Techno-economic analysis of hydrocarbon biofuels from poplar biomass

Jordan Crawford

A thesis

Submitted in partial fulfillment of the

Requirements for the degree of

Master of Science

University of Washington

2013

Committee:

Rick Gustafson (Chair)

Renata Bura

Fernando Resende

Sergey Rabotyagov

Program Authorized to Offer Degree:

School of Environmental and Forest Sciences

©Copyright 2013
Jordan Crawford

University of Washington

Abstract

Techno-economic analysis of hydrocarbon biofuels from poplar biomass

Jordan Thomas Crawford

Chair of the Supervisory Committee:
Professor of Forest Resources, Dr. Rick Gustafson
School of Environmental and Forest Sciences

Infrastructure compatible hydrocarbon biofuel that is proposed to qualify as renewable transportation fuel under the U.S. Energy Independence and Security Act of 2007 (EISA) and Renewable Fuel Standard (RFS2) is evaluated. The process uses hybrid poplar for feedstock, which undergoes dilute acid pretreatment and enzymatic hydrolysis. Sugars are fermented to acetic acid, which undergoes conversion to ethyl acetate, ethanol, ethylene, and finally a saturated hydrocarbon end product with yields of 330 liters of jet fuel per bone dry tonne feed. A lignin rich stream that is not fermented may either be burned for steam and electricity production, or gasified. During the biofuel production process, hydrogen gas is required in two unit operations and may be obtained by various methods including lignin gasification. Both technical and economic aspects of the biorefinery are analyzed, with a range of hydrogen sources considered. These include steam reforming of natural gas, gasification of lignin, and electrolysis of water using seasonal excess hydroelectric capacity in the U.S. Pacific Northwest. Cash operating costs are estimated to range from 0.67 to 0.89 USD per liter of jet fuel depending on facility capacity. Capacities of 95 to 570 million liters (25 to 150 million gallons) of polymer jet fuel per year are investigated, with capital investments in the range of 304 to 1,150 million USD. The production of alternative, intermediate products to jet fuel is briefly explored.

Table of Contents

Abstract iii
List of Tables v
List of Figures vi
1. Introduction 1
2. Hydrocarbon biofuel production 3
    2.1 Feedstock 3
    2.2 Conversion of hybrid poplar to acetic acid fermentation broth 4
    2.3 Converting fermentation broth to a hydrocarbon biofuel 6
    2.4 Hydrogen production 8
        2.4.1 Electrolysis of water 9
        2.4.2 Lignin gasification 10
        2.4.3 Natural gas steam reforming 13
        2.4.4 Scenario selection of biorefinery in combination with hydrogen production 14
3. Modeling 15
    3.1 Technical modeling 15
        3.1.1 Hybrid poplar to hydrocarbon biofuel model 15
        3.1.2 Lignin gasification model 18
        3.1.3 SMR model 21
    3.2 Economic modeling 22
        3.2.1 Capital expenses 22
        3.2.2 Operating expenses 23
        3.2.3 Discounted cash flow rate of return analysis 23
4. Results and discussion 24
    4.1 Process analysis 24
    4.2 Expense estimates 27
    4.3 Alternative products 30
5. Conclusions 31
6. Future work 33
References 34
Appendix A: Operational data from Aspen simulation A-1

List of Tables

Table 1. Cellulose, hemicellulose, and lignin content in poplar feedstock 4
Table 2. Compositional analysis of lignin, tar, and ash 10
Table 3. Summary of hydrogen production scenarios considered 15
Table 4. Hydrocarbon biofuel production reaction network 17
Table 5. Discounted cash flow analysis parameters 24
Table 6. Major biorefinery steam users 25
Table 7. Biorefinery electricity consumption by area 26
Table 8. Net biorefinery electricity 26
Table 9. Capital costs for 380 million liter/yr plant 27
Table 10. Capital costs of biorefineries of various capacity 28
Table 11. Cash operating cost and minimum fuel selling price for 380 million liter/yr plant 29
Table 12. Alternative products 31
Table A-1. RStoic reactor blocks in Aspen and reaction parameters A-1
Table A-2. Other key blocks in Aspen and simulation parameters A-3

List of Figures

Figure 1. Generalized flow diagram of biorefinery 6
Figure 2. Generalized steam plant for biorefinery 9
Figure 3. Generalized flow diagram of lignin gasification process 13
Figure 4. Economies of scale of capital expense 28
Figure 5. Operating expense economies of scale 30

1. Introduction

In 2012, ethanol comprised 94% of U.S. biofuel production, most of which was derived from corn starch [1]. The same year, a study on the U.S. gasoline market shows it is already saturated with 10% ethanol blends, and that widespread use of blends higher than 10% such as E15 will require that existing infrastructure be upgraded or replaced [2]. It is apparent that producing additional ethanol for liquid transportation fuel may be undesirable. Producing infrastructure compatible hydrocarbon biofuels will avoid some of the problems associated with ethanol production in the U.S. If produced in an economically competitive manner, hydrocarbon biofuels have great potential to displace petroleum derived transportation fuels.

Techno-economic modeling is a useful tool to study the workings of capital projects. In short, techno-economics investigate the technical performance and economic potential of hypothetical scenarios. Analyses have been performed for various eco-friendly energy related projects, such as biodiesel production [3], hydrogen production [4], hydrogen sourced power generation [5], carbon dioxide capture from coal fired power plants [6], and fast pyrolysis of biomass for fuel and energy [7, 8]. The techno-economic field combines engineering and economics – a multi-disciplinary approach necessary for any technology to transition from research to industry.

Specifically when looking at transportation fuels, lignocellulosic ethanol production is the topic of many techno-economic analyses [9]. Feedstock choice affects techno-economic outcomes, as softwoods, hardwoods, and agricultural residues have different results in ethanol production [10]. Regarding enzymatic hydrolysis, simultaneous saccharification and fermentation, or separate hydrolysis and fermentation can be used [11]. Pretreatment is the subject of intense research with many competing technologies, such as dilute sulfuric acid, sulfur dioxide catalyzed steam

explosion, controlled pH, ammonia fiber expansion, or lime pretreatment [12]. After sugars are liberated from lignocellulosic material, the fermenting organism affects yields. A range of bacteria, yeasts, and fungi have been investigated, some naturally occurring and some recombinant, with respect to ethanol production from lignocellulosic hydrolysate [13]. The complex biofuels plant uses mechanical, biological, and chemical platforms in an effort to maximize yield from feedstock and minimize cost.

The goal of the present study is to first create a representative model of a unique biofuels production method. The biorefinery, so-called due to the multiple intermediate chemicals in the process stream, is envisioned as a near-term technology. As will later be described in detail, the process ferments acetic acid from hydrolyzed biomass sugars rather than ethanol, and through chemical conversion produces an ethanol intermediate and hydrocarbon biofuel end product. This techno-economic analysis agglomerates process information from the public domain, which is set into process simulation software Aspen Plus. Quantitative results are generated, including mass, energy, and work flows. This information is available for multiple uses besides material and energy balance checks. First, environmental analysis work such as life cycle assessment may follow, and second the results are used in economic analysis. The goals of economic analysis are to estimate both capital and operating expenses of the biorefinery. Economies of scale are investigated by using the techno-economic method to generate data for multiple capacity biorefineries. In this paper we analyze four different biorefineries with capacities of 95, 190, 380, and 570 million liters (25, 50, 100, and 150 million gallons) per year output.

2. Hydrocarbon biofuel production

The following section describes a biorefinery that we envision could become a commercial technology. The overall process is described with one process train in mind for the sake of analysis, even though certain unit operations could be changed. For example, one could use any number of pretreatment options. While this biorefinery is hypothetical, it represents a possible configuration for future commercial processes.

2.1 Feedstock

Short rotation woody crops, such as hybrid poplar, present an attractive option for diversifying and expanding biomass for biofuel production. Already used for various end-uses such as fuel wood, lumber, and paper, hybrid poplar is a well-established crop with good characteristics for biofuel use. In general, it requires little fertilizer input, can be cultivated on marginal lands, has the ability to resprout after multiple harvests, and has a high biomass production [14, 15, 16, 17]. The lignocellulosic material in the wood can also be fractionated without extensive pretreatment [18] and hardwoods do not exhibit the recalcitrance reported in softwoods [19].

Hybrid poplar is chosen as a feedstock for its good growing characteristics and ability to grow at a fast rate and in diverse geographical areas [20]. Yet another advantage of hybrid poplar is its ability to be harvested at any time of the year. This means the biomass is stored in the field, on the stump, so that it can be harvested when needed by the biorefinery. Just in time harvesting reduces both the need for storage infrastructure at the biorefinery, and biomass degradation that occurs during long-term storage. The composition assumed for biomass, which falls within ranges given in literature [20], entering the biorefinery is shown in Table 1. Other minor

components of the biomass include extractives (4.5% dry wt.), acetate (2.9% dry wt.), and ash (1.9% dry wt.). It is assumed that the biomass enters the biorefinery as 50% water by weight. Although other cellulosic biomass may theoretically be used in the biofuels process of interest, hybrid poplar serves as the model feedstock.

Table 1. Cellulose, hemicellulose, and lignin content in poplar feedstock, comprising 91 wt% of the biomass. Other minor components are given in text.

Cellulose (% dry wt.)	42.0
Hemicellulose (% dry wt.)	22.9
Lignin (% dry wt.)	25.8

2.2 Conversion of hybrid poplar to acetic acid fermentation broth

Starting with chipped hybrid poplar, the first section of the process ends with a dilute fermentation product stream created by fermenting hydrolyzed cellulosic sugars. These process steps are outlined in Fig. 1. Most of the steps are commonly modeled, with the exception that the fermentation product is usually ethanol instead of acetic acid [21, 22].

