Dissertations, Master's Theses and Master's Reports

2018

EFFECTS OF CO-PRODUCT USES ON ENVIRONMENTAL AND ECONOMIC SUSTAINABILITY OF HYDROCARBON BIOFUEL FROM ONE- AND TWO-STEP PYROLYSIS OF POPLAR

Daniel G. Kulas
Michigan Technological University, dgkulas@mtu.edu

EFFECTS OF CO-PRODUCT USES ON ENVIRONMENTAL AND ECONOMIC
SUSTAINABILITY OF HYDROCARBON BIOFUEL FROM ONE- AND TWO-STEP
PYROLYSIS OF POPLAR

By

Daniel G. Kulas

A THESIS

Submitted in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

In Chemical Engineering

MICHIGAN TECHNOLOGICAL UNIVERSITY

2018

This thesis has been approved in partial fulfillment of the requirements for the Degree of MASTER OF SCIENCE in Chemical Engineering.

Department of Chemical Engineering

Thesis Advisor: *Dr. David Shonnard*

Committee Member: *Dr. Wen Zhou*

Committee Member: *Dr. Tim Eisele*

Department Chair: *Dr. Pradeep K. Agrawal*

Table of Contents

List of figures

List of tables

Preface

This master's thesis contains material previously reviewed and published in scientific journals. Full citation of these are as follows:

Chapter 1-6:

Author Contributions

Kulas	Collection of data, analysis and interpretation of data, writing of the paper, responsible for submission and review of journal article
Winjobi	Analysis and interpretation of data, paper review, and editing
Zhou	Analysis and interpretation of data, paper review, and editing
Shonnard	Conceiving of research topic, analysis and interpretation of data, paper review, and editing

Acknowledgements

List of abbreviations

AC – Activated Carbon

CCOP - Cash Cost of Production

DEPR - Depreciation

DF - Discount Factor

EXP - Expense

FCI - Fixed Capital Investment

FCOP - Fixed Cost of Production

GHG emissions – Greenhouse Gas emissions

HI – Heat Integration

ICF - Inflated Cash Flow

INV - capital investment

LCA – Life Cycle Analysis

MSP – Minimum Selling Price

NPV- Net Present Value

SA – Soil Amendment

Sc 1 – Scenario 1

Sc 2 – Scenario 2

TEA – Techno-economic Analysis

VCOP - Variable Cost of Production

WC - Working Capital

Abstract

This study investigated the environmental and economic sustainability of liquid hydrocarbon biofuel production via fast pyrolysis of poplar biomass through two pathways: a one-step pathway that converted poplar via fast pyrolysis only, and a two-step pathway that includes a torrefaction step prior to fast pyrolysis. Optimization of these fast pyrolysis-based biofuel processes were investigated through heat integration and alternative uses of the co-product biochar, which can be sold as an energy source to displace coal, soil amendment or processed into activated carbon. The impacts of optimization on the cost of hydrocarbon biofuel production as well as the environmental impacts were investigated through a techno-economic analysis (TEA) and life cycle assessment (LCA), respectively, with two-step and one-step processing compared to fossil fuels. The TEA indicates that a one-step heat integrated pathway with the production of activated carbon has a minimum selling price of $3.23/gallon compared to $5.16/gallon for a two-step heat integrated process with burning of the co-product biochar to displace coal. The LCA indicates that using the displacement analysis approach, a two-step heat integrated pathway had a global warming potential of -102 g CO_2 equivalent/MJ biofuel compared to 16 CO_2 equivalent/MJ biofuel for the heat integrated one-step pathway.

1 Introduction

Biomass is believed to be the most abundant, renewable energy feedstock and is currently under-utilized[1]. It has received research as a sustainable feedstock that can reduce the energy sector's dependence on fossil fuels, especially for the transportation sector. One advantage biomass has as a renewable energy feedstock is that it, unlike solar and wind power, can be directly converted into liquid fuels to meet transportation fuel needs. According to the 2016 Billion Ton Report, a study sponsored by the US Department of Energy, the United States has enough biomass resources to potentially produce one billion dry tons of biomass per year without negatively affecting agricultural products such as food[2]. This would produce enough bioproducts such as biofuel to displace about 30% of US petroleum consumption.

Traditionally biomass has been converted to biofuels via two processing routes, biochemical and thermochemical[3]. Biochemical conversion of biomass uses biological catalysts, such as enzymes, with microorganisms to break down biomass into oxygenated biofuels. Thermochemical conversion uses chemical catalysts and heat to break down the biomass into biofuels. The most common processing routes for thermochemical conversion is fast pyrolysis and gasification. This work focused on thermochemical conversion via fast pyrolysis of woody biomass feedstocks.

The U.S. Department of Energy's Bioenergy Technologies Office (BETO) has set the goal of reaching a minimum selling price (MSP) of $3/gallon gasoline equivalent for biomass-derived hydrocarbon fuels[4]. Current research indicates that a focus on conversion pathways that exclusively produce biofuels will not be able to achieve a MSP of $3/gallon[4,5]. One way to make biofuels cost-competitive is to capitalize on the revenue from co-products. In 2015, BETO held a workshop to discuss the use of bioproducts to enable a more sustainable production of biofuels. The conclusion was that a focus should be put on the development of bioproducts that are an environmentally favorable direct replacement for a petroleum product, act as a building block for other products and fuels, and capitalize on the inherent structure of biomass[4].

One potential co-product that, if developed, may enable biofuels to be cost-competitive is biochar. The use of biochar produced from the pyrolysis of biomass and its valorization has been identified as a promising approach to increase revenue and decrease the MSP of biofuel. Recent research has analyzed different applications for biochar[6-10]. The simplest application is to burn biochar for an energy source to displace coal for climate change mitigation benefits[8]. However this is a relatively low value use of biochar. Two higher value uses of biochar are as soil amendments and for production of activated carbon. Both of these high value uses are due to the high porosity of biochar. As a soil amendment the pores retain nutrients and water which plant roots can access when the biochar is added to soil. This increases the efficiency of applied fertilizers and has been shown to increase crop yield[9]. Research done by Roberts et al found that biochar may deliver climate change mitigation benefits and increase crop yield[9].

With activated carbon the pores adsorb pollutants in either water or air waste streams. A study by researchers at Iowa State University found that converting biochar into activated carbon using steam is profitable[10]. Arena et al. found that processing activated carbon from coconut shell instead of coal can greatly reduce the environmental burdens of activated carbon processing[11].

While environmental and economic analyses have been done on the different applications of biochar, most of the related studies in the literature have considered biochar as its own entity. Little work has been done on biochar as part of a fast pyrolysis biorefinery with the goal of reducing the MSP of biofuels. This study performed preliminary environmental and economic analysis on the various applications of biochar from poplar as a byproduct of hydrocarbon biofuel production. The applications to be studied are: 1. being burned to displace coal, 2. used as a soil amendment on fields, and 3. processed into activated carbon in the context of one-step and two-step pyrolysis pathways with and without heat integration. The goal of the study is to better understand possible trade-offs among economic and environmental indicators of sustainability for the various biochar applications from a biofuels pathway. This study also investigates the effects of process data uncertainty in the techno-economic assessment (TEA) and life cycle analysis (LCA) results.

2 Process Simulation and Optimization

2.1 Research Objectives

Development of a biorefinery simulation was necessary to assess to sustainability of new process routes. The mass and energy balances obtained from the design model serve as the inputs for the TEA and LCA presented later in this thesis.

2.2 Process Description with Co-product Options

This work focused on thermochemical conversion via fast pyrolysis of woody biomass feedstocks. Pyrolysis is a thermal depolymerization and molecular fragmentation process carried out in the absence of oxygen and at moderate temperatures (470-700 ºC)[3]. The pyrolysis reaction produces three primary co-products: non-condensable gases (CO_2, CO, H_2O, H_2), bio-oil, and char. The co-product proportions depend on the reaction's conditions and severity. The bio-oil from the pyrolysis unit is converted to biofuel through hydrotreating and hydrocracking catalytic reactions (hydrotreatment). The catalytic biofuel is suitable to a drop-in replacement for transportation fuels such as gasoline, diesel, and aviation fuel[3]. The gaseous products can be converted to hydrogen and CO_2 via a steam reformer and water gas shift reactor (hydrogen production). Pyrolysis reactions are generally carried out via two different operation conditions, slow and fast pyrolysis. Slow pyrolysis features biomass residence times between 5 and 30 minutes, a slow heating rate, and at 600 ºC. Fast pyrolysis has a much shorter residence time, 0.5 to 5 seconds, with higher heating rates and produces a higher yield of bio-oil than slow pyrolysis[3]. Due to the high heating rates, one requirement of fast pyrolysis is that the feedstock by finely ground (~2 mm) and have a low moisture content of about 5%. The grinding of the biomass feed stock (size reduction) is very energy intensive. A pre-treatment stage, torrefaction, can be used to increase the brittleness of the poplar chips and decrease the amount of electricity used in size reduction[12]. Torrefaction is a mild pyrolysis that has a residence time between 20-40 minutes at much lower temperatures than pyrolysis. Table 2.1 compares the operating conditions of torrefaction, slow, and fast pyrolysis.

Table 2.1. Comparison of torrefaction and fast pyrolysis,

	Torrefaction	Slow Pyrolysis	Fast Pyrolysis
Temperature	280 ºC	600 ºC	500 ºC
Residence Time	20-40 minutes	5-30 minutes	0.5-5 seconds

A schematic diagram of the biomass conversion at the biorefinery is shown in Figure 2.1. The biorefinery was modeled using the process simulation software Aspen Plus®. For this study a basis of 1000 dry metric tons per day of feed entering the pyrolysis reactor was modeled for both one-step and two-step pathways. This flowsheet was originally created by previous work done by Winjobi for the fast pyrolysis of pine [5].

Figure 2.1. Schematic diagram of the biofuel production pathways studied. The pathways for 1 step, 2 step, scenario 1, scenario 2, and the three uses from the co-product biochar are shown.

For this study, 1 step is defined as fast pyrolysis without torrefaction and 2 step is with torrefaction. For 2-step processing Scenario 1 (sc 1) maximizes biofuel yield by using the torrefaction bio-oil for biofuel production while Scenario 2 (sc 2) maximizes biofuel quality and burns the torrefaction bio-oil for process heat. Table 2.22 summarizes the design objectives for the two scenarios.

Table 2.2. Design objectives for the two scenarios analyzed in this study for the two step pathway.

Scenarios	Design Objective 1	Design Objective 2	Description
Scenario 1 (sc 1)	Fossil energy inputs	Maximizing bio-oil yield	Blend pyrolysis oil with torrefaction condensed liquid
Scenario 2 (sc 2)	Renewable energy inputs	Maximizing bio-oil quality	Use torrefaction condensed liquid for process heat

2.2.1 Biomass Supply Logistics

Full discussion of the biomass supply logistics can be found in detail in previous work by Winjobi[13]. The poplar is collected as forest logging residue. The wood residue is chipped on-site in the forest using a stationary reciprocating diesel-powered chipper machine. The residue chips are transported to the plant via two transport processes, a 90-mile truck transport and a 490-mile rail transport. These distances are considered representative of a logging residue collection scenario using multi-modal transport. Emission factors for biomass logistics were based on values from the Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (GREET) model[14].

2.2.2 Biomass Conversion

The poplar biomass at the proposed biorefinery goes through 4 stages to produce biofuel: drying, torrefaction, size reduction, pyrolysis, and hydrotreatment. The use of an additional pretreatment stage, torrefaction, was analyzed for its effect on the production of biofuel. The hydrogen production stage is necessary to produce the hydrogen necessary for hydrotreatment using off-gas from hydrotreatment and activated carbon processing.

2.2.2.1 Drying

The received poplar chips have an assumed moisture content of about 25% which is reduced to about 8% using an indirect contact rotary steam dryer at 110 °C, shown in Figure 2.2. The reduction in moisture content is for smoother operations of the hammer mill, shown in Figure 2.4, and optimal fast pyrolysis, shown in Figure 2.5. The dried poplar chips go to torrefaction while the exhaust is vented to the atmosphere.
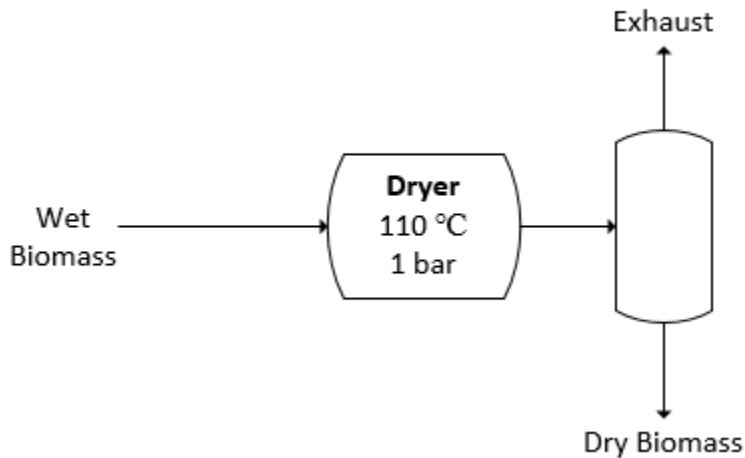
Figure 2.2. Process flow diagram for the drying stage

2.2.2.2 Torrefaction
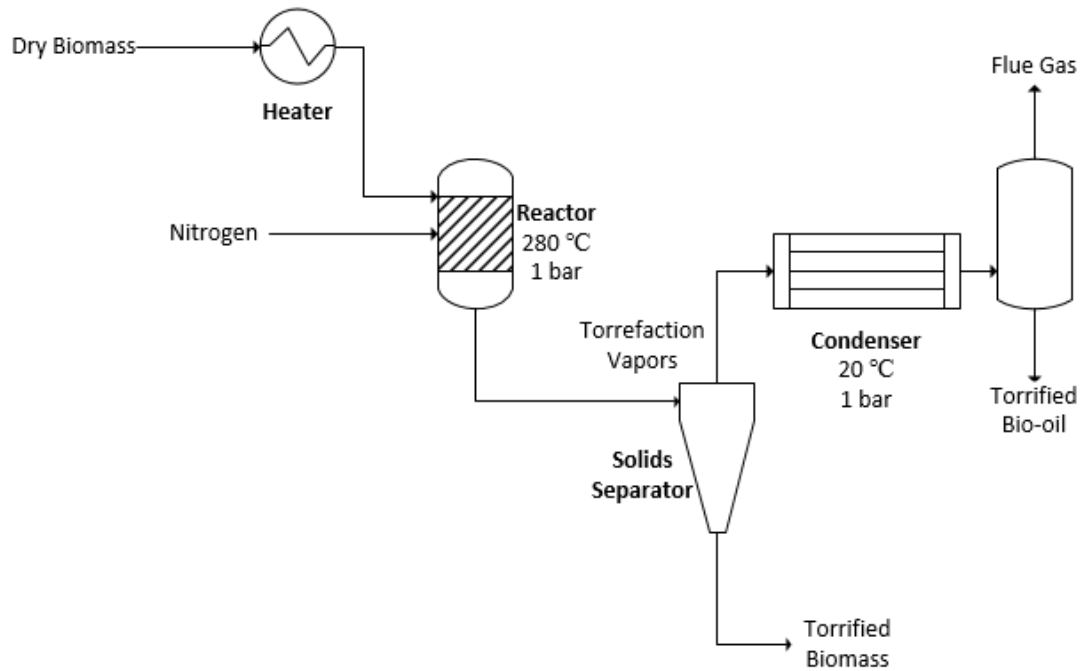
Figure 2.3. Process flow diagram for the torrefaction stage

For the two-step pathway, the poplar chips go through a pretreatment process, called torrefaction, after drying. Torrefaction is an optional stage that was analyzed to determine its effect on the production of biofuel. Torrefaction is a mild pyrolysis which can increase pyrolysis bio-oil quality and decrease the amount of electricity used in size reduction[12,15-17]. The significant reduction in electricity needed for size reduction is caused by torrefaction increasing the brittleness of the poplar chips[12]. Nitrogen is the fluidizing reactant for the fluidized-bed reactor. The torrefaction step was modeled in Aspen Plus using a yield reactor based on literature data for stream compositions[18,19]. Yields of non-condensable gases, condensed liquid (bio-oil) and torrefied solid at different torrefaction temperatures and the yield distribution of the oil and gas for torrefaction are shown as Tables 2.2 and 2.3. After torrefaction the biomass is separated from the volatiles. The volatiles are condensed, which produces the flue gas (non-condensable) and torrefied bio-oil. The torrefaction bio-oil can be added to the pyrolysis bio-oil before upgraded or it can be burned for process heat. The non-condensable flue gas is burned for process heat. Torrefaction is not present in the one-step flowsheet.

6

2.2.2.3 Size Reduction

The torrified or dried biomass, depending on the whether it is a one-step or two-step process, goes through a size reduction step via a hammer mill. The hammer mill decreases the size of the poplar chips from about 25 mm to 2 mm, which has been established by researchers as an optimal size for efficient heat transfer during fast pyrolysis[20,21].
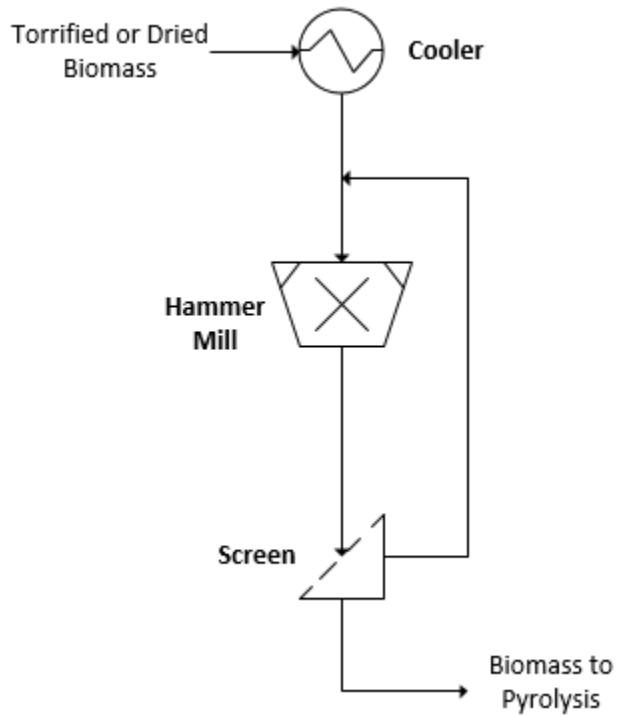
Figure 2.4. Process flow diagram for the size reduction stage

2.2.2.4 Pyrolysis
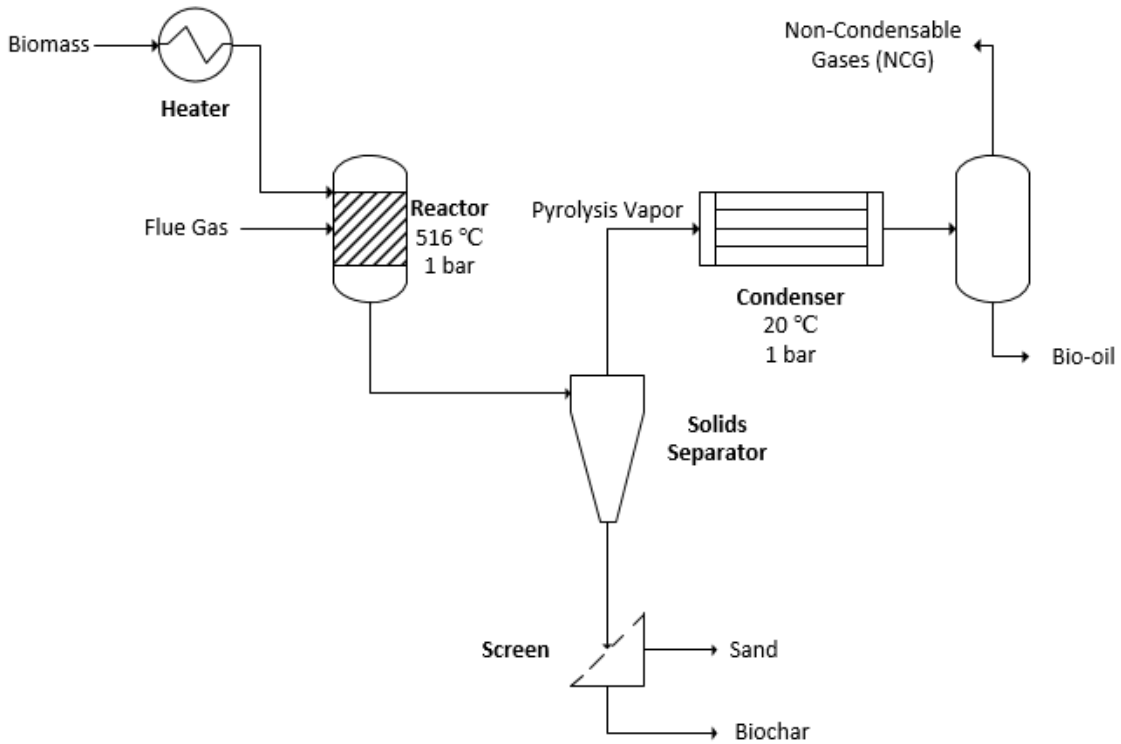
Figure 2.5. Process flow diagram for the pyrolysis stage

Fast pyrolysis of poplar/torrified solid is conducted at 516° C for a residence time of 1 second in a sand fluidized bed reactor in the absence of ozygen. Nitrogen serves as the fluidizing agent at start-up but is converted to recycled non-condensable gases (CO, CO_2) at steady state. Three products are produced from pyrolysis; bio-oil, non-condensable gases (NCG), and biochar[22]. The fast pyrolysis was modeled using a yield reactor in Aspen Plus based on literature data[23]. Table 2.3 gives the yield data for one-step fast pyrolysis, torrefaction, and two-step fast pyrolysis[23]. The presence of a torrefaction pre-treatment step before fast pyrolysis increases the yield of solid product from pyrolysis while decreasing the yield of the condensed liquid. The mass yield of gases, bio-oil and char from the torrefaction and pyrolysis of poplar were obtained from the works of Fivga[23].

