_4	0.007	metric ton
C_3H_6	0.00012	metric ton
CH_2O_2	0.00014	metric ton
NO_2	0.00014	metric ton
Waste or emissions to treatment		
Waste water	582	metric ton

Product Transportation and Distribution

For gasoline transportation, we assume transportation by barge, pipeline, and rail apportioned as 8%, 63%, and 29%, respectively. The distances for the three modes are 520 km, 400 km and 800 km, respectively. For diesel fuel transportation, we assume transportation by barge, rail and truck apportioned as 8%, 29% and 63%, respectively. The distances for the three modes are 520 km, 800 km and 50 km, respectively. Gasoline and diesel fuel are locally distributed by truck with an average travel distance of 30 km. All the assumptions and data are based on the GREET model's fast pyrolysis pathway [49]. Details of the inventory analysis for gasoline and diesel fuel transportation and distribution are shown in Table 6 and Table 7.

Table 6. Inventory data for gasoline transportation and distribution

Item	Amount	Unit
Outputs		
Delivered gasoline	82.3	metric ton
Input from material/telescope		
Gasoline	82.3	metric ton
Barge	6070	tkm
Pipeline	36800	tkm
Rail	33900	tkm
Truck 40t (distribution)	4380	tkm

Table 7. Inventory data for diesel fuel transportation and distribution

Item	Amount	Unit
Outputs		
Delivered diesel fuel	82.3	metric ton
Input from material/telescope		
Gasoline	82.3	metric ton
Barge	6070	tkm
Rail	33900	tkm
Truck 40t (transportation)	4600	tkm
Truck 40t (distribution)	4380	tkm

Vehicle Operations

Gasoline emissions are assumed for a vehicle operated using 50% conventional and 50% reformulated gasoline. Gasoline emissions are based on combustion in a spark-ignition engine while diesel fuel emissions are based on combustion in a direct-injection compression ignition engine using low-sulfur diesel. The mass density and heating value of low sulfur diesel fuel is assumed. The fuel economy for gasoline and diesel fuel is 23.4 and 28.1 miles per gallon (MPG), respectively. All of the stated assumptions and required data for assumed vehicle operations are based on default values of the GREET model [49]. The inventory data of vehicle operations on gasoline and diesel fuel bases are described in Table 8 and Table 9.

Table 8. Inventory data for vehicle operations fueled by pyrolysis derived gasoline.

Name	**Amount**	**Unit**
Outputs		
Car operation, by gasoline	1	mile
Materials and fuels		
Delivered gasoline	0.121	kg
Emission to air		
VOC	0.18	g
CO	3.75	g
NOx	0.141	g
PM10	0.029	g
PM2.5	0.015	g
Sulfur oxides	0.00612	g
CH_4	0.0146	g
N_2O	0.012	g
CO_2	371	g

Table 9. Inventory data for vehicle operations fueled by pyrolysis derived diesel fuel.

Name	**Amount**	**Unit**
Outputs		
Car operation, by diesel fuel	1	mile
Materials and fuels		
Delivered diesel fuel	0.113	kg
Emission to air		
VOC	0.088	g
CO	0.539	g
NOx	0.141	g
PM10	0.030	g
PM2.5	0.016	g
Sulfur oxides	0.002	g
CH_4	0.003	g
N_2O	0.012	g
CO_2	322	g

Results and Discussions

Fossil Energy Input

Figure 3 shows the breakdown of fossil energy input for various unit processes on the bases of gasoline and diesel fuel. The fossil energy input is separated into two parts: required fossil energy for various unit processes and co-products credits (shown as negative fossil energy input). As indicated in the figure, bio-oil production has the largest fossil energy input. It consumes 32% of the total required fossil energy among all the unit processes. In the bio-oil production unit, char is treated as a coal substitute, which contributes to 1.34 MJ/km and 1.25 MJ/km reductions to the total fossil energy input. Biomass production has the second largest fossil fuel demand of approximately 22% of the total required fossil energy for both gasoline and diesel fuel bases. Biomass preprocessing also plays a significant role, which demands approximately 21% of the total required fossil energy. Electricity consumption during biomass chopping, grinding, and drying is responsible for the largest fossil energy input for biomass preprocessing. Bio-oil upgrading consumes approximately 20% of the fossil energy input. Hydrogen as a co-product is produced from bio-oil steam reforming, which results in avoided use of natural gas in the bio-oil upgrading unit. Consequently, 5.1 MJ/km and 4.8 MJ/km are subtracted from the total fossil energy input as hydrogen credits. Due to the hydrogen and char credits, the net fossil energy input is 0.25 MJ/km and 0.23 MJ/km for gasoline and diesel fuel bases, respectively.

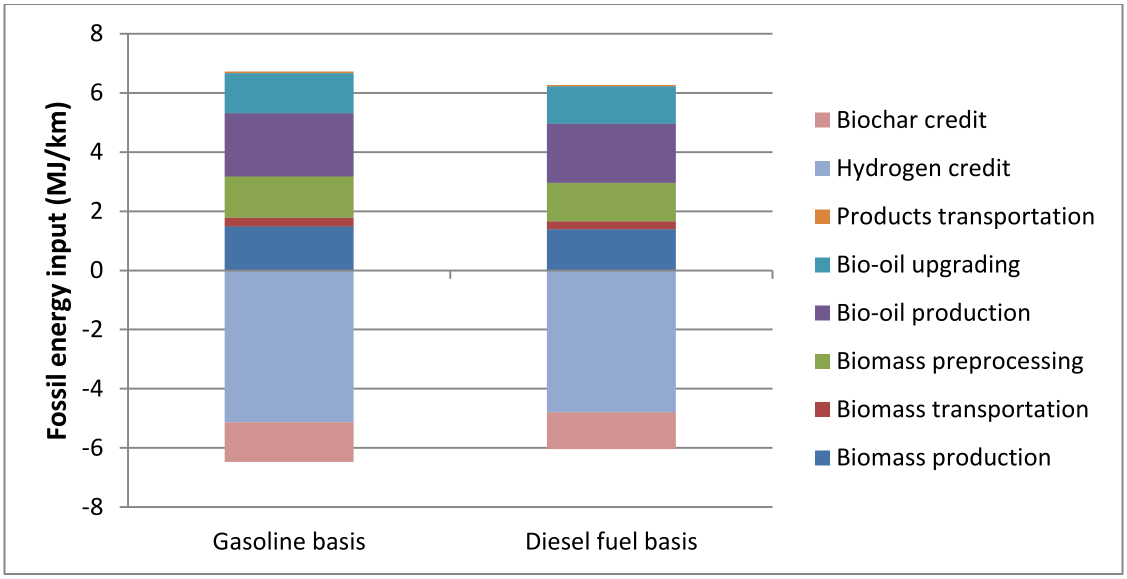


Figure 3. Fossil fuel energy inputs for various unit processes per km traveled. Note: Biochar and hydrogen credits are treated as negative fossil energy inputs.

GHG Emissions

Figure 4 details the breakdown of the various contributions of unit process to GWP for both gasoline and diesel fuel bases. In the biomass production step, GWP contributions are separated into two parts: CO_2 absorption during biomass cultivation and CO_2 emissions during biomass harvesting. For 1 kg corn production, the atmosphere can uptake 1.49 kg CO_2 during cultivation based on the U.S. Life Cycle Inventory Database (National Renewable Energy Laboratory 2012). The amount of CO_2 absorption allocated to corn stover is assumed on a basis of mass fraction. We assume corn stover occupies 38% mass fraction of total participating corn and stover; thus, the CO_2 absorption contributed by corn stover is 38% of the whole CO_2 absorption of 1 kg corn production. As a result, 1 kg corn stover could uptake 0.57 kg CO_2.

For a light-duty vehicle fueled by gasoline, the total corn stover CO_2 absorption is 0.69 kg CO_2eq/km, and the total positive GWP (excluding feedstock absorption) is 0.73 kg CO_2eq/km. Vehicle operations exhibit the largest GHG footprint, contributing 33% of total positive GWP for a gasoline basis. Bio-oil production has the second largest GHG emissions, contributing 25% of total positive GWP. This is because bio-oil production involves char and non-condensable gas combustion, which release direct GHG emissions to the environment. Biomass preprocessing has a 16% contribution to total GWP.

The large quantity of GHG emissions associated with electricity usage in biomass preprocessing is the main reason for this large GWP contribution. Bio-oil upgrading contributes 9% of the total positive GWP because the reduced GWP from avoided natural gas is subtracted from the total GWP as a hydrogen credit. This means that hydrogen production from bio-oil steam reforming as co-product makes considerable contribution to GWP reduction in this step. Biomass transportation and product distribution have the smallest contributions among all of the steps, representing 3% and 0.5% of the total positive GWP for both gasoline and diesel fuel bases.

For a light-duty vehicle using diesel fuel, the total corn stover CO_2 absorption is 0.66 kg CO_2eq/km, and the total positive GWP (excluding feedstock absorption) is 0.66 kg CO_2eq/km. It has a similar breakdown of contributions among the various unit processes but smaller GWP compared to travel in a light-duty vehicle using gasoline. This is because diesel fuel has better fuel economy than gasoline, even after considering the differences in energy content for gasoline and diesel. The net GWP traveled using gasoline and diesel fuel are 0.037 and 0.015 kg CO_2eq/km, respectively.

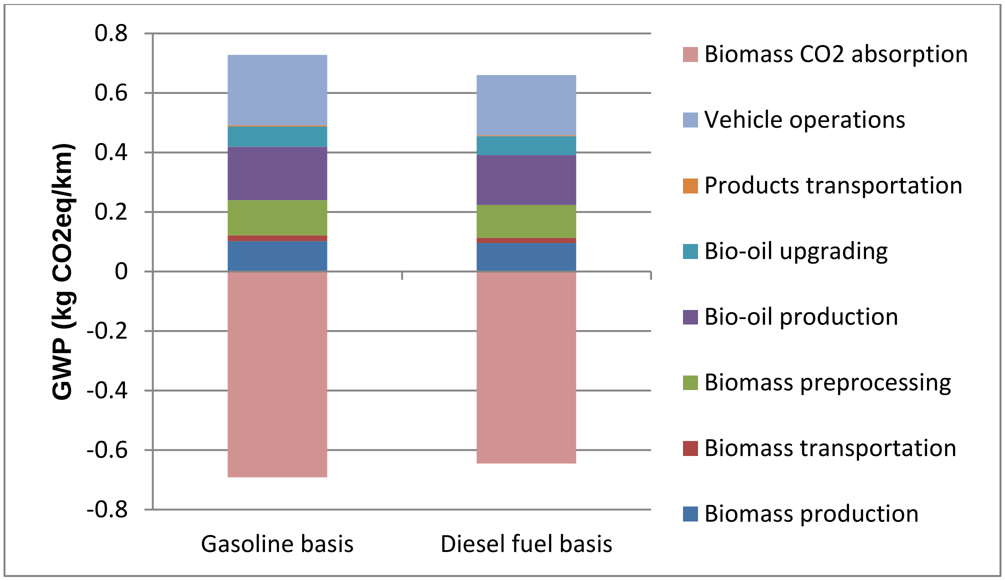


Figure 4. Contributions of unit process to global warming reported on a per km traveled basis. Note: Biomass CO_2 absorption is treated as a negative contribution to total GWP.

Other Impact Categories

Other potential environmental impacts such as acidification, eutrophication, and ecotoxicity are evaluated by TRACI 2 method. Table 10 presents the potential environmental impacts of the gasoline and diesel fuel products.

Figure 5 shows the relative contributions of different unit process to the potential environmental impacts on a gasoline basis. Biomass transportation has the largest contribution (55%) for ozone depletion among the unit processes. For smog, acidification, and eutrophication, bio-oil production has the largest contribution, which is up to 53% contribution to the total impact. Bio-oil upgrading has significant impacts on eutrophication, carcinogenics, non-carcinogenics, respiratory effects and ecotoxicity, with contributions ranging from 28% to 46%. Vehicle operations have comparatively small contributions to smog, acidification, and respiratory effects, representing less than 5%.

Table 10. Environmental profile of gasoline and diesel products (based on one km traveled by light-duty vehicle)

Impact category	Unit	Gasoline	Diesel
Ozone depletion	kg CFC-11 eq	6.93E-08	6.07E-08
Smog	kg O3 eq	0.076	0.071
Acidification	mol H+ eq	0.28	0.27
Eutrophication	kg N eq	0.17	0.16
Carcinogenics	CTUh	2.07E-08	1.92E-08
Non carcinogenics	CTUh	7.29E-08	6.82E-08
Respiratory effects	kg PM10 eq	0.00065	0.00061
Ecotoxicity	CTUe	0.45	0.42

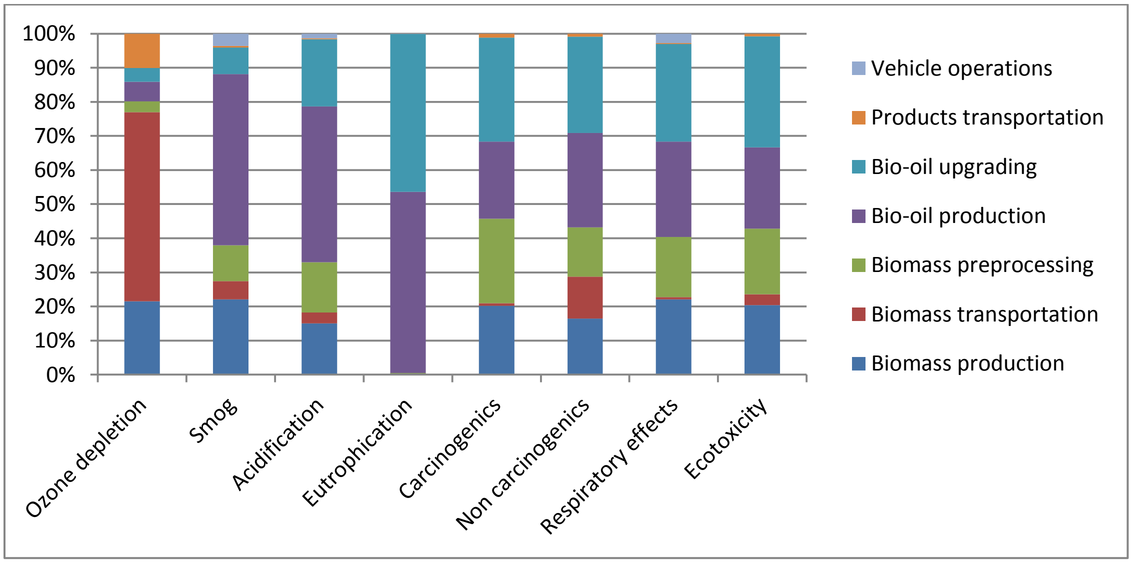


Figure 5. Contribution of unit processes to potential environmental impacts (gasoline basis).

Comparison to Previous Studies

Table 11 compares GHG emissions and fossil energy inputs determined in the present study to results from several previous LCAs of biomass-derived transportation fuels. The first case is an analysis performed by the National Renewable Energy Laboratory (NREL) [61] based on fast pyrolysis of forest residue with bio-oil hydroprocessing to gasoline and diesel fuel (Case A in Table 11) as proposed by Pacific Northwest National Laboratory (PNNL) ([19]. Compared to this case, the net GHG emissions on gasoline and diesel fuel bases for the present study are lower by 68% and 65%, respectively. This is mainly because the present study assumes hydrogen for hydrotreating comes from steam reforming of bio-oil whereas the NREL study assumes hydrogen comes from steam reforming of natural gas.

The next three cases are variations of an LCA for an integrated biorefinery based on the GREET model (Cases B1, B2 and B3 in Table11). These cases are: transportation fuels from fast pyrolysis of forest residue with hydrogen from natural gas reforming (Case B1), transportation fuels from fast pyrolysis of corn stover with hydrogen from natural gas reforming (Case B2) and transportation fuels from fast pyrolysis of corn stover with hydrogen from bio-oil reforming (Case B3). Production of both hydrogen and transportation fuels from corn stover has less GHG emissions than the other cases. For Case B1, the amount of internal hydrogen production from bio-oil reforming is only used for hydrotreating so there is no excess hydrogen as co-product. The amount of GHG emissions for the present study on a gasoline basis is 12% lower than for Case B1. The present study showed 62% and 68% reductions in GHG emissions on a gasoline basis compared to Case B2 and Case B3, respectively.

The present study is also compared to ethanol production via indirect gasification of forest residue and mixed alcohol synthesis process (Case C in Table 11) [6], which has the largest GHG emissions and fossil energy input for biofuels among the previous studies examined (0.15 CO_2eq/km and 0.258 CO_2eq/km on a gasoline basis and diesel fuel basis, respectively). Greenhouse gas emissions from petroleum-based gasoline and diesel fuel in 2005 (Case D in Table 11) are assumed to be 0.3 and 0.258 kg CO_2eq/km which are based on an well-to-wheel analysis using the GREET model [53]. Net GWP for the present study are 88% and 94% lower than petroleum-based gasoline and diesel fuel GHG emissions in 2005, respectively, which meet the criteria of 50% GHG emissions reduction mandated by RFS2.

The co-production of hydrogen and transportation fuels in the present study has the smallest GHG emissions and fossil energy input compared to the selected previous studies when transportation fuels are the only product. This indicates that the co-production of hydrogen, gasoline and diesel fuel via fast pyrolysis and upgrading of corn stover, although producing lower yields of gasoline and diesel, has lower GHG emissions and fewer fossil energy inputs than these other studies because of their use of natural gas as a source of hydrogen for upgrading.

Table 11. Comparison results of environmental impacts for 1km driven by car operated on gasoline or diesel fuel.

Gasoline basis	**GHG emissions ($kg\ CO_2eq/km$)**	**Fossil energy input (MJ/km)**
Pyrolysis gasoline for the current study	0.037	0.25
Case A: Pyrolysis gasoline from forest residue [a]	0.117	1.7
Case B1: Pyrolysis gasoline from corn stover (hydrogen from bio-oil reforming) [b]	0.0422	0.4
Case B2: Pyrolysis gasoline from corn stover (hydrogen from natural gas steam reforming) [b]	0.0975	1.22
Case B3: Pyrolysis gasoline from forest residue (hydrogen from natural gas steam reforming) [b]	0.115	1.5
Case C: Ethanol via gasification [c]	0.15	1.2
Case D: 2005 petroleum-based gasoline [d]	0.3	4.5

Diesel fuel basis	**GHG emissions ($kg\ CO_2eq/km$)**	**Fossil energy input (MJ/km)**
Pyrolysis diesel fuel for the current study	0.015	0.23
Case A: Pyrolysis diesel fuel from forest residue [a]	0.098	1.42
Case B1:Pyrolysis diesel fuel from corn stover (hydrogen from bio-oil reforming) [b]	0.0354	0.325
Case B2: Pyrolysis diesel fuel from corn stover (hydrogen from natural gas steam reforming) [b]	0.0814	1.02
Case B3: Pyrolysis diesel fuel from forest residue (hydrogen from natural gas steam reforming)[b]	0.0963	1.22
Case D: 2005 petroleum-based diesel fuel [d]	0.258	3.1

[a] Data is from NREL report [60]
[b] Data is from GREET model [61]
[c] Data is from Hsu et al. [6]
[d] Data is from GREET model [61]

Sensitivity Analysis

The sensitivity analysis of GHG emissions to various operational parameters in the production of hydrogen and transportation fuels from corn stover is illustrated in Figures 6 and 7. The parameters investigated include fuel economy, bio-oil yield, products yield, electricity consumption, biomass transportation distances and nitrogen fertilizer consumption. Sensitivity analysis is conducted by changing each operating parameter by a prescribed amount around the baseline operating conditions (expressed as a percentage of the baseline case).