The first two unit operations, pretreatment and hydrolysis convert raw cellulosic biomass into fermentable sugars. A dilute acid pretreatment is used with 1.1 wt% sulfuric acid charge and temperature of 200 ºC. This is then cooled to temperatures suitable for enzymatic hydrolysis, near 50 ºC. 91% of the cellulose is converted to six carbon sugars by the addition of enzymes. All enzymes are purchased externally for this analysis rather than being produced within the biorefinery. Next, most of the insoluble solids, comprised chiefly of lignin, are separated from the liquid stream.

As opposed to some other cellulosic ethanol processes, an acetogenic bacterium is employed to ferment hydrolyzate rather than an ethanologen. The thermophilic bacteria anaerobically ferment 94% of glucose and 92% of xylose to acetic acid. In order to maintain an acceptable pH for fermentation, the acetate product is neutralized by the addition of calcium carbonate. A solution of about 5 wt% calcium acetate leaves in the fermentation broth. A final solid-liquid separation takes place to separate out bulk biomass, which may be performed with a cross-flow filtration system.

From a carbon perspective, the process is very efficient and maintains a high percentage of biomass carbon in the end product. *Moorella thermoacetica*, previously known as *Clostridium thermoaceticum*, ferments both five and six carbon sugars with acetate as the only product [23]. This compares to fermentation with *Saccharomyces cerevisiae*, where only two-thirds of the carbon in a molecule of glucose is kept in the ethanol product, and the remaining third is fermented to the greenhouse gas carbon dioxide. With the exception of cell reproduction, the acetogenic bacterium theoretically has 100% efficiency in maintaining the carbon in the process stream. Equation 1 shows the overall chemical equation to produce ethanol from sugar using an acetogen, and includes methane as a source of hydrogen (hydrogen consumption is discussed in ensuing sections.) On a molar sugar basis, the two fermentation pathways can be compared, showing that theoretical carbon dioxide emissions are 25% lower while ethanol yields are 50% higher using an acetogen instead of an ethanologen [Eq 2].

$$C_6H_{12}O_6 + 1.5\ CH_4 \rightarrow 3\ C_2H_5OH + 1.5\ CO_2 \quad \text{[Eq 1]}$$

$$C_6H_{12}O_6 \rightarrow 2\ C_2H_5OH + 2\ CO_2 \quad \text{[Eq 2]}$$

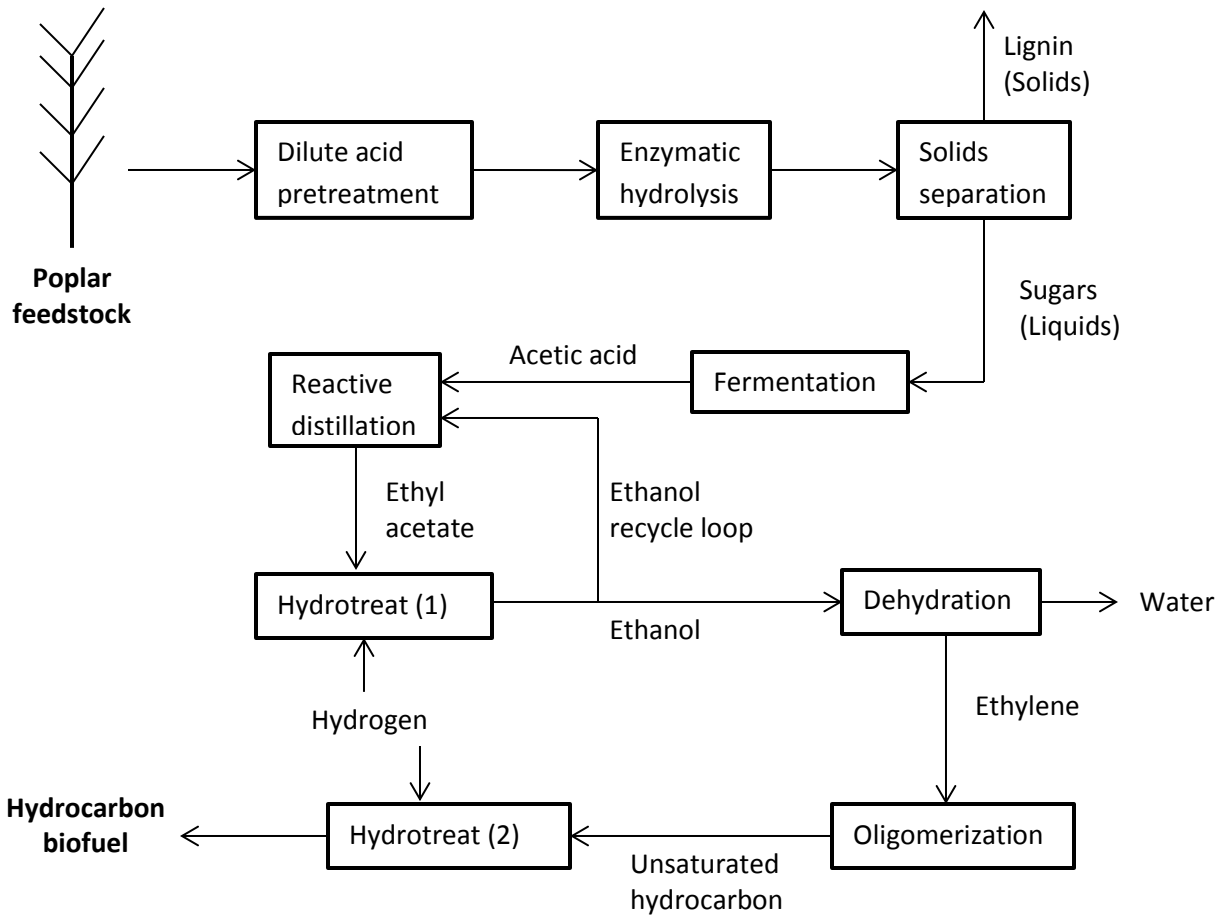

Fig. 1. Generalized flow diagram of biorefinery. This biorefinery ferments sugars to acetic acid instead of ethanol. Ethyl acetate, ethanol, and ethylene are major intermediate products towards a hydrocarbon, polymer jet fuel product. Yields are shown in Table 4.

2.3 Converting fermentation broth to a hydrocarbon biofuel

The second section in the process starts with acetic acid fermentation broth and converts it to several intermediates, including ethyl acetate, ethanol and ethylene, before finally ending with a hydrocarbon end product. These process steps are outlined in Fig. 1.

The reactive distillation unit operation plays a key role in the overall biorefinery. This unit operation combines two pieces of equipment, a reactor and a distillation column. The reaction of

interest is the creation of ethyl acetate from acetic acid and ethanol, which occurs in the middle, or reaction, section of the reactive distillation column. This reaction takes place at slightly acidic conditions by the addition of carbon dioxide, which forms calcium carbonate as the calcium acetate is protonated to form acetic acid. The bottom, or stripping section, leads to a reboiler. By constantly purging the reboiler, calcium carbonate that precipitates is removed from the system. In the top section, an azeotropic mixture of ethyl acetate, water, and ethanol is boiled off and condensed [24]. This azeotrope subsequently enters a high pressure distillation column as part of pressure swing distillation. The bottoms of the high pressure column contain a purified ethyl acetate stream, which is sent on to hydrogenation, while the tops contain an azeotrope with greater proportions of water and ethanol. The tops of the high pressure column enter the low pressure column operating under vacuum. Water exits the process stream in the bottoms of the low pressure column. The tops of the low pressure column contain ethanol and ethyl acetate, which is recycled to the reactive distillation column.

The ethyl acetate intermediate is hydrotreated, yielding two moles of ethanol for every one of the ester. This reaction occurs in the vapor phase, and achieves a high yield and selectivity. About half of the ethanol produced in the hydrogenation is recycled to the reactive distillation step, while the remaining half continues in the product stream.

In order to achieve a hydrocarbon from ethanol, the olefin ethylene is formed via the catalyzed dehydration reaction of ethanol. Next, compressed ethylene is dimerized to 1-butene. In the subsequent reactor, a 12 carbon jet fuel surrogate molecule is synthesized, still containing a carbon-carbon double bond. Finally, the unsaturated hydrocarbon is hydrotreated to a saturated end product. The hydrocarbon biofuel is water, sulfur, and nitrogen free. Overall yield is 330

liters of hydrocarbon jet biofuel per bone dry tonne (80 gallons per short ton) of hybrid poplar feedstock.

2.4 Hydrogen production

In production processes, many systems are integrally connected. Hydrogen production comprises a special case in the biorefinery of interest, and links with process heat, steam, and electricity production. Lignin is often a derivative product of ethanol production that is burned to produce process heat and steam [21, 22, 25]. However, this fraction of the biomass entering the biorefinery may be gasified to produce hydrogen, thereby maintaining a higher percentage of the biomass in the final fuel product. In a simplistic view, this is a prime solution for obtaining hydrogen, although in reality it may be overly optimistic. If lignin is gasified, there is then a lack of heating medium to produce process heat and steam. Various scenarios of hydrogen production, and therefore process heat and steam production are described herein. In all of the scenarios, one central burner-boiler system provides heat and steam for the entire biorefinery and hydrogen production facility. Steam is generated at 8,715 kPa and 510 ºC, and run through a turbine to produce lower temperature steam necessary for the process. In this way electricity is generated for biorefinery consumption. A generalized diagram of the steam system is shown in Figure 2.