Table 2.3. Torrefaction and Pyrolysis yield data for poplar (kg/kg intake poplar $\times$ 100 %)

Scenario	1 Step Pyrolysis	Torrefaction	2 Step Pyrolysis
Material	**Wt %**		
Gas	10	5	11
Condensed Liquid	78	19	65
Solid	12	76	24

Table 2.4 gives the wt% component distribution of the organics in the bio-oil from torrefaction and fast pyrolysis[19]. The main organics present in the bio-oil are levoglucosan, guaiacol, syringol, and glycol-aldehyde. The presence of a torrefaction pre-treatment step increases the guaiacol yield from fast pyrolysis. The upgrading of pyrolysis bio-oil to hydrocarbon transportation fuel was achieved by the hydrodeoxygenation of the model compounds contained in the bio-oil as outlined in previous studies[5,13,24]. Reaction pathways for the different model compounds were obtained from the literature[25-29].

Table 2.4. Bio-oil component distribution from torrefaction and pyrolysis of poplar
(kg/kg organics x 100%)

Component (wt %)	1 step Pyrolysis	Torrefaction	2 step Pyrolysis
Acetic Acid	15.11	7.53	11.54
Furfural	7.51	7.05	4.75
Furfural-Alcohol	8.17	9.85	5.02
Levoglucosan	24.00	28.95	5.00
Vanillin	4.47	5.39	11.56
Phenol	9.37	5.67	9.12
Guaiacol	4.71	5.68	26.07
Acetaldehyde	0.83	0.15	0.22
Syringol	9.25	11.16	6.73
Methylcyclopentene	3.02	3.65	3.14
Glycol-Aldehyde	12.36	14.91	16.84
Methanol	1.19	0.00	0.00

The pyrolysis NCG is recirculated to the pyrolyzer as the fluidizing agent. The co-product char produced from the pyrolysis step is carbon rich with a higher-energy content than raw biomass[30]. It can be exported to co-fire in coal power plants to improve environmental impacts for coal power plants[8,31]. In addition to being used as an energy

source to replace coal, biochar can also be exported as a higher-value product as soil amendment or activated carbon with additional processing. The selling prices of the higher-value products are in Table 3.4. The dashed box in Figure 2.1 shows the different alternatives analyzed for the biochar.

2.2.2.5 Hydrotreatment
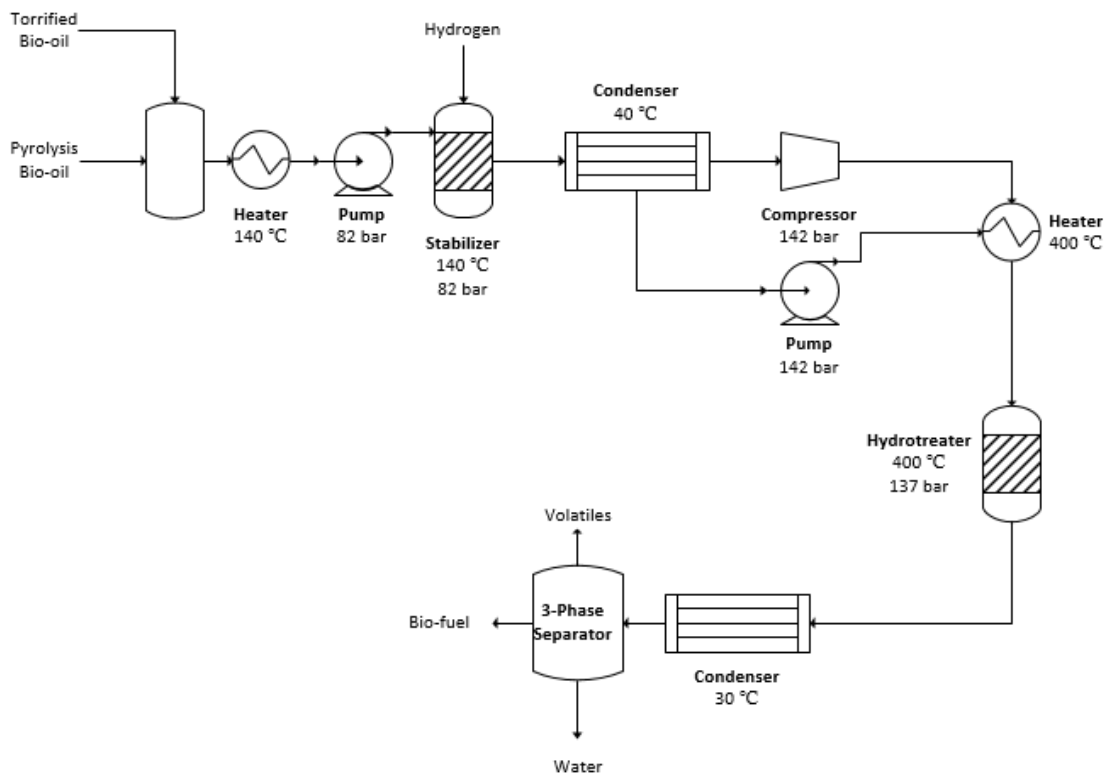
Figure 2.6. Process flow diagram for the hydrotreatment stage

Pyrolysis bio-oil has limited applications as a fuel other than direct combustion in furnaces, needing an upgrade to serve as a transportation fuel. The bio-oil is catalytically upgraded into biofuel from two catalytic steps: stabilization of bio-oil and catalytic hydrotreatment to biofuels, both using compressed hydrogen. The goal of upgrading is to increase the volatility through molecular-weight reduction, enhance storage stability, and eliminate oxygen to raise product fuel heating value[3]. Table 2.5 gives the wt% component distribution of the organics in the biofuel after catalytic upgrading of the bio-oil. Biofuel from two-step scenario 1 is catalytic upgraded bio-oil from both torrefaction and pyrolysis while scenario 2 is catalytic upgraded bio-oil from pyrolysis only. The most prevalent hydrocarbons in the biofuel are low molecular weight alkanes and cycloalkanes as well as aromatic compounds. The yields of different compounds in the bio-oil was determined using data from Fivga[23] with additional gc/ms calibration work of Klemetsrud et al[18,23].

Table 2.5. Biofuel composition distribution after catalytic upgrading of poplar bio-oil
(kg/kg organics x 100%)

Component	2 step sc 1	2 step sc 2	1 step
Methane	0.21	0.31	0.24
Ethane	4.60	4.74	6.37
Butane	5.83	7.08	2.85
Pentane	14.90	14.14	10.61
Hexane	27.65	31.07	3.72
Cyclohexane	19.90	16.72	13.99
Methylcyclohexane	3.46	3.88	30.33
Benzene	15.10	12.69	14.01
Toluene	2.66	2.98	11.86
Methylcyclopentane	3.16	3.55	3.34
Methylcyclopentene	2.53	2.84	2.68

2.2.2.6 Hydrogen Production

The required compressed hydrogen is produced by steam methane reforming of the low molecular hydrocarbons present in the non-condensable off-gas from torrefaction, hydrotreatment, and activated carbon production supplemented with natural gas as needed. A water-gas shift reactor further produces hydrogen. The pre-reforming, reforming and water-gas shift reactors were modeled as equilibrium reactors in Aspen Plus using operating conditions from literature[32]. A pressure swing adsorption (PSA) with an assumed recovery of 85% produces a high purity hydrogen stream and an off-gas stream.

The off-gas stream from hydrogen production containing unreacted CH_4, unseparated H_2, and other gases is combusted for process heat. Any excess off-gas is assumed to be sold at the price of natural gas to local industries. Nitrogen, the pyrolysis fluidizing agent, dilutes the pyrolysis NCG, causing it to have a low heating value. As a result the pyrolysis NCG is recirculated to the pyrolyzer rather than being combusted with the rest of the off gas.
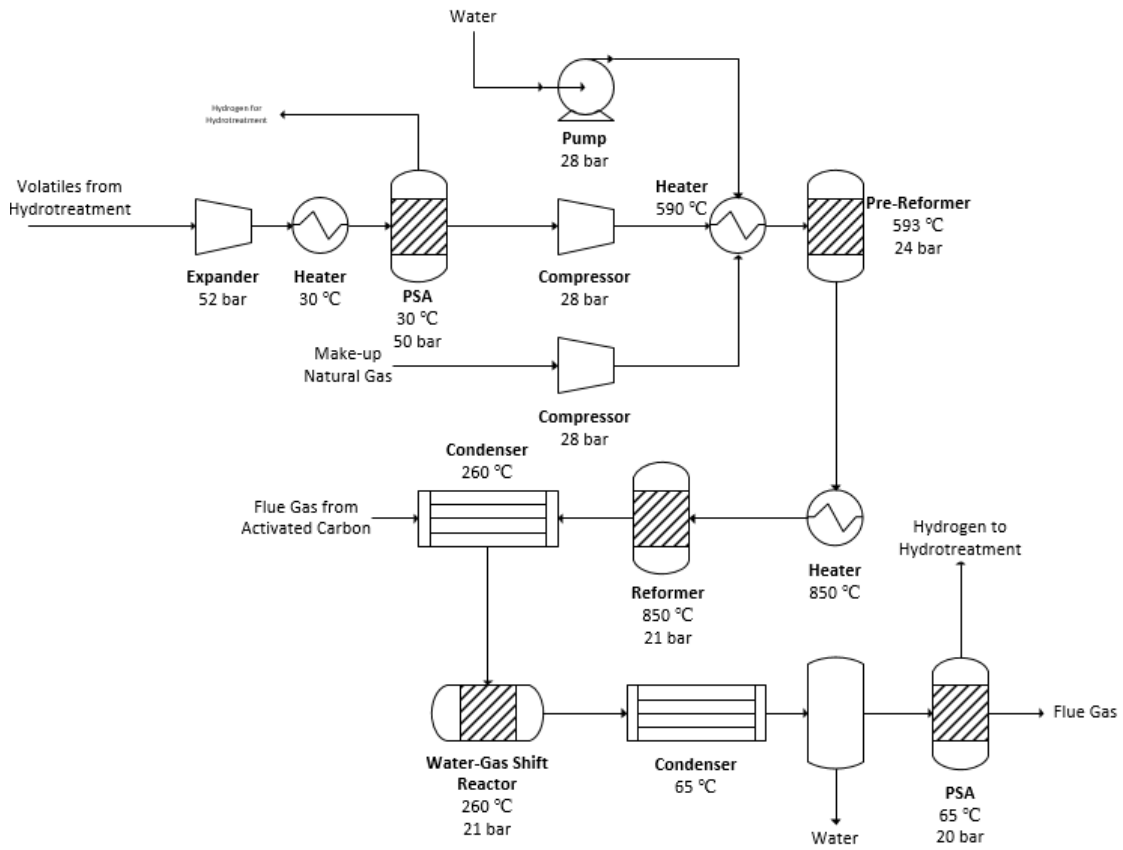
Figure 2.7. Process flow diagram for the hydrogen production stage

2.2.3 Modeling of Biochar Applications

For this study, three applications for biochar were analyzed. The three applications are burning biochar to displace coal, using biochar as a soil amendment for farm fields, and processing the biochar to produce activated carbon.

2.2.3.1 Burning Biochar to Displace Coal

Biochar may be combusted as an energy source to displace coal. The amount of coal that is displaced is calculated on an energy basis, such that the energy of the biochar is the same as that of the displaced coal. The energy content, expressed as lower heating value (LHV) of the biochar and coal is 30 MJ/kg and 33 MJ/kg respectively[33].

2.2.3.2 Soil Amendment Processes

Spreading biochar onto fields as a soil amendment can improve crop yields and fertilizer efficiency. Biochar, because of its high porosity, absorbs fertilizer and nutrients that the crops need and holds onto them until the roots use them[6]. This reduces the run-off of key nutrients and fertilizer, decreasing fertilizer usage by 7.2% according to research done by Roberts et al[9]. The biochar also decreases the N_2O emissions from the fertilizer and permanently sequesters carbon into the soil. This will be discussed further in the LCA method section.

2.2.3.3 Activated Carbon Processing
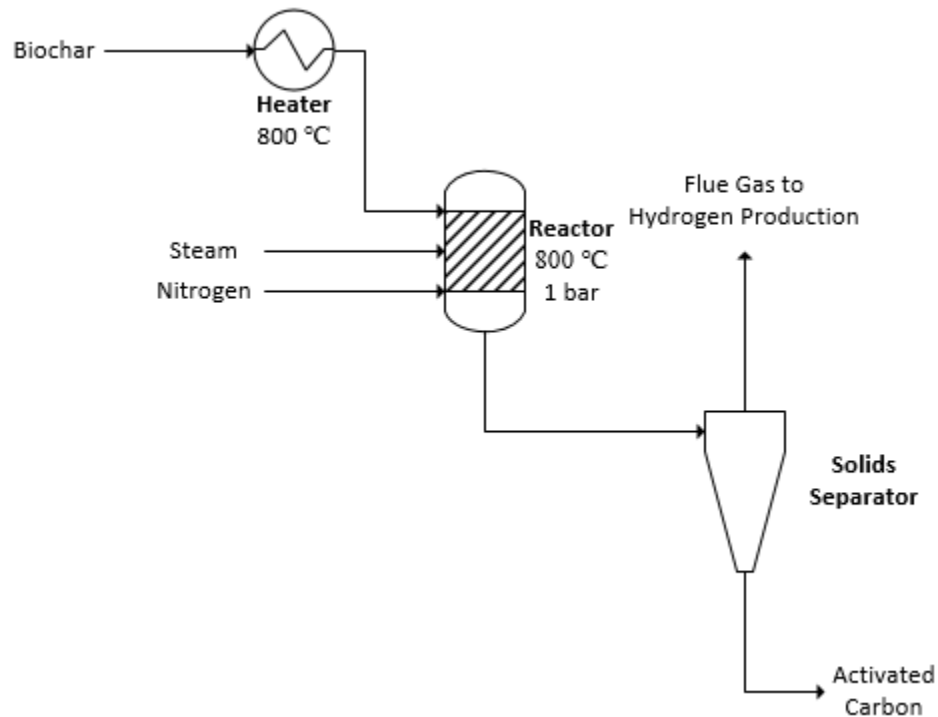
Figure 2.8. Process flow diagram for activated carbon production

Biochar is processed into activated carbon by steam activation with nitrogen as the fluidizing agent. The steam activation reaction is shown in equation 1 below and is endothermic. The steam activation is completed at 800 °C with a solids residence time of 5 minutes[10].

$$C + H_2O => H_2 + CO \qquad \Delta H = +118 \text{ kJ/mol} \qquad\qquad 2\text{-}1$$

This reaction activates the biochar by creating pores in the carbon which increases the surface area. The pores are the sites where contaminants diffuse into and immobilized during use. Activating the biochar increases these sites which improves the effectiveness

and lifespan of the activated carbon. During the creation of the pores the other components of biochar are released. The ash is released at a much slower rate than the more volatile components, causing the percent ash to increase for the activated carbon. The yield of the steam activation is 60% activated carbon and 40% off-gas. Table 2.6 below shows the ultimate and proximate analysis of the raw poplar, torrefied poplar, biochar and activated carbon[11,23,34]. The activated carbon data is taken from a study on active carbon made from coconut shells due to a lack of literature data on activated carbon from poplar.

Table 2.6a. Ultimate analysis of raw poplar, torrefied poplar, biochar, and activated carbon.

Component	Raw Poplar[16]	Torrefied Poplar[16]	Biochar[34]	Activated Carbon[8]
Carbon	46.80	54.96	83.03	82.53
Hydrogen	5.99	6.28	1.14	0.19
Nitrogen	0	0.10	1.37	0.23
Sulfur	0	0	0	0
Oxygen	46.05	36.66	6.56	4.35
Ash	1.16	2.00	7.67	12.71

Table 2.6b. Proximate analysis of raw and torrefied poplar, biochar, and activated carbon.

Component	Raw Poplar[16]	Torrefied Poplar[16]	Biochar[34]	Activated Carbon[8]
Ash	1.16	2.00	7.67	12.71
Volatile Matter	98.84	98.00	77.93	78.89
Fixed Carbon	0	0	14.4	8.4
Moisture	25	3.45	0	0

After steam activation the activated carbon is separated from the off gas and cooled. The activated carbon produced has a size of 2 mm in diameter which is categorized as granular activated carbon. Granular AC has a size range from 0.2 to 5 mm[35]. The granular AC can be further reduced in size to produced powdered AC, however this was not considered in this study. The off-gas from the steam activation is recycled to the water gas shift reactor to reclaim hydrogen. The water gas shift reaction is

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad\qquad 2\text{-}2$$

Where the carbon monoxide in the off gas is reacted with steam to produce carbon dioxide and hydrogen. The recycling of the off-gas reduces the amount of natural gas needed to produce the hydrogen for catalytic upgrade of bio-oil.

2.3 Heat Integration

The process simulations were performed with and without heat integration to investigate effects of energy efficiency measures on overall performance. Heat integration was performed in Super Target® (KBC Process Technology Ltd.) with a minimum approach temperature of 10°C. Super Target® is a pinch analysis software built to reduce energy for processes through better design. The heat duties were exported from Aspen Plus® energy analyzer and imported into Super Target®. A refrigerant was necessary for the condensation of the bio-oil from the pyrolysis unit. The heat of reaction required by the reactors were supplied externally and were not included in the heat integration, although the preheating or precooling of streams to the reactors were included.

Table 2.7. Heating and cooling utility duties for 2-step pathway scenario 1 with activated carbon. Utility duties are shown both before and after heat integration was applied.

Stage	Heating Utilities, MJ/hr		Cooling Utilities, MJ/hr	
	Before	After	Before	After
Drying	45,800	0	0	0
Size Reduction	0	0	0	0
Torrefaction	27,200	0	24,700	10,100
Pyrolysis	98,700	11,000	125,600	6,400
Hydrotreated	139,000	0	169,700	15,000
H2 production	122,000	70,000	119,600	16,000
AC Processing	54,800	37,000	31,500	0
Total	487,300	118,000	471,100	47,500

3 Techno-Economic Analysis (TEA)

3.1 Research Objectives

The techno economic analysis (TEA) was conducted to perform a preliminary economic analysis on the various applications of biochar from poplar as a byproduct of hydrocarbon biofuel production. The goal of this preliminary analysis is to determine to effect of various biochar applications on the minimum selling price of biofuel.