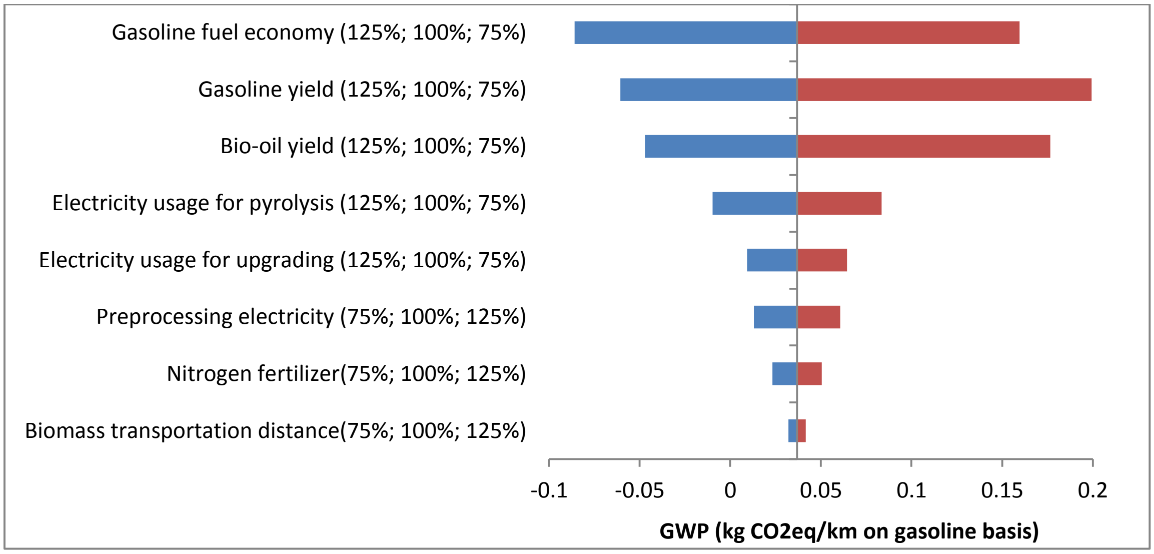


Figure 6. Sensitivity of GHG emissions to operating conditions on a gasoline basis (changes in operating parameters are expressed as a percentage of the baseline case).

As indicated in Figure 6, overall net GWP ranges from -0.086 to 0.2 kg CO_2eq/km on gasoline basis. Gasoline fuel economy has the greatest impact on GHG emissions. A ±25% variation of fuel economy on the baseline results in a -0.086 to 0.16 kg CO_2eq/km range of GWP. Yields of bio-oil and gasoline have significant impacts on GHG emissions. Low yield of gasoline (75% of the baseline) generates the highest GWP of 0.2 kg CO_2eq/km. Electricity consumption also has an important impact. If the electricity consumption for biomass fast pyrolysis varies ±25% from the baseline, GHG emissions vary from -0.01 to 0.084 kg CO_2eq/km. A variation of ±25% in bio-oil upgrading, electricity consumption, or electricity consumption for biomass preprocessing would also change GWP in a range of 0.01-0.064 kg CO_2eq/km on gasoline basis. Nitrogen fertilizer has comparatively smaller impact than the previous parameters. When nitrogen fertilizer is reduced to 75% of the baseline, a GWP of 0.023 kg CO_2 eq/km on a gasoline basis can be achieved with 92% GHG emissions reduction compared to the 2005 petroleum-based gasoline baseline.

The sensitivity analysis on a diesel fuel basis is illustrated in Figure 7. Diesel fuel economy, diesel fuel yield and bio-oil yield are the most important parameters for GWP. The overall range of GWP based on this sensitivity analysis ranges from -0.1 to 0.17 kg CO_2eq/km traveled by light-duty vehicle fueled by diesel fuel. If diesel fuel yield is only 75% of the baseline, GWP reaches its highest value of 0.17 kg CO_2eq/km. GWP reaches its lowest value of -0.1 kg CO_2eq /km if diesel fuel economy increases to 125% of the baseline. Generally, the trend of the sensitivity analysis for the diesel fuel basis is similar to the gasoline basis. But because diesel fuel has a higher fuel economy than gasoline, the GWP for biobased diesel fuel is smaller than for biobased gasoline under the same operating conditions.

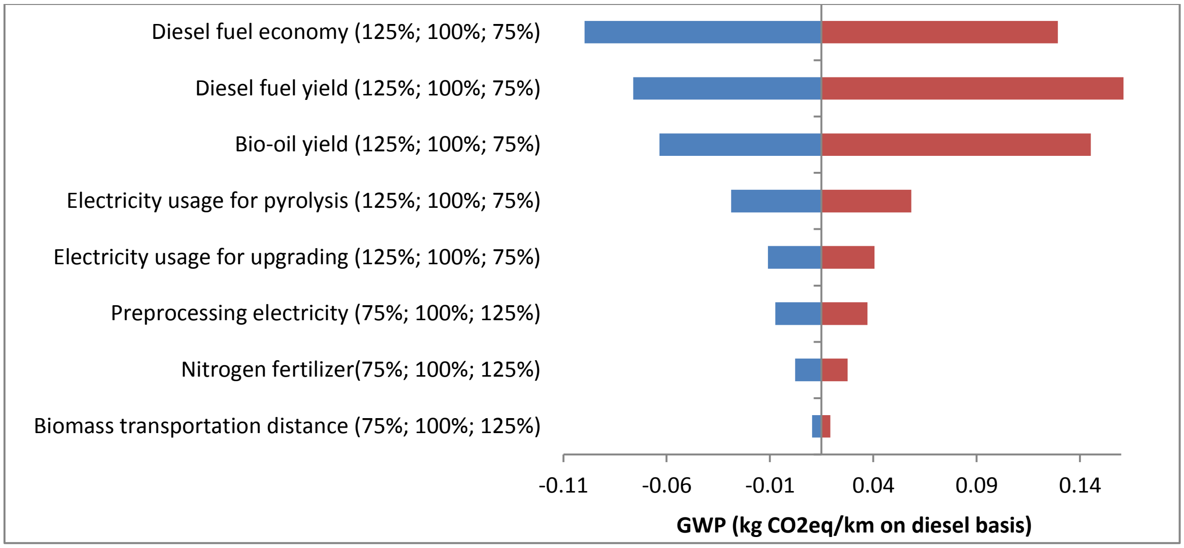


Figure 7. Sensitivity of GHG emissions to operating conditions on a diesel fuel basis (changes in operating parameters are expressed as a percentage of the baseline case).

Conclusions

A life cycle assessment of the production of hydrogen and transportation fuels from fast pyrolysis and upgrading of corn stover is examined in this study. The co-production of hydrogen and transportation fuels have lower GHG emissions and fossil energy input than scenarios where transportation fuels are the only products from pyrolysis of biomass. The results indicate that bio-oil production, biomass preprocessing, and bio-oil upgrading are the key drivers in determining overall environmental impacts of this biofuels pathway. Among the unit processes, bio-oil production has the largest energy demand and contributes the largest GHG emissions. The co-products hydrogen and char greatly reduce fossil fuel consumption in the production of transportation fuels by this pathway. Fossil energy input is 0.25 MJ and 0.23MJ per km traveled by a light-duty vehicle fueled by pyrolysis-derived gasoline and diesel fuel, respectively. The fossil energy input for this pathway is 0.25 MJ/km and 0.23 MJ/km for the gasoline and diesel fuel bases, respectively. Hydrogen for hydrotreating is produced from reforming of bio-oil instead of reforming of natural gas, so significant quantities of fossil energy are saved compared to generating hydrogen from natural gas. The net GWP is 0.037 kg CO_2eq and 0.015 kg CO_2eq per km traveled by light-duty vehicle fueled by gasoline and diesel fuel, respectively. Compared to petroleum-based gasoline and diesel fuel, GHG emissions are reduced 88% and 94%, respectively, which exceeds the RFS2 requirements. Biomass transportation has the largest impact on ozone depletion among the unit processes. Bio-oil production makes the largest contribution to smog, acidification, and eutrophication. Sensitivity analysis indicates that fuel economy is the most sensitive parameter in determining GWP. Transportation fuel yield, bio-oil yield, and electricity consumption also play significant roles in determining the GHG footprint, so there is potential to reduce GHG emissions with improvements to electricity generation.

Acknowledgements

The authors would like to acknowledge useful discussions with Tristan R. Brown in preparing this paper and the financial support of the Bioeconomy Institute and the Biobased Industry Center of Iowa State University.

References

[1] A.J. Kemppainen, D.R. Shonnard, Comparative Life-Cycle Assessments for Biomass-to-Ethanol Production from Different Regional Feedstocks, Biotechnology Progress, 21 (2005) 1075-1084.

[2] P.F. Pawelzik, Q. Zhang, Evaluation of environmental impacts of cellulosic ethanol using life cycle assessment with technological advances over time, Biomass and Bioenergy, 40 (2012) 162-173.

[3] A. Singh, D. Pant, N.E. Korres, A.-S. Nizami, S. Prasad, J.D. Murphy, Key issues in life cycle assessment of ethanol production from lignocellulosic biomass: Challenges and perspectives, Bioresource Technology, 101 (2010) 5003-5012.

[4] S. Spatari, D.M. Bagley, H.L. MacLean, Life cycle evaluation of emerging lignocellulosic ethanol conversion technologies, Bioresource Technology, 101 (2010) 654-667.

[5] S. Spatari, Y. Zhang, H.L. MacLean, Life Cycle Assessment of Switchgrass- and Corn Stover-Derived Ethanol-Fueled Automobiles, Environmental Science & Technology, 39 (2005) 9750-9758.
[6] D.D. Hsu, D. Inman, G.A. Heath, E.J. Wolfrum, M.K. Mann, A. Aden, Life Cycle Environmental Impacts of Selected U.S. Ethanol Production and Use Pathways in 2022, Environmental Science & Technology, 44 (2010) 5289-5297.

[7] L. Luo, E. van der Voet, G. Huppes, An energy analysis of ethanol from cellulosic feedstock–Corn stover, Renewable and Sustainable Energy Reviews, 13 (2009) 2003-2011.

[8] S. González-García, M.T. Moreira, G. Feijoo, Comparative environmental performance of lignocellulosic ethanol from different feedstocks, Renewable and Sustainable Energy Reviews, 14 (2010) 2077-2085.

[9] Y. Bai, L. Luo, E. Voet, Life cycle assessment of switchgrass-derived ethanol as transport fuel, Int J Life Cycle Assess, 15 (2010) 468-477.

[10] N. Kauffman, D. Hayes, R. Brown, A life cycle assessment of advanced biofuel production from a hectare of corn, Fuel, 90 (2011) 3306-3314.

[11] U.S. congress 2007 Energy Independence and Security Act of 2007 *Public Law* 110-140
[12] A.V. Bridgwater, Review of fast pyrolysis of biomass and product upgrading, Biomass and Bioenergy, 38 (2012) 68-94.

[13] S. Czernik, A.V. Bridgwater, Overview of Applications of Biomass Fast Pyrolysis Oil, Energy & Fuels, 18 (2004) 590-598.

[14] E. Heracleous, Well-to-Wheels analysis of hydrogen production from bio-oil reforming for use in internal combustion engines, International Journal of Hydrogen Energy, 36 (2011) 11501-11511.

[15] Z.W. Zhong, B. Song, M.B.M. Zaki, Life-cycle assessment of flash pyrolysis of wood waste, Journal of Cleaner Production, 18 (2010) 1177-1183.

[16] D.D. Hsu, Life cycle assessment of gasoline and diesel produced via fast pyrolysis and hydroprocessing, Biomass and Bioenergy, 45 (2012) 41-47.

[17] J. Fan, T.N. Kalnes, M. Alward, J. Klinger, A. Sadehvandi, D.R. Shonnard, Life cycle assessment of electricity generation using fast pyrolysis bio-oil, Renewable Energy, 36 (2011) 632-641.

[18] D. Iribarren, J.F. Peters, J. Dufour, Life cycle assessment of transportation fuels from biomass pyrolysis, Fuel, 97 (2012) 812-821.

[19] S.B. Jones, C. Valkenburg, C.W. Walton, D.C. Elliott, J.E. Holladay, D.J. Stevens, C. Kinchin, S. Czernik, Production of Gasoline and Diesel from Biomass via Fast Pyrolysis,

Hydrotreating and Hydrocracking: A Design Case, 2009. (Available at: http://www.pnl.gov/main/publications/external/technical_reports/pnnl-18284.pdf)

[20] A. Milbrandt, M. Mann, Hydrogen Resource Assessment: Hydrogen Potential from Coal, Natural Gas, Nuclear, and Hydro Power, 2009. NREL/TP-6A2-42773. (Available at: http://www.nrel.gov/docs/fy09osti/42773.pdf)

[21] J.A. Medrano, M. Oliva, J. Ruiz, L. Garc ía, J. Arauzo, Hydrogen from aqueous fraction of biomass pyrolysis liquids by catalytic steam reforming in fluidized bed, Energy, 36 (2011) 2215-2224.

[22] A.C. Basagiannis, X.E. Verykios, Steam reforming of the aqueous fraction of bio-oil over structured Ru/MgO/Al2O3 catalysts, Catalysis Today, 127 (2007) 256-264.

[23] C.-F. Yan, F.-F. Cheng, R.-R. Hu, Hydrogen production from catalytic steam reforming of bio-oil aqueous fraction over Ni/CeO2-ZrO2 catalysts, International Journal of Hydrogen Energy, 35 (2010) 11693-11699.

[24] E.C. Vagia, A.A. Lemonidou, Thermodynamic analysis of hydrogen production via autothermal steam reforming of selected components of aqueous bio-oil fraction, International Journal of Hydrogen Energy, 33 (2008) 2489-2500.

[25] T. Hou, L. Yuan, T. Ye, L. Gong, J. Tu, M. Yamamoto, Y. Torimoto, Q. Li, Hydrogen production by low-temperature reforming of organic compounds in bio-oil over a CNT-promoting Ni catalyst, International Journal of Hydrogen Energy, 34 (2009) 9095-9107.

[26] L. Garcia, R. French, S. Czernik, E. Chornet, Catalytic steam reforming of bio-oils for the production of hydrogen: effects of catalyst composition, Applied Catalysis A: General, 201 (2000) 225-239.

[27] M.E. Domine, E.E. Iojoiu, T. Davidian, N. Guilhaume, C. Mirodatos, Hydrogen production from biomass-derived oil over monolithic Pt- and Rh-based catalysts using steam reforming and sequential cracking processes, Catalysis Today, 133-135 565-573.

[28] S. Czernik, R. Evans, R. French, Hydrogen from biomass-production by steam reforming of biomass pyrolysis oil, Catalysis Today, 129 (2007) 265-268.

[29] F. Seyedeyn-Azad, E. Salehi, J. Abedi, T. Harding, Biomass to hydrogen via catalytic steam reforming of bio-oil over Ni-supported alumina catalysts, Fuel Processing Technology, 92 563-569.

[30] S. Thaicharoensutcharittham, V. Meeyoo, B. Kitiyanan, P. Rangsunvigit, T. Rirksomboon, Hydrogen production by steam reforming of acetic acid over Ni-based catalysts, Catalysis Today, 164 257-261.

[31] S.-p. Zhang, X.-j. Li, Q.-y. Li, Q.-l. Xu, Y.-j. Yan, Hydrogen production from the aqueous phase derived from fast pyrolysis of biomass, Journal of Analytical and Applied Pyrolysis, 92 158-163.

[32] F. Seyedeyn-Azad, E. Salehi, J. Abedi, T. Harding, Biomass to hydrogen via catalytic steam reforming of bio-oil over Ni-supported alumina catalysts, Fuel Processing Technology, 92 (2011) 563-569.

[33] T. Chen, C. Wu, R. Liu, Steam reforming of bio-oil from rice husks fast pyrolysis for hydrogen production, Bioresource Technology, 102 (2011) 9236-9240.

[34] P.J. Ortiz-Toral, J. Satrio, R.C. Brown, B.H. Shanks, Steam Reforming of Bio-oil Fractions: Effect of Composition and Stability, Energy & Fuels, 25 (2011) 3289-3297.

[35] S.-m. Liu, M.-q. Chen, J. Wang, F.-f. Min, M.-g. Chen, Hydrogen production by steam reforming for glycerol as a model oxygenate from bio-oil, in: Materials for Renewable Energy & Environment (ICMREE), 2011 International Conference on, 2011, pp. 303-307. (Available at: http://www.eia.gov/forecasts/steo/query/)

[36] Y. Zhang, T.R. Brown, G. Hu, R.C. Brown, Techno-economic analysis of two bio-oil upgrading pathways, Chemical Engineering Journal, 225 (2013) 895-904.

[37] T.R. Brown, Y. Zhang, G. Hu, R.C. Brown, Techno-economic analysis of biobased chemicals production via integrated catalytic processing, Biofuels, Bioproducts and Biorefining, 6 (2012) 73-87.

[38] T.R. Brown, M.M. Wright, R.C. Brown, Estimating profitability of two biochar production scenarios: slow pyrolysis vs fast pyrolysis, Biofuels, Bioproducts and Biorefining, 5 (2011) 54-68.

[39] Y. Zhang, T.R. Brown, G. Hu, R.C. Brown, Techno-economic analysis of monosaccharide production via fast pyrolysis of lignocellulose, Bioresource Technology, 127 (2013) 358-365.

[40] M.M. Wright, D.E. Daugaard, J.A. Satrio, R.C. Brown, Techno-economic analysis of biomass fast pyrolysis to transportation fuels, Fuel, 89, Supplement 1 (2010) S2-S10.

[41] T.L. Marker, Opportunities for Biorenewables in Oil Refineries, 2005. DOEGO15085 (Available at: http://www.osti.gov/energycitations/product.biblio.jsp?osti_id=861458)

[42] EIA, 2012 short term energy outlook, 2012. (Available at: http://www.eia.gov/forecasts/steo/query/)

[43] R.J. Plevin, M. O’Hare, A.D. Jones, M.S. Torn, H.K. Gibbs, Greenhouse Gas Emissions from Biofuels’ Indirect Land Use Change Are Uncertain but May Be Much Greater than Previously Estimated, Environmental Science & Technology, 44 (2010) 8015-8021.

[44] T. Searchinger, R. Heimlich, R.A. Houghton, F. Dong, A. Elobeid, J. Fabiosa, S. Tokgoz, D. Hayes, T.-H. Yu, Use of U.S. Croplands for Biofuels Increases Greenhouse Gases Through Emissions from Land-Use Change, Science, 319 (2008) 1238-1240.

[45] J. Fargione, J. Hill, D. Tilman, S. Polasky, P. Hawthorne, Land Clearing and the Biofuel Carbon Debt, Science, 319 (2008) 1235-1238.

[46] J.A. Mathews, H. Tan, Biofuels and indirect land use change effects: the debate continues, Biofuels, Bioproducts and Biorefining, 3 (2009) 305-317.

[47] M.M. Wright, J.A. Satrio, R.C. Brown, D.E. Daugaard, D.D. Hsu, Techno-Economic Analysis of Biomass Fast Pyrolysis to Transportation Fuels., in, Golden, CO: National Renewable Energy Laboratory, 2010, pp. 73.

[48] Y. Zhang, T.R. Brown, G. Hu, R.C. Brown, Techno-economic analysis of two bio-oil upgrading pathways, Chemical Engineering Journal.

[49] Argone National Laboratory, The greenhouse gases, regulated emissions, and energy use in tranportation (GREET) model, 2011. (Available at: http://greet.es.anl.gov/)

[50] National Renewable Energy Laboratory, U.S. life-cycle inventory database, in, Golden, CO, 2012. (Available at: https://www.lcacommons.gov/nrel/process/show/a319d03a-5895-47f7-a64b-9b026df9e3b9)

[51] IPCC 2007 Climate Change 2007:The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change (Cambridge: Cambridge University Press)

[52] M. Goedkoop, M. Oele, A. Schryver, M. Vieira, SimaPro Database Manual Methods library, PR éConsultants., 2008. (Available at: http://www.pre-sustainability.com/manuals)

[53] J. Bare, G. Norris, D. Pennington, T .McKone, The tool for the reduction and assessment of chemical and other environmental impacts, Journal of Industrial Ecology, 6 (2002) 49-78.

[54] J. Han, Elgowainy A, Palou-Rivera I, Dunn JB, Wang MQ, Well-to-Wheels Analysis of Fast Pyrolysis Pathways with GREET, 2011. (Available at: http://greet.es.anl.gov/publication-wtw_fast_pyrolysis)

[55] S. Kim, B.E. Dale, Global potential bioethanol production from wasted crops and crop residues, Biomass and Bioenergy, 26 (2004) 361-375.

