

ABSTRACT

CULBERTSON JR, CHARLES GRANT. Commercialization of Sustainable Bio-Refinery Projects for the Pulp & Paper Industry. (Under the direction of Dr. Richard Venditti, Dr. Hasan Jameel, and Dr. Ronalds Gonzalez).

The goal of this research is to present the technical and economic feasibility of bio-refining projects within the pulp and paper industry in order to create new opportunities for long-term growth whereby forest biomaterials may be effectively utilized towards fulfilling enduring customer needs. Mill curtailments, shutdowns, and consolidation of the industry (e.g. M&A activity) has created a unique opportunity to commercialize cost-advantaged technologies and products that utilize forest timber and their respective supply chain. This research incorporates systems thinking tools such as techno-economics and life-cycle assessment in order to quantify the opportunity for converting lignocellulosic biomass, predominantly softwood pine and mixed hardwoods. From this quantification, key cost-drivers of bio-refining technology are identified for continued research and development in order to improve financial returns or reduce environmental impacts of the proposed process technology.

The first study demonstrates the financial returns anticipated from extracting lignin bio-materials from a kraft pulp mill. In this work, the subtle nuances of power, heat and chemical recovery are explored as modification to the conventional kraft process are implemented. This study also details the setting for the remaining studies which explore incorporation of various bio-chemical and bio-material process technologies to the kraft pulp mill. It was determined that extracting lignin with a recovery boiler steam limiting assumption provides the highest project returns of \$71 million net present value and 53% internal rate of return for a \$23 million capital investment.

The second study explores changes to environmental impacts from the kraft pulp mill as the result of manufacturing new products while using existing assets and resources. Specifically, this study quantifies the degree of which bio-refining process technologies and their respective products are beneficial to the environment. It was determined that life-cycle greenhouse gas emissions for softwood kraft pulp (SBSK) may be reduced from 720 kg CO₂eq per air-dry metric ton to 600 kg CO₂eq with mass allocation.

From the first two studies, the valorization of kraft lignin is identified as a key factor towards to improving the financial success and environmental benefit of bio-materials. The third study examines fundamental structure-property relationships of lignin in order to identify opportunities and limitations towards incorporating this bio-material into consumer products. It was determined that low molecular weight fractions of hardwood and softwood kraft lignin exhibit glass transition temperatures as low as 70 to 85°C with good thermal stability.

The fourth study explores key cost-drivers of valorizing the lignin co-product from a majority of bio-refining technologies. In many cases, the lignin and hemi-cellulose content of wood is collected and combusted for heat and power, used within the process. This work demonstrates that it may be beneficial to collect the lignin and convert the product into higher-value materials at the expense of lost heat and power. For a conceptual lignin phenolation process, it was determined that a \$158 million capital investment may result in a \$48 million net present value and 18% internal rate of return when upgrading the lignin to \$1200/mt value for adhesive applications.

The fifth study evaluates new opportunities, beyond pulp and paper products, for converting lignocellulosic biomass to bio-chemicals that may be cost-advantaged to incumbent petro-chemicals. The purpose of this study was to explore the literature for bio-chemicals that

can be readily converted from lignocellulose via direct thermo-chemical conversion of biomass or fermentation of bio-sugars derived from lignocellulosic biomass. In this work, promising candidates such as succinic acid, quantified by the amount of potential revenue received for converting a unit of wood (e.g. \$1150/mt-hardwood), were selected for more rigorous techno-economic evaluation.

Finally, the sixth study incorporates the findings from the previous case studies in order to quantify the total opportunity of converting wood into a specific bio-chemical. In this work, the context of co-locating the process with a kraft pulp mill is evaluated against a traditional “greenfield” investment in order to quantify the savings that may be realized by utilizing existing assets within the pulp and paper industry. It was determined that an integrated bio-refinery, co-located with a kraft pulp mill, converting mixed southern hardwoods to succinic acid may generate project returns as high as \$700 million net present value and 35% internal rate of return for a \$360 million capital investment.

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Commercialization of Sustainable Bio-Refinery Projects for the Pulp & Paper Industry

by
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A dissertation submitted to the Graduate Faculty of
North Carolina State University
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

Forest Biomaterials

Raleigh, North Carolina

2017

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DEDICATION

First, this work is dedicated to my loving and infinitely patient wife Erin Lynn, daughter Eileen Lux, and the other one we haven't named yet (e.g. goddess of the hunt). This degree, and the opportunities it has afforded us, is ours to share. Your support and drive motivate me to constantly reach for more, and I can't wait to see where we end up next.

Second, I'd like to also dedicate this work to mankind's eternal companions: humility, failure and respect. Without them, we gain nothing.

BIOGRAPHY

Grant Culbertson was born and raised in eastern North Carolina in 1985 while his parents were attending bible school. Early childhood years were spent in and out of classrooms with mom and dad, and as a result, debate and fundamental questioning were a part of everyday life. It was a humble and loving start.

Grant attended K through 12 at Beaufort County's Bath Elementary and Northside High School, where he was blessed with many wonderful and caring teachers who, somehow, managed to instill a lasting appreciation for science (as well as imprinting a little work ethic) before Grant moved on to North Carolina State University.

At NCSU, Grant attended the then Department of Wood and Paper Science as another fortunate recipient of the Pulp & Paper Foundation Scholarship. He graduated with dual degrees in Chemical Engineering and Paper Science Engineering. More importantly, he met Erin Lynn Doss.

After finishing school (or so he thought), Grant followed his mentor Dr. Armindo Gaspar (one of many great mentors) and went on to serve with Novozymes as a research chemist. Not too long after, he followed his fiancé to Virginia Beach where he took a position under Mr. Bud Curtis working as a civil site design engineer for Parsons Brinckerhoff. After two years' experience working with an excellent team, Grant moved on to serve as a Nuclear Engineer for the Navy at Norfolk Naval Shipyard, prior to returning to NCSU for graduate school to work for Dr Richard Venditti and Dr. Hasan Jameel. Grant now serves at Georgia-Pacific as Chief "Luckiest-Guy-In-The-World."

ACKNOWLEDGMENTS

I've been extraordinarily fortunate to have worked with many accomplished professionals, and it would be difficult to express my deepest gratitude to all those who mentored and guided me to where I am today in 600 words or less. Consequently, I think it's important to acknowledge the "Law of Averages" and everyone that let me hang around long enough to learn something important. Also, thank you Mom, George, and Dad!

My first experience with Dr. Richard Venditti was WPS 355, where, if I wasn't fast asleep from sitting beside the softly humming over-head projector, I was busy learning everything I ever needed to know about moving a unit of fluid from A to B. He doesn't know it, but to this day, his dog-eared, self-published course-pack is sitting on my desk at work. I can't work without it. Later, he took me in as a graduate student and set me up with good projects, surrounding me with the talent and support I would need to succeed. Thank you, Dr., Venditti; this experience means the world to me.

Dr. Hasan Jameel was my first under-graduate advisor, and he encouraged me to enroll in that WPS 355 class. Now that I think of it, I suppose the two of them set me up from the beginning. Similarly, as my graduate advisor, Dr. Jameel thrust me into more than a few amazing experiences. Those experiences, as I've now learned, prepared me for the real world. Thank you, Dr., Jameel for affording me the opportunity to learn, fail, fail-again and grow as a student, professional and father.

When I started graduate school, Dr. Ronalds Gonzalez was on his way to an exciting career with SCA, but he didn't depart before leaving us with the grant for a USDA National Needs Fellowship, which I was lucky enough to obtain. With this gift from Dr. Gonzalez's

hard work, I could acquire an MBA along the way. It was hard work, but worth every minute. Thank you, Dr. Gonzalez for this once-in-a-lifetime opportunity.

Dr. Richard Phillips gave me the tools of techno-economics and instilled in me a sense of discipline needed to put them to work. His patience, generosity and demand for excellence are legendary within our department (and industry), so I was humbled when he invited me to serve as his TA for PSE 415. This was easily the most humbling and rewarding assignment that I've been given to date. Thank you again, Dr. Phillips.

I'd like to acknowledge Dr. Stephen Markham, Dr. Roger Debo, Dr. Steve Barr and the Poole College of Management's Technology Entrepreneurship and Commercialization program. Another deeply humbling experience, this program has made a lasting impact on my life.

As for my peers, I'd like to acknowledge the careful guidance from Dr. Jesse Daystar and Dr. Trevor Treasure. Their motivation and support helped me start and finish this program. The same goes for all my dear friends and colleagues in Forest Biomaterials: Carter Reeb, Robert Narron, Jing Du, Xiao Jiang, Tiago DeAssis, Remil Aguda, Neethi Rajagopalan, Barbara White, the FB graduate students and PSE under-graduate students, and every, single faculty member. All of you offered much needed encouragement and support.

Lastly, I'd like to acknowledge the time and considerable resources invested in me by my wife and family. I still can't believe you let me do this. Also, I'd like to thank Bill Frey, Subrata Sen, Mike Carroll and the team at Georgia-Pacific for supporting me and allowing me to finish my degree.

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1 INTRODUCTION TO BIO-REFINING IN THE PULP & PAPER INDUSTRY

1.1 Challenges of Bio-Refining in the Pulp & Paper Industry

The pulp and paper industry has a rich history of experience in bio-refining. In addition to fiber production for pulp and paper products, the industry has consistently been a major producer of bio-energy (largely for energy self-sufficiency) and bio-chemicals (e.g. pine chemicals recovered as co-products). While many researchers may consider recent interest in bio-refining to be a “new” opportunity for upgrading forest products and other purpose-grown biomass into sustainable bio-fuels and bio-chemicals for the 21st century, the pulp and paper industry was successfully carrying-out these operations as early as the 1940’s. Puget Sound Pulp & Timber (later acquired by Georgia-Pacific in 1963) built an industrial ethanol facility in 1945 that utilized waste hydrolysates from its sulphite pulping process. The 5 million gallon per year ethanol facility was originally built during World War II in order to supply ethanol as a chemical feedstock for butadiene and synthetic rubber production. In 1947, an additional research and development laboratory, focusing on value-added chemical uses for pulping by-products, was added as part of the mill’s continued modernization. The mill continued to thrive and grew to employ over 1,200 personnel in the 1990’s before its downsizing in 2001 (largely due to the California Energy Crisis) and ultimate closure in 2007.

Other notable examples include TEMBEC’s (formerly International Paper) mill in Temiscaming, Quebec. In addition to specialty cellulose products such as cellulose acetate and dissolving pulps, the Temiscaming site also manufactures lignosulfonates and ethanol from by-products. Of particular note is the mill’s attention and considerable investments towards pulp mill effluent treatment. Installed in the 1990’s, the mill incorporates an anaerobic

digestion unit that captures bio-methane, fermented from effluent sludge, for the purposes of generating heat and power. With continued investments, the mill even exports “green” power to the grid. The Temiscaming mill is another positive example of disciplined bio-refining concepts that have been practiced within the pulp and paper industry.

These examples highlight arguably successful process demonstrations that have been shown to improve upon existing pulp mill economics with the valorization of mill by-product streams. This is a considerably different approach when considered against recent projects requiring new technologies, tailor-made to refine a specific biomass stream. Commercializing this “transformational” biorefining technology development is difficult, and many concepts initially thought to be exciting fail in the end for a variety of reasons, five of the main ones are listed below:

1. **Lack of sufficient funding.**

Investors become impatient for achieving the technical results that they believed were initially promised by the developers (Plastics News 2016, Washington Times 2015).

2. **Initial estimate of capital for a scaled up operation was higher than expected (Ulrich 1986, Couper et al 2012).**

This differs from the first point in that technical milestones may have been achieved, but the cost of full scale operation was under-estimated based on pilot plant results

3. **Failure to anticipate the market or current market leaders who employ well-developed petrochemical technology (CFR 2013)**

Projects based on \$100 per barrel oil price may not survive \$30 per barrel raw material costs to conventional refineries. This is especially true when the bioproduct is ethanol.

4. **Projections of raw material cost or availability may have been overly optimistic.**

Purpose-grown feedstocks for bio-based processes may offer superior processing features and product yields, but the developer under-estimates the cost, time and difficulty of acquiring land (or landowners), establishing crops, harvesting, collecting, transporting and storing materials (Gonzelez et al 2012).

5. **Unforeseen “Fatal Flaws” (Fortune 2015)**

Lastly, results reported from a laboratory experiment are physically impractical (or even impossible) to extrapolate and replicate on a commercial scale. A number of process parameters discussed in more detail below can be assessed at an early stage of development, and that assessment can identify the critical technical and financial pressure points.

1.2 **Opportunity for Ligno-Cellulosic Sugars**

The knowledge gained from “2nd generation” or lignocellulosic ethanol (primarily corn stover) may be utilized towards the production of low-cost monomeric sugars, and these sugars may be utilized towards other industrial applications from commodity chemicals to high-value, niche applications. Indeed, the most recent trend observed in the biofuels industry (as a result of the 2007 to 2009 Great Recession) has been the shift in company product offering from fuel related technology to specialty chemicals production. As of 2015, up to 60% of the biofuels industry has increased its product offering from biofuels production and process technology to a mix of bioproducts such as carboxylic acids and conjugated dienes, compared with less than 15% of such specific, bioproduct offerings in 2012 (see Figure 1-1). While it is unknown to

the authors whether or not these companies planned on producing these specific chemicals prior to recent public announcements (as opposed to the author’s loosely defined “non-specific chemical” category), the sudden change in external communication, away from biofuels only discussion, is an interesting observation, suggesting a bio-refining industry’s willingness to quickly-adapt relevant technology to new opportunities that offer the greatest customer value.

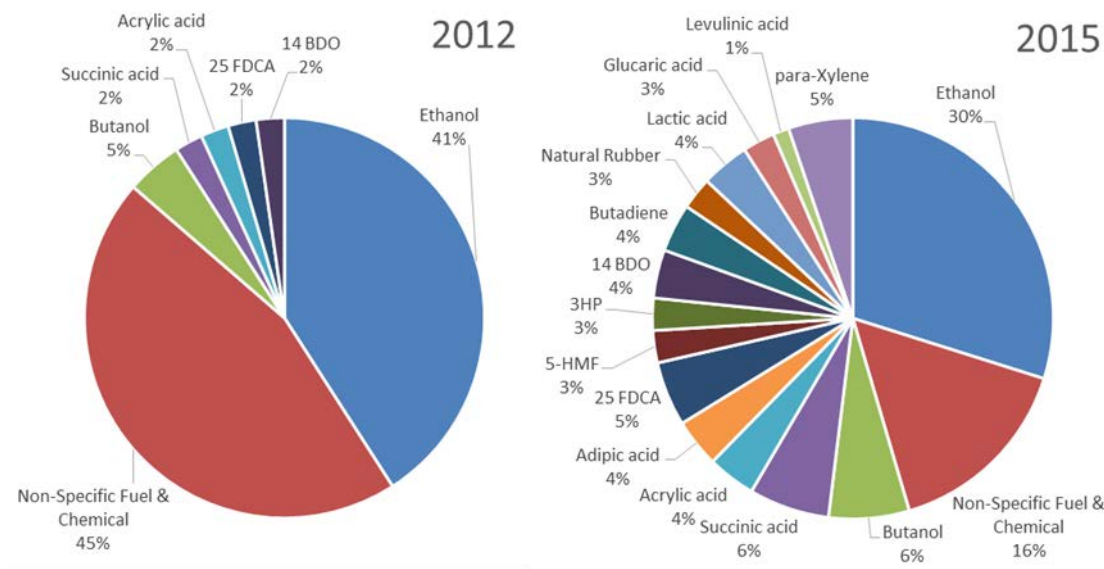


Figure 1-1: Bio-Fuels& Bio-Products Industry Composition by Product Offering (BioFuels Digest) * “25 FDCA”, 2,5 furandicarboxylic acid; “3HP”, 3-hydroxypropionic acid; “5-HMF”, 5-hydroxymethyl furfural; “14 BDO”, 1,4 butanediol

For many companies, this observed trend may be best described as an attempt at “rebranding” in order to attract additional investment towards commercialization. For one such example, Amyris ended its efforts to develop North American fuel distribution channels

in 2012 in order to focus on bio-fuels development in Brazil, and again in 2015, the company announced tolling activities in North Carolina to convert farnesene to squalene and other high-value, niche products while reporting a considerable decrease in farnesene-derived fuel sales from 2014 (Amyris, 2015). While the company continues to raise development funds through defense related grants for renewable fuels, the company continues to report new growth with specialty chemical sales in 2016 as well (Amyris, Q2 2016). An argument can be made that this strategy towards producing bioproducts, using core technology developed for the purposes of biofuels production, has helped the company survive both the Great Recession and the more recent oil bust of 2015. Additionally, leveraging the lessons learned from the five commercialization challenges referenced above may enable an opportunity for long-term growth in bioproducts, using technology originally envisioned for biofuels.

1.3 Opportunity for the Pulp & Paper Forest Products Industry

The challenges associated with developing biorefining technology may seem insurmountable to the observer. Particularly, the challenge of funding and committing to fund development activities over 10 year or greater time horizon for a low-margin commodity market that increasingly sensitive to political and market volatility may likely receive negative perception for investors accustomed to the risk-return profile associated with the information technology industry (e.g. high risk and high reward over a truncated time horizon). Furthermore, the well-accepted concept of a “lean startup” among institutional investors may not translate well to industries that rely on heavily on capital intensive investments.

For bio-refining technology, the “high risk” may be considered the engineering and design of chemical process equipment that converts lignocellulosic biomass to fuels and

chemicals, and many of the process routes envisioned pull from unit operations which are traditionally utilized in the oil & gas industry and present a significant technical hurdle with respect to solids handling that must be addressed. The “high-return”, originally characterized as the promise of large-volume sales in super-commodity markets coupled with government secured subsidies and loan guarantees, may never be realized. A prime example, KiOR, serves as a constant reminder for those involved in the biorefining industry of the disappointment that results when project returns are overstated (or impossible to achieve), and technical “fatal” flaws are not addressed (or are even ignored).

While it is important to acknowledge the difficulties of projecting project returns subject to market volatility, it is suggested that the challenge associated with technical risk, for many bio-refining technologies, may be addressed with the incorporation of existing pulp and paper industry assets and knowledge processes. In the previous example, the process technology attempted to achieve mass transfer between the catalyst and solid-state media. Those familiar with pulp and paper unit operations were sure to understand, and respect, the challenge of bringing this process to commercial scale. Historically, pulp and paper unit operations have included solids partitioning in the woodyard (e.g. chipping and screening), thermochemical conversion of a solids substrate to mixed media (e.g. wood to fiber and spent liquor), and subsequent product purification and energy recovery (e.g. kraft recovery cycle and pulp bleaching). It is worth emphasizing that these unit processes have been successfully and safely employed for over 150 years.

Another challenge that the forest products industry may address is the ability to broker and distribute cost-advantaged biomass. Unlike some newer biorefining technologies that

attempt to develop new supply chains in order to utilize a specific biomass, the forest product industry maintains a robust and stable biomass supply (Mosier et al 2005). Furthermore, recent declines in demand for forest products have left a surplus of forest based resources, both mixed hardwoods and loblolly pine in the southeast U.S., which could be efficiently utilized by biochemical manufacturers, or a bio-based economy (Wear et al 2010, Carle & Holmgren 2008, Raunikar et al 2010). As shown in Figure 1-2, the relative stability of forest based resources, specifically southern pine and hardwoods, may serve as an attractive opportunity for emerging biorefining technology.

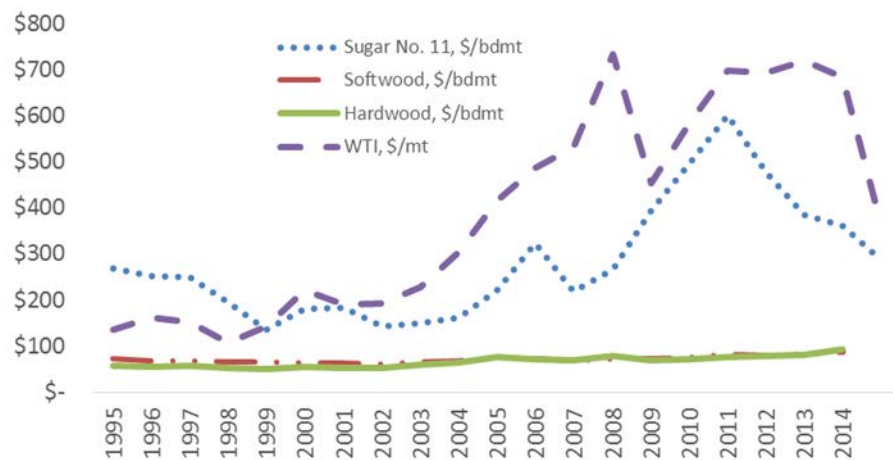


Figure 1-2: Historical Raw Material Prices. (RISI 2015, NYMEX 2015, EIA 2015) * “WTI”,

West Texas Intermediate

Lastly, the forest products industry may address the challenge of reducing capital expenditures by utilizing existing assets. The forest product industry has more recently experienced consolidation in search of higher returns, and a standard level of mill curtailments

and closures is anticipated for the industry as the marginal producers are priced out of the market (PPRC). However, during the Great Recession of 2007 to 2009, mill closures and curtailments spiked significantly, and in many cases, these assets remain off-line in order to control industry supply (PPRC & Fisher/TAPPI). This suggests a unique opportunity for the forest products industry to achieve long-term growth in bioproducts manufacturing by participating in technology development and “de-risking” the capital liability through co-location with, or repurposing of, existing assets. Again, it is worth noting that some of the most expensive of unit operations in biorefining technology share commonality with the forest product industry (e.g. power production, waste water treatment and biomass handling).

The forest products industry may be well suited to address four of the five challenges presented above (i.e. funding or expectation of returns, familiarity with required capital investment, capability as biomass brokers, and practical experience identifying “fatal flaws”), and the goal of this research is to quantify and present the potential opportunity for introducing cost-advantaged biorefining technology to the pulp and paper industry.

2 STUDY STRUCTURE & METHODOLOGY

2.1 Study Structure & Objectives

This work explores the economic opportunity and feasibility of bio-refining capital investment projects for the pulp and paper industry. The first three studies concern the integration of lignin extraction technology designed to remove lignin organics from kraft black liquor and characterization of this lignin. The later three studies concern fermenting lignocellulosic, or “biorefinery”, sugars to value-added bio-chemicals such as succinic acid and the valorization of lignin by-products. Specifically, the proposed value proposition for biorefining in the pulp and paper industry was based on three assumptions: first, that existing assets may be used in order to reduce the required capital investment required, second, that the biomass utilized in the process is cost-advantaged to current commodity, or “1st generation”, food-based sugars, and third, that there may be opportunities for variable and fixed cost reduction through economies of scale (e.g. shared labor, utilities, etc.). The scope of this work spanned the gate-to-gate production of extracted kraft lignin and succinic acid produced from wood chips, with mixed southern hardwood chips received and stored at the bio-refinery at a capacity of 500,000 “bone-dry” metric tons (bdmt) per year. The goal of this work was to quantify the value proposition for bio-refining in the pulp and paper industry and identify the context and economic drivers whereby commercial success (or profitability, as defined herein) may be achieved.

2.2 Techno-Economic Analysis

Using previously reported literature data and process modeling, techno-economic analysis (TEA) studies attempt to quantify the key financial indicators such as cash flow, net present value, internal rate of return, minimum product revenue and incremental EBITDA received for processing a unit of wood in a proposed bio-refining project.

Technoeconomic models were constructed, according to spreadsheet methodology, based on material and energy balances for a defined process system boundary. First, a process flowsheet was built in order to identify all process flow inputs and outputs relevant to each major unit operation. For this work, it was necessary to model a conceptual bio-refining process that utilizes an auto-hydrolysis pretreatment of mixed southern hardwoods with subsequent biomass deconstruction via mechanical refining and enzymatic hydrolysis. The resulting product, mixed pentose (C5) and hexose (C6) “bio-sugars” from the lignocellulosic hydrolysate, is fermented to produce succinic acid, along with additional purification and hydrogenation to 1,4 butanediol. Additional processes, including biomass combustion, pelletization or phenolation, were modeled in order to valorize by-products from the process. The process unit operations described herein employ standard equipment and unit operations found in the pulp and paper and chemical process industries.

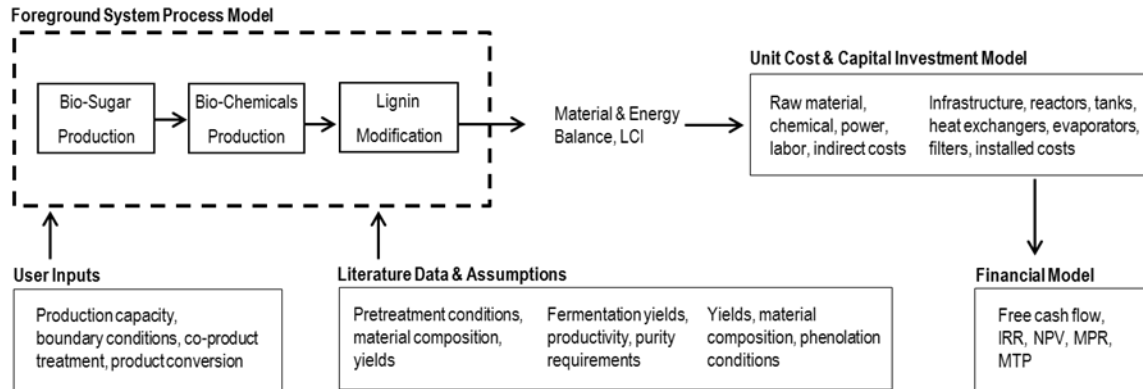


Figure 2-1: Simplified Methodology of Techno-economic Analyses

The model consists of mass balance equations that characterize and define the flow of process materials into and out of the system boundary. Pretreatment yields and carbohydrate recovery for biomass conversions (specifically, mixed hardwoods) are referenced from the literature. Common data for steam and process materials was used in order to determine the net energy consumptions for the process. Fermentation yields and productivity are also referenced from the literature; however, many assumptions were identified in the absence of detailed laboratory or process data.

Using data generated by the process model to construct a life cycle inventory (LCI, described in the next section), a financial model was constructed by determining the capital (CAPEX) and operational (OPEX) expenditures impact on total revenue generated for each scenario. Ultimately, the financial model calculated the free cash flows when considering a set of general assumptions.

2.2.1 Capital Expenditures (CAPEX)

Capital expenditures are the fixed costs associated with the equipment used in the process. All equipment costs have been estimated for year 2015 and scaled to process flows resulting from 500,000 “bone-dry” metric tons per year mixed hardwood chips consumption, accordingly. Variation of the equipment cost is expressed by the following relationship (Ulrich 1984):

$$C_v = C_u \left(\frac{v}{u} \right)^a$$

Where “ C_v ” is the purchase price of equipment at a specific capacity represented by “ v ” and “ C_u ” is the equipment cost at capacity “ u .” Since equipment costs scale disproportionately with size or capacity, the sizing exponent “ a ” is used for specific equipment.

Similarly, the cost of equipment purchased is adjusted for inflation to 2015 values using the following relationship (Ulrich 1984):

$$C_g = C_r \left(\frac{I_g}{I_r} \right)$$

Where “ C_g ” and “ I_g ” is the cost of equipment and indices in year “ g ”, and “ C_r ” and “ I_r ” is the cost of equipment and indices in year “ r .” Marshall & Swift (Marshall & Swift 2015) was used to collect inflation indices respective of the chemical engineering industry. Equipment costs were gathered from the literature where available and individual price quotes were obtained from equipment manufacturers when needed (Phillips 2010, Peters et al 1968, Peters & Timmerhaus 2003, Pirraglia et al 2010, Couper et al 2009).

2.2.2 Operational Expenditures (OPEX)

Operational expenditures (OPEX) refer to the direct and indirect variable costs associated with biomass conversion and pulp mill production. Direct costs for the production of bio-sugars and succinic acid include hardwood chips, chemicals, enzymes, nutrients, finishing materials, power, and natural gas for steam production. Indirect costs such as the cost of maintenance and overhead are derived from 2% of replacement asset value. Labor was calculated using salary estimates for approximately 90 employees required to operate the process (unless otherwise specified). Depreciation costs were calculated using 10-year straight-line depreciation. Generally, costs associated with landfilling solid waste from wastewater treatment and final product finishing materials were not considered.

An overview of the direct costs for lignin extraction, lignin valorization or bio-sugar and bio-chemical production are provided in detail according to each study's scope. Unless otherwise specified, chemical costs were collected from ICIS Chemical Business and adjusted for inflation (ICIS 2015). Natural gas prices were gathered from the U.S. Energy Information Administration (US EIA 2015). All other costs for fiber, power, and consumables were assumed are stated in each study's methodology section.

2.2.3 General Assumptions & Key Performance Indicators

Best professional judgment was used to determine the appropriate risk required for discounting future free cash flows in the financial model (e.g. 15% internal rate of return). For this study, free cash flow is defined as the unlevered sum of after tax profit and depreciation costs, less changes in working capital and new fixed capital investments. A project life of 15

years was used for evaluation of the sum of discounted cash flows according to the following equation:

$$NPV = \sum_{n=1}^t \frac{FCF_n}{(1+i)^n} + \frac{TV_t}{(1+i)^t}$$

Where the net present value “NPV” is the sum discounted free cash flows “FCF” over a specified time period “n” and discount rate “i”, with an exit fair market value “TV” in the project’s terminal year “t”. The terminal value in year 15 of the project was assumed to be five times EBITDA (Earnings Before Interest, Tax, Depreciation and Amortization). Operational costs for all process cases was based on 8,400 total annual working hours. Working capital for materials was calculated as 15% of direct costs in the coming year, and working capital for product reserves was calculated as 5% of coming year revenues. A nominal tax rate of 35% was assumed.

In addition to NPV and internal rate of return (IRR) for the project’s capital investment, the primary key performance indicators of interest in this study was the minimum product revenue (MPR), maximum transfer price (MTP), and the incremental EBITDA per unit of wood chips consumed. MPR refers to the minimum product price necessary for achieving a 15% rate of return. For the study cases where the process exports a given product for downstream conversion, the MTP refers to the maximum transfer price a neighboring downstream conversion process would be willing to accept in order to achieve a 12% rate of return for the production downstream product. Lastly, the incremental EBITDA per unit of wood chips is a desirable key performance indicator within the forest products industry, useful for comparison with traditional investment activities for this sector.

2.3 Life Cycle Assessment

Life cycle assessment (LCA) is another system thinking tool that helps to quantify and analyze key environmental performance indicators (e.g. greenhouse gas emissions, etc.). In this work, a comprehensive LCA was performed according to ISO 14044 standards, which includes three main steps, guided by the author's constant interpretation of the system being studied and the data generated, as shown in Figure 2-2. In concert with TEA, iterative analysis of the system under study and careful review of the LCA data generated helps to identify key levers whereby the proposed bio-refinery process may be optimized towards both economic returns and environmental performance, and it is often the case that process inefficiencies that contribute significantly to life cycle emissions are strong indicators of waste or sub-optimal performance.

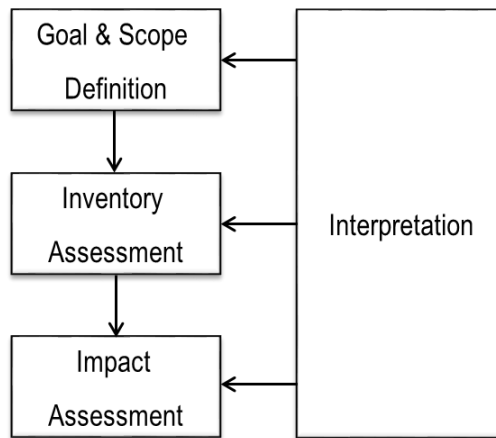


Figure 2-2: Life Cycle Assessment Methodology

2.3.1 Goal & Scope Definition

It is important to explicitly state the goal, purpose and desired outcome for the analysis. For this work, the goal was to determine the effect of bio-refinery projects on the environmental burden for pulp production (per tonne) and to compare the environmental impacts of purified lignin with phenol and alternative fuel products. Consumer use and end use was not considered in this analysis. This study also examined key hot spots in the process and raw materials consumption.

The functional unit is another key part of the LCA goal definition and serves to identify the product or service being delivered by the system under study. For example, the functional unit of 1 air dry metric tonne (ADmt, 92 wt%) SBSK pulp was used in this study. Two methods to address multiple co-products were utilized in order to determine changes to the environmental impact for pulp production: system expansion with substitution and mass and economic allocation.

With system expansion, incremental emission reductions to the SBSK pulp were a result of power and lignin product produced from the mill which was used to offset equivalent products, such as southeast grid electricity and commercial phenolic resin (PFR) in the market according to the following equation:

$$\text{Impact per Functional Unit (SBSK)} = \frac{(\sum \dot{m}_j * CF_j) - kW hr_{elec} * CF_{elec} - \dot{m}_{lignin} * CF_{PFR}}{\dot{m}_{SBSK}}$$

Where “ \dot{m}_j ” and “ CF_j ” represent the mass flow rates and TRACI characterization factors specific to the elementary flows included in the inventory analysis for the entire mill (with the subscript “j” representing the index for each individual process stream). “ $kW hr_{elec}$ ” and “ CF_{elec} ”

refers to the annual surplus (or deficit) power production from the mill and “ \dot{m}_{lignin} ” represents the mill’s lignin production capacity. The characterization factor “ CF_{PFR} ” was used to account for the credit of displacing phenolic resin (PFR) in the market.

As an alternative to the displacement assumption, mass and economic allocation methods were utilized to determine the environmental impact for each co-product: SBSK pulp (1 ADmt, 92 wt%), lignin (1 ADmt, 95 wt%) and soap (1 mt). Utilizing these two methods introduces attributional elements to the study thereby allowing a direct, cradle-to-gate comparison of the individual co-products with their respective equivalent products in the market. It is worth noting, however, that substitution of the pulp mill’s power production remains for both of these methods according to the following equation:

$$Impact\ per\ Functional\ Unit\ (co - prod) = \frac{(\sum \dot{m}_j * CF_j) - kWhr_{elec} * CF_{elec}}{\dot{m}_{co-prod}} * AF$$

Where a percentage of the system’s total emission impacts (including the credit for power production) are allocated to a single co-product according to the co-product’s specific allocation factor, “AF.” For mass and economic allocation, “AF” is described according to the following equations:

$$AF_{mass, co-prod} = \frac{\dot{m}_{co-prod}}{\sum \dot{m}_{co-prod}} = \frac{\dot{m}_{co-prod}}{\dot{m}_{total}}$$

$$AF_{econ, co-prod} = \frac{\dot{m}_{co-prod} * \frac{\$}{m_{co-prod}}}{\sum \dot{m}_{co-prod} * \frac{\$}{m_{co-prod}}} = \frac{\$_{co-prod}}{\$_{total}}$$

Where “ AF_{mass} ” represents the mass fraction of a single co-product for the system’s total products: SBSK pulp, lignin and soap. Similarly, “ AF_{econ} ” represents a single co-product’s

contribution to revenue as a fraction of the system's total revenue, "\$_{total}\$." In this instance, " $\frac{\$}{m_{co-prod}}$ " refers to the assumed market price for each co-product. For this arithmetic, the mass allocation results for each co-product will always equal one another, while slight differences can be observed with economic allocation.

The scope of the analysis spans the cradle-to-gate production of southern bleached softwood kraft (SBSK) pulp and lignin product produced at a kraft pulp mill located in Southeast U.S. The system boundary includes all of the unit operations at the mill in addition to the proposed bio-refinery process. The primary foreground systems analyzed included the pulp mill digester and brown-stock washing, evaporation, recovery boiler, and power production. Incremental changes to the process flows relative to the base case were simulated and data exported were used to build the life cycle inventory inputs and outputs. Background systems for the elementary flows into the pulp mill included softwood production and harvesting as well as chemical, fuel, landfill service and electricity production. Secondary data for the background systems were taken from the Ecoinvent database.

2.3.2 Life Cycle Inventory Assessment

Process simulations generated in this work were used to complete the material and energy balance for the base case and alternative cases proposed, and the exported results were used to build separate life cycle inventories (LCI) for each scenario. An LCI generally provides a comprehensive summary of the major material and energy inputs to the system under study. Major inputs included the wood and chemicals consumed in the pulp mill and bio-refinery process. Outputs included the pulp, lignin product, soap, and excess power produced at the

mill. The primary stack emissions at the mill were calculated for the hog fuel boilers, recovery boiler, and lime kiln

2.3.3 Life Cycle Impact Assessment

Once a complete LCI is obtained, an impact assessment methodology may be employed in order to partially quantify the environmental impacts that result from the product system's life cycle emissions. The first step is to select the desired impact categories and indicators. Generally, there are two types of impact assessment methodologies: mid-point and end-point indicators environmental impacts. End-point indicators may be concerned with an actual effect on the environment (e.g. change in temperature as a result of greenhouse gas emissions), whereas mid-point indicators usually report an equivalence point that is commonly associated with a known element of concern (e.g. gross CO₂e emissions). For this work, mid-point indicators were selected and the impact assessment was performed using the TRACI 2 V3.01 impact assessment method.

The U.S. EPA's TRACI method employs its own database for the next steps involving emission classification and impact measurement. The nine impact categories for emissions are summarized as ozone depletion, global warming, acidification, eutrophication, photochemical smog formation, human health particulate effects, human health cancer, human health noncancer, and ecotoxicity. These mid-point categories allow for the quantification of commonly known stressors that may have an impact on human health and the environment.

2.3.4 Interpretation

Reporting of mid-point indicator results from the impact assessment is not particularly useful in and of itself. Therefore, the most important step to LCA is the constant and iterative interpretation of the data generated for the product system being studied. Similar to TEA, the interpretation of LCA data helps to identify key levers, process material inputs or operating parameters, which may be optimized towards reducing negative environmental impacts. Interpretation typically involves a review of the study completeness and sensitivity to key assumptions. It is then important to identify significant issues with the system being studied and provide conclusions and recommendations for further improvement. Another key aspect of interpretation, is to provide an overview of the study's limitations (e.g. lack data or poor data quality) which helps to highlight areas of continued research towards identifying waste in the product system and, ultimately, reducing negative impacts to the environment.