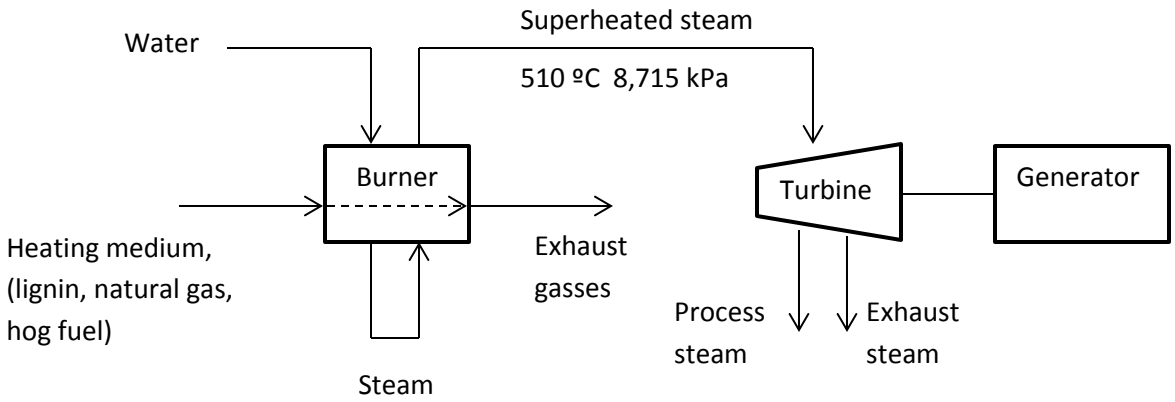

Fig. 2. Generalized steam plant for biorefinery. Various scenarios are considered for the source of the heating medium, including lignin, natural gas, and hog fuel. In all cases, the minimum amount of steam is generated that is required to run the biorefinery.

The hydrogen requirement in this biorefinery is a unique characteristic and provides many opportunities for optimization of the overall plant. Production can be achieved by any number of sources [26, 27, 28], however three hydrogen sources are initially considered for investigation: electrolysis of water using seasonal excess electricity in the U.S. Pacific Northwest (Section 2.4.1), lignin gasification (Secion 2.4.2), and natural gas steam reforming (Section 2.4.3).

2.4.1 Electrolysis of water

The U.S. Pacific Northwest traditionally has low electricity rates, due in part to the proportionally large amounts of hydro and wind power generation. The potential of these clean electricity sources to produce hydrogen can be realized through electrolysis. Based upon a 75% efficient electrolysis system, the amount of electricity required for hydrogen production is 52.5 kWh/kg gas [28,29].

While electrolysis has appealing aspects, especially with regard to carbon emissions, a preliminary calculation of the cost of hydrogen production shows that the overall process is

economically prohibitive. Even if electricity could be purchased at $0.03 per kWh, producing the required amount of hydrogen would be the equivalent of $0.20 per liter of hydrocarbon biofuel ($0.74 per gallon) in electricity expenses alone. Due to this high cost and the availability of other, more economically viable options, no further investigation of hydrogen production using electrolysis is performed.

2.4.2 Lignin gasification

Although studies have investigated gasification of whole biomass for hydrogen production [27, 30], there exists little information on lignin gasification. Using literature sources for guidance, a process model is created in Aspen to generate data on lignin gasification for hydrogen production via syngas composed of carbon monoxide, carbon dioxide, and hydrogen. As a starting point, the compositional analysis of lignin and tar, a gasification intermediate, are found as shown in Table 2 [31]. The lignin feed stream contains some carbohydrates as a result of the separations processes used in the biorefinery. An additional 4% of the dry lignin weight is carbohydrate, primarily cellulose with slight amounts of hemicellulose. Overall lignin feed to the gasification facility contains 50% moisture. A generalized block flow diagram of the lignin gasification process is shown in Figure 3.

Table 2. Compositional analysis of lignin, tar, and ash assumed to enter lignin gasification process [31]

Component	% C	% H	% O	% Ash	Empirical Formula
Lignin	59.1	2.9	6	3.1	$CH_{1.47}O_{0.51}$
Tar	66.2	7.45	26.4	-	$CH_{1.35}O_{0.3}$
Ash	-	-	-	100	-

Beginning the gasification process, the lignin feedstock is first dried from 50% to 10% moisture and preheated. The feedstock is then gasified with steam to produce 10 % char (solid carbon),

10 % tar, 2.9 % ash and 77.1 % gases. Steam is used as the gasification medium instead of oxygen or air since hydrogen is our only desired product. Gasification occurs at just above atmospheric pressure and 870 ºC. The amount of ammonia produced is negligible. Next, both char and ash are removed via a cyclone and combusted to recover heat for drying and preheating the lignin. The remaining gaseous product undergoes tar reforming to create a crude synthesis gas, or syngas. Syngas is a combination of hydrogen, carbon monoxide, and carbon dioxide.

The lignin and small amount of carbohydrates do not provide enough hydrogen required by the poplar to jet process. To account for the difference, a natural gas steam reformer is added to create additional syngas, which is mixed with the biomass based syngas stream. On a weight basis, the amount of natural gas added is equal to about 9% of the total incoming lignin and carbohydrate stream.

The mixed syngas stream is cooled and compressed to 3140 kPa and 50 ºC for further processing. A liquid phase redox system that utilizes a chelated iron solution (LO-CAT) removes hydrogen sulfide, which will poison water gas shift (WGS) reaction catalysts. It uses a readily available and regenerative catalyst and no toxic chemicals [32]. The sulfur content of lignin biomass is projected to much higher than conventional biomass due to the use of sulfur based chemicals in the biorefinery pretreatment process. However, LO-CAT alone cannot remove enough hydrogen sulfide to avoid water gas shift catalyst poisoning. Even at hydrogen sulfide concentrations as low as 0.1 ppm the catalysts might start to deactivate [27]. Thus a zinc oxide bed is used following the LO-CAT unit to further remove hydrogen sulfide from the gas stream.

High temperature (350 ºC) and low temperature (200 ºC) WGS reactors then convert most of the remaining carbon monoxide and steam into hydrogen gas and carbon dioxide. Catalysts are required for both high and low temperature reactors, consisting normally of iron oxide and chromium oxide, and copper oxide and zinc oxide respectively [27].

The resulting gases with low carbon monoxide content (roughly 70% hydrogen purity) is then cooled and demisted before entering a pressure swing adsorption (PSA) unit. It is essential to remove the entrained liquids (water and condensed hydrocarbons) because they will permanently damage the PSA adsorbent, which is a mixture of activated carbon and zeolite. It is also important that the gases are at a relatively lower temperature before entering the PSA column since the equilibrium capacity of a molecular sieve decreases with temperature and fewer impurities are adsorbed and removed. Purifying streams with original hydrogen purity less than 70% may decrease the resulting product purity and overall hydrogen recovery [27]. The purified hydrogen stream leaving the PSA unit contains 85% of the incoming hydrogen; there is an 85% recovery rate of the hydrogen. The molar purity of hydrogen gas produced is 99.9% or higher. The offgas, or reject stream of the PSA containing a majority of carbon dioxide along with other gases, is combusted in for heat energy recovery.

In total on a weight basis, about 91% of the feed for hydrogen production is from the lignin and carbohydrate stream. The balance, about 9%, is from natural gas. This compares to about 75% of the syngas being derived from the biomass, while about 25% is derived from natural gas. The overall yield is 0.073 - 0.076 kg of hydrogen per kilogram of total dry feed, which compares to 0.083 kg/kg for the gasification and processing of whole hybrid poplar chips [27].

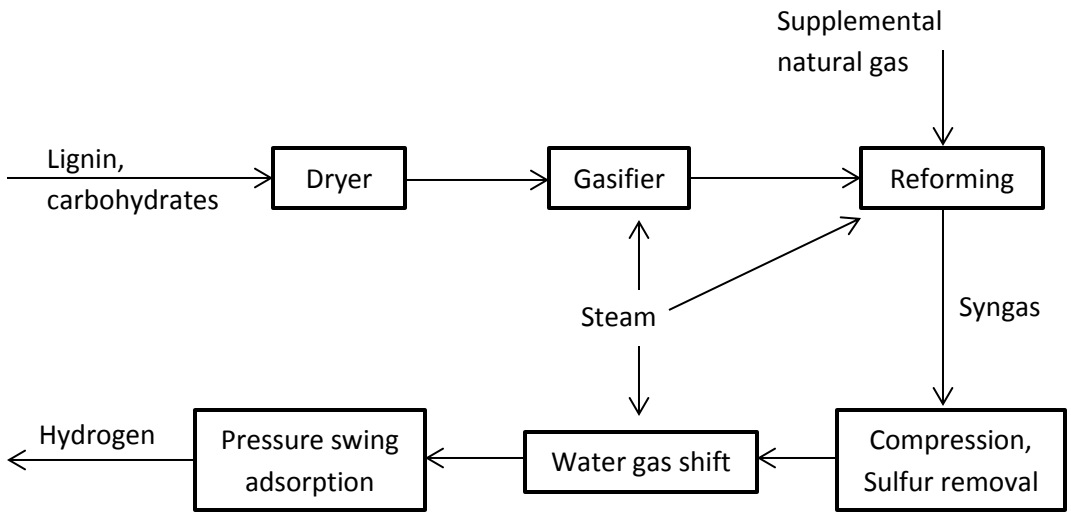

Fig. 3. Generalized flow diagram of lignin gasification process. Gasifying lignin does not provide enough hydrogen for the biorefinery process, so a minimum amount of natural gas is reformed to make up the balance. Pressure swing adsorption is used to purify the hydrogen product, the same technology that is used in other hydrogen production scenarios considered in the present analysis.

2.4.3 Natural gas steam reforming

The most common method of producing hydrogen commercially, natural gas steam reforming [29], also referred to as steam methane reforming (SMR), uses two primary reactions to form hydrogen from hydrocarbons. Methane, being the primary component of natural gas, and steam are reformed to produce syngas. To increase hydrogen yields from natural gas, the syngas then goes through low and high temperature WGS reactions. The resulting gasses then go through a PSA unit operation, as described in Section 2.4.2, to obtain a nearly pure hydrogen product.

The overall SMR process has a cold gas efficiency of 76.6% (HHV), and produces about 0.347 kg of hydrogen per kilogram of natural gas feed. This hydrogen production method is commercially well-developed. It is explored in detail, and has been combined with a carbon capture system in other studies [26, 33], although that is out of the scope of this study.