3.2 Methods

The techno economic analysis (TEA) was completed using a discounted cash flow spreadsheet in Microsoft Excel. The proposed plant has a 3 year startup period with a full life of 20 years. The TEA was designed to determine the minimum selling price (MSP) of the bio-oil that would give an internal rate of return on investment of 10% from the biorefinery using equations 3.1-2.

$$MSP = \Sigma[INV+WC+DF*((1-t)*EXP+t*DEPR)]/\Sigma[DF*PR*(1-t)] \qquad \text{3-1}$$

$$DF = (1+i)^{-j} \qquad \text{3-2}$$

where MSP is the minimum selling price, INV is the capital investment, WC is the working capital, DF is the discounted factor, t is the tax rate, EXP is the expenses, DEPR is depreciation, PR is production rate, i is internal rate of return, and j is the year. The sums are over the full life of the biorefinery. An example discounted cash flow table is shown in Table 8.1. Key inputs for the TEA are shown in Table 3.1. The IRS 7 year Modified Accelerated Cost Recovery System (MARCS) was used to evaluate the federal tax with depreciation. All costs were escalated to the base year of 2016 using the Chemical Engineering Plant Cost Index (CEPCI), which is provided monthly by the journal of Chemical Engineering.

The cost of electricity was based on delivered industrial electricity cost in the United States while the cost of natural gas was based on a 5-year average industrial delivered cost.

A sensitivity analysis was performed on the TEA results using a 15% increase or decrease on the main input parameters. This is presented in the TEA results section.

Table 3.1. Key inputs and assumptions for the techno economic analysis

Parameters	Values
Poplar Feedstock Price (dry basis)	$60 per dry metric ton^2
Project Economic Life	20 years
Internal Rate of Return (IRR)	10%
Working Capital	5% of total capital investment
Depreciation Method	7-Year MACRS
Base Year	2016
Operating Days Per Year	350 days
Natural Gas Price	$5.04 per GJ
Electricity Price	5.77 cents/kW-hr
Process Cooling Water Price	$0.16 per GJ energy removed
Refrigerant Price	$20 per GJ energy removed

3.2.1 Uncertainty Analysis

Uncertainty analysis was performed on all TEA scenarios by the analytical method, which uses error propagation[36]. The TEA sensitivity analysis, explained below in the TEA Results section, was used to determine the relationship between the change in each input parameter and change in minimum selling price (*dMSP/dParameter*), with all other input parameters held constant. The input parameters analyzed are feedstock cost, total project investment, bio-oil production, char credit value, rate of return, electricity cost, and natural cost. Each input parameter also has a variance, which were estimated from literature[37]. Error propagation combines the variances and derivatives of each parameter into a single expression of variability for the minimum selling price,

$$\sigma_{MSP} = \sqrt{\sum(Variance_{Parameter} * (\frac{dMSP}{dParameter})^2)} \qquad \text{3-3}$$

where σ_{MSP} is the standard deviation of MSP. The error bars shown on Figure 5.1, 5.3, and 5.5 are 1.96 times the standard deviation, representing the 95% confidence interval.

For the purpose of doing uncertainty analysis on the TEA it was assumed that each of the input parameters followed a modified beta distribution. The variance for the modified beta distribution can be calculated using[36]

$$\sigma^2 = \left[\frac{(b-a)}{6}\right]^2 \qquad \text{3-4}$$

where a is the minimum value and b is the maximum value found from the sensitivities of each input parameter. For example for AC selling price, a is the mode minus 20% and b is the mode plus 20%. Error propagation then combines the variance and derivative

17

values of all the input parameter using Equation 3.3 to find the standard deviation for MSP. Table 3.2 shows the variance and (*dMSP / dParameter*) values of the input parameters for 2 step sc 1 with activated carbon and heat integration. The standard deviation for this case is $0.53/gallon.

Table 3.2. The variance and (dMSP / dParameter) values for input parameters used in the TEA uncertainty analysisfor 2 step sc 1 with activated carbon and heat integration.

Input Parameters	Sensitivity[37]	*dMSP/dParameter*	Mode (m)	Variance[36]
AC Selling Price	+/- 20%	1.43E-03	$1,100	5.38E+03
Bio-oil Yield	+/- 20%	-4.19E-08	95,593,000	4.06E+13
Feed Cost, Poplar	-10 to + 30%	1.34E-02	$60.00	1.60E+01
Electricity Cost	-50% to 100%	4.13E-02	$5.77	2.08E+00
ISBL capital investment	-20% to +50%	5.98E-09	$605,485,000	4.99E+15
Interest rate	+2 percentage points	3.57E+01	10%	1.11E-05

3.2.2 Incremental Analysis

Incremental analysis was also performed to determine the uncertainty analysis on the effect of heat integration and biochar application. Incremental analysis was used to compare two cases, with the inputs to the cash flow table being the difference between the two cases for each input parameter. So for the incremental analysis on heat integration, the capital investment input was only the amount of capital expenditure needed for the heat exchangers added by heat integration, and the expense input was the reduction in utilities cost. This is detailed in Table 3.3.

Table 3.3. Incremental change in capital investment and expenses from heat integration for 2 step sc 1 with AC

Input	With HI	Without HI	Incremental Change
Total Capital Investment	$605,485,000	$576,381,000	$29,104,000
Expenses	$8,276,000	$42,216,000	-$33,940,000

The discounted cash flow table was then run using only the two inputs with incremental change shown in Table 3.3. The resulting MSP represents the incremental change between the two cases, which in this case is $0.84. This means that for 2 step sc 1 with AC performing heat integration lowers the price 84 cents. The error propagation was performed the same as described above, except on the incremental changes instead of the total amounts. A z-score was calculated using equation 3.5.

$$z_0 = \frac{0 - \mu}{\sigma}$$ 3-5

where μ is the incremental change in MSP between the two cases and σ is the standard deviation of the incremental change. The z-score can be used to calculate the profitability of the change assuming normal distribution.

For 2 step sc 1 with AC the σ is \$0.25 which results in a z-score of -1.70 when comparing the heat integrated to the non-heat integrated case. This z-score results in a 99.97% chance of the heat integrated case having a lower MSP than the non-heat integrated case.

The same approach was used to incrementally compare AC vs soil amendment for biochar application. For the same pathway, AC vs. soil amendment has a z-score of -1.51, or a 99.85% chance of the case producing activated carbon having a lower MSP than the case producing soil amendment.

3.2.3 Value of Co-product Alternatives for Biochar

The value of biochar when sold as an energy source to replace coal is \$49.60 per metric ton. This is calculated by multiplying the price of coal by the energy content of biochar divided by the energy content of coal to correct for the slightly lower energy content of biochar. The average price of bituminous coal is \$55 per metric ton[38] and the energy content for biochar and coal is 30 and 33 MJ/kg[33] respectively. Soil amendment is a higher-value product than its use as an energy source, with a price of \$352 per metric ton[39]. Activated carbon is the highest value product analyzed in this study for biochar. Its selling price is between \$1000 and \$1500 per metric ton depending on the quality of the activated carbon[10]. The selling price used in this study was assumed to be \$1100 per metric ton[7]. Table 3.4 summarizes the value of the different uses of biochar.

Table 3.4. Value of co-product alternatives for biochar

Biochar Use	Price \$/metric ton
Burn Biochar	\$49.60
Soil Amendment	\$352
Activated Carbon	\$1100

3.2.4 Equipment for Activated Carbon Processing

The equipment necessary to process biochar into activated carbon is summarized in Table 5. A nitrogen generator is needed to provide nitrogen for the fluidizing agent of the steam activation reaction. A rotary kiln is where the steam activation reaction takes place. The rotary cooler cools down the activated carbon after the reaction and the cyclone separates the activated carbon from the off gas. The cost for these equipment is shown in Table 3.5[10].

Table 3.5. Scale and costs for the equipment necessary for activated carbon processing

Equipment	Base Scale (kg/day)	Base Cost	Scaling Factor	Plant Scale (kg/day)	Plant Cost
Nitrogen Generator	6,000	$1,500,000	0.7	27,500	$4,400,000
Rotary kiln	10,000	$410,000	0.7	456,000	$5,900,000
Rotary cooler	10,000	$65,000	0.7	141,000	$410,000
Cyclone	2,400,000	$1,600,000	0.7	456,000	$500,000

3.3 Market Survey

A market survey was performed on the different alternative uses for the biochar and is summarized in Table 3.6. The proposed biorefinery has a rate of 1000 kg/hr through the pyrolysis unit and was modeled as a 2 step scenario 1 for this survey. Biochar from a 1-step pathway is much less than from a 2-step pathway, therefore our market survey is conservative. Biochar may be used as a substitute for coal to generate power in coal fired power plants. The United States combusts 670 million tons of coal per year in coal fired power plants according to the EIA[40]. Biochar can also be used as a soil amendment on farms. There are 349 million acres of farmland in the United States, which at an application rate of 5 short tons per hectare per 5 years, would use 128 million tons per year of soil amendment[41]. It can also be used to produce of activated carbon. The activated carbon market, however, is much smaller in the United States, with a demand of 0.59 million tons per year. Expanded globally the market is 1.65 million tons per year according to Research and Markets[42]. Assuming a 10% market penetration rate the activated carbon market could currently support three plants, while the other biochar alternatives can support over 100 plants. The activated carbon market, while small, is currently expanding at a rate of 5-7% per year[42]. This could further increase depending on future environmental regulations. If large industrial countries such as India and China increase their environmental regulations, the global activated carbon market will expand.

Table 3.6. Market survey data for the various applications of biochar. Data for the US market for coal and soil amendment and the global market for activated carbon is shown.

Co-product Application	Burn to Displace Coal	Soil Amendment	Activated Carbon
Demand (metric tons per year)	6.70E+08	1.28E+08	1.65E+06
Amount produced by designed plant (metric tons per year)	8.09E+04	8.09E+04	4.90E+04
# of plants at 10% penetration	827	158	3

3.4 TEA Results

3.4.1 Minimum Selling Price (MSP) of Hydrocarbon Fuel

The MSP of the hydrocarbon fuel for all scenarios of the one-step and two-step processes with and without heat integration are shown below in Figure 3.1, with a cost breakdown of these results shown in Figure 3.2. The MSP of the biofuel produced via a one-step conversion pathway is lower than the MSP estimated for the two-step pathway. This outcome is caused by the higher bio-oil yield of one-step than two step. Studies found the yield of blended bio-oil from a two-step fast pyrolysis of pine to be almost the same with the yield of oil from a one-step pathway at low torrefaction temperatures of about 290°C however, the data for poplar used in this study showed higher yield of bio-oil for the one-step pathway relative to the two-step pathway[43,44]. All scenarios producing higher value co-products from the biochar decreased the MSP of the biofuel. In general using the biochar to produce activated carbon resulted in lowest MSP for the one and two-step pathways. This is because for this scenario, revenue generated from producing the high value activated carbon outweighs the revenue generated in the other co-product utilization scenarios, despite the higher capital cost when producing activated carbon. The lowest MSP, obtained from the heat integrated one-step pathway with producing activated carbon from the biochar, was $3.23 per gallon. The use of renewable energy for process heat in Scenario 2 compared to 1 also causes a small decrease in MSP.
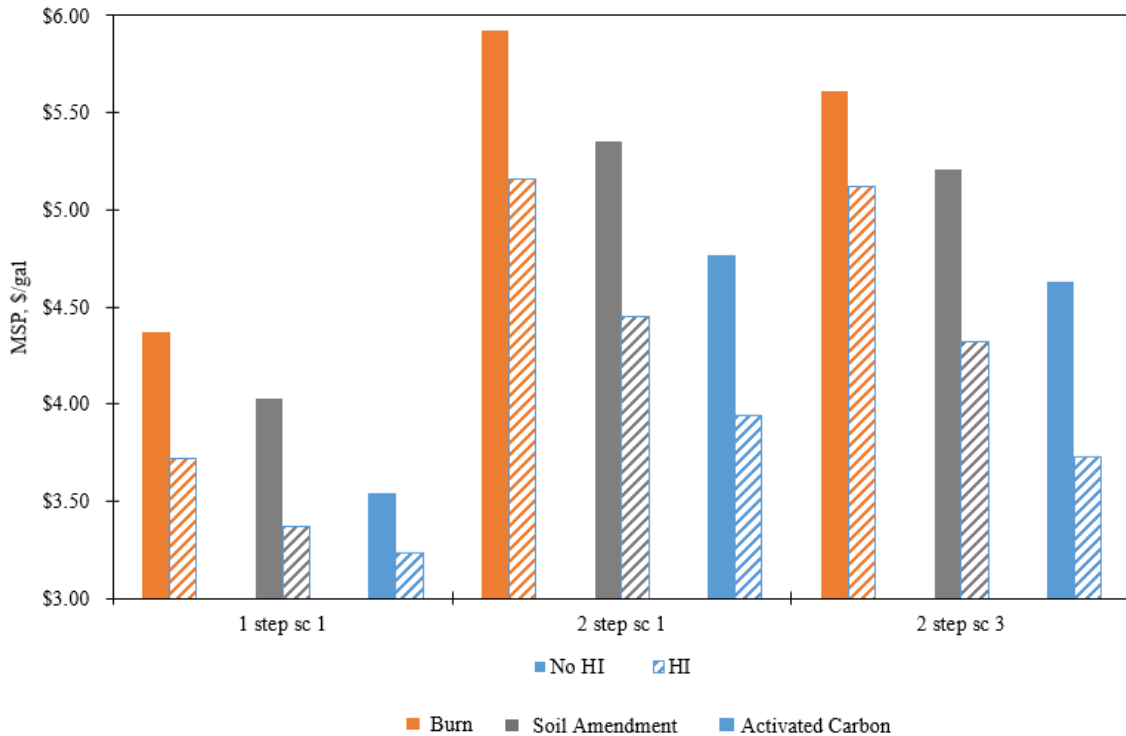
Figure 3.1. TEA results with and without heat integration

3.4.2 Economic Cost Breakdown

Figure 3.2 shows the economic breakdown for all the heat integrated cases. The most significant costs are total capital investment (TCI), feedstock, fixed cost of production (FCOP), and electricity. The most significant credits are char sales and depreciation. The effect of torrefaction can be seen by comparing the electricity costs, TCI, and biochar sales for the 1 and 2 step pathways. The two-step bars have smaller electricity costs than the one-step. The TCI and char sales for the 2 step is much larger than 1 step. A more detailed cost breakdown showing the effect of torrefaction is shown in Figure 3.3.

Figure 3.2. Breakdown of TEA results for all scenarios with heat integration. One-step activated carbon has the lowest MSP at $3.23/gal. TCI is total capital investment, including installation and indirect costs. FCOP is fixed cost of production.

Figure 3.3 compares the economic cost breakdown of the one-step and two-step scenario 1 pathways, both with processing biochar into activated carbon. This comparison shows the effect torrefaction has on the economics of the process along with a breakdown of costs among the major economic factors. Adding torrefaction significantly increases TCI through adding more equipment, while also slightly increases the feedstock required and the FCOP. The large increase in TCI is offset by the electricity requirement. Torrefaction significantly decreases the amount of electricity needed for size reduction, cutting it by approximately 50%.
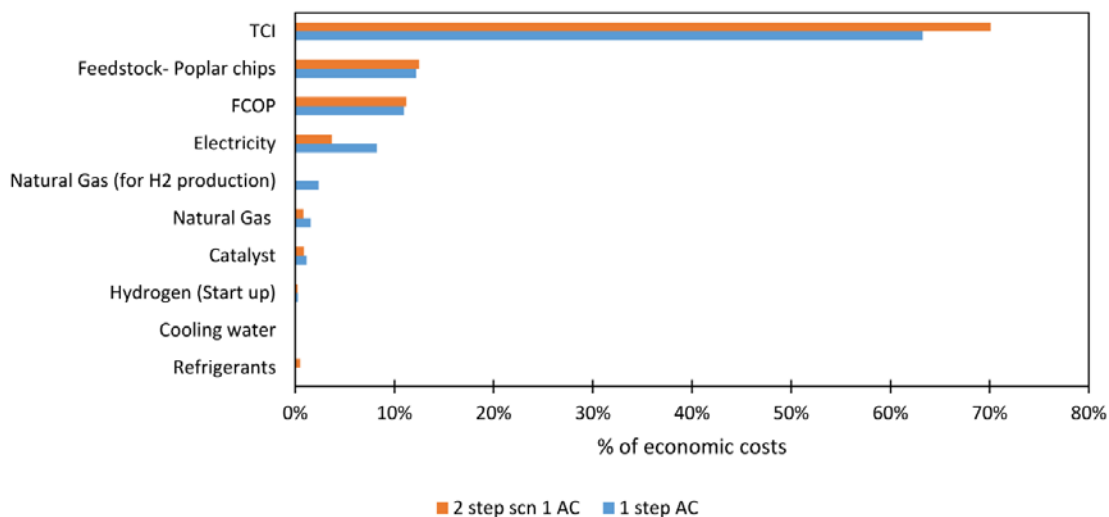
Figure 3.3. Economic cost breakdown showing the effect of torrefaction. TCI is total capital investment, including installation and indirect costs. FCOP is fixed cost of production. The MSP for 2 step scn 1 with AC is $3.94/gal and the MSP for 1 step with AC is $3.23 /gal, with heat integration (HI).

3.4.3 Sensitivity Analysis

A sensitivity analysis was performed on the best economic result, 1 step AC, shown in Figure 3.4 for the main independent input parameters by increasing and decreasing parameter values by 15% from the base value with all other parameters held constant. The input parameters analyzed are bio-oil production, total project investment, rate of return, biochar selling price, feedstock cost, electricity cost, and natural gas cost. The results show that the minimum selling price is most sensitive to a change in bio-oil production (yield), total project investment, and rate of return. For example, an increase in biofuel yield by 15% can reduce MSP from $3.23 to $2.81/gal. The minimum selling price is least sensitive to utility or feedstock cost changes. This agrees with Figure 3.2, which shows the total capital investment having a much larger influence on the selling price than utility or feedstock costs. This sensitivity analysis was used to find (dMSP/dParameter) in eqn. 3.3 for the analytical uncertainty analysis.

23

Figure 3.4. Sensitivity analysis of key variables to biofuel MSP for one-step pathway with activated carbon and HI. Each variable was changed +/-15%. The base price is $3.23/gal.

4   Life Cycle Analysis (LCA)

4.1   Life Cycle Analysis (LCA) Framework, System Definition, and Modeling Assumptions

This study evaluates the 'cradle-to-grave' impact of hydrocarbon fuel production and use via fast pyrolysis of poplar followed by an upgrade of the intermediate bio-oil to hydrocarbon biofuel. The LCA software used in this study is SimaPro® version 8.0 which provides accessible databases of environmental inventory data including ecoprofiles specific to the U.S. The LCA was created using the LCA methodology from the ISO standards (ISO 14044).

4.1.1   Goal of the LCA Study

The goal of this study is to conduct a LCA limited to greenhouse gas (GHG) emissions (commonly called a carbon footprint) of hydrocarbon biofuel production and use from the fast pyrolysis of poplar via three co-product choices for biochar, burning in coal power plants, soil amendment, and activated carbon. The LCA will be conducted through two pathways, a one-step pathway and a two-step pathway using results obtained from process simulation of the pathways.

4.1.2   System Boundary

The system boundary shows the sequence of unit processes in the pathway that is included in the assessment as shown in Figure 4.1. The hydrocarbon biofuel production chain is divided into two sections, biomass supply logistics, and biomass conversion. The biomass supply logistics includes the collection of poplar logging residues, coarse chipping of biomass in the forest, loading/unloading and transport of the biomass chips to the biofuel production site. Depending on the scenario being examined, the outputs from the system boundary varies as shown in Table 4.1. Inputs into the system are similar in almost all scenarios except for Scenario 2 where there is no input of natural gas for process heat. As earlier explained, for Scenario 2 process heat was totally supplied internally by the combustion of renewable energy sources. Steam generated from the highly exothermic hydrotreatment reaction, an output for the pathways without heat integration was utilized internally in the activated carbon processes.