3 TECHNO-ECONOMIC ANALYSIS OF LIGNIN EXTRACTION IN A KRAFT PULP MILL

3.1 Abstract

Lignin extraction from kraft black liquor on the commercial scale is a new strategy being employed by existing kraft pulp mills operating at recovery boiler capacity. Lignin extraction has demonstrated the potential to i) increase pulp mill throughput by removing black liquor solids prior to the recovery boiler to reduce loading, and ii) create a new lignin co-product for increased mill revenue. This research explores the effects of integrating a commercial scale lignin extraction process on steam usage, chemical recovery, and mill operations utilizing WinGEMS process simulation software. It was determined that, for a three kraft pulp mills producing southern bleached softwood kraft pulp, southern bleached hardwood kraft pulp and 42lb kraft linerboard, pulp production may be increased by 5.2%, 4.4% and 3.2% assuming the recovery boiler is operating at solids limiting capacity. If the recovery boiler is assumed to operate the design limit for high pressure steam, pulp production may be increased by 9.6%, 8.1% and 13.7%, respectively. After the lignin is precipitated, the dilute black liquor is returned to the evaporators resulting in evaporator economy decreases of 2.5% and additional inorganics solids loading throughout the pulp mill chemical recovery loop. The net present value (NPV) at a 15% discount rate was calculated for a variety of scenarios in which the lignin was either converted and sold as a pellet product in Europe (for a \$23 million capital investment) or burned in the lime kiln for a fuel savings credit (for a \$16 million capital investment). In all cases, lignin extraction without incremental pulp production resulted in negative project returns, and minimum product revenue (MPR) required for the lignin sales

price was determined to be \$446 to \$471/admt for the fuel pellet scenarios. For the SBSK case scenarios with lignin exported as fuel pellets, the project returns resulted in a favorable \$6 million and \$34 million NPV (16% and 34% IRR, respectively). The returns were further improved if the lignin was consumed on-site as lime kiln fuel, avoiding the additional capital costs of a pellet mill. For these SBSK cases, the returns were \$34 million for the solids limiting assumptions and \$71 million for the steam limiting assumptions (37% and 53% IRR, respectively). These scenario results were the highest project returns determined of the three pulp mill contexts considered. For the SBHK and 42lb liner case scenarios, only cases with a recovery boiler steam limiting assumption resulted in a positive project returns. For the SBSK cases, the project returns resulted in \$27 million NPV when the lignin was sold as a fuel pellet and \$24 million NPV when consumed on-site as lime kiln fuel (31% and 35% IRR, respectively). For the 42lb liner case scenarios, the project returns resulted in \$60 million NPV when the lignin was sold as a fuel pellet and \$52 million NPV when consumed on-site as lime kiln fuel (42% and 46% IRR, respectively). These results suggest that lignin extraction technology may be a profitable capital investment, provided that the recovery boiler limiting assumption is carefully considered such that incremental pulp production may be achieved.

3.2 Introduction

Success for the modern Kraft pulp mill is largely determined by economies of scale and the need to maximize production. Most often, this results in one unit operation in the Kraft pulp mill operating at max capacity: the Kraft recovery boiler. Kraft recovery boiler upgrades can be cost prohibitive to most mills, so lignin extraction to remove black liquor solids to debottleneck the recovery boiler has been suggested as an economical alternative (Axelsson et

al 2006). The strategy for implementing commercial lignin extraction is to provide an economically viable option for increasing pulp mill production while simultaneously creating a potential source of revenue and a diversification of products.

The “LignoBoost” process, developed from the Swedish national research FRAM (Future Resource-adapted Pulp Mill) program, has been demonstrated on a pilot-plant scale to remove lignin from Kraft black liquor. This process involves lignin extraction by means of CO₂ precipitation and filtration. Acid washing is performed on the resulting lignin product to remove inorganics and lower the final ash content. This process was further optimized for CO₂ precipitation and it was discovered that specific filtration resistance of precipitated lignin subjected to a condition step prior to filtration was lower than slurries filtrated directly after precipitation (Wallmo et al 2009). Additionally, higher pressure (1500 kPa) CO₂ gas allows for a precipitation yield of approximately 77% as opposed to only 35% yields using flue gases from the pulp mill process (Alen et al 1979). As for the inorganics content, the inorganic salt fraction in the Kraft black liquor is more efficiently separated by the acid precipitation and washing to lower the pH and remove inorganic ions from the lignin (Whalen 1975).

Negative effects on chemical recovery and energy efficiency are anticipated with the removal of lignin from Kraft black liquor. It was observed that by removing lignin from the black liquor, changes to the inorganic to organic ratio negatively affects the heat value of the black liquor (Perin-Levasseur 2011). Specifically, decreases in bomb calorimeter value due to less organics. For this reason, it was noted that mill’s will need to improve overall energy efficiency with the addition of lignin extraction. However, evaporator steam economy has been observed as having negligible changes (Moosayifar et al 2006). It was noted that

removing lignin from black liquor causes a reduction in viscosity and a marginal increase in boiling point elevation, suggesting a minimal effect on the evaporation process. In cases where the recovery boiler is operating at maximum capacity, the production increased by lignin extraction resulted in increases to mill steam and power deficits (Kannangara et al 2012). It was observed that for a reference mill with an overloaded recovery boiler, a 15% production increase corresponding to 15% lignin solids removal from the process reduced the higher heat value (HHV) from 13.9 MJ/kg to 13.1 MJ/kg. This was attributed to the increase in inorganic-to-organic ratio for the black liquor solids which resulted in reduced recovery boiler efficiency from 57% to 55%.

Economic analysis was performed on the “LignoBoost” process in order to examine the profitability for a number of different scenarios (Axelsson et al 2006). For pulp mills with production increases that are limited to the recovery boiler operation, the options for capacity increase studied were recovery boiler upgrade and lignin extraction. The recovery boiler load was held constant by extracting lignin from the black liquor in proportion to the production increase. Extracted lignin was sold as a biofuel. It was determined that for a lignin price of \$20/MWh, lignin separation and sale as a biofuel could be more cost advantaged than a recovery boiler upgrade. In a scenario with a steam surplus existing at a Kraft pulp mill, separated lignin can be sold as a biofuel or excess steam can be used for increased power generation which can then be exported for sale on an electrical grid. Profitability was found to be dependent on the lignin versus electricity price and cost of CO₂ for lignin precipitation. It was noted that the profitability for the lignin separation condition was lower than increased power generation at high electricity prices, suggesting that lignin should be sold as a raw

material product as opposed to a biofuel (Olsson et al 2006). This suggests the importance of developing new products where lignin can be used as a higher value raw material.

The objective of lignin extraction is to reduce recovery boiler loading allowing for increased pulp production and to introduce a new product stream to bring additional revenue to the mill. The goal of this process and financial modeling study will be to determine the profitability of the lignin extraction process installed in a Kraft pulp mill operating at recovery boiler capacity and whether or not the chemical and heat losses associated with the process will detrimentally affect operations elsewhere in the pulp mill

3.3 Methodology

3.3.1 Process Simulation

Prior to simulating the lignin extraction process it was necessary to construct a base case (BC) of a typical kraft pulp mill using simulation software to calculate the facility's material and energy balance (see Figure 3-1). The BC was modeled and analyzed representing a kraft pulp mill with annual consumption of 3,000 oven-dry metric tons per day wood chips in order to manufacture southern bleached softwood kraft pulp (SBSK), mixed hardwood bleached kraft pulp (SBHK), and unbleached softwood kraft linerboard (42lb Liner). All simulations were performed in WinGEMS v5.3, which is a material and energy balance modeling package originally developed for the pulp and paper industry. Steady state operating information was exported to detailed summary files created in Excel for financial analyses.

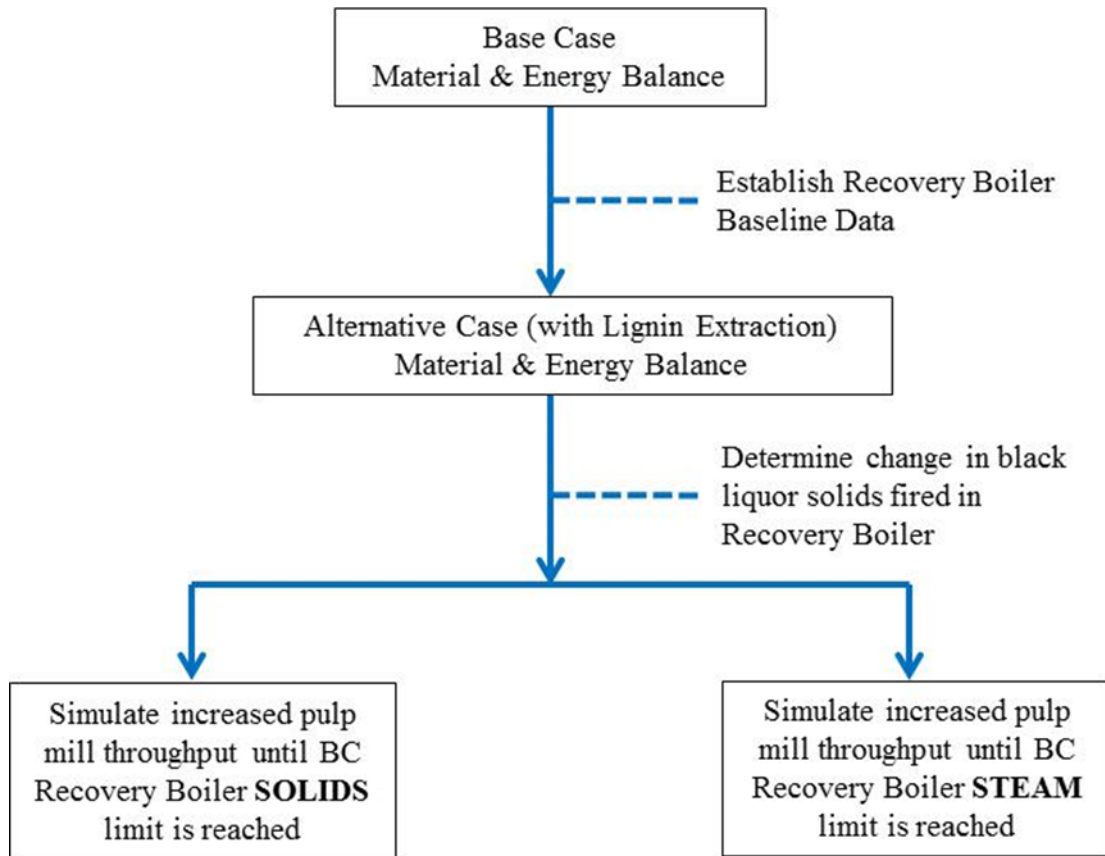


Figure 3-1: Process Simulation Methodology for Kraft Lignin Extraction

Key input data used for the process simulation is shown in Table 3-1. The model assumes effective alkali (EA) and sulfidity concentrations required to achieve an average digester yield of 45% to 55% yield, with yield as a function of an assumed optimum kappa number for each kraft pulp mill scenario (Kleppe 1970). The scenarios assume an optimum kappa number of 30 for SBSK pulps, 20 for SBHK, and 100 for kraft linerboard. The bleaching sequence (O-D0-EOP-D1-P) modeled consists of oxygen delignification (O) in the initial stage, followed by chlorine dioxide (D), alkaline extraction (E), another chlorine dioxide bleaching step (D), and a final peroxide bleaching step (P). The model also features a pulp dryer and counter-

current, multiple effect evaporators with a steam economy of 5.7 to 5.9. The process model tracks wood chip composition as lignin and carbohydrates, and the composition was assumed to have a lignin concentration of 28% wt. and carbohydrates concentration of 72% wt. for softwood. The composition for hardwoods was assumed to have 21% wt. lignin and 79% wt. carbohydrates.

Table 3-1: Key Input Data for the Kraft Pulp Mill

Woodyard, Pulping, BSW	Unit	SBSK	SBHK	42 Lb. Liner
Lignin	%	28%	21%	28%
Carbohydrates	%	72%	79%	72%
Clean Chips	OD mt/day	3000	3000	3000
EA on wood as Na2O	%	17%	14%	13%
Sulfidity	%	28%	22%	28%
WL TTA conc.	g/L as Na2O	100	100	100
Digester Yield	%	45%	48%	55%
Bleach Plant and PMs	Unit	SBSK	SBHK	42 Lb. Liner
O2 Delig.	% on pulp	2.00%	1.20%	0.00%
D0 ClO2 Charge	% on pulp	1.50%	1.00%	0.00%
EOP NaOH Charge	% on pulp	1.00%	1.10%	0.00%
EOP H2O2 Charge	% on pulp	0.40%	0.25%	0.00%
D1 ClO2 Charge	% on pulp	0.80%	1.00%	0.00%
P H2O2 Charge	% on pulp	0.35%	0.35%	0.00%
Pulp Drying (or PM)	Unit	SBSK	SBHK	42 Lb. Liner
Consistency out of Presses	%	48%	48%	53%
Dryer steam demand	lb steam/lb	2.6	2.6	1.75
Evaps and Recovery	Unit	SBSK	SBHK	42 Lb. Liner
Solids Leaving MEE	%	50%	50%	50%
Solids Leaving Concentrator	%	68%	68%	68%
Power and Steam	Unit	SBSK	SBHK	42 Lb. Liner
1250# from HFB1	klb/hr	284	284	284
1250# from HFB2	klb/hr	299	299	299

In the BC, it is assumed that production for the pulp mill is limited by the recovery boiler. There are two proposed recovery boiler limits that were explored in this work: i) a recovery boiler solids limit, and ii) a recovery boiler high pressure steam production limit. Once the BC was complete, simulation data for the recovery boiler black liquor solids and steam production limit were recorded and assumed to be the limiting operating factors for the pulp mill. The maximum black liquor solids loading rate for the recovery boiler was assumed to be 2,795 mt/day for the SBSK scenario, 2,450 mt/day for the SBHK scenario, and 2,170 mt/day for the 42lb liner scenario. The maximum high pressure (58.5 atm) steam production rate was assumed to be 408 mt/hr, 377 mt/hr and 317 mt/hr, respectively. Since the process model tracks lignin and carbohydrates separately, wood heats of formation used for the recovery boiler calculations were assumed to be 0.76 Mcal/kg for lignin and 1.46 Mcal/kg for carbohydrates (Gullichsen 1968). It is important to note that all other unit operations for the mill were assumed to have excess capacity.

The lignin extraction unit process was then incorporated to the process model and various alternative cases were simulated in order to evaluate changes in pulp mill throughput with respect to lignin production. Key assumptions for the lignin extraction process were gathered from the literature (Axelsson et al 2006, Kouisni et al 2011, Maki et al 2012) and are summarized in Table 3-2. It is important to note that for the purposes of this study, lignin extraction by means of acid precipitation was generalized and key distinctions between the proprietary processes “LignoBoost” (Valmet 2016) and “LignoForce” (NORAM 2016) were not considered (e.g. impacts of black liquor oxidation on lignin filterability and process chemical consumption).

Table 3-2: Lignin Extraction Process Input Assumptions

Lignin Extraction	Unit	Value
Production	admt/day	150
Ash Content	%	0.3%
1st Press	pH	9
2nd Press	pH	2.5
Average Filtration Rate	kg/hr-m ²	57

The alternative case attempts to model the lignin extraction process as described in the literature (Olsson et al 2006). Using operating parameters, extracted lignin composition, and a basic understanding of the process flow (see Figure 3-2), the lignin extraction process was simulated. Partially evaporated weak black liquor (WBL) was extracted from the multiple effect evaporator system. This black liquor stream was first cooled using return filtrate from the lignin extraction filter presses, which was then mixed with the black liquor stream prior to the final evaporator effect producing strong black liquor (SBL). After cooling, the lignin slurry was sent to the carbonator where the lignin slurry conditioning begins. Non-condensable gases from the acid mixing step are pulled through the carbonator (via vacuum pump) in order to cool the lignin further and recapture a portion of the volatilized sulfur. CO₂ gas was metered directly into the lignin slurry stream to condition and precipitate the lignin for filtration. The 1st filter press produces a lignin cake which was then sent to an acid mix tank, and the 1st filter press filtrate was returned to the evaporation process. The lignin slurry was further conditioned and homogenized prior to the 2nd stage filter press to produce the final lignin product. An in situ acid washing step was utilized in the filter press to remove bound inorganics from the

lignin. The 2nd filter press filtrate was then returned to WBL storage in the chemical recovery process.

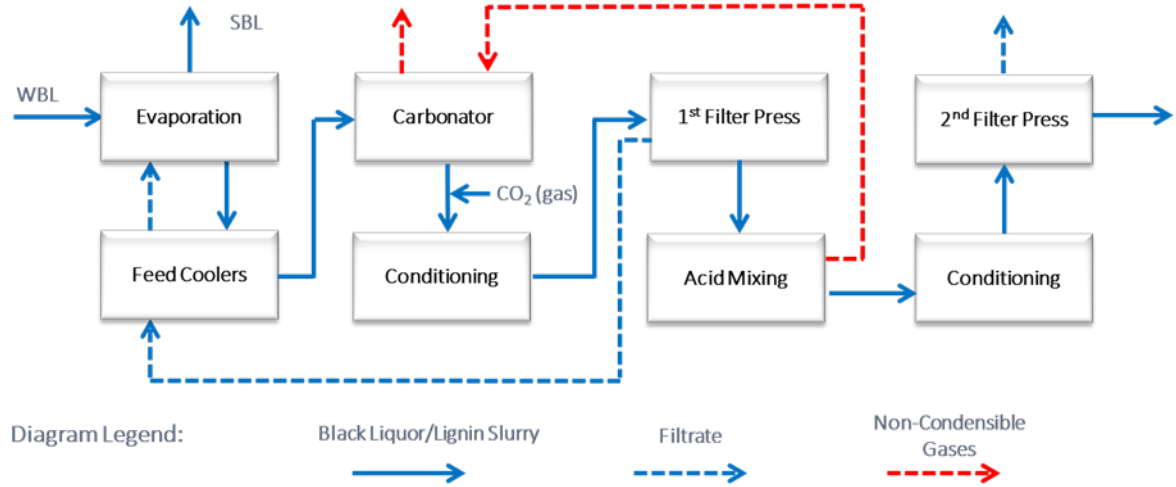


Figure 3-2: Lignin Extraction Process Flow Diagram

Six alternative cases were simulated using the process model (see Table 3-3) with respect to each of the three kraft pulp mill product scenarios for a total of eighteen alternative cases. LE-P simulated the lignin extraction process operating at a capacity of 150 admt/day (with 5% moisture content) and assumes the lignin was sold as pellets exported to Europe. LE-F simulated the lignin burned as lime kiln fuel. Similarly, SOL-P and SOL-F simulated an increase in pulp mill production up to the recovery boiler's maximum solids capacity (established in the BC) in addition to lignin extraction production. STM-P and STM-F simulated increases in pulp mill production until a recovery boiler steam limiting capacity was reached.

Table 3-3: Base & Alternative Cases Simulated

	Cases	Product	Co-Product	Recovery Boiler Capacity	Additional Capital Equipment
Base Case	BC	SBSK, SBHK, 42 Lb. Liner		Solids & Steam Limit Established	
Alternative Cases	LE-P		Lignin Pellets	Under	Pellet Plant
	LE-F		Lime Kiln Fuel	Under	Lime Kiln Mod.
	SOL-P	Δ Pulp	Lignin Pellets	Solids Limit	Pellet Plant
	SOL-F	Δ Pulp	Lime Kiln Fuel	Solids Limit	Lime Kiln Mod
	STM-P	Δ Pulp	Lignin Pellets	Steam Limit	Pellet Plant
	STM-F	Δ Pulp	Lime Kiln Fuel	Steam Limit	Lime Kiln Mod

3.3.2 Capital Expenditures (CAPEX)

Data generated by the process simulation was evaluated using Excel. The financial model was constructed by determining the capital (CAPEX) and operational (OPEX) expenditures impact on total revenue generated for each scenario. Ultimately, the financial model calculated the free cash flows when considering a set of general assumptions.

Capital expenditures are the fixed costs associated with the real equipment used in lignin extraction. All equipment costs have been estimated for year 2013 and scaled to 150 admt/day production, accordingly. Variation of the equipment cost is expressed by the following relationship (Ulrich 1984):

$$C_v = C_u \left(\frac{v}{u} \right)^a$$

Where “C_v” is the purchase price of equipment at a specific capacity represented by “v” and “C_u” is the equipment cost at capacity “u.” Since equipment costs scale disproportionately with size or capacity, the sizing exponent “a” is used for specific equipment.

Similarly, the cost of equipment purchased is adjusted for inflation to 2013 values using the following relationship (Ulrich 1984):

$$C_g = C_r \left(\frac{I_g}{I_r} \right)$$

Where “C_g” and “I_g” is the cost of equipment and indices in year “g”, and “C_r” and “I_r” is the cost of equipment and indices in year “r.” Marshall & Swift (2013) was used to collect inflation indices respective the chemical engineering industry. Equipment costs were gathered from the literature where available and individual price quotes were obtained from equipment manufacturers when needed (Phillips 2010, Peters et al 1968, Pirraglia et al 2010). Table 3-4 provides a summary of the capital expenses estimated for lignin extraction, a pellet plant, and lime kiln modifications necessary to burn lignin as lime kiln fuel.

Table 3-4: Lignin Extraction Capital Equipment Cost Estimate

	Bare Equipment Costs	Total Installed Costs	Source
Lignin Extraction	\$3,539,954	14,413,115	Phillips (2010) Peters et al (1968)
<i>Plate & Frame Filters</i>	<i>\$1,456,987</i>	<i>6,052,100</i>	
<i>Process Equipment</i>	<i>\$2,082,967</i>	<i>8,361,015</i>	
Lime Kiln Modification	\$540,195	2,243,887	Peters et al (1968)
Pellet Plant	--	7,925,638	Pirraglia et al (2010)

An average equipment factor of 4.15 was used to estimate the total installed costs. The largest single equipment costs for lignin extraction were the vertical, plate and frame filters with total installed costs greater than \$6 million for both filters. The filter quote, provided by a commercial vendor, was for 316 stainless steel plate and frame filter, and the filters were sized according to the filtration rate (57 kg/hr-m²) and modeled production capacity (150

admt/day). A sizing exponent of 0.86 was used when estimating the filters. The additional process equipment included stainless steel tanks, sized according to a 60 minute retention time, carbonator, rotary feeders, conveyors, heat exchangers, and process pumps. The process equipment was sized according to flow rates gathered from the process model.

It was assumed that in order to burn the lignin in the lime kiln that additional costs would be incurred to dry the lignin and modify the fuel feed system for the lime kiln. An indirect rotary dryer was sized assuming an average evaporation rate of 15 kg/m²-hr. The lime kiln modification included the purchase of a rotary feed system and centrifugal blower. It was assumed, that the lime kiln would be able to burn the dry lignin powder without significantly affecting flame length or operating temperature. The total installed costs for lignin extraction, drying and lime kiln modifications were estimated at \$16.6 million.

Alternative cases involving the manufacture and sale of lignin pellets was also modeled. The cost of a pellet plant was provided for by the literature and is considered a “lump sum” cost purchased in 2010 and adjusted for inflation (Pirraglia et al 2010). The pellet plant alternative cases include the pellet plant and rotary dryer cost estimates. The total installed costs for lignin extraction, drying, and pelletizing were estimated at \$22.3 million.

3.3.3 Operational Expenditures (OPEX)

Operational expenditures (OPEX) refer to the direct and indirect variable costs associated with lignin extraction and pulp mill production. Direct costs for the production of lignin include chemicals, filter consumables, power, and natural gas for drying the lignin. Indirect costs such as the cost of maintenance and overhead are derived 1% and 3% of replacement asset value. Labor was calculated using salary estimates for 5 employees required

to operate lignin extraction. Depreciation costs were calculated using 7-year MACRS. Additional costs for finishing materials and freight were considered in the pellet production cases.

Direct costs to produce SBSK, SBHK and 42lb Liner include fiber, fuel, power, chemicals, freight and finishing materials. Indirect costs such as maintenance and overhead for the pulp mill were not allocated per ton of additional pulp produced and were considered “sunk” costs. Additionally, the pulp mill was assumed to be a fully depreciated asset.

An overview of the direct costs for both lignin and pulp production are provided in Table 3-5. Chemical costs were provided by ICIS Chemical Business and adjusted for inflation (ICIS 2014). Natural gas prices were gathered from the U.S. Energy Information Administration (US EIA 2014). Freight costs were estimated using a public domain, freight calculator and it was assumed that both the lignin pellets and SBSK pulp would be exported to Europe for sale (World Freight Rates 2014). The finishing materials costs required for pelletizing the lignin were gathered from the literature and were scaled according to an annual cost. All other costs for fiber, power, and filter consumables were assumed.

Table 3-5: Direct Costs for Pulp and Lignin Production

Cost in 2013			
Pulp Mill Costs	\$ per Unit	Unit	Source
Fiber	\$79	Tonnes	Assumed
Caustic Soda	\$465	Tonnes	ICIS (2014)
Power	\$50	MWH	Assumed
Hydrogen Peroxide	\$942	Tonnes	ICIS
Lime	\$81	Tonnes	ICIS
Natural Gas (LKILN)	\$4.30	MMBtu	www.eia.gov (2014)
Sulfuric Acid	\$103	Tonnes	ICIS
Sodium Chlorate	\$549	Tonnes	ICIS
Methanol	\$546	Tonnes	ICIS
Finishing Materials	\$3.00	Tonnes SBSK	Assumed
Freight	\$94	Tonnes SBSK	Freight Calculator (2014)
Lignin Extraction	\$ per Unit	Unit	Source
Carbon Dioxide	\$79	Tonnes	CO ₂ Market Report (2011)
Sulfuric Acid	\$103	Tonnes	ICIS
Natural Gas (Drying)	\$4.30	MMBtu	www.eia.gov
Filter Consumables	\$0.55	Tonnes Lignin	Assumed
Power (Lignin Extraction)	\$50	MWH	Assumed
Finishing Materials	\$1,600,000	Per year	Pirraglia et al
Freight	\$94	Tonnes Lignin	Freight Calculator

3.3.4 General Assumptions

Best professional judgment is used to determine the appropriate risk required for the discounting future cash flows in the financial model (15% internal rate of return). A project life of 15 years was used for evaluation of lignin extraction. Pellet revenue was assigned to the lignin product to be sold as a biofuel in Europe according to the Fuel Pellet Institute reported price of \$245/admt (2014). For the alternative cases involving lignin burned as lime

kiln fuel, a credit is calculated based on natural gas savings. The revenue for SBSK , SBHK, and 42lb liner produced was gathered from RISI Price Watch and was assumed to be \$850/admt, \$800/admt, and \$650/admt, respectively (2014).

The terminal value in year 15 of the project was assumed five times EBITDA (Earnings Before Interest, Tax, Depreciation and Amortization). Operational costs for the pulp mill and lignin extraction production was based on 8,400 total annual working hours. Working capital for materials was calculated as 15% of direct costs in the coming year, and working capital for product reserves was calculated as 5% of coming year revenues. A nominal tax rate of 35% was assumed.

3.4 Results & Discussion

3.4.1 Process Changes with Lignin Extraction

Elemental sodium and sulfur were tracked in the process model and changes to inputs and outputs with the addition of lignin extraction were simulated. Incoming sodium was tracked as fresh sodium hydroxide (NaOH) in both the oxygen delignification reactors and as make-up white liquor. Where applicable, additional sodium was input to the R-10 chlorine dioxide process as sodium chlorate (NaClO₃). The process model accounts for sodium and sulfur losses throughout the pulp bleaching and chemical recovery processes, and given the specified sulfidity and effective alkali concentrations in the simulation, all cases exhibited excess sulfur which was removed from the material balance as recovery boiler precipitator catch purge. The primary sodium losses result from the recovery boiler precipitator catch purge and sodium carryover to the bleach plant.

Figure 3-3 provides an illustration of the change in fresh NaOH required (as elemental sodium) with the return of acidic filtrate in the lignin extraction cases (as elemental sulfur) to the chemical recovery loop. The acidic filtrate contains elemental sulfur from sulfuric acid (H_2SO_4 , used for washing and purifying the lignin) which results in excess sulfur in the process when returned to weak black liquor storage. The process model was designed such that the precipitator losses are controlled automatically in order to maintain the sodium-sulfur balance (based on assumed % sulfidity and % effective alkali concentrations), and the simulation removes the excess elemental sulfur by controlling the amount of electrostatic precipitator catch removed from the process. Since the electrostatic precipitator catch is primarily sodium sulfate (Na_2SO_4) and sodium carbonate (Na_2CO_3), approximately 2 to 2.4 mols of sodium are removed from the process for every mol of sulfur removed. This results in a significant increase in sodium recovery boiler precipitator catch losses with the addition of lignin extraction. Figure 3 exhibits a direct relationship with respect to increases in precipitator catch sodium losses with increased make-up white liquor (WL).

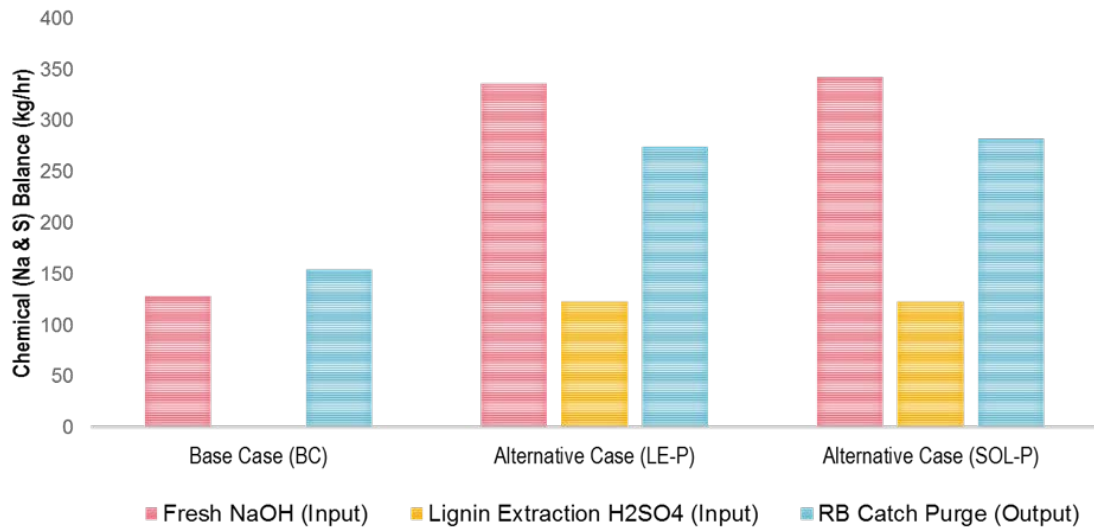


Figure 3-3: Chemical Balance with Elemental Sodium & Sulfur

Table 3-6 shows the key power and recovery data recorded by the process model for all the SBSK case scenarios. In general, the integration of lignin extraction with 150 admt/day operating capacity accounts for a solids loading to the recovery boiler drop by approximately 5.2% for the SBSK scenarios. The organic-to-inorganic ratio of the black liquor is changed slightly and the heating value of the black liquor has been accounted for in the model. It was observed that the integration of lignin extraction had a small impact on the evaporator economy with an estimated decrease from 5.76 to 5.59. In the process model, the black liquor was flashed and cooled in the lignin extraction plant and this sensible heat must be made up for with a small amount of additional steam to the evaporator train. Since the change in evaporator economy is directly related to the lignin extraction operating capacity, no other changes were observed for the alternative cases.

Table 3-6: Key Power & Recovery Data for SBSK Scenarios

Case Scenarios	SBSK	BC	LE	SOL	STM
Production Output	admt/hr	52.5	52.5	55.3	57.6
% Increase			0.0%	5.2%	9.6%
Power & Recovery	SBSK	BC	LE	SOL	STM
Recovery Boiler Solids	mt/day	2795	2650	2795	2917
Organic Content, BLS	kg/mt	476	466	466	467
X _{lignin} , BLS	%	52.10%	48.70%	48.90%	49.06%
X _{carb} , BLS	%	47.90%	51.30%	51.10%	50.94%
Inorganic Content, BLS	kg/mt	219	229	228	228
H _f , BLS	Mcal/kg	-1.10	-1.12	-1.12	-1.12
Bomb Heat Value (BHV)	Mcal/mt	3660	3606	3609	3611
Recovery Boiler Efficiency	%	65.30%	64.50%	64.50%	64.43%
HP Steam (58.5 atm)	mt/hr	408	371	393	407
Evaporator Steam Economy	mt/mt stm	5.76	5.59	5.59	5.59
Lime Kiln Fuel, Natural Gas	MJ/hr	130787	128487	135471	141132
Pulp Mill Power Production	MW	71.7	68.6	70.3	71.6
Power Consumption	MW	63.3	67.2	70.5	67.9

While the SOL cases allowed for a 5.2% increase in pulp production, the high pressure steam (58.5 atm) production is reduced from 408 mt/hr to 371 and 393 mt/hr for LE and SOL. No deficit in power production was observed as the pulp mill was capable of producing excess power for all case scenarios. Lime kiln fuel consumption decreased slightly for LE due to the decreases in green liquor processing which resulted from increased inorganics losses with the recovery boiler precipitator purge and corresponding increased make-up WL. Additionally, lime kiln fuel consumption for LE, SOL, and STM was calculated using natural gas with an assumed higher heating value (HHV) of 12,926 kcal/kg. For scenarios where lignin is combusted as lime kiln fuel, the lignin fuel consumption was calculated with an assumed

HHV of 6,402 kcal/kg. For the STM scenarios, pulp production was observed to increase by 9.6% in order to reach the BC high pressure steam production rate of 408 mt/hr.

Table 3-7 shows the key power and recovery data recorded by the process model for all the SBHK case scenarios. In this instance, the SOL cases allowed for a 4.4% increase in pulp production, slightly lower than SBSK case scenarios. High pressure steam production was reduced from 377 to 347 and 363 mt/hr for LE and SOL, and the STM scenario resulted in an 8.1% production increase. Similar trends were determined with respect to lime kiln fuel consumption, with an initial decrease for the LE scenario and then higher fuel consumption in the SOL and STM scenarios. A power deficit was observed for the SOL and STM scenarios as well, where an additional 1.5 to 3 MW power is required.

Table 3-7: Key Power & Recovery Data for SBHK Scenarios

Case Scenarios	SBHK	BC	LE	SOL	STM
Production Output	admt/hr	56.5	56.5	59.0	61.1
% Increase			0.0%	4.4%	8.1%
Power & Recovery	SBHK	BC	LE	SOL	STM
Recovery Boiler Solids	mt/day	2447	2339	2447	2537
Organic Content, BLS	kg/mt	505	498	498	499
X _{lignin} , BLS	%	45.47%	41.88%	42.04%	42.16%
X _{carb} , BLS	%	54.53%	58.12%	57.96%	57.84%
Inorganic Content, BLS	kg/mt	185	191	191	191
H _f , BLS	Mcal/kg	-1.14	-1.17	-1.17	-1.16
Bomb Heat Value (BHV)	Mcal/mt	3537	3477	3479	3481
Recovery Boiler Efficiency	%	67.20%	66.47%	66.50%	66.53%
HP Steam (58.5 atm)	mt/hr	377	347	363	376
Evaporator Steam Economy	mt/mt stm	5.77	5.62	5.62	5.62
Lime Kiln Fuel, Natural Gas	MJ/hr	116415	114827	119966	124164
Pulp Mill Power Production	MW	69.3	67.0	68.2	69.2
Power Consumption	MW	66.7	66.7	69.7	72.1

Table 3-8 shows the key power and recovery data recorded by the process model for all the 42lb Liner case scenarios. The SOL cases allowed for a 3.2% increase in pulp production. High pressure steam production was reduced from 317 to 279 and 287 mt/hr for LE and SOL, and the STM scenario resulted in an 13.7% production increase. Similar trends were determined with respect to lime kiln fuel consumption, with an initial decrease for the LE scenario and then higher fuel consumption in the SOL and STM scenarios. The 42lb Liner base case scenario exhibited a power deficit of 20 MW, and this deficit is increased to 22, 25 and 31 MW for the LE, SOL and STM cases with lignin extraction.

Table 3-8: Key Power & Recovery Data for 42 Lb. Liner Scenarios

Case Scenarios	42 Lb. Liner	BC	LE	SOL	STM
Production Output	admt/hr	71.7	71.7	74.0	81.5
% Increase			0.0%	3.2%	13.7%
Power & Recovery	42 Lb. Liner	BC	LE	SOL	STM
Recovery Boiler Solids	mt/day	2171	2111	2169	2358
Organic Content, BLS	kg/mt	472	442	445	453
X _{lignin} , BLS	%	49.88%	45.36%	45.47%	45.81%
X _{carb} , BLS	%	50.12%	54.64%	54.53%	54.19%
Inorganic Content, BLS	kg/mt	224	257	254	244
H _f , BLS	Mcal/kg	-1.11	-1.14	-1.14	-1.14
Bomb Heat Value (BHV)	Mcal/mt	3633	3580	3579	3576
Recovery Boiler Efficiency	%	64.99%	62.36%	62.59%	63.27%
HP Steam (58.5 atm)	mt/hr	317	279	287	317
Evaporator Steam Economy	mt/mt stm	5.91	5.70	5.70	5.70
Lime Kiln Fuel, Natural Gas	MJ/hr	103620	101486	104836	115707
Pulp Mill Power Production	MW	64.8	61.9	62.5	64.8
Power Consumption	MW	84.6	84.6	87.3	96.1

3.4.2 Cost Analysis

At steady state, the cash costs were calculated for the pelletizing and lime kiln modification cases. Total production costs at year 2 (full production) are illustrated in Figure 3-4 and Figure 3-5. The total costs for the pelletizing cases were calculated at approximately \$374/admt of lignin product as opposed to only \$137/admt for the lime kiln modification case. The depreciation costs were significantly higher for the pelletizing cases, but the single greatest cost was for international freight at \$98/admt. The power demand for the lignin extraction process was estimated at only 1.32 MW. However, power costs were high at \$45/admt due to the higher power consumption of 5.24 MW when including the pellet plant. Other significant costs included labor at \$52/admt and finishing materials at \$32/admt. The finishing materials represent the cost of packaging the pellet product and preparing it for shipment. These costs are avoided in the lime kiln modification cases. Other costs for chemicals and filter consumables remained the same between the pelletizing and lime kiln modification cases.