2.4.4: Scenario selection of biorefinery in combination with hydrogen production

In order to make a hydrocarbon end product from biomass and oxygenated intermediates, oxygen is removed from the process stream in the form of water. Reduction in the process is provided by hydrogen gas. How the hydrogen is obtained can play a major role in the overall techno-economics, and three scenarios are described here. Table 3 shows a summary of the scenarios, along with the key differences in heating source and lignin fate.

In the first scenario, hydrogen is produced as described in Section 2.4.2, primarily by lignin gasification. Natural gas is reformed as a supplement to lignin gasification to produce just enough hydrogen for the two hydrotreating reactions to make jet fuel. Similarly, only enough natural gas is used in the burner and boiler system to provide steam and heat for the wood to jet process and the gasification process.

Two biorefinery scenarios are considered where SMR provides all the necessary hydrogen, but differ in steam and heat production. In both of these scenarios, all of the available lignin is sent to the burner. Lignin provides approximately 55% of the heating value required by the biorefinery, while unfermented sugars and other wastes provide another 22% based on lower heating values. The balance of required heating value, about 23%, is derived from natural gas, or in an effort to reduce fossil fuel use, hog fuel.

Table 3. Summary of hydrogen production scenarios considered. Also shown are the fractions of hydrogen source material, and fractions of heating duty.

Case	Hydrogen source (wt% of total hydrogen)	Lignin fate	Burner feed (% heating value)
1	Lignin gasification (>75%) with supplemental natural gas reforming (<25%)	Gasified	Natural gas (100%)
2	Natural gas reforming (100%)	Burned	Lignin and waste (77%) with supplemental natural gas (23%)
3	Natural gas reforming (100%)	Burned	Lignin and waste (77%) with supplemental hog fuel (23%)

3. Modeling

3.1 Technical modeling

Three separate Aspen models are created: a model of the hybrid poplar to hydrocarbon biofuel with pure hydrogen inputs, a model of lignin gasification for hydrogen production, and a model of natural gas steam reforming for hydrogen production. Section 3 describes the modeling process, with assumptions and modeling characteristics stated herein.

3.1.1 Hybrid poplar to hydrocarbon biofuel model

Modeling begins by examining the basic series of unit operations necessary for the biorefinery process. An Aspen flowsheet is then developed following the process described in Sections 2.2 and 2.3, and known process parameters such as conversion percentages and losses are added. All major reactions are modeled with a RStoic block, and literature values are used for operating temperature and pressure, fractional conversion data, and heat of reaction where applicable.

Yields and conversion factors are conservative estimates in collaboration with our industry partners.

An overall reaction summary of the process is shown in Table 4 along with theoretical and practical yields. Due to incomplete conversion, selectivities lower than 100%, and recovery losses, practical yields are lower than theoretical. For example, 75 wt% of xylan is converted to xylose during pretreatment, and 91 wt% of cellulose is converted to sugars during enzymatic hydrolysis. During fermentation, 94 wt% of glucose [24] and 92 wt% of xylose are converted to acetic acid. The hydrolysis and fermentation conversion numbers are based on personal communication with our industry partner during the 2011 – 2013 timeframe of the project.

In reactive distillation, the reaction proceeds with an excess amount of ethanol and it is therefore assumed that all acetic acid is consumed in ethyl acetate production. Ethanol yield from ethyl acetate hydrotreatment is 99.5 wt% for the entire unit operation. On a single pass basis, conversions of 90% or higher are achieved [34]. The hydrotreating reaction runs in an adiabatic reactor and is slightly exothermic; however it does not require a direct source of cooling. The steps of reactive distillation, azeotrope separation, and ethyl acetate hydrotreating are combined in Table 4 yields of ethanol from acetic acid.

For ethylene production from ethanol, an adiabatic fixed bed reactor system is used. The process is an industrially well-established technology [35] with several well-known commercial processes [36]. A scrubber column is used to remove water, followed by compression in a multi-stage compressor to 3450 kPa (500 psi) with condensed water leaving the system. An adsorbent is used to remove final traces of water from the ethylene stream, modeled as a Sep block in Aspen.

The two oligomerization reactors, to produce butene from ethylene and dodecene from butene, are cooled. The second of these two reactors is modeled in a loop with a distillation column (RadFrac). The column's tops are recycled for further oligomerization, while the bottoms cut is in the jet fuel range and goes to a hydrotreatment reactor. During hydrotreating to make a saturated end product, a value of -124 kJ/mol is used for the exothermic reaction [37].

Table 4. Hydrocarbon biofuel production reaction network. Major process steps are shown with the relevant chemical equations. Theoretical and practical yields shown use a basis of one bone dry tonne of poplar. Yields are based on conservative estimates in collaboration with our industry partners.

Step	Chemistry	Cumulative Theoretical Yield	Cumulative Practical Yield
Pretreatment and hydrolysis	$Wood + H_2O \rightarrow Sugars + Lignin$	722 kg Sugars	640 kg Sugars
Fermentation	$C_6H_{12}O_6 \rightarrow 3\ CH_3COOH$ $C_5H_{10}O_5 \rightarrow 2.5\ CH_3COOH$	722 kg Acetic acid	580 kg Acetic acid
Hydrotreat (1)	$CH_3COOH + 2\ H_2 \rightarrow CH_3CH_2OH + H_2O$	554 kg Ethanol	450 kg Ethanol
Alcohol dehydration	$CH_3CH_2OH \rightarrow C_2H_4 + H_2O$	337 kg Ethylene	260 kg Ethylene
Oligomerization	$n\ C_2H_4 \rightarrow CH_3CH_2 - (CH_2CH_2)_{n-2} - CH = CH_2$	337 kg Distillate	250 kg Distillate
Hydrotreat (2)	$CH_3CH_2 - (CH_2CH_2)_{n-2} - CH = CH_2 + H_2$ $\rightarrow CH_3CH_2 - (CH_2CH_2)_{n-2} - CH_2CH_3$	341 kg Polymer jet 450 L/tonne	250 kg Polymer jet 330 L/tonne

It should be noted that the hydrocarbon end product, or polymer jet fuel, produced in modeling is a jet fuel surrogate. As a petroleum derived product, jet fuel itself is a mixture of a large number of different hydrocarbons. Because the focus of this research is on the techno-economics of producing a biomass based jet fuel, not specifically the modeled jet fuel product, one molecule is chosen as the jet fuel end product. n-Dodecane, $C_{12}H_{26}$, acts as a first approximation surrogate for Jet A, has an acceptable carbon number of 12 [38]. Dodecane also has similar physical

properties to Jet A in certain tests [39]. It is therefore chosen as the end product, jet fuel molecule to be modeled.

An analysis of the heat duties in the model is performed so that process heat may be recycled where possible. This heat analysis is done for each of the three hydrogen production scenarios described in Section 2.4.4 in order to maintain high plant efficiency. Steam and electricity production are explicitly modeled and integrated into the biorefinery. Steam is raised at high temperature and pressure, and run through a multistage turbine where process steam is exported as necessary as described in Section 2.4.

The simulation has a range of characteristics that make modeling challenging. For example, the model starts with a polar, water based stream and ends with a non-polar hydrocarbon stream. In the intermediate, a ternary azeotrope of water, ethanol, and ethyl acetate is broken with pressure swing distillation. Thermodynamic and transport property estimation methods play an essential role in determining the accuracy of a simulation model. In order to select the proper Aspen property method, general guidelines set out by Aspen are followed and applied to each unit operation separately. The model's base method is NRTL, with some unit operations operating under other property packages. For example, a flash block after dilute acid pretreatment uses NRTL with Hayden-O'Connell equation of state to account for non-idealities in the vapor phase due to high pressure.

3.1.2 Lignin gasification model

Lignin gasification includes nonpolar or mildly polar mixtures of hydrocarbon and light gases like hydrogen sulfide, carbon dioxide and hydrogen. Redlich-Kwong-Soave cubic equation of

state with Boston-Mathias alpha function (RKS-BM) is the property method used in calculating the thermodynamic and transport properties such as fugacity coefficient, viscosity, and enthalpy. It was chosen because it is recommended for gas processing applications [40]. Since there is no thermodynamic data available specifically for lignin, tar, and ash in the Aspen Plus database, they were defined as nonconventional components using compositional data shown in Table 2, Section 2.4.2. Pseudo streams containing nitrogen and sulfur are also included in the simulation to simulate the formation of sulfur and nitrogen based compounds, especially hydrogen sulfide and ammonia.

A RStoic block is used to model drying the lignin feed. A calculator block is used to control the fractional conversion so that the overall moisture of lignin goes down from 50 % to 10 %. The evaporated water vapor is then separated from the lignin stream using a FLASH2 block and it is separated for heat recovery. The heat required for drying is recovered from char combustion. In addition to lignin drying, a calculator block is used to control the mass flow rate of elemental sulfur in the conventional solid stream such that it amounts to 3% of the total wet lignin weight to simulate sulfur compounds that would be bound to the lignin stream. Another calculator block is also used to control the nitrogen mass flow rate in N_2 so that it is always 0.01 times the wet lignin mass.