A cradle-to-grave method was used to handle the biochar when it is burned to displace coal and used as a soil amendment. When the biochar is burned to displace coal, it is modeled to include combustion of coal. The soil amendment is also modeled to the grave to account for the use of biochar in the soil, the carbon sequestration, and the fertilizer savings. A cradle-to-gate approach was used to handle the activated carbon, which is modeled to the regional warehouse.

Figure 4.1. Cradle to grave system boundary for scenario 1 of a two-step hydrocarbon biofuel production with the co-product alternatives.

Table 4.1. Inputs and outputs from each scenario of the hydrocarbon biofuel production pathway.

Inputs	Outputs	
	Scenario 1	Scenario 2
Poplar	Biofuel	Biofuel
Natural gas (for hydrogen production)	Biochar to displace coal	Biochar to displace coal
Cooling water	Soil amendment	Soil amendment
Process water (for hydrogen production)	Activated carbon	Activated carbon
*Natural gas (for process heat)	Steam†	Steam†
	Off gas††	Off gas††
		Torr. condensed liquid††

*Applies to scenarios 1 & 2 only.

† Applies only to the scenarios without heat integration

†† Applies only to the heat integrated processes

26

4.1.3 Functional Unit Definition

The functional unit provides the reference to which all results in the assessment are based[45]. For this comparative environmental assessment the functional unit was set to 1 MJ of energy content of the fuel produced and combusted.

4.1.4 Allocation Methods

The pathways investigated in this study are multi-output pathways. For each case, co-products such as biochar, off-gas, and steam were produced and exported in addition to the main product hydrocarbon biofuel when applicable as shown in Table 6. For such multi-output processes, allocation is carried out so that the environmental loads are allocated to each product. This study looked at allocation using three approaches, a displacement allocation approach, an energy allocation approach, and a value allocation approach. In displacement allocation all environmental burdens are placed on the biofuel. The biofuel also receives a credit for any process or material that a co-product displaces in the market. In the case where biochar is burned, a credit is given for the amount of coal displaced at the co-fired power plant, including the combustion emissions. The steam generated from cooling the highly exothermic hydrotreatment reaction that is not used internally for activated carbon production is exported to get credits for displacing the production of steam using natural gas. Off gas and torrefaction condensed liquid not used for process heat is assumed to displace natural gas and heavy fuel oil, respectively, including their combustion. The credits received for the co-product alternatives of biochar is discussed further in the sections below. Inventories of GHG emissions for the displaced products including their combustion emissions were obtained from ecoprofiles in the ecoinvent™ database in SimaPro®. Full results of the displacement method are presented in the results section of this document.

In energy and value allocation no credits are given. An allocation factor is calculated based on the energy or value output of the biofuel compared to the total energy or value output of all the products. This allocation factor determines how the environmental burden of the process is spread out among the biofuel and its co-products. Sample calculations showing how the allocation factors were calculated are shown below.

The three different allocation methods, displacement, energy and value, were analyzed due to the different requirements from various renewable fuel standards[46]. The Renewable Fuel Standard (RFS) program in the United States was created by the Energy Independence and Security Act in 2007. This program requires that any fuel derived from cellulose, hemicellulose, or lignin (nonfood-based renewable feedstocks) must demonstrate a life cycle GHG emissions reduction of at least 60% when compared to fossil fuels, using a system expansion (displacement) allocation method. The European Union (EU) biofuel program is governed by the Renewable Energy Directive (RED), in which biofuels must achieve a minimum threshold of 35% GHG savings compared to fossil fuels using energy allocation. The Roundtable on Sustainable Biomaterial (RSB) requires that biofuels achieve 50% lower lifecycle GHG emissions compared with a fossil

fuel baseline to be certified, using an economic (value) allocation method. All three initiatives require energy content of the fuel to be the functional unit.

4.1.4.1 Sample Calculation of the Energy Allocation Factors

The allocation factors used in energy allocation for our study were calculated as shown in the sample calculation below for scenario 1 of a heat integrated two-step hydrocarbon biofuel production pathway with torrefaction. Figure 4.2 is a simplified schematic for the production pathway. The intermediate product bio-oil and co-product char exited the production pathway at the fast pyrolysis stage while co-products off-gas and activated carbon (AC) exited the production pathway at the hydrogen production, and activated carbon processing stages respectively.

Figure 4.2. Simple schematic diagram for a two-step production pathway

Stage-wise allocation factors were calculated for these three stages using equations 4.1-3. Mass flowrates and the LHV of the main product, biofuel and the co-products obtained from the model simulation for scenario 1 of a two-step pathway are shown in Table 4.2. The calculated stage-wise allocation factor for the three stages are also shown in Table 4.2.

$$Allocation\ factor_{bio-oil} = \frac{\dot{m}_{bio-oil}H_{bio-oil}}{\dot{m}_{bio-oil}H_{bio-oil} + \dot{m}_{char}H_{char}} \qquad 4\text{-}1$$

$$Allocation\ factor_{biofuel} = \frac{\dot{m}_{biofuel}H_{biofuel}}{\dot{m}_{biofuel}H_{biofuel} + \dot{m}_{off-gas}H_{off-gas}} \qquad 4\text{-}2$$

$$Allocation\ factor_{activated\ carbon\ (AC)} = \frac{\dot{m}_{AC}H_{AC}}{\dot{m}_{AC}H_{AC} + \dot{m}_{AC\ off-gas}H_{AC\ off-gas}} \qquad 4\text{-}3$$

$$AF1 = AF_{bio-oil} * AF_{biofuel} + (1 - AF_{bio-oil}) * (1 - AF_{AC}) * AF_{biofuel} \qquad 4\text{-}4$$

$$AF2 = AF_{biofuel} \qquad 4\text{-}5$$

$$AF3 = (1 - AF_{AC}) * AF_{biofuel} \qquad 4\text{-}6$$

Overall allocation factor AF1 shown in Table 4.2 is calculated with equation 4.4 and is the allocation factor for fast pyrolysis. It was applied to all the inputs and outputs for all the stages prior to and including the pyrolysis stage as shown in Figure 4.2. Overall allocation factor AF1 accounts for the burden for producing biofuel from the upgrade of bio-oil from fast pyrolysis as shown in the first term of equation 4.4, and the burden from recycling the off-gas generated from the activated carbon processing as shown in the second term of equation 4.4. Overall allocation factor AF2 shown in Table 4.2 is calculated with equation 4.5 and was applied to all the inputs and outputs from the hydrotreatment and hydrogen production stages. Allocation factor AF3 shown in Table 4.2 is calculated with equation 4.6 and is applied to the activated carbon production stages.

Table 4.2. Flow rates and LHV values for scenario 1 of a heat integrated two-step hydrocarbon biofuel production pathway with the production of activated carbon

Process Output	Mass flowrate (kg/hr)	LHV (MJ/kg)
Bio-oil	40875	17.4
Biochar	9636	30
Off gas	10250	7.45
Activated Carbon	5829	28.4
Hydrocarbon biofuel	11380	43.45
Allocation factor		
Allocation factor$_{bio-oil}$	0.71	
Allocation factor$_{biofuel}$	0.91	
Allocation factor$_{activated\ carbon}$	0.42	
AF1	0.75	
AF2	0.91	
AF3	0.38	

4.1.4.2 Sample Calculation of the Value Allocation Factors

The allocation factors used in our study for value allocation were calculated as shown in the sample calculation below for scenario 1 of a heat integrated two-step hydrocarbon biofuel production pathway with torrefaction. Figure 4.3 is a simplified schematic for the production pathway. The intermediate product bio-oil and co-product char exited the production pathway at the fast pyrolysis stage while co-products off-gas and activated carbon exited the production pathway at the hydrogen production, and activated carbon processing stages respectively.
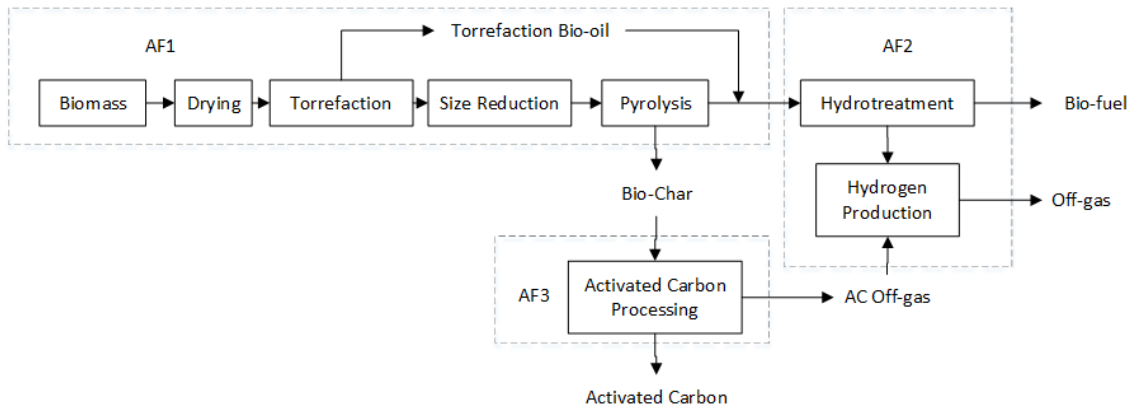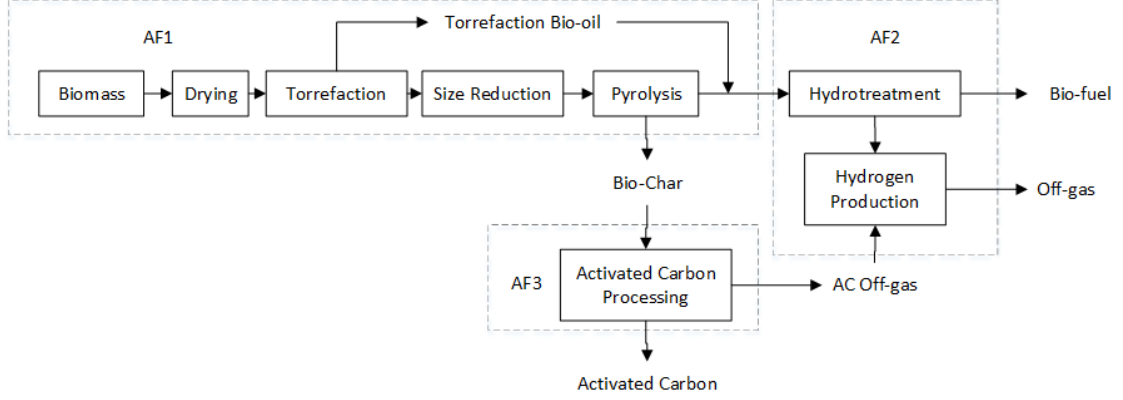
Figure 4.3. Simple schematic diagram for a two-step production pathway

Stage-wise allocation factors were calculated for these three stages using equations 4-7, 4-8, and 4-9. Mass flowrates and the market value (V) of the main product, biofuel and the co-products obtained from the model simulation for scenario 1 of a two-step pathway are shown in Table 4.3. The calculated stage-wise allocation factor for the three stages are also shown in Table 4.3.

$$Allocation\ factor_{bio-oil} = \frac{\dot{m}_{bio-oil}V_{bio-oil}}{\dot{m}_{bio-oil}V_{bio-oil} + \dot{m}_{char}V_{char}} \qquad 4\text{-}7$$

$$Allocation\ factor_{biofuel} = \frac{\dot{m}_{biofuel}V_{biofuel}}{\dot{m}_{biofuel}V_{biofuel} + \dot{m}_{off-gas}V_{off-gas}} \qquad 4\text{-}8$$

$$Allocation\ factor_{activated\ carbon\ (AC)} = \frac{\dot{m}_{AC}V_{AC}}{\dot{m}_{AC}V_{AC} + \dot{m}_{AC\ off-gas}V_{AC\ off-gas}} \qquad 4\text{-}9$$

$$AF1 = AF_{bio-oil} * AF_{biofuel} + (1 - AF_{bio-oil}) * (1 - AF_{AC}) * AF_{biofuel} \qquad 4\text{-}10$$

$$AF2 = AF_{biofuel} \qquad 4\text{-}11$$

$$AF3 = (1 - AF_{AC}) * AF_{biofuel} \qquad 4\text{-}12$$

Overall allocation factor AF1 shown in Table 4.3 is calculated with equation 4-10 and is the allocation factor for fast pyrolysis. It was applied to all the inputs and outputs for all the stages prior to and including the pyrolysis stage as shown in Figure 4.3. Overall allocation factor AF2 shown in Table 4.3 is calculated with equation 4-11 and was applied to all the inputs and outputs from the hydrotreatment and hydrogen production stages. Allocation factor AF3 shown in Table 4.3 is calculated with equation 4-12 and is applied to the activated carbon production stages.

Table 4.3. Flow rates and economic values for scenario 1 of a heat integrated two-step hydrocarbon biofuel production pathway

Process Outputs	Mass flowrate	Value
Bio-oil	14,500 gallon/hr	$0.73 per gallon
Biochar	9,636 kg/hr	$0.05 per kg
Off gas	76,349 MJ/hr	$5.04 per GJ
Activated Carbon	5,829 kg/hr	$1.10 per kg
Hydrocarbon biofuel	4,037 gallon/hr	$2.34 per gallon
Allocation factor		
Allocation factor$_{\text{bio-oil}}$	0.96	
Allocation factor$_{\text{biofuel}}$	0.97	
Allocation factor$_{\text{activated carbon}}$	0.09	
AF1	0.90	
AF2	0.94	
AF3	0.08	

4.1.5 Life Cycle Inventory

The life cycle inventory includes all material and energy inputs to each stage in the life cycle as well as the cradle-to-gate or grave inventory of greenhouse gas emissions and energy demand for those inputs[47].

4.1.5.1 Biomass Supply Logistics

Full discussion of the biomass supply logistics can be found in detail in previous work by Winjobi[13]. CO_2 emissions due to direct and indirect land use changes are not considered in our assessment because we assume that sustainable practices will be adopted by leaving a portion of the logging residue in the forest to sustain soil C stocks[5]. Recent studies have demonstrated minimal direct and indirect land use change effects when logging and mill residues are utilized.[2,48] Emission factors for biomass logistics were based on values from the Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (GREET) model[14].

4.1.5.2 Biomass Conversion

4.1.5.2.1 Drying of Biomass

Biomass is received at the conversion facility at an assumed moisture content of 25%. This is reduced though drying to about 8% for smoother operations of the hammer mills and for optimal fast pyrolysis[21]. The drying step was modeled in Aspen Plus and the estimated heat duty from the simulation was used to quantify the amount of either natural gas or renewable fuels required to generate the required steam.

4.1.5.2.2 Torrefaction of Biomass

For the two-step pathway torrefaction comes after drying. The torrefaction step was modeled in Aspen Plus using a yield reactor based on literature data for stream compositions as described previously[18,19]. Yields of non-condensable gases, condensed liquid and torrefied solid and the component distribution of the oil and gas for torrefaction are shown in Tables 2.2 and 2.3 in Chapter 2. The emissions from this step are based on the process heat supplied (via natural gas or renewable energy) and cooling water required to condense the torrefaction condensed liquid. Torrefaction, as a pretreatment, causes the solid product to be more brittle, significantly reducing electricity inputs for size reduction[12].

4.1.5.2.3 Size Reduction of Poplar Chips

Further reduction in the size of the poplar chips to a size of about 2mm is required to ensure that the biomass is processed in the pyrolyzer. The size reduction was assumed to be carried out using hammer mills driven by electricity delivered to the plant using US grid electricity mix.

4.1.5.2.4 Fast Pyrolysis

Fast pyrolysis of raw/torrified poplar at a temperature of 516° C was modeled using a yield reactor in Aspen Plus based on literature data[23]. The yield data and distribution of the representative compounds in the bio-oil used in the model are shown in Tables 2.2 and 2.3 in Chapter 2. The emissions from this step are based on the process heat supplied (natural gas or renewable energy) and cooling water required for quick quench of pyrolysis vapors.

4.1.5.2.5 Upgrade of Bio-oil

This study assumed whole bio-oil upgrade through catalytic hydrotreatment to remove the oxygen contained in the bio-oil as water and CO_2 by phase separation[49]. The upgrade is achieved by a stabilization step followed by a hydrotreatment step. The reaction pathways of the representative compounds are discussed in detail in previous work by

Winjobi[13]. The emission inventories for this step include process heat requirements and cooling water used for cooling the highly exothermic hydrotreatment step.

4.1.5.2.6 Hydrogen Production

The hydrogen required for the upgrade step was produced on-site by steam methane reforming. The pre-reforming, reforming and water-gas shift reactors were modeled as equilibrium reactors in Aspen Plus using operating conditions from literature[32]. Natural gas was used to supplement the off-gas from hydrotreatment and activated carbon production in order to provide excess hydrogen for upgrading. Inputs and the emissions inventory for this step include natural gas used to complement the off-gas, process heat requirements, cooling water required for the water-gas shift reactor, process water required to generate steam for reactions, and fossil CO_2 produced from the combustion of off-gas based on the natural gas input. The remaining CO_2 produced from off-gas combustion is biogenic. The life cycle inventory of the catalyst utilized for the catalytic upgrade was not accounted for in this study because previous studies have shown that the life cycle inventory of the catalyst has little effect on the overall life cycle emission of the pathway[32,50,51].

A detailed description of the modeling of the biomass conversion can be found in previous work by Winjobi[13].

4.1.5.3 Biochar Applications

4.1.5.3.1 Burning Biochar to Displace Coal

For the case in which biochar is burned in a coal-fired power plant, the biochar displaces coal. The amount of coal that is displaced is calculated on an energy basis, such that the energy content of the biochar is the same as that of the displaced coal. The emissions saved from coal displaced was modeled using the ecoinvent profile for US average of bituminous coal production and use in combustion. Biochar can also be modeled to displace natural gas for electricity. However, this study modeled the displacement of coal due to the close similarity in properties (ultimate and proximate analysis) of biochar and coal.[52]

4.1.5.3.2 Soil Amendment Application

 Biochar may be applied to farm fields as a soil amendment to increase crop yield, increase fertilizer efficiency, decrease N_2O emissions, and permanently sequester carbon in the soil. A typical application rate of 5 ton/ha was used in this study[6]. It has yet to be determined experimentally the maximum amount of biochar that can be applied to field crops, yet rates as high as 50 ton/ha have shown crop improvements[53]. This indicated that continuing to add biochar to soils over an extended period of time can provide additional benefits.

Carbon sequestration: About 80% of the carbon in biochar is considered stable, which means it will stay sequestered in the soil for over 100 years[6]. This is modeled as a carbon credit in SimaPro® by taking an input from nature of CO_2 equivalent to the sequestered carbon content in the biochar. This credit is from removing the carbon in the biochar, and thus the equivalent CO2, from the biogenic cycle over the long term.

Improved fertilizer use efficiency: A study on N retention on highly weather soils found a 7.2% increase on total N recovery in soils fertilizer with biochar compared with no-biochar present [54]. In this LCA the 7.2% savings is assumed to be the same for P_2O_5 and K_2O and is multiplied by the fertilizer application rates to calculate total fertilizer avoided. The fertilizer application rates were averaged from corn, soybean, winter wheat, and spring wheat data from NASS surveys for N, P_2O_5, and K_2O and are 88.5, 56.5, and 78.8 kg/ha respectively[55]. The inventory of GHG emissions for the displaced synthetic fertilizers (N, P_2O_5, and K_2O) are from the US average in the GREET model[14].

Soil N_2O emissions: Several studies have found that biochar reduces the N_2O soil emissions that result from applying N fertilizer[56,57]. A laboratory study on poultry litter biochar showed that biochar reduced N_2O emissions by 40-80%[57]. Another study in Japan showed a 89% suppression of N_2O emissions from the application of biochar[56]. These results indicate that the level of N_2O emission suppression is not equal for every case. For this analysis it was assumed that the reduction of soil N_2O emissions from the application of N fertilizer is 50%. It is estimated that typically 1.325% of the N in the N fertilizer is converted into N in N_2O emissions[14].