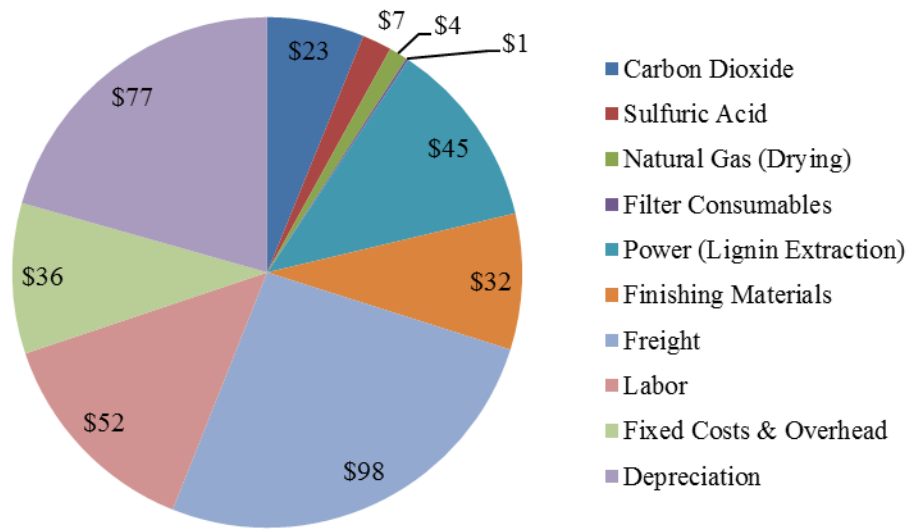


Figure 3-4: Year 2 Lignin Extraction Costs, For the Pelletizing Cases (\$/admt lignin)

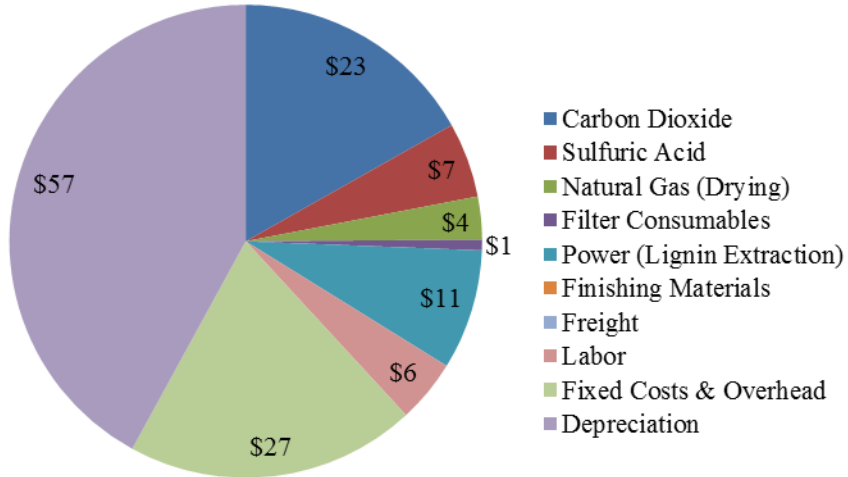


Figure 3-5: Year 2 Lignin Extraction Costs, For the Lime Kiln Modification Cases (\$/admt lignin)

The incremental costs for additional pulp tons with the SBSK, SBHK and 42lb Liner cases are shown in Table 3-9. For this analysis, indirect costs associated with the pulp mill production were not allocated to the total costs and were assumed to be “sunk” costs. The total direct costs were calculated to be \$604/admt of increased SBSK pulp production, \$488 for SBHK and \$446 for 42lb Liner. SBSK tons have the highest fiber costs at \$218/admt, while the SBHK and 42lb Liner cases have lower fiber costs at \$203 and \$160/admt due to higher pulp mill yields. Similar to the pellet products, it was assumed that the SBSK would be exported to Europe with freight costs of \$98/admt, and this assumption for incurred freight costs was included with the SBHK and 42lb Liner cases as well. Chemical costs for caustic soda were calculated at \$74/admt for the SBSK case and include fresh NaOH for bleaching as well as make-up white liquor, while the SBHK and 42lb Liner cases have lower caustic soda costs at \$63 and \$69/admt, respectively. However, the most notable incremental costs associated with lignin extraction are costs incurred from decreased power production due to extracting combustible organics from the black liquor and increasing the inorganics load to the recovery boiler. The SBSK case resulted in the highest incremental power costs of \$157/admt and the SBHK and 42lb Liner cases were \$81 and \$113/admt, respectively.

Table 3-9: Year 2 Pulp Mill Production Costs (\$/admt additional pulp produced)

\$/admt Product	SBSK	SBHK	42 Lb. Liner
Fiber	\$218	\$203	\$160
Caustic Soda	\$74	\$63	\$69
Power	\$157	\$81	\$113
Hydrogen Peroxide	\$14	\$11	\$0
Lime	\$3	\$2	\$1
Natural Gas (LKILN)	\$7	\$6	\$2
Sulfuric Acid	\$3	\$2	\$0
Sodium Chlorate	\$25	\$17	\$0
Methanol	\$2	\$2	\$0
Finishing Materials	\$3	\$3	\$3
Freight	\$98	\$98	\$98
Total	\$604	\$488	\$446

3.4.3 Key Financial Indicators

Generally, lignin sold as a pellet product was observed to produce more revenue at \$245/admt as compared to the lime kiln fuel credit of \$110/admt lignin (from displacing equivalent natural gas at \$4.30/MMBtu). However, no profit from the sale of pellets was observed for these cases due to the overwhelming cash costs (\$374/admt) when compared to the assumed pellet revenue of \$245/admt. Again, the revenue for SBSK, SBHK, and 42lb Liner produced was assumed to be \$850/admt, \$800/admt, and \$650/admt, respectively. Assuming a discount rate of 15%, the financial model was used to calculate the net present value (NPV) for all cases (as shown in Figure 3-6).

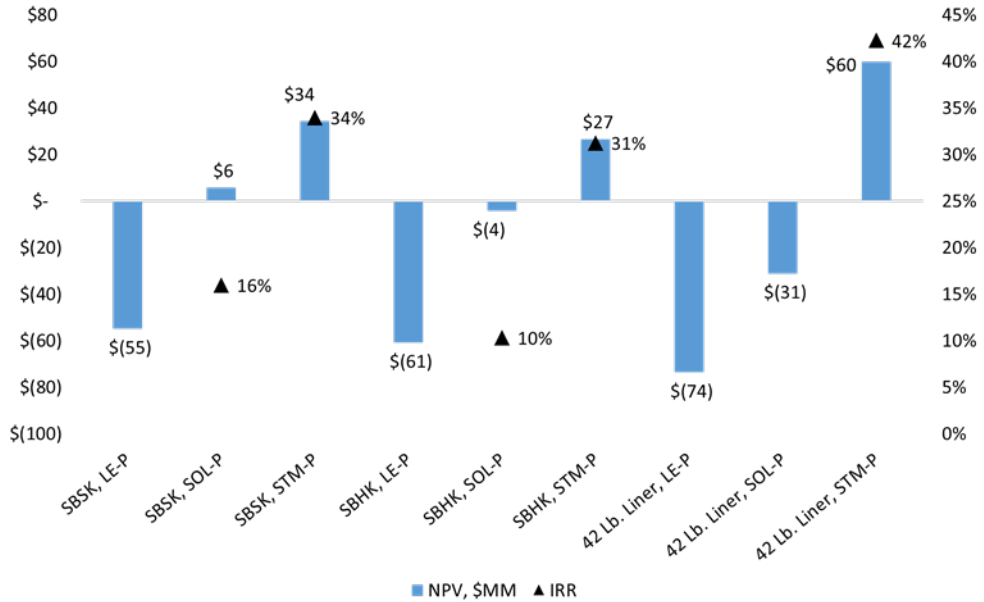


Figure 3-6: Key Financial Indicators (NPV \$MM, IRR %) for All Scenarios, with Lignin Exported as Fuel Pellets

The financial model results indicate that the sale of lignin pellets alone, without any increase in pulp mill production, would not result in a return on investment. For the SBSK scenarios, LE-P was shown to have a NPV of negative \$55 million, while the SOL-P and STM-P cases were \$6 and \$34 million NPV, corresponding with 5.2% and 9.6% incremental pulp production increases. For the SBHK SOL-P case, the incremental pulp production was only 4.4%, which results in negative \$4 million NPV despite a higher contribution margin per incremental ton produced when compared with SBSK (\$312/admt EBITDA as opposed to \$246). The 42lb Liner SOL-P case was considerably worse with only a 3.2% pulp production increase and \$204/admt contribution margin which resulting in a negative \$31 million NPV. However, the 42lb Liner STM-P case performed exceptionally better than the other STM cases

for SBSK and SBHK with \$60 million NPV, primarily a result of the additional 13.7% pulp production increases.

These results demonstrate the sensitivity to the recovery boiler limiting assumption. Extracting 150 admtd/day lignin from the black liquor resulted in 38 mt/hr decrease in high steam pressure for both the 42lb Liner and SBSK case scenarios. For the pulp mill producing 42lb Liner, the black liquor heating value is lowered by 57 Mcal/mt from 3633 to 3576 Mcal/mt due to increases in inorganics and decreases in organics content. On the other hand, the SBSK case resulted in black liquor heating value being lowered by only 49 Mcal/mt, from 3660 to 3611 Mcal/mt. Therefore, the 42lb Liner case allows for a higher pulp production increase (13.7% as opposed to 9.6% for the SBSK STM case) due to the ability to push more solids through the recovery boiler by making-up equivalent high pressure steam with a lower heat quality black liquor. Alternatively, when considering a solid limiting assumption, the higher relative inorganics content of the 42lb Liner case scenario liquor allows for only a 3.2% pulp production increase as opposed to the 5.2% for SBSK. This suggests that careful consideration must be given to the recovery boiler limiting assumption when considering a lignin extraction capital investment project.

Financial results for the lime kiln modification cases are shown in Figure 3-7. In the lime kiln modification cases, revenue was realized as a fuel savings credit. For this reason, the SBSK case scenarios performed better where more natural gas was being consumed as opposed to the SBHK and 42lb Liner cases (130,000 MJ/hr as opposed to 116,000 and 103,000, respectively). The SBSK lime kiln fuel cases resulted in \$34 and \$71 million for SOL and STM case assumptions, much higher than the fuel pellet case scenarios. Alternatively, both the

SBHK and 42lb Liner cases resulted in slightly lower NPV as compared with the fuel pellet case scenarios. This suggests that SBSK pulp mills may be advantaged with a lime kiln modification to consume extracted lignin as an alternative to natural gas.

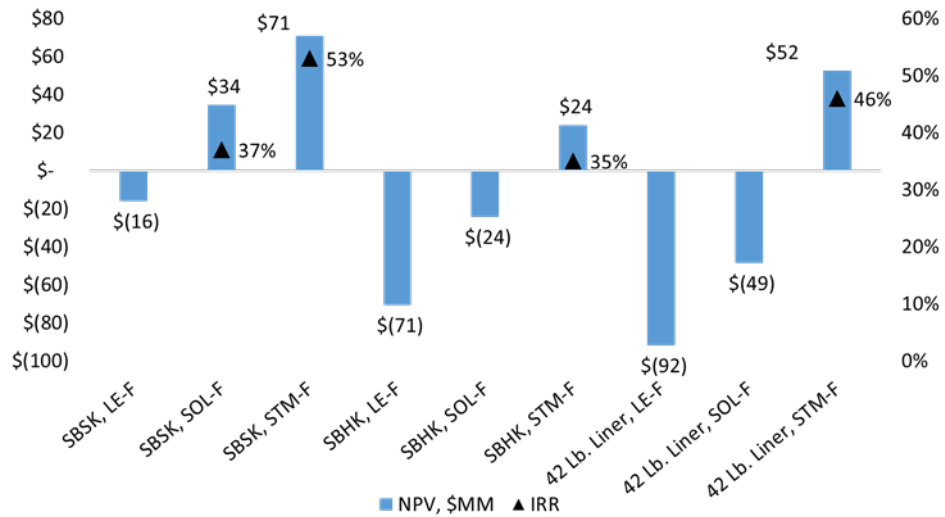


Figure 3-7: Key Financial Indicators (NPV \$MM, IRR %) for All Scenarios, with Lignin as Lime Kiln Fuel

Table 3-10 provides results for the minimum product revenue (MPR) necessary from lignin sales in order to receive a 15% internal rate of return. If no incremental pulp production increases are realized, the lignin must sell for a price between \$445 to \$470/admt assuming the lignin is pelletized and exported off-site. When the lignin is consumed internally, on-site in the lime kiln, the MPR may be as low as \$197/admt for the SBSK case scenario but is considerably higher for the SBHK and 42lb Liner scenarios (\$402 and \$541/admt, respectively). However, the MPR was reduced significantly for the SOL and STM cases where revenue received from incremental pulp ton sales offsets the revenue required from lignin

sales. For the SBSK cases, lignin may be sold for \$244 and \$74/admt for the SOL and STM case assumptions. For the SBHK cases, lignin may be sold for \$263 and \$104/admt. 42lb Liner must be sold for \$354/admt if the recovery boiler limiting assumption is based on solids fired; however, no revenue is needed from lignin sales when considering a steam limiting assumption. These results suggest that valorization of the lignin may be necessary if incremental increases to pulp production are not achievable with the lignin extraction project (i.e. there exists other production capacity limiting unit processes such as machine speed, evaporator capacity, etc. which cannot be reasonably improved in a cost-effective manner). Phenol, for example, has a market price of \$900 to \$1200/mt which is significantly higher than the fuel value of \$160/mt for unmodified lignin.

Table 3-10: Summary, Including Minimum Product Revenue (MPR),

Case Scenario	MPR	NPV, \$MM	IRR	EBITDA/mt-wood
SBSK, LE-P	\$446	-\$55		
SBSK, SOL-P	\$244	\$6	16%	\$180
SBSK, STM-P	\$74	\$34	34%	\$192
SBHK, LE-P	\$457	-\$61		
SBHK, SOL-P	\$263	-\$4	10%	\$155
SBHK, STM-P	\$104	\$27	31%	\$184
42 Lb. Liner, LE-P	\$471	-\$74		
42 Lb. Liner, SOL-P	\$354	-\$31		
42 Lb. Liner, STM-P	-\$22	\$60	42%	\$160
SBSK, LE-F	\$197	-\$16		
SBSK, SOL-F		\$34	37%	\$187
SBSK, STM-F		\$71	53%	\$198
SBHK, LE-F	\$402	-\$71		
SBHK, SOL-F	\$227	-\$24		
SBHK, STM-F		\$24	35%	\$97
42 Lb. Liner, LE-F	\$541	-\$92		
42 Lb. Liner, SOL-F	\$335	-\$49		
42 Lb. Liner, STM-F		\$52	46%	\$102

Lastly, for the cases where incremental pulp production was achievable, the incremental EBITDA per ton of wood consumed was considered. The SBSK cases resulted in the highest incremental EBITDA with \$180 to \$192/mt-wood for the fuel pellet scenarios and \$187 to \$198/mt-wood for the lime kiln fuel scenarios. For the lime kiln fuel cases, no incremental EBITDA was achieved for the SBHK and 42lb Liner solids limiting case scenarios.

3.4.4 Sensitivity Analysis

Figure 3-8 provides a sensitivity analysis for the SBSK case scenario with a recovery boiler steam limiting assumption. Key financial indicators for a lignin extraction capital investment project were determined to be most sensitive to achievable incremental pulp production and the pulp market price. By comparison, the NPV was considerably less sensitive to the lignin sales price and capital investment required for lignin extraction. This suggests that additional capital investment towards improving production capacity may be warranted in order to achieve the incremental pulp production increases necessary for an adequate project return.

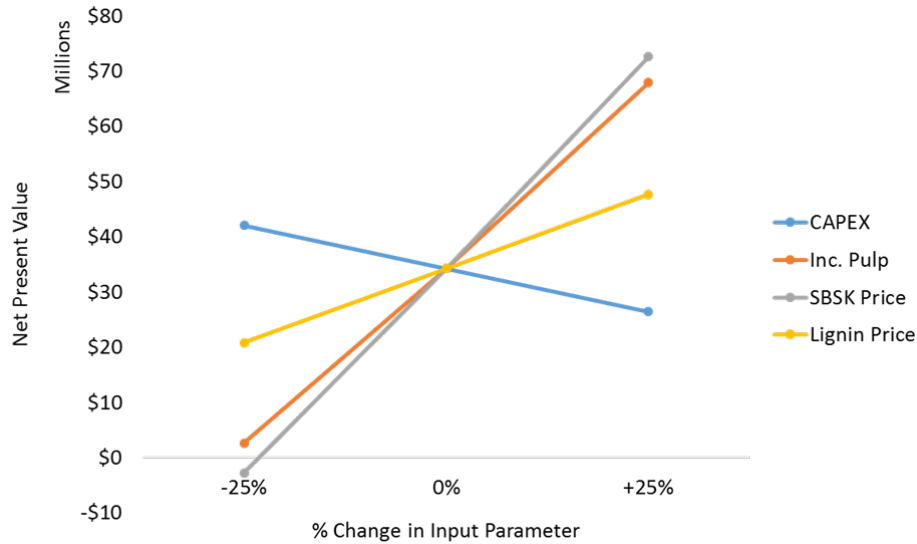


Figure 3-8: Net Present Value Sensitivity to % Change in Input Parameters for SBSK-SOL-P Case Scenario

3.5 Conclusions

Three kraft pulp mill scenarios, each consuming 3,000 bdmt/day wood chips, were simulated with an integrated lignin extraction process using WinGEMS v5.3. The process model was used to conduct a thorough material and energy balance in order to determine the impact of lignin extraction operating at 150 admt/day. It was determined that for a pulp mill producing southern bleached softwood kraft (SBSK) pulp, extracting lignin from black liquor solids allowed for an approximate 5.2% increase in pulp production assuming a recovery boiler solids limit. In the case of the recovery boiler operating at maximum steam production, extracting lignin from black liquor solids allowed for a 9.6% increase in pulp production. After the lignin is precipitated, the dilute black liquor is returned to the evaporators resulting in

evaporator economy decreases of 2.5% and additional inorganics solids loading throughout the pulp mill chemical recovery loop. Similarly, a pulp mill producing southern bleached hardwood kraft (SBHK) pulp may increase pulp production by 4.4% and 8.1%, and a mill producing 42lb kraft linerboard may increase pulp production by 3.2% and 13.7%.

The net present value (NPV) at a 15% discount rate was calculated for a variety of scenarios in which the lignin was either converted and sold as a pellet product in Europe or burned in the lime kiln for a fuel savings credit. In all cases, lignin extraction without incremental pulp production resulted in negative project returns, and minimum product revenue (MPR) required for the lignin sales price was determined to be \$446 to \$471/admt for the fuel pellet scenarios. This suggests that significant valorization of the lignin may be necessary in order to justify a lignin extraction capital investment project without increases to incremental pulp production.

The NPV for the various case scenarios were improved considerably with increases to pulp production, but the project returns were determined to be highly sensitive to the recovery boiler limiting assumptions which determines the amount of increased pulp. For the SBSK case scenarios with lignin exported as fuel pellets, the project returns resulted in a favorable \$6 million and \$34 million NPV (16% and 34% IRR, respectively). The returns were further improved if the lignin was consumed on-site as lime kiln fuel, avoiding the additional capital costs of a pellet mill. For these SBSK cases, the returns were \$34 million for the solids limiting assumptions and \$71 million for the steam limiting assumptions (37% and 53% IRR, respectively). These scenario results were the highest project returns determined of the three pulp mill contexts considered.

For the SBHK and 42lb Liner case scenarios, only cases with a recovery boiler steam limiting assumption resulted in a positive project returns. For the SBHK cases, the project returns resulted in \$27 million NPV when the lignin was sold as a fuel pellet and \$24 million NPV when consumed on-site as lime kiln fuel (31% and 35% IRR, respectively). For the 42lb Liner case scenarios, the project returns resulted in \$60 million NPV when the lignin was sold as a fuel pellet and \$52 million NPV when consumed on-site as lime kiln fuel (42% and 46% IRR, respectively).

Finally, the project returns were determined to be most sensitive to achievable incremental pulp production and the pulp market price, and by comparison, the key financial indicators were considerably less sensitive to the lignin sales price and capital investment required for lignin extraction. This suggests that additional capital investment towards improving production capacity may be warranted in order to achieve the incremental pulp production increases necessary for an adequate project return.

4 LIFE CYCLE ASSESSMENT OF LIGNIN EXTRACTION IN A SOFTWOOD KRAFT PULP MILL

4.1 Abstract

Lignin extracted from kraft pulp mills located in the southeast United States represent an emerging opportunity for novel biomaterials from wood, a renewable resource. The lignin extraction process has demonstrated the potential to create a new lignin co-product for increased mill revenue. The objective of this work was to examine the environmental life cycle impact of integrating a commercial scale lignin extraction process to an existing kraft pulp mill producing southern bleached softwood kraft (SBSK) pulp. This life cycle assessment study includes a cradle-to-gate analysis of the production of SBSK pulp from southern loblolly pine, with and without lignin extraction, using a detailed mass and energy balance modeled in WinGEMS V5.3 simulation software. The functional unit for this study was 1 ADmt (air dry metric tonne) SBSK pulp. Both system expansion and mass allocation were used to account for placement of environmental burdens to both products. Key differences in TRACI environmental impacts were observed using mass allocation, with global warming potential for the SBSK pulp product with lignin extraction reported as 602 kg CO₂eq per ADmt SBSK pulp as compared to 722 kg CO₂eq per ADmt SBSK pulp for the base case without lignin extraction. When system expansion was utilized, the global warming potential for the SBSK pulp product was reported as 234 kg CO₂eq. This reduction was primarily due to the displacement of petroleum derived phenolic resins by the lignin co-product credited to the SBSK pulp. Sodium chlorate and natural gas was identified as a key “hotspot,” or process stream contributing significantly to environmental burdens at the mill. Overall, this study

demonstrated that the kraft pulp mill system has reduced environmental impact with the addition of a lignin co-product.

4.2 Introduction

Success for the modern Kraft pulp mill is largely determined by economies of scale and the need to maximize production. Most often, this results in one unit operation in the kraft pulp mill operating at max capacity: the kraft recovery boiler. Kraft recovery boiler upgrades can be cost prohibitive to most mills, so lignin extraction to remove black liquor solids in order to debottleneck the recovery boiler has been suggested as an economical alternative (Axelsson et al., 2006). The strategy for implementing commercial lignin extraction is to provide an economically viable option for increasing pulp mill production while simultaneously creating a potential source of revenue and a diversification of products.

The current application for kraft lignin as a raw material for the manufacture of low-cost carbon fibers was explored in order to provide lighter, low-cost materials for automobile construction and to improve economics of biorefineries that produce a lignin product (Baker & Rials, 2013). Additionally, extracted kraft lignin has been found to have a low degree of polymerization and contained low quantities of oxygen containing functional groups making it a viable feedstock for biomaterials production (Nagy, Kosa, Theliander, & Ragauskas, 2010).

Lignin fiber manufacture was previously demonstrated through the use of thermal spinning (Kadla, Kubo, Venditti, & Gilbert, 2002). A porous, hollow-core lignin fiber was produced from lignin and synthetic polymer blends. The blended polymer allows for disruption of the extensive cross-linking in lignin, the primary cause for the poor visco-elastic properties that

prevent fiber spinning. By improving lignin fiber manufacturing techniques, lignin has been shown to be viable raw material for commercial application.

Extracted lignin, from a pilot plant developed by FPInnovations, has also been used as a replacement for phenols in the preparation of lignin-based phenol formaldehyde resins (Maki et al, 2012). These resins are used as adhesives for wood products such as oriented strand board (OSB), and product testing showed that up to a 50% substitution of the phenol allows for OSB shear strength values comparable to a control group.

Kraft lignin also offers a competitive environmental advantage to products derived from petroleum based raw materials. Life cycle assessments performed on extracted kraft lignin determined that the product may be preferable to synthetic organic compounds of similar molecular complexity (Bernier, Lavigne, & Robidoux, 2013). This is due to the energy efficiency of lignin extraction over organic compound synthesis. It should also be noted that the dominant contributors to life cycle environmental impact from the kraft recovery process are the result of the chemical and energy input production chains (Rehnstrom, 2003).

The purpose of this study was to analyze the cradle-to-gate life cycle environmental impacts for a kraft pulp mill producing southern bleached softwood kraft (SBSK) pulp in order to determine reductions to environmental impact per unit of SBSK pulp produced with the addition of a commercial lignin extraction process. Additionally, this study determined the environmental impact for a lignin co-product using mass allocation.

4.3 Methodology

4.3.1 Goal Definition

Lignin can be readily separated from kraft black liquor, thereby lowering the black liquor solids content, with acid precipitation and separation (filtration) according to Axelsson et al, 2006. A benefit to implementing lignin extraction at a kraft pulp mill is to reduce recovery boiler loading, allowing for increased pulp production, and introduce a new product stream to bring additional revenue to the mill. A comprehensive process model of a kraft pulp mill was used to perform a life cycle assessment (LCA) using ISO 14044 standards. For this assessment, the goal was to determine the effect of lignin extraction on the environmental burden for pulp production (per tonne) and to compare the environmental impacts of purified lignin with phenol and alternative fuel products. In addition to its fuel value, lignin sold from the kraft pulp mill can potentially displace phenol in phenol formaldehyde adhesives, and a one-to-one substitution of the extracted lignin product with phenolic resin was assumed. Consumer use and end use was not considered in this analysis. This study also examined key hot spots in the process and raw materials consumption.

4.3.2 Functional Unit

The functional unit of 1 air dry metric tonne (ADmt, 92 wt%) SBSK pulp was used in this study. Two methods to address multiple coproducts were utilized in order to determine changes to the environmental impact for SBSK pulp production: system expansion with substitution and mass and economic allocation. With system expansion, incremental emission reductions to the SBSK pulp were a result of power and lignin product produced from the mill

which was used to offset equivalent products, such as southeast grid electricity and commercial phenolic resin (PFR) in the market according to the following equation:

$$\text{Impact per Functional Unit (SBSK)} = \frac{(\sum \dot{m}_j * CF_j) - kW hr_{elec} * CF_{elec} - \dot{m}_{lignin} * CF_{PFR}}{\dot{m}_{SBSK}}$$

Where “ \dot{m}_j ” and “ CF_j ” represent the mass flow rates and TRACI characterization factors specific to the elementary flows included in the inventory analysis for the entire mill (with the subscript “j” representing the index for each individual process stream). “ $kW hr_{elec}$ ” and “ CF_{elec} ” refers to the annual surplus (or deficit) power production from the mill and “ \dot{m}_{lignin} ” represents the mill’s lignin production capacity. The characterization factor “ CF_{PFR} ” was used to account for the credit of displacing phenolic resin (PFR) in the market. In this equation, only the production of SBSK was considered for the functional unit. It is worth noting that system expansion with respect to substitution of the bioenergy displacing grid electricity from fossil fuels is widely accepted as a method to obtain a functional unit that is wood product only (Brander & Wylie, 2011). Credits received for substituting non-wooden products with wood products on the other hand is generally “not advisable, because the substitution criteria is too complex” (Jungmeier et al, 2002). In this study, careful consideration was given to the efficacy of displacing phenolic resin (PFR) with kraft lignin, and it is considered a reasonable assumption that equivalent mechanical properties can be obtained by simple mass substitution of phenolic resins in many wood adhesive formulations, as demonstrated in the literature (Kousini et al, 2011). However, the displacement assumption used in this study does not consider overall market trends for the phenolic resin market (as recommended by Weidema, Frees & Nielsen, 1999) and it is likely that lignin exported for wood adhesive applications will

not displace 100% of phenolic resin such that manufacturers decrease its production capacity (and overall use of phenolic resin) in the future.

As an alternative to the displacement assumption, mass and economic allocation methods were utilized to determine the environmental impact for each co-product: SBSK pulp (1 ADmt, 92 wt%), lignin (1 ADmt, 95 wt%) and soap (1 mt). Utilizing these two methods introduces attributional elements to the study thereby allowing a direct, cradle-to-gate comparison of the individual co-products with their respective equivalent products in the market. It is worth noting, however, that substitution of the pulp mill's power production remains for both of these methods according to the following equation:

$$\text{Impact per Functional Unit (co - prod)} = \frac{(\sum \dot{m}_j * CF_j) - kWhr_{elec} * CF_{elec}}{\dot{m}_{co-prod}} * AF$$

Where a percentage of the system's total emission impacts (including the credit for power production) are allocated to a single co-product according to the co-product's specific allocation factor, "AF." For mass and economic allocation, "AF" is described according to the following equations:

$$AF_{mass, co-prod} = \frac{\dot{m}_{co-prod}}{\sum \dot{m}_{co-prod}} = \frac{\dot{m}_{co-prod}}{\dot{m}_{total}}$$

$$AF_{econ, co-prod} = \frac{\dot{m}_{co-prod} * \frac{\$}{m_{co-prod}}}{\sum \dot{m}_{co-prod} * \frac{\$}{m_{co-prod}}} = \frac{\$_{co-prod}}{\$_{total}}$$

Where " AF_{mass} " represents the mass fraction of a single co-product for the system's total products: SBSK pulp, lignin and soap. Similarly, " AF_{econ} " represents a single co-product's contribution to revenue as a fraction of the system's total revenue, " $\$_{total}$." In this instance,

“ $\frac{\$}{m_{co-prod}}$ ” refers to the assumed market price for each co-product. For this arithmetic, the mass allocation results for each co-product will always equal one another, while slight differences can be observed with economic allocation.

4.3.3 Scope Definition & System Boundaries

The scope of the analysis spans the cradle-to-gate production of southern bleached softwood kraft (SBSK) pulp and lignin product produced at a kraft pulp mill located in Southeast U.S. The operating capacity for this study was 440,000 ADmt/year (air dry metric tonnes per year) SBSK pulp and 150 ADmt/day for the lignin extraction unit (LignoBoost). The system boundary includes all of the unit operations at the mill in addition to the lignin extraction unit. The primary foreground systems analyzed included the pulp mill digester and brown-stock washing, evaporation, recovery boiler, and power production. Incremental changes to the process flows relative to the base case were simulated and data exported were used to build the life cycle inventory inputs and outputs. Background systems for the elementary flows into the pulp mill included softwood production and harvesting as well as chemical, fuel, landfill service and electricity production. Secondary data for the background systems were taken from the Ecoinvent database, and data for the softwood production supply chain was referenced from Daystar et al, 2012.

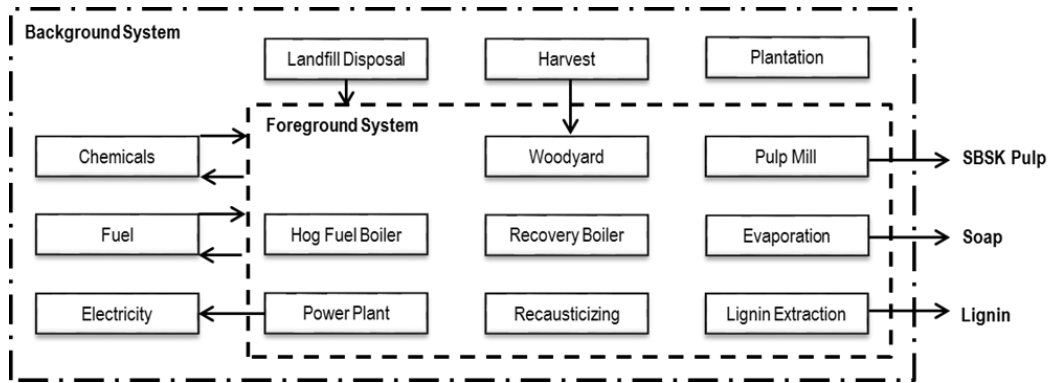


Figure 4-1: System Boundaries for the Kraft Pulp Mill Operating with Lignin Extraction

For the scenarios simulated in this study, excess power is generated by the pulp mill's power plant, and the system boundary was expanded to include the offset of electricity production. A credit was given to reduce the pulp mill's environmental burden for the equivalent production of electricity (natural gas) at a power plant in the U.S. When analyzing the system using system expansion, an additional credit is given for the displacement of petroleum derived chemicals (phenolic resin) with lignin produced in the pulp mill on an equivalent mass basis. No credit is given to the production of soap (valuable fatty acids extracted from evaporation used to manufacture crude tall oil, CTO) because it is assumed that specialty chemicals produced from CTO intermediates serve established markets representing little opportunity to displace petroleum derived products. The environmental burdens were summed and allocated to the total SBSK pulp production. For mass and economic allocation, the environmental burdens were allocated to each of the three main products (SBSK pulp, soap and lignin) as either a percentage of the total mass or revenue. The credit for power production

remained as it was considered impractical to allocate environmental burdens from the pulp mill on a mass or economic basis.

4.3.4 Process Simulation

Prior to simulating the lignin extraction process it was necessary to construct a base case (BC) of a typical kraft pulp mill using simulation software to calculate the facility's material and energy balance (Figure 4-2). The BC was modeled and analyzed representing a kraft pulp mill with annual production at 440,000 ADmt/year of SBSK pulp. All simulations were performed in WinGEMS v5.3, which is a material and energy balance modeling package originally developed for the pulp and paper industry. Steady state operating information was exported to detailed summary files created in Excel for the life cycle inventory analyses.

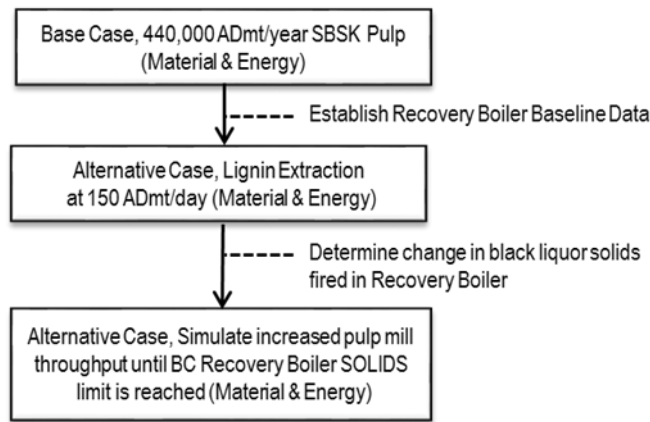


Figure 4-2: Process Simulation Methodology

Key input data used for the process simulation is shown in Table 4-1. The model assumes effective alkali (EA) and sulfidity concentrations required to achieve an average

digester yield of 44.6%. The bleaching sequence (O-D0-EOP-D1-P) modeled consists of oxygen delignification (O) in the initial stage, followed by chlorine dioxide (D), alkaline extraction (E), another chlorine dioxide bleaching step (D), and a final peroxide bleaching step (P). The model also features a pulp dryer and counter-current, multiple effect evaporators with a steam economy of 5.76 kg water evaporated per kg of fresh low pressure (2.7 atm) steam. The process model tracks softwood as lignin and carbohydrates, and the composition was assumed to have a lignin concentration of 28% wt. and carbohydrates concentration of 72% wt. Extractives are not tracked independently with respect to the raw material composition. Instead, approximately 2% of the dissolved carbohydrates and lignin is removed from digester to account for turpentine losses, and 1% is removed from the evaporators to account for the production of tall oil fatty acid.

Table 4-1: Key Input Data for the Kraft Pulp Mill

Woodyard, Pulping, BSW	Unit	Value
Clean SW Chips to Digester	OD mt/day	3,000
EA on Wood as Na ₂ O	%	17%
Sulfidity	%	28%
WL TTA conc.	g/L as Na ₂ O	100
Digester Yield	%	45%
Bleach Plant	Unit	Value
D0 ClO ₂ Charge	% on pulp	2.0%
EOP NaOH Charge	% on pulp	1.0%
EOP H ₂ O ₂ Charge	% on pulp	0.4%
D1 ClO ₂ Charge	% on pulp	1.0%
P H ₂ O ₂ Charge	% on pulp	0.4%
Paper Machine	Unit	Value
Consistency out of Presses	%	48%
Dryer Steam Demand	mt steam/mt water	2.6
Evaporators	Unit	Value
Solids Leaving Evaporators	%	50%
Solids Leaving Concentrator	%	68%

For this study, heating values for the black liquor were calculated for the proposed alternative cases (as opposed to using the default winGEMS value of 1.107 Mcal/kg) using literature heats of formation values (Gullichsen, 1968), -0.76 Mcal/kg for lignin and -1.46 Mcal/kg for carbohydrate, and the following equation:

$$H_f = x_{lignin} * -0.76 \frac{Mcal}{kg} + x_{carb} * -1.46 \frac{Mcal}{kg}$$

Where “ x_{lignin} ” and “ x_{carb} ” represent mass fractions of the lignin and carbohydrate content in the black liquor. Calculated heats of formation values were then exported directly to the “KFURN” block in winGEMS for recovery boiler modeling. It is likely that as a portion of the organics are removed by lignin extraction the heating value of the strong black liquor

will decrease and there will be a small penalty in reduction efficiency as a result of the increased inorganics concentration. This study explored the significance of such impacts on the entire pulp mill process.

For the BC, as shown in Table 4-2, it was assumed that production for the pulp mill is limited by the recovery boiler. Once the BC was complete, simulation data for the recovery boiler black liquor solids limit were recorded and assumed to be the limiting operating factor for the pulp mill. The maximum black liquor solids loading rate for the recovery boiler was assumed to be 2,795 mt/day. All other unit operations for the mill were assumed to have excess capacity.

Table 4-2: Process Simulation Case Scenarios

	Cases	SBSK Pulp (ADmt/year)	Lignin (ADmt/day)	Soap (mt/day)	Net Power (MW)	Recovery Boiler Capacity
Base Case	BC	440,000	0	36	8.4	Solids Limit
Alternative Cases	LE-P	440,000	150	36	1.4	Under
	SOL-P	464,000	150	38	-0.2	Solids Limit

The lignin extraction unit process was then incorporated to the process model and various alternative cases were simulated in order to evaluate changes in pulp mill throughput with respect to lignin production. Key assumptions for the lignin extraction process were gathered from the literature and are shown in Table 4-3. Of the three alternative cases that were simulated using the process model, LE-P simulated the lignin extraction process operating at a capacity of 150 ADmt/day (with 5% moisture content) and assumes the lignin was sold as a pelletized product. Similarly, SOL-P simulated an increase in pulp mill production up to the recovery boiler's maximum solids capacity (established in the BC) in addition to lignin

extraction production. There are limitations to the process model with respect to simulating volatized H₂S as a result of precipitation in the lignin extraction process. To account for the sulfur balance, it is assumed that volatized H₂S will be captured by the NCG (non-condensable gas) system and scrubbed with 1st pass filtrate, from the lignin extraction filter press, prior to being returned to the evaporators. It is believed that this assumption represents the most conservative approach to accounting for potential excess sulfur in the mill resulting from the addition of lignin extraction and determining impacts to the mill's elemental sodium and sulfur balance.

Table 4-3: Lignin Extraction Process Input Assumptions

Lignin Extraction	Unit	Value
Production	ADmt/day	150
Moisture Content	%	5%
Ash Content	%	0.3%
1st Press	pH	9
2nd Press	pH	2.5

4.4 Results & Discussion

4.4.1 Process Changes with Lignin Extraction

Elemental sodium and sulfur were tracked in the process model and changes to inputs and outputs with the addition of lignin extraction were simulated. Incoming sodium was tracked as fresh sodium hydroxide (NaOH) in both the oxygen delignification reactors and as make-up white liquor. Additional sodium was input to the R-10 chlorine dioxide process as sodium chlorate (NaClO₃). The process model accounts for sodium and sulfur losses throughout the pulp bleaching and chemical recovery processes, and given the specified

sulfidity and effective alkali concentrations in the simulation, all cases exhibited excess sulfur which was removed from the material balance as recovery boiler precipitator catch purge. The primary sodium losses result from the recovery boiler precipitator catch purge and sodium carryover to the bleach plant.

