IOWA STATE UNIVERSITY Digital Repository

Graduate Theses and Dissertations

Graduate College

2015

Techno-economic, uncertainty, and optimization analysis of commodity product production from biomass fast pyrolysis and bio-oil upgrading

Wenhao Hu Iowa State University

Follow this and additional works at: http://lib.dr.iastate.edu/etd Part of the <u>Mechanical Engineering Commons</u>

Recommended Citation

Hu, Wenhao, "Techno-economic, uncertainty, and optimization analysis of commodity product production from biomass fast pyrolysis and bio-oil upgrading" (2015). *Graduate Theses and Dissertations*. 14400. http://lib.dr.iastate.edu/etd/14400

This Thesis is brought to you for free and open access by the Graduate College at Iowa State University Digital Repository. It has been accepted for inclusion in Graduate Theses and Dissertations by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.

Techno-economic, uncertainty, and optimization analysis of commodity product

production from biomass fast pyrolysis and bio-oil upgrading

by

Wenhao Hu

A thesis submitted to the graduate faculty

in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Major: Mechanical Engineering

Program of Study Committee: Mark Mba Wright, Major Professor Robert C. Brown Marjorie R. Rover

Iowa State University

Ames, Iowa

2015

Copyright © Wenhao Hu, 2015. All rights reserved

DEDICATION

To my grandmother and my parents

TABLE OF CONTENTS

	Page
DEDICATION	ii
TABLE OF CONTENTS	iii
ACKNOWLEDGMENTS	v

ABSTRACT	vi
CHAPTER 1. GENERAL INTRODUCTION	1

CHAPTER 2. COMPARATIVE TECHNO-ECONOMIC ANALYSIS OF ADVANCED BIOFUELS, BIOCHEMICALS, AND HYDROCARBON CHEMICALS

Abstract	
Introduction	13
Methodology	15
Bio-oil production and collection	16
Bio-oil upgrading	19
Bio-refinery economic analysis	
Results and discussion	
Conclusion	31
Acknowledgments	
Conflict of interest	
References	33

CHAPTER 3. TECHNO-ECONOMIC ANALYSIS OF PRODUCTS SELECTION AND	
OPTIMIZATION FROM BIOMASS FAST PYROLYSIS AND BIO-OIL	
UPGRADING	36
Abstract	36
Introduction	37
Methodology	39
Process model description	40
Product portfolio selection and cost analysis	45
Results and Discussion	48
Conclusion	54
Acknowledgments	55
Conflict of interest	55
Reference	55
CHAPTER 4. GENERAL CONCLUSIONS	59
Conclusions	59
Future Work	60

ACKNOWLEDGMENTS

First and foremost, I want to thank my family for their unconditional support and encouragement. Without their help, encouragement and exhortation, I wouldn't be here and persistently pursue my M.S degree.

Second, I am especially grateful to my major professor Mark Mba Wright. Thank you for giving me this opportunity and supporting me to participant in the research of biorenewable technology. Your support, encouragement and tutelage made this work possible. During my mater degree period, I learned a lot of knowledge about this growing bio-technology which was totally new to me. I believe that these knowledge will greatly impact me in my future career. Your enthusiasm for research, generosity and efficient works also set me a model. I am glad to have you as my mentor and these years would be the memorable time in my life.

Third, I am also very thankful to my committee members, Dr. Brown and Dr. Rover. The papers and this thesis could not be completed without your contributions and efforts. I gratefully appreciate your time and insightful suggestions for my research.

As a member of Dr. Wright's research group, I enjoyed working with my colleagues. I would like to thank the postdoc, Qi Dang, for her advices and help in research. Special thanks for Wenqin Li, Boyan Li and Ntaliya Apanovich, thanks for all of your friendship and support over these time.

Finally, thanks a lot for the Iowa State University and the Department of Mechanical Engineering. Special thanks to all of the administration staffs in the Department of Mechanical Engineering. Special thanks to Amy, Deb, and Neely for helping me a lot during my study in Iowa State University.

v

ABSTRACT

Advanced biofuel is a promising replacement to fossil fuels for the purpose of protecting the environment and securing national energy supply, but the high cost of producing advanced biofuels makes it not as competitive as petroleum-based fuels. Recent technology developments in biomass fast pyrolysis and bio-oil upgrading introduced several innovative pathways to convert bio-oil into other commodity products, such as bio-asphalt, bio-cement, dextrose and benzene, toluene, xylene (BTX). Before commercializing these products, a comprehensive techno-economic analysis should be employed to examine the economic feasibility of producing them. This thesis compared the economic performance of biofuels, biochemicals, and hydrocarbon chemicals portfolios and optimized the product selection of an integrated biorefinery.

Based on a fast pyrolysis and bio-oil fractionation system, three product portfolios were proposed: biofuels (gasoline and diesel), biochemicals (bio-asphalt, cement and dextrose) and hydrocarbon chemicals (BTX and olefins). The production process, operating costs and capital costs were simulated based on the model data, experimental data, and literature data. Minimum product selling price (MPSP), maximum investment cost (MIC) and net present value (NPV) were used to evaluate and compare the economic performance of three portfolios with a 10% internal rate of return (IRR). A bio-refinery concept integrating all products was proposed to improve the flexibility to respond to changes in the market prices of the proposed products. The ratio of bio-oil upgrading to different product groups was manipulated to maximize the NPV under different price situations.

Several major conclusions were drawn from this study. Due to high capital costs and operating costs associated with biofuels production, hydrocarbon chemical and biochemical

vi

products can be attractive bio-refinery products. However, there has been limited development of the hydrocarbon chemical and biochemical product technologies. This study attempts to address this risk by evaluating the uncertainty in the NPV and MIC. In particular, the biochemicals scenario has the highest MIC, which indicates that it has the greatest potential for remaining profitable with increased capital investment. The hydrocarbon chemicals production yields relatively high revenues and is more robust to fluctuations in market prices based on historical data. Biofuels production is economically attractive only when the price of transportation fuels is at historically high values.

CHAPTER 1. GENERAL INTRODUCTION

In the 20th century, most research efforts were dedicated to develop petroleum, coal and natural gas based commodity products to meet the growing energy demand of the increasing population [1]. Currently, fossil fuels and products are not considered environmentally friendly and sustainable for human development. In addition, the dependence on foreign petroleum has become a concern for energy policymakers. The desires of finding a clean and sustainable energy source have driven more efforts and investment into developing substitutes of fossil fuels. Biofuels, as a promising substitute, have attracted increasing attention for its sustainability, resource availability and positive economic effects.

Biofuel is any type of liquid or gaseous fuel that is derived from recent biological materials [2]. Recent biological materials are also called biomass, which can be energy crops, wood residues, agricultural residues, municipal waste and others. Based on the source of biomass, biofuels are classified into first generation biofuels, which are produced from sugarcane and corn starch, and second generation biofuels, which are derived from non-food biomass. The biomass potential in the U.S. is 1.1-1.6 billion tons per year and it could supply energy content of over one-third of total petroleum consumption in the U.S. if they are fully taken advantage of [3]. Due to the accessibility of biomass, biofuels can be produced in every country and thus have the potential of reducing foreign energy dependence. Rural areas that have abundant biomass resources will be benefitted greatly from the development of biofuels. Several researches have shown the sustainability of biofuels production and demonstrated that greenhouse gas (GHG) emissions can be reduced by replacing petroleum-derived fuels with biofuels [4–7].

In the United States, biofuel production received great support from the government in the form of favorable policies. Petroleum industry received a federal tax credit which encouraged

the blending of ethanol with gasoline in 1978 and biodiesel received a similar tax credit in 2004 [8]. In order to stimulate the biofuel production, the U.S. Environmental Protection Agency (EPA) released the Renewable Fuel Standard (RFS) in 2005 which increased the minimum amount of biofuel production from 4 billion gallons in 2006 to 7.5 billion gallons in 2013 [9]. The Energy Independence and Security Act (EISA) of 2007 replaced the RFS with a more comprehensive RFS2, which increased the total renewable fuel requirement from 9 billion gallons in 2008 to 36 billion gallons per year by 2022 [9]. EISA also divided renewable fuel into four categories based on the life-cycle GHG emission reductions and set volume requirement for each of them. At least 21 billion gallons of renewable fuel should be advanced biofuels and no more than 15 billion gallons should come from corn ethanol or biodiesel [9]. Cellulosic biofuel, as next-generation biofuel, was mentioned specifically in the RFS2 which mandates the production of cellulosic biofuels from 100 million gallons in 2008 to 16 billion gallons in 2022 [9].

Cellulosic biofuel is derived from lignocellulosic biomass, which includes agricultural residues, virgin biomass, energy crops, and municipal solid waste. Among different conversion pathways of cellulosic biomass, the thermochemical pathway has received high attention for its ability to produce hydrocarbons[10]. Thermochemical conversion usually produces multiple and complex products in a short reaction time. Sometimes catalysts are added to improve the quality or spectrum of the product [11]. Combustion, gasification, pyrolysis, and solvolysis have been investigated as thermochemical pathways for biomass conversion [12–18]. A variety of liquid and gaseous products can be produced from thermochemical processing of biomass as shown in Figure 1.



Figure 1. Strategies for production of fuels from lignocellulosic biomass[19]

Pyrolysis was used for charcoal production thousands of years ago, but only in the past 30 years fast pyrolysis has become of a considerable interest in biofuel production [11]. The liquid product from fast pyrolysis, which is also called bio-oil, offers this technology significant logistical and economic advantages over other thermochemical conversion methods because the liquid product can be stored or transported to where it is needed [20]. Fast pyrolysis is a rapid thermal decomposition of organic compounds at moderate temperature in the absence of oxygen. Liquids, solids and gases are produced in the process and the product distributions vary with

biomass type, pyrolysis temperature and vapor residence time. Short vapor residence time, up to 2 seconds, and reaction temperature of 500 °C favor the production of liquid products. The yields of bio-oil can be up to 75 wt% of dry biomass feed [21]. Bio-oil can be directly used for heat and power generation or subsequently upgraded to biofuels and chemicals. Charcoal, one of the by-products, can be burned with process gases to provide process heat or can be upgraded to biochar for soil amendment.

Mohan et al. gave the details about fast pyrolysis process from biomass to bio-oil and introduced the application of bio-oil [22]. The high viscosity, chemical instability, high oxygen content and corrosiveness make bio-oil incompatible with current fuel system [23]. Further upgrading is required to make bio-oil more valuable and available in transportation fuels or chemical markets. Renewable transportation fuels are the focus of current research efforts in finding a substitute to fossil fuels. Elliott et al. [24] developed several catalyst formulations for hydroprocessing of bio-oil to produce hydrocarbon products, which can be used to supplement petroleum refinery feedstock. Stevens et al. [25] designed a plant that produces infrastructureready renewable gasoline and diesel from biomass through fast pyrolysis, hydrotreating and hydrocracking and evaluated its economic feasibility. Susanne et al. [26] designed a process and evaluated the economics for the conversion of lignocellulosic biomass to hydrocarbon via fast pyrolysis and hydrotreating bio-oil pathway. Commodity chemicals always have high market value and thus many investments have been attracted into the research of producing chemicals from renewable resources. Vispute et al. [27] developed five catalytic hydroprocessing of whole bio-oil and aqueous phase bio-oil pathways to produce aromatic hydrocarbons and light olefins. Ru/C and Pt/C were chosen as the catalysts for hydroprocessing and zeolite was the catalyst of fluid catalytic cracking (FCC). Cheng et al. [28] developed a bifunctional Ga/ZSM-5 catalyst for

fast pyrolysis of lignocellulosic biomass to produce benzene, toluene and xylenes (BTX). Hydrogen is another main product that can be produced from biomass. Takanabe et al. [29] investigated a pathway to generate hydrogen from bio-oil via steam reforming over Pt/ZrO₂ followed by gas-shift reaction. Vagia and Lemonidou [30] analyzed the thermodynamics of hydrogen production via steam reforming the aqueous faction of bio-oil and concluded that hydrogen from bio-oil steam reforming is competitive with hydrogen from natural gas steam reforming. Hydrogen generation via aqueous phase bio-oil steam reforming can be integrated into bio-oil upgrading process to provide hydrogen for deoxygenation [31]. Sugars are the most important component in the bio-oil and have high value, they can be upgraded to various hydrocarbon. Kuzhiyil et al. [32] developed an acid treatment method to increase the sugar yields during fast pyrolysis. Rover et al. [33] found a two-stage water wash method of removing pyrolytic sugars from bio-oil and detoxification method to get clean sugars. Charcoal is the main by-product in fast pyrolysis process and there are several publications investigating the production of biochar from biomass [34,35]. Some studies also explored some new routes for bio-oil utilization, for example asphalt and gluconic acids [36,37].