[56] L.O. Pordesimo, B.R. Hames, S. Sokhansanj, W.C. Edens, Variation in corn stover composition and energy content with crop maturity, Biomass and Bioenergy, 28 (2005) 366-374.

[57] S. Mani, L.G. Tabil, S. Sokhansanj, Grinding performance and physical properties of wheat and barley straws, corn stover and switchgrass, Biomass and Bioenergy, 27 (2004) 339-352.

[58] L. Zhang, Y. Ninomiya, Emission of suspended PM10 from laboratory-scale coal combustion and its correlation with coal mineral properties, Fuel, 85 (2006) 194-203.

[59] X. Gao, H. Wu, Biochar as a Fuel: 4. Emission Behavior and Characteristics of PM1 and PM10 from the Combustion of Pulverized Biochar in a Drop-Tube Furnace, Energy & Fuels, 25 (2011) 2702-2710.

[60] C. Koroneos, A. Dompros, G. Roumbas, N. Moussiopoulos, Life cycle assessment of hydrogen fuel production processes, International Journal of Hydrogen Energy, 29 (2004) 1443-1450.

[61] D.D. Hsu, Life Cycle Assessment of Gasoline and Diesel Produced via Fast Pyrolysis and Hydroprocessing, 2011. NREL/TP-6A20-49341.

CHAPTER V

LIFE CYCLE ASSESSMENT OF COMMODITY CHEMICLAS PRODUCTION FROM FOREST RESIDUE VIA FAST PYROLYSIS

A paper submitted to International Journal of Life Cycle Assessment

Yanan Zhang, Guiping Hu and Robert C. Brown

Abstract

This life cycle assessment evaluates and quantifies the environmental impacts of replacing chemicals currently produced from fossil fuels with renewable chemicals produced from forest residue via fast pyrolysis with hydrotreating/fluidized catalytic cracking (FCC) pathway.

The assessment's input data are taken from Aspen Plus and GREET (Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation) modeling. SimaPro 7.3 software is employed to calculate the environmental impacts.

The results indicate that the net fossil energy input is 49.1 MJ to produce one kilogram of chemicals and the net Global Warming Potential (GWP) is 0.79 kg CO_2eq per kg chemicals produced under the current chemicals production pathway. Sensitivity analysis indicates that bio-oil yields and chemical yields play the most important roles in determining the greenhouse gas footprints.

Fossil energy consumption and GHG emissions could be reduced if commodity chemicals are produced via forest residue fast pyrolysis with hydrotreating/FCC pathway instead of conventional petroleum-based production pathways.

Introduction

Aromatics and olefins are two main types of petrochemicals and have a wide range of applications. Aromatics can be used to produce a number of petrochemical intermediates including styrene, phenol, purified terephthalic acid (PTA), and phthalic anhydride (PA) [1]. The most important commercial olefins are ethylene, propylene, and butadiene, all of which can be used to manufacture rubbers, polymer resins, and other chemical intermediates [2]. In 2012, the aromatics production capability of the U.S. petroleum refining sector reached 296,911 barrels per day [3]. The demand for light olefins in the U.S. is expected to increase at a compounded annual growth rate (CAGR) of 3.4% over the period 2010-2020, reaching approximately 68.4 million tons by 2020 [4]. Petrochemicals are generally produced from fossil feedstocks such as the refining of crude oil or the processing of natural gas. Global petrochemicals feedstock consumption is projected to rise through 2025 with the greatest proportion coming from naphtha and coal, increasing about 100 million tons and 70 million tons by 2025, respectively [5]. Among all the regions, North America leads in the feedstock consumption, accounting for 17% of world feedstock consumption in 2010 [5]. The U.S. Energy Information Administration (EIA) has projected a 2.4% annual growth rate for crude oil prices from 2010-2035 [6]. Increasing oil prices and projected growth in consumption of fossil feedstocks together drive a growing interest in investigating alternative feedstocks for commodity chemicals production. A variety of alternative feedstocks are under consideration, including coal, unconventional natural gas, plastic waste, tar and heavy oil, and biomass [7, 8]. Feedstocks of non-fossil resources (lignocellulosic biomass, etc.) within the petrochemical industry have also gained increasing interest [9-13].

Biomass can be converted into basic chemicals through thermochemical conversion (gasification, pyrolysis, and liquefaction/hydrothermal upgrading) or biochemical conversion (fermentation and anaerobic digestion) [14]. The biochemical process is a complex process, and there are technical issues and challenges, such as low bulk density feedstock, high viscosity substrate, high enzymes cost, and low fermentability of some substrates [15-17]. The energy use and CO_2 emissions for basic chemicals production from biomass is fully examined by Ren and Patel [7]. The pathways examined in that study include steam cracking of naphtha derived from the Fischer-Tropsch processing (FT) of biomass, dehydration of ethanol (ethanol is derived from biomass via syngas fermentation or via direct fermentation), and the processing of methanol to olefins (methanol is derived from biomass via syngas). For thermochemical conversion, the process of chemicals production from biomass gasification is relatively slow and typically requires large, complicated, and expensive equipment [18, 19].

Brehmer et al. [9] has utilized a limited energetic and exergetic analysis using life cycle assessment (LCA) to evaluate the maximum fossil fuel feedstock replacement potential and concludes that the best potential for biomass to replace fossil fuel is as an alternative feedstock source for the petrochemical industry. Hermann et al. [20] analyzed the CO2 emissions and fossil energy use for bulk chemicals production using industrial biotechnology and found that more than 100% savings in nonrenewable energy use and greenhouse gas emissions are already possible with current state of the art biotechnology. Hipolito [21] evaluated the environmental loads associated to the production of chemicals (phenolic compounds, acetone, polyhydroxybutyric acid and polylactic acid) from lignocellulose biomass scenarios and compared these environmental loads to the petrochemical equivalents. Hipolito [21] concluded that the production of chemicals from biomass could contribute to possible reductions between 37% and 48% on greenhouse gas emissions and up to 80% fossil fuel can be saved while ecotoxicity indicators present much lower values for the production of chemicals from biomass.

But chemicals from biomass may increase other impact categories such eutrophication and acidification, human toxicity, photochemical oxidant formation, water depletion, and particulate matter formation. A number of other similar LCA studies discussed the environmental impacts of biopolymers or bioplastics production from biomass [22-27]. Yates and Barlow [28] made a thoughtful review from these existing biopolymers production LCA studies especially for polylactic acid (PLA), polyhydroxyalkanoates (PHA), and starch-based biopolymers. It is demonstrated as well that reductions in non-renewable energy use and GHG emissions can be achieved from biopolymers production, but higher impacts in other categories were commonly reported [28].

Although some LCA studies have been done on the intermediate chemicals or biopolymers, rare LCA studies are reported on basic commodity chemicals (benzene, toluene, xylene etc.) production from biomass. Recently, fast pyrolysis has attracted considerable interest as a means for converting biomass into valuable fuels or energy. With the growing interest in fast pyrolysis technology, the related economic and environmental impacts of pyrolysis-based energy systems are under extensive examination [29-36]. Vispute et al. [37] combined a two-stage hydrotreating process with FCC to form an integrated catalytic process for the high-yield production of valuable commodity chemicals (i.e., olefins and aromatics). For previous study, Zhang et al.[36] compared this chemicals production pathway with the transportation fuels production from fast pyrolysis pathway and found that the IRR of the chemicals production pathway is much higher than that of transportation fuels production pathway. In this paper, life cycle assessment is conducted to evaluate and quantify the environmental impacts of renewable commodity chemicals production via forest residue fast pyrolysis and hydrotreating/FCC upgrading. A variety of environmental impacts are evaluated, including the fossil energy input, GHG emissions, acidification, ozone depletion, ecotoxicity, smog, etc.

Descriptions for the Chemicals Production Pathway

In the chemicals production pathway, the bio-oil yield is assumed to be 52% of the dry mixed wood, based on the previous techno-economic analysis study [37]. Bio-oil generation from the raw feedstock includes five steps: biomass preprocessing, biomass fast pyrolysis, bio-oil recovery, solids removal, and heat generation. In the biomass preprocessing step, the raw biomass is assumed to be 25 wt.% moisture and chopped to a 10 mm diameter. It is dried to 7 wt.% moisture content and ground to particles of 3 mm diameter. Steam generated in the combustion area is used to dry the biomass and then recycled to the combustion area to increase its temperature. This consists of a recycling steam process and 1% of the steam input is assumed to be the makeup steam. In the fast pyrolysis step, biomass particles are converted into non-condensable gases, bio-oil vapors, and solid char phases in a fluidized bed reactor operating at 500^{o}C and ambient pressure. Bio-oil vapors are recovered using a condenser and an electrostatic precipitator. In the solids removal step, the pyrolysis products are cleaned by removing 90% of the entrained char and solid particles through cyclones. Finally, in the combustion step, the non-condensable gases are combusted to provide the heat for the pyrolysis process. The excess char is treated as a low-value coal substitute for local usage such as heat generation. Portion of the combusted non-condensable gases are compressed and sent to the pyrolyzer as the carrier gases.

After bio-oil production, a two-stage hydrotreating and FCC process is employed to upgrade the aqueous phase of the bio-oil to commodity chemicals. Process configurations based on Vispute et al. [37] are adopted for this pathway. A liquid-liquid (L-L) extractor is employed to separate the whole bio-oil into the aqueous phase and the water-insoluble fraction. The aqueous phase undergoes a two-stage hydrotreating process, which consists of a low-temperature hydrotreatment and a high-temperature hydrotreatment. The low-temperature hydrotreatment stage is carried out in a hydrotreater operating at 125 ℃ and 100 bar pressure and the high-temperature hydrotreatment stage is carried out at 250 ℃ and 100 bar pressure. After the two-stage hydrotreating process, fluidized catalytic cracking is performed on the hydrotreated aqueous phase of the bio-oil over HZSM-5 catalyst at 600 ℃. The FCC process converts the aqueous phase to commodity chemicals. Natural gas is steam-reformed to produce hydrogen via a two-stage catalytic process, and the hydrogen is used for the hydroprocessing steps. Because natural gas contains enough sulfur to poison reforming catalysts, reforming is preceded by a desulfurization step. In the first stage of reforming, steam reacts with the natural gas in a steam methane reformer (SMR) at 700 ℃ –1100 ℃ to yield syngas. In the second stage, low-temperature Water-Gas-Shift (WGS) reaction occurs at about 250 ℃ to generate t hydrogen from the syngas. The hydrogen is separated from the syngas through a Pressure Swing Adsorption (PSA) unit and the rest of the gas is treated as exhaust gas.

LCA Goal and Scope Definition

The goal of this LCA study is to analyze the environmental impacts of the chemicals production from forest residue via fast pyrolysis with hydrotreating/FCC upgrading. The system for this LCA is divided into five unit processes: biomass production, biomass transportation, biomass preprocessing, bio-oil production, and bio-oil upgrading. The system boundary is illustrated in Figure 1, which contains land, energy and material resources consumptions as well as air emissions, solid waste and water emissions in the process. Bio-oil production unit is a combination of biomass fast pyrolysis, bio-oil recovery, solids removal, and heat generation, which is shown as the sub-block in the system boundary diagram. The biomass fast pyrolysis and upgrading facility is assumed to be an integrated facility, where the biomass is preprocessed and converted to intermediate bio-oil that is ultimately upgraded to the commodity chemicals. Electricity usage is assumed to be medium-voltage electricity produced at U.S. The indirect land-use change effects and chemicals distributions are not considered in the LCA study. This study is a general study for chemicals production from forest residue fast pyrolysis and location-specific energy carriers associated with feedstocks are not considered.

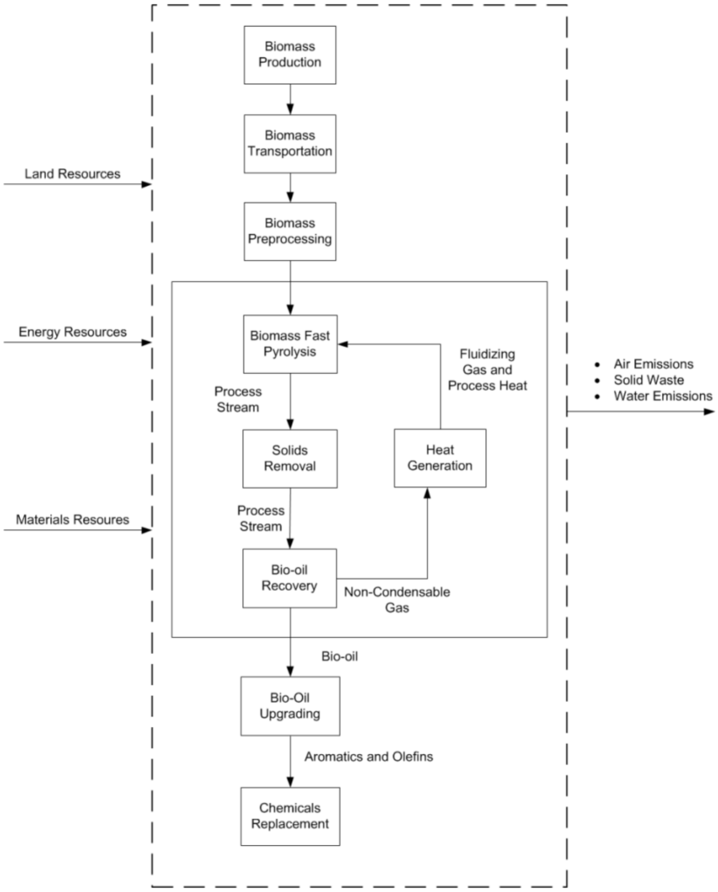


Figure 1. Life cycle system boundary for the chemicals production from forest residue via fast pyrolysis and upgrading.

The Aspen Plus model for the chemical production process is based on a previous process model of chemical production via fast pyrolysis [36, 38]. In this study, we have updated the bio-oil recovery modeling. The modified Aspen Plus model assumes an nth plant facility with mature technology processing 2000 metric tons/day of dry mixed wood feedstock. SimaPro 7.3 is used to develop and link primary unit processes related to the current chemicals production pathway. Materials and energy associated with the unit processes are collected as the inventory data which is set as primary materials and energy in SimaPro 7.3. Then the built-in Ecoinvent v.2.2 database in SimaPro 7.3 provides life cycle inventories for secondary materials and energy required in those primary unit processes. The required primary materials and energy inputs associated with the unit processes of the LCA are derived from this modified Aspen Plus model in combination with a GREET model [39]. The functional unit for interpreting the LCA results is 1 kg of chemicals. The IPCC 2007 GWP 100a method is employed to calculate the GWP. The Cumulative Energy Demand (CED) method is used to estimate the fossil energy input for chemical production pathway. Other potential environmental impacts (smog, acidification, ecotoxicity etc.) are evaluated by the TRACI2 method.

Inventory Analysis

Biomass Collection and Biomass Transportation

We assume biomass is produced through the collection of forest residue. The input data for the biomass collection step is detailed in Table 1 and based on data from Fan et al. [33]. In this study, forest residue is treated as a waste product. The inputs for biomass collection include the fuel consumption associated with the forwarding and the grinding of the biomass and the cost of the equipment used [33].

Table 1. Inventory data of biomass collection.

Item	Amount	Unit
Outputs		
Collected forest residue	1	kg
Resources		
Biomass energy	18	MJ
Materials and fuels		
Diesel fuel	7.38	g
Building machine	18.4	p

Note: “p” is one process unit in SimaPro; the process unit incorporates all input resources.

The wet forest residue, which contains 25 wt.% moisture, is transported by 40-ton trucks. The total weight of the transported wet forest residue is 2670 metric tons and the transportation distance is 150 miles one way, based on the GREET model developed by Argonne National Laboratory [39]. Detailed input data for the biomass transportation is summarized in Table 2.

Table 2. Inventory data of biomass transportation.

Item	Amount	Unit
Outputs		
Delivered forest residue	2670	metric ton
Input from material		
Truck 40t	710000	tkm
Collected forest residue	2670	metric ton

Note: tkm is one unit in SimaPro and indicates transporting 1 ton commodity by 1km.

Biomass Preprocessing

Steam is employed in the dryer to remove water from the wet forest residue. We assume a makeup of steam for biomass drying process, representing 1% of the recycling steam. For the inventory analysis of biomass preprocessing, electricity and steam usage are considered as the material inputs. Water vapor from the drying process is treated as an emission to the environment. Detailed inventory data is shown in Table 3.

Table 3. Inventory data of biomass preprocessing.

Item	Amount	Unit
Outputs		
Pretreated forest residue	2140	metric ton
Materials and fuels		
Delivered forest residue	2670	metric ton
Steam	255	metric ton
Electricity for chopping	44600	kwh
Electricity for grinding	109000	kwh
Electricity for compressor	170000	kwh
Emission to air		
Water	523	metric ton

Bio-oil Production

The entire inventory analysis for bio-oil production is shown in Table 4. Non-condensable gases generated during fast pyrolysis process are combusted to provide heat for the pyrolyzer. Char generated during pyrolysis is treated as coal substitute with an assumed heating value that is 50% of the displaced coal. Char is locally consumed such as combusted in the boiler for heat generation, so char transportation is not considered. Electricity, air, and process water are considered to be inputs while bio-oil and char are considered to be outputs. Process water is mainly used in bio-oil recovery and air is employed to support combustion of non-condensable gases. Emissions from bio-oil production include carbon oxides, hydrocarbons, nitrogen oxides, sulfide, and ash. Ash separated from the cyclones is used in sanitary landfills as waste treatment.

Table 4. Inventory data of bio-oil production.

Item	Amount	Unit
Outputs		
Forest residue bio-oil	1040	metric ton
Char	219	metric ton
Avoided Products		
Coal	110	metric ton
Resources		
Air	2165	metric ton
Process water	9590	metric ton
Materials and fuels		
Pretreated forest residue	2140	metric ton
Electricity for pyrolysis	450000	kwh
Emission to air		
N_2	1660	metric ton
O_2	21.7	metric ton
CO_2	928	metric ton
Water	432	metric ton
Waste or emissions to treatment		
Ash	11	metric ton

Bio-oil Upgrading

The final products from the hydrotreating/FCC pathway are aromatics and olefins. The total yield of chemicals is 243 metric ton/day. The inventory inputs involved in this step are: air, catalysts, process water, electricity, natural gas, and bio-oil. Natural gas is used to produce the hydrogen for the two-stage hydrotreating processes. Process water includes the water used for gas cooling and separation processes. Waste water from bio-oil upgrading is assumed to be sent to a waste water treatment plant. Details of the inventory analysis are shown in Table 5. Chemical products include aromatics and olefins like benzene, toluene, and xylene. Table 6 details the composition of the commodity chemical.

Table 5. Inventory data of bio-oil upgrading.

Item	Amount	Unit
Outputs		
Chemicals	243	metric ton
Resources		
Air	370	metric ton
Process water	2840	metric ton
Materials and fuels		
Bio-oil	1040	metric ton
Electricity for upgrading	103000	kwh
Natural gas	60	metric ton
Zeolite powder	0.79	metric ton
ZnO catalyst	0.24	metric ton
Heat	116000	MJ
Emission to air		
N_2	284	metric ton
O_2	14.2	metric ton
CO	39	metric ton
CO_2	395	metric ton
Water	388	metric ton
Sulfur	1.56	metric ton
SO_2	0.263	metric ton
Waste or emissions to treatment		
Waste water	1010	m^3

Table 6. Commodity chemicals composition.

Chemicals	Weight
Ethylene	22.9%
Propene	38.5%
Butylene	10.2%
Benzene	7.6%
Toluene	14.1%
Xylene	5.5%
Ethylbenzene	0.7%
Styrene	0.4%
Indene	0.1%
Naphthalene	0.1%

Results and Discussions

Fossil Energy

Figure 2 includes the breakdown of fossil energy input for individual unit processes for chemicals production.

Fossil energy input is separated into two parts: required fossil energy and products credits (shown as negative fossil energy input). The bio-oil production step and bio-oil upgrading steps consume the largest portion of the required fossil energy, both representing 28% of the total fossil energy. Biomass transportation and biomass production consume relatively smaller portions, 11% and 7% of the total required fossil energy input, respectively.