Figure 4-3 provides an illustration of the change in fresh NaOH required (as elemental sodium) with the return of acidic filtrate in the lignin extraction cases (as elemental sulfur) to the chemical recovery loop. The acidic filtrate contains elemental sulfur from sulfuric acid (H_2SO_4 , used for washing and purifying the lignin) which results in excess sulfur in the process when returned to weak black liquor storage. The process model was designed such that the precipitator losses are controlled automatically in order to maintain the sodium-sulfur balance (based on 28% sulfidity and 17% effective alkali concentrations), and the simulation removes the excess elemental sulfur by controlling the amount of electrostatic precipitator catch removed from the process. Since the electrostatic precipitator catch is primarily sodium sulfate (Na_2SO_4) and sodium carbonate (Na_2CO_3), approximately 2 to 2.4 mols of sodium are removed from the process for every mol of sulfur removed. This results in a significant increase in sodium recovery boiler precipitator catch losses with the addition of lignin extraction. Figure 3 exhibits a direct relationship with respect to increases in precipitator catch sodium losses with increased make-up white liquor (WL).

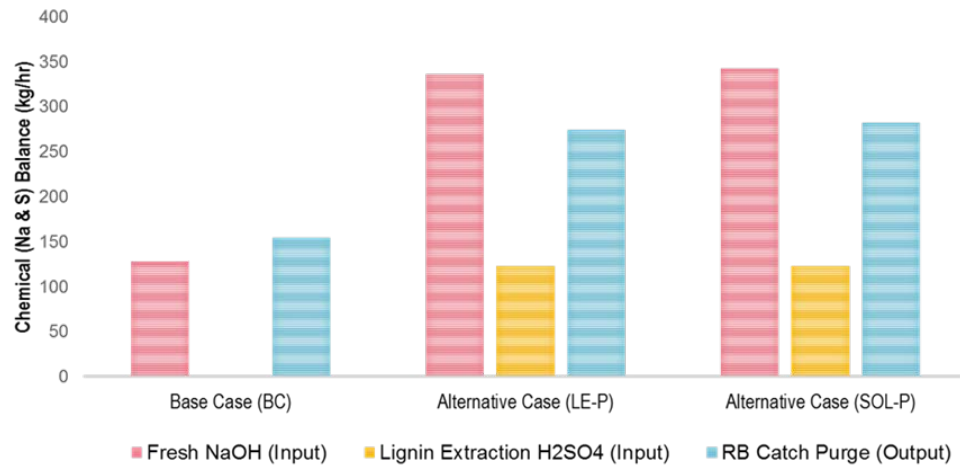


Figure 4-3: Chemical Balance with Elemental Sodium & Sulfur

It was observed that the integration of lignin extraction had a small impact on the evaporator economy with an estimated decrease from 5.76 to 5.59 as shown in Table 4-4. In the process model, the black liquor was flashed and cooled in the lignin extraction plant and this sensible heat must be made up for with a small amount of additional steam to the evaporator train. Since the change in evaporator economy is a function of the lignin extraction operating capacity, no other changes were observed for the alternative cases.

Table 4-4 provides the key power and recovery data recorded by the process model for all cases. In general, the integration of lignin extraction with 150 ADmt/day operating capacity accounts for a solids loading to the recovery boiler drop by approximately 5.2%. The organic-to-inorganic ratio of the black liquor solids (BLS) is changed slightly and the heating value of the black liquor has been accounted for in the model.

Table 4-4: Key Power & Recovery Data

Power & Recovery		BC	LE-P	SOL-P
Recovery Boiler Solids fired	mt/day	2795	2650	2795
Organic Content, BLS	kg/mt	476	466	466
X _{lignin} , BLS	%	52.1%	48.7%	48.9%
X _{carb} , BLS	%	47.9%	51.3%	51.1%
Inorganic Content, BLS	kg/mt	219	229	228
H _f , BLS	Mcal/kg	-1.095	-1.119	-1.118
Bomb Heat Value (BHV), BLS	Mcal/mt	3660	3606	3609
Recovery Boiler Efficiency	%	65.3%	64.5%	64.5%
High Pressure Steam (58.5 atm)	mt/hr	408	371	393
Evaporator Steam Economy	mt/mt steam	5.76	5.59	5.59
Lime Kiln Fuel, Natural Gas	MJ/hr	130787	128487	135471
Pulp Mill Power Production	MW	71.7	68.6	70.3
Pulp Mill Power Consumption	MW	63.3	67.2	70.5

The SOL-P scenario allowed for a 5.2% increase in pulp production, the high pressure steam (58.5 atm) production is reduced from 408 mt/hr to 371 and 393 mt/hr for LE-P and SOL-P. No deficit in power production was observed for the BC and LE-P scenarios since the pulp mill was capable of producing excess power, whereas the SOL-P scenario only exhibited a minor deficit in power production. Lime kiln fuel consumption decreased slightly for LE-P and SOL-P due to the decreases in green liquor processing which resulted from increased inorganics losses with the recovery boiler precipitator purge and corresponding increased make-up WL. Additionally, lime kiln fuel consumption for LE-P and SOL-P was calculated using natural gas with an assumed higher heating value (HHV) of 12,926 kcal/kg.

4.4.2 Inventory Analysis

The process simulation was used to complete the material and energy balances for the base case and alternative cases. The results were used to build separate life cycle inventories (LCI) for each scenario as shown in

Table 4-5. Major inputs included the softwood and chemicals consumed in the pulp mill and lignin extraction unit operation. Outputs included the SBSK pulp, lignin product, soap, and excess power produced at the mill. The primary stack emissions at the mill were calculated for the hog fuel boilers, recovery boiler, and lime kiln.

Table 4-5: Life Cycle Inventory Data for a Kraft Pulp Mill, with Lignin Extraction

Outputs	BC	LE-P	SOL-P	SOL-P, -25%	SOL-P, +25%
Power & Recovery					
CO ₂ eq (kg/hr), Total	250488	240443	248490	249572	247645
CO ₂ eq (kg/hr), Lime Kiln	16400	16113	16977	16820	17117
CO ₂ eq (kg/hr), Recovery	90534	91860	91531	91931	91428
CO ₂ eq (kg/hr), Hog Fuel	143554	132470	139982	140821	139099
SO ₂ eq (kg/hr)	162.7	164.1	167.2	166.8	168.0
Production					
Lignin (ADmt/hr)	0.00	6.11	6.11	4.59	7.63
Power (MWhr/hr)	71.7	68.6	70.3	70.4	70.1
SBSK Pulp (ADmt/hr)	52.5	52.5	55.3	54.6	56.0
Soap (mt/hr)	1.52	1.51	1.57	1.56	1.59
Solid Residue (mt/hr)	6.07	6.55	6.87	6.67	7.07
Inputs					
Power & Recovery					
NaOH (mt/hr)	0.22	0.60	0.60	0.51	0.70
Na ₂ SO ₄ (mt/hr)	0.00	0.00	0.00	0.00	0.00
CaO (mt/hr)	2.52	2.48	2.61	2.59	2.64
Natural Gas (MJ/hr)	130787	128487	135471	134110	136555
Power (MWhr/hr)	63.3	67.2	70.5	69.0	71.8
Bleaching					
NaOH (mt/hr)	0.94	0.94	0.99	0.97	1.00
H ₂ O ₂ (50%, mt/hr)	0.74	0.74	0.77	0.76	0.78
H ₂ SO ₄ (mt/hr)	0.23	0.23	0.24	0.24	0.25
R10					
H ₂ SO ₄ (mt/hr)	1.15	1.15	1.21	1.20	1.23
NaClO ₃ (mt/hr)	2.26	2.26	2.38	2.35	2.41
CH ₃ OH (mt/hr)	0.23	0.23	0.24	0.23	0.24
Lignin Extraction					
CO ₂ (mt liq/hr)	0.00	1.74	1.74	1.31	2.17
H ₂ SO ₄ (mt liq/hr)	0.00	0.40	0.40	0.30	0.50
Natural Gas (MJ/hr)	0.00	6315	6365	4736	7943
Woodyard					
SW Feed (mt/hr)	139.4	139.4	146.6	144.8	148.5

The simulated kraft pulp mill produces between 70 to 75 MW of power, and for most cases, there was an energy surplus at the mill. The only fossil fuel consumption at the mill was in the lime kiln, where natural gas is burned to calcine calcium carbonate into lime for the

causticizing plant. The direct inputs for the lignin extraction process were purchased commercial carbon dioxide gas and concentrated sulfuric acid.

Transport for the raw materials (chemicals) and softwood feedstock is provided for by batch transport. For the LCIA, this service is provided for by “Transport, lorry >28t, fleet average” Ecoinvent data with an assumed batch carrier distance of 108 and 216 kilometers for the softwood feedstock and raw materials, respectively. This is indicative of a supply radius of 80 and 160 kilometers with a tortuosity factor of 1.35, typical in the Southeast U.S.

4.4.3 Impact Assessment

The impact assessment was performed using the TRACI 2 V3.01 Impact Assessment Method and the results are shown in Table 4-6. The system expansion calculations were performed, where credits are given by displacing grid electricity and petroleum derived phenolic resin. Significant reductions in GHG emissions were observed for the alternative cases with the production of lignin used to offset phenolic resin production in the market. Decreases in ecotoxicity for the pellet product scenarios are a result of the phenolic resin displaced in the market, where typically, phenolic resin is produced from petroleum sources.

Table 4-6: Characterization Results for the SBSK Pulp with System Expansion. The functional unit is 1 ADmt for SBSK (92 wt%).

Per ADmt SBSK Pulp	BC	LE-P	SOL-P
GW, kg CO ₂ eq	7.22E+02	2.34E+02	1.94E+02
AD, H+ moles eq	3.23E+02	3.08E+02	3.21E+02
CG, kg benzene eq	2.80E+00	1.54E+00	1.65E+00
NCG, kg toluene eq	5.78E+04	5.72E+04	5.86E+04
RE, kg PM2.5 eq	1.27E+00	1.19E+00	1.24E+00
EU, kg N eq	5.14E-01	-1.15E-01	-7.98E-02
OD, kg CFC-11 eq	3.77E-05	2.99E-05	3.12E-05
EC, kg 2,4-D eq	1.04E+03	6.50E+02	6.74E+02
SM, kg NO _x eq	2.64E+00	1.46E+00	1.55E+00

Table 4-7 shows the environmental impacts of SBSK pulp, lignin and soap using mass allocation. With mass allocation, the emissions are allocated according to the mass fraction of each product manufactured at the mill, therefore the emissions on a per tonne basis are the same for all three different products. When the SBSK was analyzed using mass allocation, decreases in GHG emissions were observed due to decreased throughput in the chemical recovery loop. The decrease is primarily due to less make-up lime with lignin extraction and increased production. However, slight increases in non-carcinogenics correlate with incremental increases in natural gas burned in the lime kiln with each additional tonne of SBSK pulp production.

Table 4-7: Characterization Results for the SBSK Pulp with Mass Allocation. Note: For mass allocation, Lignin has the same values. The functional unit is 1 ADmt for SBSK (92 wt%),

1ADmt lignin (95 wt%), or 1mt of Soap.

SBSK Pulp or Lignin	BC	LE-P	SOL-P
GW, kg CO ₂ eq	7.02E+02	6.02E+02	5.50E+02
AD, H ⁺ moles eq	3.14E+02	3.36E+02	3.45E+02
CG, kg benzene eq	2.73E+00	2.80E+00	2.84E+00
NCG, kg toluene eq	5.61E+04	5.67E+04	5.80E+04
RE, kg PM2.5 eq	1.24E+00	1.36E+00	1.40E+00
EU, kg N eq	5.00E-01	5.09E-01	5.12E-01
OD, kg CFC-11 eq	3.67E-05	3.92E-05	4.00E-05
EC, kg 2,4-D eq	1.01E+03	1.01E+03	1.01E+03
SM, kg NO _x eq	2.57E+00	2.48E+00	2.51E+00

Table 4-8 shows the environmental impacts for the SBSK pulp, lignin and soap using economic allocation. The emissions per tonne of co-product are different due to the individual prices. In this study, it is assumed that any additional SBSK pulp must be sold to the broader European market for approximately \$850/ADmt (RISI Price Watch, 2014) due to increasing

demand as compared with the saturated North American market. For the lignin pellet product, a fuel value of \$245/ADmt (Fuel Pellet Institute, 2014) was assumed as a conservative estimate. The soap by-product recovered from evaporation of the black liquor is primarily used for the production of crude tall oil, so a value of \$117/mt is assumed (ICIS Chemical Pricing, 2014). Environmental burdens allocated to the SBSK pulp are higher when using economic allocation instead of mass allocation because pulp sales account for over 96% of revenue for all cases. Lignin and soap were shown to have significantly less environmental burdens as compared with their respective mass allocation values since sales for the co-products account for only 3% and 1% of total mill revenue.

Table 4-8: Characterization Results for the SBSK Pulp with Economic Allocation. The functional unit is 1 ADmt for SBSK (92 wt%), 1ADmt lignin (95 wt%), or 1mt of Soap.

SBSK Pulp	BC	LE-P	SOL-P
GW, kg CO ₂ eq	7.20E+02	6.64E+02	6.04E+02
AD, H+ moles eq	3.21E+02	3.71E+02	3.79E+02
CG, kg benzene eq	2.79E+00	3.09E+00	3.12E+00
NCG, kg toluene eq	5.75E+04	6.26E+04	6.36E+04
RE, kg PM2.5 eq	1.27E+00	1.51E+00	1.54E+00
EU, kg N eq	5.12E-01	5.61E-01	5.62E-01
OD, kg CFC-11 eq	3.76E-05	4.33E-05	4.39E-05
EC, kg 2,4-D eq	1.03E+03	1.11E+03	1.11E+03
SM, kg NO _x eq	2.63E+00	2.74E+00	2.75E+00
Lignin	BC	LE-P	SOL-P
GW, kg CO ₂ eq	0.00E+00	1.91E+02	1.83E+02
AD, H+ moles eq	0.00E+00	1.07E+02	1.15E+02
CG, kg benzene eq	0.00E+00	8.92E-01	9.46E-01
NCG, kg toluene eq	0.00E+00	1.80E+04	1.93E+04
RE, kg PM2.5 eq	0.00E+00	4.34E-01	4.67E-01
EU, kg N eq	0.00E+00	1.62E-01	1.70E-01
OD, kg CFC-11 eq	0.00E+00	1.25E-05	1.33E-05
EC, kg 2,4-D eq	0.00E+00	3.21E+02	3.38E+02
SM, kg NO _x eq	0.00E+00	7.89E-01	8.35E-01
Soap	BC	LE-P	SOL-P
GW, kg CO ₂ eq	9.92E+01	9.15E+01	8.76E+01
AD, H+ moles eq	4.43E+01	5.11E+01	5.50E+01
CG, kg benzene eq	3.85E-01	4.27E-01	4.52E-01
NCG, kg toluene eq	7.93E+03	8.63E+03	9.23E+03
RE, kg PM2.5 eq	1.75E-01	2.08E-01	2.24E-01
EU, kg N eq	7.07E-02	7.74E-02	8.15E-02
OD, kg CFC-11 eq	5.18E-06	5.97E-06	6.37E-06
EC, kg 2,4-D eq	1.42E+02	1.54E+02	1.62E+02
SM, kg NO _x eq	3.63E-01	3.77E-01	4.00E-01

Both system expansion and mass allocation were used to account for placement of environmental burdens to the co-products. Key differences in TRACI environmental impacts were observed, with global warming potential for the SBSK pulp product with lignin extraction reported as 194 kg CO₂eq (carbon dioxide equivalents) per ADmt SBSK pulp for system expansion as compared to 722 kg CO₂eq per ADmt SBSK pulp for the base case (without

lignin extraction). This reduction was primarily due to the displacement of petroleum derived phenolic resins by the lignin co-product credited to the SBSK pulp. For mass allocation, a smaller decrease to global warming emissions was observed for lignin extraction relative to the base case with GWP reported at 550 kg CO₂eq per ADmt SBSK pulp. Similarly, for the mass allocation scenarios, a lignin co-product with GWP of 550 kg CO₂eq per ADmt lignin was significantly lower than phenolic resin with 3911 kg CO₂eq per ADmt. Furthermore, significant decreases for the lignin co-product relative to phenolic resin were observed for every TRACI impact category.

As for economic allocation, revenue from the sale of lignin and soap represents less than 5% of total mill revenues. This accounts for the large difference between environmental burdens per ADmt SBSK pulp as compared with the lignin and soap.

4.4.4 Hot Spot Analysis

Gonzalez-Garcia et al, 2009, provided a hot spot analysis when comparing life cycle inventories and impact assessments for both totally chlorine free (TCF) and elemental chlorine free (ECF) pulp mills. Impacts to ozone layer depletion, global warming and ecotoxicity were shown to result primarily from chemical production and direct emissions from energy production. As shown in Table 4-9, a similar heat map was used to provide an overview of the life cycle emissions from the mill.

Table 4-9: Relative Contribution of Process Inventory to Environmental Impact Categories.

Data is based on the SOL-P scenario. Other scenarios are similar these results.

Process Inventory	GW	AD	CG	NCG	RE	EU	OD	EC	SM
NaOH, 50%	10%	4%	9%	3%	6%	9%	8%	18%	4%
CaO	6%	0%	0%	0%	1%	1%	5%	1%	1%
H2O2, 50%	3%	1%	4%	5%	1%	2%	4%	12%	1%
H2SO4	1%	6%	2%	1%	7%	2%	1%	1%	1%
NaClO3	22%	8%	39%	46%	13%	16%	16%	50%	8%
CH3OH	0%	1%	0%	1%	1%	0%	1%	0%	0%
CO2 (gas)	4%	1%	3%	1%	1%	3%	4%	3%	1%
Nat. Gas	84%	58%	28%	42%	63%	13%	43%	10%	21%
Emissions	722%	1%	0%	0%	0%	0%	0%	0%	0%
Soft. W.	-759%	16%	2%	1%	5%	14%	0%	3%	50%
Solid Residue	0%	0%	11%	0%	0%	35%	1%	1%	0%
Transport	1%	1%	0%	0%	0%	1%	2%	0%	2%
Transport, F.	7%	4%	1%	0%	2%	4%	15%	1%	12%
Power	0%	0%	0%	0%	0%	0%	0%	0%	0%

The hot spot analysis for the pulp mill indicates major contributors to global warming potential and respiratory effects from chemical recovery operations. This is largely due to the consumption of natural gas in the lime kiln which is used to calcine CaCO₃ to CaO. With lignin extraction, the recycling of acid filtrate from the lignin extraction process results in a buildup of inorganics in the chemical recovery process, thereby increasing the throughput in the lime kiln. The result is a slight increase in natural gas consumption per unit of SBSK pulp produced. The consumption of sodium chlorate (NaClO₃), used for the production of chlorine dioxide for pulp bleaching, was also shown to be a significant contributor for a majority of the impact categories. It is worth noting that the hot spot for global warming potential from calculated direct emissions is more than offset by the large credit provided by the use of softwood, which is considered negative due to sequestered CO₂ from photosynthesis (Daystar

et al, 2012). However, the use of softwood is the most significant contributor to smog emissions, resulting from plantation and harvesting activities.

4.4.5 High Value Product Comparison

A direct comparison of the environmental impacts reported, utilizing mass allocation, for the SBSK pulp and lignin as compared with similar, high value products on the market is provided in Table 4-10. Data for the environmental impacts of the high value products selected were gathered directly from the Ecoinvent database. The results for the SBSK pulp were similar with the market pulp, as “Sulphate pulp, ECF bleached, at plant – RER (Europe region)”, with respect to global warming potential. However, the SBSK pulp exhibits significantly higher non-carcinogenics (58,000 kg toluene eq as opposed to 4,400 kg toluene eq) and ecotoxicity (1,000 kg 2,4-D eq as opposed to 140 kg 2,4-D eq) impacts. This is primarily due to the sodium chlorate consumption required for chlorine dioxide generation, given the assumed bleaching sequence common to the southeast United States.

Table 4-10: Comparison of the Characterization Results, for the SBSK Pulp and Lignin utilizing Mass Allocation, with the High Value Products. Data for high value products was gathered from Ecoinvent. The functional unit is 1 ADMT for SBSK (92 wt%) and 1ADMT lignin (95 wt%).

Per ADmt SBSK Pulp or Lignin	BC	LE-P	SOL-P	Market Pulp	Wood Pellet	Phenolic Resin, PFR	Acrylonitrile, AN
GW, kg CO ₂ eq	7.02E+02	6.02E+02	5.50E+02	5.21E+02	6.72E+01	4.12E+03	3.14E+03
AD, H+ moles eq	3.14E+02	3.36E+02	3.45E+02	2.43E+02	1.71E+01	6.89E+02	8.31E+02
CG, kg benzene eq	2.73E+00	2.80E+00	2.84E+00	2.55E+00	9.24E-02	1.51E+01	4.69E+00
NCG, kg toluene eq	5.61E+04	5.67E+04	5.80E+04	4.42E+03	3.04E+02	7.02E+04	3.36E+04
RE, kg PM2.5 eq	1.24E+00	1.36E+00	1.40E+00	1.17E+00	7.69E-02	3.37E+00	2.43E+00
EU, kg N eq	5.00E-01	5.09E-01	5.12E-01	1.99E+00	1.15E-02	6.31E+00	1.79E+01
OD, kg CFC-11 eq	3.67E-05	3.92E-05	4.00E-05	4.51E-05	3.31E-06	1.36E-04	1.69E-04
EC, kg 2,4-D eq	1.01E+03	1.01E+03	1.01E+03	1.44E+02	2.12E+01	4.59E+03	5.38E+02
SM, kg NO _x eq	2.57E+00	2.48E+00	2.51E+00	3.21E+00	1.63E-01	1.25E+01	4.29E+00

Further review of the Ecoinvent database suggests sodium chlorate consumption is approximately 0.7 kg NaClO₃ per bone-dry metric tonne (BDmt). This is considerably less than the R-10 process model in this study which consumes 46.7 kg per BDmt SBSK pulp. As a result, the percent contribution from sodium chlorate consumption to non-carcenogenics and ecotoxicity is 46-50% as compared with an 11% contribution to the sulphate pulp inventory provided in Ecoinvent. It is worth noting that the sodium chlorate consumption simulated in this study is similar to the data provided by NREL's "LCA Commons V2.0", which is 61.7 kg NaClO₃ per BDmt for "Pulp, kraft market, bleached, average production, at mill" (Gaudreault, 2014), and it is believed that this adequately represents an average consumption of sodium chlorate in North America higher than European consumption, commiserate with key differences in the bleaching sequence and mill practice. This example highlights the

limitations of LCA studies performed on North American pulp mills (or any North American manufacturing processes) that utilize the Ecoinvent database, and researchers using Ecoinvent in this manner must exercise caution and provide careful attention to the key regional differences in both process engineering and supply chain management when reporting environmental burdens per unit product.

The lignin co-product was reported as having significantly less environmental impacts across all midpoint indicators when compared directly with PFR, “Phenolic resin, at plant/RER U,” and AN, “Acrylonitrile from Sohio process, at plant/RER WITH US ELECTRICITY U.” This suggests that a lignin bio-polymer is an attractive candidate for commercialization, from an environmental improvement perspective, when targeting adhesive or carbon fiber applications. However, it should be noted that further conversion of the lignin bio-polymer to improve its purity, reactivity or process-ability will reduce the relative performance advantage over petroleum derived products as more raw materials and energy are incorporated into the supply chain. This emphasizes the need for further developing lignin process schema that utilize fewer reagents, solvents and energy.

As for fuel related applications, the environmental burdens associated with the lignin co-product were shown to be significantly higher than “wood pellets, moisture=10%, at storehouse – RER.” This suggests that extracted lignin sold for fuel applications external to the mill are less preferred over potential bio-polymer applications. Furthermore, incorporating extracted kraft lignin as a binder for wood pellets (to improve pellet durability) may increase the environmental impacts attributed to the final product.

4.4.6 Sensitivity Analysis

A sensitivity analyses was performed to determine changes to environmental impact categories for different commercial lignin extraction production capacities. For the SOL-P case, a $\pm 25\%$ sensitivity analyses for the design capacity of 150 ADmt/day lignin production rate was simulated, and the incremental pulp production was increased according to the recovery boiler operating capacity for each scenario. As shown in

Table 4-5 and Figure 4-4, impacts for global warming (kg CO₂eq per ADmt SBSK) and eutrophication (kg N eq per ADmt SBSK) were shown to change significantly with respect to lignin extraction operation capacity when using system expansion.

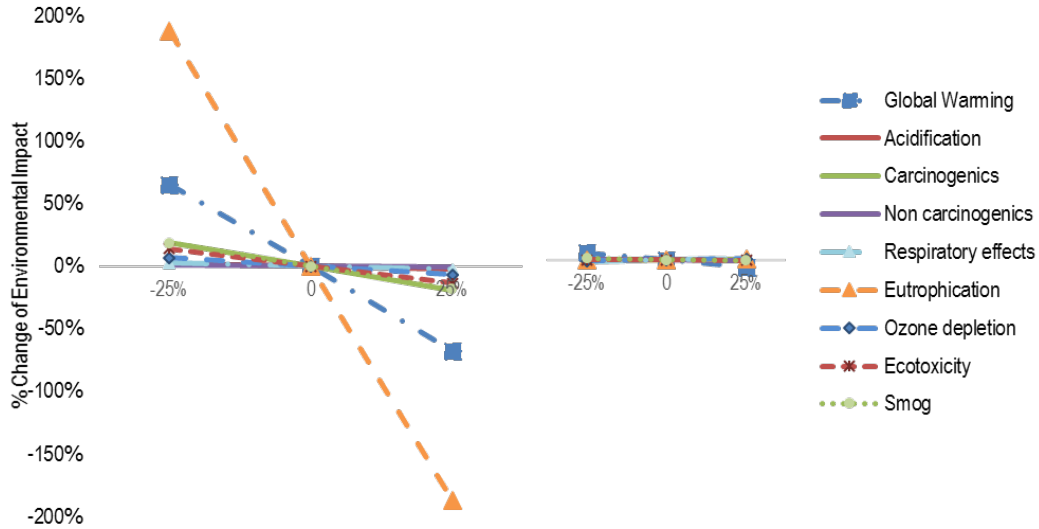


Figure 4-4: Sensitivity of the % Difference of Environmental Impacts to the Production Capacity of Commercial Lignin Extraction, with System Expansion (shown left) and Mass Allocation (shown right) for the SOL-P Case

For the lignin extraction cases, less organics were combusted resulting in lower direct CO₂ eq emissions from the recovery boiler while emissions from the lime kiln and hog fuel boilers were shown to increase according to incremental pulp production. As shown with the sensitivity analysis for system expansion in Figure 4-4, the primary driving force affecting global warming potential and eutrophication was the credit being given for offsetting petroleum derived phenolic resin, which exhibits a high CO₂eq and N eq values. Increasing

lignin extraction production capacity by 25% was shown to increase incremental pulp production an additional 1.3% (to a total 6.51% increase in incremental pulp production at 188 ADmt/day lignin production). Similarly, a 1.3% decrease in incremental pulp production was observed for a 25% decrease in lignin production to 113 ADmt/day (to 3.89% incremental pulp production). All other chemical and power consumption rates were shown to increase and decrease linearly with incremental pulp production.

As shown in Figure 4-4 for mass allocation, global warming potential changes moderately (+/- 10%) as a result of lignin extraction production when using mass allocation. This is primarily due to the lack of an emission credit for displacing phenolic resin in the market. With all emissions allocated directly to production throughput, the change in direct emissions correlates with lignin extraction production. That is, a 25% decrease in lignin extraction production corresponds to more lignin combusted where as a 25% increase corresponds to less lignin combusted, thereby lowering the direct CO₂eq emissions for the mill.

4.5 Conclusions

Using system expansion, the simulated kraft pulp mill system was observed as having reduced environmental impact with the addition of a lignin co-product in part due to reduced stack emissions from the recovery boiler as a result of fewer combusted organics. Commercial lignin extraction was shown to have the potential to demonstrate marked improvement for the reduction of environmental impacts at the kraft pulp mill. From this study, it was determined that this reduction with the addition of lignin extraction is achieved by reducing fossil fuel and raw material (chemical) consumption at the mill per unit of SBSK pulp produced. In other words, by debottlenecking the recovery boiler, overall mill production efficiency is improved

by 5% at the lignin extraction design capacity of 150 ADmt/day for the 440,000 ADmt/year SBSK pulp producing mill.

The results for the environmental burdens of a lignin biopolymer produced from lignin extraction at a kraft pulp mill when using mass allocation were shown to be significantly less when compared with potential high value products such as phenolic resin or acrylonitrile monomers. This suggests that lignin is a sustainable bio-material. However, the lignin product was shown to have significantly higher environmental burdens as compared with wood pellets, suggesting it is not a suitable displacement for wood pellets when exported from the mill.

A hot spot analysis of the kraft pulp mill was also performed, and sodium chlorate used for chlorine dioxide generation and natural gas used in the lime kiln were shown to be significant contributors to overall mill environmental burdens.

5 IMPACT OF WOOD SPECIES & MOLECULAR WEIGHT ON LIGNIN

THERMAL PROPERTIES

5.1 Abstract

This study analyzes the glass transition temperature for the lignin fractions and suggests that T_g primarily depends on molecular weight for lignin, regardless of the isolation method or legacy feedstock. Decreases in glass transition temperature were observed for softwood kraft lignin (SWKL), hardwood kraft lignin (HWKL) and dilute acid-enzymatic hydrolysis lignin (DAHL) fractions with low molecular weight. Similarly, thermal stability (as measured by mass loss and decomposition activation energies) was shown to decrease with decreasing MW. The lowest molecular weight fraction for softwood kraft lignin (SWKL.F3) exhibited the lowest glass transition temperatures between 69 to 86 °C, while maintaining good thermal stability up to 220 °C. Glass transition temperatures as low as 94 °C were observed for the lowest molecular weight fraction for hardwood kraft lignin (HWKL.F3), while also maintaining good thermal stability. DAHL fractions showed only slight decreases in glass transition temperature, while suffering from poor thermal stability at temperature below 190 °C. Decomposition energies for both softwood and hardwood kraft lignin were shown to be similar at 40 kJ/mol, while DAHL lignin fractions were shown as having energies as low as 11 kJ/mol at 300 °C. Whole lignin fractions appear to exhibit simple linear mixing rules for their constituent parts and only slight interactions resulting from thermally induced crosslinking were observed based on rise of glass transition temperatures upon subsequent reheats. This indicates that small MW fractions impart some plasticizing effect to the whole lignin fraction.

5.2 Introduction

Representing approximately 20 to 35% of lignocellulosic materials by mass, lignin is an abundant amorphous, phenolic heteropolymer. Lignin plays a critical role in plant-life by imparting strength, rigidity and hydrophobicity to the plant cell wall. It helps to enable the transport of water and nutrients through the plant and it helps to protect the plant against insects and pathogens. (Boerjan et al 2003, Heitner et al 2016). Lignin is synthesized in the plant cell wall via polymerization of monolignols (hydroxycinnamyl alcohol monomers). These monolignols primarily include 4-hydroxycinnamyl alcohol (p-coumaryl, or “H” type), 4-hydroxy-3-methoxycinnamyl alcohol (coniferyl, or “G” type), and 4-hydroxy-3,5-dimethoxycinnamyl alcohol (sinapyl, or “S” type). For forest products, gymnosperms (e.g. softwood) predominantly contain “G” type lignin and dicotyledonous angiosperms (e.g. hardwoods) contain “G” and “S” type lignin.

Generally, lignocellulosic biomass is recalcitrant to thermal, mechanical and chemical degradation due to the lignin, and breaking the biomass down to its constituent parts requires significant energy and effort. Lignin isolated from various industrial processes can exhibit significantly different material properties. For this reason, lignin material isolated from the plant cell wall is classified according to A) the process, or method, used to extract the lignin and B) the legacy feedstock. As a result of the many different methods for isolating lignin from dozens of wood species (both commercial and non-commercial), the wide range of said properties has limited the commercialization of products based on lignin raw materials (Wang et al 2016).

In the forest products industry, there are four commercially relevant or actively researched lignin isolation, or “pulping”, process technologies employed to remove lignin from the plant cell wall and liberate a fiber useful for bleaching and paper manufacture (see Table 5-1). The first and most widely recognized is the kraft process that utilizes highly alkaline cooking liquors comprised of sodium hydroxide and sodium sulfide in order to fragment the lignin by cleaving alpha and beta aryl ether bonds at temperatures ranging from 150 to 190 °C for 30 to 90 minutes (Smook 1982).

Table 5-1: Industrial Lignin Fragmentation, or “Pulping”, Process Technologies

Lignin Isolation Process	Reagents & Conditions	Major Reactions
Kraft	NaOH, Na ₂ S, pH 14+, 150 – 190 °C, 30 to 90 minutes	Aryl ether bond cleavage, condensation, sulfur condensation
Acid Sulfite	H ₂ SO ₃ , pH 1.5 – 2 (or 4 – 5), 140 – 160 °C, 6 – 8 hours	Aryl ether bond cleavage, condensation, sulfonation
Organosolv	Ethanol (or other organic solvents), pH 4 – 10, 140 – 220 °C, 30 to 90 minutes	Aryl ether bond cleavage, condensation
Dilute acid (or “auto”) hydrolysis	H ₂ SO ₄ (or hot-water), pH 3 – 4, 170 – 180 °C, 1 to 4 hours	Lignin recovered as enzymatic hydrolysis residue after saccharification, aryl ether bond cleavage, condensation

The second is the acid sulfite process where sulfurous acid, or its alkali salts, are used to fragment the lignin at temperatures ranging from 140 to 160 °C for 6 to 8 hours. While the aryl ether bonds are also cleaved, the lignin fragments are sulfonated in the process producing lignosulfonates, a well-known industrial scale lignin product (Rødsrud et al 2012). Even though lignosulfonates are a valuable co-product, the acid sulfite process is used less and less as many mills have converted to the cost-advantaged kraft process, where the alkaline chemicals used can be recovered. The number of acid sulfite mills has diminished significantly since the 1980s, down from over 60 mills to less than 10 in North America (FisherSolve 2016).

Lastly, organosolv and dilute acid hydrolysis processes are of increasing interest for bio-refining research, where the goal may be to remove the lignin from the lignocellulosic substrate prior to saccharification for the purposes of yielding monomeric sugars for bio-fuels or biochemicals production (Lindner & Wegener 1988, Lora & Aziz 1985, Humbird et al 2011). The organosolv process employs an organic solvent that aids in solubilizing the lignin fragments during pretreatment. Lignin isolated from this method is suitable for valorization due to its lack of residual sulfur. The dilute acid (or auto) hydrolysis utilizes acid catalysts, most notably sulfuric acid, in order to break apart the wood substrate prior to enzymatic hydrolysis. The resulting enzymatic hydrolysis residue is an insoluble lignin product with residual hemicellulose content. Valorization of this lignin is of interest in order to further improve bio-refinery economics.

Utilization of industrial lignin is currently limited to known lignosulfonate chemistry or fuel combustion for energy and chemical recovery. High value applications such as bio-composite manufacture or polymer blending often require that the lignin be subsequently modified. Furthermore, since the lignin is an amorphous, highly crosslinked macromolecule with no melting point, lignin modification or addition to polymer products is limited to a brief window of temperatures and processing conditions where a softening point prior to self-condensation and thermal decomposition is available (Wang, Kelley & Venditti 2016, Cui et al 2013).

Lignin and isolated lignin fractions have been studied and it has been suggested that processing conditions may be improved with lower molecular weight fractions (Saito et al 2014, Duval et al 2016, Li & McDonald 2014). The purpose of this study is to continue this

work and provide a head-to-head comparison of lignin thermal properties for three industrial lignin types of increasing research interest. The goal of the study is to provide useful and added insight towards the valorization of these materials.

5.3 Methodology

5.3.1 Materials

For this study, three types of lignin were used:

1. Domtar's "Biochoice" softwood kraft lignin (SWKL)
2. Suzano Limerira – Lignin from a eucalyptus kraft pulp mill (HWKL), graciously provided by Suzano Limerira.
3. Lignin residue from dilute acid pretreatment and enzymatic hydrolysis (higher carbohydrate content), denoted DAHL

The SWKL was extracted via the commercially available "Lignoboost" process. In this process, kraft black liquor at approximately 35% solids is collected, cooled and treated with CO₂ gas, where the lignin begins to precipitate at around pH 10. The precipitated lignin is then filtered and transferred to an acidulation vessel where the pH is again lowered to 2, and a subsequent acid washing step removes remaining inorganic impurities from the kraft pulping process. For this process, the legacy feedstock was softwood loblolly pine harvested in the southeast U.S.

The HWKL was extracted from a Brazilian kraft pulp and the legacy feedstock was eucalyptus. For this lignin, however, only CO₂ precipitation was employed, and no in situ acid washing or acidulation was utilized. HWKL samples received were diluted to 5% solids, brought to a pH of +13 with sodium hydroxide and then subsequently precipitated with

hydrochloric acid to a pH of 2. The resulting HWKL was then filtered using glass filter with fine coarseness and washed an additional seven times with 0.1 N dilute sulfuric acid.

The DAHL was prepared from mixed hardwood chips (predominantly *P. trichocarpa*). The chips were added to a pressure vessel, diluted to 10% solids, charged with sulfuric acid (2% wt. on oven-dry wood), and heated with 150 psig steam to a temperature of 180°C for 90 minutes. The resulting “pulp” was cooled to room temperature, diluted to 5% solids and then saccharified with enzymes for 48 hours with a 5 FPU per oven-dry gram substrate. The resulting enzymatic hydrolysis residue (DAHL) was then thoroughly washed and pressed to 55% solids.

5.3.2 Fractionation – Partitioning of the Lignin by Molecular Weight

Each commercial lignin was solubilized in a acetone-methanol mixture (70:30 v/v), optimized according to Hildebrand solubility parameter (Hildebrand & Scott 1950):

$$\delta = \sqrt{\frac{\Delta H_v - RT}{V_m}}$$

Where “ ΔH_v ” is the heat of vaporization of the compound, “R” is the ideal gas constant (8.314 J/mol-K), “T” is the temperature, and “ V_m ” is the molar volume of the compound. The parameter provides a numerical estimate of the degree of interaction between materials and serves as an indicator of solubility. For this study, a δ of 11 cal^{1/2}-cm^{-3/2} was assumed for the lignin samples (Schuerch 1952, Duval et al 2016), and the 70:30 v/v acetone-methanol mixture was selected according to a δ of 11.1 cal^{1/2}-cm^{-3/2} in order to fully solubilize the whole lignin fractions.

The lignin samples were dissolved in the acetone-methanol mixture and sequentially precipitated with an organic solvent of lower solubility (i.e., ethyl acetate with δ of 9.1 cal^{1/2}-cm^{-3/2}, and 1:1 v/v, ethyl acetate-petroleum ether with a δ of 8.4 cal^{1/2}-cm^{-3/2}) such that the dissolved lignin was split between insoluble and soluble fractions. The insoluble fraction is generally characterized as having higher molecular weight than the soluble portion. This process was performed twice to provide three distinct lignin fractions denoted “F1”, “F2” and “F3.” The first fraction F1 is the lignin fraction with a δ of 11.1 cal^{1/2}-cm^{-3/2}, the second F2 with a δ of 9.1 and the third F3 with a δ of 8.4. Each sample was then washed thoroughly with deionized water and vacuum freeze dried.