Numerous studies have already been conducted to explore the potential of lignocellulosic biomass fast pyrolysis to promote the commercialization cellulosic biofuels. To investigate the economic feasibility of advanced biofuel refinery, techno-economic analysis of fast pyrolysis have been widely conducted. Wright et al. [38] examined corn stover fast pyrolysis to bio-oil with subsequent upgrading to naphtha and diesel range fuel and \$3.09 along with \$2.11 per gallon of gasoline equivalent value was achieved for fuel products. Brown et al. [39] performed an updated techno-economic analysis of fast pyrolysis and hydroprocessing of biomass to transportation fuels and electricity based on the previous study. In this study, the minimum

product selling price (MPSP) of \$2.57 per gallon of gasoline and diesel was achieved. Zhang et al. [40] modeled a woody biomass fast pyrolysis refinery that produced monosaccharides, hydrogen and transportation fuel, and examined its economic feasibility. Internal rate of return (IRR) method was used to assess the economic performance and 11.4% was achieved based on the market price of products. Thilakaratne et al. [41] compared two catalytic pyrolysis pathways of converting microalgae into drop-in fuels with different feedstock dewatering methods. The MPSPs of \$1.8 per liter and \$1.49 per liter were calculated for two pathways. Brown et al. [42] evaluated the economic feasibility of five fast pyrolysis and bio-oil upgrading scenarios in which commodity chemicals were produced through integrated catalytic processing (ICP). To optimize the bio-refinery concept, several studies have investigated fast pyrolysis bio-refinery using life cycle assessment method and developed optimization methods for fast pyrolysis products selection and supply chain management [43–47].

Numerous studies have investigated the economic feasibility of cellulosic biofuels production. Normally the transportation fuel production is the intended product of a bio-refinery, but the fluctuations in petroleum prices make it difficult to guarantee the profit of the refinery. There are more alternative products generated from fast pyrolysis which might offer the biorefinery more economic benefits and stability. The objective of this research is to explore the economic performance of advanced bio-refineries with multiple categories of products based on the state-of-the-art fast pyrolysis and bio-oil upgrading technologies. The organization of the thesis is as follows:

In Chapter two, we conduct techno-economic analysis of three product portfolios from biomass fast pyrolysis: transportation fuels, biochemicals and hydrocarbon chemicals. The fast pyrolysis process is simulated in the Aspen PlusTM software and products yields are calculated

based on model, experimental, and literature data. A modified discounted cash flow rate of return spreadsheet is used to summarize the production process consumption, estimate the capital cost and annual operating costs, calculate the net present value and minimum fuel selling price, and finally determine the economic feasibility. The uncertainty analysis of bio-refinery net present value is implemented using Monte-Carlo method based on products historical prices.

Based on the previous work in chapter two, a bio-refinery concept that integrates three product categories is proposed. Multiple product selection strategy gives the bio-refinery more flexibility when the market for the intended product is changing. In order to find the best product combination based on different product price situations, a Mathematica model is created to optimize the distribution of products and find the highest net present value. In the meantime, the capital costs and annual operating costs are adjusted by the ratio of product groups. The optimal product selection under different market situations is determined.

The thesis is summarized and concluded in chapter four. Some thoughts for future research directions are given in the concluding chapter.

References

- S. N. Naik, V. V. Goud, P. K. Rout, and A. K. Dalai, "Production of first and second generation biofuels: A comprehensive review," *Renew. Sustain. Energy Rev.*, vol. 14, pp. 578–597, 2010.
- [2] M. Giampietro, S. Ulgiati, and D. Pimentel, "Feasibility of Large-Scale Biofuel Production," *Bioscience*, vol. 47, no. 9, pp. 587–600, 1997.
- [3] U. S. D. of Energy, "US Billion Ton Update: Biomass supply for a bioenergy and bioproducts industry," 2011.
- [4] J. Han, A. Elgowainy, J. B. Dunn, and M. Q. Wang, "Life cycle analysis of fuel production from fast pyrolysis of biomass," *Bioresour. Technol.*, 2013.

- [5] R. Luque, L. Herrero-Davila, J. M. Campelo, J. H. Clark, J. M. Hidalgo, D. Luna, J. M. Marinas, and A. a. Romero, "Biofuels: a technological perspective," vol. 1, no. 5, 2008.
- [6] B. D. Solomon, "Biofuels and sustainability," *Ann. N. Y. Acad. Sci.*, vol. 1185, pp. 119–134, 2010.
- [7] Q. Dang, C. Yu, and Z. Luo, "Environmental life cycle assessment of bio-fuel production via fast pyrolysis of corn stover and hydroprocessing," *Fuel*, vol. 131, pp. 36–42, 2014.
- [8] C. Panoutsou, A. Bauen, and I. C. London, "Policy regimes and funding schemes to support investment for next- generation biofuels in the USA and the EU-27," pp. 685–701, 2013.
- [9] U.S. EPA, "Renewable Fuel Standard (RFS)," 2005. [Online]. Available: http://www.epa.gov/otaq/fuels/renewablefuels/index.htm. [Accessed: 17-Mar-2015].
- [10] J. R. Regalbuto, "The sea change in US biofuels' funding: from cellulosic ethanol to green gasoline," *Biofuels, Bioprod. Biorefining*, vol. 5, pp. 495–504, 2011.
- [11] A. V. Bridgwater, "Review of fast pyrolysis of biomass and product upgrading," *Biomass and Bioenergy*, vol. 38, pp. 68–94, 2012.
- [12] R. C. Brown, *Thermochemical Processing of Biomass: Conversion into Fuels, Chemicals and Power*, First. John Wiley & Sons, Ltd., 2011.
- [13] P. C. Munasinghe and S. K. Khanal, "Biomass-derived syngas fermentation into biofuels," *Biofuels*, vol. 101, no. 13, pp. 79–98, 2011.
- [14] J. B. Binder and R. T. Raines, "Fermentable sugars by chemical hydrolysis of biomass.," *Proc. Natl. Acad. Sci. U. S. A.*, vol. 107, pp. 4516–4521, 2010.
- [15] F. Guo, Z. Fang, C. C. Xu, and R. L. Smith, "Solid acid mediated hydrolysis of biomass for producing biofuels," *Prog. Energy Combust. Sci.*, vol. 38, no. 5, pp. 672–690, 2012.
- [16] D. R. Vardon, B. K. Sharma, G. V. Blazina, K. Rajagopalan, and T. J. Strathmann, "Thermochemical conversion of raw and defatted algal biomass via hydrothermal liquefaction and slow pyrolysis," *Bioresour. Technol.*, vol. 109, pp. 178–187, 2012.
- [17] D. López Barreiro, W. Prins, F. Ronsse, and W. Brilman, "Hydrothermal liquefaction (HTL) of microalgae for biofuel production: State of the art review and future prospects," *Biomass and Bioenergy*, vol. 53, no. 0, pp. 113–127, 2013.
- [18] R. Davis, L. Tao, E. C. D. Tan, M. J. Biddy, G. T. Beckham, C. Scarlata, J. Ross, J. Lukas, D. Knorr, and P. Schoen, "Process Design and Economics for the Conversion of Lignocellulosic Biomass to Hydrocarbons : Dilute-Acid and Enzymatic Deconstruction of

Biomass to Sugars and Biological Conversion of Sugars to Hydrocarbons Process Design and Economics for the Conversion," 2013.

- [19] G. W. Huber and J. a. Dumesic, "An overview of aqueous-phase catalytic processes for production of hydrogen and alkanes in a biorefinery," *Catal. Today*, vol. 111, pp. 119– 132, 2006.
- [20] A. V Bridgwater, D. Meier, and D. Radlein, "An overview of fast pyrolysis of biomass."
- [21] S. Czernik and A. V Bridgwater, "Overview of applications of biomass fast pyrolysis oil," *Energy & Fuels*, 2004.
- [22] D. Mohan, C. U. Pittman, and P. H. Steele, "Pyrolysis of wood/biomass for bio-oil: A critical review," *Energy and Fuels*, vol. 20, pp. 848–889, 2006.
- [23] Q. Zhang, J. Chang, T. Wang, and Y. Xu, "Review of biomass pyrolysis oil properties and upgrading research," *Energy Convers. Manag.*, vol. 48, pp. 87–92, 2007.
- [24] D. C. Elliott, T. R. Hart, G. G. Neuenschwander, L. J. Rotness, and A. H. Zacher, "Catalytic hydroprocessing of biomass fast pyrolysis bio-oil to produce hydrocarbon products," *Environ. Prog. Sustain. Energy*, 2009.
- [25] S. Jones, J. Holladay, C. Valkenburg, D. Stevens, C. Walton, C. Kinchin, D. Elliott, and S. Czernik, "Production of Gasoline and Diesel from Biomass via Fast Pyrolysis, Hydrotreating and Hydrocracking: A Design Case," Richland, WA, 2009.
- [26] J. Susanne, M. Pimphan, L. Snowden-Swan, A. Padmaperuma, E. Tan, A. Dutta, J. Jacobson, and K. Cafferty, "Process Design and Economics for the Conversion of Lignocellulosic Biomass to Hydrocarbon Fuels Fast Pyrolysis and Hydrotreating," Golden, CO., 2013.
- [27] T. P. Vispute, H. Zhang, A. Sanna, R. Xiao, and G. W. Huber, "Renewable chemical commodity feedstocks from integrated catalytic processing of pyrolysis oils.," *Science*, vol. 330, pp. 1222–1227, 2010.
- [28] Y. T. Cheng, J. Jae, J. Shi, W. Fan, and G. W. Huber, "Production of renewable aromatic compounds by catalytic fast pyrolysis of lignocellulosic biomass with bifunctional Ga/ZSM-5 catalysts," *Angew. Chemie - Int. Ed.*, vol. 51, pp. 1387–1390, 2012.
- [29] K. Takanabe, K. I. Aika, K. Seshan, and L. Lefferts, "Sustainable hydrogen from bio-oil -Steam reforming of acetic acid as a model oxygenate," J. Catal., vol. 227, pp. 101–108, 2004.
- [30] E. C. Vagia and A. a. Lemonidou, "Thermodynamic analysis of hydrogen production via autothermal steam reforming of selected components of aqueous bio-oil fraction," *Int. J. Hydrogen Energy*, vol. 33, pp. 2489–2500, 2008.