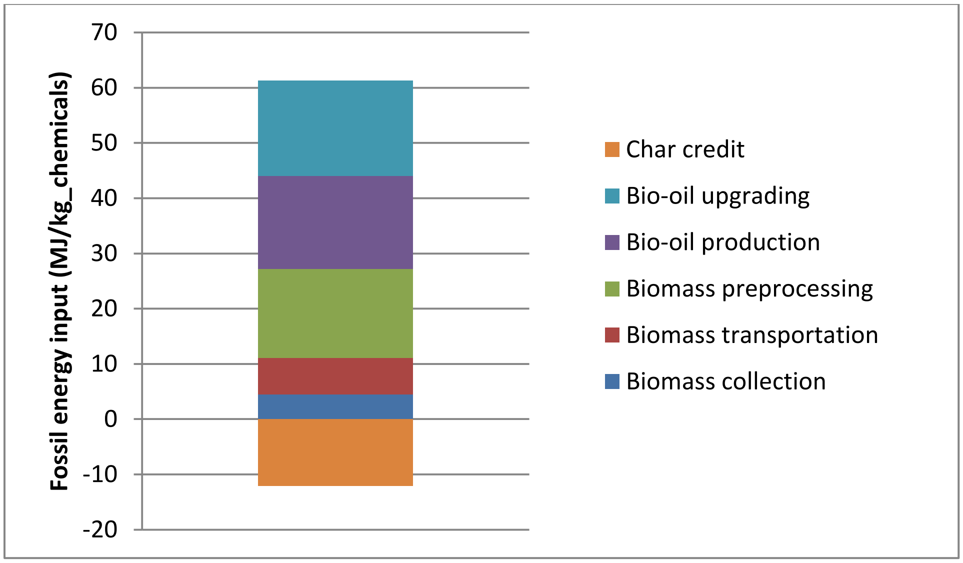


Figure 2. Fossil energy input for various unit processes
(Note: Products credits are treated as negative fossil energy input.)

Conventional chemicals are petroleum-based products. In this study, chemicals are produced from renewable feedstocks and treated as substitutes for petroleum-based chemicals. Biochar generated in pyrolysis contributes as a credit, which reduces fossil energy input by 12.1

MJ per kg chemicals production. Accounting for all fossil energy inputs and credits, net fossil energy input is 49.1 MJ per kg chemicals production.

GHG Emissions

The contributions of various unit processes to GWP are shown in Figure 3. Contributions to GWP are separated into two parts: positive GWP and negative GWP. Positive GWP contributions come from biomass production, biomass transportation, biomass preprocessing, bio-oil production, and bio-oil upgrading. Negative GWP contributions come from carbon fixation by biomass and char credit. For biomass absorption, it is assumed that the atmosphere can take up 0.942 kg CO_2 per kg of forest residue during the biomass growth [40]. Biochar is treated as products credit since it is used as coal substitute.

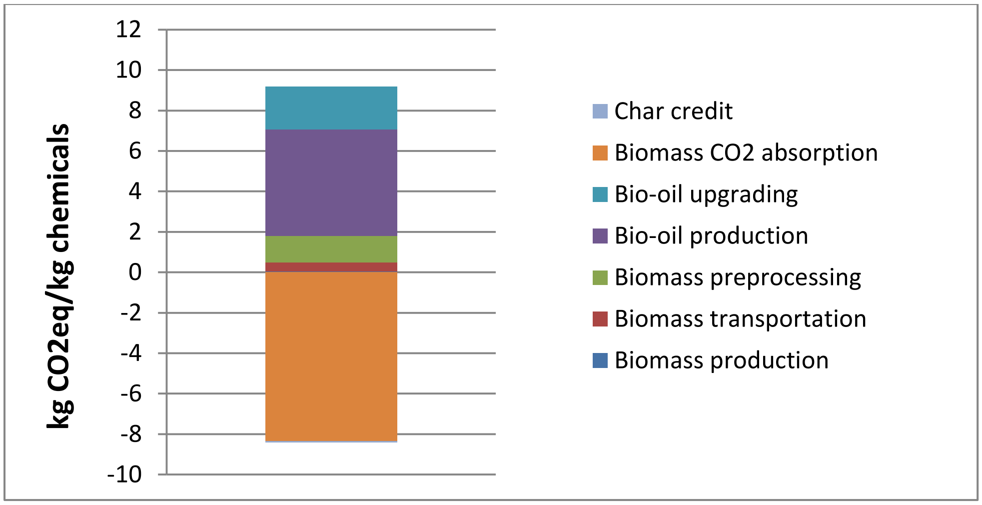


Figure 3. Contributions of unit process to GWP reported per kg of chemicals production (Note: Biomass CO_2 absorption and the products credits are treated as negative contributions to total GWP.)

Total positive GWP is 9.1 kg CO_2eq per kg chemicals production. Among all of the unit processes, bio-oil production step has the largest GHG emissions, contributing 57% of the total positive GWP. Bio-oil upgrading and biomass preprocessing steps represent 23% and 14% of total positive GWP, respectively. Biomass transportation contributes 5% of the total positive GWP and biomass production makes the smallest contribution to GHG emissions, contributing just 0.6% of total GWP. Total CO_2 absorption from growth of biomass is 8.3 kg CO_2eq per kg of chemicals. Biochar makes little contribution to GWP reduction, saving just 0.07 kg CO_2eq per kg chemicals. As a result, net GWP is 0.79 kg CO_2eq per kg chemicals.

Other Impact Categories

Table 7 presents the potential environmental impacts as evaluated by the TRACI 2 method and the relative contributions of individual unit processes to potential environmental impacts are presented in Figure 4. Biomass transportation has the largest impact on ozone depletion, contributing 83% of the total impact. Bio-oil production has the greatest impact on eutrophication, contributing 85% to the total impact. Bio-oil upgrading contributes almost the rest of 15% of the eutrophication. During the bio-oil production and bio-oil upgrading processes, nitrogen gases are emitted which results in the eutrophication impacts. Char has larger contributions to reductions of ecotoxicity and carcinogenics compared to other environmental impacts.

Table 7. Potential environmental impacts.

Impact category	Unit	Data
Ozone depletion	kg CFC-11 eq	1.05E-06
Smog	kg O_3 eq	0.243
Acidification	mol H+ eq	1.38
Eutrophication	kg N eq	1.21
Carcinogenics	CTUh	1.17E-07
Non-carcinogenics	CTUh	5.16E-07
Respiratory effects	kg PM10 eq	0.0037
Ecotoxicity	CTUe	2.38

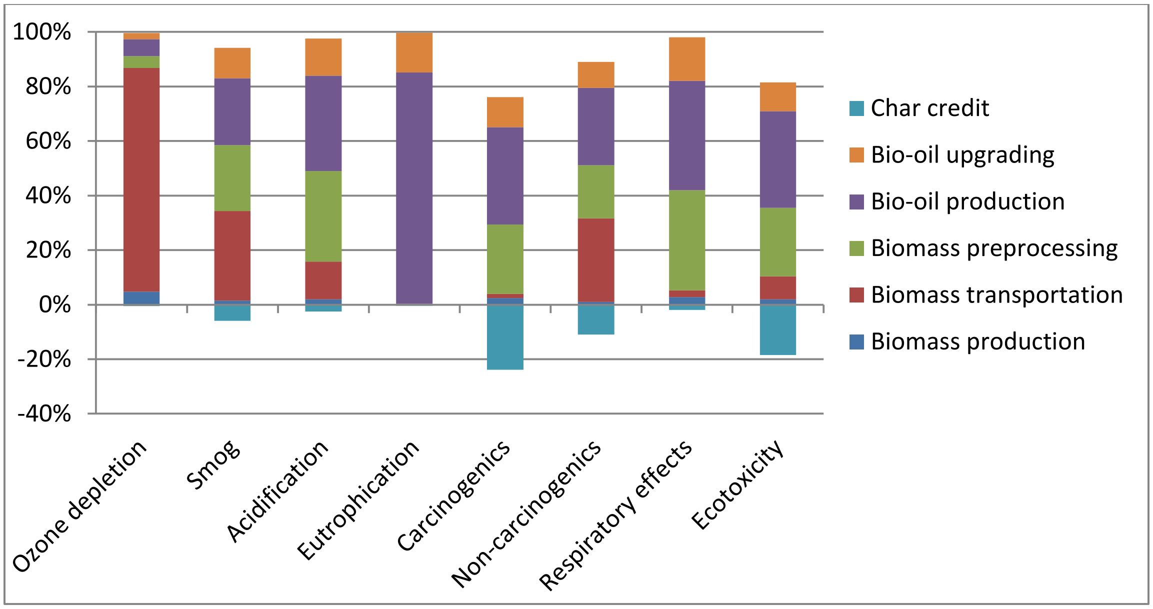


Figure 4. Potential environmental impacts for various impact categories.

Comparison to Other Chemical Production Pathways

Table 8 describes several pathways selected for comparison. Generally, steam cracking is considered the key petrochemicals conversion pathway [41]. Naphtha steam cracking routes based on Ren and Patel [7] are selected for comparison. In these pathways, a variety of energy sources, including crude oil, natural gas, coal, and lignocellulosic biomass, are considered for the chemicals production. Table 9 compares the GHG emissions and fossil energy input in this study to the results from other production pathways.

Table 8. Descriptions for compared chemical production pathways.

Compared pathways[a]	Descriptions
Oil byproduct CC	Fluidized catalytic cracking of byproducts derived from crude oil
Oil Naphtha SC	Steam cracking of naphtha derived from crude oil
Waste Naphtha SC	Steam cracking of naphtha derived from plastic waste gasification
Ethane SC	Steam cracking of ethane derived from natural gas
Methane FT Naphtha SC	Steam cracking of Fischer-Tropsch naphtha derived from gas-to-liquids process of methane
Ligno FT Naphtha SC	Steam cracking of Fischer-Tropsch naphtha derived from biomass gasification
Coal-ligno FT Naphtha SC	Steam cracking of Fischer-Tropsch naphtha derived from coal and biomass gasification
Coal FT Naphtha SC	Steam cracking of Fischer-Tropsch naphtha derived from coal gasification
Coal direct Naphtha SC	Steam cracking of naphtha derived from direct liquefaction of coal

[a] Note: All of the abbreviations of the pathways are adopted from the study of Ren and Patel [7].

Table 9. Comparison results of different chemical production pathways.

Pathways	GHG emissions (kg CO_2eq/kg chemicals)	Fossil energy input (MJ/kg chemicals)
Current study	0.79	49.1
Compared pathways[a]		
Oil byproduct CC	1	11
Oil Naphtha SC	0.9	10.3
Waste Naphtha SC	1.2	20
Ethane SC	1	11.4
Mthane FT Naphtha SC	1	28.7
Ligno FT Naphtha SC I	-3.5	-6
Ligno FT Naphtha SC II	-7.1	-72
Coal-ligno FT Naphtha SC	-1	76.7
Coal FT Naphtha SC I	5.1	46
Coal FT Naphtha SC II	7.8	84.7
Coal Direct Naphtha SC	6.5	77.1

[a] Note: The fossil energy input and GHG emissions data are calculated based on Tables 2-7 and Figures 3 and 4 in Ren and Patel [7].

As indicated in Table 9, among all of the pathways, coal-based pathways (Coal FT Naphtha SC I, Coal FT Naphtha SC II, and Coal Direct Naphtha SC) have the greatest GHG emissions and fossil energy inputs. Coal based pathways are to produce chemicals via steam cracking of coal-derived naphtha. Coal-based pathways can consume three to eight times more fossil energy and release five to eight times more GHG emissions than other petroleum-based (oil, natural gas, etc.) pathways. Lignocellulose biomass-derived chemicals have the negative GHG emissions (included the carbon fixation from biomass growth) and negative fossil energy input. Ligno FT Naphtha pathways are to produce chemicals via steam cracking of FT naphtha derived from biomass gasification. Ligno FT Naphtha II represents the maximum co-generation of electricity and the minimum output of FT liquids and it has the largest saving of GHG emissions and fossil energy input. Ligno FT Naphtha I, on the other hand, represents the minimum co-generation of electricity and the maximum output of FT liquids. This indicates that electricity production from biomass derived synthesis gas could save larger GHG emissions as well as fossil energy. Other petroleum-based pathways (oil, natural gas et. al) have comparable smaller GHG emissions and fossil energy than coal-based pathways but larger GHG emissions and fossil energy than lignocellulos biomass-based pathways.

Compared to the studied pathways, the GHG emissions related to the current pathway is smaller than all the petroleum-based chemicals production pathways (coal, natural gas, oil etc.). This is because carbon fixation from biomass growth for current production pathway largely reduces the GHG emissions compared to petroleum-based pathways. Also, the fossil energy input for the current pathway is smaller than the coal-based pathways. But compared to chemicals production via steam cracking of biomass-derived naphtha pathways, fast pyrolysis process has larger GHG emissions and fossil energy input. This is because the pyrolytic lignin is treated as the waste so bio-oil is not fully utilized.

Sensitivity Analysis

We select bio-oil yield, chemicals yield, electricity consumption, biomass transportation distances, and catalysts as the operating parameters for sensitivity analysis according to the previous techno-economic analysis [42] as well as their contributions in the inventory input. Each of these operating parameters is changed by a prescribed amount in relation to the baseline operating conditions (expressed as a percentage of the baseline case ranging from 75% to 125%) to see the effect on GHG emissions.

The overall GWP ranges from -1.0 to 3.8 kg CO_2eq, as indicated in Figure 5. Commodity chemicals are the main products, so the yield of commodity chemicals has the most significant impact on the GHG emissions based on the same amount of emissions. The increase of bio-oil yield could raise the final yields of chemicals so it is also a significant parameter for GHG emissions. A variation of bio-oil yield from 125% to 75% may result in a -0.6 to 3.1 kg CO_2eq kg chemicals range of GWP. Electricity consumption for biomass pyrolysis and bio-oil preprocessing are the secondary important parameters for GHG emissions. This is because electricity consumption for biomass pyrolysis and preprocessing occupy the majority of inventory inputs. If electricity consumption for biomass pyrolysis or bio-oil preprocessing has a variation of $\pm$25% on the baseline, GWP varies from 0.4 to 1.2 kg CO_2eq per kg chemicals. Biomass-upgrading electricity consumption and transportation distance have comparable smaller impact on the GHG emissions. A variation of $\pm$25% in biomass-upgrading electricity consumption and transportation distance result in a 0.7 to 0.9 kg CO_2eq per kg chemicals range of GWP. Quantity of catalysts used has very little impact on GWP.

The results of sensitivity analysis show that chemical yield and bio-oil yield are the most sensitive GHG emissions factors which indicates the increase of plant efficiency for pyrolysis process or bio-oil upgrading to chemicals process could largely save the GHG emissions. In addition, the reduction of electricity consumptions related to the production processes could also reduce the carbon footprints.

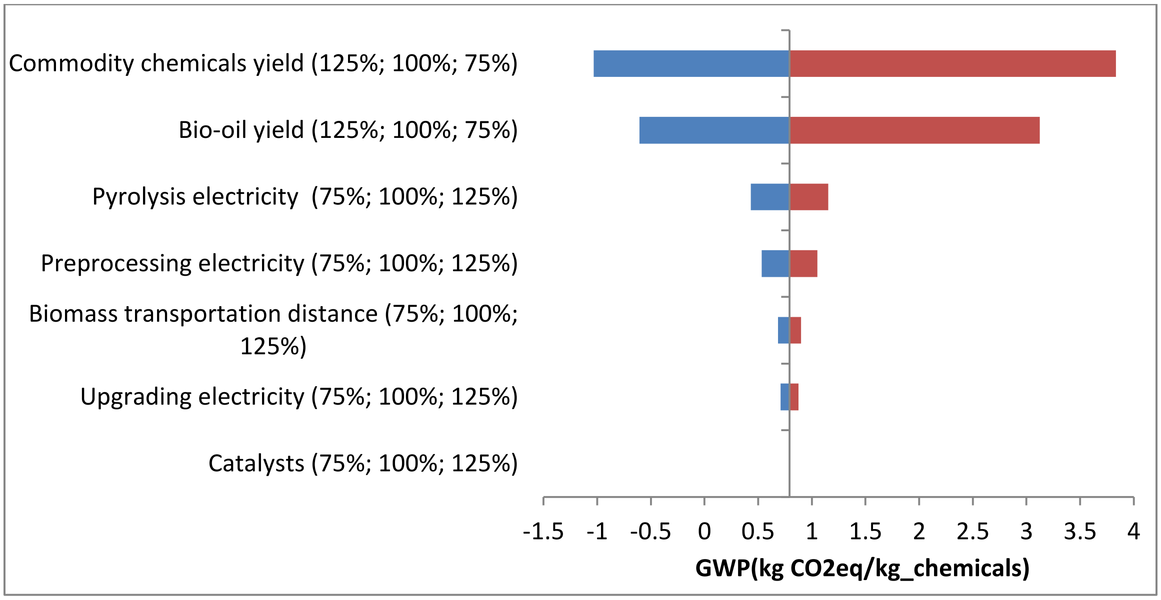


Figure 5. Sensitivity of GWP to operating conditions for chemicals production from forest residue (changes in operating parameters expressed as a percentage of the baseline case).

Conclusions

The life cycle assessment of chemicals production via forest residue fast pyrolysis and hydrotreating/FCC upgrading is examined in this study. Renewable chemicals are evaluated as substitutes for fossil-based chemicals and char is treated as a substitute for coal. Among production processes, bio-oil production is the key driver of the fossil energy input and GHG emissions. Bio-oil production contributes the largest GHG footprint (57% of total positive GWP) and the largest fossil energy demand (28% of the total required fossil energy) among all unit processes. Total fossil energy input is 49.1 MJ per kg chemicals and GWP is 0.79 kg CO_2eq per kg chemicals. In contrast to conventional petrochemical production pathways, fossil energy input and GWP are smaller for the current chemicals production pathway, which indicates that fossil energy consumption and GHG emissions could be reduced if commodity chemicals is produced via forest residue fast pyrolysis with hydrotreating/FCC upgrading processes. Biomass transportation makes the largest contribution to and bio-oil production makes the largest contribution to eutrophication. Sensitivity analysis indicates that bio-oil yield and chemicals yields play the most important roles in determining GHG footprint.

Acknowledgements

The authors would like to acknowledge the financial support of the Bioeconomy Institute and the Biobased Industry Center of Iowa State University

References

[1] ICIS, Aromatics & Aromatic Chemicals Information from ICIS, 2013. (Available at: http://www.icis.com/v2/chemicals/petrochemicals_aromatics.aspx)

[2] ICIS, Olefins & Olefin Chemicals Information from ICIS, 2013. http://www.icis.com/V2/chemicals/petrochemicals_olefins.aspx)

[3] EIA, Production Capacity of Operable Petroleum Refineries, 2012. (Available at: http://www.eia.gov/dnav/pet/PET_PNP_CAPPROD_A_(NA)_8PR_BSD_A.htm)

[4] GBI Research, Light Olefins Americas Market to 2020 - Cost Effective Ethylene from Shale Gas-Derived Ethane and On-Purpose Technology for Propylene to Promote Industry Growth, 2012. (Available at: http://www.marketresearch.com/GBI-Research-v3759/Light-Olefins-Americas-Cost-Effective-6744067/)

[5] CHEMSYSTEMS, Feedstock options for the petrochemcial indusy, 2013. (Available at: http://www.chemsystems.com/about/cs/news/items/PPE%20PCMD%20Feedstocks%202011.cfm)

[6] EIA, Annual Energy Outlook, 2012. (Available at:http://www.eia.gov/)

[7] T. Ren, M.K. Patel, Basic petrochemicals from natural gas, coal and biomass: Energy use and CO2 emissions, Resources, Conservation and Recycling, 53 (2009) 513-528.

[8] J. McFarlane, S. Robinson, Survey of Alternative Feedstocks for Commodity Chemical Manufacturing, 2007. Oak Ridge National Laboratory Report No. ORNL/TM-2007/28 (Available at: http://info.ornl.gov/sites/publications/files/Pub8760.pdf)

[9] B. Brehmer, R.M. Boom, J. Sanders, Maximum fossil fuel feedstock replacement potential of petrochemicals via biorefineries, Chemical Engineering Research and Design, 87 (2009) 1103-1119.

[10] C.H. Christensen, J. Rass-Hansen, C.C. Marsden, E. Taarning, K. Egeblad, The Renewable Chemicals Industry, ChemSusChem, 1 (2008) 283-289.