For the DAHL samples, there is an additional fraction that was insoluble in the acetone-methanol mixture denoted as “F0.”

5.3.3 Gel Permeation Chromatography

The molecular weight (MW) of the lignin fractions were determined by gel permeation chromatography (GPC). The vacuum dried lignin fractions were acetylated with acetic anhydride and pyridine (1/1, v/v) at room temperature for 72 hours in the dark, away from direct light. The concentration of the lignin in this solution was approximately 50 mg/L. The acetylated lignin samples were then precipitated in deionized ice water, washed thoroughly and vacuum freeze dried. Prior to injection of each 200 μ L sample, the acetylated samples were dissolved in tetrahydrofuran (THF) at a 1000 ppm concentration and filtered with a 0.45 μ m PTFE (e.g. Teflon) filter. A Shimadzu LC 20-AD chromatograph equipped with a UV detector set at 280 nm was used. THF was used as the eluent at a flow rate of 0.7 mL/min at 35 C. Two styragel linear columns linked in series were used (Styragel HR 1 7.8 x 300mm

and Styragel HR 5E 7.8 x 300mm). Monodispersed polystyrene standards, ranging from 0.82 to 1860 kg/mol, were used for calibration, and molecular weights were calculated using Millennium software.

5.3.4 Fourier Transform Infrared Spectroscopy

The Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a Perkin Elmer FTIR spectrophotometer. Finely ground non-acetylated lignin fractions were analyzed using ZnSe crystals. All spectra were obtained by accumulation of 256 scans, with resolution of 1 cm⁻¹, from 400 to 4000 cm⁻¹. Condensation indices were analyzed as the sum of minima from 1050 to 1600 cm⁻¹ divided by the sum of maxima from 1000 to 1650 cm⁻¹ according to methods by Faix et al 1992. Carbonyl group content was also analyzed according to Faix et al (1992) by examining the absorption at 1700 to 1750 cm⁻¹ and 1600 cm⁻¹.

5.3.5 Thermal Analysis

The thermal transitions and properties were analyzed using a TA Discovery Series Q100 differential scanning calorimeter (DSC), with aluminum hermetic pans. All samples were purged with nitrogen gas (50 mL/min) and measured against an empty reference pan. Approximately 5 mg of lignin fraction samples were added to each pan, and the samples were first annealed at 90 °C for 20 minutes and then subjected to a 20 °C/min heating rate.

The thermal history for the lignin fractions was recorded at multiple, sequential heat and cooling temperature ramps in order to measure the increase in glass transition temperatures as a result of thermally induced crosslinking and self-condensation (Cui et al 2013, Fenner & Lephardt 1981). As shown in Figure 5-1, the DSC protocol cured the lignin fractions for 2

minutes at temperatures ranging from 190 °C to 250 °C, in 20 °C increments. Changes in thermal behavior were recorded and analyzed for each cycle, and the glass transition temperature (T_g) was determined as the mid-point of the change in the heat capacity associated with the glass transition using TA instruments' Universal Analysis software.

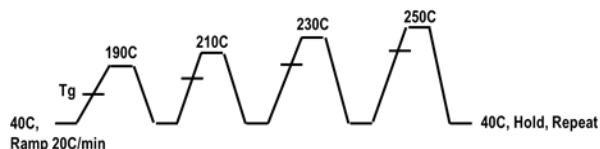


Figure 5-1: DSC Protocol to Analyze Changes in Thermal Behavior

Thermal decomposition for the lignin fractions were analyzed by thermal gravimetric analysis (TGA) using a TA Discovery Series Q500 TGA instrument. 10 mg of lignin fraction were added to a platinum pan, purged with nitrogen gas and then heated at 20 °C/min up to 900 °C. Thermal decomposition reactions were modeled for a non-isothermal process with a linear heating rate according to Murugan et al 2008.

5.4 Results & Discussion

5.4.1 Fractionation & GPC

As seen in Table 5-2, the SWKL, HWKL and DAHL lignin samples were partitioned into three distinct fractions by increasing molecular weight. Approximately, 88% to 94% of the original lignin samples were recovered and the recorded data was normalized for mass closure. For the SWKL and HWKL samples, the first fraction, denoted F1, exhibited a higher average MW than the whole unfractionated lignin, while the second and third samples (F2 &

F3) were consistently lower in MW. For all fractionated samples, the polydispersity decreases for the subsequent, lower MW fractions. All samples, regardless of the isolation process or legacy feedstock, exhibited a final fraction with comparable MW and PD (780 – 900 Da and 1.3 – 1.5, respectively).

Table 5-2: Molecular Weights & Mass Balance for Isolated Lignin Fractions

Lignin Fraction	δ, cal^{1/2}-cm^{-3/2}	Molecular Weight (Da)	Polydispersity	% Mass	Normalized % Mass	CI*	CG*
SWKL		6129	4.20				
SWKL F1	11.1	8843	2.92	46%	51%	0.64	0.70
SWKL F2	9.1	2729	1.60	30%	34%	0.83	0.68
SWKL F3	8.4	881	1.37	13%	15%	0.83	0.63
HWKL		2700	2.19				
HWKL F1	11.1	5996	1.97	31%	35%	0.38	0.56
HWKL F2	9.1	2180	1.63	47%	53%	0.47	0.57
HWKL F3	8.4	787	1.31	11%	12%	0.45	0.54
DAHL		+30000**	+3**				
DAHL F0	Insoluble	36719	38.57	73%	77%	0.66	0.73
DAHL F1	11.1	nd	nd	2%	2%	0.58	0.69
DAHL F2	9.1	3623	2.13	13%	14%	0.60	0.65
DAHL F3	8.4	905	1.48	6%	7%	0.74	0.64

*CI, condensation indices; CG, carbonyl groups (Tolbert et al 2014)

**Only 10% of the whole DAHL fraction was soluble in THF, and these results reflect the soluble portion

For the SWKL samples, a higher polydispersity (PD) was observed, consistent with other previously published studies (Cui et al 2014, Li & McDonald 2014, Saito et al 2014). The higher MW fraction SWKL.F1 accounted for over 50% of the of the whole SWKL sample, SWKL.F2 was approximately 35% and the lowest MW fraction SWKL.F3 accounted for 15% of the sample. The HWKL lignin samples exhibited a lower overall MW than the SWKL samples with the second fraction HWKL.F2 accounting for over 50% by mass. As with the

SWKL samples, HWKL exhibited a similar low MW fraction accounting for less than 15% by mass. The DAHL samples were predominantly insoluble with DAHL.F0 accounting for over 75% of the sample. However, lower MW fractions less than 3600 Da were recovered accounting for less than 25% of the sample.

5.4.2 FTIR

As seen in Figure 5-2, the infrared spectra for the fractionated lignin samples were recorded and analysis is provided in Table 5-2. As expected, typical bands for G-type lignin were observed for all samples at 1260 cm^{-1} , with the HWKL and DAHL spectra exhibiting lower peak intensity. Bands for the S-type lignin were observed for the HWKL and DAHL samples at 1330 cm^{-1} (even without acetylation). All of the fractionated lignin samples exhibited characteristic O-H stretching at $3000\text{ to }3500\text{ cm}^{-1}$ and C-H stretching at 2850 and 2930 cm^{-1} . Condensation indices were analyzed as the sum of minima from $1050\text{ to }1600\text{ cm}^{-1}$ divided by the sum of maxima from $1000\text{ to }1650\text{ cm}^{-1}$ according to methods by Faix et al 1992. The minima selected for determining condensation indices were $1549, 1481, 1439, 1400, 1294, 1260, 1173, \text{ and } 1063\text{ cm}^{-1}$. The maxima selected were $1607, 1514, 1464, 1425, 1325, 1267, 1219, 1117, \text{ and } 1034\text{ cm}^{-1}$. As observed in previously reported studies, spectra data for fractionated lignin samples reported that least condensed lignin structures are more soluble in organic solvents (McDonald & Li 2014, Schorr et al 2014).

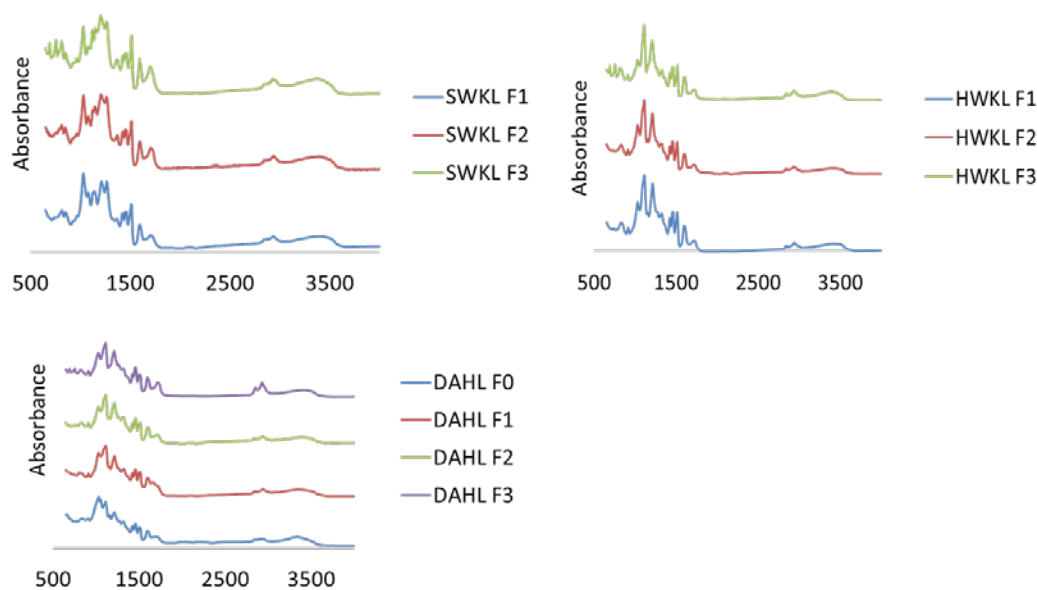


Figure 5-2: Lignin FTIR Spectra by Infrared Wavelength (cm^{-1})

Carbonyl group content was also determined by comparing the absorption spectra at 1720 to 1730 cm^{-1} for C=O stretching against the peak at 1600 cm^{-1} for aromatic skeletal vibrations (see Table 5-2). The lower MW fractions exhibited a higher carbonyl group content, with the SWKL.F3 fraction containing the most. The HWKL fractions exhibited the lowest amount of carbonyl groups. While it is tempting to surmise that higher carbonyl group content would be indicative of less condensation, only a weak negative relationship was observed between condensation indices and carbonyl group content for the SWKL samples ($R^2 = 0.55$) and no relationship was observed for the HWKL and DAHL lignin samples ($R^2 < 0.1$) when using FTIR. Alternatively, a weak positive relationship was observed for all fractions ($R^2 = 0.39$). Additional work to quantify carbonyl groups by hydroxylamine-hydrochloride titration

(Nicolaidis 1984) and degree of condensation by thioacidolysis (Rolando & Lapierre 1992) may be required.

5.4.3 Thermal Analysis & Discussion

The glass transition temperature (T_g) provides an indication of the polymer's transition from glass to a liquid or rubbery state, and it is associated with the energy required to allow individual molecules to move independently of one another. As a result, T_g values typically increase according to increases in the polymer's molecular weight and cross-linking density (Wang, Kelley & Venditti 2016). As seen in Table 5-3 and Figure 5-3, all of the lignin samples exhibit higher T_g for higher MW fractions and lower T_g for lower MW fractions, and these results are in good agreement with previously reported findings (Wang, Kelley & Venditti 2016).

Table 5-3: Differential Scanning Calorimetry for Isolated Lignin Fractions

Lignin Fraction	1st T_g (°C)	Final T_g (°C)	1st ΔC_p (J/g - °C)	Final ΔC_p (J/g - °C)	T_g Rise
SWKL	154	166	0.45	0.24	11.9
SWKL F1	193	201	0.18	0.15	8.8
SWKL F2	162	175	0.27	0.24	13.1
SWKL F3	69	86	0.30	0.27	17.0
HWKL	191	208	0.26	0.20	17.7
HWKL F1	202	203	0.24	0.23	1.5
HWKL F2	177	180	0.30	0.25	3.3
HWKL F3	94	108	0.35	0.28	13.1
DAHL	154	190	0.23	0.18	36.5
DAHL F0	163	190	0.23	0.17	27.4
DAHL F1	193	223	0.11	0.09	29.8
DAHL F2	161	193	0.56	0.27	32.4
DAHL F3		226		0.32	

Unfractionated SWKL was observed as having T_g from 154 to 166 °C, HWKL showed 190 to 208 °C, and DAHL with 154 to 190 °C. For the lower MW fractions, significantly lower glass transitions were observed for the SWKL and HWKL fractions. In order to examine the mixing relationship between the lignin fractions, Gordon & Taylor's (1952) empirical method for predicting T_g in miscible polymer blends based on the composition of the blend and the T_g of the individual components was utilized, as shown in the following equation:

$$T_g = \frac{w_1 T_{g1} + K' w_2 T_{g2}}{w_1 + K' w_2}$$

Where “w₁” and “w₂” denotes the weight fractions of the individual components and “K'” is the fitting constant that indicates the nature of the interactions between said components. For linear mixing systems, K' may be equal to 1. Interestingly enough, the predicted T_g versus whole fraction T_g for fractionated lignin samples indicated only a weak linear mixing relationship (R² = 0.53). This suggests the presence of specific intermolecular interactions between the blend components (Lu & Weiss 1992). Various researchers have reported these interactions as free radical initiated self-polymerization and cross-linking, which have been shown to increase the lignin polymer's MW (Pucciariello et al 2004, Jeong et al 2013, Luong et al 2013, Cui et al 2013, Kubo & Kadla 2005).

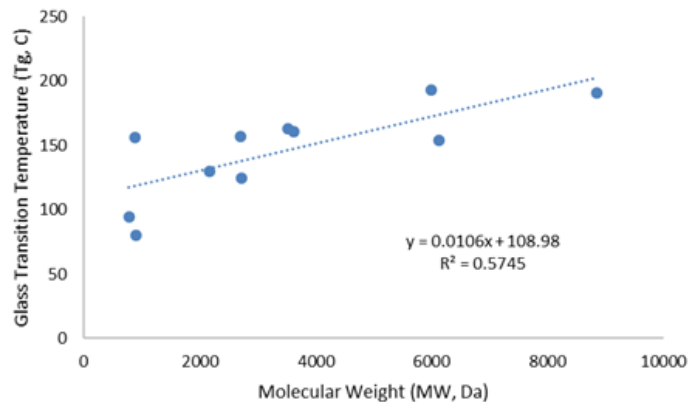


Figure 5-3: Glass Transition Temperatures (1st Heating) versus Molecular Weight for Lignin Fractions

To better examine the relationship between glass transition temperature and thermally induced cross-linking of the lignin, the rise of the glass transition temperature and the change in specific heat capacity were examined with subsequent reheats in order to analyze cross-linking behavior for the lignin fractions. The change in specific heat capacity (ΔC_p) at the glass transition serves as an indication of the differences of molecular mobility between the glass and rubbery states. For these lignin fractions, it is believed that T_g is greater than the cure temperature such that the reaction rate for free radical initiated self-polymerization is limited by the relative mobility of the molecules (Wisnarakkit & Gillham 1990). That is, lower MW fractions were shown to exhibit higher rises in glass transition temperatures (see Table 5-3). Venditti & Gillham (1997) provide a useful method for approximating fractional conversion from the uncured to the cured state based on the rise in glass transition temperatures, as shown in the following equation:

$$\ln(T_g) = \frac{(1-x)\ln(T_{g0}) + \frac{\Delta C_{p\infty}}{\Delta C_{p0}} x \ln(T_{g\infty})}{(1-x) + \frac{\Delta C_{p\infty}}{\Delta C_{p0}} x}$$

Where “x” denotes the fixed conversion from 0 to 1, and the subscripts “0” and “∞” indicate values for the uncured and cured states. This method is suitable for analyzing lignin fractions since it can also be used to model systems that are comprised of copolymers of unreacted segments. As shown in Figure 5-4, mostly linear relationships were observed for glass transition temperature as a function of estimated fractional conversion.

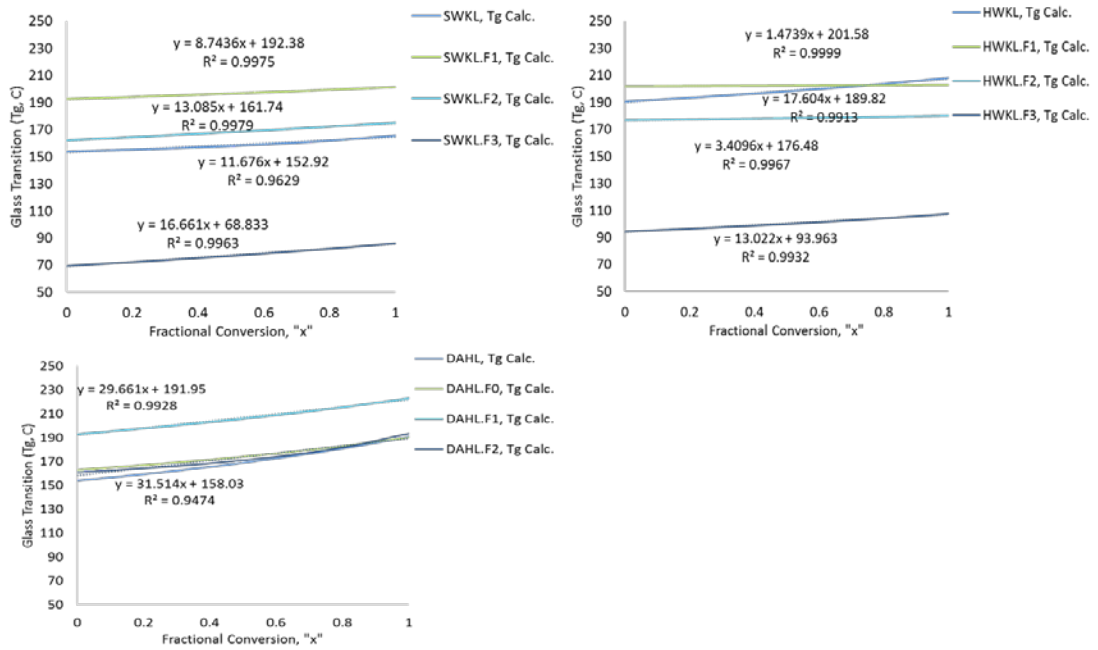


Figure 5-4:Lignin Glass Transition Temperature versus Fractional Conversion

For this work, fractional conversion for the lignin was not measured directly and no fit data is provided. However, based on the small changes observed in glass transition temperature and specific heat capacity, key differences between the lignin fractions are noted.

The higher MW fractions SWKL.F1 and HWKL.F1 were both noted as having the lowest increase in glass transition temperatures upon curing, while the low MW fractions SWKL.F3 and HWKL.F3 had higher increases. SWKL.F1 increased less than 10 °C from 193 to 201 °C and HWKL.F3 increased more than 17 °C from 69 to 86 °C. Similarly, HWKL.F1 increased by only 1 °C from 202 to 203 °C, yet HWKL.F3 exhibited a T_g rise similar to SWKL.F3 by 13 °C from 94 to 108 °C. This may present a significant challenge for engineers attempting to blend unmodified low molecular weight lignin fractions with existing polymers in that even though the glass transition temperatures are low enough to mix with common polymers (e.g. HDPE, PET, etc.), these same fractions may be subject to a higher degree of polycondensation and crosslinking upon heating.

DAHL lignin fractions exhibited a significantly higher T_g rise from 25 to 35 °C for the whole and high MW fractions. Results for the low MW fraction DAHL.F3 were inconclusive due to mass loss upon heating, which is believed to have had a significant impact on the DSC results. As shown in Table 5-4 and Figure 5-5, over 25% of the DAHL.F3 fraction's mass was lost at 220 °C upon heating.

Table 5-4: Thermal Decomposition for Isolated Lignin Fractions

Lignin Fraction	ΔT	E, kJ/mol	R ²	Δ Mass Loss, %	Mass Loss, % 300°C	Molecular Weight, Da
SWKL	300 to 450 °C	38	0.96	63%	24%	6129
	220 to 300 °C	29	1.00	17%		
	190 to 220 °C	32	1.00	3%		
SWKL.F1	300 to 450 °C	40	0.99	58%	17%	8843
	220 to 300 °C	41	1.00	13%		
	190 to 220 °C	48	1.00	2%		
SWKL.F2	300 to 450 °C	41	0.98	60%	18%	2729
	220 to 300 °C	12	0.98	9%		
	190 to 220 °C	7	1.00	2%		
SWKL.F3	300 to 450 °C	35	0.99	59%	31%	881
	220 to 300 °C	15	0.99	16%		
	190 to 220 °C	12	1.00	4%		
HWKL	300 to 450 °C	33	0.92	57%	21%	2700
	220 to 300 °C	11	0.93	11%		
	190 to 220 °C	23	1.00	4%		
HWKL.F1	300 to 450 °C	44	0.97	63%	14%	5996
	220 to 300 °C	41	1.00	12%		
	190 to 220 °C	72	1.00	2%		
HWKL.F2	300 to 450 °C	46	0.98	63%	15%	2180
	220 to 300 °C	11	0.97	7%		
	190 to 220 °C	15	0.99	2%		
HWKL.F3	300 to 450 °C	38	0.97	58%	27%	787
	220 to 300 °C	12	0.99	13%		
	190 to 220 °C	20	1.00	5%		
DAHL	300 to 450 °C	11	0.96	33%	58%	3523
	220 to 300 °C	27	0.98	35%		
	190 to 220 °C	16	1.00	7%		
DAHL.F0	300 to 450 °C	24	0.98	47%	31%	36719
	220 to 300 °C	20	1.00	18%		
	190 to 220 °C	29	1.00	6%		
DAHL.F1	300 to 450 °C	32	0.92	58%	21%	
	220 to 300 °C	50	1.00	18%		
	190 to 220 °C	52	1.00	2%		
DAHL.F2	300 to 450 °C	37	0.96	59%	19%	3623
	220 to 300 °C	24	0.99	12%		
	190 to 220 °C	33	1.00	3%		
DAHL.F3	300 to 450 °C	13	0.99	34%	48%	905
	220 to 300 °C	6	0.98	16%		
	190 to 220 °C	20	0.98	10%		

In order to further examine the thermal stability for all lignin fractions, thermal gravimetric analysis was used to examine mass loss as a function of temperature and linear heating rate under a nitrogen atmosphere. As shown in previous studies, the kraft lignin whole fractions were observed as being moderately stable up to 300 °C (Brodin et al 2010), and Fenner and Lephardt (1981) used FTIR evolved gas analysis in order to attribute mass loss up to 300 °C to the elimination of formic acid, formaldehyde, carbon dioxide, sulfur dioxide and water resulting from the degradation of phenylpropane side chains.

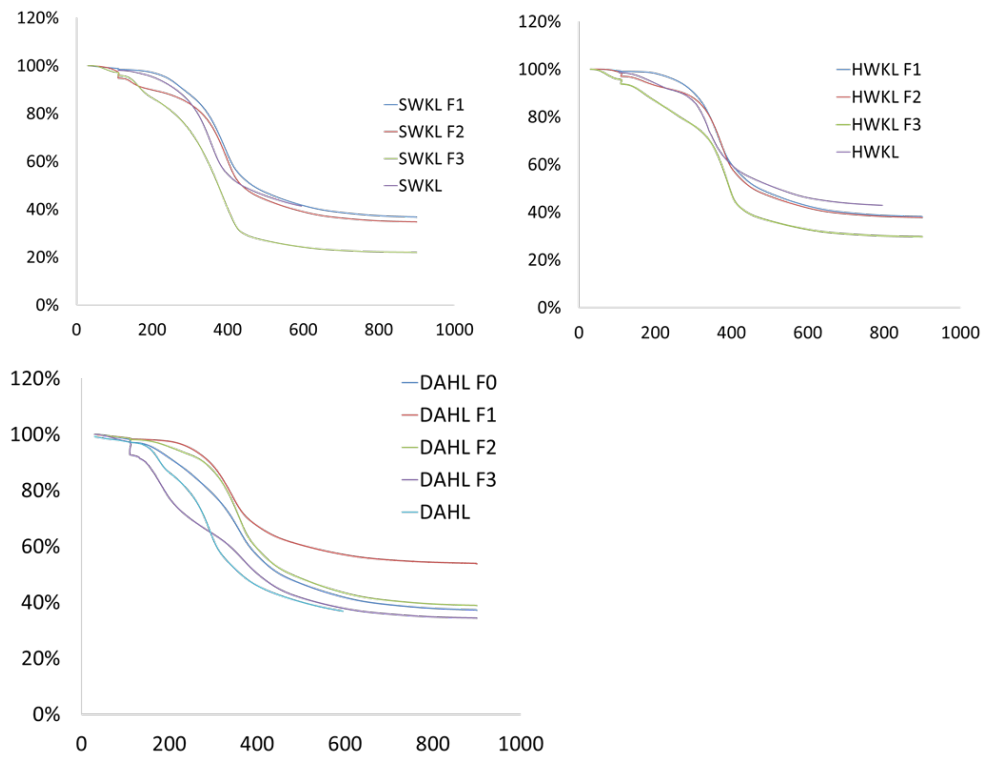


Figure 5-5: Thermal Gravimetric Analysis for the Isolated Lignin Fractions

For this study, the degradation reactions during pyrolysis of the lignin fractions were modeled using a non-isothermal method according to Murugan et al 2008, as shown in the following equation:

$$\int_0^{\alpha} \frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta} \int_0^T e^{-E/RT} dT$$

Where “ α ” is the mass loss coefficient, “A” is the pre-exponential factor for an Arrhenius relationship, “ β ” is the linear heating rate, “T” is the temperature, and “R” is the universal gas constant, “n” is the reaction order, and “E” is the decomposition activation energy. Solving for a first order reaction (n=1), the equation becomes:

$$\ln \left[\frac{-\ln(1-\alpha)}{T^2} \right] = \ln \left[\frac{AR}{\beta E} \left(1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT}$$

Assuming “ $2RT/E$ ” is significantly less than 1, a plot of “ $\ln \left[\frac{-\ln(1-\alpha)}{T^2} \right]$ ” versus $1/T$ will provide a slope where the decomposition energy “E” may be calculated from the slope. The data was fit to the model for three distinct heating regions 190 to 220 °C, 220 to 300 °C, and 300 to 450 °C, with R^2 values all above 0.92. The decomposition activations energies are reported in Table 5-4.

For SWKL lignin fractions, decomposition activation energies from 300 to 450 °C were the same for all fractions at 40 kJ/mol. However, for the SWKL.F2 and SWKL.F3 fractions, the decomposition energies for mass loss below 300 °C were significantly less than 40 kJ/mol and increased with increasing temperature. For SWKL.F1, the decomposition energies for mass loss below 300 °C were higher than 40 kJ/mol. This suggests relatively poor thermal stability for low MW fractions relative to the higher MW fraction.

A similar trend was noted for the HWKL samples. All of the HWKL samples exhibited decomposition energies between 33 to 46 kJ/mol from 300 to 450 °C. However, each of the HWKL fractions was observed as having the lowest decomposition energies from 220 to 300 °C, where a majority of the mass loss up to 300 °C occurs upon heating.

Again, for the DAHL samples, the lowest decomposition activation energies and the highest mass losses at 300 °C were observed. DAHL was shown to be the least thermally stable of the lignin analyzed in this study, and the low MW fraction DAHL.F3 exhibited approximately 22% mass loss below 190 °C. This finding suggests that despite low MW and low observed glass transition temperatures, unmodified whole and fractionated DAHL are unsuitable for thermoplastic polymer blending applications.

Lastly, as shown in Figure 5-6, mass loss at 300 °C for all samples was shown to decrease logarithmically with increases in MW.

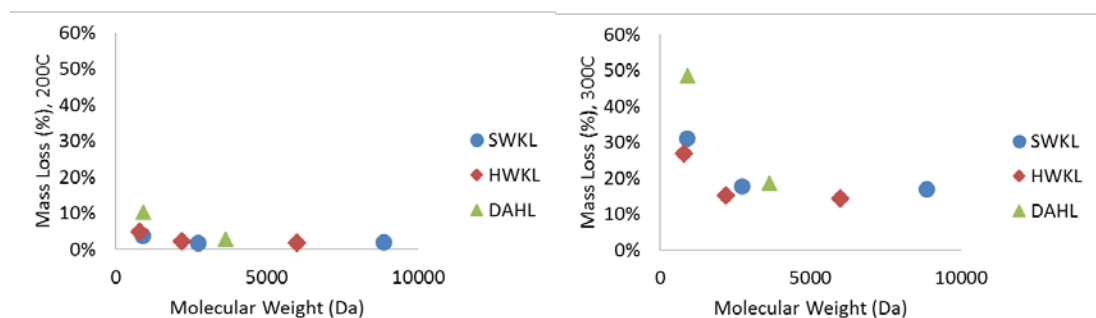


Figure 5-6: Lignin Mass Loss at 200 °C & 300 °C versus Molecular Weight

5.5 Conclusions

Glass transition temperature for the lignin fractions analyzed in this study primarily depends on molecular weight. Decreases in glass transition temperature were observed for SWKL, HWKL and DAHL lignin fractions with low MW. Similarly, thermal stability (as measured by mass loss and decomposition activation energies) was shown to decrease with decreasing MW. SWKL.F3 exhibited the lowest glass transition temperatures between 69 to 86 °C, while maintaining good thermal stability up to 220 °C. Glass transition temperatures as low as 94 °C were observed for HWKL.F3, while also maintaining good thermal stability. DAHL fractions showed only slight decreases in glass transition temperature, while suffering from poor thermal stability at temperature below 190 °C. Decomposition energies for both softwood and hardwood kraft lignin were shown to be similar at 40 kJ/mol, while DAHL lignin fractions were shown as having energies as low as 11 kJ/mol at 300 °C.

Finally, whole lignin fractions appear to exhibit simple linear mixing rules for their constituent parts and only slight interactions resulting from thermally induced crosslinking were observed based on rise of glass transition temperatures upon subsequent reheating above the glass transition temperature. This suggests that small MW fractions may impart some plasticizing effect to the whole lignin fraction.

6 TECHNO-ECONOMIC ANALYSIS OF LIGNIN PHENOLATION

6.1 Introduction

Lignin phenolation has been proposed as a means of improving the reactivity of lignin bio-materials (Calvo-Flores 2010, Argyropoulos 2016). One specific application where this may be useful is with respect to phenol formaldehyde resins, and cost-advantaged phenol formaldehyde (PF) production may be of interest to the forest products industry where over 80% of PF resins are consumed towards the manufacture of engineered wood products, oriented strand board (OSB) and plywood. There may be immediate market opportunities for phenolated lignin products applied towards thermosetting resin applications, where the estimated market volume is over 6 million metric tons per year globally. Furthermore, phenol prices range from \$900 to \$2000/mt (ICIS Chemical).

Unmodified lignin is not miscible with non-polar amorphous solids and it exhibits only moderate chemical reactivity in adhesive applications (Pucciariello et al 2004, Kadla & Kubo 2004, Argyropoulos et al 2015). For this reason, the addition of lignin towards bio-polymer applications typically results in a sharp decrease in performance, as indicated by the conceptual Figure 6-1. The goal of lignin phenolation is to improve its reactivity and “value-in-use” with thermo-setting systems, and ultimately, improve product properties with increased lignin substitution. The value proposition assumes that PF resin customers will pay an equivalent price (based on substituted phenol) for cost advantaged phenolated lignin, assuming no compromise to product performance is experienced. The goal of this work is to provide a techno-economic assessment for the unit operations required to phenolate lignin and determine how the process chemistry affects cost drivers and safety.

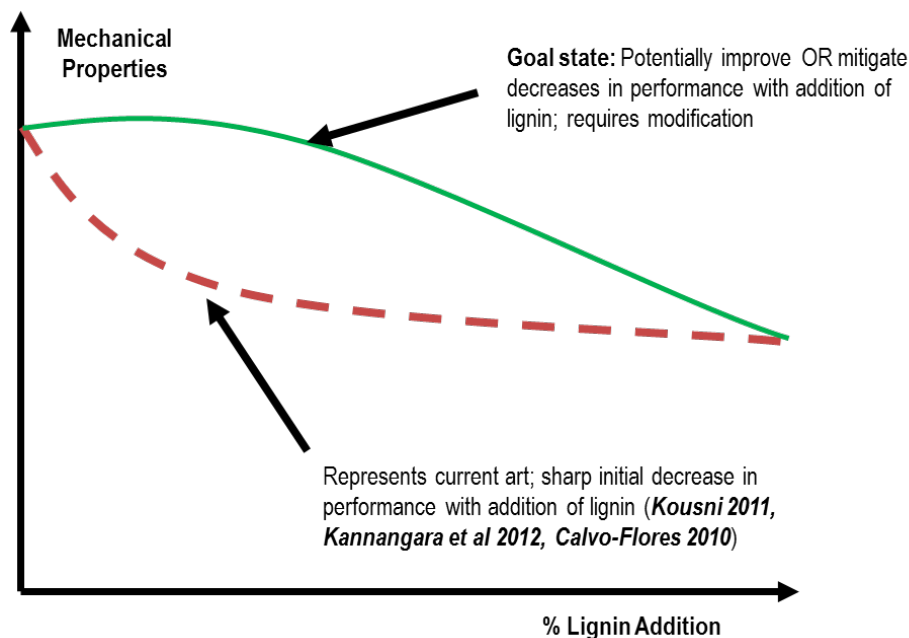


Figure 6-1: Changes in Bio-Polymer Mechanical Properties with Lignin Addition (Concept)

6.2 Methodology

6.2.1 Process Description & Functional Unit

It has been shown that phenol may be substituted at the alpha position of a mono-lignol unit by acid catalysis, thereby increasing its reactivity (Podschun et al 2015). For the purposes of this study, a conceptual process was modeled according to a laboratory procedure that calls for acid catalysis of kraft lignin or bio-refinery lignin residue. As shown in Figure 6-2, the process involves low-temperature drying of the starting lignin material, in order to prevent thermal decomposition, and 5% addition of sulfuric acid to the lignin in the presence of a surplus of phenol (e.g. 5 parts phenol to 3 parts lignin). The acid catalysis is then carried out at 90°C for 2 hours.

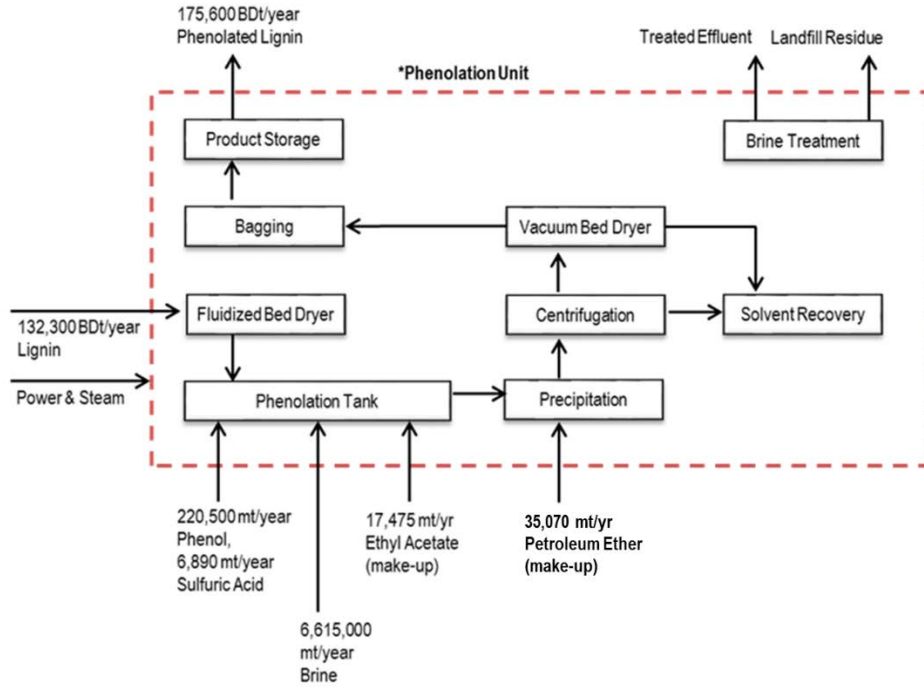


Figure 6-2: Process Flow Diagram for Lignin Phenolation

Once the reaction is complete, the phenolated lignin is subjected to an intense purification process. First, the reaction media is washed with a brine solution to remove all impurities and sent to an industrial decanter for separation of the brine from the phenolated lignin and excess phenol. Next, the purified phenolated lignin is solubilized with ethyl acetate and precipitated once more with petroleum ether in order to remove the excess phenol. The phenolated lignin slurry is then centrifuged and dried in a low-temperature vacuum dryer in order to recover the solvents and excess phenol. The solvents are then sent to a solvent recovery system (e.g. distillation). Excess brine is sent to wastewater treatment, and finally, the dry phenolated lignin product is bagged and sent to product storage. The functional unit

for this study was 1 mt of phenolated lignin product. The reference capacity for this process is 132,000 mt/year lignin which is used to produce 175,000 mt/yr phenolated lignin.

6.3 Results & Discussion

6.3.1 Capital Expenditures (CAPEX)

As shown in Table 6-1, the total installed costs for the conceptual lignin phenolation process is \$158 million, with bare equipment costs at \$48 million. The largest contributor to the capital investment is the solvent recovery system required for the purification of the phenolated lignin product. The other significant items are the centrifuges and waste water treatment facilities required for recovery and treatment of the brine solution.

Table 6-1: Total Installed Costs for Lignin Phenolation

Unit Capex, \$ MM	Bare Equipment Cost	Total Installed Cost
Ribbon Blender	\$1.5	\$4.7
Column-1	\$15.2	\$47.8
Column-2	\$14.7	\$50.3
Waste Treatment Plant	\$4.4	\$15.1
CSR-1	\$0.9	\$2.8
CSR-2	\$0.9	\$2.8
CSR-3	\$1.7	\$5.9
Centrifuge	\$6.8	\$23.1
Fluidized Bed Dryer	\$0.4	\$1.4
Vacuum Fluidized Bed Dryer	\$0.4	\$1.4
Product Storage	\$0.9	\$3.0
Total	\$47.7	\$158.2

6.3.2 Cost Analysis

Figure 6-3 provides an overview of the costs associated with lignin phenolation. The single largest costs are associated with the phenol consumed in the reaction and solvent losses

(assumed to be less than 1%) during solvent recovery as ambient air losses. The next largest cost is the natural gas consumption required to produce the 23 MMBtu of process heat demand per mt phenolated lignin. Fuel value of \$150/mt was considered for the starting lignin, which would feasibly represent the opportunity cost for not combusting the lignin in a bio-refinery process, and this cost was allocated to the phenolation process as a raw material cost. The total unit cost for the phenolated lignin product was estimated to be \$450/mt.