In gasification, a RYield block is first used to stimulate the decomposition of lignin into carbon (solid), hydrogen, oxygen, tar, ash and char. Ash is removed while char is combusted. The solid carbon, hydrogen, tar and oxygen, along with steam (240 kPa, 130 ºC), are sent to a RGibbs block and gasified. RGibbs provides a good approximation for the final product composition through Gibbs free energy minimization when the exact reaction mechanisms and kinetics are

not well known. However, RGibbs is not capable of predicting the formation of solid char (solid carbon) and tar (brown or black liquefied mixtures of phenols, polycyclic aromatic hydrocarbons, heterocyclic compounds and possibly other hydrocarbons); hence RYield is used first to convert 10 % of the overall lignin weight into water and 10 % of the dry lignin into tar, another 10 % into char with specified yield and composition, 2.9 % into ash and the remaining dry lignin mass into carbon, hydrogen gas and oxygen gas [Eq 3]. Sensitivity blocks are used to find the steam and reaction temperature that result in optimal hydrogen yields. Equation 4 shows the overall conversion of lignin and steam into hydrogen and carbon monoxide. The tar reformer is set up similarly to the gasifier: a RYield first decomposes all of the tar into carbon, hydrogen and oxygen [Eq 5], after which they are sent to RGibbs and reformed with steam (240 kPa, 130 ºC). A stoichiometric amount of water is used to reform tar into carbon monoxide and hydrogen, shown by the overall reaction in Equation 6.

$$CH_{1.47}O_{0.51}\,(Lignin) \rightarrow C + 0.735H_2 + 0.255O_2 \;[Eq\ 3]$$

$$CH_{1.47}O_{0.51}\,(Lignin) + 0.49H_2O \rightarrow 1.225H_2 + CO \;[Eq\ 4]$$

$$CH_{1.35}O_{0.3}\,(Tar) \rightarrow C + 0.675H_2 + 0.15O_2 \;[Eq\ 5]$$

$$CH_{1.35}O_{0.3}\,(Tar) + 0.7H_2O \rightarrow 1.375H_2 + CO \;\;[Eq\ 6]$$

In sulfur removal modeling, the gas is desulfurized in two RStoic blocks, a LO-CAT reactor and zinc oxide bed. The reactions involved in reoxidizing the LO-CAT solution using air (in which hydrogen sulfide is oxidized to elemental sulfur and water) are simplified in Equation 7. The remaining hydrogen sulfide is removed via zinc oxide bed [Eq 8] modeled as RStoic. It is assumed that any remaining sulfur is present only in negligible quantities.

$$H_2S + \frac{1}{2}O_2 \rightarrow S + H_2O \;\;[Eq\ 7]$$

$$ZnO + H_2S \rightarrow ZnS + H_2O \;\;[Eq\ 8]$$

Both high and low temperature water gas shift reactors with 350 and 200˚C reactor temperatures respectively are modeled as REquil with zero temperature approach [27]. Approach temperature is defined as the difference between the measured outlet temperature and the temperature that would yield the measured conversion of a component at equilibrium (in our case, carbon monoxide) [27]. It is assumed the reaction is at equilibrium and thus temperature approach is zero. Since the water gas shift reaction itself is slightly exothermic, lower reactor temperature tends to result in better yield but slower reaction and vice versa. This explains the use of high and low temperature reactors instead of just one WGS reactor.

Hydrogen gas separation and purification is performed in a PSA unit modeled as a Sep2 block, with split fractions specified to achieve expected product yield and selectivity [27, 41].

3.1.3 SMR model

Natural gas reforming, or SMR, is a widely used, widely studied, advanced and mature production process [26, 29, 33, 41]. The bulk of the data for the SMR process is derived from an Idaho National Lab report [26], due to the multiple scenarios provided in the report. For example, in efforts to reduce carbon dioxide emissions, a carbon capture system could be included in future studies.

In the SMR model, the reformer is modeled as a RGibbs block, and the high and low temperature WGS reactions are modeled as REquil blocks using methods similar to those described for lignin gasification. A PSA unit is used as the final hydrogen separations and purification operation, and is used as described previously.

3.2 Economic modeling

3.2.1 Capital expenses

The capital cost is estimated using a well-known method of factored estimation, and may include uncertainties of as much as ±30% [21, 25]. The method used starts with costs of major pieces of equipment based on literature or software estimation. Using the flow data generated during process simulation, the cost of major pieces of equipment is scaled based on Equation 9. The flow components, $Flow_a$ and $Flow_b$, are simply mass, heat, or work data generated from simulation. The scaling exponent, n, is found in literature and is different for various types of equipment, but usually is in the range of 0.5 to 0.8.

$$Cost_a = Cost_b \times \left(\frac{Flow_a}{Flow_b}\right)^n \text{[Eq 9]}$$

The scaled cost is then multiplied by an installation factor, and updated to 2011 USD using the Chemical Engineering Plant Cost Index. Waste water treatment and cooling tower systems are not modeled explicitly in Aspen; the capital cost of these two systems however is modeled and included in the final capital expense. Hydrogen production as well as burner and boiler systems are included in the capital estimate, along with all equipment necessary to convert poplar biomass to the hydrocarbon end product.

The installed equipment comprises the bare module cost, which is then multiplied by a factor of 1.68 to include additional costs. These costs are comprised of a contingency, contractor fee, site development, auxiliary buildings, off-sites, and utilities. The final estimated capital expense is grassroots, which refers to a completely new facility although it does not include the cost of land.

3.2.2 Operating expenses

Operating expense estimation is done as follows: A list of inputs and outputs of the biorefinery model is compiled. This includes raw materials entering the biorefinery, and waste and byproducts exiting the facility. Costs are associated with each item, based on literature sources or publicly available industry quotes. Some costs, such as enzymes, are not narrowly defined but may be estimated based on literature [42]. Fixed costs comprise around 20% of the cash cost to produce the biofuel, and include labor, maintenance, overhead, administration, and various other support activity costs. Labor costs are estimated by number of employees and salary, while other fixed costs are estimated by factors of labor or capital. Any excess electricity is to be sold to a nearby grid at $0.06 per kWh, although the excess amount is small. Based on simulation results, a cost per hour, year, or liter of hydrocarbon fuel may be estimated.

3.2.3 Discounted cash flow rate of return analysis

One way to measure and compare the profitability of investments, a discounted cash flow rate of return (DCFROR), or internal rate of return (IRR) analysis takes into account an entire project timespan. In summary, the analysis manipulates the jet fuel selling price to find the break-even point at which the project net present value is zero. This calculation is performed by iteration with a specified discount rate, and the final price is the minimum jet fuel selling price on a volume basis. The minimum selling price is the minimum price that the fuel must be sold for in order to break even under the assumed discount rate. Selling the product for a higher price will increase the internal rate of return, while selling for a lower price will reduce the rate of return.

Key parameters of the analysis are shown in Table 5. The two discount rates are chosen for two different purposes. First, a 7% discount rate is chosen as a baseline for social opportunity cost of capital, based on appropriate discounting from a benefit-cost analysis point of view [43]. A higher, 15% discount rate is used for comparison and reflects a discount rate that would be more attractive to investors.

Table 5. Discounted cash flow analysis parameters

Parameter	**Value**
Discount rates (nominal, compounded yearly)	7, 15%
Project lifetime (plant operation)	20 years
Construction time	3 years
Depreciation method	MACRS
Equity share	100%
Tax rate	0%
Working capital (% of FCI)	10%, returned at project completion

Modified Accelerated Cost Recovery System (MACRS) is used for depreciation allowance as it is currently the accepted system in the U.S. A pre-tax position, or rate of 0%, is chosen due to the fact that cellulosic biofuels is an emerging industry with the potential for substantial government subsidy and tax breaks.

4. Results and discussion

4.1 Process analysis

Analysis of process simulation gives insights into technical feasibility of different processes. Hydrogen, steam, and electricity play a large interconnected role within the biorefinery, and are analyzed here.

Considering hydrogen production, it is readily apparent that natural gas reforming is much less complex, and much more industrially proven than lignin gasification. A noteworthy amount of hydrogen is consumed in jet fuel production, about 0.12 kg per liter of jet fuel.

Steam and heat play a critical role in this specific biorefinery. The lignin and waste biomass alone does not provide enough heat when burned or hydrogen when gasified for the jet fuel process. The following tables show steam consumption and related electricity production, based on a 380 million liter per year facility. Table 6 summarizes consumption in major steam consumer unit operations. Pretreatment is the largest consumer, and due to the steam being injected directly into the biomass process stream, no condensate is returned.

Table 6. Major biorefinery steam users

Process	**kg steam per liter jet fuel**	**Steam temperature, pressure**
Pretreatment	3.6	280 ºC, 1310 kPa
Pressure swing distillation column (1)	1.5	280 ºC, 1310 kPa
Pressure swing distillation column (2)	1.2	175 ºC, 450 kPa
Ethanol to ethylene	1.3	580 ºC, 450 kPa
Oligomerization reboiler	0.1	580 ºC, 450 kPa

Net electricity production in the envisioned biorefineries is low compared to similar studies that produce ethanol [21] instead of a hydrocarbon. This is due to the extra processing steps involved in the acetogen production pathway to produce ethanol, additional processing steps to make a hydrocarbon fuel instead of only ethanol, and the necessary hydrogen production. The low electricity production may affect life cycle assessment results due to excess electricity not being able to displace fossil fuel-produced electricity [17].

Table 7 shows electricity consumption by process area. The last two items cover hydrogen production and differ substantially due to syngas compression. In natural gas reforming, the gas feed is already pressurized, whereas for lignin gasification the lignin feed is at near atmospheric pressure and energy must be utilized to pressurize the system. The results of this systematic disparity come to light in Table 8, where net electricity production is shown. In the case where hydrogen is derived from natural gas reforming, excess electricity is produced and may be sold. When hydrogen is derived via lignin gasification, a deficit of electricity exists and so must be purchased. While the difference is relatively small, it may have impacts on both economics and environmental assessments.

Table 7. Biorefinery electricity consumption by area

Process	**kWh/liter jet**
Feedstock handling	0.032
Pretreatment	0.210
Hydrolysis and fermentation	0.095
Ethylene compressor	0.100
Wastewater treatment	0.270
Utilities	0.110
Boiler pump	0.026
Natural gas reforming	0.079
Lignin gasification	0.350

Table 8. Net biorefinery electricity

	Natural gas reforming	Lignin gasification
Consumed (kWh/liter jet)	0.93	1.19
Generated (kWh/liter jet)	0.98	1.00
Net (kWh/liter jet)	0.05	-0.19

4.2 Expense estimates

Using methods described in Section 3.2, capital costs are estimated. Table 9 shows costs of a 380 million liter per year facility broken down into three major areas. Information is given for the two hydrogen production scenarios of natural gas reforming and lignin gasification. It is assumed that a burner boiler system burning lignin, other waste products, and hog fuel costs the same as the same system with natural gas substituted for hog fuel.