[11] B.E. Dale, 'Greening' the chemical industry: research and development priorities for biobased industrial products, Journal of Chemical Technology & Biotechnology, 78 (2003) 1093-1103.

[12] M. Gavrilescu, Y. Chisti, Biotechnology—a sustainable alternative for chemical industry, Biotechnology Advances, 23 (2005) 471-499.

[13] L.B. Schilling, Chemicals from alternative feedstocks in the United States, FEMS Microbiology Reviews, 16 (1995) 101-110.

[14] I. Fahmi, S. Cremaschi, Stage-Gate Representation of Feedstock Development for Chemical Process Industry, Foundations of Computer-Aided Process Operations, 2012. (Available at: http://focapo.cheme.cmu.edu/2012/proceedings/data/papers/012.pdf)

[15] G. Stephanopoulos, Challenges in Engineering Microbes for Biofuels Production, Science, 315 (2007) 801-804.

[16] Y. Lin, S. Tanaka, Ethanol fermentation from biomass resources: current state and prospects, Applied Microbiology and Biotechnology, 69 (2006) 627-642.

[17] Y. Chen, Biomass to Fuels: Thermo-chemical or Bio-chemical Conversion?, Ferment Technology, 1 (2012) e104. (Available at: http://www.omicsgroup.org/journals/biomass-to-fuels-thermo-chemical-or-bio-chemical-conversion-2167-7972.1000e104.pdf)

[18] Y. Xu, M.A. Hanna, L. Isom, "Green" Chemicals from Renewable Agricultural Biomass - A Mini Review The Open Agriculture Journal, 2 (2008) 54-61.

[19] J.R. Salge, B.J. Dreyer, P.J. Dauenhauer, L.D. Schmidt, New process to produce completely renewable fuels and chemicals, 2006. (Available at: http://scitizen.com/future-energies/new-process-to-produce-completely-renewable-fuels-and-chemicals_a-14-235.html)

[20] B.G. Hermann, K. Blok, M.K. Patel, Producing Bio-Based Bulk Chemicals Using Industrial Biotechnology Saves Energy and Combats Climate Change, Environmental Science & Technology, 41 (2007) 7915-7921.

[21] M.G. Hipolito, Life Cycle Assessment of platform chemicals from fossil and lignocellulosic biomass scenarios, 2011.(Available at: http://www.diva-portal.org/smash/get/diva2:458493/FULLTEXT01.pdf)

[22] M. Heyde, Ecological considerations on the use and production of biosynthetic and synthetic biodegradable polymers, Polymer Degradation and Stability, 59 (1998) 3-6.

[23] V. Dornburg, I. Lewandowski, M. Patel, Comparing the Land Requirements, Energy Savings, and Greenhouse Gas Emissions Reduction of Biobased Polymers and Bioenergy, Journal of Industrial Ecology, 7 (2003) 93-116

[24] W. Groot, T. Borén, Life cycle assessment of the manufacture of lactide and PLA biopolymers from sugarcane in Thailand, Int J Life Cycle Assess, 15 (2010) 970-984.

[25] V. Piemonte, Bioplastic Wastes: The Best Final Disposition for Energy Saving, J Polym Environ, 19 (2011) 988-994.

[26] S. Kim, B.E. Dale, Energy and Greenhouse Gas Profiles of Polyhydroxybutyrates Derived from Corn Grain: A Life Cycle Perspective, Environmental Science & Technology, 42 (2008) 7690-7695.

[27] L.R. Lynd, M.Q. Wang, A Product-Nonspecific Framework for Evaluating the Potential of Biomass-Based Products to Displace Fossil Fuels, Journal of Industrial Ecology, 7 (2003) 17-32.

[28] M.R. Yates, C.Y. Barlow, Life cycle assessments of biodegradable, commercial biopolymers—A critical review, Resources, Conservation and Recycling, 78 (2013) 54-66.

[29] N. Kauffman, D. Hayes, R. Brown, A life cycle assessment of advanced biofuel production from a hectare of corn, Fuel, 90 (2011) 3306-3314.

[30] E. Heracleous, Well-to-Wheels analysis of hydrogen production from bio-oil reforming for use in internal combustion engines, International Journal of Hydrogen Energy, 36 (2011) 11501-11511.

[31] Z.W. Zhong, B. Song, M.B.M. Zaki, Life-cycle assessment of flash pyrolysis of wood waste, Journal of Cleaner Production, 18 (2010) 1177-1183.

[32] D.D. Hsu, Life cycle assessment of gasoline and diesel produced via fast pyrolysis and hydroprocessing, Biomass and Bioenergy, 45 (2012) 41-47.

[33] J. Fan, T.N. Kalnes, M. Alward, J. Klinger, A. Sadehvandi, D.R. Shonnard, Life cycle assessment of electricity generation using fast pyrolysis bio-oil, Renewable Energy, 36 (2011) 632-641.

[34] D. Iribarren, J.F. Peters, J. Dufour, Life cycle assessment of transportation fuels from biomass pyrolysis, Fuel, 97 (2012) 812-821.

[35] Y. Zhang, T.R. Brown, G. Hu, R.C. Brown, Techno-economic analysis of monosaccharide production via fast pyrolysis of lignocellulose, Bioresource Technology, 127 (2013) 358-365.

[36] Y. Zhang, T.R. Brown, G. Hu, R.C. Brown, Techno-economic analysis of two bio-oil upgrading pathways, Chemical Engineering Journal, 225 (2013) 895-904.

[37] T.P. Vispute, H. Zhang, A. Sanna, R. Xiao, G.W. Huber, Renewable Chemical Commodity Feedstocks from Integrated Catalytic Processing of Pyrolysis Oils, Science, 330 (2010) 1222-1227.

[38] T.R. Brown, Y. Zhang, G. Hu, R.C. Brown, Techno-economic analysis of biobased chemicals production via integrated catalytic processing, Biofuels, Bioproducts and Biorefining, 6 (2012) 73-87.

[39] Argone National Laboratory, The greenhouse gases, regulated emissions, and energy use in tranportation (GREET) model, 2011. (Available at: http://greet.es.anl.gov/)

[40] D.D. Hsu, D. Inman, G.A. Heath, E.J. Wolfrum, M.K. Mann, A. Aden, Life Cycle Environmental Impacts of Selected U.S. Ethanol Production and Use Pathways in 2022, Environmental Science & Technology, 44 (2010) 5289-5297.

[41] IEA, Energy Statistic Mannual, 2004. (Available at: http://www.iea.org/training/toolsandresources/energystatisticsmanual/)

[42] Y. Zhang, T.R. Brown, G. Hu, R.C. Brown, Comparative techno-economic analysis of biohydrogen production via bio-oil gasification and bio-oil reforming, Biomass and Bioenergy, 51 (2013) 99-108.

CHAPTER VI

INTEGRATED SUPPLY CHAIN DESIGN FOR COMMODITY CHEMICALS PRODUCTION VIA WOODY BIOMASS FAST PYROLYSIS AND UPGRADING

A paper accepted by Bioresource and Technology

Yanan Zhang, Guiping Hu and Robert C. Brown

Abstract

This study investigates the optimal production planning and facility locations for commodity chemicals (BTX, etc.) production via woody biomass fast pyrolysis and hydroprocessing pathway. The locations and capacities of distributed preprocessing hubs and centralized biorefinery facilities are optimized by a mixed integer linear programming (MILP) model. In this integrated supply chain system, decisions on biomass chipping methods (roadside chipping, and facility chipping) are taken into account. The objective of this supply chain model is to maximize the profit for a 20-year project based on this chemicals production pathway. The capital cost, operating cost, revenues for the biorefinery facilities are based on the techno-economic analysis. In addition to the economic objective, the objective of minimizing life cycle GHG emissions is also incorporated into this model, which forms a multi-objective optimization problem. The proposed approach is illustrated through a case study in Minnesota, where Minneapolis-St. Paul is set as the chemicals distribution hub.

Introduction

The growing interest in biofuels production has generated much related research in economic analysis, environmental assessment, and supply chain system design [1-12]. Biomass logistics are complicated by the bulky, distributed nature of biomass and by the high volumes of low energy density materials to be collected and transported to the conversion facilities [13]. The unique nature of biomass feedstock provides great impetus for the exploration of sustainable and robust supply chain systems.

Numerous studies have been devoted to optimal design and operational planning of the bioethanol supply chain. You et al. [12] developed a multi-objective mixed integer linear programming (MILP) model which addresses the optimal design and planning of the cellulosic ethanol supply chain under economic, environmental, and social objectives. Dunnett et al. [14] proposed a system model to optimize the lignocellulosic bioethanol supply chain under assumptions of energy integration. Bai et al. [15] optimized biofuel refinery location and supply chain planning for bioethanol production, taking into account of traffic congestion issues. Giarola et al. [11] developed a stochastic modeling framework adopting a scenario-based approach to assess the effects of trading Greenhouse Gas (GHG) emissions allowances under market uncertainty for bioethanol production.

Researchers have also been aggressively exploring the supply chain design for biomass-derived transportation fuels (gasoline and diesel fuel). You et al. [16] presented the optimal design and planning of a biomass-to-liquids (BTL) supply chain under economic and environmental criteria. You’s design was based on a distributed preprocessing and centralized conversion network. Kim et al. [17] designed an optimal biomass supply chain network for transportation fuels production under uncertainty and then analyzed the robust design with Monte Carlo simulation. Elia et al. [18] developed a nationwide supply chain optimization framework for a BTL system using hardwood biomass for gasoline, diesel, and jet fuel production.

While much research is devoted to the use of biomass for fuels, there has been a concurrent growing interest in the use of biomass for the biobased products, such as renewable chemicals [19-23]. A survey on the alternative feedstocks for commodity chemicals manufacturing was conducted by Oak Ridge National Laboratory [24] and biomass was recognized as one of the most promising alternative feedstocks for commodity chemicals production. Various production pathways, such as gasification, fermentation, and pyrolysis, were analyzed. Brehmer et al. [19] evaluated the maximum fossil fuel replacement potential for a variety of feedstocks and reported a high potential for biomass to replace fossil fuel in the petrochemical industry. Christensen et al. [20] discussed the possibility of establishing a renewable chemicals industry and reported that from both economic and ecological perspectives, such an industry might be most advantageous to secure the optimal use of abundant, but limited, bioresources.

Vispute et al. [25] proposed a novel integrated catalytic thermochemical pathway to convert woody biomass to commodity chemicals, such as benzene, toluene, and xylene aromatic hydrocarbons (BTX). In this pathway, the bio-oil produced from woody biomass fast pyrolysis undergoes two-stage hydrotreatment followed by fluid catalytic cracking (FCC). Due to the high selectivity of commodity chemicals products attainable using this production pathway, the pathway has garnered significant attention and has inspired further examination of its economic feasibility and environmental effects. A techno-economic study has been conducted to examine the five commodity chemicals production scenarios, one of which was Vispute’s two-stage hydrotreating followed by FCC. Vispute’s pathway is found to be the most profitable among the five scenarios [26]. Another techno-economic study concluded that this chemicals production pathway is economically feasible, in which the facility internal rate of return was predicted to be as high as 13% for a 20-year project [5]. A life cycle assessment was conducted to examine the environmental performance and found that chemicals production via the integrated catalytic processing pathway could reduce GHG emissions significantly compared to the petroleum-based chemicals production [27].

Although there have been many studies of supply chain design and optimization for biofuel production, there have been few papers addressing supply chain design and optimization for renewable chemicals production from woody biomass via the thermochemical pathway. In this paper, a supply chain network is designed and optimized for the biobased chemical production pathway, using MILP modeling to optimize the locations and capacities of distributed preprocessing hubs and centralized biorefinery facilities. This paper examines both economic and environmental criteria in a multi-objective framework that allows analysis of trade-offs between economic feasibility and environmental impact. A case study for the state of Minnesota is presented to illustrate the integrated supply chain network design model.

Methodology

Integrated Catalytic Processing Pathway

Vispute et al. [25] has proposed an integrated catalytic processing pathway for commodity chemicals production via woody biomass (Figure 1). In this pathway, woody biomass is preprocessed (chopped, dried, and grinded) and then sent to a pyrolyzer to produce bio-oil. The bio-oil undergoes phase separations through a liquid-liquid extractor, resulting in separate water insoluble and aqueous phases. The water insoluble phase consists mainly of pyrolytic lignin, which is treated as a co-product. The aqueous phase is sent to a low temperature hydrotreating process (125^{o}C, 100 bar). And then the hydrotreated bio-oil is sent to a high temperature hydrotreating process for further hydrodeoxygenation (200^{o}C, 100 bar) over catalysts. After the two-stage hydrotreating process, FCC is performed on the hydrotreated aqueous phase to produce commodity chemicals. In addition to the primary raw material the woody biomass, hydrogen is needed for the two-stage hydrotreating process. Hydrogen is produced through the steam reforming of natural gas. Natural gas usually contains sulfur, so the gas goes through a desulfurizer for purification before entering the steam methane reformers and water gas shift reactors. The produced hydrogen is then separated from the syngas and send to the hydrotreaters.

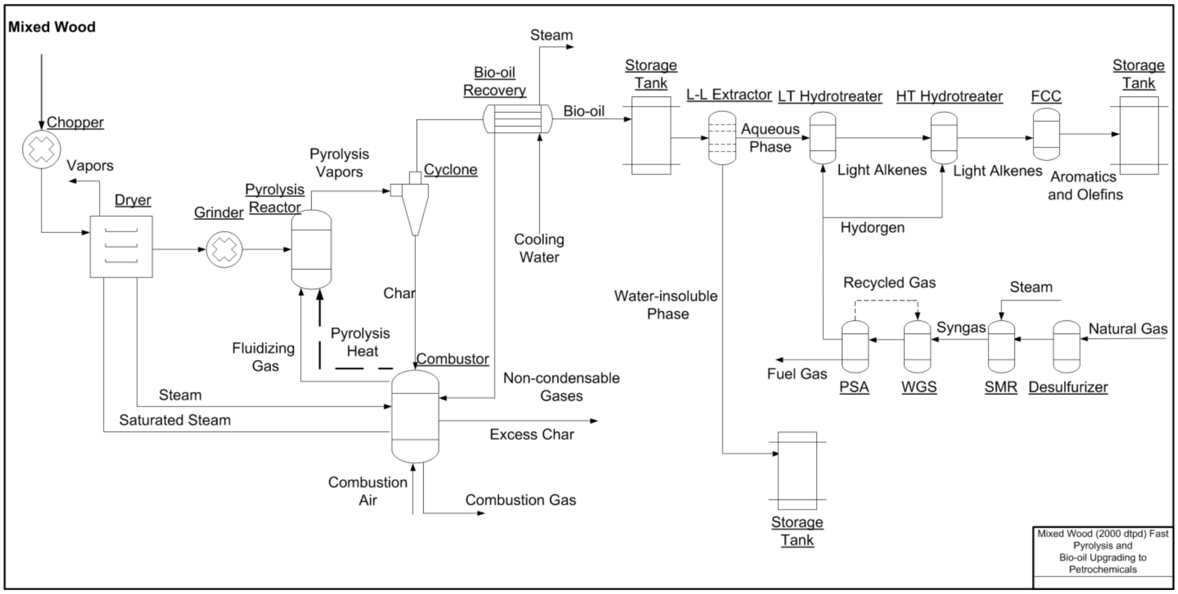


Figure 1. Process diagram for mixed wood fast pyrolysis and bio-oil upgrading to commodity chemicals (Adapted from Zhang et al. [30]).

Supply Chain Model Description

In this paper, the optimal plant sizes, locations, biomass and product flows are considered as the decision variables for the integrated supply chain design. Table 1 (shown as Table A1 in the Appendix A) shows descriptions for decision variables and the parameters for the economic and environmental objectives.

Figure 2 illustrates the supply chain network schematics for chemicals production via woody biomass fast pyrolysis and upgrading. First, the woody biomass is harvested and collected from location i. Two types of woody biomass are considered: raw forest residue and the residue chipped with a road-side chipping method. Both woody biomass types need to be preprocessed for size and moisture reduction before conversion. For biomass preprocessing, two methods are considered. One method is distributed preprocessing, where multiple preprocessing centers are located close to biomass sources. The other method is integrated preprocessing, where the biomass is gathered into one integrated facility. The integrated facility has a preprocessing facility and the biorefinery facility. All the preprocessing facilities are to chop, dry, and grind the biomass to reduce the moisture and sizes. Then the preprocessed biomass is sent to the biorefinery facilities. Chemicals and co-products are produced at the integrated facility location. The co-products are char and lignin which are left at the local location and the chemicals are transported to the distribution center.

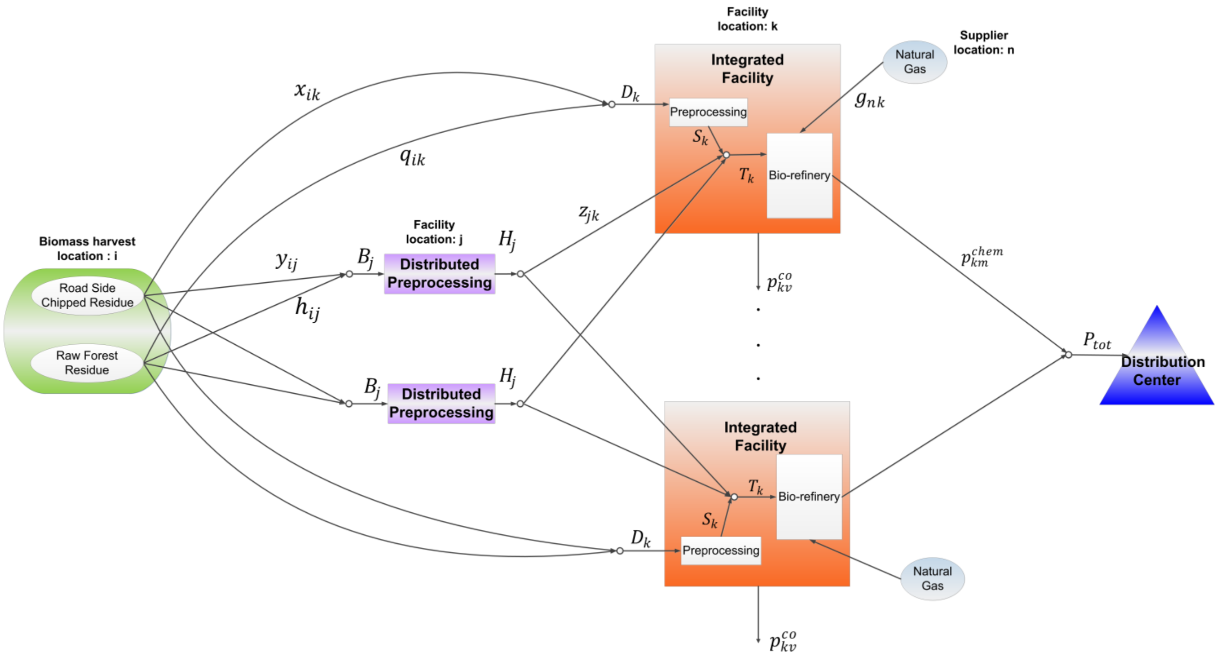


Figure 2. Supply chain schematic for chemicals production via woody biomass fast pyrolysis.

Model Formulation

Economic Objective

The economic objective is to maximize the net present profit for a 20-year project producing commodity chemicals via woody biomass fast pyrolysis and upgrading:

$$max\,PROFIT = \sum_{t=1}^{ny} \varphi_t \big(COST_t^{Revenue} - COST^{VarOper} - COST^{FixOper} - COST^{Collect} - COST^{Trans}\big) - COST^{Capital} \quad (1)$$

The $PROFIT$ is a function of the annual revenue ($COST_t^{Revenue}$), annual variable operating cost ($COST^{VarOper}$), annual fixed operating cost ($COST^{FixOper}$), annual biomass collection cost ($COST^{Collect}$), annual biomass transportation cost ($COST^{Trans}$), the plant capital cost ($COST^{Capital}$) and the discount factor (φ_t).