- [31] C. a. Fisk, T. Morgan, Y. Ji, M. Crocker, C. Crofcheck, and S. a. Lewis, "Bio-oil upgrading over platinum catalysts using in situ generated hydrogen," *Appl. Catal. A Gen.*, vol. 358, pp. 150–156, 2009.
- [32] N. Kuzhiyil, D. Dalluge, X. Bai, K. H. Kim, and R. C. Brown, "Pyrolytic sugars from cellulosic biomass," *ChemSusChem*, vol. 5, pp. 2228–2236, 2012.
- [33] M. R. Rover, P. A. Johnston, T. Jin, R. G. Smith, R. C. Brown, and L. Jarboe, "Production of clean pyrolytic sugars for fermentation," *ChemSusChem*, vol. 7, pp. 1662–1668, 2014.
- [34] D. C. Elliott, G. G. Neuenschwander, and T. R. Hart, "Hydroprocessing bio-oil and products separation for coke production," *ACS Sustain. Chem. Eng.*, 2013.
- [35] D. A. Laird, R. C. Brown, J. E. Amonette, and J. Lehmann, "Review of the pyrolysis platform for coproducing bio-oil and biochar," *Biofuels, Bioprod. Biorefining*, vol. 3, pp. 547–562, 2009.
- [36] D. Santhanaraj, M. R. Rover, D. E. Resasco, R. C. Brown, and S. Crossley, "Gluconic Acid from Biomass Fast Pyrolysis Oils: Specialty Chemicals from the Thermochemical Conversion of Biomass," *ChemSusChem*, vol. 7, pp. 3132–3137, 2014.
- [37] J. Peralta, H. M. R. D. Silva, R. C. Williams, M. R. Rover, and A. V. A. Machado, "Development of an Innovative Bio-binder Using Asphalt-Rubber Technology," *Int. J. Pavement Res. Technol.*, vol. 6, no. 4, pp. 447–456, 2013.
- [38] M. M. Wright, J. A. Satrio, R. C. Brown, D. E. Daugaard, and D. D. Hsu, "Techno-Economic Analysis of Biomass Fast Pyrolysis to Transportation Fuels," *Fuel*, vol. 10, pp. S2–S10, 2010.
- [39] T. R. Brown, R. Thilakaratne, R. C. Brown, and G. Hu, "Techno-economic analysis of biomass to transportation fuels and electricity via fast pyrolysis and hydroprocessing," *Fuel*, vol. 106, pp. 463–469, 2013.
- [40] Y. Zhang, T. R. Brown, G. Hu, and R. C. Brown, "Techno-economic analysis of monosaccharide production via fast pyrolysis of lignocellulose," *Bioresour. Technol.*, vol. 127, pp. 358–365, 2013.
- [41] R. Thilakaratne, M. M. Wright, and R. C. Brown, "A techno-economic analysis of microalgae remnant catalytic pyrolysis and upgrading to fuels," *Fuel*, 2014.
- [42] T. R. Brown, Y. Zhang, G. Hu, and R. C. Brown, "Techno-economic analysis of biobased chemicals production via integrated catalytic processing," *Biofuels, Bioprod. Biorefining*, 2011.

- [43] B. H. Gebreslassie, M. Slivinsky, B. Wang, and F. You, "Life cycle optimization for sustainable design and operations of hydrocarbon biorefinery via fast pyrolysis, hydrotreating and hydrocracking," *Comput. Chem. Eng.*, vol. 50, pp. 71–91, 2013.
- [44] P. E. Murillo-alvarado, J. Mar, M. Serna-gonza, and M. M. El-halwagi, "Optimization of Pathways for Biore fi neries Involving the Selection of Feedstocks, Products, and Processing Steps," 2013.
- [45] A. T. Ubando, A. B. Culaba, K. B. Aviso, D. K. S. Ng, and R. R. Tan, "Fuzzy mixedinteger linear programming model for optimizing a multi-functional bioenergy system with biochar production for negative carbon emissions," *Clean Technol. Environ. Policy*, pp. 1537–1549, 2014.
- [46] A. Kelloway and P. Daoutidis, "Process synthesis of biorefineries: Optimization of biomass conversion to fuels and chemicals," *Ind. Eng. Chem. Res.*, 2014.
- [47] Y. Zhang and M. M. Wright, "Product Selection and Supply Chain Optimization for Fast Pyrolysis and Biorefinery System," *Ind. Eng. Chem. Res.*, vol. 53, pp. 19987–19999, 2014.

CHAPTER 2. COMPARATIVE TECHNO-ECONOMIC ANALYSIS OF ADVANCED BIOFUELS, BIOCHEMICALS, AND HYDROCARBON CHEMICALS PRODUCTION VIA THE PYROLYSIS PLATFORM

A paper to be submitted to *Biomass and Bioenergy* Wenhao Hu, Qi Dang, Mark M. Wright, Marjorie Rover, Robert C. Brown

Abstract

This study evaluates the techno-economic feasibility of three product portfolios from a biomass fast pyrolysis bio-refinery: biofuels, biochemicals, and hydrocarbon chemicals. The bio-refinery design is based on the fast pyrolysis and five-stage recovery system developed by Iowa State University. It can produce drop-in transportation fuels; infrastructure materials such as bio-asphalt and bio-cement, and dextrose in the biochemicals scenario; and hydrocarbon aromatics and olefins are produced in the hydrocarbon chemicals scenario. The bio-refinery converts 65.87 wt% of corn stover biomass into bio-oil. The bio-oil is fractionated into five stage fractions and upgraded through different pathways based on the chosen portfolio. Minimum product selling prices (MPSP) are calculated based on a 30-year discounted cash flow rate of return analysis with a target 10% internal rate of return (IRR).

We estimated MPSPs of \$3.09/gallon for biofuels, \$461.32/MT for biochemicals, and \$1113.83/MT for hydrocarbon chemicals. Monte-Carlo analysis is used to determine maximum investment cost (MIC) and the net present value (NPV) distribution based on 20-year historical prices. The mean MICs are estimated to be \$162 MM, \$525 MM and \$283 MM for biofuels scenario, biochemicals scenario and hydrocarbon chemicals scenario, respectively. The net present value distributions are \$-243.42±268.9 MM for the biofuels scenario, \$412.03±374.1

MM for the biochemicals scenario, and \$82.08±16.6 MM for the hydrocarbon chemicals scenario. Biofuels, biochemicals and hydrocarbon chemicals portfolios have 18%, 100% and 100% chance that net present values are positive respectively, which indicates that producing biochemicals and hydrocarbon chemicals could be more competitive than producing biofuels alone.

Introduction

Global concerns over climate change and energy resources have driven interest in replacing fossil products with clean and sustainable alternatives. Biomass is a suitable resource for the production of a variety of fuels, chemicals, and infrastructure (asphalt and cement) materials via biochemical and thermochemical processing. Through fast pyrolysis, one of several thermochemical platforms, we can convert biomass into products that can substitute those derived from fossil fuels. Previous studies have shown that biomass fast pyrolysis produces bio-oil which can be upgraded into gasoline and diesel, chemicals, and infrastructure materials [1–4].

Fast pyrolysis is the rapid thermal decomposition of organic materials into liquid, vapor and solid products in the absence of oxygen at temperatures of about 500 °C with residence time of 0.5 to 2 seconds [5–7]. The selectivity of fast pyrolysis products depends on the composition of biomass, temperature, and reaction residence time [6]. The liquid product is commonly known as bio-oil, and it contains oxygenated organic compounds. The gases, also known as noncondensable gases (NCG), are a low-Btu natural gas substitute. The solids are called bio-char, and they include carbon, alkali and alkaline earth metals, and ash. Each of these products can be commercialized into various markets, but there is currently no large-scale commercial market based on these systems.

There are several studies that have evaluated the commercialization of multiple fast pyrolysis products. Wright et al. [1] examined two 2000 tons corn stover bio-refineries to produce naphtha and diesel range fuels with on-site hydrogen generation or merchant hydrogen. With capital costs of \$911 and \$585 million, \$6.55 and \$3.41 per gasoline gallon equivalent (gge) product values was achieved. Brown et al. [8] presented a pathway for fast pyrolysis and hydroprocessing of biomass to transportation fuels and electricity and achieved minimum product selling price (MPSP) of \$2.57/gal which was competitive with petroleum. Zhang et al. [2] explored the economic feasibility of a 2000 dry metric ton biomass per day fast pyrolysis facility producing monosaccharides, hydrogen and transportation fuels. Based on the market price of products, 11.4% internal rate of return was achieved. Brown et al. [3] evaluated the economic feasibility of producing biobased commodity chemicals based on fast pyrolysis facility with five different catalytic upgrading processes. There are hundreds of compounds in bio-oil [9]. This property makes bio-oil available to be upgraded towards specialty product. Santhanaraj et al. [10] presented a novel route to produce the specialty chemical gluconic acid from biomass fast pyrolysis oils without additional by-products. Bio-char is a very important by-product in the fast pyrolysis facility because of its potential agronomic and carbon sequestration value [11]. Laird et al. [12] gave a review of pyrolysis platform for coproducing renewable fuels and biochar which is a promising means of producing large amount of fuels while reducing emission of greenhouse gases at the same time. Brown et al. [13] estimated the profitability of producing biochar through slow pyrolysis and fast pyrolysis and concluded that coproducing gasoline and biochar via fast pyrolysis was commercially feasible. Zhang et al. [14] utilized a mixed-integer nonlinear programming model (MINLP) to determine the biomass supply, facility selection and optimal distribution of different products for an integrated fast pyrolysis bio-refinery supply

chain. A few studies have developed optimization frameworks for the selection of fast pyrolysis products within a supply chain framework [15–17]

In this study, a techno-economic analysis is conducted to evaluate the minimum product selling price (MPSP), maximum investment cost (MIC) and net present value (NPV) of multiple product portfolios from a biomass fast pyrolysis bio-refinery. The analysis employs recent experimental data [9, 18] to compare the commercialization potential of hydrocarbon chemicals (benzene, toluene, and xylene (BTX)) and biochemicals (bio-asphalt, bio-cement, and dextrose) to the traditional fast pyrolysis to fuels approach. Previous studies have evaluated the production of multiple products from a single fast pyrolysis bio-refinery including chemicals. To our knowledge, this is the first study to compare the production of our biomass-based biochemicals and hydrocarbon chemicals to fuels production via fast pyrolysis. By comparing their MPSPs, MICs and NPVs, we seek to determine favorable market conditions for the commercialization of a multi-product fast pyrolysis bio-refinery.

The structure of this article is as follows: first we describe the three portfolio options for fuels, biochemicals, and hydrocarbon chemicals; second, we evaluate the MPSPs for each of the portfolios; third, we determine the MIC and NPV uncertainties of the various scenarios based on historical market prices.

Methodology

Red oak is employed as the biomass feedstock in this study, and the bio-refinery is designed to process 2000 dry metric ton of red oak per day. The properties of the red oak feedstock are provided in Table 1. There are five basic processing areas: biomass pretreatment, biomass pyrolysis, solid removal, bio-oil fractionation, bio-oil upgrading and co-generation. The

following analysis will be divided into three parts: bio-oil production and collection, bio-oil upgrading and bio-refinery economic analysis.

Constituent (wt %)		Ultimate Analysis (wt %)		Proximate Analysis (wt %)		
Hemicellulose	20.0	Carbon	48.7	Moisture	3.86	
Cellulose	29.8	Hydrogen	6.8	Volatiles	81.9	
Lignin	43.3	Nitrogen	0.072	Fixed Carbon	12.56	
Extractives	3.3	Oxygen	44.03	Ash	0.39	
Ash	0.3	Sulfur	0.002	Other	1.28	
Other	3.3	Ash	0.39			

Table 1. Properties of Red Oak[19]

Bio-oil production and collection

In the biomass pretreatment section, biomass is first chopped, dried and ground to 3 mm diameter particles [1]. The chopping process grinds biomass into 10 mm particles in order to improve the drying performance by increasing the particle surface area and reducing the heat input required to remove moisture. The grinding process is employed to enhance the fast pyrolysis performance in a fluidized bed reactor [1]. The drying process is required because high moisture content in biomass can contribute to lower products yields. In this study, we assume the moisture of red oak is reduced from 25 wt% to less than 7 wt%. For the biochemicals scenario, an additional acid treatment is applied to the chopped biomass in order to improve the sugar yields during fast pyrolysis. A sulfuric acid solution is adopted in this paper with an acid to water mass ratio of 1:1 [20].



Biomass Conversion System

Figure 2. Schematic of bio-oil conversion system

Pretreated biomass then enters the fluidized bed reactor where fast pyrolysis takes place. The pyrolyzer is operated at around 500 °C under ambient pressure without oxygen. Biomass is decomposed into a mixture of pyrolysis vapor, non-condensable gases, aerosols, char and ashes in a very short residence time. Before the vapor is condensed and collected as bio-oil, it passes through a high volume and efficient cyclone where solids and ash are removed at 95% efficiency. Part of the bio-char collected in this section is burned in the combustion section to provide process heat for biomass pretreatment and pyrolysis.