Table 9. Capital costs for 380 million liter/yr jet plant. The costs are broken down into three major areas for comparison purposes.

Fixed capital, $ million	**Natural gas reforming**	**Lignin gasification**
Feedstock through ethanol	502	502
Alcohol to hydrocarbon	113	113
Steam plant and hydrogen production (reforming/gasification)	149	284
Total	$764	$882

The factored estimation method is applied to four different capacity biorefineries. Economies of scale can be seen in the range of capacities investigated, from 95 to 570 million liters of biofuel per year. This is shown in Figure 4 for the two different cases of hydrogen production, where the capital dollars per capacity is plotted against capacity. In Table 10, the absolute capital cost estimates are shown.

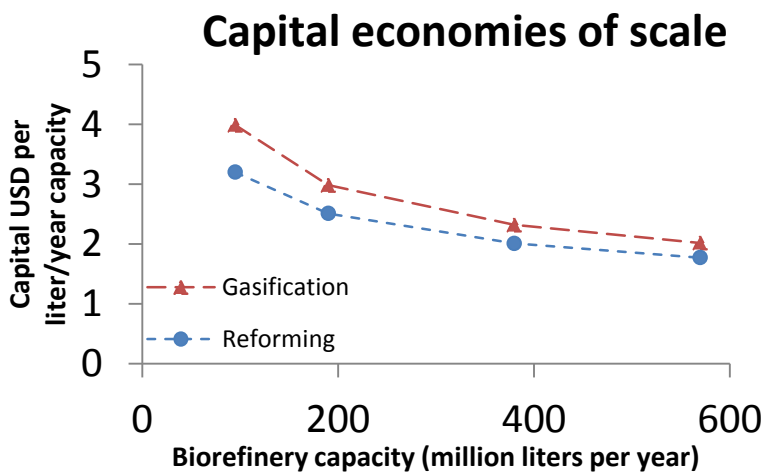

Fig. 4. Economies of scale of capital expense for four different capacity biorefineries. This also shows sensitivity to scale or capacity. As would be expected based on the economies of scale principle, large biorefineries are shown to have lower cost per unit capacity.

Table 10. Fixed capital costs of biorefineries of various capacity (million USD)

Capacity (million L/yr)	**95**	**190**	**380**	**570**
Reforming capital	304	477	764	1,010
Gasification capital	379	567	882	1,150

In estimating operating expenses, three scenarios from Section 2.4.4 are explicitly displayed. Table 11 shows an operating expense breakdown in USD for a facility that produces 380 million liters of jet fuel per year. Feedstock is assumed to be bought at the facility gate, chipped, at 77 USD per bone dry tonne ($70/ton), and natural gas is priced at 0.0033 USD per MJ ($3.50/ million Btu) on a higher heating value basis. Hog fuel is purchased at 55 USD per dry tonne ($50/ton), but is assumed to contain 45 wt% moisture and have a heating value of 11 MJ/kg (4700 Btu/pound [44]) when burned. Electricity is sold at 0.06 USD per kWh. All assumptions for the discounted cash flow analysis are discussed in Section 3.2.3, where 7 and 15% discount rates are used.

Table 11. Cash operating cost and minimum fuel selling price for 380 million liter/year facility. Operating costs are broken down into major groupings and shown for the three hydrogen production scenarios described in Section 2.4.4. It can be seen that the two cases of natural gas reforming are nearly identical in cost, while the two largest differences for the lignin gasification case are electricity and fixed manufacturing costs.

Operating cost	**USD per liter**		
	Reforming, natural gas in boiler	Reforming, hog fuel in boiler	Gasification
Feedstock	0.23	0.23	0.23
Cellulase enzymes	0.13	0.13	0.13
Fermentation nutrients	0.02	0.02	0.02
Other raw materials	0.08	0.08	0.08
Waste disposal	0.01	0.01	0.01
Electricity	-0.003	-0.003	0.011
Reforming/Gasification O&M	0.01	0.01	0.01
Natural gas (and hog fuel)	0.09	0.08	0.10
Fixed manufacturing costs	0.12	0.12	0.13
Total cash cost	**$0.69**	**0.69**	**0.73**
Minimum selling price with 7% discount	**$0.91**	**0.90**	**0.98**
Minimum selling price with 15% discount	**$1.09**	**1.08**	**1.18**

Minimum selling prices are plotted in Figure 5, where economies of scale become apparent with decreasing minimum selling prices as plant capacity increases. As the discount rate increases, economies of scale also become more pronounced. Cash cost is defined here as the actual production cost to make one liter of hydrocarbon fuel, not including any discount, tax, capital depreciation, or other factors. The cash cost is only comprised of the operating costs, both fixed and variable, and includes any credit for electricity sold. For comparison, the global average price paid at the refinery for aviation jet fuel from January through November, 2013 was $0.78/L ($2.96/gallon) [45].

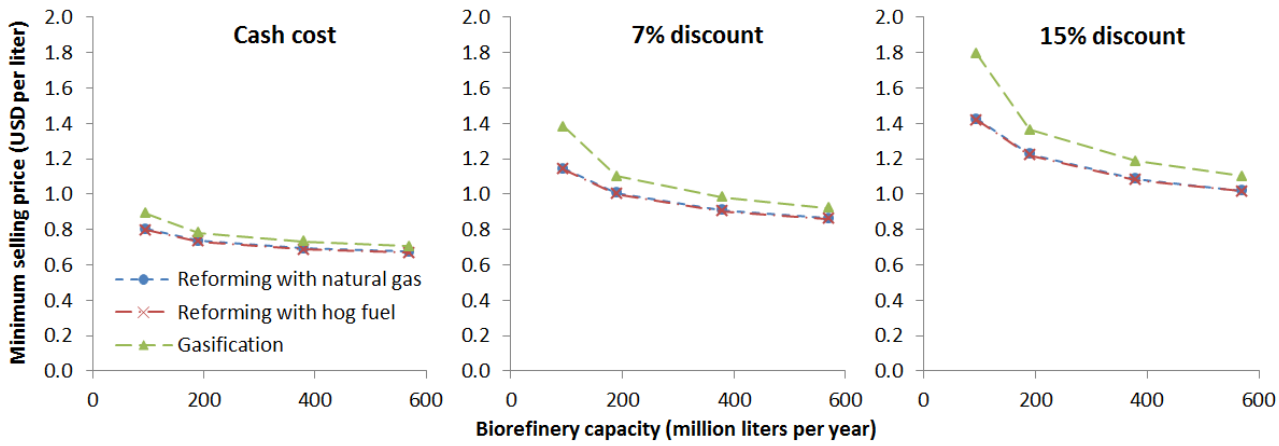

Fig. 5. Operating expense economies of scale. The cash cost is compared with minimum selling prices using 7% and 15% discount rates. It can be seen that increasing the discount rate increases operating cost economies of scale.

4.3 Alternative products

While this analysis focuses on jet fuel production, it is worth noting that several chemical intermediates are marketable products themselves. Acetic acid, ethyl acetate, ethanol, and ethylene are all intermediates to polymer jet fuel production. Separation and purification to a chemical commodity purity is not explored here, although the biorefinery as envisioned already has relatively pure streams of ethyl acetate, ethanol, and ethylene. We envision the recovery of these streams would be relatively easy and inexpensive. Producing and selling more than one product reduces risk in the biorefinery via product diversification.

Table 12 explores theoretical revenue options of a biorefinery built with the capacity to produce 380 million liters per year of jet fuel. The biorefinery could alternatively produce the shown amounts of ethanol, ethylene, or ethyl acetate, and given the estimated selling prices [45, 46] could actually increase revenue compared to producing only jet fuel.

Table 12. Alternative products. Shown here are four different setups a single biorefinery could have, but does not include any capital reduction allowance. The table shows the revenue produced if each of the products were produced separately at 100% capacity, given the referenced selling price.

Product	Annual capacity at 100% production	Estimated selling price	Annual revenue at 100% production
Jet fuel	380 million L	$0.80/L [45]	$300 million
Ethanol	600 million L	$0.55/L [46]	$330 million
Ethylene	285,000 tonnes	$1320/tonne [46]	$375 million
Ethyl acetate	475,000 tonnes	$1320/tonne [46]	$625 million

5. Conclusions

A unique biorefinery is explored to produce a hydrocarbon biofuel as part of the push for infrastructure compatible cellulosic biofuels. A high yield of 330 liters of hydrocarbon biofuel per tonne of biomass feedstock is achieved in large part due to the use of acetogenic bacteria that do not produce carbon dioxide as a co-product during fermentation. Compared to an ethanologen process, the present biorefinery has more unit operations and goes through more intermediate products to produce ethanol. From ethanol, a polymer fuel is produced further increasing the complexity of the biorefinery in order to make a more valuable end product.

A challenge in the process is sourcing hydrogen required for the biorefinery. With the bulk of the current hydrogen in the world being produced from natural gas, a fossil fuel, the environmental impact of the hydrogen must be considered when looking at the overall biofuel produced. While the additional operating expenses of hydrogen production are not huge (about 15% of total cash operating expenses), it does add significant capital expense as well as a degree of complexity to the biorefinery. Lignin gasification is a less mature, more complex hydrogen production method that leaves the biorefinery with a lack of heating source for process heat and steam, while natural gas reforming uses fossil fuel in the biofuel production. On a positive note,

we show that hog fuel can viably be used as a heating fuel source with nearly the same economics as burning natural gas. Hog fuel has the advantage of being a biogenic source of heat, rather than the fossil fuel natural gas, which will affect environmental analyses.