The N_2O emissions are reduced two ways: the increase in fertilizer efficiency and the decrease in N_2O emissions from the soil. The increase in fertilizer efficiency causes less fertilizer to be applied which decreases N_2O emissions. Equation 4-13 calculates the amount of N_2O emissions avoided per ton of biochar applied. With the assumptions used in this study 0.39 kg of N_2O emissions will be avoided per ton of biochar.

$$N_2O \text{ emissions savings} = 88.47 \frac{N\,kg}{ha} * (7.2\% * 1.33\% + 92.8\% * 50\% * 1.33\%) * \frac{44\,kg\,N_2O}{14\,kg\,N} * \frac{ha}{5\,ton} \quad \text{4-13}$$

4.1.5.3.3 Soil Amendment Scenarios and Results

The research of using biochar as a soil amendment is currently young and ongoing. As such there is much uncertainty over how long the benefits of using biochar as a soil amendment last. A life cycle assessment (LCA) of biochar systems by Roberts et al [9] assumes that the soil amendment only has one year of benefits while a LCA on greenhouse gas mitigation benefits of biochar by Cowie et al [58] assumes that the soil amendment provides 10 years of constant benefits. In this study both cases, 1 year and 10 years of benefits, were analyzed along with a linear and exponential decay over 10 years to represent a middle case. Table 4.4 shows the percentage of the benefits per year each of the cases have. These percentages are multiplied by the maximum avoided fertilizer usage and N_2O emissions in the LCA.

Table 4.4. Percentage of fertilizer and emission benefits per year for the soil amendment cases

Year	1	2	3	4	5	6	7	8	9	10
Constant for 10 years	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%
Linear Decline	100%	90%	80%	70%	60%	50%	40%	30%	20%	10%
1 year Only	100%	0%	0%	0%	0%	0%	0%	0%	0%	0%
Exponential decay	100%	77%	60%	46%	36%	28%	22%	17%	13%	10%

The LCA results for the soil amendment scenarios along with the other biochar uses are shown in Figure 4.4. The main environmental benefit from soil amendment is the sequestration of carbon in the soil, not the avoided fertilizer usage and N_2O emissions. Thus altering the length of time the soil amendment is functional does not have a large effect on the CO_2 equivalent, especially when compared to activated carbon. When compared to burning char and receiving a coal credit, the length of time does matter. The soil amendment with only 1 year of benefits is worse environmentally than burning the char while the soil amendment with 10 years of benefits is better environmentally. The reason for the 1 year of SA benefits being worse environmentally than burning the char is that only 80%, not 100%, of the carbon in the soil amendment is sequestered. This partial sequestration does not fully compensate for the amount of coal extracted. There are also additional environmental burdens from the extraction and transport of the coal that also make the substitution of coal combustion more beneficial than 1 year SA. In the other SA cases the accumulation of fertilizer benefits over the 10 years makes up for this difference. For this study the middle case of 10 years with exponential decay was used.
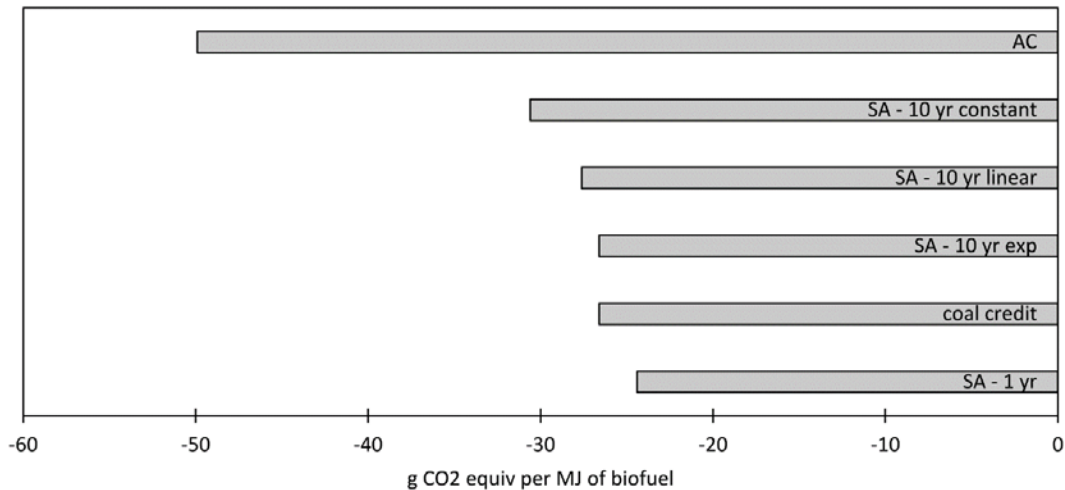
Figure 4.4. LCA results for all biochar applications, including all soil amendment cases, activated carbon, and burning char for a coal credit.

4.1.5.3.4 Activated Carbon Credit

The majority of virgin activated carbon today is made from bituminous coal[59]. Activated carbon can also be made from renewable sources such as coconut shell and wood. The average energy demand for granular activated carbon is 79.8 MJ/kg and the average global warming potential is 9.3 kg CO_2 eq/kg[53]. This was input into SimaPro® to model the activated carbon that is displaced though the production of activated carbon from biochar.

For the end of life treatment, the activated carbon can be either recycled, combusted as co-gen fuel in a coal plant, or disposed in a landfill depending on what substance the activated carbon is used to absorb. As the exact substance the AC absorbs cannot be accurately modeled, this was not included in the study. The LCA inventory used for an activated carbon is modeled as "cradle-to-use" for both the biogenic AC as well as the fossil AC. The end of life state impacts were not modeled assuming that they are the same for both, and thus cancel in the analysis.

4.1.6 Input Table for Inventory Analysis

A list of products and inputs of materials and energy for one-step biofuel production without heat integration are included in Table 4.5 on the basis of 1 MJ of hydrocarbon biofuel produced. The names of ecoprofiles selected in the LCA software SimaPro are also listed in the input table. Similar input tables for all scenarios with and without heat integration for 1- and 2-step pathways are included in 8.1.

Table 4.5. LCA inputs including ecoprofile names, for one-step hydrocarbon biofuel production from poplar without heat integration with burning biochar to replace coal.

Products	Amount	Unit
Hydrocarbon biofuel	1	MJ
Biochar (displaces coal)	0.009	kg
Fossil CO_2 (from combustion of H_2 production off-gas)	0.025	kg
Steam (displaces natural gas generated steam)	0.051	kg
Material Inputs		
Poplar (8 % moisture content)	0.103	kg
Process water, ion exchange, production mix, at plant, from surface water RER S[a] (to generate steam for hydrogen production)	0.045	kg
Natural gas, from high pressure network (1-5 bar), at service station/US* US-EI U[a] (for hydrogen production)	0.009	kg
Water, completely softened, at plant[a] (cooling water, pyrolysis stage)	4.56	kg

36

Water, completely softened, at plant[a] (cooling water, hydrotreatment stage)	5.49	kg
Water, completely softened, at plant[a] (cooling water, hydrogen production stage)	5.65	kg
Process Energy Inputs or Outputs (negative values)		
Electricity, medium voltage US[a] (size reduction)	0.034	kWh
Electricity, medium voltage US[a] (hydrotreatment)	0.004	kWh
Electricity, medium voltage US[a] (hydrogen production)	0.010	kWh
Natural gas, burned in industrial furnace low-NOx> 100kW[a] (biomass drying)	0.064	MJ
Natural gas, burned in industrial furnace low-NOx> 100kW[a] (pyrolysis)	0.269	MJ
Natural gas, burned in industrial furnace low-NOx> 100kW[a] (hydrotreatment)	0.18	MJ
Natural gas, burned in industrial furnace low-NOx> 100kW[a] (hydrogen production)	0.06	MJ
Bituminous coal, combusted in industrial boiler NREL/US[a]	-0.008	kg
Steam, for chemical processes, at plant/US-US-EI U[a]	-0.041	kg

a – Ecoinvent profile names in SimaPro®

4.1.7 Carbon Accounting

This life cycle carbon footprint accounts only for the fossil fuel carbon, not the biogenic carbon. The biogenic carbon is associated with the production and use of biomass resources. Emissions from the combustion of char biofuel were not included in our CO_2 accounting as they are biogenic. We are assuming that poplar biomass is provided using sustainable forest management practices, such that negligible change in forest above and below ground carbon results from the utilization of this resource. The most likely harvest scenario to achieve this sustainability goal is collection of rapidly decomposing logging residues from ongoing harvesting operations for other forest products.

4.1.8 Impact Assessment Methods

The impact assessment method for this LCA are the global warming impacts of all greenhouse gases using IPCC 2013 GWP 100a in SimaPro®. The IPCC 2013 was developed by Intergovernmental Panel on Climate Change and contains the climate change factors with a timeframe of 100 years.

4.1.9 Uncertainty Analysis

Uncertainty analysis of LCA results was performed by a Monte Carlo simulation in SimaPro that incorporates the associated uncertainty in the life-cycle inventory data used in this study into the LCA results. All the input data in this LCA were described using appropriate profiles in SimaPro except the credit for soil amendment which was modeled using literature data. For the data described by the SimaPro profiles, the default uncertainties in SimaPro were used in the Monte Carlo simulation. These default uncertainties in SimaPro were mostly quantified using a lognormal distribution with the geometric mean standard deviation estimated either using the pedigree matrix by Weidema or basic uncertainty factors based on expert judgment[60]. For soil amendment credit, a standard deviation of 0.1 was used to quantify the uncertainty in the data using a normal distribution. Each Monte Carlo simulation performed 1000 runs for the uncertainty analysis. The histogram output from this simulation for 2 step sc 1 with activated carbon and heat integration with displacement allocation is shown in Figure 4.5. The outside red lines on the figure represent the 95% confidence interval and were used on the figures in the manuscript. The y-axis on Figure 4.5 is the probability while the x-axis is GHG emissions in kg CO_2 eq.
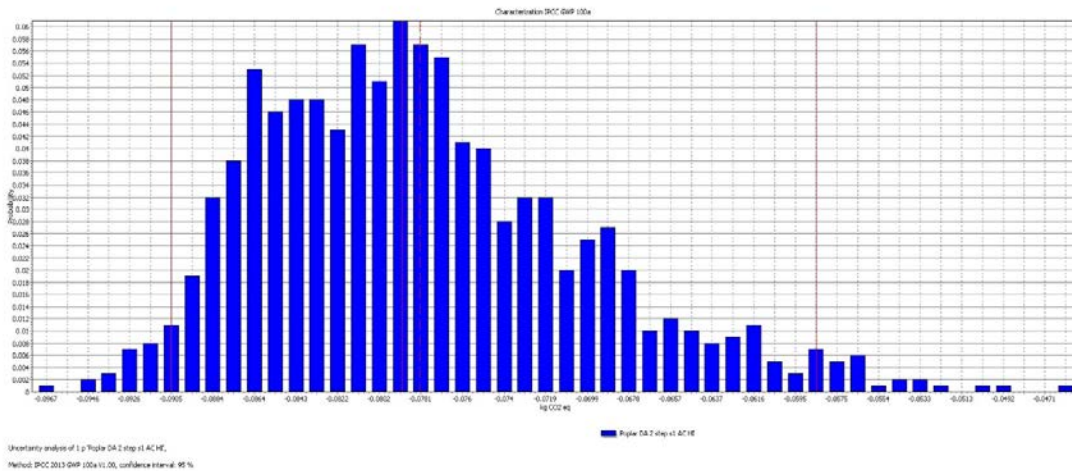
Figure 4.5. Monte Carlo simulation output on LCA results for 2 step sc 1 with activated carbon and heat integration with displacement allocation. The two outside red lines represent the upper and lower confidence interval while the center red line is the mean result.

4.2 LCA Results

4.2.1 Displacement Allocation Results

The results from the displacement LCA are shown below in Figure 4.6. The GHG emissions produced via a one-step conversion pathway are higher than the GHG

estimated for the two-step pathway. This is due to the higher char yields and lower size reduction energy demands caused by torrefaction in the 2-step pathway. All of the uses for biochar give large GHG emission credits compared to emissions. The credits for burning biochar to replace coal are similar to the credit for using biochar as a soil amendment. Activated carbon has a higher GHG credit than the other alternatives. This is caused by the activated carbon displacing the coal usually used to produce activated carbon along with the fossil fuels consumed to process the coal into activated carbon. The use of renewable energy for process heat in Scenario 2 compared to 1 also causes a small decrease in GHG emissions. The lowest GHG emission is from 2 step Scenario 2 with activated carbon at -102 g CO_2 eq. per MJ of fuel.

Hydrogen production and size reduction have the largest GHG emissions among the process sections. The GHG emissions from hydrogen production are much lower for pathways with activated carbon (AC) than the other pathways due to the recycling of the AC off gas. Recycling the off gas from the production of activated carbon increases the amount of hydrogen produced during hydrogen production thereby reducing the amount of fossil derived natural gas and subsequently reducing the emissions from hydrogen production. The two-step conversion pathway has a lower size reduction energy demand than the one-step pathway due to torrefaction.

Figure 4.6. Breakdown of LCA (displacement allocation) results for all scenarios with heat integration. Two-step scenario 2 with activated carbon has the lowest GHG emissions at -102 g CO_2/MJ fuel.

4.2.2 Energy Allocation Results

In addition to the displacement allocation LCA, LCAs using both energy and value allocation were analyzed. Greenhouse gas emissions (GHG) were again used as the impact category and the LCA was carried out in SimaPro 8.0. Results for the energy allocation LCA are shown below in Figure 4.7.

Energy allocation distributes the environmental burden among all the products on an energy basis and is calculated based on the energy content of the main product and co-products. There are no credits given for fossil fuels or fertilizer avoided as in the displacement allocation method. Sample calculations of the energy allocation factors were previously.

Figure 4.7 shows the heat integrated results for all scenarios. As with displacement allocation, the two step pyrolysis has lower GHG emissions than the one step pyrolysis. The decrease of the size reduction electricity usage from torrefaction is the main cause of the difference between one and two step. Also one step pyrolysis has a higher bio-oil yield than two step pyrolysis. The higher yield increases the amount of energy in the biofuel product compared to the char, or the allocation factor. The higher allocation factor increases the environmental burden carried by the biofuel for one step versus two step.

The results for the burning biochar and the soil amendment are identical for energy allocation. This is because using the biochar as a soil amendment does not change the energy content of the biochar and this allocation method does not consider any credits from displacing fertilizer or coal. The activated carbon cases have lower GHG emissions than the burning or soil amendment due to the recycling of the activated carbon off gas to the hydrogen production unit.

Figure 4.7. Breakdown of LCA (energy allocation) results for all scenarios with heat integration. Two-step scenario 2 with activated carbon has the lowest GHG emissions at 17.4 g CO2/MJ fuel.

4.2.3 Value Allocation Results

Value allocation distributes the environmental burden among all the products on a value basis and is calculated based on the market value of the main product and co-products. The market value for the biofuel was taken to be equal to the market value of gasoline. There are no credits given for fossil fuels or fertilizer avoided as in the displacement allocation method. Sample calculations of the value allocation factors were shown previously. Results for the value allocation LCA are shown in Figure 4.8.

Figure 4.8 shows the heat integrated results for all scenarios. As with displacement allocation, the two step pyrolysis has lower GHG emissions than the one step pyrolysis. The decrease of the size reduction electricity usage from torrefaction is the main cause of

the difference between one and two step. Also one step pyrolysis has a higher bio-oil yield than two step pyrolysis. The higher yield increases the amount of value in the biofuel product compared to the char, or the value allocation factor. The higher allocation factor increases the environmental burden carried by the biofuel for one step versus two step.

Higher value co-products for biochar decreases the value allocation factor by decreasing the amount of value in the biofuel product compared to the biochar. Thus the biofuel produced with soil amendment has a lower environmental burden than when the biochar is burned using the value allocation method. The activated carbon cases also have lower GHG emissions than the burning or soil amendment due to the recycling of the activated carbon off gas to the hydrogen production unit.
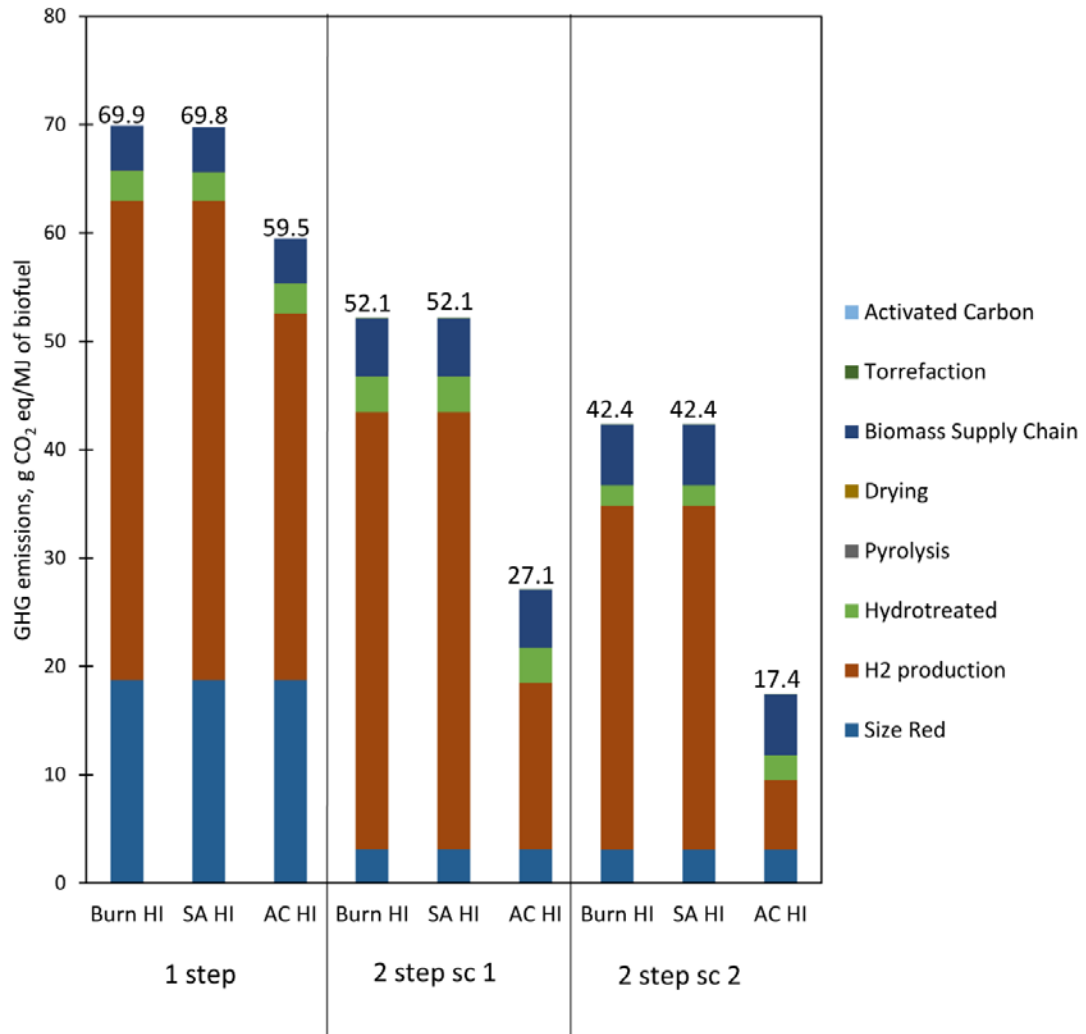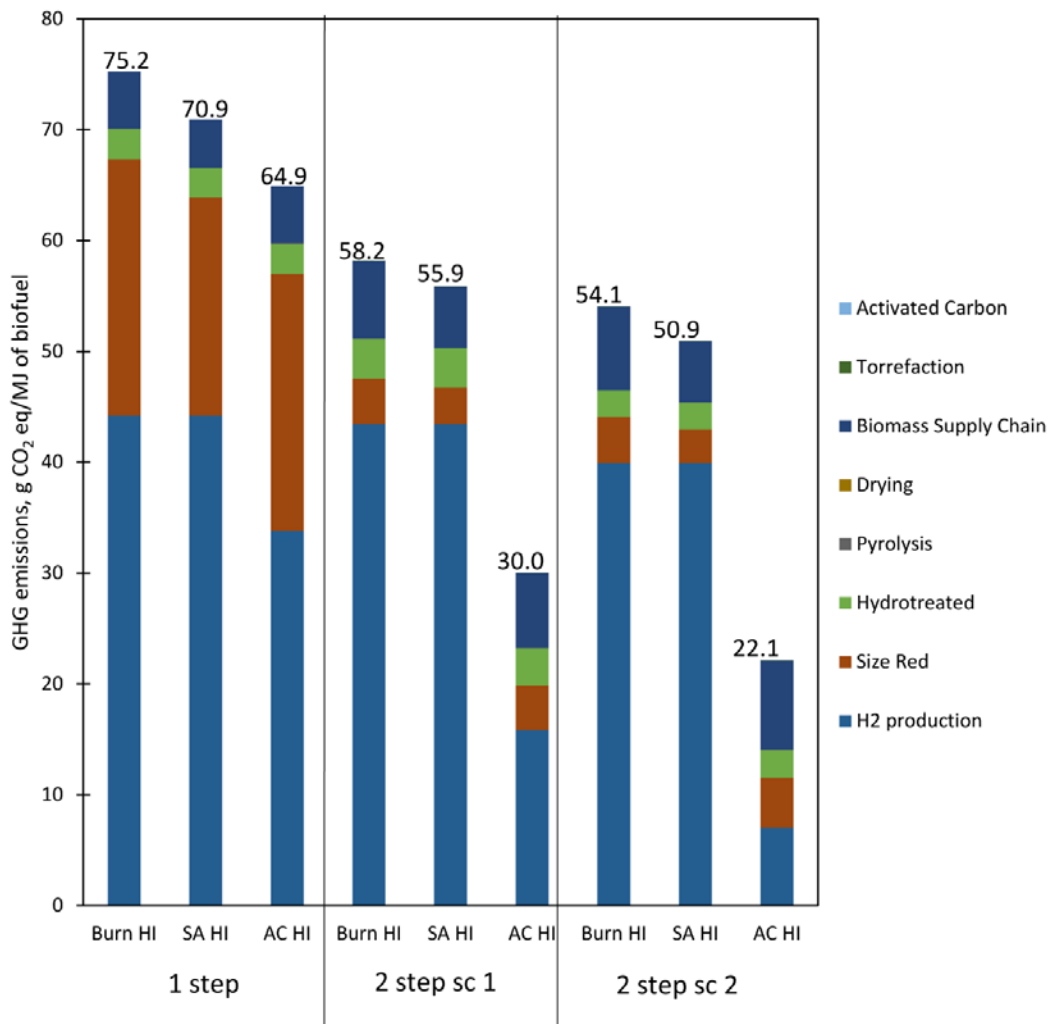

Figure 4.8. Breakdown of LCA (value allocation) results for all scenarios with heat integration. Two-step scenario 2 with activated carbon has the lowest GHG emissions at 22.1 g CO2/MJ fuel.