Figure 3. Schematic of bio-oil fractionation system

Bio-oil is recovered as distinct stage fractions using a five-stage bio-oil fractionation system developed at Iowa State University as shown in Figure 3 [9]. Stage fraction (SF) 1&2 are designed to recover levoglucosan and other compounds with high dew points, so SF 1&2 consist of sugars and the majority of water-insoluble content which consists primarily of phenolic oligomers [9]. SF 1&2 are also designated as heavy ends. SF 3&4 are designed to collect monomeric phenols and other compounds with similar dew points. Therefore most of SF 3&4, which are called mid ends, are phenols and alkylated phenols as well as part of the acids [9]. Most of the acids, furans, water, and part of the monomeric phenols are collected in SF 5, which is also named light ends[9]. Non-condensable gases (NCG) from this section are combusted to provide heat for whole system.

Bio-oil contains more than one hundred compounds and five-stage fractionation system divides bio-oil into stage fractions with diverse chemical and physical properties, which makes it possible to upgrade them into various products. The chemical compounds detected in bio-oil fractions using GC/MS are given in Table 2 [9]. In this paper, different target products will be evaluated in different portfolios according to the properties of each stage fraction.

Levoglucosan	Additional phenolic compounds
Acetic acid	Phenol
Furans	2-Methylphenol
2-Furan methanol	3-Methylphenol
5-Methyl-2-furancarboxaldehyde	4-Methylphenol
3-Methyl-2(5H)-furanone	2-Ethylphenol
Furfural	3-Ethylphenol
5-Hydroxymethyl-2-furancarboxaldehdye	2.4-Dimethylphenol
Dimethoxy phenols	2,5-Dimethylphenol
2,6-Dimethoxyphenol	3,4-Dimethylphenol
1-(4-Hydroxy-3,5-dimethoxyphenyl) ethanone	Benzenediol
4-Methyl-2,6-dimethoxyphenol	Hydroquinone
Monomethoxy phenols	Ketones
2-Methoxyphenol	l-Hydroxy-2-propanone
2-Methoxy-4-methylphenol	3-Hydroxy-2-butanone
4-Ethyl-2-methoxyphenol	2-Methyl-2-cyclopenten-1-one
Eugenol	2H-pyran-2-one
Isoeugenol	3-Methyl-1,2-cyclopentanedione
Vanillin	

Table 2. Chemical compounds detected in bio-oil fractions using GC/MS

Bio-oil upgrading

To produce transportation fuels, first four stage fractions (SF1-SF4) go through a twostage hydroprocessing process [21]. First-stage hydroprocessing happens in the reduction reactor under 140 °C and 121 bar, long chain molecules and oligomers are broken down to monomers. Under 370 °C and 121 bar, monomers are hydrotreated into gasoline and diesel range hydrocarbons in the second stage reactor. This hydrotreated bio-oil is called stabilized bio-oil. Then a refining process is applied to separate gasoline and diesel. Distillation bottoms will be hydrocracked into gasoline and diesel in a hydrocracker.



Figure 4. Schematic of biofuels production

In the biochemicals portfolio, dextrose, bio-asphalt and bio-cement are the main products. Most of the water-soluble sugars exist in the heavy ends fractions [9]. A simple two-stage water washing and detoxification process can recover a stream with high concentration of these sugars [22]. These sugars can be hydrolyzed to monosaccharide using 400mM sulfuric acid solution [23]. Dextrose equivalent (DE) value is used to differentiate glucose-rich syrup and dextrose. Dextrose's DE is greater than 60 [24], while glucose syrup has 38-44 DE [25]. Sugar analysis shows that the pyrolytic sugars have more than 90% of monomers, and it is high enough to consider the syrup as dextrose even though the DE value is undetermined [2]. Sugar yields achieve around 15 wt% of the bio-oil and 16.9 wt% yield can be achieved with additional biomass pretreatment [2,23]. The raffinate from heavy ends washing is water-insoluble phenolic oligomers. These products present similar performance to asphaltic bitumen, which means it has the potential to replace the bitumen or used as the modifier of a bituminous binder [26]. Due to the scarcity of commercialization data of this technology, we assume this product value is similar to fossil-based asphalt. Light ends are recovered as an aqueous phase, which contains large quantities of water and light oxygenated organic compounds. The major constituent is acetic acid, which can be converted into calcium acetate by adding limestone. This acetate can be used

to produce gelled fuel by mixing it with ethanol or can be combined with urea and seeded with urease-producing bacteria, then sprayed on soil or other pavement materials to produce concrete. Both products need further study for commercialization. In this study, calcium acetate is sold as the final product.



Figure 5. Schematic of biochemicals production

Commodity chemicals, such as BTX have high market value. In the hydrocarbon chemicals scenario, aromatic hydrocarbon (BTX, ethylbenzene) and olefins (Ethylene, propylene, Butylene) are chosen as the target products. SF 1&2 go through the same water washing process to separate water-soluble fraction, then the water-soluble fraction is mixed with the remaining stage fractions for upgrading. Two-stage hydrotreating followed by FCC of aqueous phase bio-oil upgrading method which is developed by Vispute et al. [27] is adopted. First stage hydrotreating happens at 398 K and 100 bar hydrogen pressure over Ru/C catalyst in a low temperature hydrotreator while the second stage hydrotreating is carried out at 523 K with 100 bar hydrogen pressure over Pt/C catalyst in a high-temperature hydrotreator. Subsequent fluidized catalytic cracking (FCC) occurs at 873 K over HZSM-5 catalyst. Hydrogen is purchased near-site for hydroprocessing.



Figure 6. Schematic of hydrocarbon chemicals production

Table 3 gives the hydrogen consumption, carbon yields and carbon selectivity for each product. According to the model data, the empirical formula for SF 1&2 is $CH_{1.34}O_{0.51}$. Here we assume the elements are uniformly distributed in the water-insoluble and water-soluble fractions. The carbon mole number of aqueous phase bio-oil is summarized from the process model for the final product yield calculation. Raffinate from SF 1&2 washing is sold as boiler fuel at coal price. In the MPSP analysis, the raffinate price is set to \$60/MT as the boiler fuel. In the uncertainty analysis, we employ coal prices stochastically chosen from the Monte-Carlo simulation.

Process	Hydrogen consumption	Carbon yields and carbon selectivity (%)					
Ru/H ₂ +Pt/H ₂ +Zeolite	(g/100 g of carbon m feed)	Aromatics		Olefins			
		18.3		43.0			
		Ca	rbon sel	ectivity (%)	Olefins 43.0 ity (%) Ethylene 32.0 Propylene 53.8 Butylene 14.2		
	0.1	Benzene	27.0	Ethylene	32.0		
	0.1	Toluene	49.3	Propylene	53.8		
		Xylene	19.1	Butylene	14.2		
		EthylBenzene 2.3					

Table 3. Final products carbon yields and carbon selectivity[27]

Bio-refinery economic analysis

Equipment size and cost estimation are calculated from Aspen Economic Analyzer software and scaled for different scenarios. Peter and Timmerhaus factors for installation cost are employed to estimate the total project cost[28]. The type of depreciation is double declining balance (DDB), and the depreciation period for the general plant and steam system are 7 and 20 years respectively. The bio-refinery construction period is 2.5 years and capital investment spent in this period is 8% for first year, 60% for second year and 32% for third year. The revenues, variable costs and fixed cost during start-up years are 50%, 75% and 100% of normal. Income tax rate is set to be 39%. A Lang factor of 5.6 is used to calculate the total project investment. A modified discounted cash flow rate of return (DCFROR) spreadsheet is employed to calculate the MPSPs of products for a target IRR of 10% over a 30-year period. MIC estimation is another value in which industry is interested to assess the maximum investment that should be invested into the project based on current market condition. Here we set the operating cost to a fixed value and use Monte-Carlo simulation to calculate MIC distribution using modified DCFROR spreadsheet based on historical prices with a target of 0 NPV and 10% IRR.

Table 5 gives the details of operating variables employed in this paper. The feedstock is assumed to be \$80/metric ton. Hydrogen price is assumed to be purchased near-site hydrogen production facility and set to be \$1.5/kg. The natural gas and electricity prices are based on the averages for EIA 20-year price forecasts[29]. Sulfuric acid and limestone prices are collected online [30,31]. Char produced by facility is sold for \$20/MT based on the low heating value of char.

The market price of commodity products are unstable and fluctuate due to the market conditions so fixed product prices are insufficient to adequately estimate the economic potential

of a bio-refinery. To investigate the influence of these fluctuations, the historical market prices of commodity products over past 20 years (1995-2014) are collected and used to find their price distribution. Sample sets of 3000 random picked group product prices are incorporated into the DCFROR spreadsheet to calculate the bio-refinery NPV. Finally, NPV distributions are generated to illustrate the economic potential of bio-refinery.

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
Engineering	32%
Construction	34%
Legal and contractors fees	23%
Indirect cost (IC)	0.89 * TPEC
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. Methodology for capital cost estimation for nth plant[28]

Commodity	Price
Feedstock	\$80/MT
Hydrogen	\$1.5/kg
Natural gas	\$0.26/kg
Pt/C	\$56.29/kg
Ru/C	\$5.60/kg
Zeolite	\$1.6/kg
Sulfuric Acid	\$200.0/MT
Limestone	\$17.0/MT
Electricity	\$0.062/kWh
Process water	\$0.52/MT
Char	\$20/MT

Table 5. Material parameters employed in the evaluation

Results and discussion

The bio-refinery uses red oak as feedstock, and it is designed to process 2000 metric tons dry biomass per day. The same pyrolysis and fractionation system is employed in all three scenarios, the system is modeled in the Aspen PlusTM software and the yields of stage fractions are summarized in Table 6. Model and process yields are simulated based on the experimental data from laboratory in Iowa State University. The total bio-oil yields is 65.87 wt% of dry biomass, which is within the range of previous studies. Char and NCG yields are 13.04 wt% and 21.09 wt%, respectively. In the facility, all the NCG and 135 tons of char are burned in the combustor to provide process heat for the whole system.

The yields of final products for each scenario are illustrated in Table 7. For the fuel scenario, 173,000 gal gasoline and diesel are produced per day. For the alternative scenario, 480 tons per day infrastructure material and 222 tons per day dextrose syrup are produced. In the

chemical scenario, the total yields of olefins and aromatics are 246.2 tons per day and 87.9 tons per day.

	Mass yields based on 2000 MT dry biomass (MT)	wt % (dry biomass base)
SF1	274.25	13.71%
SF2	408.29	20.41%
SF3	86.82	4.34%
SF4	33.01	1.65%
SF5	515.1	25.76%
Total Bio-oil	1317.47	65.87%
Char	260.8	13.04%
NCG	421.73	21.09%

 Table 6. Stage fraction yields from Aspen Plus model

Products yields for three scenarios based on 2000 MT dry biomass					
Diofuels	Gasoline	96,790	gal		
Biolueis	Diesel	76,144	gal		
	Asphalt	426.00	MT		
Biochemicals	Dextrose	222.65	MT		
	Calcium Acetate	52.99	MT		
	Butylene	32.73	MT		
	Ethylene	73.89	MT		
	Propylene	124.24	MT		
	Benzene	24.63	MT		
Hydrocarbon	Toluene	45.47	MT		
Chemicals	Xylene	17.76	MT		
	Ethylebenzene	2.14	MT		
	Indene	0.45	MT		
	Naphthalene	0.45	MT		
	Styrene	12.26	MT		

Table 7. Final products yields for three portfolios

The fixed capital investments for the three scenarios are \$317, \$162 and \$216 million, respectively. The details of them are shown in Figure 7. The differences in the investments are mainly because of the high costs of the bio-oil upgrading process. The installed equipment cost for upgrading process are \$100 and \$35 million for biofuels scenario and hydrocarbon chemicals scenario, respectively. The upgrading process of the biofuels scenario includes bio-oil stabilization, refining and hydrogen generation. The installed costs of these three sections are \$23.2 MM, \$13.4 MM and \$63.3 MM. For the hydrocarbon chemicals portfolio, the installed equipment cost of the upgrading process is \$35 MM and consists primarily of hydroprocessing, FCC, and separation units. In this scenario, hydrogen is purchased instead of producing on-site, so the equipment investment is reduced while \$10 million cost for hydrogen purchase is added to the annual operating cost. Upgrading processes are relatively simple in the biochemicals scenario, and several storage tanks are needed for sugar hydrolysis. The equipment cost for this section is included in the balance of plant cost.