The discounted factor φ_t is used to calculate the net present. Annual interest r is assumed to be 10% for the 20-year project (2011-2032). The discount factor is shown below:

$$\varphi_t = \frac{1}{(1+r)^{t-1}} \quad (2)$$

The annual revenue $COST_t^{Revenue}$ is the sum of the revenue from chemicals product and the revenue from the co-products at individual plant location in year t as described in Equation 3. The annual revenue is not same for every year since the selling price of the chemical product m in year t (c_{mt}^{chem}) is assumed to be changing every year. The prices of chemicals throughout the years are predicted based on EIA petroleum price prediction.

$$COST_t^{Revenue} = \sum_{k=1}^{K} \sum_{v=1}^{V} p_{kv}^{co}\, c_v^{co} + \sum_{k=1}^{K} \sum_{m=1}^{M} p_{km}^{chem}\, c_{mt}^{chem} \quad (3)$$

The annual variable operating cost $COST^{VarOper}$ is a sum of variable operating costs for the distributed preprocessing facilities, integrated preprocessing facilities, and integrated biorefinery facilities, which is shown in Equation 4. The variable operating costs include the costs for plant operation, such as electricity, process water, and catalysts.

$$COST^{VarOper} = \sum_{k=1}^{K} T_k c_k^{VCenB} + \sum_i^I \sum_j^J h_{ij} c^{VPre} + \sum_i^I \sum_j^J y_{ij} c^{VPre2} + \sum_i^I \sum_k^K q_{ik} c^{VPre} + \sum_i^I \sum_k^K x_{ik} c^{VPre2} \quad (4)$$

The annual fixed operating cost $COST^{FixOper}$ is defined by Equation 5. The fixed operating cost includes the salaries, overhead, and maintenance costs for the distributed preprocessing facilities and integrated facilities.

$$COST^{FixOper} = \sum_{j=1}^{J} \sum_{l=1}^{L} r_{lj}\, c_l^{FD} + \sum_{k=1}^{K} \sum_{l=1}^{L} u_{lk} c_l^{FC} \quad (5)$$

The annual biomass collection cost $COST^{Collect}$ is the sum of collection costs for raw biomass and roadside chipped biomass given in Equation 6.

$$COST^{Collect} = \sum_{i=1}^{I} \sum_{j=1}^{J} h_{ij}\, c_i^{CR} + \sum_{i=1}^{I} \sum_{k=1}^{K} q_{ik}\, c_i^{CR} + \sum_{i=1}^{I} \sum_{j=1}^{J} y_{ij}\, c_i^{CC} + \sum_{i=1}^{I} \sum_{k=1}^{K} x_{ik}\, c_i^{CC} \quad (6)$$

The annual biomass transportation cost $COST^{Trans}$ includes the transportation costs of all of the materials (biomass, chemicals, and natural gas), as shown in Equation 7.

$$COST^{Trans} = \sum_{i=1}^{I} \sum_{j=1}^{J} h_{ij}\, c^{TR} \tau d_{ij} + \sum_{i=1}^{I} \sum_{k=1}^{K} q_{ik}\, c^{TR} \tau d_{ik} + \sum_{i=1}^{I} \sum_{j=1}^{J} y_{ij}\, c^{TC} \tau\, d_{ij} + \sum_{i=1}^{I} \sum_{k=1}^{K} x_{ik}\, c^{TC} \tau d_{ik} + \sum_{j=1}^{J} \sum_{k=1}^{K} z_{jk}\, (c^{TPre} \tau d_{jk} + c^{DFC}) + \sum_{n=1}^{N} \sum_{k=1}^{K} g_{nk}\, c^{TN} d_{nk} + \sum_{k=1}^{K} P_k\, c^{TP} \tau d_k^{DC} \quad (7)$$

The plant capital cost, the sum of capital investment for all of the facilities, is assumed to be invested in the current year, so the discount factor is not applied (see Equation 8).

$$COST^{Capital} = \left(\sum_{j=1}^{J} \sum_{l=1}^{L} r_{lj}\, c_l^{CapiD} + \sum_{k=1}^{K} \sum_{l=1}^{L} u_{lk}\, c_l^{CapiC} \right) \quad (8)$$

Environmental Objective

The environmental objective for GHG-emissions minimization is defined as follows:

$$min\ \ E_{TOT} = E^{Collection} + E^{Transport} + E^{Production}$$

where:

$$E^{Collect} = \sum_{i=1}^{I}\sum_{j=1}^{J} h_{ij}\, e_i^{CR} + \sum_{i=1}^{I}\sum_{k=1}^{K} q_{ik}\, e_i^{CR} + \sum_{i=1}^{I}\sum_{j=1}^{J} y_{ij}\, e_i^{CC} + \sum_{i=1}^{I}\sum_{k=1}^{K} x_{ik}\, e_i^{CC} \quad (9)$$

$$E^{Trans} = \sum_{i=1}^{I}\sum_{j=1}^{J} h_{ij}\, e^{TR}\tau d_{ij} + \sum_{i=1}^{I}\sum_{k=1}^{K} q_{ik}\, e^{TR}\tau d_{ik} + \sum_{i=1}^{I}\sum_{j=1}^{J} y_{ij}\, e^{TC}\tau\, d_{ij} +$$

$$\sum_{i=1}^{I}\sum_{k=1}^{K} x_{ik}\, e^{TC}\tau d_{ik} + \sum_{j=1}^{J}\sum_{k=1}^{K} z_{jk}\, e^{TPre}\tau d_{jk} + \sum_{k=1}^{K} P_k\, e^{TP}\tau d_k^{DC}$$

$$+ \sum_{n=1}^{N}\sum_{k=1}^{K} g_{nk}\, e^{TN}\tau d_{nk} \quad (10)$$

$$E^{Production} =$$

$$\sum_{k=1}^{K} T_k e^{CenB} + \sum_i^I \sum_j^J h_{ij} e^{Pre} + \sum_i^I \sum_j^J y_{ij} e^{Pre2} + \sum_i^{\mathrm{I}} \sum_k^K q_{ik} e^{Pre} + \sum_i^I \sum_k^K x_{ik} e^{Pre2} \quad (11)$$

In Equation 9, $E^{Collect}$ is the CO$_2$-equivalent GHG emissions associated with the biomass collection processes. Here e_i^{CR} is the emission of a collection-unit amount of raw biomass from harvest site i, and e_i^{CC} is the emission of a collection-unit amount of roadside chipped biomass. In Equation 10, E^{Trans} is the CO$_2$-equivalent GHG emissions associated with the materials transportation processes. The term e^{TR} is the emission of a transporting-unit amount of raw biomass, e^{TC} is the emission of a transporting-unit amount of roadside chipped biomass, and e^{TPre} is the emission of a transporting-unit amount of preprocessed biomass. The term e^{TN} is the emission of a transporting unit amount of natural gas, and e^{TP} is the emission of a transporting unit amount of chemicals. In Equation 11, $E^{Production}$ is the emissions associated with the biomass conversion processes. Here e^{Pre} is the emission of raw biomass preprocessing process, e^{Pre2} is the emission of roadside chipped biomass preprocessing process and e^{cenB} is the emission of a converting unit amount of preprocessed biomass at biorefinery facility location k.

Biomass Supply Constraints

In this section, the mass balance of biomass flows and facility capacities constraints are included. The total collected biomass F_i should not exceed the total biomass allowed for collection in harvesting location i. In Equation 12, α is the sustainability factor, which illustrates the allowed collection percentage of the available biomass.

$$F_i \leq \alpha A_i, \forall i \tag{12}$$

The total collected biomass F_i can be categorized into two types: raw biomass and roadside chipped biomass. They both can be transported to either the distributed preprocessing facility location j or the integrated facility location k. In Equations 13-15, y_{ij} and h_{ij} are the amount of transported raw biomass and roadside chipped biomass from harvest location i to distributed preprocessing location j. x_{ik} and q_{ik} are the amount of raw biomass and roadside chipped biomass transported from harvest location i to integrated facility location k. ε is the loss factor for the biomass transportation process. B_j is the total received biomass (raw biomass and roadside chipped biomass) in distributed preprocessing facility location j, and D_k is the total biomass (raw biomass and roadside chipped biomass) received in integrated preprocessing facility location k.

$$\sum_{j=1}^{J}\left(y_{ij} + h_{ij}\right) + \sum_{k=1}^{K}(x_{ik} + q_{ik}) = F_i(1-\varepsilon), \forall i \tag{13}$$

$$\sum_{i=1}^{I}\left(y_{ij} + h_{ij}\right) = B_j, \forall j \tag{14}$$

$$\sum_{i=1}^{I}(x_{ik} + q_{ik}) = D_k, \forall k \tag{15}$$

Distributed Preprocessing Facility Constraints

The distributed preprocessing facility constraints are shown in Equations 16-20.

$$B_j \leq \sum_{l=1}^{L} Cap_l^{Dis} r_{lj}, \forall j \tag{16}$$

For each candidate location j, there is at most one facility with capacity level l.

$$\sum_{l=1}^{L} r_{lj} \leq 1, \forall j \tag{17}$$

The total number of distributed preprocessing facilities at location j with capacity level l should not exceed the maximum number Num^{Dis}.

$$\sum_{l=1}^{L} \sum_{j=1}^{J} f_{lj} \leq Num^{Dis}, \forall j \tag{18}$$

For equations 8 and 9, the received biomass B_j is preprocessed with a yield β of H_j at distributed preprocessing facility location j and then H_j is transported to the integrated biorefinery location k.

$$B_j \beta = H_j, \forall j \tag{19}$$

$$\sum_{k=1}^{K} z_{jk} = H_j, \forall j \tag{20}$$

Integrated Facility Constraints

The total biomass (raw biomass and roadside chipped biomass) received in integrated preprocessing facility location k is presented as D_k. As indicated in Equation 21, the received biomass is preprocessed to dry biomass with a yield β of S_k at location k. The total preprocessed biomass T_k is the sum of preprocessed biomass from integrated preprocessing facility S_k and that from distributed preprocessing facility $\sum_{j=1}^{J} z_{jk}$, as described in Equation 22. In the integrated biorefinery facility location k, the preprocessed biomass T_k is converted to various chemicals, as shown in Equation 23. μ_m is the conversion rate for specific chemical m, and p_{km}^{chem} is the production quantity of chemical m at location k. In addition to the chemicals, the co-products pyrolytic lignin and biochar are produced at integrated biorefinery facility. In Equation 24, γ_v is the conversion rate for co-products and p_{kv}^{co} is the production of co-product v at location k.

$$D_k\beta = S_k, \forall k \tag{21}$$

$$\sum_{j=1}^{J} z_{jk} + S_k = T_k, \forall k \tag{22}$$

$$T_k\mu_m = p_{km}^{chem}, \forall k \tag{23}$$

$$T_k\gamma_v = p_{kv}^{co}, \forall k, \forall v \tag{24}$$

The total preprocessed biomass for the integrated biorefinery facility at location k should not exceed the capacity of the integrated biorefinery Cap_l^{Cen} if facility level l is selected (Equation 25). At most one facility can exist in one location as indicated in Equation 26. In Equation 27, the total number of facilities should not exceed the maximum facility number Num^{Cen}due to budget constraints.

$$T_k \leq \sum_{l}^{L} u_{lk} {Cap^{Cen}}_l, \forall k \tag{25}$$

$$\sum_{l=1}^{L} u_{lk} \leq 1, \forall k \tag{26}$$

$$\sum_{l}^{L} \sum_{\mathrm{k}=1}^{K} u_{lk} \leq Num^{Cen} \tag{27}$$

Natural Gas and Chemicals Constraints

In Equation 28, the total natural gas demand at the biorefinery locations is the sum of natural gas flows from various natural gas suppliers. The supplied natural gas from location n to all biorefinery facilities should not exceed the available natural gas in supply location n as indicated in Equation 29. In Equation 30, natural gas demand is calculated as a factor θ of the preprocessed total biomass T_k at biorefinery location k. The total chemicals production P_{tot} (Equation 31) is the sum of all types of chemical m produced from all of the integrated facility locations. In Equation 32, the total chemicals production should not exceed the maximum chemicals demand.

$$\sum_{n=1}^{N} g_{nk} = Q_k, \forall k \tag{28}$$

$$\sum_{k=1}^{K} g_{nk} \leq NG_n, \forall n \tag{29}$$

$$Q_k = \theta T_k, \forall k \tag{30}$$

$$\sum_{k=1}^{K} \sum_{m=1}^{M} p_{km}^{chem} = P_{tot} \tag{31}$$

$$P_{tot} \leq T^{max} \tag{32}$$

$$x_{ik}, q_{ik}, y_{ij}, h_{ij}, z_{jk}, g_{nk,}, \geq 0, r_{lj}, u_{lk} \in \{0,1\}, \forall i, j, k, n, l, m, v, t \tag{33}$$

Result and Discussion

Data Sources

In this paper, forest residue is the feedstock and the state of Minnesota is employed for the case study. The amount of available forest residue is obtained from the National Renewable Energy Laboratory [28]. Each county in Minnesota is considered as a candidate harvesting site, a potential distributed preprocessing facility location, and potential integrated facility location. The Minneapolis-St. Paul metro area has the most convenient transportation resources; therefore, Minneapolis-St. Paul is selected to be the distribution center. The chemicals demand data are based on the commodity flow survey for Minnesota [29]. All of the chemicals are assumed to be transported to the distribution center in Minneapolis-St. Paul. The information about the natural gas suppliers and their gas availability is obtained from the U.S. Energy Information Administration [30].

Five capacity levels (L1, L2, L3, L4, and L5) are considered for distributed preprocessing and integrated facilities; L1, L2, L3, L4, and L5 correspond to 100, 200, 500, 1000, and 2000 metric ton/day dry biomass processing capacities. The 2000 metric ton/day capacity plant is selected as the reference plant and the bio-oil conversion rate is assumed to be 52 wt.% of dry biomass. The capital costs for the distributed and integrated facilities are based on the techno-economic analysis [5, 26]. A scale factor of n=0.6 is employed to estimate the capital costs. In Equation 34, S_{new} and S_0 represent the new plant size and the reference plant size, and C_{new} and C_0 are the capital costs for the new plant and the reference plant.

$$C_{new} = C_0 \left(\frac{S_{new}}{S_0}\right)^n \tag{34}$$

For biomass preprocessing, two methods are considered. One is to preprocess biomass in distributed preprocessing facilities and the other is to preprocess biomass in integrated preprocessing facilities. Table 2 details the capital costs and the fixed operating cost for the distributed preprocessing facility and for the integrated preprocessing and biorefinery facility at various levels [5]. The fixed operating cost includes salaries, overhead, maintenance, and insurance. The maintenance fees are assumed to be 6% of the facility capital cost. The overhead and insurance are assumed to be 2% and 1.5% of the total salaries, respectively.

The variable costs for the distributed preprocessing facility and integrated preprocessing facility for same biomass are assumed to be the same. But for raw biomass and roadside chipped biomass preprocessing, variable operating costs are different. For roadside chipped biomass preprocessing process, the variable operating cost does not include chopping cost in Table 3. For the environmental impact assessment, all GHG emissions related to biomass collection, materials transportation, and production processes are based on the Aspen Plus, SimaPro and GREET models [5, 27]. The emission for the distributed preprocessing facility and integrated preprocessing facility for same biomass are assumed to be the same. But raw biomass preprocessing and roadside chipped biomass preprocessing have different emissions. The variable operating costs for facilities and emissions data are derived from the reference plant data (Table 3) [5, 27].

The 2012-2035 chemicals prices are based on the techno-economic analysis [5]. The correlations between each chemical species and petroleum price are used to calculate the prices for the next 20 years. The chemical yield and market prices for the next 20 years are shown in Table 4. The co-products yields include char, pyrolytic lignin, and fuel gas. The prices of the co-products are \$18.21, \$22.05, and \$200 per metric ton for char, pyrolytic, and fuel gas respectively.

Table 2. Total capital costs and fixed operating costs for various levels of facilities.

Level	**Capacity (dry metric ton/day)**	**Total Capital Cost ($million)**	
		Distributed Preprocessing Facility	Integrated Facility
L1	100	6.6	37.3
L2	200	10	56.5
L3	500	17.3	97.9
L4	1000	26.2	148.3
L5	2000	39.7	224.9
Level	**Capacity (dry metric ton/day)**	**Fixed Operating Cost ($million)**	
		Distributed Preprocessing Facility	Integrated Facility
L1	100	2	3.2
L2	200	2.2	3.9
L3	500	2.5	5.3
L4	1000	2.8	7.1
L5	2000	3.3	9.8

Table 3. Variable unit operating cost and emissions.

Preprocessing Facility	**\$/metric ton**
Electricity for chopping	0.83
Electricity for grinding	2.025
Electricity for compressor	6.425
Total	**9.28**

Integrated Biorefinery Facility	**\$/metric ton**
Solid disposal	0.1
Natural gas	5.58
Process water	0.18
Electricity	15.96
Catalyst	7.17
Total	**28.99**

Emissions	**kg CO_2eq/(metric ton mile)**
Raw biomass collection **(kg CO_2eq/metric ton)**	4.76
Road chipped biomass collection **(kg CO_2eq/metric ton)**	14.2
Raw biomass transportation	0.55
Road chipped biomass transportation	0.26
Preprocessed biomass transportation	0.13
Natural gas transportation	0.23
Chemicals transportation	0.26
Raw biomass preprocessing **(kg CO_2eq/metric ton)**	149.77
Roadside chipped biomass preprocessing **(kg CO_2eq/metric ton)**	133.4
Biorefinery facility production **(kg CO_2eq/metric ton)**	215.35

The collection costs for raw biomass and roadside chipped biomass are based on Leinonen [31]. Forest haulage cost is \$9.8/ton for raw forest residue. The stumpage price for the forest residue is assumed to be \$5/metric ton. So the collection cost for raw biomass is \$15.8 /metric ton. For roadside chipped forest residue, there is a \$9.8/ton haulage cost, \$9.8/ton chipping cost, and stumpage cost of \$5/metric ton. Therefore, the collection cost for roadside chipped forest residue is \$26.6/metric ton.

Table 4. Chemical yields and calculated prices for the next 20 years.