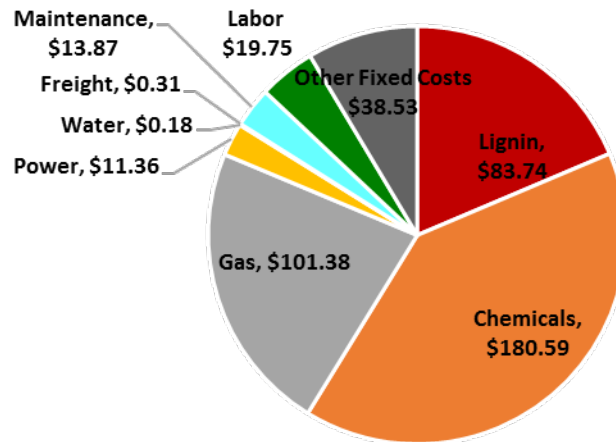


Figure 6-3: Unit Costs for Phenolated Lignin

6.3.3 Revenue Analysis & Key Financial Indicators

As shown in Figure 6-4, a lignin phenolation capital investment project has the potential to generate over \$215 million in annual revenue from the sale of 175,000 mt/yr phenolated lignin product. More importantly, the generous margins (+60%) associated with the phenolated lignin price assumption of \$1200/mt, less the much-lower-by-comparison unit

costs of \$450/mt, provides a project return of \$48 million and 18% IRR which may be applied directly to a bio-refinery project.

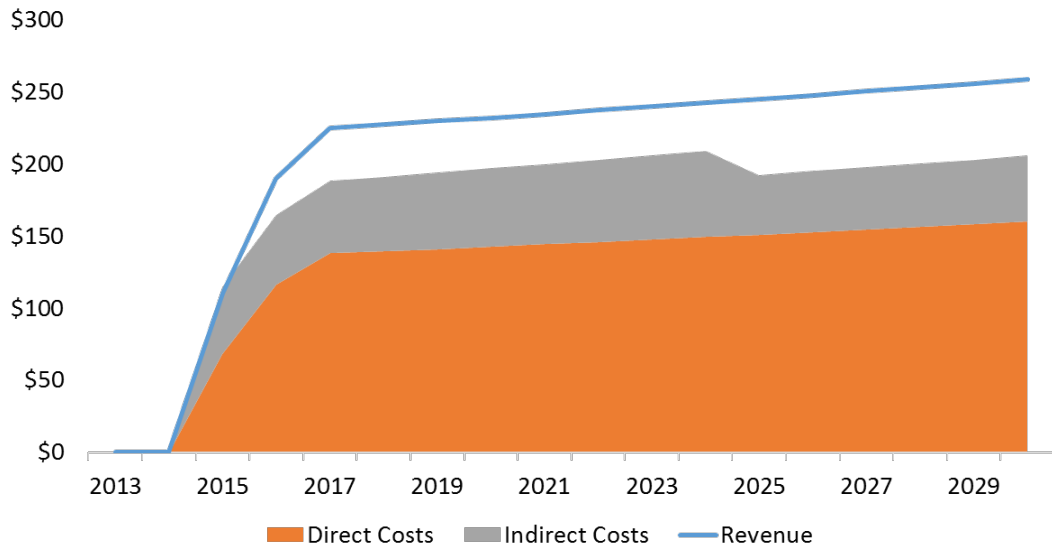


Figure 6-4: Revenue & Cost Projects for Lignin Phenolation

6.3.4 Sensitivity Analysis

One of the more important findings from this analysis is shown in Figure 6-5, the conceptual phenolation process is equally sensitive to changes in capital investment cost and phenolation price. That is, a 25% increase in capital investment costs may be offset by a 25% increase in price in order to achieve an equivalent internal rate of return. This suggests that additional capital investment towards the valorization of lignin may be justified.

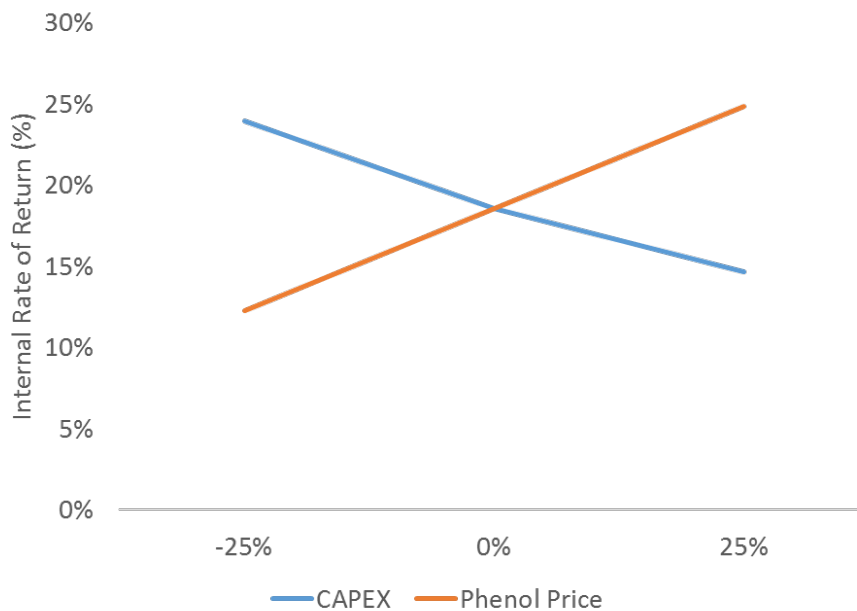


Figure 6-5: Sensitivity of Internal Rate of Return to % Changes in Input Parameters

6.4 Conclusions

In this study, a conceptual lignin phenolation process was modeled according to a laboratory procedure that calls for acid catalysis of kraft lignin or bio-refinery lignin residue. The goal of lignin phenolation is to improve its reactivity and ultimately improve product properties with increased lignin substitution of phenol in phenol formaldehyde (PF) resin systems. Again, the value proposition assumes that PF resin customers will pay an equivalent price (\$1200/mt, based on substituted phenol) for cost advantaged phenolated lignin, assuming no compromise to product performance is experienced, and at a reference capacity of 175,000 mt/yr phenolated lignin, the expected project returns may be \$48 million NPV and 18% IRR. Therefore, the capital investment requirement, unit costs, and incremental revenue

from the conceptual phenolation process will be applied to the techno-economic analysis of a bio-refinery process in order to valorize the lignin co-product and achieve additional project returns. It is suggested that lignin valorization is a significant economic driver towards successful bio-refinery commercialization.

7 PRODUCT DEVELOPMENT IN THE BIO-BASED ECONOMY: SCREENING CONVERSION TECHNOLOGIES & PATHWAYS FOR FOREST-BASED CHEMICALS

7.1 Abstract

In the emerging bio-chemical market, there are many chemicals that can be converted from food-based and lignocellulosic carbohydrates. Each chemical product and its respective conversion pathway will require significant resources for successful commercialization. Primarily intended as a new product development (NPD) tool for forest products industry management, a simple prioritization metric was used in order to screen and evaluate the commercialization potential of a bio-chemical with respect to its potential profitability. In the early stages of research, commercially relevant yields are largely unknown, therefore, this study employs a molecule economy of 1 to 1 as a starting point (i.e. product molecule to monomeric sugar). These theoretical yield assumptions were then compared against actual yields reported in the literature, and since the results exhibited a positive linear correlation ($R^2 = 0.42$), this simple model is suggested as a starting point for NPD management. In this work, fermentation technology for the efficient production of succinic acid was determined to be the most promising of bio-chemical candidates for commercialization over the short-term. This is due to high level of demonstrated yields in the literature, value-added functionality of the dicarboxylic acid and versatility of succinic acid product family to fulfill market needs in a variety of high-value intermediate chemical applications.

7.2 Introduction

In recent years, it has been suggested that a growing bio-chemical market will promote rural and regional economies (Golden & Handfield, 2014). However, the successful commercialization of bio-chemicals and bio-materials remains a significant challenge (USDA 2008, Werpy et al 2004, Kajaste 2014, Dale 2003). This is primarily due to the technical feasibility of proposed bio-chemical production routes, large capital investment, insufficient market demand which translates to lower product prices, lower operating margins and high production costs relative to equivalent petro-chemical markets and the price volatility of raw materials (de Jong et al 2012, Nelson et al 2010, Lipinsky 1981, Werpy et al 2004).

It is estimated that roughly 2/3 of the global petro-chemicals market volume could be satisfied with bio-chemicals providing equivalent or better performance (Nelson et al 2010, de Jong et al 2012). While it is technically feasible to produce a majority of petro-chemical based products from bio-chemical equivalents, it is important to understand that most of these products belong to mature markets where stable growth is currently satisfied with petro-chemical production. In this instance, the product price for any chemicals serving mature markets is a function of the marginal producer (Landsburg, 2008). This suggests that firms seeking to serve these markets with new bio-based technology are limited solely to “cost-advantaged” business propositions, which historically have been unattainable due to low conversion yields and excessive production costs (de Jong 2012, Werpy 2004, Danner & Braun 1999). Alternatively, bio-chemicals targeting the specialty and fine chemicals markets may encounter premium prices, however, new commercial bio-chemical operations run the risk of quickly saturating these smaller markets. Therefore, selecting a bio-chemical product for

commercialization is an iterative exercise of constant market evaluation and a careful analyses of the fundamental bio-chemical conversion pathway with respect to conversion efficiencies and operational costs.

One of the principle advantages of petro-chemical conversion processes is the ability to achieve relatively high product yields by converting raw materials into a variety of co-products, thereby simultaneously increasing revenue and decreasing non-value added waste (Lipinsky, 1981). Bio-chemical conversion processes on the other hand, are often designed and specifically tailored to produce a single product, which may result in unintended consequences such as relatively lower yields and significant waste (i.e. low value lignin, waste cell mass from fermentation, etc.). This implies, given limited data, that the highest cost driver for any chemical conversion pathway is raw material costs and chemical consumption. Fortunately, recent advances in microbiology and catalyst development have enabled researchers to dramatically improve upon yield and reduce bio-based production costs (Jang et al 2012, Dale 2003, Song & Lee 2005, Gallezot 2012, Ling & Aden 2009, Bozell 2008).

Raw material price volatility is of primary concern regarding emerging market opportunities for bio-chemicals. With established commodity chemicals, the product price is closely tied to the price of oil, which is increasingly volatile (Lee & Ni 2002, Kannegiesser et al 2008). Generally, liquid natural gas containing ethane and propane are used to produce C2 and C3 olefins, while petroleum distillates and BTX (benzene, toluene and xylene) are used to produce C4 compounds via steam reforming. Since approximately 8% - 15% of liquid fossil fuel consumption is for the production of commodity chemicals, long-run volatility associated with

these raw material prices may create attractive market opportunities for bio-chemicals in the near future (USDA 2008, Shen 2009).

Bio-chemicals produced from lignocellulosic sugars may also serve as an attractive alternative to bio-chemicals derived from food-based sugars since the raw material prices for wood products are relatively stable (see Figure 7-1). Specifically, lignocellulosic biomass is suggested as an attractive feedstock due to its abundant supply in the U.S (Mosier et al 2005). Furthermore, recent declines in demand for forest products have left a surplus of forest based resources, both mixed hardwoods and loblolly pine in the southeast U.S., which could be efficiently utilized by bio-chemical manufacturers, or a bio-based economy (Wear et al 2010, Carle & Holmgren 2008, Raunikar et al 2010).

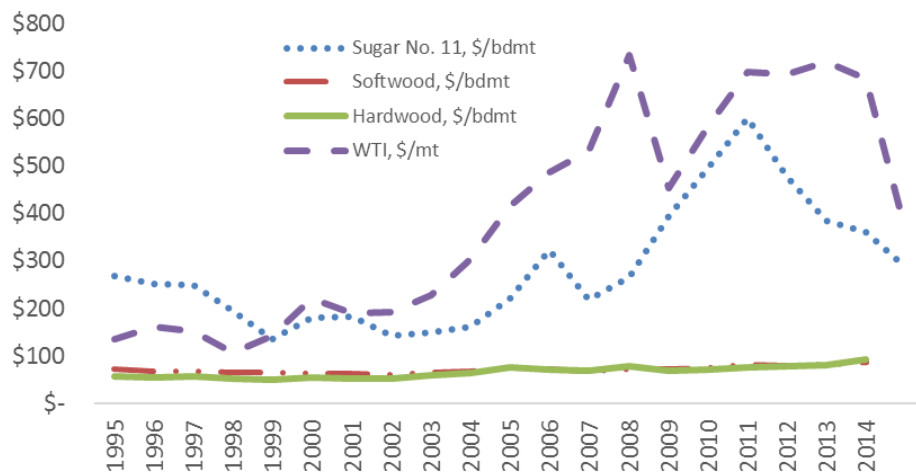


Figure 7-1: Historical Raw Material Prices. (RISI 2015, NYMEX 2015, EIA 2015)

7.2.1 The Challenge of New Product Development in Forest Products

The forest products industry may also be well suited to differentiate itself in the biofuels and bio-chemical industry by utilizing core capabilities such as wood harvesting and transport in an established supply chain, solids partitioning in the woodyard (e.g. chipping and screening), thermochemical conversion of a solids substrate to mixed media (e.g. wood to fiber and spent liquor from the pulping process), and subsequent product purification and energy recovery (e.g. kraft recovery cycle and pulp bleaching). It is worth emphasizing that these unit processes have been successfully and safely employed for over 150 years. Paradoxically, however, these core capabilities are also “core rigidities” (as described by Leonard-Barton, 1992) which dramatically inhibit new product development. For example, drawing parallels between kraft pulping chemistry and fermentation technology may be a daunting task for management, and it is difficult to envision the “why” or “how” a forest products company may leverage core capabilities to enter new chemicals markets.

Management in the forest products industry and other stakeholders with an interest in bio-chemicals commercialization will likely experience difficulty in determining the gross opportunity each conversion technology presents. In the early stages of project development it is important to communicate the relative value of the technology being developed. Management faced with deciding which technology to pursue for commercialization require a simple metric and method for screening potential candidates which merit further study. This work provides such a metric for examining the potential value that a bio-chemical may possess as a function of its conversion yield and applies it to a group of newly researched bio-chemical conversion technologies proposed in the literature; in this example, the revenue received for

converting a unit of hardwood with a typical starting raw material cost of \$70 to \$90 per “bone-dry” metric ton.

7.2.2 New Opportunities for Bio-Based Chemicals from Forest Products

Chemicals produced from biomass are considered “flexible” with respect to biomass source and “adaptable” with respect to genetic manipulation (Lipinsky, 1981). Petroleum derived chemicals on the other hand are considered “inflexible” but compensate with respect to efficient and effective conversion technology and economies of scale. For this reason, lignocellulosic fractionation was identified as a promising avenue for taking advantage of inexpensive and potentially chemically useful biomass feedstocks (Lipinsky, 1981). Special emphasis should be placed on potential commercial processes with the ability to improve genetic strains and broaden the range of potential substrates and product ranges for the microorganism, including the valorization of lignin which serves to improve the overall yield of value-added products from the process (Danner & Braun, 1999).

The objective of this work is to present a simple screening methodology for ranking bio-chemical conversion technologies and pathways quantitatively, according to their estimated economic maximum potential margin per unit of biomass feedstock. Specifically, this analysis is intended as an early stage-gate opportunity assessment for known technology and organic chemical conversion pathways. Furthermore, this work attempts to screen the most promising, technically viable bio-chemical conversion technologies based on a prioritization of the estimated revenue received for converting a unit of biomass to a final desired product. This work builds upon earlier reviews that attempted to evaluate the commercialization potential of promising bio-chemical conversion pathways, qualitatively.

7.3 Methodology

7.3.1 Conversion Pathway & Bio-Chemical Product Search Criteria

A comprehensive analysis of bio-chemicals derived from lignocellulosic biomass was provided by U.S. Department of Energy's "Top Value Added Chemicals" (Werpy et al 2004). In this report, potential bio-chemicals were evaluated according to synthesis pathways (i.e. number of conversion steps), number of "Building Block" derivatives (i.e. succinic acid to 1,4 butanediol, polybutylene succinate, tetrahydrofuran, etc.) and a general qualitative assessment of market potential based on industry experience. While this report is helpful in cataloging the technically feasible bio-chemicals and their respective target markets, it offers little suggestion with respect to a quantifiable commercialization potential. Jang et al (2012) provided significant technical detail with respect to microorganism fermentation. Their analysis included a thorough discussion of research constraints and opportunities associated with each product and its respective micro-organism technology, but most discussion regarding revenue or cost drivers was not included.

Other techno-economic analyses on bio-chemicals have recently been structured around the evaluation of bio-refinery process schema using linear programming and non-linear mixed integer programming (NLMIP), mathematical algorithms (Zondervan et al 2011, Tang et al 2013, Sharma et al 2011, Sammons et al 2008). Sophisticated algorithms are employed in order to optimize a variety of process and product options for a variety bio-refinery process schema. First, an objective function is programmed according to the bio-refineries primary goal, usually profit maximization, and then functions for a series of system constraints such as yield, waste generated and fixed capital investments, are added to the algorithm. The model

can then “predict” a suitable product mix and process design by optimizing the system against the specified constraints. Unfortunately, while powerful in theory, Cooper et al (1997) reported that complicated multi-decision models such as this are not particularly useful in the new product development process at early stage due to a lack of reliable information and that the primary weakness with these approaches to product portfolio management is the heavy reliance on accurate data for many process inputs (Marion & Myer 2011). Furthermore, the new product or process design reported as “optimal” from any specific objective function may ultimately conflict with the strategy and direction set forth by the firm’s management, resulting in wasteful allocation of scarce resources. In practice, many firm’s reported using a simpler scoring system in order to prioritize and sort a variety of new product options for further development (Cooper & Kleinschmidt 1991).

For this work, it was important to establish search criteria for bio-chemical when reviewing the literature. Generally, technology that converts sugars directly to hydrated intermediate and commodity chemicals were given priority (Dale, 2003). It assumed that chemicals fitting this search criteria will exhibit a higher manufacturing yield and increased carbon efficiency (Kajaste, 2013) which will provide a higher overall value. Products must also serve markets that demonstrate new and expanding growth, and bio-chemicals were selected based on the intended downstream market’s relative size and growth (see Table 7-1). In general, the products selected can be grouped into three general product families: i) dicarboxylic acids, ii) alcohols and iii) conjugated dienes.

Table 7-1: Overview of Prospective Bio-Chemicals

Compound	Formula	MW*	CAS**	Biomass Conversion Reagents	Commercial Use	Reference Fossil Fuel
1,3 Propanediol	C3H8O2	76	504-63-2	Microorganism, Nutrients	Engineered Polymers, Textiles, Polyesters, Polyurethanes	C2 & C3 Olefins
1,3 Butadiene	C4H6	54	106-99-0	Microorganism, Nutrients, Acetic Acid	Rubber Products	C2 - C4 Olefins, Butane
1,4 Butanediol	C4H10O2	90	110-63-4	H2 (Gas), Pd Catalysts	Solvents, Commodity Polymers, Polyurethanes	C2 & C3 Olefins, BTX
2,5 FDCA	C6H4O5	156	3238-40-2	Pd Catalysts	Commodity Polymers, Polyesters	
3HP	C3H6O3	90	503-66-2	Microorganism, Nutrients	Engineered Polymers, Polyesters, Acrylic acid	
Acrylamide	C3H5NO	71	79-06-1	Enzymes	Engineered Polymers, Coatings, Adhesives	C2 & C3 Olefins
Acrylic Acid	C3H4O2	72	79-10-7	H2 (Gas), Metal Oxide Catalysts	Engineered Polymers, Coatings, Adhesives	C2 & C3 Olefins
Adipic Acid	C6H10O4	146	124-04-9	Metal Oxide Catalysts	Engineered Polymers (Predominantly Nylon 6,6)	BTX
Ethanol	C2H6O	46	64-17-5	Microorganism, Nutrients	Super-Commodity	
Fumaric Acid	C4H4O4	116	110-17-8	Microorganism, Nutrients	Polyesters, Polyols. Also food plasticizer and acidulant.	BTX, Butane
Furfural	C5H4O2	96	98-01-1	Dilute H2SO4	Solvents, Adhesives, Agrochemicals	
Glutamic Acid	C5H9NO4	147	617-65-2	Microorganism, Nutrients	Food Additive, Amino Acid	
Glutaric Acid	C5H8O4	132	110-94-1	KCN	Polyesters, Plasticizers	C2 - C4 Olefins, Butane
Itaconic Acid	C5H6O4	130	97-65-4	Microorganism, Nutrients	Synthetic Rubber, Carbon Fiber, Coatings	
Lactic Acid	C3H6O3	90	50-21-5	Microorganism, Nutrients	Commodity Polymers	
Levulinic Acid	C5H8O3	116	123-76-2	Dilute H2SO4	Solvents, Plasticizers, Polyols	

Table 7-1: Continued

Compound	Formula	MW*	CAS**	Biomass Conversion Reagents	Commercial Use	Reference Fossil Fuel
Malic Acid	C ₄ H ₆ O ₅	134	97-67-6	Microorganism, Nutrients	Food Acidulant	
Malonic Acid	C ₃ H ₄ O ₄	104	141-82-2	Metal Oxide Catalysts	Polyesters, Coatings	
Methyl Acrylate	C ₄ H ₆ O ₂	86	96-33-3	Methanol	Engineered Polymers	C2 & C3 Olefins
Oxalic Acid	C ₂ H ₂ O ₄	90	144-62-7	Nitric Acid	Cleaning, Bleaching	C2 & C3 Olefins
Sorbitol	C ₆ H ₁₄ O ₆	182	50-70-4	H ₂ Gas, Raney Nickel Catalyst	Food Additive, Moisture Stabilizer	
Succinic Acid	C ₄ H ₆ O ₄	118	110-15-6	Microorganism, Nutrients	Engineered Polymers, Polyesters	
Tetrahydrofuran	C ₄ H ₈ O	72	109-99-9	Non-specific Catalysts	Elastomers, Solvents, Coatings	C2 & C3 Olefins, BTX
Xylitol	C ₅ H ₁₂ O ₅	152	87-99-0	H ₂ Gas, Raney Nickel Catalyst	Food Additive	
Glycerol	C ₃ H ₈ O ₃	92	56-81-5	Microorganism, Nutrients	Food Additive, Moisturizer, Preservative	C2 & C3 Olefins
Gluconic Acid	C ₆ H ₁₂ O ₇	196	526-95-4	Pd Catalysts	Industrial Cleaner, Sizing Agent	
Glucaric Acid	C ₆ H ₁₀ O ₈	210	576-42-1	Non-specific Catalysts	Phosphate Replacement for Detergents	
Acrylonitrile	C ₃ H ₃ N	53	107-13-1	NaBr, NaOH	ABS Resins & Nitrile Rubbers, Acrylamide (Carbon) Fibers	C2 & C3 Olefins
Butanol	C ₄ H ₉ OH	74	71-36-3	Microorganism, Nutrients	Coatings, Solvents, Fuel, Polyesters	C2 & C3 Olefins

*Molecular Weight (MW) **Chemical Abstract Service (CAS) Number

7.3.2 Price Assumptions

All prices are gathered as quotes from either ICIS chemical pricing (a division of Reed Business Information) or Alibaba's chemical marketplace unless otherwise noted. ICIS chemical prices are from 2006 & 2008 and Alibaba quotes were gathered in 2015. When applicable, prices taken from these references are inflated according to specific raw material price indices. For example, butadiene prices taken from 2006 are inflated to current market prices using historical commodity price data for RSS3 (rubber smoke sheet 3). It is assumed that the product prices change proportionally with changes with the cost of respective raw materials. The authors chose not to incorporate risk management tools in this analysis in order to assess the raw material price volatility. However, the methodology provided herein can easily be adapted to utilize such tools (e.g. Monte Carlo simulation, etc.) provided the user possesses the appropriate data set. Others may wish to eschew statistical methods and incorporate their own price models based on relevant industry experience or a thorough analyses of manufacturing costs for the marginal producer. It is understood that such work is constant, evolving, exhaustive and contextual depending on the user's (or management's) point of view. The purpose of this study is not to explore the validity (or voracity) of previously published price information. Any assumed prices reported herein are intended to provide the reader with an approximation of revenue received for biomass conversion to a specific chemical in order to better quantify and prioritize the opportunity for this particular subset of chemical conversion technologies. Furthermore, the authors maintain that the relatively low price-volatility of North American hardwoods and softwoods may enable significant value creating opportunities in bio-chemical manufacture for the forest products industry.

In some instances, specific chemical abstract service (CAS) number chemicals do not possess commercial markets or the intended "bio-chemical" business proposition targets a market outside of the existing specialty chemical market for the respective chemical (i.e. the chemical is a "substitute" and not a direct "replacement"). For example, Glutamic acid is a widely manufactured amino acid, but the target biomaterial applications proposed in this and other works require the manufacture of commercial quantities far beyond the current market application. In this instance, a log-log linear regression model was used in order to estimate the price of commercial quantities based on price data gathered as smaller quantities (Hart & Sommerfield 1997, Qi et al 2015), as described by the following equation:

$$P = aQ^b$$

Where "P" in dollar per kilogram is the product price at a specific quantity, "Q", in grams. The values "a" and "b" represent best fit parameters, and "b" is the discount factor which is a negative number representing the regressed discount for economies of scale. It should be noted that the group discount factor calculated for this work was -0.67 and that most literature cites the use of -0.75 as an appropriate discount factor (Qi et al 2015, Stuart et al 2012).

7.3.3 Prioritization Example

This study attempts to prioritize selected bio-chemicals for commercialization based on the potential revenue received from converting one metric tonne (mt) of sugar, or mixed hardwoods, to any of the aforementioned chemicals. For example, the calculation of revenue received for converting one mt of sugar (glucose) to succinic acid is presented in Figure 7-2.

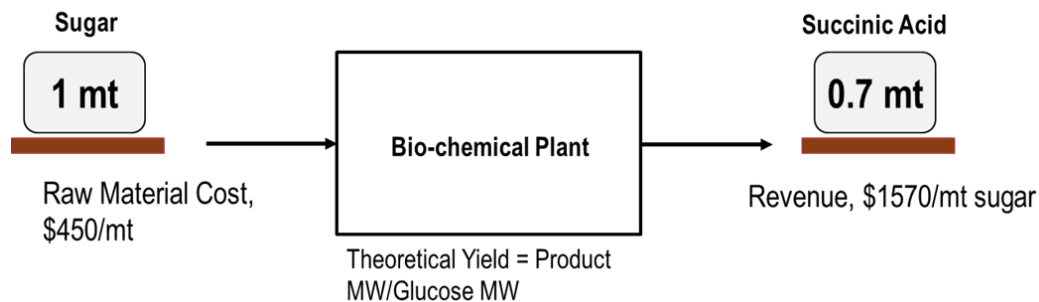


Figure 7-2: Example of Converted Revenue Calculation

First, the price of succinic acid is gathered from industry price quotes or calculated according to the methodology provided by Hart & Sommerfield, 1997. In this instance, a price of \$2400 per mt succinic acid is assumed, and the assumed transfer price (i.e. established price between two entities) of sugar is \$450 per metric ton. The assumed, or theoretical, molar yield is 1 mol product (or succinic acid in this example) per mol of glucose. The calculated yield in this instance is 65.6% (e.g. 118 g/mol succinic acid divided by 180 g/mol glucose), or 0.656 mt of sugar per 1 mt of converted glucose. Therefore, the revenue received for converting sugar at the hypothetical bio-chemical plant gate to succinic acid is the product yield multiplied by the assumed price (i.e. \$2400/mt succinic acid multiplied by 0.656 mt succinic acid/mt sugar). In this example, the value of 1 mt of sugar at the bio-chemical plant gate is then estimated to be \$1570. The difference between this revenue received for converting 1 mt of glucose and the cost of the raw material (i.e. the sugar transfer price) represents the maximum revenue that can be received for converting the sugar to a bio-chemical product. Of course, this does not account for additional operational costs such as reagents, separation and purification items, and it is only intended as a starting point for further discussions. That is, if

the revenue calculated in this manner were less than the starting cost of the raw material before such additional costs are even considered, then it is suggested that other bio-chemicals exhibiting a higher value be investigated first.

7.4 Results

The prioritization methodology presented was then repeated for prospective bio-chemicals shown in Table 7-1 that could feasibly be produced from sugars, or bio-chemicals produced from mixed hardwoods, and the results for revenue received per unit of biosugar converted (\$/mt glucose) are presented in Figure 7-3, alongside the unit price for each chemical (\$/mt). In many cases, as a result of significant yield losses, the revenue received for converting a unit of biosugar is considerably less than the product price. Estimating feasible yields in a manner similar to Straathof (2014), the theoretical molar yields are all considered to be 1 mol product per 1 mol sugar, except for specific instances for fermentation technology where the microorganism has demonstrated the ability to produce 2 mols of product per mol of glucose (i.e. conversion of glucose to ethanol with *Z. mobilis* which demonstrates). Conversion pathways examined include catalytic conversion in addition to fermentation technology.

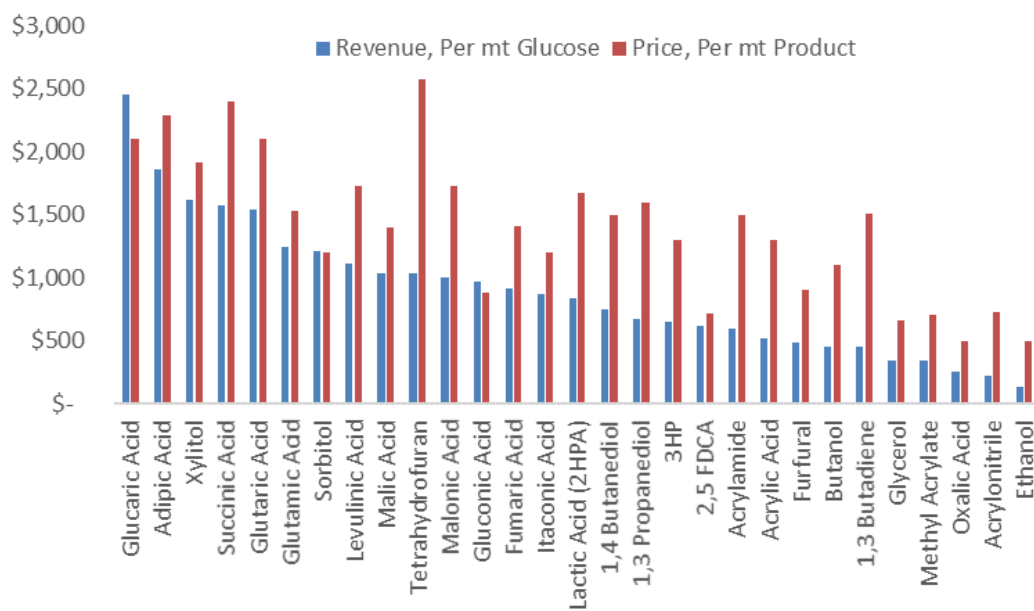


Figure 7-3- Prioritization of Bio-Chemicals Based on Revenue Received per MT Glucose

Next, conversion technologies and best yields reported in the literature were collected and analyzed for the selected bio-chemicals, and the prioritization method was repeated using these reported values. The challenge presented with gathering this data is reflected in the manner with which different researchers from different scientific fields choose to report their results. The results can either be reported in final concentration (g/L), mass yield (g/g substrate) or molar yield (mol/mol substrate). In many cases, the specific definition of yield is not defined by the authors. With little doubt, the lack of reporting consistency combined with the magnitude of recently published literature regarding bio-chemical conversion technology continues to frustrate decision making efforts by firm management and industry stakeholders interested in commercializing new product technology. It is suggested that this underscores

the need for a simple and consistent prioritization metric for allocating resources in the early stages of new product development.

As shown in Table 7-2, the prioritization method was repeated using reported literature values, and while the rank order is different, the results are similar in that higher molecular weight, oxygenated carboxylic acids are prioritized above alcohols and lower molecular weight and less oxygenated compounds. In several cases, such as succinic acid, fermentation technology has advanced enabling molar yields as high as 1.5 mol product per mol glucose (Song & Lee 2006). It is suggested that bio-chemical candidates demonstrating reported yields at or above their theoretical molar yields and calculated values above the raw material market price merit further study.

Next, the reported yields were used in order to determine the revenue received for converting 1 bdmt of mixed hardwoods to the final bio-chemical product in a manner similar to that reported by Sammons et al (2008). The approximate yield for converting the biomass to lignocellulosic sugars was multiplied by the reported yields for converting glucose to the respective bio-chemical product to give an overall process yield. An assumed yield of 0.34 bdmt glucose and 0.12 bdmt xylose per bdmt mixed hardwoods was used (i.e. approximately 80% recovery of the southern hardwood glucan and xylan content reported by Tunc & van Heiningen, 2008), and since a majority of the literature reviewed only reported bio-chemical conversion yields for glucose, a 75% conversion efficiency is assumed for converting the xylose. It is understood that this is a generous assumption that must be investigated further, and that in many cases, any conversion of the xylose may not be technically feasible. For instance, sorbitol cannot be catalytically converted from xylose in a single process step. The

authors have accounted for this with the dilute acid and metal oxide catalytic conversion schemes and have not included the conversion of xylose into the value of the converted mixed hardwoods.

As seen in Figure 7-4 and Figure 7-5, a side by side comparison exhibits good agreement between the bio-chemicals ranked according to theoretical molar yields and reported yields ($R^2 = 0.42$). Again, these results depict the revenue received for converting a unit of mixed hardwoods (in this case, 1 bone-dry metric ton) to a specific chemical. With a few exceptions, higher molecular weight and oxygen content molecules are commiserate with higher converted revenue for the biomass, or mixed hardwoods ($R^2 = 0.28$ and $R^2 = 0.15$, respectively). This suggests that previous criteria set forth in the literature (Dale 2003, Kajaste 2014) with respect to maintaining the oxygen content of the sugar through bio-chemical conversion to a final product is critical to providing increased functionality and improving financial performance.

Table 7-2: Prioritization of Bio-Chemicals Based on Revenue Received per MT Glucose

Rank	Compound	Theoretical Yield (g/g)*	Reported Yield (g/g)	Apprx. Market Volume (MMmt)	Reference	Price, Per mt Product	Revenue, Per mt Glucose
1	Succinic Acid	0.7	1.1	0.03 - 2.5	Song & Lee, 2005	\$2,400	\$2,640
2	Glutaric Acid	0.7	0.9	0	Paris et al, 1963	\$2,107	\$1,832
3	Xylitol	0.8	0.9	0.125 - 0.5	Granstrom et al, 2007	\$1,913	\$1,626
4	Lactic Acid (2HPA)	0.5	0.9	0.48 - 1.07	Wang et al, 2011	\$1,672	\$1,555
5	Tetrahydrofuran	0.4	0.6	0.15 - 2.4	Lee & Baek, 2008	\$2,571	\$1,471
6	Adipic Acid	0.8	0.6	2.5	Boussie et al, 2014	\$2,289	\$1,325
7	Glucaric Acid	1.2	0.6	0 - 4.75	Kiely & Hash,2010	\$2,100	\$1,260
8	Levulinic Acid	0.6	0.7	0.02	Hayes et al 2008 (BioFine)	\$1,729	\$1,238
9	Sorbitol	1.0	1.0	1.8 - 2.3	Ullmann's	\$1,200	\$1,212
10	Fumaric Acid	0.6	0.8	0.23 - 0.346	Zhang et al, 2012	\$1,410	\$1,100
11	1,4 Butanediol	0.5	0.7	2 - 2.5	Yim et al 2011	\$1,493	\$1,067
12	Acrylic Acid	0.4	0.8	1 - 4.5	Lange et al, 2014	\$1,300	\$1,040
13	Gluconic Acid	1.1	1.1	0.06	Biella et al, 2001	\$885	\$964
14	1,3 Propanediol	0.4	0.5	0.12	Nakamura & Whited, 2003	\$1,600	\$816
15	Itaconic Acid	0.7	0.6	0.005 - 0.01	Liao et al, 2010	\$1,200	\$732
16	Malic Acid	0.7	0.5	0.09 - 0.147	Zhang et al, 2011	\$1,393	\$655
17	Glutamic Acid	0.8	0.4	1	Delaunay et al, 1999	\$1,527	\$603
18	2,5 FDCA	0.9	0.8	2.2	*Yi et al, 2015	\$713	\$571
19	Methyl Acrylate	0.5	0.8	0.4 - 0.5	Ullmann's	\$702	\$545
20	Oxalic Acid	0.5	1.0	0.19	Ullmann's	\$500	\$487
21	Furfural	0.5	0.6	0.8	Ullman's	\$900	\$576

Table 7-2: Continued

Rank	Compound	Theoretical Yield (g/g)*	Reported Yield (g/g)	Apprx. Market Volume (MMmt)	Reference	Price, Per mt Product	Revenue, Per mt Glucose
22	Malonic Acid	0.6	0.3	0.016 - 0.02	Gokarn et al, 2007	\$1,728	\$459
23	Glycerol	0.5	0.7	2 - 3.1	Wang et al, 2001	\$664	\$432
24	Butanol	0.4	0.3	3.6 - 9	Ullmann's	\$1,100	\$363
25	3HP	0.5	0.2	0 - 4.5	Kumar et al, 2013	\$1,300	\$299
26	1,3 Butadiene	0.3	0.2	10.5	Baek et al, 2014	\$1,506	\$262
27	Ethanol	0.3	0.5	38.5 - 41	Humbird et al, 2010	\$499	\$254
28	Acrylamide	0.4	0.02	0.16 - 0.25	Kang et al 2014	\$1,500	\$24
29	Acrylonitrile	0.3	0.02	5.9 - 6.7	Le Notre et al 2011	\$731	\$12

*Theoretical yields assume 1 mol product per mol glucose and are not the maximum feasible yield. In many cases, research has shown that reported yields exceed the authors' definition of "theoretical yield"; particularly for technologies that employ anaerobic fermentation.