Figure 7. Fixed capital investment for three scenarios

The biofuels scenario has annual operating costs of \$105 million, while the biochemicals scenario has annual operating costs of \$68 million, and the hydrocarbon chemicals scenario has annual operating costs of \$79 million. Feedstock, natural gas and hydrogen have higher impacts on the operating cost. To meet the 10% IRR rate, MPSP is calculated to be \$3.09/gal for biofuels, \$461.32/MT for biochemicals and \$1113.12/MT for hydrocarbon chemicals. This price is the average price for the products in each scenario. Similar to the previous TEA analysis, products yields, fixed capital costs and biomass cost have higher impacts on the MPSP. Figure 8 gives the detail compositions of the MPSP for three scenarios.



Figure 8. Annualized operating costs for three scenarios

MPSPs give us a criterion of the product prices, but in practice market prices are volatile throughout the project's 30-year life. The fluctuation of commodity products price will impact the NPV. Uncertainty analysis enables the evaluation of MIC and NPV changes due to product price changes. Monte-Carlo simulation is adapted in the uncertainty analysis. The changing variables in the Monte-Carlo analysis are the selling prices of main products. Figure 9 gives the price distribution of main products. Due to the scarcity of price information for chemicals, toluene and xylene prices are assumed to have the same distribution with benzene but different mean values. Other low yields hydrocarbon aromatics are sold at a mean price of benzene, and olefins are sold based on available price information from the literature in which toluene is \$1186/MT and xylene is \$1404/MT [32].

Commodity	Probability	Average	10th	90th
	Distribution		Percentile	Percentile
Gasoline Price (\$/gallon)		2.498	1.573	3.578
Diesel Price (\$/gallon)		2.638	1.558	3.919
Dextrose Price (\$/ton)		563.9	401.8	737.2
Asphalt Price (\$/ton)		950.2	415.9	1491.
Cement Price(\$/ton)		240.3	222.3	256.9
Benzene Price (\$/ton)		1356.	1222.	1495.

Figure 9. Products historical prices distribution

Three thousand facility maximum investment costs and net present values are generated from Monte-Carlo simulation. Through the analysis, the facility MICs for three scenarios are \$162.14±181.3 MM for biofuels scenario, \$524.69±308.7 MM for biochemicals scenario and \$282.84±14 MM for hydrocarbon chemicals scenario. The facility NPVs for three scenarios are found to be \$-243.42±268.9 MM for biofuels scenario, \$412.03±374.1 MM for biochemicals scenario and \$82.08±16.6 MM for hydrocarbon chemicals scenario. Figure 10 shows the probability density distribution of MICs and NPVs for the three scenarios.

For the mean value of the MIC analysis. The MICs are \$162 MM, \$525 MM and \$283 MM for biofuels scenario, biochemicals scenario and hydrocarbon chemicals scenario, respectively. Compared to calculated capital cost, the MIC of biofuels scenario is much lower than the required capital cost while the MICs of biochemicals scenario and hydrocarbon chemicals scenario are higher than the required capital costs. It means that fuels production has less potential to be profitable while biochemicals and hydrocarbon chemicals production have higher potential to be profitable and are more flexible.

For the cumulative probability distribution of the NPV analysis, around 18% of the biofuels scenario NPVs are profitable (NPV > 0). For the biochemicals and hydrocarbon chemicals scenarios, 100% of NPVs are expected to be profitable based on historical market prices. It means that there is a high risk to invest fuel plant while lower risk to invest in biochemicals and hydrocarbon chemicals production. However, there are other technical (feasibility) and market constraints (demand) that should be considered in a commercialization plan.



Figure 10. Probability density distribution of MICs and NPVs

Conclusion

This paper evaluates the economic feasibility of biomass fast pyrolysis and three product portfolios based on the fast pyrolysis and fractionation system developed by Iowa State University. The biochemicals scenario producing infrastructure materials and hydrocarbon chemicals scenario producing BTX and olefins are compared to a conventional fast pyrolysis biofuels production facility. Through the process model analysis, both scenario facilities have much lower capital costs and annual operating costs. In addition, the high product values from these two scenarios make the bio-refinery have a higher potential to be profitable. For the target of 10% IRR, MPSP gives a straightforward approach to examine the economic feasibility of this facility by comparing it to current market prices. We estimated MPSPs of \$3.09/gal for biofuels scenario, \$461.62/MT for biochemicals scenario, and \$1113.83/MT for hydrocarbon chemicals and mean MICs of \$162 MM for biofuels scenario, \$525 MM for biochemicals scenario and \$282 MM for hydrocarbon chemicals scenario. The high volatility of market prices increases the commercialization uncertainty of these portfolios. Monte-Carlo simulation is used to analyze the uncertainty of the facility. The net present value distributions are estimated as -\$243.42±268.9 MM for the biofuels scenario, \$412.03±374.1 MM for the biochemicals scenario and \$82.08±16.6 MM for the hydrocarbon chemicals scenario. The uncertainty analysis indicates that 18%, 100% and 100% of NPVs are expected to be profitable at a 10% IRR for the biofuels, biochemicals, and hydrocarbon chemicals scenarios. These results suggest that a fast pyrolysis bio-refineries could be more competitive if it integrates new products into their portfolios.

Acknowledgments

The authors would like to acknowledge the financial support from Bioeconomy Institute at Iowa State University.

Conflict of interest

All authors declare no conflicts of interest in this paper.

References

- [1] Wright MM, Satrio JA, Brown RC, Daugaard DE, Hsu DD. Techno-Economic Analysis of Biomass Fast Pyrolysis to Transportation Fuels. Fuel 2010;10:S2–10.
- [2] Zhang Y, Brown TR, Hu G, Brown RC. Techno-economic analysis of monosaccharide production via fast pyrolysis of lignocellulose. Bioresour Technol 2013;127:358–65.
- [3] Brown TR, Zhang Y, Hu G, Brown RC. Techno-economic Analysis of Biobased Chemicals Production via Integrated Catalytic Processing 2012;6:73–87.
- [4] Zhang Y, Brown TR, Hu G, Brown RC. Techno-economic analysis of two bio-oil upgrading pathways. Chem Eng J 2013;225:895–904.
- [5] Mohan D, Pittman CU, Steele PH. Pyrolysis of wood/biomass for bio-oil: A critical review. Energy and Fuels 2006;20:848–89.
- [6] Bridgwater A V. Review of fast pyrolysis of biomass and product upgrading. Biomass and Bioenergy 2012;38:68–94.
- [7] Zhang Q, Chang J, Wang T, Xu Y. Review of biomass pyrolysis oil properties and upgrading research. Energy Convers Manag 2007;48:87–92.
- [8] Brown TR, Thilakaratne R, Brown RC, Hu G. Techno-economic analysis of biomass to transportation fuels and electricity via fast pyrolysis and hydroprocessing. Fuel 2013;106:463–9.
- [9] Pollard AS, Rover MR, Brown RC. Characterization of bio-oil recovered as stage fractions with unique chemical and physical properties. J Anal Appl Pyrolysis 2012;93:129–38.
- [10] Santhanaraj D, Rover MR, Resasco DE, Brown RC, Crossley S. Gluconic Acid from Biomass Fast Pyrolysis Oils: Specialty Chemicals from the Thermochemical Conversion of Biomass. ChemSusChem 2014;7:3132–7.
- [11] Han J, Elgowainy A, Dunn JB, Wang MQ. Life cycle analysis of fuel production from fast pyrolysis of biomass. Bioresour Technol 2013.
- [12] Laird DA, Brown RC, Amonette JE, Lehmann J. Review of the pyrolysis platform for coproducing bio-oil and biochar. Biofuels, Bioprod Biorefining 2009;3:547–62.
- [13] Brown TR, Wright MM, Brown RC. Estimating profitability of two biochar production scenarios: Slow pyrolysis vs fast pyrolysis. Biofuels, Bioprod Biorefining 2011;5:54–68.

- [14] Zhang Y, Wright MM. Product Selection and Supply Chain Optimization for Fast Pyrolysis and Biorefinery System. Ind Eng Chem Res 2014;53:19987–99.
- [15] Gebreslassie BH, Slivinsky M, Wang B, You F. Life cycle optimization for sustainable design and operations of hydrocarbon biorefinery via fast pyrolysis, hydrotreating and hydrocracking. Comput Chem Eng 2013;50:71–91.
- [16] Ubando AT, Culaba AB, Aviso KB, Ng DKS, Tan RR. Fuzzy mixed-integer linear programming model for optimizing a multi-functional bioenergy system with biochar production for negative carbon emissions. Clean Technol Environ Policy 2014:1537–49.
- [17] Kelloway A, Daoutidis P. Process synthesis of biorefineries: Optimization of biomass conversion to fuels and chemicals. Ind Eng Chem Res 2014;53:5261–73.
- [18] Rover MR, Johnston PA, Whitmer LE, Smith RG, Brown RC. The effect of pyrolysis temperature on recovery of bio-oil as distinctive stage fractions. J Anal Appl Pyrolysis 2013;105:262–8.
- [19] Ellens CJ. Design, optimization and evaluation of a free-fall biomass fast pyrolysis reactor and its products. Iowa State University, 2009.
- [20] Kuzhiyil N, Dalluge D, Bai X, Kim KH, Brown RC. Pyrolytic sugars from cellulosic biomass. ChemSusChem 2012;5:2228–36.
- [21] Susanne J, Pimphan M, Snowden-Swan L, Padmaperuma A, Tan E, Dutta A, et al. Process Design and Economics for the Conversion of Lignocellulosic Biomass to Hydrocarbon Fuels - Fast Pyrolysis and Hydrotreating. Golden, CO.: 2013.
- [22] Rover MR, Johnston PA, Jin T, Smith RG, Brown RC, Jarboe L. Production of clean pyrolytic sugars for fermentation. ChemSusChem 2014;7:1662–8.
- [23] Choi YS, Johnston PA, Brown RC, Shanks BH, Lee K-H. Detailed characterization of red oak-derived pyrolysis oil: Integrated use of GC, HPLC, IC, GPC and Karl-Fischer. J Anal Appl Pyrolysis 2014;110:147–54.
- [24] Wyman C. Handbook on Bioethanol: Production and Utilization, 1st ed. Washington DC.: 1996.
- [25] Jackson EB. Sugar Confectionery Manufacture. 2nd ed. Chapman & Hall, New York: Springer; 1995.
- [26] Peralta J, Silva HMRD, Williams RC, Rover MR, Machado AVA. Development of an Innovative Bio-binder Using Asphalt-Rubber Technology. Int J Pavement Res Technol 2013;6:447–56.

- [27] Vispute TP, Zhang H, Sanna A, Xiao R, Huber GW. Renewable chemical commodity feedstocks from integrated catalytic processing of pyrolysis oils. Science 2010;330:1222– 7.
- [28] Peters M, Timmerhaus K, West R. Plant Design and Economics for Chemical Engineers. Fifth. McGraw Hill, New York: 2003.
- [29] EIA. Annual Energy Outlook 2011. Washington DC.: 2011.
- [30] Young's Sand & Gravel n.d. Available from: http://www.youngssandandgravel.com/pricelist.htm (accessed January 2, 2015).
- [31] Sulfuric Acid Market and Cost Information n.d. Available from: http://www.sulphuric-acid.com/sulphuric-acid-on-the-web/Market-Info.htm (accessed December 15, 2014).
- [32] Wang K, Ou L, Brown T, Brown RC. Beyond ethanol: a techno-economic analysis of an integrated corn biorefinery for the production of hydrocarbon fuels and chemicals. Biofuels, Bioprod Biorefining 2014.

CHAPTER 3. TECHNO-ECONOMIC ANALYSIS OF PRODUCTS SELECTION AND OPTIMIZATION FROM BIOMASS FAST PYROLYSIS AND BIO-OIL UPGRADING

A paper to be submitted to *Biomass and Bioenergy* Wenhao Hu, Qi Dang, Mark M. Wright, Robert C. Brown

Abstract

A novel integrated bio-refinery design producing multiple products via the fast pyrolysis platform is introduced in this work. Three different product portfolios targeting certain markets, namely biofuels, biochemicals (bio-asphalt, calcium acetate, dextrose) and hydrocarbon chemicals, are proposed and investigated. The Net Present Value (NPV) is employed as the indicator to evaluate the performance of the bio-refinery. The study employs historical price data to determine low, medium, and high prices for each product. By choosing three price levels for products of each portfolio, a total of twenty-seven scenarios are explored, and the NPV of each scenario is maximized based on the allocation ratios to the various product portfolios. The results indicate that under most price scenarios a hydrocarbon chemicals portfolio generates a relatively higher NPV compared to the alternatives and fuels portfolios whereas the fuel portfolio performs better when gasoline prices are \$1601/tonne (\$4.4/gallon) or greater.