Yield		Chemicals Price ($/metric ton)									
% of preprocessed biomass		**y1**	**y2**	**y3**	**y4**	**y5**	**y6**	**y7**	**y8**	**y9**	**y10**
Benzene	0.859	1280	1322	1355	1330	1350	1361	1370	1378	1387	1398
Toluene	1.587	1068	1102	1128	1109	1124	1133	1140	1147	1154	1162
Xylenes	0.616	1105	1139	1164	1145	1161	1169	1176	1183	1189	1198
Ethylene	2.582	1297	1336	1367	1344	1363	1373	1381	1389	1397	1407
Propylene	4.342	1514	1570	1613	1581	1607	1621	1633	1644	1656	1670
Butylene	1.146	750	750	750	750	750	750	750	750	750	750
Ethylbenzene	0.075	1270	1270	1270	1270	1270	1270	1270	1270	1270	1270
Styrene	0.046	850	850	850	850	850	850	850	850	850	850
Indene	0.016	850	850	850	850	850	850	850	850	850	850
Naphthalene	0.016	850	850	850	850	850	850	850	850	850	850
		y11	**y12**	**y13**	**y14**	**y15**	**y16**	**y17**	**y18**	**y19**	**y20**
Benzene	0.859	1409	1420	1431	1442	1453	1463	1473	1484	1498	1509
Toluene	1.587	1172	1181	1189	1198	1207	1215	1223	1232	1242	1252
Xylenes	0.616	1207	1215	1224	1232	1241	1248	1256	1265	1275	1284
Ethylene	2.582	1418	1429	1439	1450	1460	1469	1479	1489	1502	1513
Propylene	4.342	1686	1701	1716	1730	1745	1758	1771	1787	1805	1821
Butylene	1.146	750	750	750	750	750	750	750	750	750	750
Ethylbenzene	0.075	1270	1270	1270	1270	1270	1270	1270	1270	1270	1270
Styrene	0.046	850	850	850	850	850	850	850	850	850	850
Indene	0.016	850	850	850	850	850	850	850	850	850	850
Naphthalene	0.016	850	850	850	850	850	850	850	850	850	850

*y1-y20 indicates the year 1 to year 20 (2010-2030)

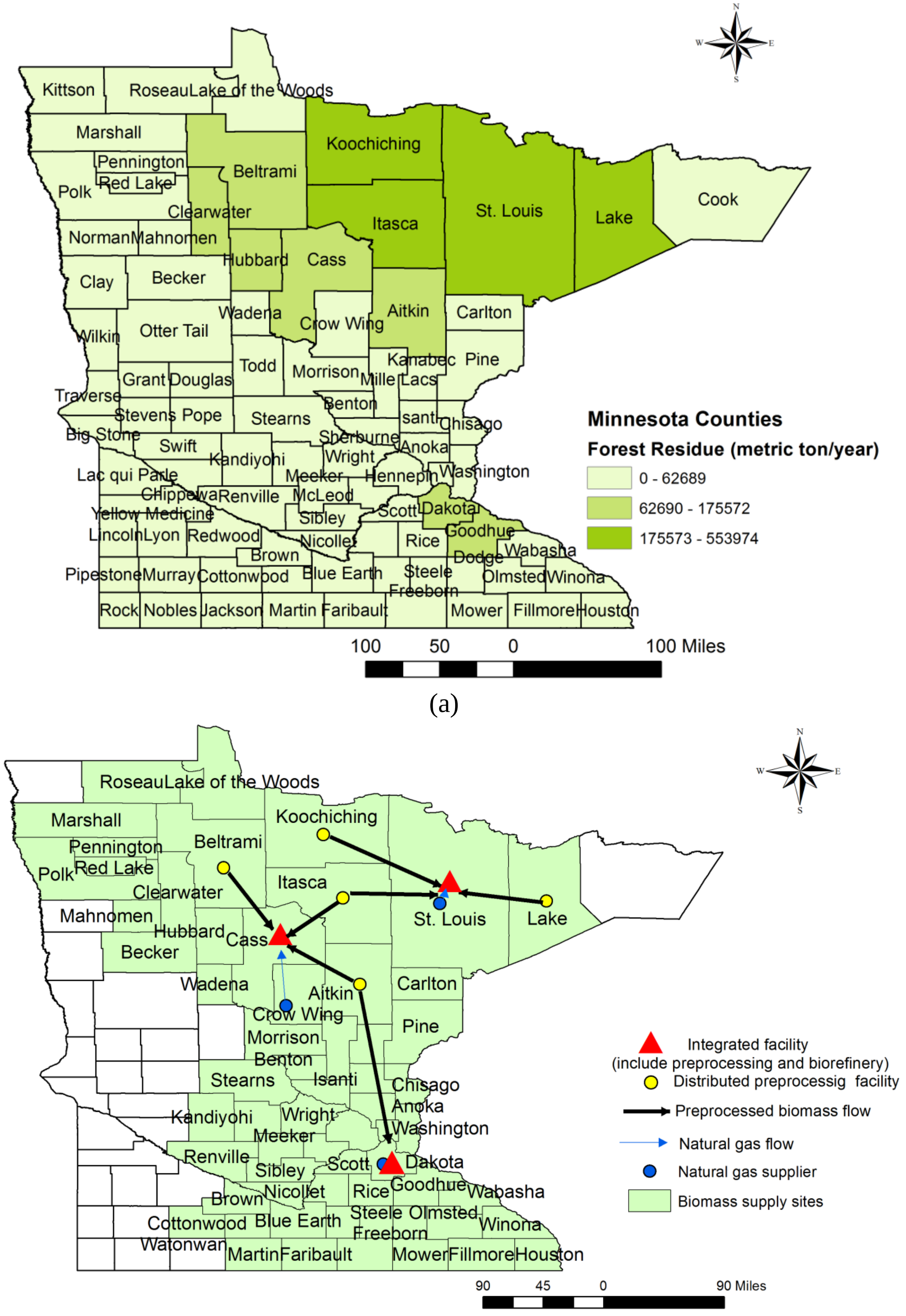
*Butylene, ethylbenzene, styrene, indene and naphthalene are assumed to have fixed prices.

The costs of the harvesting methods of forest residues also have been reported by Leinonen [31]. The four harvest methods include bundle, terrain chip, road chip, and plant chip. The road transportation costs for raw forest residue and roadside chipped forest residue are $12.8/ton and $18.3/ton for 80 km. As calculated, the variable transportation costs for raw forest residue and roadside chipped forest residue are assumed to be $0.41/metric-ton-mile and $0.28/metric-ton-mile. The preprocessed forest residue is transported by the trucks with a fixed transportation cost of $3.32/metric ton for wood chips loading and unloading and a variable transportation cost of $0.124/metric-ton-mile [32]. The transportation cost of commodity chemicals is assumed to be same as the national average truck shipping cost of $0.286/metric-ton-mile [33]. The transportation cost of natural gas via pipeline is assumed to be same as the national average oil pipeline cost of $0.0297/metric-ton-mile [33]. The distances between counties are based on the great circle distances calculated based on the latitudes and longitudes. Circuitry factors are incorporated to estimate the actual transportation distances. The circuitry factors are assumed to be 1.27 [34] and 1.1 for truck and pipeline, respectively [35].

This model employs MATLAB to collect the data and uses geographic information system (GIS) software to map the biomass availability and locations. The mathematical model is coded in GUSEK and solved with Gurobi.

Results and Analysis for Economic Objective Model

The economic objective model is developed to determine the economic feasibility and optimal capacities and locations of the distributed preprocessing facilities and integrated facilities in Minnesota by maximizing the net present profit for a 20-year project. Figure 3a shows the forest residue availability. The northern Minnesota has the most abundant forest residue sources, especially in Lake, Itasca, St. Louis, Koochiching, Cass, Aitkin, Hubbard, Clearwater, and Beltrami Counties. The forest residue in those nine counties represents 70% of the total forest residue in Minnesota. Among these counties, St. Louis County has the largest amount of forest residue, representing approximately 19% of the total forest residue in Minnesota. The optimal locations for the distributed preprocessing, integrated facilities, and natural gas suppliers locations are illustrated in Figure 3b. The results predict that three integrated facilities (include the preprocess facility and biorefinery facility) and five distributed preprocessing facilities would be built in the state of Minnesota.



(a)

(b)

Figure 3. Forest residue availability and optimal facility locations for Minnesota State.

In St. Louis County and Cass County, two of the integrated facilities with the highest capacity level (L5, 2000 metric ton/day) are molded to be built. Although Dakota County contains only 6% of the forest residue in Minnesota, it is located very near Minneapolis-St Paul and thus reduce significant amount of transportation costs. So an integrated facility is modeled to be built in Dakota with capacity L4 (1000 metric ton/day). The five distributed preprocessing facilities are modeled to be built in Aitkin (L3), Beltrami (L4), Itasca (L3), Koochiching (L3), and Lake (L3) Counties. These facilities are modeled to be built in the counties rich in forest residue for convenient collection of biomass. The biomass mass flows for the distributed preprocessing facilities and their locations are shown in Table 5.

Table 5. Mass flows for the distributed preprocessing facilities.

Biomass	**Location1**	**Location2**	**Mass flow (metric ton/year)**
h	Aitkin	Aitkin	113965.8
h	Carlton	Aitkin	51866.1
h	Crow Wing	Aitkin	50287.87
h	Morrison	Aitkin	11498.38
h	Pine	Aitkin	46521.15
h	Beltrami	Beltrami	171182.7
h	Clearwater	Beltrami	123937.1
y	Lake of the Woods	Beltrami	47419.13
h	Mahnomen	Beltrami	8135.4
y	Marshall	Beltrami	19046.63
h	Pennington	Beltrami	1570.725
y	Polk	Beltrami	39340.28
h	Red Lake	Beltrami	810.225
y	Roseau	Beltrami	30625.72
h	Itasca	Itasca	248718.6
h	Koochiching	Itasca	8882.725
h	Koochiching	Koochiching	274139.3
h	Lake	Lake	274139.3

Note: h represents the raw biomass transported from harvest site to distributed preprocessing location; y represents the roadside chipped biomass transported from harvest site to distributed preprocessing location.

The main biomass mass flows to the three integrated facilities (integrated preprocessing and biorefinery) are shown in Table 6. Most of the biomass arriving at the St. Louis County or Cass County integrated preprocessing facilities is raw biomass or preprocessed biomass from distributed preprocessing facilities. The third integrated facility, located in Dakota County, receives raw biomass and road chipped biomass from near biomass harvest sites and preprocessing biomass from Aitkin County. The raw biomass is preprocessed and converted to commodity chemicals at this integrated facility. Each integrated facility has a natural gas supplier nearby.

Table 6. Main mass flows for the integrated facilities.

Biomass	**Location1**	**Location2**	**Mass flow (metric ton/year)**
x	Becker	Cass	16231.6
q	Cass	Cass	114896
q	Crow Wing	Cass	10833.9
q	Hubbard	Cass	108658.9
q	Wadena	Cass	23519
z	Aitkin	Cass	80671.5
z	Beltrami	Cass	285133.8
z	Cass	Cass	176819.8
z	Itasca	Cass	164724.8
q	Anoka	Dakota	2674.4
x	Blue Earth	Dakota	3860
q	Chisago	Dakota	2499.9
q	Dakota	Dakota	164281.6
x	Fillmore	Dakota	29177.9
q	Goodhue	Dakota	72581.9
q	Hennepin	Dakota	2771
x	Houston	Dakota	22204.7
x	Kanabec	Dakota	11933
x	Mille Lacs	Dakota	11931
x	Morrison	Dakota	4305.4
q	Olmsted	Dakota	8146.1
x	Renville	Dakota	12757.9
x	Sherburne	Dakota	3118.05
q	Wabasha	Dakota	17722.6
x	Winona	Dakota	12728.6

Table 6 continued

z	Aitkin	Dakota	96148.3
z	Dakota	Dakota	257526.7
q	Lake	St. Louis	6049.4
q	St. Louis	St. Louis	540124.7
z	Koochiching	St. Louis	176819.8
z	Lake	St. Louis	176819.8
z	St. Louis	St. Louis	352282.2

Note: q means the transported raw biomass from harvest site to integrated preprocessing location; x means the road side chipped biomass from harvest site to integrated preprocessing location; z means the preprocessed biomass from distributed preprocessed location to the integrated biorefinery location.

A breakdown of the total cost is shown in Figure 4. The facility capital cost is the largest expenditure, representing 33% of the total cost. The production cost accounts for 30% of the total cost, which includes the fixed operating cost (19.4%) and the variable operating cost (10.3%). The remainder of the cost comes from the biomass collection and transportation cost, which are 18.9% and 18%, respectively. The transportation cost includes the costs of transporting the biomass, commodity chemicals, and the natural gas. The biomass transportation is the largest among them, representing 13.9% of the total cost.

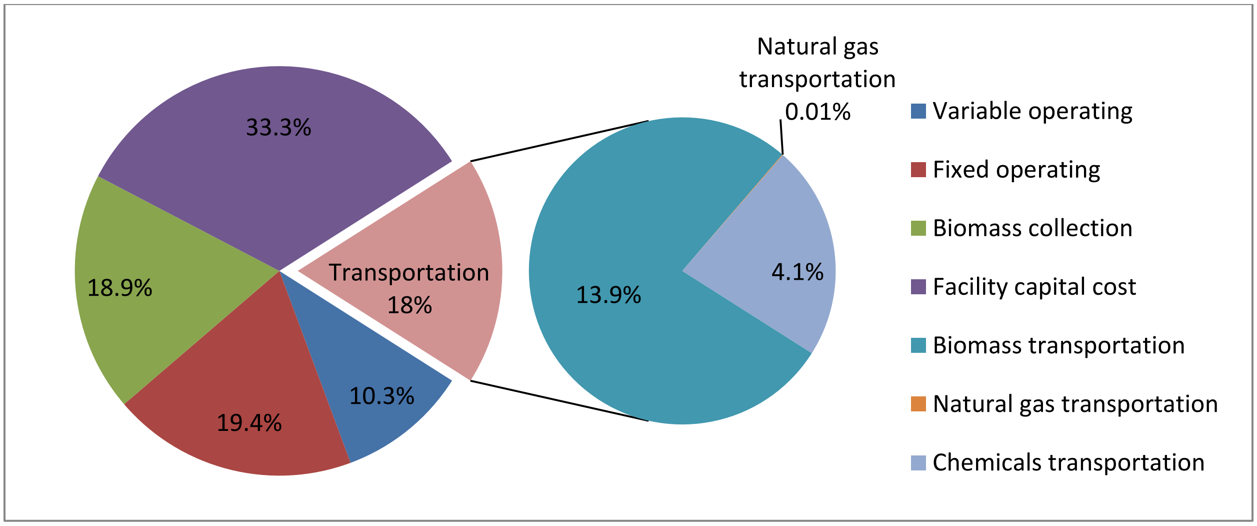


Figure 4. Breakdown of total cost for 20-year project.

Factors Influencing Project Profitability

Figure 5 describe the effect of variable factors on the project profitability. The commodity chemicals demand is directly related to project revenues. Figure 5(a) shows the effect of chemicals demand on project profitability. Here the relative chemicals demand in x-axis represents ratio of chemical demand to baseline demand. The profitability increases directly with increasing chemicals demand from 25% to 75% of the current production. Profitability increases to $494 million when chemicals demand reaches 75% of the baseline. After that, profitability stays constant even as the chemicals demand increases. This is because the forest residue is not sufficient to achieve the largest profitability possible when the chemicals demand is 75% of the baseline. So even when the chemicals demand increases, the biomass supply is not sufficient to meet the demand.

Based on the analysis of effect of chemicals demand variation on total profitability, it is illustrated that the biomass availability plays a significant role in the total profitability. Seasonal and other factors (competition of biomass etc.) cause variation in biomass availability and thus lead to different optimal solutions. Figure 5(b) illustrates the effect of variation of biomass availability on the project profitability. Here the relative biomass availability in the x-axis means ratio of biomass availability to baseline availability. The project profitability increases as the biomass availability increases. As discussed, the project profitability is limited by insufficient biomass. When there is an increase in biomass availability, the project profitability will increase significantly.

The competition for this feedstock will lead to increasing forest residue price. Biomass collection cost is an important parameter for the project profitability, representing 18.9% of the total capital cost. The effect of variation in biomass collection cost on project profitability is analyzed in Figure 5(c). Here the relative biomass collection cost in x-axis is ratio of biomass of collection cost with respect to the baseline biomass collection cost. It is illustrated that when the biomass collection cost is reduced to 25% of the baseline, the maximum profitability for the project increases to $812 million. The profitability decreases to just $165 million when the biomass collection cost is twice the baseline cost.

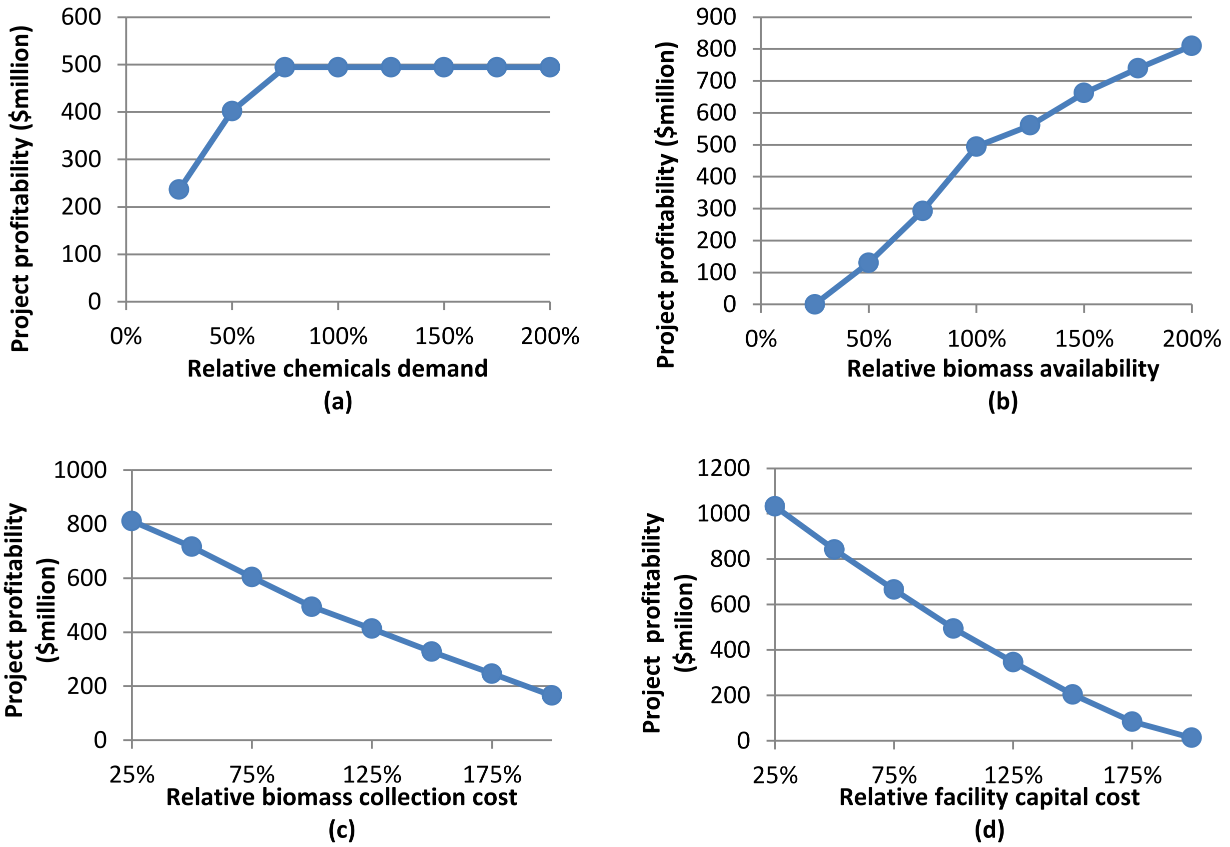


Figure 5. Effects of chemicals demand, biomass availability, biomass collection cost and facility capital cost on project profitability.

Facility capital cost is the largest contributor to project profitability. As indicated in Figure 5(d), if the facility cost is double the baseline, there is project profitability will drop to zero. Here the relative facility capital cost in x-axis is ratio of facility capital cost with respect to the baseline.

Results and Analysis for Economic-environmental Multi-objective Model

The multi-objective model is formulated to analyze the trade-off between minimizing GHG emissions and while maximizing project profits. The ε-constraint method is used to solve this multi-objective problem. The Pareto curve generated by all of the optimal solutions is shown in Figure 6. The GHG emissions reduce from 843 million kg CO_2eq per year to zero while the total 20-year profitability decreases from 494 million dollars to zero.

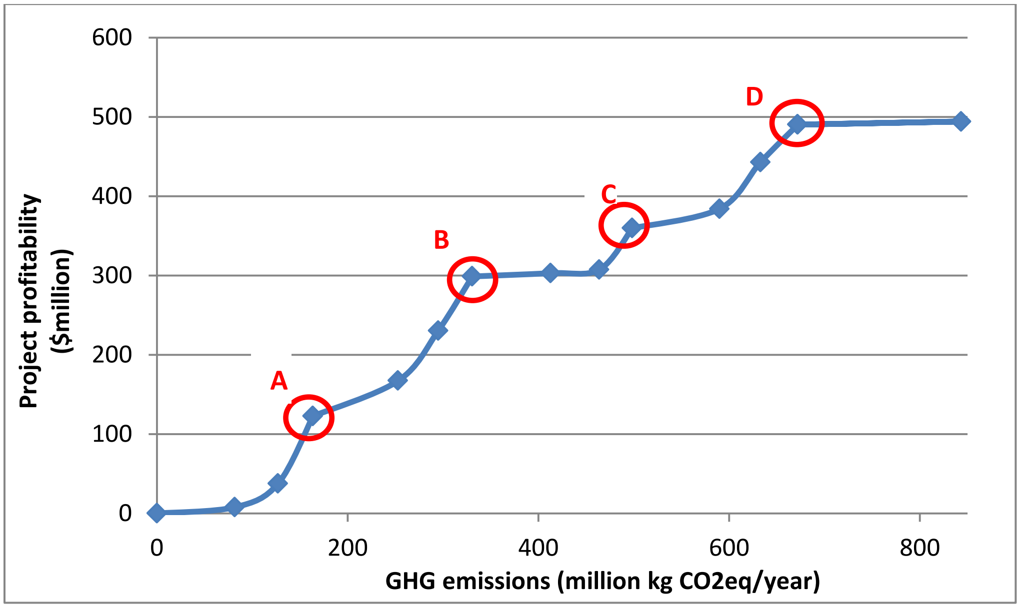


Figure 6. Pareto curve for the economic-environmental multi-objective optimization for supply chain of commodity chemicals production via woody biomass fast pyrolysis.