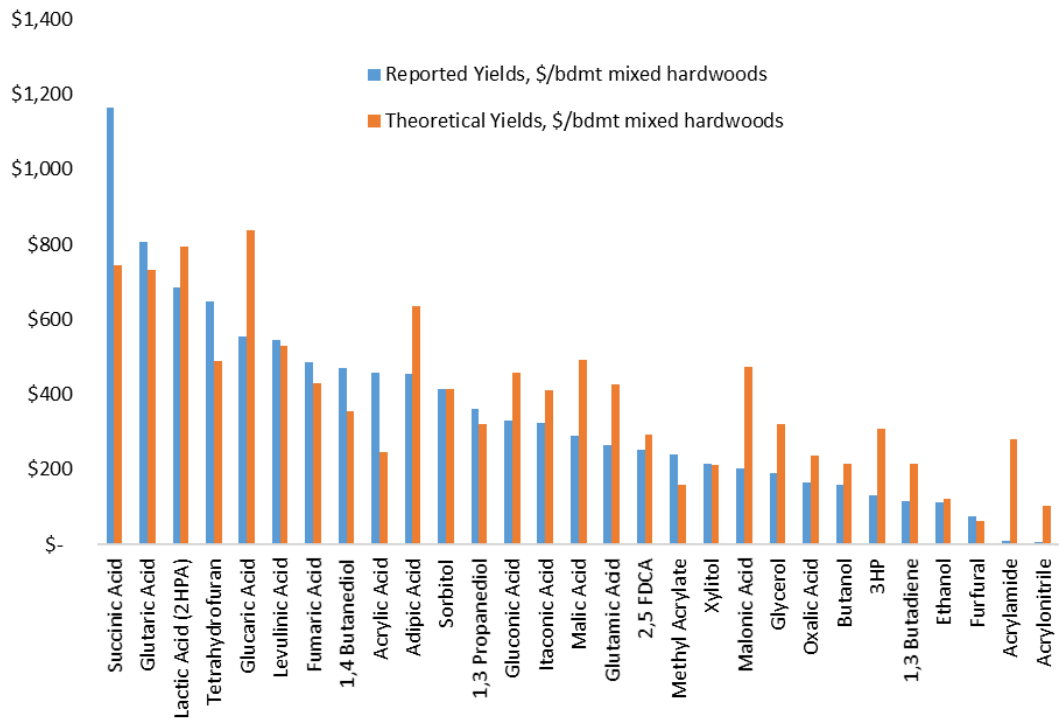


Figure 7-4: Prioritization of Bio-Chemicals Based on 1 BDMT Mixed Hardwoods.

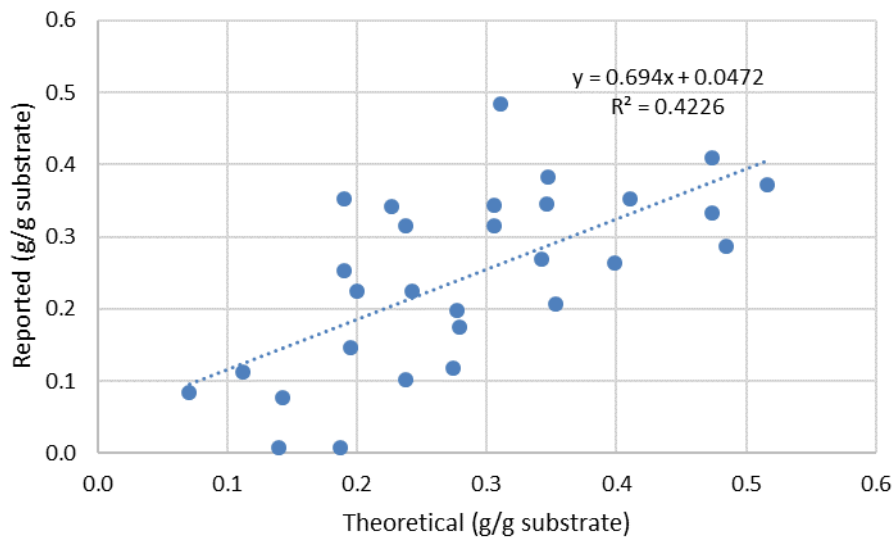


Figure 7-5: Correlation between Reported and Theoretical Molar Yields

7.5 Discussion

Cooper et al (1997) discuss the importance of project “funneling” with respect to new product development. Specifically, the concept of prioritizing projects for new product development is not a simple exercise of choosing one project as a clear, definitive winner of the firm’s commercialization resources. Instead, the techniques employed by firm management with respect to new product portfolio management serves as a form a triage for scarce funding. As the author’s concluded, many firms discovered that projects regarded as seemingly less successful or apart from the firm’s core business often consumed an excess or majority of exploratory research and development resources, and in an attempt to mitigate waste, firm management constantly employ a scoring based model and prioritization metric in choosing which projects to investigate further. Furthermore, it is understood that even before research and development resources are allocated, the activity of managing the new product portfolio itself is a costly use of firm resources. For this reason, the prioritization method presented in this work is intended to serve as a starting discussion for decision making and further investigation. As Bozell & Petersen (2010) suggest, the decision to proceed with commercialization of any bio-based product is ultimately a decision based on the product’s fit within the firm’s business plan, final product cost and purity, justification of the required capital investment, and market needs.

7.5.1 Succinic Acid Product Family

Succinic acid serves as a “platform” chemical in that it can be used as an intermediate for the production of tetrahydrofuran (THF), 1,4 butanediol (1,4 BDO) and glutaric acid (Jang et al 2012, Bozell & Petersen 2010, Gallezot 2012, Werpy et al 2004). 1,4 BDO in particular

is an attractive intermediate molecule with an established market for the production of commercially relevant engineered polymers and polyesters (Haas et al 2005, Sauer et al 2008, Bechtold et al 2008). Song & Lee (2005) provide a comprehensive overview of succinic acid production performance characteristics for a variety of engineered microorganisms. In general, yields between 0.86 to 1.10 g succinic acid per g glucose were reported, with concentrations from 24 to 105 g per L.

A. succinogenes, *E. coli* and *M. succiniciproducens* were noted by Song & Lee (2005) as being the best candidates for succinic acid production. Developed from bovine rumen, *M. succiniciproducens* is likely the most desirable microorganism for the fermentation of lignocellulosic sugars with high yields and high productivity reported in the literature. Kim et al (2004) observed that it utilizes xylose more efficiently than other bacterium and suggested using it for the fermentation of untreated wood hydrolysate to reduce commercial succinic acid production feedstock costs. *M. succiniciproducens* produces succinic acid from a variety of sugars under CO₂ conditions at a pH of 6 to 7.5, with productivity reported as high as 3.9 g/L-h (Lee et al 2003). Major by-products include acetic and formic acids. It is also a capnophilic bacterium (CO₂ loving) and it was predicted that a succinic acid yield of 1.71 mol per mol glucose could be achieved under an enriched CO₂ environment, while 1.86 mol succinic acid is capable with CO₂-H₂ gas mixture (Hong et al 2004). While promising, the increased succinic acid yields from using enriched gases also leads to increased major by-products (mixed acids) which must be separated and purified, further complicating the process design and increasing costs (Zeikus et al 1999, .

1,4 BDO can be produced via aqueous phase hydrogenation of succinic acid and Minh et al (2010) reported that a 15 wt% solution of succinic acid could be easily converted to 1,4 BDO using bimetallic catalysts to achieve a 65% mass yield. This single, subsequent process step requires additional hydrogen gas and the reaction demonstrates good selectivity. By-products predominantly include gamma-butyrolactone which can be separated and further converted into value-added products such as glutaric acid. Glutaric acid can be prepared by ring opening of gamma-butyrolactone (Paris et al 1963). However, it requires 1 mol potassium cyanide to achieve a yield of 1.28 g per g gamma-butyrolactone. The patent by Lee & Baek (2008) describes catalytic dehydration of 1,4-butanediol to produce THF, whereby a reactive distillation scheme allows for the recovery and recycle of unreacted 1,4 BDO such that the molar yield is 1 mol THF per mol 1,4 BDO. Alternatively, Yim et al (2011) utilized engineered *E. coli* for the direct production of 1,4 BDO from glucose, achieving final concentration up to 18 g per L for a variety of substrates, including lignocellulosic sugars. However, the maximum theoretical yield was determined to be 0.37 g 1,4 BDO per g glucose. Again, yield is of particular importance since conventional fossil fuel based routes typically feature 85-90% yields from either BTX or C2 & C3 olefins from liquid natural gas (Haas et al 2005).

Several companies have made recent attempts towards commercializing succinic acid production from bio-sugars. Most notably, BioAmber has begun production at its commercial plant located in Sarnia, ON, with a nameplate capacity of 30,000 mt per year. The company even announced off-take and equity participation from its supply chain partner, Vinmar, towards the production of bio-based butanediol (Baker 2016). Similarly, Myriant Corporation started its 10,000 mt/yr succinic acid plant in 2013 at Lake Providence, LA (Myriant 2013).

7.5.2 3-Hydroxypropionic Acid (3HP) Product Family

Another promising bio-chemical include 3-hydroxypropionic acid (3HP) that can be readily converted into a family of products, including malonic acid, 1,3 propanediol (1,3 PDO), acrylic acid and methyl acrylate (Kumar et al 2013). It can be fermented from both glucose and glycerol by a variety of microorganisms Molar yields for a glycerol substrate range from 0.35 to 0.55 mol/mol with varying low concentrations and selectivity. A major byproduct with fermentation, however, is another value-added bio-chemical intermediate, 1,3 PDO, with overall yields in excess of 80%. Molar yields for glucose were reported to be as high as 0.46 mol/mol when using engineered *E. coli*. More recent work in metabolic engineering for microorganisms that produce 3HP and 1,3 PDO has strived to enhance propionic acid tolerance which is acutely toxic to the microorganism, thereby driving costs such as cell culture and distillation due to low concentrations significantly (Zhang & Yang 2009, Nakamura & Whited 2003, Xiu et al 2008). Zhou et al (2013) used engineered *P. denitrificans* and *K. pneumoniae* in order to achieve yields between 0.62-0.67 mol 3-HP per mol glycerol substrate, respectively. Additionally, several recently published patents report high efficiencies and selectivity for the production of 3HP using “resistant modified” microorganisms (Horikawa et al 2013, Lynch et al 2011, Zhang et al 2011).

More Specifically, 1,3 PDO is conventionally produced via fermentation of glycerol using *Clostridium butyricum*, exhibiting a yield of 0.65 g per g glycerol substrate (Biebl et al 1999, Gonzalez-Pajuelo et al 2005). Nakamura & Whited (2003) reported a yield of 0.51 g 1,3 PDO per g glucose when using metabolically engineered *E. coli*, but again the final concentrations in the fermentation titer are low. As mentioned previously, 1,3 PDO is an

attractive intermediate for the production of polyesters and other high value, engineered polymers. It is worth noting that 1,3 PDO is one of the few bio-based chemicals that is successfully produced in commercial quantities by DuPont-Tate and Lyle under the “Susterra” brand (DuPont 2006).

As for the production of glycerol from sugar (since 1,3 PDO and 3HP are produced more efficiently using glycerol as a substrate), glycerol can be produced from *S. cerevisiae* via a sulfite or alkaline process which retards the co-production of ethanol and improves selectivity (Wang et al 2001). The typical reported mass yield is around 25%, but osmotolerant yeasts such as *Z. acidifaciens* can suggest mass yields in excess of 65% (or 0.65 g glycerol per g sugar) can be achieved. While this is a significant improvement towards the production of glycerol from biomass, it is important to note that glycerol production from fossil fuels (a diesel by-product) is considered more economical. That being said, this fermentation technology and process routes described in the literature will likely benefit from the option of being able to choose between one feedstock or the other depending on raw material prices.

While it has been suggested that acrylic acid could be prepared from 3HP, recent research and patent literature suggest alternate routes for greater mass efficiency. The Shell oil patent by Lange (2014) can reportedly produce acrylic acid from any C3-oxygenate using catalytic dehydrogenation to produce propanoic acid as an intermediate. This proposed bio-based route is a four step process that produces acrylic acid from glucose and boasts a mass efficiency (defined as total mass of produce over total mass of feed, including other reactants such as methane) and effectively yields 2 mols acrylic acid per mol glucose. Propanoic acid is a minor product from conversion of 1,3 PDO with selectivity reported elsewhere of only

18% with 100% conversion of the 1,3 PDO (Sato et al 2008). The balance is propanal which may serve as a viable feed for Lange's process. This implies that 1 mol of acrylic acid can be produced per mol of 1,3 PDO or 3HP such that the yields for those compounds are the overall process limiting factor and cost driver. A techno-economic analysis by Straathof et al (2005) confirmed that the 2 mols acrylic acid per mol glucose, regardless of the conversion route, is an important performance benchmark required for process economic feasibility, and the authors reported an attractive 34% internal rate of return (IRR) provided that this maximum theoretical yield can be achieved.

Provided that the production of acrylic acid from 1,3 PDO or 3HP is technically feasible, other downstream markets for acrylate esters can be made available with the additional of a primary alcohol. For example, methyl acrylate can be readily prepared from acrylic acid at near 100% yield by the addition of methanol (Ullman's). Other value added chemicals from 3HP include malonic acid, which can be obtained by catalytic oxidation of 3HP for 100% molar yields (Gokarn et al 2007).

7.5.3 Glutamic Acid for Acrylamide Production

It is possible to produce acrylonitrile, the principle component for ABS (acrylonitrile-butadiene-styrene) resins and nitrile rubbers, from glutamic acid, a commercially manufactured amino acid. Le Notre et al (2011) reported the production of acrylonitrile via a two-step reaction scheme which produces 3-cyanopropanoic acid via oxidative decarboxylation of glutamic acid using sodium bromide and sodium hypochlorite. The molar yield for the first step was reported as 70% (or 0.7 mol/mol) which is then followed by a subsequent palladium catalyzed decarbonylation elimination reaction step to produce

acrylonitrile with a 17% molar yield. An overall effective 12% molar yield on glutamic acid was reported, corresponding to a mass yield of only 0.04 g acrylonitrile per g glutamic acid. Certainly, significant work is needed to improve the yield and selectivity for this reaction scheme in order for the bio-based production of acrylonitrile to be considered financially feasible.

However, the efficient production of bio-based acrylonitrile would allow for the production of bio-based acrylamide. Since the amidation of acrylic acid is considered too difficult or impractical, the conventional fossil fuel route for acrylamide is through acid catalysis of acrylonitrile (Ullmann's). Today, copper catalysts are used and conversion yields greater than 50% are achievable with minimal waste generation. However, the catalyst poisoning and shortened catalyst life are significant cost drivers for acrylamide production. As an alternative, bio-catalysts such as the enzyme N. hydratase are becoming a more attractive reagent for this process, whereby acrylamide can be produced from acrylonitrile with 93% mass yields (Kang et al 2014).

Glutamic acid and lysine are bulk amino acid products that have been produced commercially since the 1950's with *C. glutamicum*, with the main application as a food additive (Hermann et al 2003). Recent advances in metabolic engineering have significantly improved product yields on glucose (Kalinowski et al 2003). Delaunay et al (1999), used recombinant *C. glutamicum* to produce 85 g glutamate from 215 g glucose (or 0.4 g per g glucose). This was largely attributed to an over expression of phosphoenolpyruvate carboxylase (PEPc) and pyruvate carboxylase (Pc) in the microorganism. Furthermore, Peters-Wendisch et al (2001) demonstrated that pyruvate carboxylase (Pc) is a significant bottleneck

for the production of glutamic acid and lysine, and it was shown that overexpressing this enzyme allowed for over five-fold increase in glutamate yield. This suggests that recent advances in metabolic engineering could dramatically increase yield and lower production costs for glutamic acid, increasing its financial viability as a bio-chemical intermediate.

7.5.4 Lactic Acid

Successfully commercialized in the late 1990s and early 2000s by the Cargill and Dow joint venture now known as “Natureworks”, lactic acid is easily the most established non-fuel bio-chemical, which, along with bio-based glycerol from seed oils, accounts for nearly 80% of the global bio-chemicals market (Patel et al 2005). Wang et al 2011 reported mass yields as high as 0.93 g lactic acid per g glucose when using peanut meal as a nutrient for *Sporolactobacillus*. However, Abdel-Rahman et al (2011) were careful to point out the challenges of producing lactic acid from lignocellulosic sugars, which is significantly inhibited by the formation of by-products due to heterofermentation of pentose sugars and the carbon catabolite repression caused by the heterogeneity of the hydrolysate-sugar composition. While hexose (or glucose) sugars are easily fermented, the selectivity of lactic acid from pentose sugars (or xylose) is significantly lower with equimolar amounts of lactic acid and acetic acid produced, ultimately increasing the costs of separation and purification. Two approaches towards addressing the issues that arise with composition heterogeneity are to either metabolically engineer the microorganism to co-ferment C5 & C6 sugars with little by-product formation, or use mixed cultures (“engineered microorganism consortia”) of different microorganisms that are optimized to ferment C5 or C6 sugars, respectively (Brenner et al 2008, Okano et al 2010). Finally, the experience and techniques developed for addressing this

issue with optimization of lactic acid production from lignocellulosic sugars may be applied to other fermentation technology as well.

7.5.5 Fuel & Sugar Alcohols

Xylitol and sorbitol have well established markets as food additives, functioning as artificial sweeteners and moisture stabilizers, and both are conventionally produced via catalytic dehydrogenation of their respective pre-cursor sugars, xylose and glucose, in the presence of a Raney nickel catalyst with typical mass yields in the range of 50-60% or higher depending on the starting purity of the sugar or molasses stream (Ullmann's). Recently, xylitol production by fermentation has come of interest due to the high yields associated with metabolically engineered *S. cerevisiae* and *Candida* which have both been shown to produce xylitol from both glucose and xylose (Cirino et al 2006). Granstrom et al (2007) reported yields as high as 0.85 g xylitol per g glucose and went on to suggest that higher yields and productivity could lower the production cost of xylitol significantly below conventional methods. However, the only additional use suggested for xylitol was as a raw material for the production of rare sugars such as xylulose, ribulose, arabinose and other rare sugars which may have some use in bio-medical research and applications.

Ethanol and butanol remain promising fuel alcohols for the future, and in addition to fuel use, applications such as dehydration of ethanol to produce ethylene glycol or acid catalysis of n-butanol to produce butyl acetate are of commercial interest (Nelson et al 2010, Tao & Aden 2009, Patel 2005, Shen et al 2009). *Z. mobilis* allows for the production of 2 mols ethanol per mol glucose and 5 mols ethanol per mol xylose (Humbird et al 2011). Butanol production can be high as 0.33 g per g glucose, and even with the low selectivity demonstrated

by Clostridia microorganisms, the value-added fermentation byproducts include acetone and ethanol (Ullmann's). However, even with the demonstrated high fermentation yields, the cost of purifying and distilling the fuel remains a significant expense considering the large scale of many proposed ethanol and butanol plants, and provided that fuel value is effectively the lowest possible value allocated to the product, it's not surprising that many firms are shifting towards the conversion of these alcohols to value-added bio-chemicals for the near future.

7.5.6 Other Dicarboxylic & Carboxylic Acids

Levulinic acid was a promising platform bio-chemical for converting biomass, specifically, to value added chemicals. It can be readily converted to a variety of solvents, plasticizers and polyols via dilute sulfuric acid hydrolysis of the biomass. Hayes et al (2006) reported yields from the "BioFine" process of 0.716 g levulinic acid per g hexose with the remaining by-product as formic acid. However, the relative severity of the process conditions, requiring low pH and high temperature, leads to excess corrosion of the process equipment, thereby increasing costs and frustrating the commercialization efforts.

Glucaric acid serves as a promising replacement for phosphate detergents, which are increasingly banned due to its problems associated with eutrophication. Kiely & Hash (2010) reported in their patent the use of nitric acid oxidation to oxidize glucose and xylose to alderic acids glucaric acid and xylaric acid. Their novel method appears to have higher selectivity and yields compared to other methods for producing alderic acids, primarily due to the oxidation in a closed reactor under milder conditions where nitric acid is fully recovered by distillation and reused. Glucaric acid mass yields using the methods described were from 30% to 60% (as g glucaric acid per g glucose). Xylaric acid mass yields were closer to 83% on the xylose

substrate. Boussie et al (2014) hold a similar patent that covers the hydrodeoxygenation of glucose to glucaric acid using solid catalysts, without the need for nitric acid. Additionally, this patent covers further deoxygenation steps to produce adipic acid (a major precursor to nylon 6,6 production), with mass yields as high as 0.579 g adipic acid per g glucose reported. This is significantly higher than fermentation and catalytic conversion routes reported in the literature where adipic acid is produced via a muconic acid intermediate at yields of 0.181 g per g glucose and a theoretical max of only 0.34 g per g glucose (Niu et al 2002). Of important note, the glucaric acid product intended for detergent applications can be separated and sold as a mono or disodium glucarate salt which must be further crystallized and purified. This implies that unlike other dicarboxylic applications targeting polymers, the purification of the product to its acid form via ion exchange or electro-dialysis is not necessary which could dramatically reduce the operating costs and capital investment required for manufacture. Glucaric acid produced via fermentation exhibits significantly lower yields (Moon et al 2010).

Gluconic acid is an attractive industrial cleaner and sizing agent and is readily produced from glucose via catalytic oxidation. Biella et al (2002) reported high selectivity and yields approaching 100% conversion of glucose to gluconic acid with gold and palladium catalysts. However, the most important observations with respect to the catalytic reaction include a rapid decrease in activity of the catalyst from its initial levels (a decline that cannot be completely reversed despite efforts at reactivation), the need for highly purified glucose solutions, and the formation of various byproducts as a result of insufficient catalyst specificity and the tendency of the substrate to undergo side reactions under the prevailing reaction conditions. The economic viability of the process depends largely on the activity, selectivity, lifetime, and cost

of the catalyst, as well as on the measures required for product purification and the energy demands (Ullmann's). Furthermore, the inherent impurities associated with the heterogeneous composition of lignocellulosic sugars may preclude biomass such as mixed hardwoods from commercialization.

Fumaric acid is another important intermediate that could be used for the production of polyols and polyesters, and it is primarily used as a food plasticizer and acidulant. A Thyssenkrup Uhde GmbH patent by Adreas et al (2013) reported efficient production of fumaric acid using yeast to obtain a yield of 48.5 g fumaric acid per 40 - 60 g glucose with +80% selectivity at a pH 5.5 – 7. This is considerably higher than values reported elsewhere in the literature and approaches the theoretical limit (Gu et al 2013, Zhang et al 2012). The difficulties with achieving high fumaric acid yield is due the co-production of byproducts like ethanol. An important and successful lesson with respect to metabolic engineering of microorganism for high yield dicarboxylic acid production was reported by Zhang et al (2012). In their work, the authors overexpress endogenous pyruvate carboxylase (PYC) and exogenous phosphoenolpyruvate carboxylase (PEPC) to increase carbon flux toward oxaloacetate, instead of acetaldehyde, which is the preferred pathway for ethanol production. The result was an increase in fumaric yield from 0.62 g fumaric acid per g glucose for the wild type to 0.78 g/g with the PEPC transformant. The pyruvate pathway to oxaloacetate yields malate and then fumarate whereas the pyruvate pathway to acetaldehyde yields ethanol (Kenealy et al 1986).

2,5 furandicarboxylic acid (2,5 FDCA) has been explored as a replacement for terephthalic acid, which is a major chemical intermediate for the production of many engineered and commodity polymers such as polyethylene terephthalate (PET) and Lycra. Yi

et al (2015) reported the direct conversion of fructose and glucose in a triphasic system in order to achieve 78% and 50% mass yields, respectively, 5-hydroxymethylfurfural (5-HMF) as an intermediate. It is proposed that the triphasic system will allow for a “one-pot” production step potentially reducing capital costs dramatically. Similarly, selective aerobic oxidation of HMF using platinum and metal oxide catalysts results can achieve 99% molar yield of 2,5 FDCA (Ait-Rass et al 2015), and 5-HMF can be prepared from glucose in an aqueous medium with indium trichloride as a catalyst resulting in a 79% molar yield with levulinic acid as a by-product (Shen et al 2014). Alternatively, 5-HMF can be prepared from glucose at nearly 100% molar yields with ionic liquids as the solvent system (Hu et al 2012, Chidambaram & Bell 2010, Zakrzewska et al 2010, Tong et al 2010, Thananattachon et al 2010).

Finally, several patents exist for the efficient fermentation of glucose and lignocellulosic sugars to produce itaconic acid, with yields as high as 0.61 g per g glucose reported (Liao & Chang 2010). Itaconic is another important precursor to the production of high-value synthetic rubbers and carbon fibers. It can also be used in a variety of coating applications (Ullmann's).

7.5.7 Butadiene

As shown in Figure 7-6, the market for butadiene is perhaps the most volatile of the bio-chemicals examined. This is predominantly due to the fact that 70% of the global demand is fulfilled by natural rubber (or latex) grown in southeast Asia, where due to a lack of government consortia and farmer subsidies the supply from the region is difficult to forecast and manage. While the price of rubber in 2015 has decreased to approximately \$1300 to \$1600 per mt, it is worth noting that a global supply shortfall of only 2% - 5% (or 180,000 mt) natural

rubber in 2010 and 2011 is responsible for past price peaks above \$6000 per mt (International Rubber Study Group 2011). Global consumption of rubber and butadiene is in excess of 10 million mt and growing, making bio-chemical based butadiene an attractive opportunity.

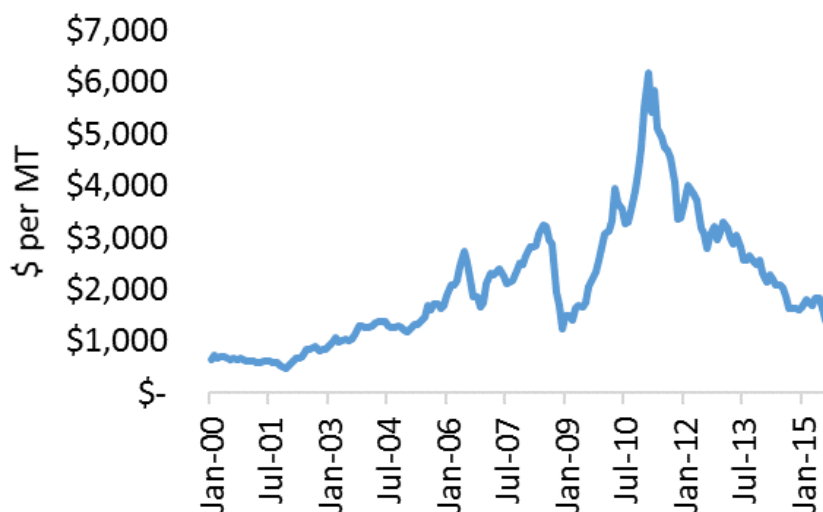


Figure 7-6: Price History for Rubber Smoke Sheet #3 (RSS3)

Butadiene can be produced via esterification and pyrolysis of 2,3 butanediol, or 2,3 BDO (Othmer et al 1954, Schlecter et al 1945). Before steam cracking of petroleum distillates was discovered to produce butadiene, this alternative bio-based chemical conversion route was pursued, using fermentation of glucose to produce 2,3 BDO, during World War II when natural rubber supplies in the Pacific and southeast Asia were constrained. Ultimately, the research and development towards producing butadiene from 2,3 BDO was abandoned due to the consumption of 1 mol acetic acid per mol butadiene during pyrolysis preventing the process from being economical viable (Xiu et al 2008). Recent work by Baek et al (2014) reported

that butadiene can be produced from the 2,3 BDO intermediary at 70% yield with 100% recovery of acetic acid with only loss of formic acid which can be compensated for as a by-product acid present in the fermentation liquor. Other recent work has shown efficient production of 2,3 BDO by *S. cerevisiae* with yields approaching 0.3 g per g glucose at high titer final concentrations (Kim et al 2013, Nan et al 2014). More importantly, efficient conversion of cellobiose has demonstrated which may serve to dramatically reduce enzyme costs associated with converting pre-treated biomass to monomeric sugars.

7.5.8 Prioritization of Bio-Chemical Products & Target Markets for the Pulp & Paper Industry

As mentioned previously (and shown in Figure 7-1), the stability of prices in North America has made mixed hardwoods an attractive 2nd generation feedstock. There are also many potential opportunities to significantly reduce the cost of bio-refineries by “co-locating” bio-chemical conversion plants to existing pulp and paper mill infrastructure (Stuart et al 2012, Zondervan et al 2011). More specifically, opportunities for reduced capital expenses can be realized by using areas of the mill that are under-utilized due to closure of pulp machine, such as the woodyard for biomass processing, hot water pre-hydrolysis (or Kamyr) reactors for pretreatment, and existing water and wastewater treatment facilities (Phillips et al 2013).

Based on the analysis presented in this work, technologies that target the succinic acid product family are attractive candidates for further commercialization. Succinic acid, THF, glutaric acid and 1,4 BDO are each in the top 8 in order of maximum value potential for converted mixed hardwoods. Glucaric acid is another strong candidate due to the attractive

value proposition presented for the sizable detergent industry and ability to sell the product in its alderate salt form.

The next most attractive opportunities for commercialization include the 3HP product family, with the promise of manufacturing bio-based 1,3 PDO (from lignocellulosic sugars, specifically) and acrylic acid which each have high value engineered polymer markets. 2,5 FDCA also demonstrate the potential for strong value as a replacement for major intermediate chemicals such as terephthalic acid used in commodity polymers.

Butadiene was shown to have a converted revenue of \$112 just barely above the assumed transfer price of \$70 per bdmt mixed hardwoods, and while this is not as attractive at first thought when compared to the other bio-chemicals such as dicarboxylic acids, it is important to note that the price assumed in this work reflects historically low prices for rubber products. Bio-based butadiene would also serve the 2nd largest chemical market in terms of volume for the bio-chemicals analyzed. This, coupled with the historical volatility for the market and average 10-year prices over \$2700 per mt RSS3, makes butadiene a promising long-term commercialization project. With a price of \$2700, the calculated revenue using yields reported in the literature would be \$207 per bdmt of mixed hardwoods, and a record high price of \$6500 translates to \$500 per bdmt of mixed hardwoods.

The only two bio-chemicals not meeting the benchmark cut-off of \$70 per bdmt of mixed hardwoods were acrylonitrile and acrylamide. At this time, the yields reported by Le Notre et al (2011) are excessively low (less than 1/10th of their theoretical yields) in comparison to other candidates. This suggests that efforts to produce bio-based acrylonitrile and acrylamides would require significant early-stage or exploratory research and development

resources in order to improve the yields of the decarboxylation and decarbonylation reaction schemes. However, the pursuit may be warranted with recent advances in catalyst synthesis and large target markets (approximately 6 million mt annually for acrylonitrile).

7.6 Conclusions

Forest product industry management interested in exploring new and disruptive technologies in the emerging bio-fuels and bio-chemicals industry may desire a simple model, or new product development (NPD) tool, for screening commercially relevant opportunities. In this work, a product yield and price-driven calculation was employed in order to screen a list of relevant bio-chemical conversion technologies. In the early stages of research, commercially relevant yields are largely unknown, therefore, this study employs a molecule economy of 1 to 1 as a starting point. These theoretical yield assumptions are then compared against actual yields reported in the literature (Figure 7-4 and Figure 7-5). Since there is a positive linear correlation ($R^2 = 0.42$), the authors suggest this model as a starting point for NPD management. It is suggested that the “theoretical yield” approach can be considered in minutes, whereas the gathering of technical (and often proprietary) laboratory data can require hundreds of hours and considerable resources.

Bio-chemicals with potential revenue received for converting one unit of biomass that are less than the market price of the raw material (assumed \$70 per bdmt for mixed hardwoods) can be removed from immediate consideration until the market price for the raw material plummets, the value of a specific chemical increases considerably, or microorganism or catalyst technology advances to allow an effective yield to approach or achieve the maximum theoretical yield. Fermentation technology for the efficient production of succinic acid was

determined to be the most promising of bio-chemical candidates for commercialization over the short-term. This is due to high level of demonstrated yields in the literature, value-added functionality of the dicarboxylic acid and versatility of succinic acid product family to fulfill market needs in a variety of high-value intermediate chemical applications. Significant costs associated with the production of succinic acid include the microorganism culture and the downstream costs associated with separation and purification since the product cannot be sold or utilized in its salt-succinate form.

8 TECHNO-ECONOMIC ANALYSIS OF SUCCINIC ACID PRODUCTION FROM A FOREST PRODUCTS BIO-REFINERY

8.1 Abstract

This study explores the technical and economic feasibility of succinic acid production from the fermentation of lignocellulosic sugars, produced in a “biorefinery”. Specifically, the proposed value proposition for biorefining in the pulp and paper industry was based on three assumptions: first, that existing assets may be used in order to reduce the required capital investment, second, that the biomass utilized in the process is cost-advantaged to current commodity, or “1st generation”, food-based sugars, and third, that there may be opportunities for variable and fixed cost reduction through economies of scale (e.g. shared labor, utilities, etc.). The scope of this analysis spanned the gate-to-gate production of succinic acid produced from wood chips, with mixed southern hardwood chips received and stored at the bio-refinery at a capacity of 500,000 “bone-dry” metric tons (bdmt) per year.

Using previously reported literature data and process modeling, this TEA study attempted to quantify the minimum product revenue (MPR), maximum transfer price (MTP) and incremental EBITDA for succinic acid with respect to multiple, feasible process case scenarios. For the case scenarios identified, succinic acid can be manufactured and sold to an open market, or exported directly to a known off-taker (e.g. towards 1,4 BDO production) with MPR as low as \$1,100/mt when assuming a co-location or repurpose scenario. When coupled with a greenfield 1,4 butanediol, none of the investment cases were determined to be economically feasible (at an assumed market price of \$2,000/mt BDO), although the additional free cash flow provided by a co-product from non-sugar process residue - phenolated lignin -

sales does result in 11% IRR. Integrated production of 1,4 butanediol and phenolated lignin when co-located with or repurposing a pulp mill resulted in 16% IRR-\$31 million NPV and 18% IRR-\$76 million NPV. MPR for 1,4 butanediol produced with these assumptions was less than \$1,900/mt, or below the assumed market price. The value of this study is in determining the key cost drivers for succinic acid production from lignocellulosic sugars that may be improved with further research.

8.2 Introduction

Succinic acid is a notable fermentation product that serves as a “platform” chemical in that it can be used as an intermediate for the production of tetrahydrofuran (THF), 1,4 butanediol (1,4 BDO) and glutaric acid (Jang et al 2012, Bozell & Petersen 2010, Gallezot 2012, Werpy et al 2004). 1,4 BDO in particular is an attractive intermediate molecule with an established market for the production of commercially relevant engineered polymers and polyesters (Haas et al 2005, Sauer et al 2008, Bechtold et al 2008). 1,4 BDO is currently produced via aqueous phase hydrogenation of succinic acid and Minh et al (2010) reported that a 15 wt% solution of succinic acid could be easily converted to 1,4 BDO using bimetallic catalysts to achieve a 65% mass yield. This single, subsequent process step requires additional hydrogen gas and the reaction demonstrates good selectivity.

To date, succinic acid has been produced from starch-based sugars, namely glucose. Several companies have made recent attempts towards commercializing succinic acid production. Most notably, BioAmber has a 2,000 ton per year demonstration facility in Pomacle, France and has recently begun production at its commercial plant located in Sarnia, ON, with a nameplate capacity of 30,000 tons per year (BioAmber 2014). The company even

announced off-take and equity participation from its supply chain partner, Vinmar, towards the production of bio-based 1,4 butanediol (Baker 2016).

Similarly, Myriant Corporation offers a fermentation technology platform capable of producing succinic acid, 1,4 butanediol, polybutylene succinate (PBS), tetrahydrofuran (THF), and phthalic anhydride (adipic acid substitute), and it started its 10,000 tons per year succinic acid plant in 2013 at Lake Providence, LA (Reuters 2014, BFD 2014, Myriant 2013). Succinity, a joint venture between Corbion Purac and BASF, recently began production at its commercial facility located in Montmelo, Spain with an annual capacity of 10,000 tons per year of bio-succinic acid (Succinity 2014, Progressive Media 2014). Reverdia is a joint venture between DSM and Roquette to produce bio-based succinic acid. Its first commercial facility, located in Spinola, Italy, was constructed in 2012 with an annual capacity of 10,000 tons per year. However, it is not clear whether or not Reverdia has successfully shipped any commercial quantities to its customers, although it plans to target the Chinese plastics market with PBS (Reverdia 2014).

Genomatica is a key technology provider for commercial succinic acid and has licensing agreements with BASF, Novamont, and Braskem. Genomatica first achieved commercial production at its demonstration facility in 2012 when it produced 5 million pounds of succinic acid in under 5 weeks (Genomatica 2014). The Novamont facility in Italy produces approximately 40 million pounds annually, and there are reported plans to expand with partners to construct facilities in North America greater than 100 million pounds annually. The joint venture agreement with Braskem allows exclusive license to use Genomatica technology in North America (Global Data 2014).

From the key players identified in the bio-succinic acid market, it is estimated that the current average annual production capacity in Europe and North America is approximately 40,000 to 70,000 tons per year, with planned production capacity expansions up to 150,000 tons per year by 2017. It is important to note that the apparent global market consumption of succinic acid is largely unknown, but potential market sizes may be estimated based on end-use applications for succinic acid. PBS for example is known to offer performance and product attributes comparable to premium polypropylene resins (Fujimaki 1998, Park et al 2010), with a global market volume in excess of 58 million tons per year. 1,4 BDO, potentially manufactured from succinic acid, is another commodity chemical, with an estimated total market volume of 2 million tons per year, used to make the chemical intermediate THF. 1,4 BDO is also used to make polyester polybutylene terephthalate (PBT) which is used to make plastics and fibers (e.g. Spandex).

The objective of this study is to explore the economic opportunity and feasibility of fermenting lignocellulosic, or “biorefinery”, sugars to succinic acid. As noted, current bio-succinic acid is manufactured from food-based sugars and it is assumed that the raw material price volatility of commodity sugar and starch may be cost-prohibitive over time. For example, an analysis of sugar futures (NYMEX, Sugar No.11) over the past 15 years exhibits an average sugar price of \$320/mt, with a standard deviation of \$140/mt, high of \$600/mt and an 80% probability of \$440/mt or less. By comparison, hardwoods exhibit an average price of \$70/bdmt, with a standard deviation of \$12/bdmt and an 80% probability of \$80/bdmt or less (RISI). Furthermore, production of sugars from sustainably managed North American wood offers additional economic potential from valuable co-products that can be upgraded (e.g.

phenolation of lignin residue) to high value products that cannot be achieved with the starch based approach to bio-refining. Therefore, it is desirable to explore opportunities in the forest products and pulp and paper industry whereby succinic acid can be produced from cost-advantaged feedstocks, with well-established supply chain infrastructure, in order to address the large potential market for this platform chemical. It is realistic to assume opportunities exist for reducing the capital investment required by co-locating with an existing pulp and paper mill. Especially, given the declining demand for production of communication papers, where more than 10 million tons of kraft pulp capacity has closed in the last 10 years (RISI, PPRC). Additionally, this work will explore subsequent conversion of succinic acid to the commodity chemical 1,4 BDO which is of equal interest in bio-chemicals production.

8.3 Methodology

8.3.1 Process & Financial Modeling

A technoeconomic model was constructed, according to spreadsheet methodology, based on material and energy balances for a defined process system boundary. First, a process flowsheet was built in order to identify all process flow inputs and outputs relevant to each major unit operation. For this work, it was necessary to model a conceptual bio-refining process that utilizes an auto-hydrolysis pretreatment of mixed southern hardwoods with subsequent biomass deconstruction via mechanical refining and enzymatic hydrolysis. The resulting product, mixed pentose (C5) and hexose (C6) “bio-sugars” from the lignocellulosic hydrolysate, is fermented to produce succinic acid, along with additional purification and hydrogenation to 1,4 butanediol.