Fixed capital costs of \$162 MM, \$216 MM and \$317 MM and annual operating costs of \$73 MM, \$89 MM and \$104 MM are estimated for a 2000 tonne/day bio-refinery producing biochemicals, hydrocarbon chemicals and biofuels, respectively. Relatively high capital and operating cost make biofuels production unfavorable when compared to the biochemicals and hydrocarbon chemicals production scenarios.

Introduction

Environmental quality, energy security and economic development are important factors related to energy utilization. Incentives for improving environmental quality, securing energy supply and promoting economic development have drawn interest towards finding renewable and clean substitutes for petroleum-derived products. Biomass are organic materials from recent biological origin that are a clean and renewable alternative to fossil resources. They can be converted into heat, stationary power, transportation fuels and commodity chemicals through chemical processing. The total sustainable availability of biomass in the U.S. is 1.1-1.6 billion tons per year, which is equivalent to 19.3-28.1 billion GJ energy [1]. If this resource is fully developed, it could replace over one third of the total petroleum consumption in the U.S. [1].

Thermochemical conversion is a proven pathway to producing biofuels, biochemical, and bioproducts from biomass [2]. Thermochemical conversion technologies include liquefaction, gasification and pyrolysis, which are frequently used for the thermal degradation of biomass [3]. Fast Pyrolysis is investigated in this paper as the pathway to convert biomass into hydrocarbon-based transportation fuels, biochemicals and hydrocarbon chemicals. Fast pyrolysis is a rapid thermal decomposition of organic compounds occurring in the absence of oxygen at moderate temperature of around 500 °C and short residence time, yielding a mix of liquids, gases and solids [4]. The yield of each compound varies with feedstock composition, pyrolysis temperature and residence time [4]. The liquid pyrolysis product is known as bio-oil, and it can represent up to 75 wt% of biomass [5,6]. Increasing the heating rate, reducing the residence time and rapid cooling of the pyrolysis vapors favor higher bio-oil yield [7]. Bio-oil is usually a dark brown liquid with distinctive smoky odor which consists of hundreds of different compounds derived from decomposition of cellulose, hemicellulose and lignin in the woody biomass [5,8]. Bio-oil

can be directly used in burner systems, diesel engines, turbines and Stirling engines, or it can be upgraded into a variety of hydrocarbon fuels and chemicals [5,9–11]. Fast pyrolysis was chosen for this study because of its ability to generate a portfolio of products at a lower cost than other thermochemical pathways [12]

There is a growing literature on pathways for upgrading bio-oil into valued-added products. Elliott et al. [10] proposed a catalytic hydroprocessing method followed with hydrocracking to upgrade bio-oil into alkenes and aromatics, which can serve as a petroleum refinery feedstock for transportation fuel applications. Peralta et al. [13] developed a bio-binder using s rubber-modified fractionated bio-oil for flexible pavements. Vispute et al. [11] found that bio-oil can be upgraded into industrial commodity chemical feedstock through catalytic hydroprocessing and fluid catalytic cracking (FCC). All of these products are targeting existing markets, but those upgrading systems have not been commercialized in large-scale. There are some papers that have examined the economic feasibility of commercialization of fast pyrolysis products. Zhang et al. [14] evaluated the production of monosaccharide along with hydrogen and transportation fuels via fast pyrolysis. Wright et al. [15] examined a fast pyrolysis facility that converts corn stover to naphtha and diesel range fuels and the fuel product values were estimated to be \$3.09 and \$2.11 per gallon of gasoline equivalent (GGE) for hydrogen production and purchase scenarios, respectively. Brown et al. [16] evaluated the economic feasibility of the five scenarios in Vispute's paper to produce biobased commodity chemicals using Integrated Catalytic Processing (ICP). Zhang et al. [17] compared two bio-oil upgrading pathways that produce transportation fuel along with hydrogen and commodity chemicals. Previous technoeconomic analysis (TEA) papers have focused on fast pyrolysis facilities designed for producing a single product such as transportation fuels or commodity chemicals. Hydrogen production was

often combined with transportation fuel production to provide hydrogen for bio-oil hydroprocessing. The economic performance of these technologies have often been quantified by calculating either the internal rate of return (IRR) or minimum product selling price (MPSP). However, industrial deployment of fast pyrolysis technologies has been limited and its commercialization potential is subject to high uncertainty [18,19].

Diverse product portfolios are one approach to reducing commercialization risk. Various authors have investigated the product selection and optimization of bio-refineries generating multiple products[20–23]. These studies combine feedstock selection, facility location, and product selection to maximize project profitability. This article focuses on the conceptual design of a single bio-refinery producing transportation fuel, hydrogen, biochemicals (bio-asphalt, calcium acetate, dextrose) and hydrocarbon chemicals (benzene, toluene, and xylene). The contribution of this study is in the techno-economic evaluation of the alternative products portfolio within the context of an integrated bio-refinery.

Methodology

This study employs material and energy balance data from an Aspen PlusTM chemical process to determine the process performance of converting biomass into fuels, biochemicals, and hydrocarbon chemicals. The analysis estimates capital and operating costs for a commercial-scale bio-refinery based on the process model results. The facility is modeled with a fixed input capacity for processing 2000 metric ton per day (MTPD) of biomass. Product yields vary based on the ratio of bio-oil upgraded through each portfolio. The yields of all products are substituted into the discounted cash flow rate of return (DCFROR) model to estimate capital costs based on scaling factors and the net present value (NPV) for a fixed IRR of 10%. The portfolio production

distributions are varied to optimize the NPV, and contour plots of the variables space are generated to validate the optimal portfolio allocations.

Process model description

The bio-refinery conceptual design is based on the fast pyrolysis and bio-oil fractionation system developed at Iowa State University. Figure 11 shows the generalized process diagram. There are six main processes: biomass pretreatment, fast pyrolysis, solids removal, bio-oil recovery, bio-oil upgrading, and co-generation. The process converts raw biomass into products from bio-oil upgrading and excess char. Non-condensable gases are consumed for heat within the process.



Figure 11. Generalized Schematic of bio-oil production and upgrading

The bio-refinery employs red oak as its process feedstock, and red oak ultimate and proximate analyses are shown in the Table 8. In the pretreatment section, biomass is first chopped to an approximately 10 mm diameter particle. For the production of dextrose, higher sugar content is preferred in the bio-oil. To increase the sugar yield, an acid treatment is adopted and sulfuric acid (0.4 wt% of dry biomass) is infused unto the biomass in a continuous spray rotary drum after chopping [14]. After acid treatment, the biomass moisture is reduced to below 7 wt% in a steam rotary dryer. After drying, the biomass particle is ground to about 3mm diameter. In the pyrolysis section, biomass is rapidly heated to 500 °C in a fluidized bed reactor

and decomposed to condensable vapors, non-condensable gases (NCG), aerosols and solids. Fast pyrolysis product distributions are modeled in the Aspen PlusTM software based on the experimental data by Pollard et al. [24].

Ultimate Analysis (dry basis)		Proximate Analysis (wet basis)		
Element	wt %	Element	wt %	
Carbon	48.7	Moisture	3.86	
Hydrogen	6.8	Volatiles	81.9	
Nitrogen	0.072	Fixed Carbon	12.56	
Oxygen	44.03	Ash	0.39	
Sulfur	0.002	Other	1.28	
Ash	0.39			

Table 8. Ultimate and proximate analysis of as received red oak[24]

Before the hot stream from reactor is condensed as bio-oil, it goes through a clean-up process in solids removal section where a high volume and efficiency cyclone removes the solids from the stream at 95% efficiency. The solids consist of char mixed with ashes and alkali metals. In the bio-oil recovery section, a five-stage fractionation system is employed to collect condensable vapors into five stage fractions (SF1-5) with distinct compositions.



Five-Stage Bio-oil Fractionation System

Figure 12. Diagram of five-stage bio-oil fractionation system

SF1, 3, and 5 are condensed using shell-and-tube heat exchanger condensers. SF 2 and 4 are collected by ESPs which consists of cylindrical steel pipes and a central cylindrical rod electrode. SF 1-2 are designed to recover levoglucosan and other high dew point compounds. SF 3-4 are designed to capture the compounds that have similar dew points to that of phenol. SF 5 is designed to gather light oxygenated compounds and water. SF 1-2 are designated as *heavy ends* which consist of sugars and phenolic oligomers. SF 3-4 are called *middle cut* and contain monomeric phenol and furans as well as part of the acids. The aqueous phase SF 5 is also named *light end* which contains water, acids, furans and some monomeric phenols.



Figure 13. Stage fractions 1-5 upgrading pathways, intermediate and final products, and portfolio categories

The distinctive compositions of each stage fraction makes them suitable for upgrading to different products. Figure 13 summarizes the stage fraction upgrading pathways considered in this study and final products. SF1&2 can be upgraded to gasoline and diesel blend-stock fuels via hydroprocessing or can be upgraded to dextrose through sugar extraction and hydrolysis. Sugar extraction yields phenolic oligomers, which can be upgraded into an asphalt binder through a rubber modifying process. The sugars can alternatively be hydroprocessed and treated in a fluid catalytic cracking (FCC) unit to produce aromatics and olefins. SF3 and 4 are the most versatile

fractions, and they can be upgraded through any of the aforementioned pathways except for sugar extraction. SF5 can be steam reformed to produce hydrogen based on its high moisture and acids content. Alternatively, SF5 can be employed as a substrate for producing cement. We group these products into three categories: biofuels, biochemicals and hydrocarbon chemicals. Biofuels portfolio includes hydrogen, gasoline, and diesel. Biochemicals portfolio includes asphalt binder, cement, and dextrose. Aromatics and olefins are included in hydrocarbon chemicals portfolio.

In the biofuels scenario, gasoline and diesel are the main products and hydrogen is produced for hydroprocessing. A two-stage hydroprocessing process is adopted to upgrade SF 1-4 into gasoline and diesel range hydrocarbon [26]. Distillation process is followed to separate gasoline and diesel range hydrocarbons, and hydrocracking is employed to convert distillation residues to lighter hydrocarbons. Hydroprocessing requires hydrogen at a ratio of 3-5 wt. % of the feed. Thus, SF 5 is steam reformed to produce hydrogen with additional natural gas input [15,27].

In the biochemicals scenario, dextrose, asphalt and cement are chosen as the product combination. The sugars and phenolic oligomers in SF 1-2 are recovered through a simple two-stage water washing process that separates water-soluble sugars from water-insoluble oligomers [28]. These sugars are mostly monosaccharides along with levoglucosan and some disaccharides, and they can be hydrolyzed to produce a glucose-rich syrup, which can be valued as dextrose [14]. The water-insoluble raffinate left from water washing has similar properties to petroleum-derived bitumen. The bio-asphalt produced from bio-oil can be used as modifier, extender or even replacement for petroleum asphalt [29]. Peralta has successfully developed a bio-binder using asphalt-rubber technology [13]. There is no available data to fully evaluate the economic

feasibility of this technology, so the water-insoluble raffinate along with SF 3-4 is valued as raw material for bio-asphalt at the market price for asphalt. The most distinct feature of SF 5 is high acetic acid content. Acetic acid can be converted into calcium acetate, which can be used to produce gelled fuel and bio-cement, by adding limestone [30]. In this paper, calcium acetate is sold as the final product considering that both acetic acid upgrading technologies have not been commercially developed.