4.2.4 Fossil Fuel Energy Demand

In addition to GHG emissions, a second impact assessment was analyzed for both the best economic and environmental case, 1 step and 2 step sc 2 with activated carbon respectively, using displacement allocation. This was done using Cumulative Energy Demand in SimaPro, focusing on the energy demand on nonrenewable fossil fuels. For the 1 step with activated carbon, shown in Table 4.6, the fossil energy demand is 1.08 MJ fossil energy per MJ of biofuel without heat integration and 0.27 MJ fossil energy per MJ of biofuel with heat integration. For the 2 step sc 2 with activated carbon, the fossil energy demand is -0.18 MJ fossil energy per MJ of biofuel without heat integration and -1.08 MJ fossil energy per MJ of biofuel with heat integration. The fossil energy demand is negative for 2 step sc 2 because of the displacement credits from activated carbon. This result agrees with the GHG emissions analysis findings, in which the 2 step sc 2 is better environmentally than the 1 step. For both cases heat integration lowers the fossil energy demand ~0.8 MJ of fossil energy per MJ biofuel. Of the selected cases analyzed, only the 1 step without heat integration puts in more energy from nonrenewable fossil fuels into the process than is received from the biofuels.

Table 4.6. Fossil fuel energy demand for selected cases.

	1 step with AC		2 step sc 2 with AC	
Case	**Without HI**	**With HI**	**Without HI**	**With HI**
MJ of fossil energy/MJ biofuel	1.08	0.27	0.18	-1.08

4.3 Conclusion

From this study, we can conclude that co-product use alternatives will have a very large effect on the carbon footprint and fossil energy demand of pyrolysis-based hydrocarbon biofuels produced in a 1-step or 2-step conversion pathway. In addition, heat integration has very large positive energy savings and environmental benefits for pyrolysis-based hydrocarbon biofuels. For the displacement allocation method, two-step scenario 2 with activated carbon shows the best result, at -102 g CO_2 eq. per MJ of biofuel. The same trends and best case are also seen in the energy and value allocation method, with one-step having higher emissions than two-step and scenario 2 having lower emissions than scenario 1. All three allocation methods show the two-step scenario 2 with activated carbon as having the lowest GHG emissions.

5 Trade-Off Analysis

5.1 Research Objectives

A trade-off analysis was completed to compare the TEA and LCA results presented in Ch 3 and 4 respectively. The analysis was done through the use of trade-off plots, which plot the MSP on the x-axis and the GHG emissions on the y-axis. This plot is useful in showing the economic and environmental trade-offs when comparing different scenarios or cases. Cases closer to the lower left corner are the preferred, as they demonstrate having both a low MSP and low GHG emissions. In this study trade-off analysis was conducted to determine the effect of the one-step vs two-step pathway, heat integration, and co-product applications on the economic and environmental results.

5.2 Hydrocarbon Biofuel Compared to Fossil Gasoline

A trade-off plot was generated to compare the economic and environmental results of all scenarios to that of petroleum gasoline. Figure 5.1 compares biofuel GHG emissions and MSP with those for petroleum gasoline (shown in the dashed lines) for the three different scenarios with and without heat integration along for displacement allocation. All but 2 of the cases have less GHG emissions than gasoline. Both of the cases with higher GHG emissions are one-step without heat integration. All of the cases still have a MSP well above that of gasoline, with the best cases being ~$1.50 higher. This difference has been lowered though through the work done in this study.

Figure 5.1 can also be used to compare the one-step vs two-step pathway. In general the two-step pathway has lower GHG emissions but a higher MSP than the one-step pathway. This is because torrefaction causes a lower bio-fuel yield but a larger char yield. The lower bio-fuel yield increases the MSP as there is less biofuel being produced. The larger char yield improves the biofuel's GHG emissions through displacement credits.

For each of the three pathway scenarios, the point to the upper right is the original case, which had no heat integration and burning biochar to displace coal. From this point the results exhibit large changes in GHG emissions and MSP with the application of heat integration and higher value co-products. Sections 5.3 and 5.4 take a closer look at the effects of both heat integration and co-product application separately.
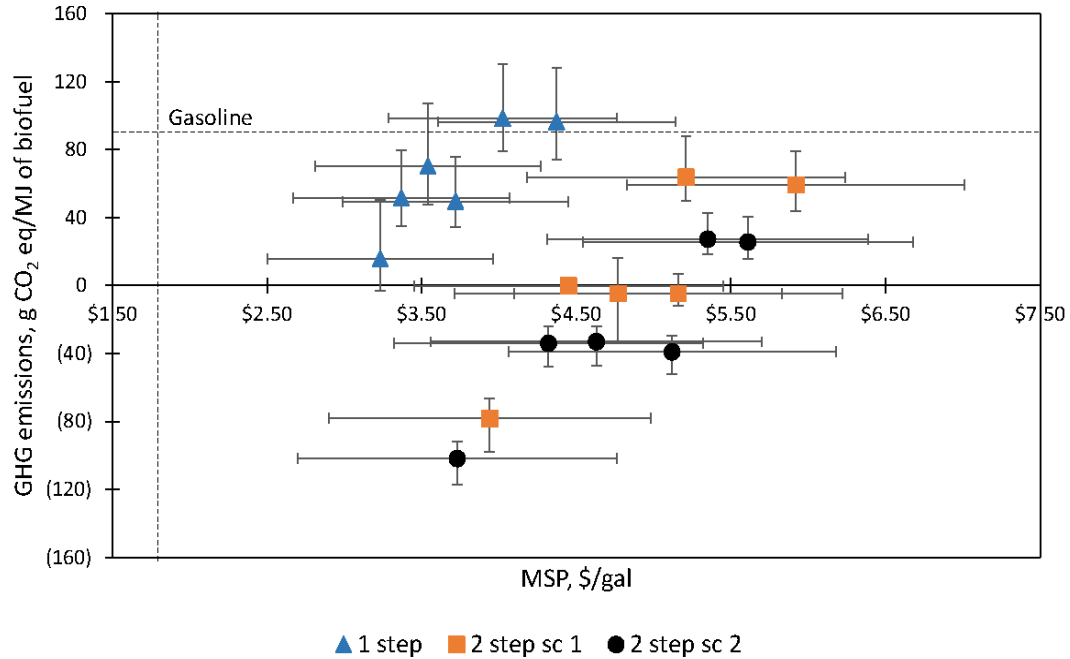
Figure 5.1. Trade-off plot comparing displacement allocation GHG emissions vs minimum selling price for all scenarios. The GHG emissions and wholesale selling price (1) for gasoline are shown for comparison.

5.3 Effect of Heat Integration

5.3.1 Displacement Allocation

Figure 5.2 shows the effect of heat integration on all cases for two-step scenario 2. For all the cases, heat integration lowers the MSP of biofuel about $0.80/gal and decreases the GHG emissions about 70 g CO_2 eq. / MJ of biofuel. This trend is similar in magnitude for the other two scenario pathways. The MSP error bars shown on Figure 5.2 for the heat integrated case do significantly overlap with the error for the non-heat integrated case, bringing uncertainty into the positive conclusion regarding HI. However the majority of this uncertainty is in the sunk cost in capital investment that heat integration does not significantly affect. Thus it can be reasonably concluded with low economic risk that heat integration does improve the economics of the production of biofuel. Error bars for GHG emissions do not overlap when comparing HI with no HI cases, and therefore there is very low risk in concluding that HI improves emissions.

Figure 5.2. Trade-off plot showing the effect of heat integration for displacement allocation method for two-step scenario 2. The light points are without heat integration while the dark points are with heat integration.

5.3.2 Energy Allocation

Figure 5.3 shows the effect of heat integration on all cases for two-step scenario 1 using energy allocation. For all the cases, heat integration lowers the MSP of biofuel about $0.80/gal and decreases the GHG emissions about 60 g CO_2 eq. / MJ of biofuel. This trend is similar in magnitude for the other two scenario pathways.
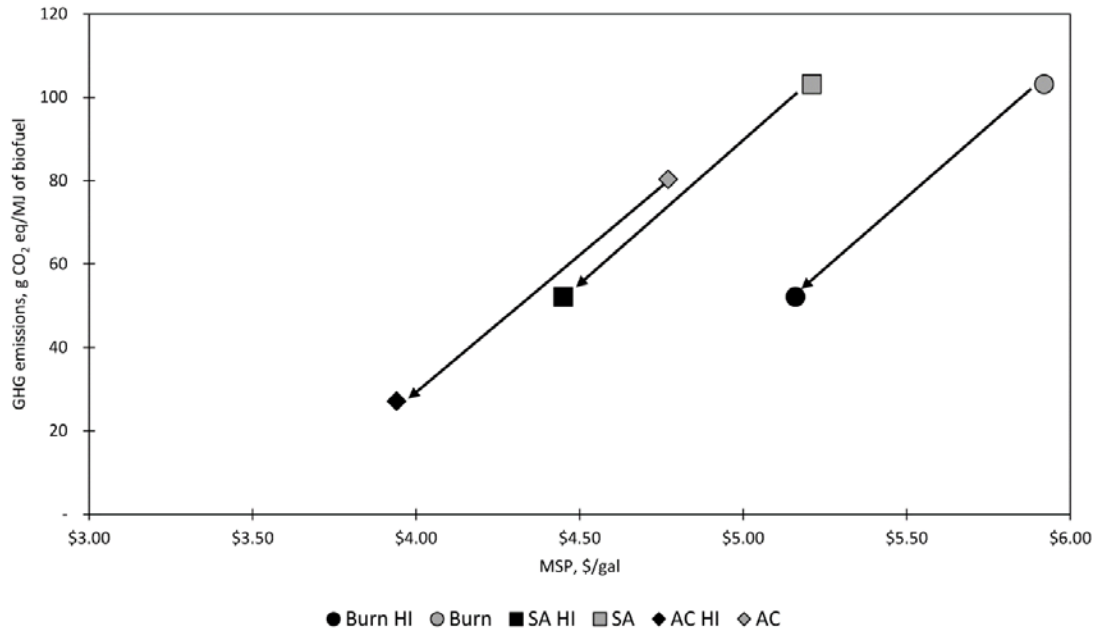
Figure 5.3. Trade-off plot showing the effect of heat integration for energy allocation method for two-step scenario 1. The light points are without heat integration while the dark points are with heat integration.

5.3.3 Value Allocation

Figure 5.4 shows the effect of heat integration on all cases for two-step scenario 1 for value allocation. For all the cases, heat integration lowers the MSP of biofuel about $0.80/gal and decreases the GHG emissions about 70 g CO_2 eq. / MJ of biofuel. This trend is similar in magnitude for the other two scenario pathways.
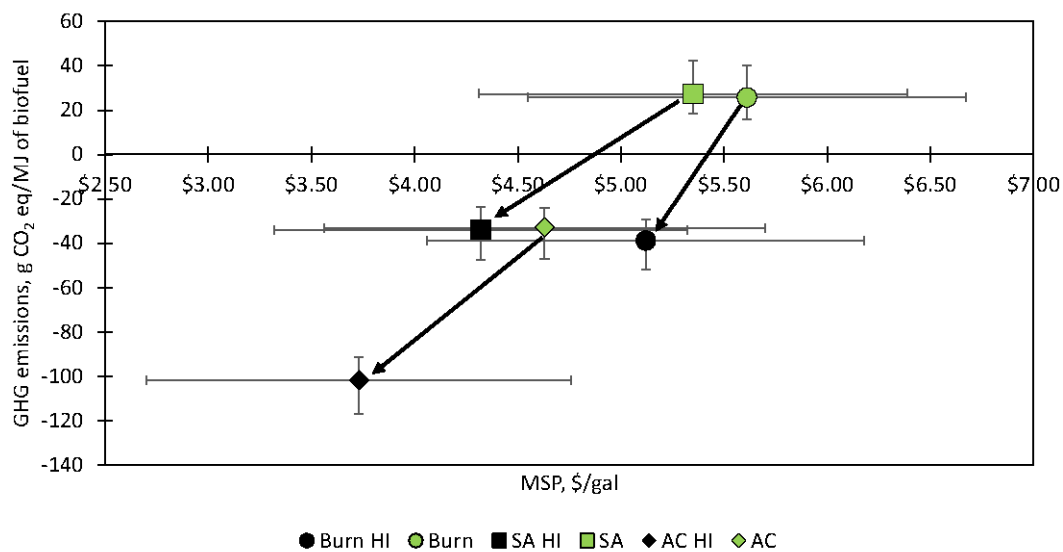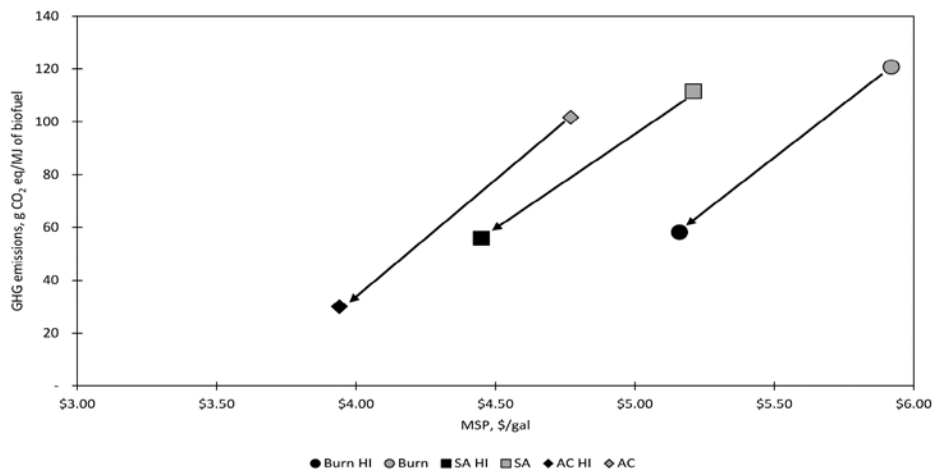

Figure 5.4. Trade-off plot showing the effect of heat integration for value allocation method for two-step scenario 1. The light points are without heat integration while the dark points are with heat integration.

5.4 Effect of Co-product Use Alternatives for Biochar

Trade-off plots were also made to analyze the effect of the different co-product uses for biochar on the economic and environmental impact of biofuel. This was done for displacement, energy, and value allocation.

5.4.1 Displacement Allocation

Figure 5.5 shows the effect of different co-product uses on the economic and environmental results for all scenarios with heat integration and displacement allocation. For all cases the soil amendment and burning char are similar in GHG emissions, with soil amendment having a lower MSP. Processing the char to produce activated carbon lowers both the MSP ($0.50-$1.40/gal) and GHG emissions (40-80 g CO_2 eq./MJ) depending on case (1- or 2-step). Overall the higher value co-products decrease the MSP of the biofuel without substantially hurting the environmental emissions, and with the AC alternative having particularly large GHG savings. The error bars shown on Figure 5.5 show that the MSP error bars for each bio-char application overlap with each other, reducing the probability that the differences in MSP are realizable. However, just like with heat integration, the majority of this uncertainty is in the sunk cost in capital investment that the biochar application only contributes about 8% of the total capital investment. Thus it can be reasonably concluded that higher value co-products decrease the MSP of the biofuel while also decreasing the GHG emissions.

Figure 5.5. Trade-off plot for all scenarios with heat integration showing the effect of different co-products from biochar for displacement allocation method.

48

The same trends found using displacement allocation are also found using energy and value allocation, shown below. For all allocation methods, heat integration and producing activated carbon lowers the MSP and GHG emissions. The best case for all three scenarios is activated carbon with heat integration for any of the three allocation methods.

5.4.2 Energy Allocation

Figure 5.6 shows the effect of different co-product uses on the economic and environmental results for all scenarios with heat integration and energy allocation. For all cases the soil amendment and burning char are similar in GHG emissions, with soil amendment having a lower MSP. Processing the char to produce activated carbon lowers both the MSP ($0.50-$1.40/gal) and GHG emissions (10-30 g CO_2 eq./MJ) depending on case (1- or 2-step). Overall the higher value co-products decrease the MSP of the biofuel without substantially hurting the environmental emissions. The GHG savings from the AC alternative are not as large with energy allocation as with displacement allocation however.