Strong economies of scale are shown, especially in biorefineries in the capacity range of 95 to 380 million liters per year. We show that process economics have the potential to improve with alternative products. From an operating expense standpoint we show that calculated minimum jet fuel selling prices can result in positive cash flow, but will not yield a reasonable return. We estimate the cash operating cost to be $0.67/L at the cheapest configuration, a 570 million liter per year facility that uses natural gas reforming and hog fuel for heat generation. A discount rate of 7% makes the minimum selling price $0.86/L, which is higher than the 2013 average price paid at the refinery of $0.78/L [45]. Although we did not consider any carbon tax or government incentives, these could make jet fuel production profitable in the short term.

Considering the significant capital investment required to build these facilities, the previous 20 years' volatility in petroleum prices, and the political fluctuations that can be associated with subsidies or a carbon tax, building a biorefinery as described would incur a large amount of risk and necessitate a high internal rate of return to attract private investors. However, there are ways to reduce risk such as selling more than one product at a time and netting a premium for "green" fuels and chemicals. Future work may investigate in further detail where to build these biorefineries and what, if any, incentives are required.

6. Future Work

A techno-economic analysis with the broad scope of the present study has many areas where additional work may be performed. One area that has potential large real-world connection is water consumption. A detailed analysis of water within the biorefinery would provide valuable information. Besides the biorefinery processing streams, the waste water treatment area and cooling tower area have large roles in the water cycle. The waste water treatment area for the present study is largely based on NREL [21] designs, and there is significant room for improvement when looking at a WWT system for the specific biorefinery of this study.

Other areas for future work include different aspects of operating economics. For example, a market analysis of the alternative products mentioned in Section 4.3 may be performed. Below are some questions that could be investigated:

- How best to sell multiple products to reduce risk in biorefinery, and how long or short term contracts could affect prices
- Would building the facility to only produce ethanol (reduction in capital investment) have significant impacts on operating expenses?
- How would a carbon tax affect economics? What carbon price is necessary for 15% IRR?
- How would RINs affect economics?

In addition to these questions, an economic sensitivity analysis would be valuable. For example, how would a price of $80/BDT for feedstock affect the minimum jet fuel selling price? Additional sensitivity analyses would provide insight on what variables have the most effect on the process yield, or process economics.

References

[1] United States Department of Agriculture. U.S. Bioenergy Statistics – website: http://www.ers.usda.gov/data-products/us-bioenergy-statistics.aspx. Washington DC USA. October 2013.

[2] U.S. Energy Information Administration. Biofuels Issues and Trends. Washington DC USA. October 2012.

[3] Marchetti JM, Miguel VU, Errazu AF. Techno-economic study of different alternatives for biodiesel production. Fuel Processing Technology 2008; 89:740-748. DOI 10.1016/j.fuproc.2008.01.007

[4] Mueller-Langer F, Tzimas E, Kaltschmitt M, Peteves S. Techno-economic assessment of hydrogen production processes for the hydrogen economy for the short and medium term. International Journal of Hydrogen Energy 2007; 32:3797-3810. DOI 10.1016/j.ijhydene.2007.05.027

[5] Zoulias EI, Lymberopoulos N. Techno-economic analysis of the integration of hydrogen energy technologies in renewable energy-based stand-alone power systems. Renewable Energy 2007; 32:680-696. DOI 10.1016/j.renene.2006.02.005

[6] Singh D, Croiset E, Douglas PL, Douglas MA. Techno-economic study of CO_2 capture from an existing coal-fired power plant: MEA scrubbing vs. O_2/CO_2 recycle combustion. Energy Conversion and Management 2003; 44:3073-3091. DOI 10.1016/S0196-8904(03)00040-2

[7] Bridgwater AV, Toft AJ, Brammer JG. A techno-economic comparison of power production by biomass fast pyrolysis with gasification and combustion. Renewable and Sustainable Energy Reviews 2002; 6:181-248.

[8] Wright MM, Daugaard DE, Satrio JA, Brown RC. Techno-economic analysis of biomass fast pyrolysis to transportation fuels. Fuel 2010; 89:S2-S10. DOI 10.1016/j.fuel.2010.07.029

[9] Gnansounou E, Dauriat A. Techno-economic analysis of lignocellulosic ethanol: A review. Bioresource Technology 2010; 101:4980-4991. DOI 10.1016/j.boirtech.2010.02.009

[10] Sassner P, Galbe M, Zacchi G. Techno-economic evaluation of bioethanol production from three different lignocellulosic materials. Biomass and Bioenergy 2008; 32:422-430. DOI 10.1016/j.biombioe.2007.10.014

[11] Wingren A, Galbe M, Zacchi G. Techno-Economic Evaluation of Producing Ethanol from Softwood: Comparison of SSF and SHF and Identification of Bottlenecks. Biotechnology Progress 2003; 19:1109-1117. DOI 10.1021/bp0340180

[12] Yang B, Wyman CE. Pretreatment: the key to unlocking low-cost cellulosic ethanol. Biofuels, Bioprod. Bioref 2008; 2:26-40. DOI 10.1002/bbb.49

[13] Olsson L, Hahn-Hägerdal B. Fermentation of lignocellulosic hydrolysates for ethanol production. Ezyme and Microbial Technology 1996; 18:312-331.

[14] Keoleian GA, Volk TA. Renewable energy from willow biomass crops: Life cycle energy, environmental and economic performance. Crit. Rev. Plant Sci. 2005; 24(5–6):385–406.

[15] Stephenson AL, Dupree P, Scott SA, Dennis JS. The environmental and economic sustainability of potential bioethanol from willow in the UK. Bioresour. Technol. 2010; 101(24):9612–9623.

[16] González-García S, Gasol CM, Gabarrell X, Rieradevall J, Moreira MT, Feijoo G. Environmental profile of ethanol from poplar biomass as transport fuel in Southern Europe. Renewable Energy 2010; 35(5):1014–1023.

[17] Budsberg E, Rastogi M, Puettmann ME, Caputo J, Balogh S, Volk TA, Gustafson R, Johnson L. Life-Cycle Assessment for the Production of Bioethanol from Willow Biomass Crops via Biochemical Conversion. Forest Products Journal 2012; 62(4):305-313.

[18] Sassner P, Galbe M, ZacchiG. Steam pretreatment of Salix with and without SO2 impregnation for production of bioethanol. Appl. Biochem. Biotechnol 2005; 121–124:1101–1117.

[19] Mansfield SD, Mooney C, Saddler JN. Substrate and enzyme characteristics that limit cellulose hydrolysis. Biotechnol. Prog 1999; 15(5):804–816.

[20] Sannigrahi P, Ragauskas, AJ, Tuskan GA. Poplar as a feedstock for biofuels: A review of compositional characteristics. In: Dale BE, editor. Biofuels, Bioproducts and Biorefining 2010; 4:209-226. DOI: 10.1002/bbb.206

[21] Humbird D, Davis R, Tao L, Kinchin C, Hsu D, Aden A, Schoen P, Lukas J, Olthof B, Worley M, Sexton D, Dudgeon D. Process Design and Economics for Biochemical Conversion of Lignocellulosic Biomass to Ethanol, NREL/TP-5100-47764. National Renewable Energy Laboratory. Golden, CO, United States, 2011.

[22] Treasure T, Gonzalez R, Jameel H, Phillips RB, Park S, Kelley S. Integrated process, financial, and risk modeling of cellulosic ethanol from woody and non-woody feedstocks via dilute acid pretreatment. In: McMillan J, Decker S, program chairs. Proceedings of 35th Symposium on Biotechnology for Fuels and Chemicals. Portland, OR, United States. 2013; 70.

[23] Andreesen JR, Schaupp A, Neurauter C, Brown A, Ljungdahl L. Fermentation of Glucose, Fructose, and Xylose by Clostridium thermoaceticum: Effect of Metals on Growth Yield, Enzymes, and the Synthesis of Acetate from CO_2. Journal of Bacteriology,1973; 114(2):743-751.

[24] ZeaChem, Inc. Process for Producing Ethanol. US Patent No. 7,964,379 B2, June 21, 2011.

[25] Hamelinck C, Hooijdonk G, Faaij A. Ethanol from lignocellulosic biomass: techno-economic performance in short-, middle- and long-term. Biomass and Bioenergy 2005; 28:384-410. DOI: 10.1016/j.biombioe.2004.09.002

[26] Wood RA. HTGR-Integrated Hydrogen Production via Steam Methane Reforming (SMR) Process Analysis, TEV-953. Idaho National Laboratory. Idaho Falls, ID, United States, 2010.

[27] Spath, P., A. Aden, T. Eggeman, M. Ringer, B. Wallace, and J. Jechura. "Biomass to Hydrogen Production Detailed Design and Economics Utilizing the Battelle Columbus Laboratory Indirectly Heated Gasifier." National Renewable Energy Laboratory, May 2005.

[28] Levene JI, Mann MK, Margolis R, Milbrandt A. An Analysis of Hydrogen Production from Renewable Electricity Sources, NREL/CP-560-37612. National Renewable Energy Laboratory. Golden, CO, United States, 2005.

[29] Koroneos C, Dompros A, Roumbas G, Moussiopoulos N. Life cycle assessment of hydrogen fuel production processes. International Journal of Hydrogen Energy 2004; 29:1443-1450. DOI 10.1016/j.ijhydene.2004.01.016

[30] Koroneos C, Dompros A, Roumbas G. Hydrogen production via biomass gasification – A life cycle assessment approach. Chemical Engineering and Processing 2008; 47:1261-1268. DOI 10.1016/j.cep.2007.04.003

[31] Nunn TR, Howard JB, Longwell JP, Peters WA. Product Compositions and Kinetics in the Rapid Pyrolysis of Milled Wood Lignin. Industrial & Engineering Chemistry Process Design and Development 1985; 24(3):844-52.

[32] Nagl GJ. Small Capacity Sulfur Recovery Units. – website: http://www.merichem.com/resources/technical_papers/small_capacity/index.php. Merichem Company.