For the hydrocarbon chemicals scenario, Vispute et al. [11] developed five upgrading pathways to produce commodity chemicals (aromatics and olefins) from whole bio-oil or aqueous phase bio-oil. In this paper, the two-stage hydroprocessing followed by FCC of aqueous phase bio-oil pathway is adopted to produce olefins and aromatics, such as benzene, toluene, and xylene (BTX). The aqueous phase bio-oil in this scenario is the combination of SF 3-4 and water-soluble fraction from SF 1 and 2. The same washing process is used to separate the water-soluble fraction and water-insoluble fraction of SF 1 and 2. The water-insoluble raffinate is also sold as bio-asphalt raw material. In this scenario, there is a high demand of hydrogen for hydroprocessing of aqueous phase. However, all stage fractions are upgraded, so the hydrogen is purchased from merchant sources for hydroprocessing. Table 9 shows the carbon yields and selectivity of final products of this upgrading pathway.

Catalysts	Carbon yields (%)			
	Aromatics		Olefins	
	Benzene	4.94	Ethylene	13.76
Ru/H ₂ +Pt/H ₂ +Zeolite	Toluene	9.02	Propylene	23.13
	Xylene	3.31	Butylene	6.11
	EthylBenzene	0.42		

Table 9. Process catalysts and carbon yields of aromatics and olefins[11]

Product portfolio selection and cost analysis

The concept of the bio-refinery in this paper is to simultaneously produce three categories of products and maximize the net present value. The high variability and correlations between the prices of transportation fuels, commodity chemicals and petroleum price results in a high price fluctuation for these products [17]. Thus, there is a wide range of a potential NPVs for this bio-refinery concept based on fluctuations of the market prices. To investigate the impact of these market prices, we evaluate up to 27 scenarios of combinations of portfolio prices.

First, each portfolio is analyzed separately to find the base case stream flows of intermediates, final product yields, annual operating costs and bare equipment costs. Then all three portfolios are integrated into a single bio-refinery concept design. In this design, the feedstock input rate is constant, and the ratio of bio-oil upgraded through each technology is varied. The size and output of the upgrading equipment for each platform is scaled linearly by their input flow rates. Equipment costs through a power law with the ratio of new stream flow to old stream flow and a scaling factor of 0.7 [31] The fixed capital costs are calculated using Peter and Timmerhaus factors [32]. Table 10 gives the breakdowns of installation cost factor based on the total purchased equipment cost (TPEC). This approach provides a baseline capital cost for an integrated bio-refinery designed for a particular product distribution. In practice, an integrated bio-refinery can incur additional capital costs due to larger equipment sizes, increased process complexity, and unit redundancy that are not considered in this estimate. Furthermore, installation costs are based on an nth plant design in which all major engineering breakthroughs and technical innovations have been demonstrated.

Parameter	Assumption		
Total purchased equipment cost (TPEC)	1*TPEC		
Purchased equipment installation	0.39*TPEC		
Instrumentation and controls	0.26*TPEC		
Piping	0.1*TPEC		
Electrical systems	0.31**TPEC		
Buildings (including services)	0.29*TPEC		
Yard improvements	0.12*TPEC		
Service facilities	0.55*TPEC		
Total installed cost (TIC)	3.02 *TPEC		
Engineering	0.32*TPEC		
Construction	0.34*TPEC		
Legal and contractors fees	0.23*TPEC		
Indirect cost (IC)	0.89 * TPEC		
Total direct and indirect costs (TDIC)	TIC + IC		
Contingency	0.2*TDIC		
Fixed capital investment (FCI)	TDIC + Contingency		
Working capital (WC)	0.15* FCI		
Land use	0.06* TPEC		
Total capital investment (with land)	FCI +WC + Land		

Table 10. Methodology for capital cost estimation for nth plant

In this study, the red oak purchase cost is set to \$80/MT. Water and electricity prices are based on the EIA 20-year forecast [33]. For the fuel scenario, natural gas is purchased for hydrogen generation through steam reforming and the price is set to \$0.26/kg [33]. The catalysts for hydroprocessing and steam reforming are set to \$18.25/lb and 3.6 cents/kscf H₂. In the biochemicals scenario, sulfuric acid is consumed for sugar hydrolysis and limestone is used to

convert acids into calcium acetate. Their prices are set to \$200/MT and \$17/MT for sulfuric acid and limestone, respectively[34,35]. For hydrocarbon chemicals production, hydrogen and catalyst account for most of the raw material cost. The hydrogen is assumed to be purchased from a near-site facility without storage and transportation cost, which results in a hydrogen price of \$1.5/kg. Ru, Pt and zeolite are chosen as the catalysts for chemicals production and prices are \$2.5/lb, \$25.3/lb and \$0.72/lb, respectively. The excess char is sold for \$20/MT based on its heating value as a coal substitute.

Parameters	Assumption
Equity	40%
Loan Interest	7.5%
Loan Term, years	10
Depreciation type	DDB
General Plant	7
Steam/Electricity System	20
Construction Period	2.5
% Spent in Year -3	8%
% Spent in Year -2	60%
% Spent in Year -1	32%
Start-up Time	0.5
Revenues (% of Normal)	50%
Variable Costs (% of Normal)	75%
Fixed Cost (% of Normal)	100%
IRR	10%
Income Tax Rate	39%

Table 11. Discounted Cash Flow Rate of Return analysis assumptions

The historical prices of gasoline, diesel, asphalt, cement, dextrose and BTX are collected to find the price distributions. Three prices, low, medium and high, for each product are chosen for the NPV analysis based on the historical data. A discounted cash flow rate of return model is developed using Mathematica to calculate the best product allocation ratio to maximize the NPV for different product price scenarios. Table 11 presents the main assumptions for the 30-year DCFROR analysis.

Results and Discussion

The fast pyrolysis and bio-oil recovery process are modeled in the Aspen PlusTM software. Based on the experimental data, the processes and yields are simulated and adjusted in the established model. The yield of bio-oil is 65.87 wt% of dry biomass and each stage fraction yield is illustrated in Table 12. SF 1&2 yields are maximized to get more sugars and phenolic oligomers which can be either upgraded to transportation fuels or sold as asphalt binder. SF 5 contains water and acids, which can be steam reformed for H₂ or processed into calcium acetate. There are two more important products, char and NCG. Char and NCG account for 13.04 wt% and 21.09 wt% of dry biomass, which are 261 metric tonne per day (MTPD) and 422 MTPD, respectively. All of the NCG and a portion of the char are burned in the combustor to provide process heat for the whole system. There are 126 MTPD of excess char that is sold for \$20/MT.

Stage fractions	wt %
SF1	20.81%
SF2	30.99%
SF3	6.59%
SF4	2.5%
SF5	39.11%

Table 12. Mass distribution of bio-oil stage fractions from Aspen Plus

According to the simulation, 266 MTPD gasoline and 245MTPD diesel can be produced with full production capacity. If the facility is dedicated to produce biochemicals, 223 MTPD glucose-rich syrup, which can be considered as dextrose, along with 426 MTPD asphalt binder modifier and 53 MTPD calcium acetate can be produced. For the hydrocarbon chemicals production, the yield of aromatics is 87.9 MTPD and the yield of olefins is 246.2 MTPD. Table 13 gives the detailed yields of aromatics and olefins.

Name	Output (MTPD)
Butylene	32.73
Ethylene	73.89
Propylene	124.24
Benzene	24.63
Toluene	45.47
Xylene	17.76
Ethylebenzene	2.14
Indene	0.45
Naphthalene	0.45
Styrene	12.26

 Table 13. Chemicals yields from the SF 3, 4, 5 and water-soluble fraction of SF 1&2

The total fixed investment cost is the sum of the installed equipment cost, indirect costs and project contingence. In this project, equipment costs are varied because of the ratio of different products. This facility is based on the fast pyrolysis system and five-stage bio-oil fractionation system developed by Iowa State University, and the capacity is fixed so that the equipment costs of the pretreatment, pyrolysis and recovery sections are fixed. The installed costs for those sections are \$92 MM. The upgrading section for the transportation fuel portfolio includes bio-oil hydroprocessing, refining and hydrogen generation, which account for about \$100 MM. The upgrading section for chemical production includes two-stage hydroprocessing followed by a FCC and the installed equipment cost is \$35 MM [17]. For the biochemicals portfolio, the condensed bio-oil fractions are collected and stored without additional processing. Storage costs are included in the balance of plant cost category. The remaining costs, which include cogeneration, cooling plant and balance of plant, are \$12 MM. When all products are integrated into a single facility, the corresponding upgrading capital costs for each scenario are scaled by a power law with a factor of 0.7.

In order to explore the performance of the facility under different market conditions, three price levels are generated according to the historical price distribution. The three price levels for each product are given in Table 14. As shown in Table 14, product prices range from \$228/MT for calcium acetate to \$1804/MT for xylene.

	Prices (\$/MT)	Low	Average	High
Diofriol	Gasoline	480	909	1601
Dioluei	Diesel	428	808	1575
	Dextrose	347	570	603
Biochemicals	Asphalt Binder Modifier	382	960	1852
	Calcium Acetate	228	241	262
	Benzene	1052	1355	1753
Hydrocarbon Chemicals	Toluene	860	1186	1556
	Xylene	1062	1404	1804

Table 14. Prices combination for all products

There are twenty-seven price combinations for different product groups. Under each price scenario, the yield ratio of each product group is varied to maximize the NPV of the bio-refinery. The products ratio and optimal NPV condition for each scenario is shown in Table 15.

G	Prices		Portfolio Distribution					
Scenario	Biofuel	Biochemicals	Chemicals	Biofuel	Biochemicals	Chemicals	ττι ν (φιτιτι)	
1	Low	Low	Low	0	0	1	314	
2	Low	Low	Average	0	0	1	365	
3	Low	Low	High	0	0	1	426	
4	Low	Average	Low	0	0	1	634	
5	Low	Average	Average	0	0	1	685	
6	Low	Average	High	0	0	1	745	
7	Low	High	Low	0	1	0	1194	
8	Low	High	Average	0	1	0	1194	
9	Low	High	High	0	0	1	1238	
10	Average	Low	Low	0	0	1	314	
11	Average	Low	Average	0	0	1	365	
12	Average	Low	High	0	0	1	426	
13	Average	Average	Low	0	0	1	634	
14	Average	Average	Average	0	0	1	685	
15	Average	Average	High	0	0	1	745	
16	Average	High	Low	0	1	0	1194	
17	Average	High	Average	0	1	0	1194	
18	Average	High	High	0	0	1	1238	
19	High	Low	Low	1	0	0	477	
20	High	Low	Average	1	0	0	477	
21	High	Low	High	1	0	0	477	
22	High	Average	Low	0	0	1	634	
23	High	Average	Average	0	0	1	685	
24	High	Average	High	0	0	1	745	
25	High	High	Low	0	1	0	1194	
26	High	High	Average	0	1	0	1194	
27	High	High	High	0	0	1	1238	

Table 15. Net present value and product distributions under different price combination scenarios

Under most scenarios, maximizing hydrocarbon chemicals production yields the highest NPV. There are two scenarios where the biochemicals portfolio is optimal: either the biochemicals have high prices, or the hydrocarbon chemicals have low or average prices. There are only three scenarios in which producing biofuels is the most profitable option. This occurs when biochemicals prices are low. Hydrocarbon chemicals generate a higher NPV than biofuels when biochemicals prices are medium or high because the water-insoluble fraction in the hydrocarbon chemical production scenario is marketed as asphalt binder modifier with a higher market value than boiler fuel.

A NPV triangle contour plot was generated for each scenario. Contour plots for scenarios 16 to 19 are shown in this paper to illustrate the analysis results. Three different optimal results are shown in those four plots. The black spot in the plots represents the product distribution ratio with the highest NPV.

The plots for scenarios 16 and 17 are similar. These scenarios have medium biofuels prices, high biochemicals prices, and low to medium hydrocarbon chemical prices. The black spots in the first two plots are located on the lower right corner which means producing more biochemicals products will generate higher NPVs. The contour lines indicate that hydrocarbon chemicals are the second best choice of products given these market conditions, and biofuels generate the lowest revenue.

In scenario 18, biofuels and biochemicals have medium and high prices respectively, and hydrocarbon chemicals have a historically high price. In this case, hydrocarbon chemicals are the preferred product followed by biochemicals.

In scenario 19, fuels have a high price and the other products have low prices. Fuels are the desirable product in this case. However, the NPV for fuel production in this scenario is lower than the NPV of scenarios 16-18.