The results for the burning biochar and the soil amendment are identical for energy allocation because the soil amendment application does not change the energy content of the biochar. The activated carbon cases have lower GHG emissions due to the recycling of the activated carbon off gas to the hydrogen production unit.
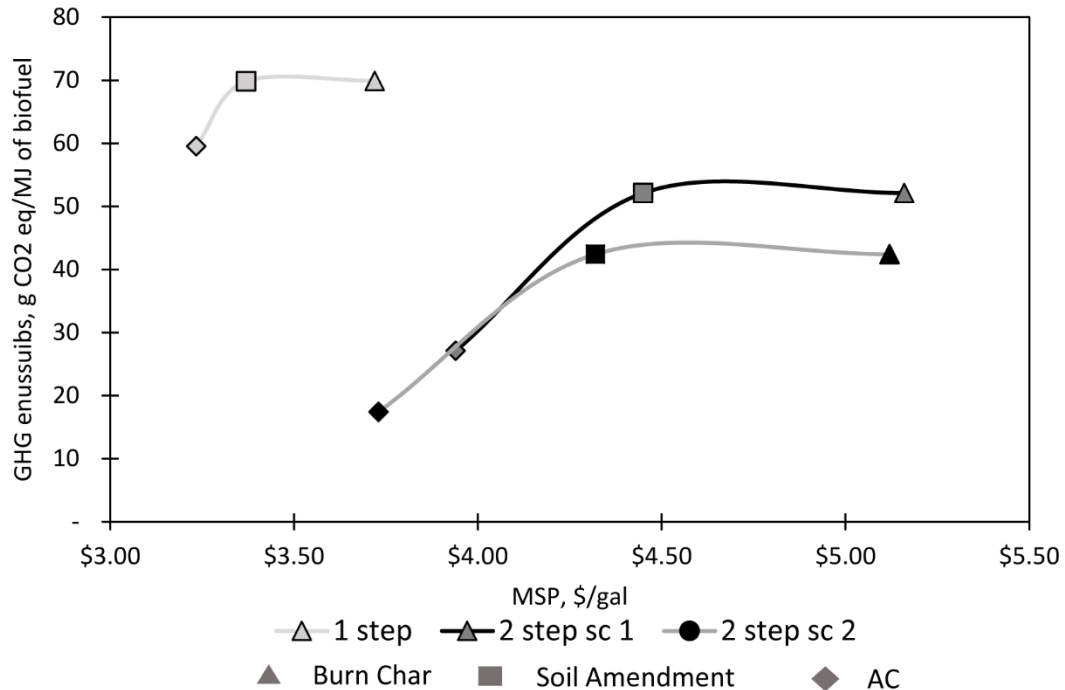
Figure 5.6. Trade-off plot for all scenarios with heat integration showing the effect of different co-products from biochar using the energy allocation method.

5.4.3 Value Allocation

Figure 5.7 shows the effect of different co-product uses on the economic and environmental results for all scenarios with heat integration and energy allocation. For all cases the soil amendment and burning char are similar in GHG emissions, with soil amendment having a lower MSP. Processing the char to produce activated carbon lowers both the MSP ($0.50-$1.40/gal) and GHG emissions (10-40 g CO_2 eq./MJ) depending on case (1- or 2-step). Overall the higher value co-products decrease the MSP of the biofuel without substantially hurting the environmental emissions. The GHG savings from the AC alternative are larger for the 2-step pathways than the 1-step pathway due to the larger char yield from the torrefaction step.

Higher value co-products for biochar decreases the value allocation factor by decreasing the amount of value in the biofuel product compared to the biochar. Thus the biofuel produced with activated carbon has the lowest environmental burden using the value allocation method. The activated carbon cases also have lower GHG emissions than the burning or soil amendment due to the recycling of the activated carbon off gas to the hydrogen production unit.
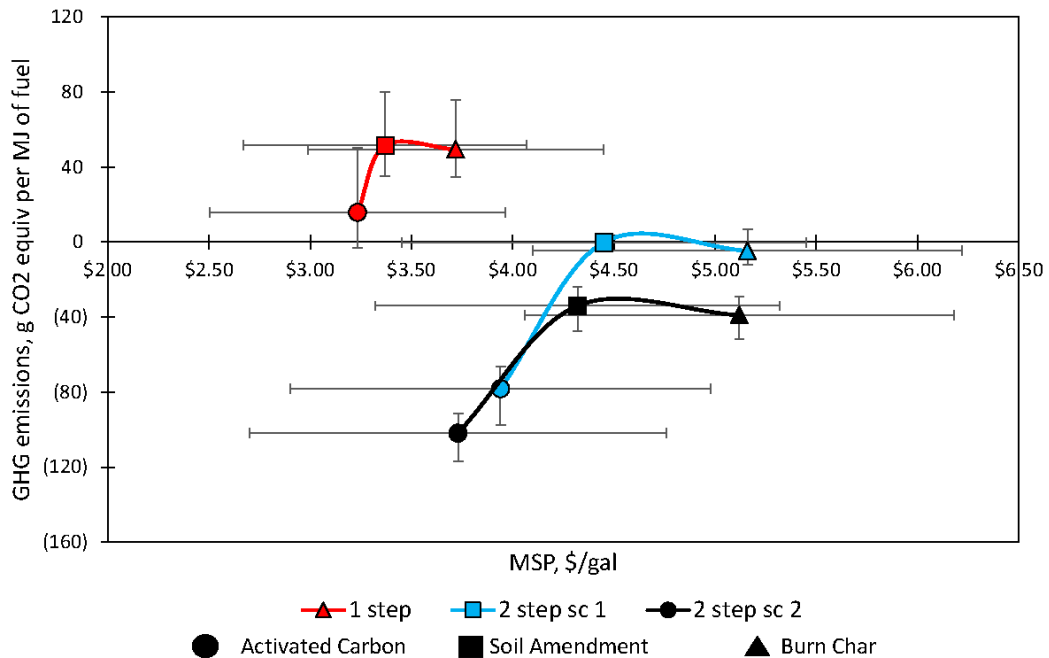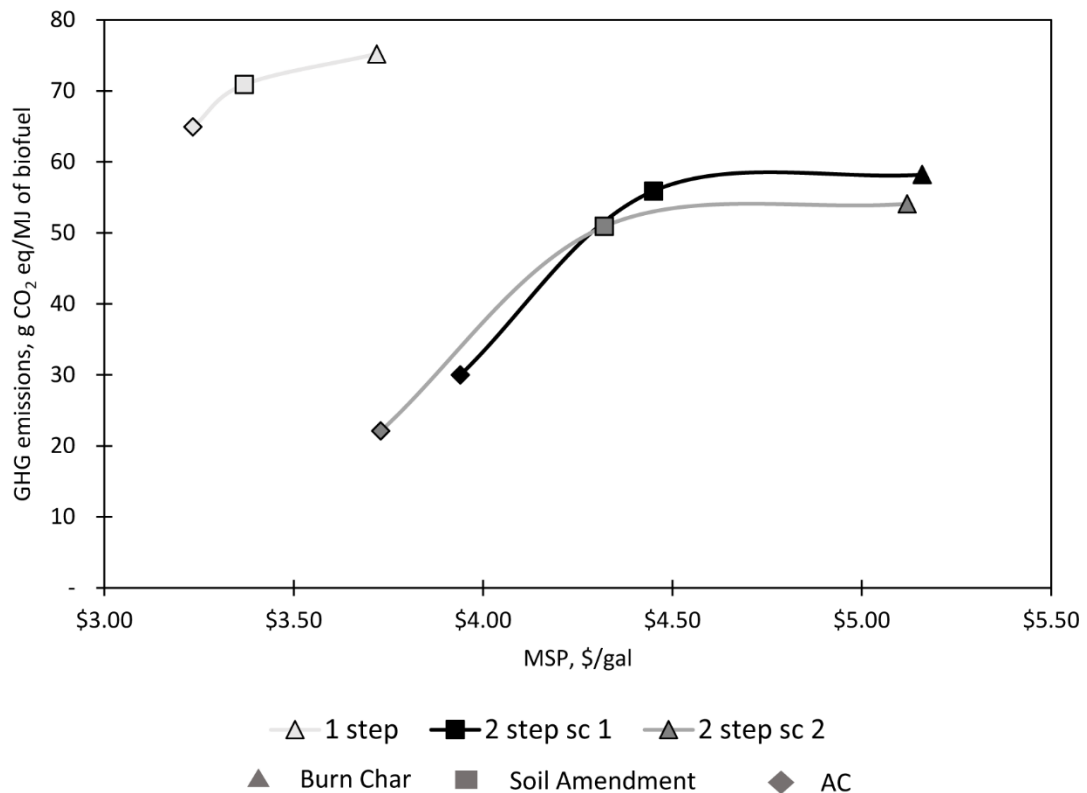

Figure 5.7. Trade-off plot for all scenarios with heat integration showing the effect of different co-products from biochar for value allocation method.

5.5 Effect of Using Biochar as a Substitute for Natural Gas Instead of Coal

A last scenario was run to analyze the effect of using biochar as a substitute for natural gas instead of coal. However, natural gas is often the marginal source of electricity, and thus using coal may overstate the economic and environmental benefit of burning biochar. The 2-step pathway scenario 2 was run to compare the effect of the two substitutes. Using biochar as a substitute for natural gas instead of coal for 2 step sc 2 Burn HI that has the highest amount of biochar increases the MSP from $5.12/gal to $5.15/gal and the GHG emissions from -38.9 to -32.8 gCO_2eq/MJ. This difference is minimal compared to the error of this preliminary study and does not affect the trade-off trends discussed above.

6 Conclusions and Recommendations for Future Work

This thesis research investigated the sustainability of biofuel production through two pathways: a one-step fast pyrolysis of biomass and a two-step torrefaction-fast pyrolysis of biomass, using the product's minimum selling price and life cycle GHG emissions of the pathways as the indicators for sustainability. This research examined the impact of different uses of by-products and heat integration on these sustainability indicators.

The TEA sensitivity analysis results obtained show how sensitive the economic and environmental impacts are to the yield of biofuel. Extensive study and experiments on the fast pyrolysis of woody biomass are necessary to decrease the uncertainty on the yield of biofuel before broad conclusions can be drawn on the cost competitiveness of proposed innovative technologies.

One way to decrease the biofuel yield's uncertainty is through the development of kinetic models. The kinetic models would give better insight in the torrefaction, fast pyrolysis, hydrotreatment reactors, and activated carbon reactors, showing how reaction temperature and residence time can affect product distribution and species concentrations. This could result in more accurate economic and environmental impact assessments. The knowledge of how reaction temperature and residence time affect the biofuel yield and composition would also allow the determination of optimal process conditions for the best economic or environmental result.

Further research into the fertilizer and emission benefits of soil amendment is also needed to fully understand the environmental benefits of using biochar as a soil amendment. Currently research is lacking into the length of time the benefits last for, with it being unknown whether soil amendment provides fertilizer and emission decreases after the first year. In this research this uncertainty was addressed through the use of several cases analyzing how different lengths of time affected the environmental result. Further research would decrease this uncertainty of the environmental benefits of soil amendment.

In summary, this research conducted a model-based life cycle carbon footprint analysis and techno-economic analysis hydrocarbon biofuel production and use from one- and two-step pyrolysis of poplar logging residues with catalytic upgrading. The main objective was to better understand the effects of co-product char uses on the TEA and LCA results on GHG emissions, recognizing that by including other important environmental indicators, the results and conclusions may be different. In conclusion, the economic and environmental performance of hydrocarbon biofuel production is enhanced greatly by biochar use as a high value product compared to its use as an energy carrier displacing fossil coal. Processing biochar into activated carbon decreases the MSP of biofuel to $3.23 per gallon while providing climate change mitigation benefits. Heat integration creates more favorable economics and reduces GHG emissions of the hydrocarbon biofuel pathway by reducing MSP by about $0.80/gal and decreases the GHG emissions about 70 g CO_2 eq. / MJ. The inclusion of torrefaction prior to pyrolysis

increased the MSP of the biofuel, but decreased the environmental burden of the biofuel. This economic-environmental tradeoff with the 2-step pathway may be mitigated through policy incentives or a market price on carbon emissions.

7 Reference List

(1)   Andress, D.; Nguyen, T. D.; Das, S. Reducing GHG emissions in the United States' transportation sector. *Energy for Sustainable Development* **2011,** *15* (2), 117-136.

(2)   U.S. Department of Energy. 2011. U.S. Billion-Ton Update: Biomass Supply for a Bioenergy and Bioproducts Industry. R.D. Perlack and B.J. Stokes (Leads), ORNL/TM-2011/224. Oak Ridge National Laboratory, Oak Ridge, TN. 227p.

(3)   Kole, C.; Joshi, C. P.; Shonnard, D. R. *Handbook of bioenergy crop plants*, ed.; CRC Press, 2012.

(4)   Bailey, A.; Leong, G. J.; Fitzgerald, N. *Bioproducts to Enable Biofuels Workshop Summary Report*; Report No. 2015.

(5)   Winjobi, O. Techno-economic and life cycle assessments of biofuel production from woody biomass through torrefaction-fast pyrolysis and catalytic upgrading. PhD Dissertation, Michigan Technological University, **2017.**

(6)   Blackwell, P.; Riethmuller, G.; Collins, M. Biochar application to soil. *Biochar for environmental management: science and technology* **2009,** *1*, 207-226.

(7)   Gu, Z.; Wang, X. Carbon materials from high ash bio-char: a nanostructure similar to activated graphene. *Am. Trans. Eng. Appl. Sci* **2013,** *2* (1), 15-34.

(8)   Huang, Y.-F.; Syu, F.-S.; Chiueh, P.-T.; Lo, S.-L. Life cycle assessment of biochar cofiring with coal. *Bioresource technology* **2013,** *131*, 166-171. DOI 10.1016/j.biortech.2012.12.123

(9)   Roberts, K. G.; Gloy, B. A.; Joseph, S.; Scott, N. R.; Lehmann, J. Life cycle assessment of biochar systems: estimating the energetic, economic, and climate change potential. *Environmental science & technology* **2009,** *44* (2), 827-833. DOI 10.1021/es902266r

(10)   del Campo, B. G. Production of activated carbon from fast pyrolysis biochar and the detoxification of pyrolytic sugars for ethanol fermentation. PhD Dissertation, Iowa State University, **2015.**

(11)   Arena, N.; Lee, J.; Clift, R. Life Cycle Assessment of activated carbon production from coconut shells. *Journal of Cleaner Production* **2016,** *125*, 68-77. DOI 10.1016/j.jclepro.2016.03.073

(12)   Phanphanich, M.; Mani, S. Impact of torrefaction on the grindability and fuel characteristics of forest biomass. *Bioresource technology* **2011,** *102* (2), 1246-1253. DOI 10.1016/j.biortech.2010.08.028

(13)   Winjobi, O.; Zhou, W.; Kulas, D.; Nowicki, J.; Shonnard, D. R. Production of
Hydrocarbon Fuel using Two-Step Torrefaction and Fast Pyrolysis of Pine. Part 2:
Life-Cycle Carbon Footprint. *ACS Sustainable Chemistry & Engineering* **2017**,
DOI 10.1021/acssuschemeng.7b00373.

(14)   Wang, M. The greenhouse gases, regulated emissions, and energy use in
transportation (GREET) model: Version 1.5. *Center for Transportation Research,
Argonne National Laboratory* **2008**.

(15)   Arias, B.; Pevida, C.; Fermoso, J.; Plaza, M. G.; Rubiera, F.; Pis, J. Influence of
torrefaction on the grindability and reactivity of woody biomass. *Fuel Processing
Technology* **2008,** *89* (2), 169-175. DOI 10.1016/j.jclepro.2016.03.073

(16)   Boateng, A.; Mullen, C. Fast pyrolysis of biomass thermally pretreated by
torrefaction. *Journal of Analytical and Applied Pyrolysis* **2013,** *100*, 95-102. DOI
10.1016/j.jaap.2012.12.002

(17)   Ru, B.; Wang, S.; Dai, G.; Zhang, L. Effect of torrefaction on biomass
physicochemical characteristics and the resulting pyrolysis behavior. *Energy &
Fuels* **2015,** *29* (9), 5865-5874. DOI 10.1021/acs.energyfuels.5b01263

(18)   Klemetsrud, B.; Ukaew, S.; Thompson, V. S.; Thompson, D. N.; Klinger, J.; Li,
L.; Eatherton, D.; Puengprasert, P.; Shonnard, D. Characterization of products
from fast micropyrolysis of municipal solid waste biomass. *ACS Sustainable
Chemistry & Engineering* **2016,** *4* (10), 5415-5423. DOI
10.1021/acssuschemeng.6b00610

(19)   Klemetsrud, B.; Eatherton, D.; Shonnard, D. Effects of Lignin Content and
Temperature on the Properties of Hybrid Poplar Bio-Oil, Char, and Gas Obtained
by Fast Pyrolysis. *Energy & Fuels* **2017,** *31* (3), 2879-2886. DOI
10.1021/acs.energyfuels.6b02836

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

(21)   Bridgwater, A.; Toft, A.; Brammer, J. A techno-economic comparison of power
production by biomass fast pyrolysis with gasification and combustion.
Renewable and Sustainable Energy Reviews **2002,** *6* (3), 181-246.

(22)   Neupane, S.; Adhikari, S.; Wang, Z.; Ragauskas, A.; Pu, Y. Effect of torrefaction
on biomass structure and hydrocarbon production from fast pyrolysis. *Green
Chemistry* **2015,** *17* (4), 2406-2417. DOI 10.1039/C4GC02383H

(23)   Fivga, A. Comparison of the effect of pre-treatment and catalysts on liquid quality
from fast pyrolysis of biomass Aston University, 2012.

(24)   Winjobi, O.; Shonnard, D. R.; Zhou, W. Production of Hydrocarbon Fuel Using
         Two-Step Torrefaction and Fast Pyrolysis of Pine. Part 1: Techno-economic
         Analysis. *ACS Sustainable Chemistry & Engineering* **2017,** *5* (6), 4529-4540.
         DOI 10.1021/acssuschemeng.7b00372

(25)   He, Z.; Wang, X. Hydrodeoxygenation of model compounds and catalytic
         systems for pyrolysis bio-oils upgrading. *Catalysis for sustainable energy* **2012,**
         1, 28-52. DOI 10.2478/cse-2012-0004

(26)   Zacher, A. H.; Olarte, M. V.; Santosa, D. M.; Elliott, D. C.; Jones, S. B. A review
         and perspective of recent bio-oil hydrotreating research. *Green Chemistry* **2014,**
         16 (2), 491-515. DOI 10.1039/C3GC41382A

(27)   Furimsky, E. Catalytic hydrodeoxygenation. *Applied Catalysis A: General* **2000,**
         199 (2), 147-190. DOI 10.1016/S0926-860X(99)00555-4

(28)   Odebunmi, E. O.; Ollis, D. F. Catalytic hydrodeoxygenation: I. Conversions of o-,
         p-, and m-cresols. *Journal of Catalysis* **1983,** *80* (1), 56-64. DOI 10.1016/0021-
         9517(83)90229-4

(29)   Vispute, T. Pyrolysis oils: characterization, stability analysis, and catalytic
         upgrading to fuels and chemicals. **2011**.

(30)   Winjobi, O.; Zhou, W.; Shonnard, D. R. Production of Hydrocarbon Fuel using
         Two-Step Torrefaction and Fast Pyrolysis of Pine. Part 1: Techno-economic
         Analysis *ACS Sustainable Chemistry & Engineering* **2017**,
         DOI:10.1021/acssuschemeng.7b00372 10.1021/acssuschemeng.7b00372.

(31)   Peters, J. F.; Iribarren, D.; Dufour, J. Biomass pyrolysis for biochar or energy
         applications? A life cycle assessment. *Environmental science & technology* **2015,**
         49 (8), 5195-5202. DOI 10.1021/es5060786

(32)   Jones, S. B.; Meyer, P. A.; Snowden-Swan, L. J.; Padmaperuma, A. B.; Tan, E.;
         Dutta, A.; Jacobson, J.; Cafferty, K. *Process design and economics for the
         conversion of lignocellulosic biomass to hydrocarbon fuels: fast pyrolysis and
         hydrotreating bio-oil pathway*; Report No. 2013.

(33)   The Engineering ToolBox. Standard Grade Coal - Heating Values. Source:
         https://www.engineeringtoolbox.com/coal-heating-values-d_1675.html

(34)   Bahrton, A.; Horowitz, G.; Cerrella, G.; Bonelli, P.; Cassanello, M.; Cukierman,
         A. Fourth Biomass Conference of the Americas, 1999; p 549-554.

(35)   Desotec. Granular Activated Carbon (GAC). Source:
         https://www.desotec.com/en/carbonology/carbonology-academy/granular-
         activated-carbon-gac

(36)   O'Donnell, B. R.; Hickner, M. A.; Barna, B. A. Economic Risk Analysis: Using Analytical and Monte Carlo Techniques. *Chemical Engineering Education* **2002,** *36* (2), 94-99.

(37)   Towler, G.; Sinnott, R. K. *Chemical engineering design: principles, practice and economics of plant and process design*, ed.; Elsevier, 2012.