[33] Molburg JC, Doctor RD. Hydrogen from Steam-Methane Reforming with CO_2 Capture. Prepared at Argonne National Laboratory for 20th Annual International Pittsburgh Coal Conference. June 2003.

[34] Zhang B, Lin L, Zhuang J, Liu Y, Peng L, Jiang L. Hydrogenation of Ethyl Acetate to Ethanol over Ni-Based Catalysts Obtained from Ni/Al Hydrotalcite-Like Compounds. Molecules 2010; 14:5139-5152. DOI 10.3390/molecules15085139

[35] Chematur Engineering Group. Ethylene from Ethanol. Karlskoga, Sweden.

[36] Morschbacker A. Bio-Ethanol Based Ethylene. Journal of Macromolecular Science, Part C: Polymer Reviews 2009; 49:79-84. DOI 10.1080/15583720902834791

[37] Rogers DW, Skanupong S. Heats of Hydrogenation of Sixteen Terminal Monoolefins. The Alternating Effect. The Journal of Physical Chemistry 1974; 78(25):2569-2572.

[38] Edwards T, Maurice LQ. Surrogate Mixtures to Represent Complex Aviation and Rocket Fuels. Journal of Propulsion and Power 2001; 17(2):462-466. DOI 10.2514/2.5765

[39] Colket M, Edwards T, Williams S, Cernansky NP, Miller DL, Egolfopoulos F, Lindstedt P, Seshadri K, Dryer FL, Law CK, Friend D, Lenhert DB, Pitsch H, Sarofim A, Smooke M, Tsang W. Development of an Experimental Database and Kinetic Models for Surrogate Jet Fuels. 45th AIAA Aerospace Sciences Meeting and Exhibit, Reno, NV, USA. Paper No. AIAA 2007-770. January 2007. DOI 10.2514/6.2007-770

[40] Aspen Technology. Aspen Plus V7.3 user guide. Burlington, MA, USA, 2011.

[41] Boyce CA, Crews MA, Ritter R. Time for a new hydrogen plant? Hydrocarbon Engineering. February 2004.

[42] Klein-Marcuschamer D, Oleskowicz-Popiel P, Simmons BA, Blanch, HW. The Challenge of Enzyme Cost in the Production of Lignocellulosic Biofuels. Biotechnology and Bioengineering 2012; 109(4):1083-1087. DOI 10.1002/bit.24370

[43] Burgess DF, Zerbe RO. Appropriate Discounting for Benefit-Cost Analysis. Journal of Benefit-Cost Analysis 2011; 2(2):Article 2. DOI 10.2202/2152-2812.1065

[44] Sharpe D. Comparing Waste Wood Boilers. – website: http://ir.library.oregonstate.edu/xmlui/bitstream/handle/1957/5039/Compare_Waste_Wood_ocr.pdf?sequence=1. Western Dry Kiln Association. May 2002.

[45] International Air Transportation Association (IATA). Fuel Price Analysis. – website: http://www.iata.org/publications/economics/fuel-monitor/Pages/price-analysis.aspx. 2013.

[46] Chang J (ed). Indicative Chemical Prices A-Z. – website: http://www.icis.com/chemicals/channel-info-chemicals-a-z/#top. ICIS.

Appendix A

Operational data from Aspen simulation

Table A-1. RStoic reactor blocks in Aspen and reaction parameters

Reactor	Reaction Condition 1		Reaction Condition 2		Reaction	Fractional Conversion	Of Component	Heat of Reaction
pretreatment	200	C	0	Vapor Fraction	CELLULOS(CISOLID) + H2O --> GLUCOSE	0.014	CELLULOS(CISOLID)	
					H2O + XYLAN(CISOLID) --> XYLOSE	0.75	XYLAN(CISOLID)	
					XYLAN(CISOLID) --> 2 FURFURAL + H2O	0.05	XYLAN(CISOLID)	
					GALACTAN(CISOLID) + H2O --> GALACTOS	0.61	GALACTAN(CISOLID)	
					GALACTAN(CISOLID) --> HMF + 2 H2O	0.05	GALACTAN(CISOLID)	
					H2O + ARABINAN(CISOLID) --> ARABINOS	0.75	ARABINAN(CISOLID)	
					ARABINAN(CISOLID) --> 2H2O + FURFURAL	0.05	ARABINAN(CISOLID)	
					ACETATE(CISOLID) --> AACID	1	ACETATE(CISOLID)	
					2 H2O + FURFURAL --> ARABINAN(CISOLID)	1	FURFURAL	
					2 H2O + HMF --> 1.2273 ARABINAN(CISOLID)	1	HMF	
					LIGNIN(CISOLID) --> LGNSOL	0.05	LIGNIN(CISOLID)	
enzymatic hydrolysis	50	C	1	atm	CELLULOS(CISOLID) + H2O --> GALACTOS	0.0593	CELLULOS(CISOLID)	
					CELLULOS(CISOLID) + H2O --> GLUCOSE	0.855	CELLULOS(CISOLID)	
primary fermentation	58	C	1	atm	GLUCOSE --> 3 AACID	0.94	GLUCOSE	
					2 XYLOSE --> 5 AACID	0.92	XYLOSE	
					2 ARABINOS --> 5 AACID	0.85	ARABINOS	
					GALACTOS --> 3 AACID	0.85	GALACTOS	
					GLUCOSE + 1.1428571 NH3 --> 5.71428571 MOORELLA(CISOLID) +2.57142857 H2O +0.28571429 CO2	0.017	GLUCOSE	
					XYLOSE + 0.952381 NH3 --> 4.76190476 MOORELLA(CISOLID) + 2.14285714 H2O + 0.23809524 CO2	0.019	XYLOSE	

Reactor	Reaction Condition 1		Reaction Condition 2		Reaction	Fractional Conversion	Of Component	Heat of Reaction
seed train	58	C	1	atm	GLUCOSE + 1.1428571 NH3 --> 5.71428571 MOORELLA(CISOLID) + 2.57142857 H2O + 0.28571429 CO2	0.017	GLUCOSE	
					XYLOSE + 0.952381 NH3 --> 4.76190476 MOORELLA(CISOLID) + 2.14285714 H2O + 0.23809524 CO2	0.019	XYLOSE	
reactive distillation	72	C	1	atm	ETHANOL + AACID --> ETOAC + H2O	1	AACID	
					LIME(CISOLID) + CO2 --> CACO3(CISOLID) + H2O	1	LIME(CISOLID)	
ethyl acetate hydrotreat	500	psi	0	MMkcal/hr	ETOAC + 2 H2 --> 2 ETHANOL	0.995	ETOAC	-74.98 MJ/kmol, 77F ref. temp., 1 atm ref. pressure, liquid ref. phase
ethanol to ethylene	375	C	50	psig	ETHANOL --> C2H4 + H2O	0.982	ETHANOL	10920 cal/mol, 425C ref. temp., 50 psig ref. pressure, vapor ref. phase
					2 ETHANOL --> 2 H2O + BUTENE	0.013	ETHANOL	10920 cal/mol, 425C ref. temp., 50 psig ref. pressure, vapor ref. phase
oligomerization (1) dimer	200	C	500	psi	2 C2H4 --> BUTENE	0.99	C2H4	
oligomerization (2)	200	C	500	psi	3 BUTENE --> DODECENE	0.975	BUTENE	
					2 C2H4 --> BUTENE	0.3	C2H4	
final hydrotreating	200	C	500	psi	DODECENE + H2 --> DODECANE	1	H2	-29.7 kcal/mol, 77F ref. temp., 1 atm ref. pressure, vapor ref. phase
burner	0	atm	0	MMkcal/hr	N/A (Combustion tab, check "Generate combustion reactions")			

Table A-2. Other key blocks in Aspen and simulation parameters

Block	**Nearby unit operations**	**Conditions**			
Flash2	After pretreatment	1	atm	0	cal/sec
RadFrac (1st pressure swing distillation)	After reactive distillation	Calculation type	Equilibruim		
		Number of stages	25		
		Condenser	Total		
		Reboiler	Kettle		
		Valid phases	Vapor-Liquid		
		Convergence	Strongly non-ideal liquid		
		Reflux ratio	1.7	mole	
		Bottoms to feed ratio	0.6	mass	
		Feed stage	12	above-stage	
		pressure	10	bar, stage 1/condenser	
RadFrac (2nd pressure swing distillation)	After reactive distillation	Calculation type	Equilibruim		
		Number of stages	20		
		Condenser	Total		
		Reboiler	Kettle		
		Valid phases	Vapor-Liquid		
		Convergence	Strongly non-ideal liquid		
		Reflux ratio	2.4	mole	
		Bottoms to feed ratio	0.2	mass	
		Feed stage	10	above-stage	
		pressure	500	mmHg-vac, stage 1/condenser	

Block	Nearby unit operations	Conditions			
RadFrac (scrubbing column)	Before compressor, ethylene/water scrubber	Calculation type	Equilibruim		
		Number of stages	14		
		Condenser	None		
		Reboiler	None		
		Valid phases	Vapor-Liquid		
		Convergence	Standard		
		Incoming stream	1	above-stage	
		Recycle stream	15	above-stage	
		Pressure	1	atm	
Mcompr	Ethylen compressor, before oligomerization	Number of stages	5		
		Compressor model	Isentropic		
		Fix discharge pressure from last stage	500	psi	
		Heat capacity calculation	Rigorous		
		Cooler (at each stage)	38	C	
		Pressure drop (at each stage)	0.1	bar	
RadFrac (Oligomerization)	After oligomerization	Calculation type	Equilibruim		
		Number of stages	10		
		Condenser	None		
		Reboiler	Kettle		
		Valid phases	Vapor-Liquid		
		Convergence	Petroleum/Wide-boiling		
		Bottoms to feed ratio	0.915	mass	
		Feed stage	1	On-stage	
		pressure	147	psi	