Figure 14. Selected net present value triangle contour plots

The fixed capital investments (FCI) and annual operating costs for these four scenarios are summarized in Table 16. The scenarios which have same optimal product selection result will have same FCI and annual operating cost. The difference of FCI are mainly because of biooil upgrading section. It has been discussed above. Feedstock cost and utilities (water and electricity) are the main cost for the bio-refinery, and they are \$52.6 MM and \$16.3MM respectively. There is no high cost for upgrading in biochemicals production. Only sulfuric acid and limestone cost \$1.5 MM per year. For scenario 18, the extra operating costs lie in hydrogen cost and hydrotreating and hydrocracking catalysts costs, which are about \$10 MM and \$7MM. The high operating cost of scenario 19 is the result of high cost of natural gas and catalysts. Natural gas cost about \$20 MM per year and catalysts for hydrotreating, hydrocracking and steam reforming cost \$13 MM per year. The high capital cost and annual operating cost make biofuels production unfavorable compared to biochemicals and hydrocarbon chemicals production.

Scenario	Fixed Capital Cost (\$ MM)	Annual operating cost (\$ MM)
16 & 17 (Alternative)	162	73
18 (Chemical)	216	89
19 (Fuel)	317	104

Table 16. Fixed capital cost and annual operating cost for selected scenarios

Conclusion

Based on the fast pyrolysis and fractionation bio-oil recovery system, multiple bio-oil upgrading pathways are considered in this paper. Three product portfolios designed for various markets are proposed and an integrated bio-refinery concept, which includes all three groups of products, is introduced. The performance of the bio-refinery is evaluated based on the NPV, and the optimal performance is found from varying the ratio of different product groups. Three price levels for each product group are chosen to evaluate the performance of the bio-refinery under different market conditions. Twenty-seven scenarios in total are explored and optimal NPVs are found along with the product distributions. Hydrocarbon chemicals portfolio generates relatively

higher NPV when compared to biochemicals and biofuels scenarios. The biofuels portfolio also is attractive at high fuel prices, but its NPV is lower than producing hydrocarbon chemicals. The fixed capital cost for biochemicals scenario, hydrocarbon chemicals scenario and biofuels scenario are \$162 MM, \$216 MM and \$317 MM, respectively. The annual operating costs for three scenarios are \$73 MM, \$89 MM and \$104 MM.

These results suggest that integrating the production of hydrocarbon chemicals and biochemicals such as bio-asphalt, dextrose, and bio-cement can lead to increased bio-refinery NPV. However, further research must be done to understand the additional costs of constructing and operating an integrated bio-refinery. Furthermore, both basic research and engineering development are needed to develop these novel hydrocarbon chemicals and biochemicals upgrading pathways.

Acknowledgments

The authors would like to acknowledge the financial support from Bioeconomy Institute at Iowa State University.

Conflict of interest

All authors declare no conflicts of interest in this paper.

References

- [1] Energy USD of. US Billion Ton Update: Biomass supply for a bioenergy and bioproducts industry. vol. 7. 2011.
- [2] Regalbuto JR. The sea change in US biofuels' funding: from cellulosic ethanol to green gasoline. Biofuels, Bioprod Biorefining 2011;5:495–504.

- [3] Wright MM, Brown RC. Comparative economics of biorefineries based on the biochemical and thermochemical platforms. Biofuels, Bioprod Biorefining 2007.
- [4] Bridgwater A V. Review of fast pyrolysis of biomass and product upgrading. Biomass and Bioenergy 2012;38:68–94.
- [5] Czernik S, Bridgwater A V. Overview of applications of biomass fast pyrolysis oil. Energy & Fuels 2004.
- [6] Bridgwater A V, Meier D, Radlein D. An overview of fast pyrolysis of biomass n.d.
- [7] Mohan D, Pittman CU, Steele PH. Pyrolysis of wood/biomass for bio-oil: A critical review. Energy and Fuels 2006;20:848–89.
- [8] Chaala A, Ba T, Garcia-Perez M, Roy C. Colloidal properties of bio-oils obtained by vacuum pyrolysis of softwood bark: Aging and thermal stability. Energy and Fuels 2004;18:1535–42.
- [9] Takanabe K, Aika KI, Seshan K, Lefferts L. Sustainable hydrogen from bio-oil Steam reforming of acetic acid as a model oxygenate. J Catal 2004;227:101–8.
- [10] Elliott DC, Hart TR, Neuenschwander GG, Rotness LJ, Zacher AH. Catalytic hydroprocessing of biomass fast pyrolysis bio-oil to produce hydrocarbon products. Environ Prog Sustain Energy 2009.
- [11] Vispute TP, Zhang H, Sanna A, Xiao R, Huber GW. Renewable chemical commodity feedstocks from integrated catalytic processing of pyrolysis oils. Science 2010;330:1222– 7.
- [12] Anex RP, Aden A, Kazi FK, Fortman J, Swanson RM, Wright MM, et al. Technoeconomic comparison of biomass-to-transportation fuels via pyrolysis, gasification, and biochemical pathways. Fuel 2010.
- [13] Peralta J, Silva HMRD, Williams RC, Rover MR, Machado AVA. Development of an Innovative Bio-binder Using Asphalt-Rubber Technology. Int J Pavement Res Technol 2013;6:447–56.
- [14] Zhang Y, Brown TR, Hu G, Brown RC. Techno-economic analysis of monosaccharide production via fast pyrolysis of lignocellulose. Bioresour Technol 2013;127:358–65.
- [15] Wright MM, Satrio JA, Brown RC, Daugaard DE, Hsu DD. Techno-Economic Analysis of Biomass Fast Pyrolysis to Transportation Fuels. Fuel 2010;10:S2–10.
- [16] Brown TR, Zhang Y, Hu G, Brown RC. Techno-economic analysis of biobased chemicals production via integrated catalytic processing. Biofuels, Bioprod Biorefining 2011.

- [17] Zhang Y, Brown TR, Hu G, Brown RC. Techno-economic analysis of two bio-oil upgrading pathways. Chem Eng J 2013;225:895–904.
- [18] Brown TR, Wright MM. Techno-economic impacts of shale gas on cellulosic biofuel pathways. Fuel 2014.
- [19] Liu G, Wright MM, Zhao Q, Brown RC. Catalytic fast pyrolysis of duckweed: Effects of pyrolysis parameters and optimization of aromatic production. J Anal Appl Pyrolysis 2015;112:29–36.
- [20] Zhang Y, Wright MM. Product Selection and Supply Chain Optimization for Fast Pyrolysis and Biorefinery System. Ind Eng Chem Res 2014;53:19987–99.
- [21] Gebreslassie BH, Yao Y, You F. Multiobjective optimization of hydrocarbon biorefinery supply chain designs under uncertainty. Proc IEEE Conf Decis Control 2012:5560–5.
- [22] Li Y, Brown T, Hu G. Optimization Model for a Thermochemical Biofuels Supply Network Design. J Energy Eng 2014:04014004. Available from:http://ascelibrary.org/doi/abs/10.1061/(ASCE)EY.1943-7897.0000158.
- [23] Gebreslassie BH, Slivinsky M, Wang B, You F. Life cycle optimization for sustainable design and operations of hydrocarbon biorefinery via fast pyrolysis, hydrotreating and hydrocracking. Comput Chem Eng 2013;50:71–91.
- [24] Pollard AS, Rover MR, Brown RC. Characterization of bio-oil recovered as stage fractions with unique chemical and physical properties. J Anal Appl Pyrolysis 2012;93:129–38.
- [25] Ellens CJ. Design, optimization and evaluation of a free-fall biomass fast pyrolysis reactor and its products. Iowa State University, 2009.
- [26] Susanne J, Pimphan M, Snowden-Swan L, Padmaperuma A, Tan E, Dutta A, et al. Process Design and Economics for the Conversion of Lignocellulosic Biomass to Hydrocarbon Fuels - Fast Pyrolysis and Hydrotreating. Golden, CO.: 2013.
- [27] Jones S, Holladay J, Valkenburg C, Stevens D, Walton C, Kinchin C, et al. Production of Gasoline and Diesel from Biomass via Fast Pyrolysis, Hydrotreating and Hydrocracking: A Design Case. Richland, WA: 2009.
- [28] Rover MR, Johnston PA, Jin T, Smith RG, Brown RC, Jarboe L. Production of clean pyrolytic sugars for fermentation. ChemSusChem 2014;7:1662–8.
- [29] Peralta J, Williams RC, Rover M, Silva HMRD. Development of Rubber-Modified Fractionated Bio-Oil for Use as Noncrude Petroleum Binder in Flexible Pavements. Transp Res Board 2012. Available from:http://hdl.handle.net/1822/22357.

- [30] Ivanov V, Chu J. Applications of microorganisms to geotechnical engineering for bioclogging and biocementation of soil in situ. Rev Environ Sci Biotechnol 2008.
- [31] Wright M, Brown RC. Establishing the optimal sizes of different kinds of biorefineries. Biofuels, Bioprod Biorefining 2007;1:191–200.
- [32] Peters M, Timmerhaus K, West R. Plant Design and Economics for Chemical Engineers. Fifth. McGraw Hill, New York: 2003.
- [33] EIA. Annual Energy Outlook 2011. Washington DC.: 2011.
- [34] Sulfuric Acid Market and Cost Information n.d. Available from: http://www.sulphuricacid.com/sulphuric-acid-on-the-web/Market-Info.htm (accessed December 15, 2014).
- [35] Young's Sand & Gravel n.d. Available from: http://www.youngssandandgravel.com/pricelist.htm (accessed January 2, 2015).

CHAPTER 4. GENERAL CONCLUSIONS

Conclusions

Under the policy stimulus of Renewable Fuel Standard (RFS) and Revised Renewable Fuel Standard (RFS2), cellulosic biofuels, as the most promising substitute of fossil-based transportation fuels, have received high industrial attention and research investment. Fast pyrolysis is a widely studied technology that produces bio-oil which is highly versatile because it can be upgraded to such products as transportation fuels. Due to recent low petroleum prices, the adoption and commercialization of biomass-derived fuels has been limited. Producing alternative products or adding valuable by-products can provide bio-refineries with economic benefits and make them more competitive. This study evaluated the economic feasibility of different product portfolios from biomass fast pyrolysis.

Bio-asphalt, bio-cement and dextrose were chosen as the products for biochemicals scenario and BTX and olefins are produced in hydrocarbon chemicals scenario. Those two scenarios were compared to the traditional biofuels production via techno-economic analysis. As shown in this study, the bio-refineries which produce biochemicals and hydrocarbon chemicals required lower capital cost and operating cost. With the target of 10% IRR, the MPSPs were estimated to be 3.09/gal for biofuels, \$461.62/MT for biochemicals, and \$1113.83/MT for hydrocarbon chemicals. The uncertainty analysis showed that the biochemicals scenario and the hydrocarbon chemicals scenario have high probability of being profitable and the biofuels scenario has much lower chance of being profitable. MIC analysis indicated that the biochemicals scenario had higher investment allowance while biofuels scenario had much lower limit than the required investment.

To give the bio-refinery more flexibility when the market changes, multiple products combinations are integrated into the bio-refinery in chapter 3. Three price levels are generated based on the historical prices and used to evaluate the performance and optimize the product selection. Hydrocarbon chemicals are most frequently chosen as the best product selection because of its high value and valuable by-products. Transportation fuels can also be the optimal product when petroleum prices are high.

Future Work

The process simulation is essential for techno-economic analysis. The production of biochemicals and hydrocarbon chemicals through fast pyrolysis is still under development, and more details of how upgrading processes can be integrated to optimize the production line of market ready products is required. With biofuels, the upgrading process technology needs to be improved to increase the yield of transportation fuels and reduce the capital costs. There are uncertainties in biomass supply, operating costs and product yields that can be incorporated into techno-economic analysis. Char is an important by-product of fast pyrolysis, and it can be further used to increase economic profitability and improve environmental impacts. The environmental impact is one of the primary considerations choosing between biorenewable products and fossil products. For the production of biofuels and hydrocarbon chemicals, policy constraints can be incorporated into the economic analysis. These extensions will contribute a more comprehensive insight to the future of biorenewable products.