(38)   U.S. Energy Information Administration. Daily Prices in Energy. Source: https://www.eia.gov/todayinenergy/prices.php

(39)   Hunt, J.; Biohar Price Sheet. Pacific Biochar, 2017. Source: https://pacificbiochar.com/biochar-price-sheet/

(40)   Short-Term Energy Outlook. U.S. Energy Information Administration, **2017**. Source: https://www.eia.gov/outlooks/steo/

(41)   Major Land Uses. United States Department of Agriculture, **2012**. Source: https://www.ers.usda.gov/data-products/major-land-uses/major-land-uses/#Cropland

(42)   Global and China Activated Carbon Industry Report 2017-2021. *Research and Markets* **2017**.

(43)   Wigley, T. B. Improving the quality of bio-oil by fast pyrolysis of acid leached and torrefied Pinus radiata. **2015**.

(44)   Westerhof, R. J.; Brilman, D. W. F.; Garcia-Perez, M.; Wang, Z.; Oudenhoven, S. R.; Kersten, S. R. Stepwise fast pyrolysis of pine wood. *Energy & fuels* **2012,** *26* (12), 7263-7273. DOI 10.1021/ef301319t

(45)   Weidema, B.; Wenzel, H.; Petersen, C.; Hansen, K. The product, functional unit and reference flows in LCA. *Environmental News* **2004,** *70*, 1-46.

(46)   Shonnard, D.; Solomon, B. Special Issue on Pan American Biofuel and Bioenergy Sustainability. *Springer* **2015**.

(47)   Owens, J. Life-cycle assessment: Constraints on moving from inventory to impact assessment. *Journal of industrial ecology* **1997,** *1* (1), 37-49. DOI 10.1162/jiec.1997.1.1.37

(48)   Brack, D. Woody Biomass for Power and Heat: Impacts on the Global Climate. *Environment, Energy and Resources Department, Chatham House, February* **2017**.

(49)   Wildschut, J.; Arentz, J.; Rasrendra, C.; Venderbosch, R.; Heeres, H. Catalytic hydrotreatment of fast pyrolysis oil: model studies on reaction pathways for the

carbohydrate fraction. *Environmental progress & sustainable energy* **2009,** *28* (3), 450-460. DOI 10.1002/ep.10390

(50)   Snowden-Swan, L. J.; Spies, K. A.; Lee, G.; Zhu, Y. Life cycle greenhouse gas emissions analysis of catalysts for hydrotreating of fast pyrolysis bio-oil. *Biomass and Bioenergy* **2016,** *86*, 136-145. DOI 10.1016/j.biombioe.2016.01.019

(51)   Benavides, P. T.; Cronauer, D. C.; Adom, F.; Wang, Z.; Dunn, J. B. The influence of catalysts on biofuel life cycle analysis (LCA). *Sustainable Materials and Technologies* **2017,** *11*, 53-59. DOI 10.1016/j.susmat.2017.01.002

(52)   Abdullah, H.; Wu, H. Biochar as a fuel: 1. Properties and grindability of biochars produced from the pyrolysis of mallee wood under slow-heating conditions. *Energy & Fuels* **2009,** *23* (8), 4174-4181. DOI 10.1021/ef900494t

(53)   Alhashimi, H. A.; Aktas, C. B. Life cycle environmental and economic performance of biochar compared with activated carbon: A meta-analysis. *Resources, Conservation and Recycling* **2017,** *118*, 13-26. DOI 10.1016/j.resconrec.2016.11.016

(54)   Steiner, C.; Glaser, B.; Geraldes Teixeira, W.; Lehmann, J.; Blum, W. E.; Zech, W. Nitrogen retention and plant uptake on a highly weathered central Amazonian Ferralsol amended with compost and charcoal. *Journal of Plant Nutrition and Soil Science* **2008,** *171* (6), 893-899. DOI 10.1002/jpln.200625199

(55)   Fertilizer Use and Price. United States Department of Agriculture, 2013. Source: https://www.ers.usda.gov/data-products/fertilizer-use-and-price/

(56)   Yanai, Y.; Toyota, K.; Okazaki, M. Effects of charcoal addition on N2O emissions from soil resulting from rewetting air-dried soil in short-term laboratory experiments. *Soil Science & Plant Nutrition* **2007,** *53* (2), 181-188. DOI 10.1111/j.1747-0765.2007.00123.x

(57)   Van Zwieten, L.; Singh, B.; Joseph, S.; Kimber, S.; Cowie, A.; Chan, K. Y. Biochar and emissions of non-CO2 greenhouse gases from soil. *Biochar for environmental management: science and technology* **2009,** *1*, 227-250.

(58)   Cowie, A. L.; Cowie, A. J.; Solutions, R. C. Life cycle assessment of greenhouse gas mitigation benefits of biochar. *Report to IEA Bioenergy Task* **2013,** *38*, 136-145.

(59)   Calgo Carbon Corporation, C. C. Investor Presentation. **2011**. Source: http://www.getfilings.com/sec-filings/110329/CALGON-CARBON-CORPORATION_8-K/l42277exv99w1.htm

(60)   Weidema, B. P.; Wesnaes, M. S. Data quality management for life cycle inventories—an example of using data quality indicators. *Journal of cleaner production* **1996,** *4* (3-4), 167-174. DOI 10.1016/S0959-6526(96)00043-1

8 Cash Flow Table

Table 8.1. Cash flow table for 2 step sc 1 with activated carbon and heat integration.

YEAR j	INV (FCI)	WC 0.05*(FCI)	Working Time %	Production Rate kg/yr	Producton rate kg/yr, adjusted	EXP (CCOP) (FCOP)	EXP (CCOP) (VCOP)	DEPR	ICF (Infl)	(1+i)$^{-i}$ 10%	NPV with inflation
0	$ -	-	-	-	-	-	-	-	$ -	1.00	$ -
1	$ 181,645,463	-	-	-	-	-	-	-	$ (181,645,463)	0.91	$ (181,645,463)
2	$ 302,742,439	-	-	-	-	-	-	-	$ (302,742,439)	0.83	$ (302,742,439)
3	$ 121,096,975	$ 30,274,244	50%	47,796,265	23,341,527	$ 23,017,915	$ (7,371,020)	$ 86,523,789	$ (131,258,375)	0.75	$ (133,307,777)
4	-	-	90%	86,033,276	38,195,225	$ 23,017,915	$ (13,267,836)	$ 148,283,246	$ 45,561,585	0.68	$ 31,119,176
5	-	-	100%	95,592,529	38,581,036	$ 23,017,915	$ (14,742,040)	$ 105,899,305	$ 31,685,438	0.62	$ 19,674,164
6	-	-	100%	95,592,529	35,073,669	$ 23,017,915	$ (14,742,040)	$ 75,625,061	$ 21,089,453	0.56	$ 11,904,446
7	-	-	100%	95,592,529	31,885,154	$ 23,017,915	$ (14,742,040)	$ 54,069,800	$ 13,545,111	0.51	$ 6,950,784
8	-	-	100%	95,592,529	28,986,503	$ 23,017,915	$ (14,742,040)	$ 54,009,251	$ 13,523,919	0.47	$ 6,309,008
9	-	-	100%	95,592,529	26,351,367	$ 23,017,915	$ (14,742,040)	$ 54,069,800	$ 13,545,111	0.42	$ 5,744,449
10	-	-	100%	95,592,529	23,955,788	$ 23,017,915	$ (14,742,040)	$ 27,004,626	$ 4,072,300	0.39	$ 1,570,048
11	-	-	100%	95,592,529	21,777,989	$ 23,017,915	$ (14,742,040)	-	$ (5,379,319)	0.35	$ (1,885,418)
12	-	-	100%	95,592,529	19,798,172	$ 23,017,915	$ (14,742,040)	-	$ (5,379,319)	0.32	$ (1,714,017)
13	-	-	100%	95,592,529	17,998,338	$ 23,017,915	$ (14,742,040)	-	$ (5,379,319)	0.29	$ (1,558,197)
14	-	-	100%	95,592,529	16,362,125	$ 23,017,915	$ (14,742,040)	-	$ (5,379,319)	0.26	$ (1,416,543)
15	-	-	100%	95,592,529	14,874,659	$ 23,017,915	$ (14,742,040)	-	$ (5,379,319)	0.24	$ (1,287,766)
16	-	-	100%	95,592,529	13,522,418	$ 23,017,915	$ (14,742,040)	-	$ (5,379,319)	0.22	$ (1,170,696)
17	-	-	100%	95,592,529	12,293,107	$ 23,017,915	$ (14,742,040)	-	$ (5,379,319)	0.20	$ (1,064,269)
18	-	-	100%	95,592,529	11,175,552	$ 23,017,915	$ (14,742,040)	-	$ (5,379,319)	0.18	$ (967,518)
19	-	-	100%	95,592,529	10,159,593	$ 23,017,915	$ (14,742,040)	-	$ (5,379,319)	0.16	$ (879,562)
20	-	-	100%	95,592,529	9,235,993	$ 23,017,915	$ (14,742,040)	-	$ 24,894,925	0.15	$ (799,601)

$ (547,167,191)

8.1 Cash Flow Table Abbreviations

Tax Rate, t=35%

Inflation, i=10%

INV - Capital Investment

FCI - Fixed Capital Investment

WC - Working Capital

DF - Discount Factor

EXP – Expense

CCOP – Cash Cost of Production

FCOP - Fixed Cost of Production

VCOP - Variable Cost of Production

ICF – Inflated Cash Flow

NPV- Net Present Value

DEPR - Depreciation

8.2 Cash Flow Equations

$$NPV = SICF*DF \qquad\qquad 8\text{-}1$$

$$DF = (1+i)^{-j} \qquad\qquad 8\text{-}2$$

$$ICF = INC\text{-}INV\text{-}WC\text{-}EXP\text{-}TAX \qquad\qquad 8\text{-}3$$

$$TAX = t*(INC\text{-}EXP\text{-}DEPR) \qquad\qquad 8\text{-}4$$

$$INC = PR*SP \qquad\qquad 8\text{-}5$$

Set NPV=0 and solve for SP

$$MSP = \Sigma[INV+WC+DF*((1\text{-}t)*EXP+t*DEPR)]/\Sigma[DF*PR*(1\text{-}t)] \qquad\qquad 8\text{-}6$$

9 Input Tables for Inventory Analysis

A list of products and inputs of materials and energy are included in Tables H1 on the basis of 1 MJ of hydrocarbon biofuel produced. The names of ecoprofiles selected in the LCA software SimaPro are also listed in the input table. Table 9.1 shows the inputs for the one-step pathway for burning char to displace coal and processing biochar to produce activated carbon, both with and without heat integration. Table 9.2 shows the same cases for scenario 1 with the two-step fast pyrolysis pathway and Table 9.3 shows the input data for scenario 2 for the two-step pathway. The input data for using biochar as a soil amendment is not shown as all the material and energy inputs, other the displacement credit for biochar, are the same as for burning char to displace coal. The displacement credit for soil amendment is discussed in detail in 4.1.5.3.3 Soil Amendment Scenarios and Results.

Table 9.1. Inputs including ecoprofile names, for one-step hydrocarbon biofuel production from poplar.

Products	Burn char With HI	Burn char No HI	Activated Carbon With HI	Activated Carbon No HI	Unit
Hydrocarbon biofuel	1	1	1	1	MJ
Biochar	0.009	0.009	0.009	0.009	kg
Activated Carbon	0	0	0.006	0.006	kg
Fossil CO_2 (from combustion of H_2 production off-gas)	0.025	0.025	0.011	0.011	kg
Steam (displaces natural gas generated steam)	0	0.051	0	0.047	kg
Material Inputs					
Poplar (8 % moisture content)	0.103	0.103	0.103	0.103	kg
Process water, ion exchange, production mix, at plant, from surface water RER S[a] (to generate steam for hydrogen production)	0.045	0.045	0.052	0.052	kg
Natural gas, from high pressure network (1-5 bar), at service station/US* US-EI U[a] (for hydrogen production)	0.009	0.009	0.004	0.004	kg
Water, completely softened, at plant[a] (cooling water, pyrolysis stage)	0.88	4.56	0.78	4.56	kg
Water, completely softened, at plant[a] (cooling water, hydrotreatment stage)	2.55	5.49	2.58	5.49	kg

Water, completely softened, at plant[a] (cooling water, hydrogen production stage)	1.54	5.65	0.48	6.46	kg
Water, completely softened, at plant[a] (cooling water, activated carbon production stage)	0	0	0	0.75	kg
Process Energy Inputs or Outputs (negative values)					
Electricity, medium voltage US[a] (size reduction)	0.034	0.034	0.034	0.034	kWh
Electricity, medium voltage US[a] (hydrotreatment)	0.004	0.004	0.004	0.004	kWh
Electricity, medium voltage US[a] (hydrogen production)	0.010	0.010	0.010	0.010	kWh
Electricity, medium voltage US[a] (activated carbon production)	0	0	0.005	0.005	kWh
Natural gas, burned in industrial furnace low-NOx> 100kW[a] (biomass drying)	0	0.064	0	0.064	MJ
Natural gas, burned in industrial furnace low-NOx> 100kW[a] (pyrolysis)	0	0.269	0	0.269	MJ
Natural gas, burned in industrial furnace low-NOx> 100kW[a] (hydrotreatment)	0	0.182	0	0.174	MJ
Natural gas, burned in industrial furnace low-NOx> 100kW[a] (hydrogen production)	0	0.060	0	0.170	MJ
Natural gas, burned in industrial furnace low-NOx> 100kW[a] (activated carbon production)	0	0	0	0.060	MJ
Bituminous coal, combusted in industrial boiler NREL/US[a]	-0.008	-0.008	-0.008	0	kg
Natural gas, burned in industrial furnace low-NOx> 100kW[a] (off-gas)	0	0	0	0	MJ
Steam, for chemical processes, at plant/US-US-EI U[a]	0	-0.041	0	-0.038	kg

a – Ecoinvent profile names in SimaPro®

Table 9.2. Inputs including ecoprofile names, for scenario 1 of two-step hydrocarbon biofuel production from poplar.

Products	Burn char With HI	Burn char No HI	Activated Carbon With HI	Activated Carbon No HI	Unit
Hydrocarbon biofuel	1	1	1	1	MJ
Biochar	0.019	0.019	0.019	0.019	kg
Activated Carbon	0	0	0.012	0.012	kg
Fossil CO_2 (from combustion of H_2 production off-gas)	0.024	0.024	0	0	kg
Steam (displaces natural gas generated steam)	0	0.054	0.037	0.037	kg
Material Inputs					
Poplar (8 % moisture content)	0.147	0.147	0.147	0.147	kg
Process water, ion exchange, production mix, at plant, from surface water RER S[a] (to generate steam for hydrogen production)	0.044	0.044	0.040	0.040	kg
Natural gas, from high pressure network (1-5 bar), at service station/US* US-EI U[a] (for hydrogen production)	0.009	0.009	0	0	kg
Water, completely softened, at plant[a] (cooling water, torrefaction stage)	0.037	1.19	0.49	1.19	kg
Water, completely softened, at plant[a] (cooling water, pyrolysis stage)	0.70	6.07	0.31	6.07	kg
Water, completely softened, at plant[a] (cooling water, hydrotreatment stage)	2.17	8.20	0.73	8.20	kg
Water, completely softened, at plant[a] (cooling water, hydrogen production stage)	2.64	5.75	0.77	5.79	kg
Water, completely softened, at plant[a] (cooling water, activated carbon production stage)	0	0	0	1.53	kg
Process Energy Inputs or Outputs (negative values)					
Electricity, medium voltage US[a] (size reduction)	0.006	0.006	0.006	0.006	kWh

Electricity, medium voltage US[a] (hydrotreatment)	0.005	0.005	0.005	0.005	kWh
Electricity, medium voltage US[a] (hydrogen production)	0.013	0.013	0.012	0.012	kWh
Electricity, medium voltage US[a] (activated carbon production)	0	0	0.011	0.011	kWh
Natural gas, burned in industrial furnace low-NOx> 100kW[a] (biomass drying)	0	0.093	0	0.093	MJ
Natural gas, burned in industrial furnace low-NOx> 100kW[a] (torrefaction)	0	0.055	0	0.055	MJ
Natural gas, burned in industrial furnace low-NOx> 100kW[a] (pyrolysis)	0	0.200	0	0.200	MJ
Natural gas, burned in industrial furnace low-NOx> 100kW[a] (hydrotreatment)	0	0.281	0	0.281	MJ
Natural gas, burned in industrial furnace low-NOx> 100kW[a] (hydrogen production)	0	0.023	0	0.035	MJ
Natural gas, burned in industrial furnace low-NOx> 100kW[a] (activated carbon production)	0	0	0.070	0.111	MJ
Bituminous coal, combusted in industrial boiler NREL/US[a]	-0.018	-0.018	0	0	kg
Natural gas, burned in industrial furnace low-NOx> 100kW[a] (off-gas)	-0.108	0	-0.070	0	MJ
Steam, for chemical processes, at plant/US-US-EI U[a]	0	-0.043	-0.029	-0.029	kg

a – Ecoinvent profile names in SimaPro®

Table 9.3. Inputs including ecoprofile names, for scenario 2 of two-step hydrocarbon biofuel production from poplar.

Products	Burn char With HI	Burn char No HI	Activated Carbon With HI	Activated Carbon No HI	Unit
Hydrocarbon biofuel	1	1	1	1	MJ
Biochar	0.022	0.007	0.022	0.022	kg
Activated Carbon	0	0	0.013	0.013	kg
Fossil CO_2 (from combustion of H_2 production off-gas)	0.023	0.023	0	0	kg
Steam (displaces natural gas generated steam)	0	0.059	0.033	0.033	kg
Material Inputs					
Poplar (8 % moisture content)	0.163	0.163	0.163	0.163	kg
Process water, ion exchange, production mix, at plant, from surface water RER S[a] (to generate steam for hydrogen production)	0.038	0.038	0.038	0.038	kg
Natural gas, from high pressure network (1-5 bar), at service station/US* US-EI U[a] (for hydrogen production)	0.009	0.009	0	0	kg
Water, completely softened, at plant[a] (cooling water, torrefaction stage)	0.64	1.32	0.36	1.32	kg
Water, completely softened, at plant[a] (cooling water, pyrolysis stage)	0.30	6.71	0.27	6.71	kg
Water, completely softened, at plant[a] (cooling water, hydrotreatment stage)	2.25	5.57	0.72	5.57	kg
Water, completely softened, at plant[a] (cooling water, hydrogen production stage)	0.66	4.81	0.70	5.25	kg
Water, completely softened, at plant[a] (cooling water, activated carbon production stage)	0	0	0	1.69	kg
Process Energy Inputs or Outputs (negative values)					
Electricity, medium voltage US[a] (size reduction)	0.006	0.006	0.006	0.006	kWh

Electricity, medium voltage US[a] (hydrotreatment)	0.003	0.003	0.003	0.003	kWh
Electricity, medium voltage US[a] (hydrogen production)	0.011	0.011	0.009	0.009	kWh
Electricity, medium voltage US[a] (activated carbon production)	0	0	0.012	0.012	kWh
Natural gas, burned in industrial furnace low-NOx> 100kW[a] (biomass drying)	0	0	0	0.100	MJ
Natural gas, burned in industrial furnace low-NOx> 100kW[a] (torrefaction)	0	0	0	0.063	MJ
Natural gas, burned in industrial furnace low-NOx> 100kW[a] (pyrolysis)	0	0	0	0.221	MJ
Natural gas, burned in industrial furnace low-NOx> 100kW[a] (hydrotreatment)	0	0	0	0.100	MJ
Natural gas, burned in industrial furnace low-NOx> 100kW[a] (hydrogen production)	0	0	0	0	MJ
Natural gas, burned in industrial furnace low-NOx> 100kW[a] (activated carbon production)	0	0	0	0.123	MJ
Bituminous coal, combusted in industrial boiler NREL/US[a]	-0.020	-0.006	0	0	kg
Natural gas, burned in industrial furnace low-NOx> 100kW[a] (off-gas)	-0.39	0	-0.046	0	MJ
Steam, for chemical processes, at plant/US-US-EI U[a]	0	-0.047	-0.026	-0.026	kg

a – Ecoinvent profile names in SimaPro®

10 Copyright Documentation

Figure 10.1. Copyright clearance for Chapters 1-6