In the Pareto curve, there is one integrated facility with capability L4 (1000 metric ton/day) in St. Louise for Point A. For point B, two distributed preprocessed facilities with capacity L3 are modeled to be built in Koochiching and Lake. One integrated facility is modeled to be built with capacity of L5 level (2000 metric ton/day) in St. Louis. The emissions for Point B are 331 million kg CO2eq /year and the profitability is $300 million. From point A to point B, the optimal solution includes only one integrated facility (built in St. Louis County). After point B, other integrated facilities are modeled to be built in addition to the integrated facility in St.

Louis County. For points C, two integrated facilities are modeled to be built which are located in St. Louis (L5, 2000 metric ton/day) and Beltrami (L4, 1000 metric ton/day) and the distributed preprocessing facilities are built in Itasca, Lake and Koochiching. Point D is a good point where two integrated facilities and five distributed preprocessing facilities are modeled to be built. The two integrated facilities are located in St. Louis (L5, 2000 metric ton/day) and Case (L5, 2000 metric ton/day). The five distributed preprocessing facilities are located in Itasca, Lake, Koochiching, Aitkin, and Beltrami.

The Pareto curve illustrates the trade-offs between economics and environmental effects. When the production capacity is comparatively small, the profitability grows fast with a small increase of GHG emissions. After a certain production capacity (point B), however, the profitability grows much slowly. From point A to point D, the optimal integrated facility locations always include St. Louis County, which indicates that St. Louis County is the most favorable location to build the integrated chemicals plant.

Conclusions

This study investigates the economic feasibility and the optimal production planning and facility locations for commodity chemicals production via woody biomass fast pyrolysis. The economic objective model results show that the distributed facilities biomass chipping is preferable to the roadside chipping method for forest residue. The harvest sites rich in biomass resources are the preferable locations for building biorefinery facilities. Influences of parameters on economic objective model show that the biomass availability and facility capital costs are the most important factors for the project profitability. The economic-environmental multi-objective model results illustrate the trade-off between economic and environmental considerations.

Acknowledgements

The authors would like to acknowledge the financial support of the Bioeconomy Institute and the Biobased Industry Center of Iowa State University and the National Science Foundation under Grant Number EPS-1101284.

References

[1] Y. Zhang, G. Hu, R.C. Brown, Life cycle assessment of the production of hydrogen and transportation fuels from corn stover via fast pyrolysis, Environmental Research Letters, 8 (2013) 025001.

[2] H.v. Blottnitz, M.A. Curran, A review of assessments conducted on bio-ethanol as a transportation fuel from a net energy, greenhouse gas, and environmental life cycle perspective, Journal of Cleaner Production, 15 (2007) 607-619.

[3] E.D. Larson, A review of life-cycle analysis studies on liquid biofuel systems for the transport sector, Energy for Sustainable Development, 10 (2006) 109-126.

[4] C.N. Hamelinck, G.v. Hooijdonk, A.P.C. Faaij, Ethanol from lignocellulosic biomass: techno-economic performance in short-, middle- and long-term, Biomass and Bioenergy, 28 (2005) 384-410.

[5] Y. Zhang, T.R. Brown, G. Hu, R.C. Brown, Techno-economic analysis of two bio-oil upgrading pathways, Chemical Engineering Journal, 225 (2013) 895-904.

[6] Y. Zhang, T.R. Brown, G. Hu, R.C. Brown, Comparative techno-economic analysis of biohydrogen production via bio-oil gasification and bio-oil reforming, Biomass and Bioenergy, 51(2013) 99-108.

[7] J.D. Stephen, W.E. Mabee, J.N. Saddler, Biomass logistics as a determinant of second-generation biofuel facility scale, location and technology selection, Biofuels, Bioproducts and Biorefining, 4 (2010) 503-518.

[8] J.R. Hess, C.T. Wright, K.L. Kenney, Cellulosic biomass feedstocks and logistics for ethanol production, Biofuels, Bioproducts and Biorefining, 1 (2007) 181-190.

[9] H. An, W.E. Wilhelm, S.W. Searcy, A mathematical model to design a lignocellulosic biofuel supply chain system with a case study based on a region in Central Texas, Bioresource Technology, 102 (2011) 7860-7870.

[10] I.M. Bowling, J.M.a. Ponce-Ortega, M.M. El-Halwagi, Facility Location and Supply Chain Optimization for a Biorefinery, Industrial & Engineering Chemistry Research, 50 (2011) 6276-6286.

[11] S. Giarola, N. Shah, F. Bezzo, A comprehensive approach to the design of ethanol supply chains including carbon trading effects, Bioresource Technology, 107 (2012) 175-185.

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

[13] J. Tallaksen, Biomass Gasification: A Comprehensive Demonstration of a Community Scale Biomass Energy System -Chapter 6: Guidelines for Developing a Sustainable Biomass, 2011.(Available at: http://renewables.morris.umn.edu/biomass/documents/USDA_Report/SII_SupplyChain.pdf)

[14] A. Dunnett, C. Adjiman, N. Shah, A spatially explicit whole-system model of the lignocellulosic bioethanol supply chain: an assessment of decentralised processing potential, Biotechnol Biofuels, 1 (2008) 1-17.

[15] Y. Bai, T. Hwang, S. Kang, Y. Ouyang, Biofuel refinery location and supply chain planning under traffic congestion, Transportation Research Part B: Methodological, 45 (2011) 162-175.

[16] F. You, B. Wang, Life Cycle Optimization of Biomass-to-Liquid Supply Chains with Distributed–Centralized Processing Networks, Industrial & Engineering Chemistry Research, 50 (2011) 10102-10127.

[17] J. Kim, M.J. Realff, J.H. Lee, Optimal design and global sensitivity analysis of biomass supply chain networks for biofuels under uncertainty, Computers & Chemical Engineering, 35 (2011) 1738-1751.

[18] J.A. Elia, R.C. Baliban, C.A. Floudas, B. Gurau, M.B. Weingarten, S.D. Klotz, Hardwood Biomass to Gasoline, Diesel, and Jet Fuel: 2. Supply Chain Optimization Framework for a Network of Thermochemical Refineries, Energy & Fuels, 27 (2013) 4325-4352.

[19] B. Brehmer, R.M. Boom, J. Sanders, Maximum fossil fuel feedstock replacement potential of petrochemicals via biorefineries, Chemical Engineering Research and Design, 87 (2009) 1103-1119.

[20] C.H. Christensen, J. Rass-Hansen, C.C. Marsden, E. Taarning, K. Egeblad, The Renewable Chemicals Industry, ChemSusChem, 1 (2008) 283-289.

[21] B.E. Dale, 'Greening' the chemical industry: research and development priorities for biobased industrial products, Journal of Chemical Technology & Biotechnology, 78 (2003) 1093-1103.

[22] M. Gavrilescu, Y. Chisti, Biotechnology—a sustainable alternative for chemical industry, Biotechnology Advances, 23 (2005) 471-499.

[23] L.B. Schilling, Chemicals from alternative feedstocks in the United States, FEMS Microbiology Reviews, 16 (1995) 101-110.

[24] Oak Ridge National Laboratory, Survey of Alternative Feedstocks for Commodity Chemical Manufacturing, 2007. (Available at: http://info.ornl.gov/sites/publications/Files/Pub8760.pdf)

[25] T.P. Vispute, H. Zhang, A. Sanna, R. Xiao, G.W. Huber, Renewable Chemical Commodity Feedstocks from Integrated Catalytic Processing of Pyrolysis Oils, Science, 330 (2010) 1222-1227.

[26] T.R. Brown, Y. Zhang, G. Hu, R.C. Brown, Techno-economic analysis of biobased chemicals production via integrated catalytic processing, Biofuels, Bioproducts and Biorefining, 6 (2012) 73-87.

[27] Y. Zhang, G. Hu, R.C. Brown, Life cycle assessment of commodity chemicals production from forest residue via fast pyrolysis, 2013.Technical Report, Iowa State University.

[28] NREL, Forest and Primary Mill Residues, 2013. (Available at: http://www.nrel.gov/gis/data_biomass.html)

[29] BTS. 2007. Commodity Flow Survey 2007. Table 12. Shipment Characteristics by NAICS and Commodity for Metropolitan Area of Origin: 2007. Available at: http://www.rita.dot.gov/bts/sites/rita.dot.gov.bts/files/publications/commodity_flow_survey/2007/metropolitan_areas/minneapolis_st_paul_st_cloud_mn_wi_csa_mn_part/index.html

[30] EIA, Natural Gas Annual Respondent Query System, 2011. (Available at: http://www.eia.gov/cfapps/ngqs/ngqs.cfm?f_report=RP7)

[31] A. Leinonen, Harvesting Technology of Forest residues for fuel in the USA and Finland, 2004. (Available at: http://www.vtt.fi/inf/pdf/tiedotteet/2004/T2229.pdf)

[32] E. Searcy, P. Flynn, E. Ghafoori, A. Kumar, The relative cost of biomass energy transport, Appl Biochem Biotechnol, 137-140 (2007) 639-652.

[33] BTS, Average Freight Revenue per Ton-mile. Bureau of Transportation Statistics, 2012.

[34] J.G. Rogers, J.G. Brammer, Analysis of transport costs for energy crops for use in biomass pyrolysis plant networks, Biomass and Bioenergy, 33 (2009) 1367-1375.

[35] CBO, Energy use in freight transportation, Congressional Budget Office, 1982.

CHAPTER VII

CONCLUSIONS

Work in this dissertation has investigated the development of integrated assessment platform for biofuels production. This integrated assessment platform using separate modules to evaluate process engineering, economic feasibility, logistics of supply, and environmental impact within a general framework. The separated modules include: process simulation (module A), economics analysis (module B), life cycle assessment (module C), and supply chain & logistics optimization (module D). In this dissertation, the specific instance of production of drop-in biofuels using fast pyrolysis and upgrading is employed as the case study to examine this methodology. Two different bio-oil upgrading pathways are examined using this integrated assessment platform. One is the FCC of hydrotreated water-soluble bio-oil to produce commodity chemicals and the other is hydrotreating/hydrocracking the bio-oil to produce transportation fuels. The preliminary results prove that this developed integrated assessment methodology is a powerful tool to evaluate the biofuels production via fast pyrolysis pathway. Through this methodology, the fast pyrolysis technology could be fully examined. Chapter 3 focuses on Techno-economic analysis of fast pyrolysis technology results show that chemicals and fuels production from fast pyrolysis Fast pyrolysis is a promising technology to convert biomass to valuable chemicals and fuels.

This integrated platform has a wide application. A variety of feedstock can be examined for biofuels production including corn stover, forest residue, woody biomass, switch grass, algae, and wastes. In addition to fast pyrolysis system, it can be also extended to other biomass conversion pathways such as biomass gasification, biomass fermentation, Fischer-Tropsch (FT) synthesis, bio-oil reforming. A variety of products can be evaluated by this integrated assessment platform including hydrogen, biodiesel, gasoline, ethanol, biochar, and bio-based chemicals. Via the integrated assessment extension, the overall sustainability of bioenergy systems could be evaluated for plenty of research projects and commercial applications. In addition to the bioenergy system, the other alternative energy sources (e.g. nuclear, natural gas, geothermal, hydrogen) can also be evaluated though this integrated assessment platform.

Future Work

The process simulation (module A) is essential for other modules (module B, C, and D) since it supplies all the material and energy data. Although the heating integrations for the chemical process models have been done, the heating exchange networks have not been optimized. In the future, the heat exchange network could be optimized before the economic analysis. The life cycle assessment (module C) examined the chemicals and transportation fuels production environmental impacts. For chemicals production via forest residue fast pyrolysis pathway, it assumes many generic inputs related to electricity production and feedstock source without specific location considerations. However the forest residue availability and electricity generation are varied on different locations. So for future research work, the location-specific energy carriers associated with those feedstocks should be included. The case study for logistic optimization (module D) is about the chemicals production so that there is no related policy incorporated into the supply chain design and optimization. For other biofuels research such as bioethanol production, the policy constraints could be incorporated into to the supply chain design and optimization. In addition, the uncertainties of the biofuels supply chain should be explored using robust optimization method.

APPENDIX A

DESCRIPTIONS OF SUBSCRIPTS, DECISION VARIABLES AND PARAMETERS IN CHAPTER 5.

Table A1. Description of subscripts, decision variables and parameters.

Subscripts		
i	1,2, …, I	Biomass candidate harvest locations
j	1,2, …, J	Candidate distributed preprocessing facility locations
k	1,2, …, K	Candidate integrated facility locations
n	1,2, …, N	Natural gas candidate supplier locations
l	1,2, …, L	Allowed facility capacity levels
t	1,2, …, ny	Project years
v	1,2, …, V	Co-products species
m	1,2, …, M	Chemicals species
Decision Variables		
r_{lj}	binary	Equal to one if a distributed preprocessing facility of capacity level l exists in candidate facility location *j*
u_{lk}	binary	Equal to one if an integrated facility of capacity level l exists in candidate facility location *k*
x_{ik}	metric ton/year	Amount of roadside chipped biomass transported from harvest location *i* to integrated preprocessing facility location *k*
y_{ij}	metric ton/year	Amount of roadside chipped biomass transported from harvest location *i* to distributed preprocessing facility location *j*
h_{ij}	metric ton/year	Amount of raw biomass transported from harvest location *i* to integrated preprocessing facility location *k*
q_{ik}	metric ton/year	Amount of raw biomass transported from harvest location *i* to distributed preprocessing facility location *j*
z_{jk}	metric ton/year	Amount of preprocessed biomass transported from distributed preprocessing facility location *j* to integrated biorefinery facility location *k*
g_{nk}	metric ton/year	Amount of natural gas transported from natural gas supplier location g to integrated biorefinery facility location *k*
p_{km}^{chem}	metric ton/year	Amount of chemical m transported from integrated biorefinery facility location *k* to fixed distribution center
p_{kv}^{co}	metric ton/year	Amount of co-product v in integrated biorefinery facility location *k*
F_i	metric ton/year	Total amount of transported biomass from harvest location *i* to other locations

B_j	metric ton/year	Total amount of transported biomass from harvest locations to the preprocessing facility location *j*
H_j	metric ton/year	Total amount of preprocessed biomass from the distributed preprocessing facility location *j*
D_k	metric ton/year	Total amount of raw biomass transported to integrated preprocessing facility location *k*
S_k	metric ton/year	Total amount of preprocessed biomass from the integrated preprocessing facility location *k*
T_k	metric ton/year	Total amount of preprocessed biomass for integrated biorefinery facility location *k*
Parameter		
A_i	metric ton/year	Biomass availability in harvest location *i*
F_i	metric ton/year	Total collected biomass in harvest location *i*
Cap_l^{Dis}	metric ton/year	Capacity level *l* for the distributed preprocessing facility
Cap_l^{Cen}	metric ton/year	Capacity level *l* for the integrated facility
NG_n	metric ton/year	Natural gas availability in supply location *n*
T^{max}	metric ton/year	The maximum products demand
c_i^{CR}	$/metric ton	Unit collection cost for raw biomass in location *i*
c_i^{CC}	$/metric ton	Unit collection cost for roadside chipped biomass in location *i*
c^{TR}	$/(metric ton mile)	Unit transportation cost for raw biomass
c^{TC}	$/(metric ton mile)	Unit transportation cost for roadside chipped biomass
c^{TPre}	$/(metric ton mile)	Unit transportation cost for preprocessed biomass
c^{TN}	$/(metric ton mile)	Unit transportation cost for natural gas
c^{TP}	$/(metric ton mile)	Unit transportation cost for chemicals
c^{DFC}	$/metric ton	Fixed transportation cost for unit biomass
d_{ij}	mile	Distance from harvest location *i* to distributed preprocessing location j
d_{ik}	mile	Distance from harvest location *i* to the integrated facility location *k*
d_{jk}	mile	Distance from distributed preprocessed location *j* to the integrated facility location *k*
d_{nk}	mile	Distance from natural gas supplier location n to the integrated facility location *k*
d_k^{DC}	mile	Distance from integrated facility location *k* to the distribution center location
c_l^{FD}	$/year	Fixed operating cost for distributed preprocessing facility at capacity level *l*
c_l^{FC}	$/year	Fixed operating cost for the integrated facility at capacity level *l*
c_l^{CapiD}	$	Capital cost for distributed preprocessing facility at capacity level *l*
c_l^{CapiC}	$	Capital cost for integrated facility at capacity level *l*
c^{VPre}	$/metric ton	Variable operating cost for raw biomass preprocessing
c^{VPre2}	$/metric ton	Variable operating cost for roadside chipped biomass preprocessing

c^{VCenB}	\$/metric ton	Variable operating cost for biorefinery facility
c_{vt}^{co}	\$/metric ton	Price of co-product *v* in year *t*
c_{mt}^{chem}	\$/metric ton	Price of chemical m year *t*
e_i^{CR}	kg CO_2eq/metric ton	Emissions of unit raw biomass collection
e_i^{CC}	kg CO_2eq/metric ton	Emissions of unit roadside chipped biomass collection
e^{TR}	kg CO_2eq/(metric ton mile)	Emissions of unit raw biomass transportation
e^{TC}	kg CO_2eq/(metric ton mile)	Emissions of unit roadside chipped biomass transportation
e^{TPre}	kg CO_2eq/(metric ton mile)	Emissions of unit preprocessed biomass transportation
e^{TN}	kg CO_2eq/(metric ton mile)	Emissions of unit natural gas transportation
e^{TP}	kg CO_2eq/(metric ton mile)	Emissions of unit chemicals transportation
e^{Pre}	kg CO_2eq/metric ton	Emissions of converting unit raw biomass in preprocessing facility
e^{Pre2}	kg CO_2eq/metric ton	Emissions of converting unit roadside chipped biomass in preprocessing facility
e^{CenB}	kg CO_2eq/metric ton	Emissions of converting unit biomass in integrated biorefinery facility
φ_t		Discounted factor of year *t*
r		Interest rate
α		Biomass collection factor
ε		Biomass loss factor
β		Preprocessed biomass conversion rate in preprocessing facility
μ_m		Conversion rate of chemical *m*
γ_v		Conversion rate of co-products *v*
Num^{Dis}		Maximum number of the distributed preprocessing facilities
Num^{Cen}		Maximum number of the integrated facilities
θ		Natural gas demand rate based on preprocessed biomass

APPENDIX B

NOMENCLATURE

CSET	Center for Suitable Energy Technologies
GHG	Greenhouse Gas
EPA	Environmental Protection Agency
RFS	Renewable Fuel Standard
FCC	Fluidized catalytic cracking
BTL	Biomass-to-Liquid
FT	Fischer–Tropsch
ARS	Agricultural Research Service
IIFB	Internally Interconnected Fluidized Bed
R&D	Research and Development
IRR	Internal Rate of Return
NREL	National Renewable Energy Laboratory
FBFP	Fluidized Bed Fast Pyrolysis
LCA	Life cycle assessment
WTW	Well-to-Wheel
CVaR	Value at Risk
PFD	Process Flow Diagram
DCFROR	Discounted Cash Flow Rate of Return
MSP	Minimum Selling Price
GREET	Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation
FCI	Fixed Capital Investment
RIN	Renewable Identification Numbers

TEA	Techno-economic Analyses
MTPD	metric tons per day
L-L	Liquid-Liquid
SMR	Steam Methane Reformer
WGS	Water Gas Shift
PSA	Pressure Swing Adsorption
PNNL	Pacific Northwest National Laboratory
EIA	Energy Information Administration
WTI	West Texas Intermediate
NPV	Net Present Value
ILUC	Indirect Land Use Change
GWP	Global Warming Potential
CED	Cumulative Energy Demand
LHV	Low Heating Value
GHSV	Gas Hourly Space Velocities
MPG	Miles per Gallon
PTA	Purified Terephthalic Acid
PA	Phthalic Anhydride
CAGR	Compounded Annual Growth Rate
PLA	Poly Lactic Acid
PHA	Poly Hydroxy Alkanoates
MILP	Mixed Integer Linear Programming