Co-products from non-sugar process components comprise approximately 50% of the input biomass. Thus, additional processes, including biomass combustion, pelletization or phenolation of lignin, were modeled in order to valorize by-products from the process. The process unit operations described herein employ standard equipment and unit operations found in the pulp and paper and chemical process industries.

The model consists of mass transport equations that characterize and define the flow of process materials into and out of the system boundary. Pretreatment yields and carbohydrate recovery for biomass conversions (specifically, mixed hardwoods) are referenced from the literature. Common mass transport data for steam and process materials was used in order to determine the net energy consumptions for the process. Fermentation yields and productivity are also referenced from the literature; however, many assumptions were identified in the absence of detailed laboratory or process data.

Using data generated by the process model to construct a life cycle inventory (LCI), a financial model was constructed by determining the capital (CAPEX) and operational (OPEX) expenditures impact on total revenue generated for each scenario. Ultimately, the financial model calculated the free cash flows when considering a set of general assumptions.

8.3.2 Capital Expenditures (CAPEX)

Capital expenditures are the fixed costs associated with the equipment used in the process. All equipment costs have been estimated for year 2015 and scaled to process flows resulting from 500,000 “bone-dry” metric tons per year mixed hardwood chips consumption, accordingly. Storage tanks and heat exchanger costs were estimated using Best Professional

Judgement. Variation of the equipment cost is expressed by the following relationship (Ulrich 1984):

$$C_v = C_u \left(\frac{v}{u} \right)^a$$

Where “C_v” is the purchase price of equipment at a specific capacity represented by “v” and “C_u” is the equipment cost at capacity “u.” Since equipment costs scale disproportionately with size or capacity, the sizing exponent “a” is used for specific equipment.

Similarly, the cost of equipment purchased is adjusted for inflation to 2015 values using the following relationship (Ulrich 1984):

$$C_g = C_r \left(\frac{I_g}{I_r} \right)$$

Where “C_g” and “I_g” is the cost of equipment and indices in year “g”, and “C_r” and “I_r” is the cost of equipment and indices in year “r.” Marshall & Swift (Marshall & Swift 2015) was used to collect inflation indices respective of the chemical engineering industry. Equipment costs were gathered from the literature where available and individual price quotes were obtained from equipment manufacturers when needed (Phillips 2010, Peters et al 1968, Peters & Timmerhaus 2003, Pirraglia et al 2010, Couper et al 2009).

8.3.3 Operational Expenditures (OPEX)

Operational expenditures (OPEX) refer to the direct and indirect variable costs associated with biomass conversion and pulp mill production. Direct costs for the production of bio-sugars and succinic acid include hardwood chips, chemicals, enzymes, nutrients, finishing materials, power, and natural gas for steam production. Direct costs for the production of 1,4 butanediol include hydrogen, catalysts, additional fuel and power. By-

product credits from the hydrogenation of succinic acid were not considered. Indirect costs such as the cost of maintenance and overhead are derived from 2% of replacement asset value. Labor was calculated using salary estimates for approximately 90 employees required to operate the process. Depreciation costs were calculated using 10-year straight-line depreciation. Costs associated with landfilling solid waste from wastewater treatment and final product finishing materials were not considered.

An overview of the direct costs for both bio-sugar and succinic acid production are provided in Table 8-1. Chemical costs were collected from ICIS Chemical Business and adjusted for inflation (ICIS 2015). Natural gas prices were gathered from the U.S. Energy Information Administration (US EIA 2015). All other costs for fiber, power, and consumables were assumed.

Table 8-1: Unit costs for Bio-Refinery Raw Materials & Reagents

Raw Materials & Reagents	Annual Inflation	Unit Cost	Unit
Mixed Southern Hardwoods	0.50%	\$72.80	bdmt
Hydrolyzed Starch	2%	\$440	bdmt
Cellulytic Enzymes	0%	\$6.67	kg
Ammonia	2%	\$713	mt
Hydrochloric Acid	2%	\$285	mt
Corn Steep Liquor	2%	\$55.44	mt
Natural Gas	2%	\$4.50	MMBtu
Power	2%	\$56	MW hr
Carbon Dioxide (Gas)	2%	\$100	mt
Hydrogen	2%	\$1,100	mt

8.3.4 General Assumptions & Key Financial Indicators

Best professional judgment was used to determine the appropriate risk required for discounting future free cash flows in the financial model (e.g. 15% internal rate of return). For this study, free cash flow is defined as the unlevered sum of after tax profit and depreciation costs, less changes in working capital and new fixed capital investments. A project life of 15 years was used for evaluation of the sum of discounted cash flows according to the following equation:

$$NPV = \sum_{n=1}^t \frac{FCF_n}{(1+i)^n} + \frac{TV_t}{(1+i)^t}$$

Where the net present value “NPV” is the sum discounted free cash flows “FCF” over a specified time period “n” and discount rate “i”, with an exit fair market value “TV” in the project’s terminal year “t”. The terminal value in year 15 of the project was assumed to be five times EBITDA (Earnings Before Interest, Tax, Depreciation and Amortization). Operational costs for all process cases was based on 8,400 total annual working hours. Working capital for materials was calculated as 15% of direct costs in the coming year, and working capital for product reserves was calculated as 5% of coming year revenues. A nominal tax rate of 35% was assumed, and tax loss carryforward was applied.

In addition to NPV and internal rate of return (IRR) for the project’s capital investment, the primary key performance indicators of interest in this study was the minimum product revenue (MPR), maximum transfer price (MTP), and the incremental EBITDA per unit of wood chips consumed. MPR refers to the minimum product price necessary for achieving a 15% rate of return. For the study cases where the process exports dry succinic acid crystals

for downstream conversion, the MTP refers to the maximum transfer price a neighboring hydrogenation plant would be willing to accept in order to achieve a 12% rate of return for the production of 1,4 butanediol. Lastly, the incremental EBITDA per unit of wood chips is a desirable key performance indicator within the forest products industry, useful for comparison with traditional investment activities for this sector.

8.3.5 Goal Definition

The goal of this study was to quantify the MPR, MTP and incremental EBITDA for succinic acid with respect to multiple, feasible process case scenarios. Specifically, this work explores the context of repurposing all or a significant portion of existing assets commonly found at a kraft pulp mill and reallocating the biomass used for pulp manufacture towards biochemical production. For the case scenarios identified, succinic acid can be manufactured and sold to an open market, or exported directly to a known off-taker (e.g. 1,4 BDO production).

8.3.6 Functional Unit

The functional unit for all cases was 1 metric ton of succinic acid, or “H2SA”, except where noted. All revenue and operating costs analyzed, including by-product credits, were allocated to the functional unit and used in the cash flow analyses.

8.3.7 Scope Definition & System Boundaries

The scope of this analysis spans the gate-to-gate production of succinic acid produced from wood chips. As shown in Figure 8-1, the mixed southern hardwood chips are received and stored at the bio-refinery at a capacity of 500,000 “bone-dry” metric tons (bdmt) per year. This figure was chosen as a baseline for all cases evaluated since it is roughly equivalent to a

single kraft pulp mill fiber-line (i.e. a fraction of the total pulp and paper making process equipment dedicated to digestion, washing, bleaching and pulp storage), which serves as the basis for co-location and mill repurposing scenarios.

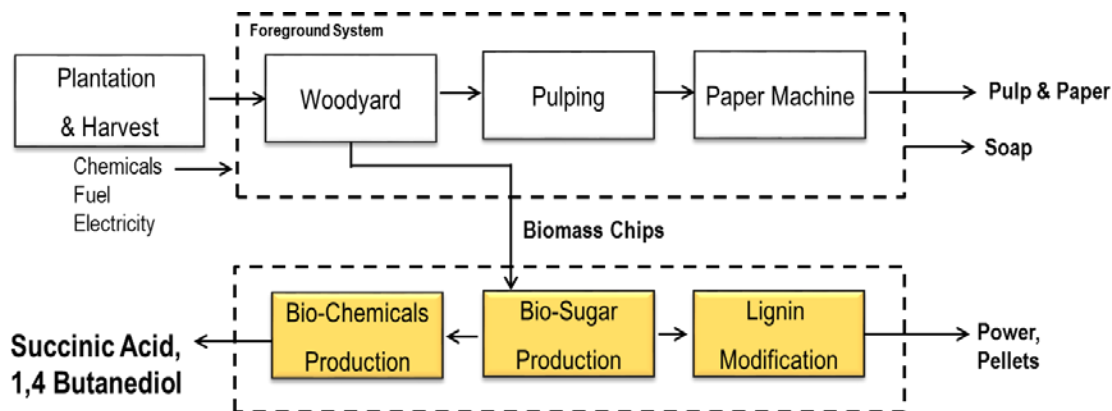


Figure 8-1: Bio-Refinery General Block Flow Diagram

The primary foreground systems analyzed included the pulp mill digester, evaporation, power production, fermentation, purification, and, in some cases, hydrogenation of succinic acid and phenolation of the enzymatic hydrolysis residue (e.g. “biorefinery” lignin). The process model used to quantify the life cycle inventory for the primary foreground system utilized secondary data gathered from peer-reviewed literature. It is noted that there exists a considerable degree of uncertainty – especially around the cost of the all-important hydrolytic enzymes that convert polysaccharides to monomeric, fermentable, sugars - associated with financial modeling of conceptual bio-chemical conversion processes where literature data is used, and continued iterations of the techno-economic model are absolutely necessary as new, more accurate information can be used to update major process input assumptions.

8.4 Process Description

After biomass receipt and storage, the wood chips are loaded into a continuous digester and charged with 150 psig steam to 10% wt. A temperature of 180C is maintained for 90 minutes in order to auto-hydrolyze the wood fiber matrix, which solubilizes lignin and hemicellulose while preserving the glucan content of the cellulose. Reaction kinetics for autohydrolysis are well studied in the literature (Ek 2009, Young & Akhtar 1998) Operating and yield assumptions were collected and are reported in Table 8-2 (also, see supplemental information for more detailed process assumptions). The digested wood pulp is then mechanically refined in order to further deconstruct the fiber matrix and increase the cellulose surface area prior to enzymatic hydrolysis. The pulp is filtered and “pre”-hydrolysates are sent to an ion-exchange unit in order to remove 90% of solubilized pretreatment by-products which are known to inhibit enzyme activity (e.g. acetic and formic acid from hydrolyzed hemicellulose). The prehydrolysate is then added back to the pulp slurry and saccharified across three enzymatic hydrolysis tanks at 50C for 48 hours. The enzyme is added to the system at 5 FPU (filter paper units) per gram of substrate, and a gravity clarifier is used to separate solids from the sugar hydrolysates between the first and second stages of enzymatic hydrolysis. This strategy is employed in order to increase residence time and reduce enzyme efficiency loss during enzymatic hydrolysis. Finally, the remaining solids residue (e.g. lignin and unhydrolyzed carbohydrates) is filtered and pressed to a 50% solids cake and the filtrate product is collected and concentrated prior to fermentation. A more detailed process description for bio-sugar production is provided in the Life Cycle Inventory Analysis section.

Table 8-2: Operating & Yield Assumptions for the Bio-Refinery Process

Input Assumption	Value	Unit
Mixed Southern Hardwood Consumption	500,000	Bdmt/yr
Feedstock Carbohydrate Content	0.68	Unit/unit feedstock
Carbohydrate Recovery (Monomeric)	0.623	Unit/unit feedstock-carbohydrate
Bio-Sugar Purity	0.915	Unit/unit sugar-product
Enzyme Addition	6.67	Kg/bdmt substrate
Succinic Acid Yield	0.79*	Unit/unit sugar
Succinic Acid Recovery	0.75	Unit/unit succinic acid produced
Succinic Acid Purity	0.972	Unit/unit succinic acid-product
1,4 Butanediol Yield	0.50**	Unit/unit succinic acid
1,4 Butanediol Purity	0.999	Unit/unit 1,4 butanediol-product

*Succinic acid yields as reported (Song & Lee 2005) **1,4 butanediol yields as reported

in Minh et al 2010

The most efficient process for SA manufacture is likely provided for with fermentation by the bacterium *E. coli* (Song & Lee, 2005). After fermentation, the media is centrifuged to recycle cells. Micro-filtration and ultra-filtration are used to remove residual cell debris and proteins. From here, SA can be removed by a direct vacuum distillation and crystallization process as described in Luque et al, 2008. After separation, the filtrate is then mixed with activated carbon to further remove contaminants thereby reducing color. Next, the purified SA filtrate is condensed via vacuum distillation. After distillation, the SA filtrate is sent to a crystallizer and titrated with hydrochloric acid to a pH of 4.2. At pH 4.2, SA crystals form and the SA crystal slurry is removed from the crystallizer bottoms. The SA crystal slurry is then filtered and the SA crystals are washed with process water, with the filtrate returned to vacuum distillation. Purified SA crystals are then dried with hot air in rotary dryer.

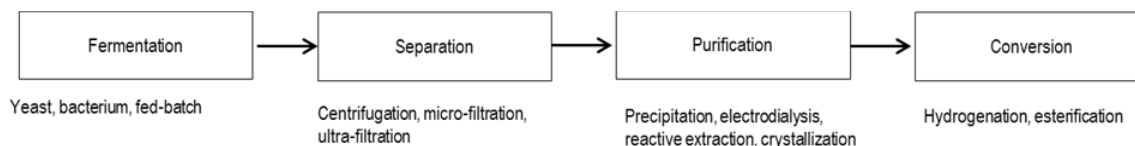


Figure 8-2: Characteristics of Succinic Acid Unit Operations

The chemical 1,4 butanediol (1,4 BDO) may be produced readily from succinic acid by hydrogenation and hydrogenolysis (Minh et al 2010, US20110245515). Purified succinic acid may be dissolved in water to a 10% wt. concentration and fed directly to a hydrogenation reactor operating at 150C. The reactor may be loaded with 1 g catalyst per g succinic acid and reacted for 10 to 24 hours, or until 100% molar conversion of the succinic acid is complete. Depending on the catalyst and reaction conditions, the molar selectivity of 1,4 butanediol may be 65 to 90%, and notable by-products include tetrahydrofuran (THF), gamma-butyrolactone (GBL), and n-butanol. For the purposes of this study, it was assumed that the selectivity of 1,4 butanediol was 65% and the selectivity of each co-product was 12% (Minh et al 2010). The resulting reaction mixture must then be purified by means of distillation. It was assumed that catalysts employed in this process would be supported on carbon and therefore no catalyst recovery from the reactor effluent would be required. The catalyst was assumed to be 3% Re-3% Ru-94% carbon with a catalyst cost of \$73/kg and 3-year life. Other reagents included hydrogen gas required in order to sufficiently reduce the succinic acid to its respective products.

8.4.1 Review of Succinic Acid Fermentation

To summarize, for most the micro-organisms reviewed (except for one strain of recombinant *E. coli*), anaerobic fermentation at pH 6 to 7.5 is required for the optimum SA production, unless otherwise stated. Fed-batch fermentation was commonly noted as the most efficient means for SA production.

One of the purported benefits of selecting yeast for SA production is a low pH fermentation (Raab et al, 2010). Since the pKa of succinic acid is 4.2, yeast fermentation with engineered *Saccharomyces cerevisiae* at a pH of 3 yields the SA product in its protonated form, H₂SA. H₂SA can be crystallized directly without the need for neutralization or precipitation steps which require additional reagents and create waste by-products (Kurzrock & Weuster-Botz, 2010). A yield of 0.11 mol H₂SA per mol glucose was reported by Raab et al, 2010.

However, it is likely that H₂SA recovered from a low pH fermentation broth will have considerable contaminants depending on the selectivity of the engineered *S. Cerevisiae*. While other acid by-products are miscible in the fermentation broth, any H₂SA that crystallizes in the fed batch reactor will be difficult to separate from the cell debris and proteins. If this is to be avoided, fermentation media will need to be diluted such that the H₂SA concentration is well below the reported 5.8 wt% solubility limit at 20C. For this reason, it is necessary to re-dissolve the separated SA crystals and filter with activated carbon or ion-exchange to remove contaminants prior to a re-crystallization step. This additional step would, of course, require additional ammonia (NH₃) and hydrochloric acid (HCl) for pH control.

Another potential benefit to using *S. cerevisiae* over engineered bacterium would be the micro-organism's ability to ferment C5 sugars. In a hypothetical "2nd generation" succinic

acid plant, where the legacy feedstock is ligno-cellulosic biomass, the mixed C5 and C6 sugar product may be more suited for the yeast based succinic acid process. Also, yeast is widely considered to be more tolerable to industrial applications, where sanitation controls are necessarily expensive.

Song & Lee, 2005, provide a comprehensive overview of the SA production performance characteristics for a variety of engineered micro-organisms, as shown in Table 8-3. In general, yields between 0.86 to 1.10 g SA per g glucose were reported, with concentrations from 24 to 105 g per L.

Table 8-3: Succinic Acid Production Performance (compiled by Song & Lee, 2005)

Micro-organism	SA Conc. (g/L)	Yield (g SA/g glucose)	Productivity (g/L-h)	Cell Conc. (g/L)
<i>A. succinogenes</i>	33.9	0.86	0.88	
<i>M. succiniciproducens</i>	14	0.7	1.87	3.44
<i>A. succiniciproducens</i>	33	0.93	1.1	
<i>E. coli</i>	99.2	1.1	1.3	

A. succinogenes and *M. succiniciproducens* were noted by Song & Lee as being the best candidates for SA production. *A. succinogenes* is capable of producing large amounts of SA from a variety of carbon sources including glucose, arabinose, cellobiose, fructose and xylose, and it is more tolerant to high glucose concentrations in the fermentation media (US Patent 5,573,931). It is also capable of increased SA production in the presence of high CO₂ concentrations, with ethanol and formic acid as by-products. More reduced sugars such as arabitol, result in further increases to SA production as compared with glucose (Van der Werf et al, 1997). The SA production performance for strain 130Z was reported in US Patent's 5,573,931 (1996) and 5,504,004 (1996), as shown in Table 8-4.

Table 8-4: *A. succinogenes* (strain 130Z) 1 L Batch Fermenter Product & By-Product Titer

Product/By-Product	Concentration (g/L)	pKa	Solubility (g/L)
Glucose (consumed)	98.3		
Succinic Acid	66.4	4.2	58
Corn Steep Liquor	15		
MgCO ₃ (pH Control)	80		
Acetic	12.0	4.76	<i>miscible</i>
Formic	8.7	3.77	<i>miscible</i>
Propionic	2.5	4.88	<i>miscible</i>
Pyruvic	4.3	2.5	<i>miscible</i>

Developed from bovine rumen, *M. succiniciproducens* is likely the most desirable micro-organism for the fermentation of lignocellulosic sugars with high yields and high productivity reported in the literature. Kim et al, 2004, observed that it utilizes xylose more efficiently than other bacterium and suggested using it for the fermentation of untreated wood hydrolysate to reduce commercial SA production feedstock costs. *M. succiniciproducens* produces SA from a variety of sugars under CO₂ conditions at a pH of 6 to 7.5, with productivity reported as high as 3.9 g/L-h (Lee et al, 2003). Major by-products include acetic and formic acids. It is also a capnophilic bacterium (CO₂ loving) and it was predicted that an SA yield of 1.71 mol SA per mol glucose could be achieved under an enriched CO₂ environment, while 1.86 mol SA is capable with CO₂-H₂ mixture (Hong et al, 2004). While promising, the increased SA yields from using enriched gases also leads to increased major by-products (mixed acids) which must be separated and purified, further complicating the process design.

A. succiniciproducens produces succinic acid and acetic acid as major products under anaerobic conditions. Lee et al, 2001, showed that *A. succiniciproducens* can efficiently utilize glucose, sucrose, maltose, lactose and fructose, and that by using glycerol, the SA yield was

1.33 mol SA per mol glycerol with a high ratio of SA to acetic acid (25.8:1). It was also suggested that wood hydrolysate may be a suitable feedstock (Lee et al, 2000). However, *A. succiniciproducens* suffers from poor cell growth unless enriched with CO-H₂ gas (Lee et al, 1999). Several variant strains were developed and evaluated by Lee et al in order to reduce the acetic acid by-products, but it remains a disadvantage to SA production.

Wild type *E. coli* typically produces succinic acid as a minor by-product while primarily fermenting glucose to ethanol. However, Hong et al, 2003, predicted theoretical yields of 1.647 mol SA per mol glucose by metabolic flux analysis. Eventually, strain NZN111 was developed by Stols & Donnelly, 1997, for SA production with limited by-products and has since been used as the starting strain for metabolic engineering. Strain AFP111, one of the derived strains, was shown to produce 1 mol SA per mol glucose with a productivity of 0.87 g/L-h. Another metabolically engineered *E. coli* strain was shown to produce SA by aerobic fermentation with a yield of 0.85 mol SA per mol glucose (Lin et al, 2005). However, pyruvic and acetic acid were major by-products. As with the other bacteria, major by-products (mixed acids) from SA production was observed as the main disadvantage to bacterium for the fermentation micro-organism.

8.4.2 Decision Criteria for Selecting Fermentation Organism

It is commonly stated in the literature that separation and purification costs from downstream processing should account for approximately 60% of total SA production costs (Bechthold et al, 2008). While commercial SA production is currently in its infancy, technology for citric acid production is a suitable, well-established comparable processing technology for cost benchmarking SA production. Due to the high costs, micro-organisms are

selected, metabolically engineered and evaluated to reduce downstream processing costs and, ultimately, simplify the process design. For this reason, designing a co-located SA production plant is not as simple as choosing the “best-in-class” process equipment and bolting it alongside an existing kraft pulp mill. It will be difficult to develop a specific process schema suitable for more than one micro-organism. Therefore, it is important to remain flexible with respect to lingo-cellulosic feedstock specifications as well as selected process equipment when considering which micro-organism and process to develop for commercialization.

Simply stated, the process must be built according to the available micro-organism and the required customer specifications for the end SA product. Furthermore, it must be recognized that considerable changes will be required in the near term to an existing SA production plant such that new, more advanced micro-organisms can be facilitated. It should be noted that various micro-organism strains developed from competing laboratories will likely surpass any strain selected for commercialization shortly after project selection.

In selecting a suitable process for techno-economic evaluation, the following decision criteria were evaluated and ranked for each process schema reviewed in the literature, as shown in Table 8-5.

Table 8-5: Decision Criteria for Succinic Acid Production Schema

Criteria	<i>A. succinogenes</i>	<i>M. succiniciproducens</i>	<i>A. succiniciproducens</i>	<i>E. coli</i>	<i>S. cerevisiae</i>
Theoretical & Applied Yield	6	6	7	9	2
Technology Readiness	4	4	3	4	5
Time-to-Revenue	4	5	3	5	7
Intellectual Property	3	4	3	4	1
Safety	4	7	4	7	8
Process Steps	4	7	4	7	8
Versatility	3	6	3	6	4
Total	28	39	27	42	35

Although *M. succiniciproducens* offers a modest yield for SA as compared with other micro-organisms, it was generally preferred due to its versatility to legacy feedstock and is likely a suitable candidate for the conversion of lignocellulosic sugars. Furthermore, since it exhibits reasonable cell growth and mortality it was viewed as more robust over the competing three bacterium. With regards to safety, it was viewed as a suitable candidate for direct vacuum distillation and crystallization implying that the downstream processing will require limited reagents and generate fewer by-products.

S. cerevisiae was identified as being the simplest and safest method for SA production, but it remains unclear whether the yield is viable for commercial production. Also, the only advantage *S. cerevisiae* possesses over bacterium is direct crystallization of SA from the fermentation broth, requiring fewer process steps. In theory, the SA purity should be much higher but it's not clear whether or not any advantage with respect to reduced mixed acids production can be achieved.

E. coli is the clear winner with regards to yield. However, the micro-organism produces considerable mix acid by-products making unsuitable for direct vacuum distillation and crystallization. In fact, *E. coli*, *A. succinogenes* and *A. succiniciproducens* will all likely require some form of ion-exchange and electro dialysis, increasing the number of process steps. Likewise, the alternative reactive extraction (currently used for commercial citric acid production) requires additional reagents and extractant solvents which are costly and increase the level of safety precautions considerably. For this reason, these bacteria were seen as having the lowest “technology readiness” and “time-to-revenue.” Furthermore, opportunities for obtaining intellectual property were considered low and licensing costs from companies such as Genomatica undesirable.

Another important note from the literature, the original patents filed in 1996 for the *A. succiniogenes* strain 130Z, developed by Guettler et al, and the metabolically engineered *E. coli* strain NZN111, developed by Stols & Donnelly, expired in 2013, suggesting the current rush in commercial SA development. More market research and analyses into the history of these micro-organisms and their respective laboratories is needed to better understand the key players and the direction of the specialty bio-chemical industry as a whole.

8.4.3 Review of Separation Technology

Regardless of the micro-organism selected, SA produced will require separation from the fermentation media. First, the residual cell mass is centrifuged from the fermentation broth and is either recycle or removed as waste fertilizer (another potential co-product to be investigated). The SA filtrate is then filtered with micro-filtration units to remove cell debris and then ultra-filtration units to remove proteins and other organics.

A decanter centrifuge uses high rotational speeds to separate solid particles from a liquid slurry. This device is commonly used in the food processing and wastewater treatment industries. Typically, the centrifuge is oriented horizontally with the slurry fed to the center of the centrifuge, as shown in Figure 8-3. Inside the device, a large diameter rotating bowl is centered with the degree of slope designed specific to the characteristics of the fermentation media. Clarified liquid is removed from the top of the centrifuge and the solid cell mass is removed from the bottom as the solids are collected along the beach via a scroll conveyor. One of the key advantages to a decanter centrifuge over a screw press or belt filter is that the degree of separation can be manipulated by changing the rotational speed with the electric motor. This implies that a centrifuge is more suitable to handle the daily variations of slurry composition by giving operators more control. Furthermore, other solid-liquid separation systems such as a plate and frame filter press are likely too expensive for this application.

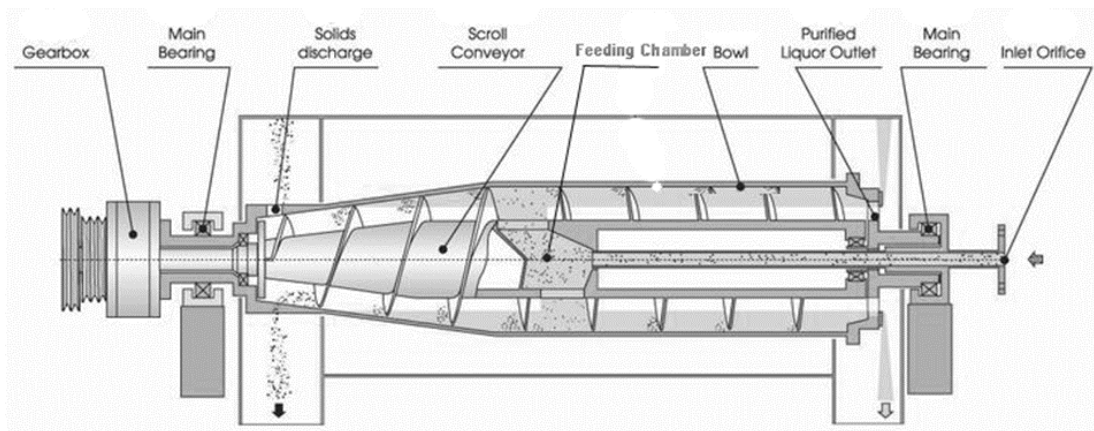


Figure 8-3: Decanter Centrifuge Diagram (GN Centrifuge, 2014)

The largest disadvantage to the decanter centrifuge is its inability to separate colloidal solids and its high energy consumption. A typical 400 GPM centrifuge has a 90 KW power requirement. The centrifuge also requires expensive metallurgy in its construction in order to mitigate abrasive damage further increasing capital costs. NREL provides a 2010 quote for a centrifuge unit sized to process 411 mt/hr of fermentation media at the cost of \$6.5 million (Humbird et al, 2011). It is assumed that the centrifuge is capable of producing a solid stream to a 30-40% consistency.

The centrifuged SA supernatant must be subsequently treated using micro-filtration, which is a physical separation using membranes. Membranes are typically composed of cellulose acetate or polysulfone and are selected according to their flexibility and suitability to the desired application. Alternatively, a metal or alumina membrane can be used as well. As shown in Figure 8-4, the membranes are designed for either screen filters, where the membrane pore size blocks larger particles along a flat surface, or depth filters, where the particles are captured inside the filter media. Similarly, the filter elements can be assembled for cross-flow filtration, where a portion of the feed stream is continuously returned to the previous step, or dead-end filtration, where all of the feed stream must pass through the filter media.

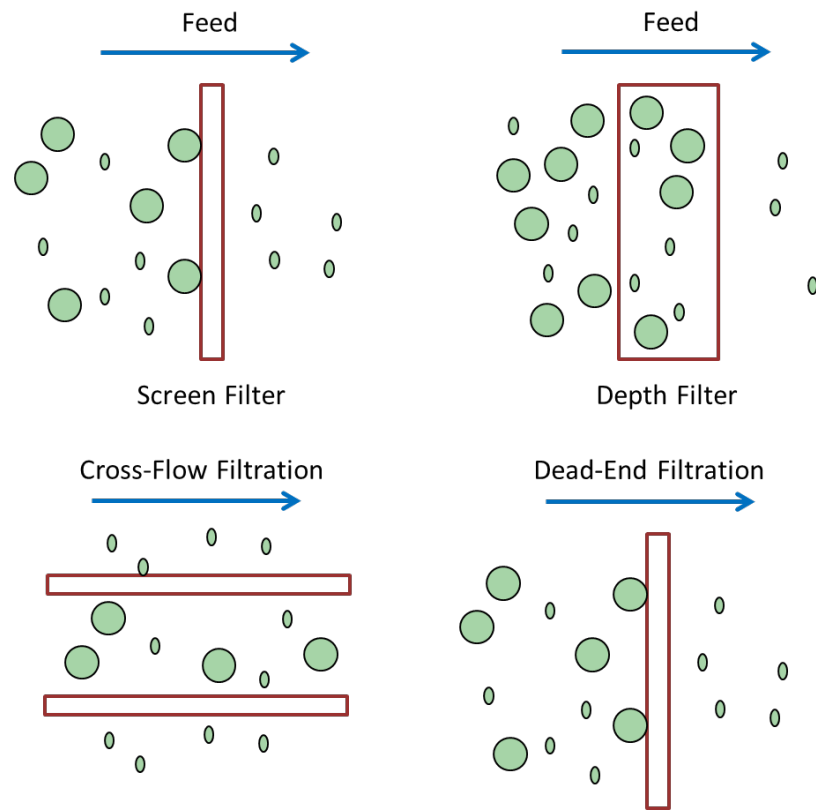


Figure 8-4: Filtration Equipment Characteristics

Micro-filtration is a versatile solid separating platform, and the selection of filtration media and design will largely depend on the composition of the SA filtrate. It is important to select filtration units with while considering tendency for fouling, viscosity, temperature and operating pressures. Fouling must be corrected by back-washing the filters regularly or utilizing “clean-in-place” procedures requiring hazardous cleaning agents and detergents. Regardless, portions of the micro-filtration unit must be brought off-line regularly for

maintenance and their operation is necessarily sensitive to any changes to the fermentation media. That being said, micro-filtration is largely regarded as a “low-risk” operation.

Ultra-filtration is similar to micro-filtration in both design and operation only with smaller pore sizes, and the filter media is typically sized according to molecular weight cut-off. It should also be noted that SA losses with the filtered residual cell debris and proteins are considered minimal, or less than 1%.

8.4.4 Review of Purification Technology

The purification of SA crystals can be complex, so for the purposes of this review, the technology was evaluated according to its degree of simplicity. Simplicity is considered by the number of process steps, reagents and waste by-products generated as a result of the inability to recover the reagents used.

As shown in the Figure 8-5 process diagram, SA salt is precipitated from the fermentation broth by the addition of calcium hydroxide (Datta et al, 1992). In this single step, only an 85% yield is reported with the addition of calcium hydroxide. Residual cell mass is removed as waste fertilizer using a centrifuge, and the supernatant is filtered such that the Ca+SA- product can be recovered for acidulation. Part of the filtrate is recycled back to the fermenter and the remaining portion is removed as wastewater. The Ca+SA- product is then sent to the acid mixing tank and washed with concentrated sulfuric acid. In this step, a stoichiometric consumption of H₂SO₄ is required and the SA product is converted to its acid form. A subsequent neutralization step with additional lime is required after acid mixing to neutralize the product. A filtration unit removes calcium sulfate (gypsum) from the process, and after that, an ion exchange unit removes residual cationic and anionic debris. The

remaining H₂SA solution, which is less than 5.8 wt% H₂SA, must be concentrated with a vacuum distillation unit. At approximately 6 wt%, the purified H₂SA begins to precipitate as SA crystals, and the concentrated SA solution is sent to a crystallizer. It is assumed that the practical yield for this process is between 60 to 70%. For this reason, as well as the waste disposal burden and costly reagents, classic industrial precipitation is not suitable for commercialization.

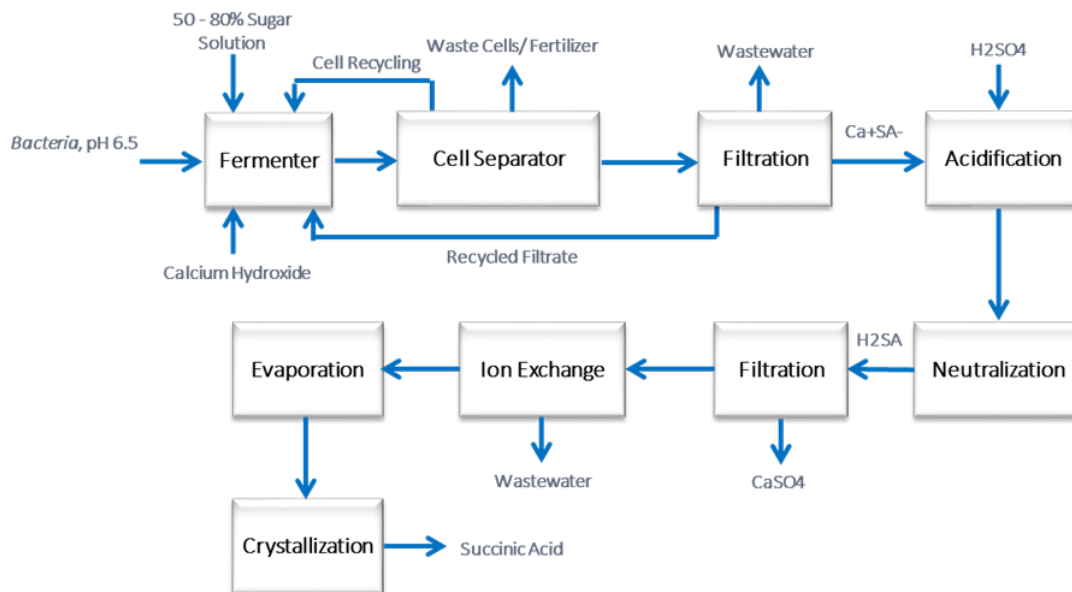


Figure 8-5: Classic Precipitation of Succinic Acid with Calcium Hydroxide

Similar to the classic precipitation with calcium hydroxide, precipitation with ammonia can also be performed allowing for the potential recovery of the base, thereby minimizing reagents (Berglund et al, 1999). As shown in Figure 8-6, ammonia is added directly to the fermentation broth and the diammonium succinate salt is recovered from the filtrate and

precipitated with sulfuric acid and ammonium bisulfate. The precipitated H₂SA is then recovered, and the waste filtrate containing spent ammonium sulfate is sent to a thermal cracking unit for regeneration of the acid, sulfuric acid and ammonium bisulfate, and ammonia. The key advantage to this purification process is the ability to partially regenerate reagents, but similar to classic precipitation, succinic acid was shown to exhibit low selectivity to ammonia (Yedur et al, 2001). Furthermore, only a 93% yield of the SA recovered from purification based on available diammonium succinate were observed, allowing for only an 80% overall yield.

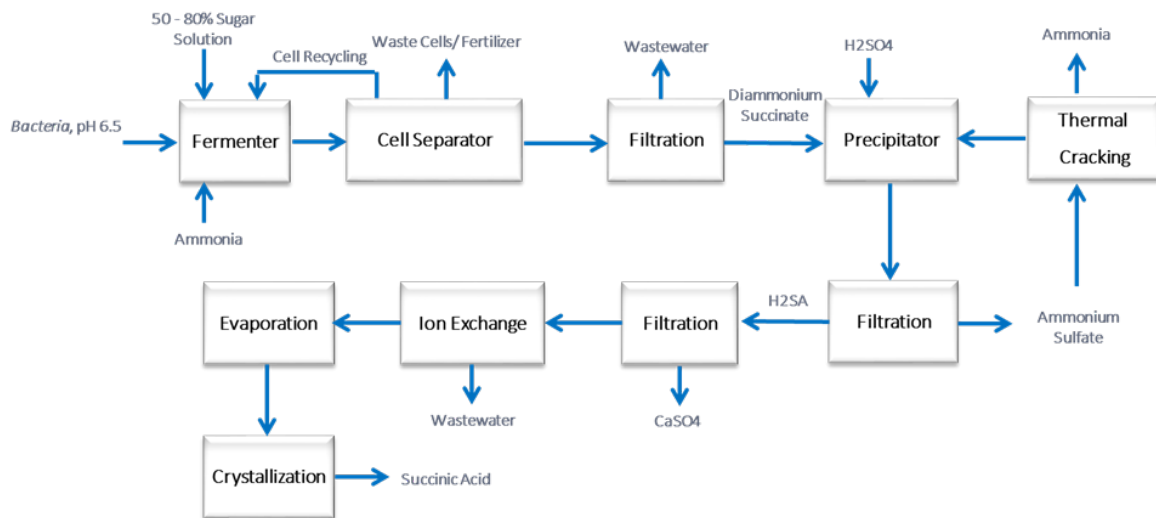


Figure 8-6: Precipitation of Succinic Acid with Ammonia

Zeikus et al, 1999, proposed the purification of succinic acid using two electro dialysis units in series to achieve a moderate yield, approximately 60%, and high purity, 99%, without the use of salts for pH control. As shown in Figure 8-7, sodium hydroxide is added to the

fermentation broth to produce sodium succinate. A desalting electro dialysis unit removes the sodium succinate salt from the remaining non-ionic impurities, and a subsequent water splitting electro dialysis unit separates the sodium ions from the succinate ions by donating a proton and a hydroxyl ion. Sodium hydroxide is then recovered and returned to the fermenter for pH control, while the remaining H₂SA is treated with ion exchange to remove residual cationic and anionic impurities. Finally, the purified H₂SA can be concentrated, crystallized and dried.

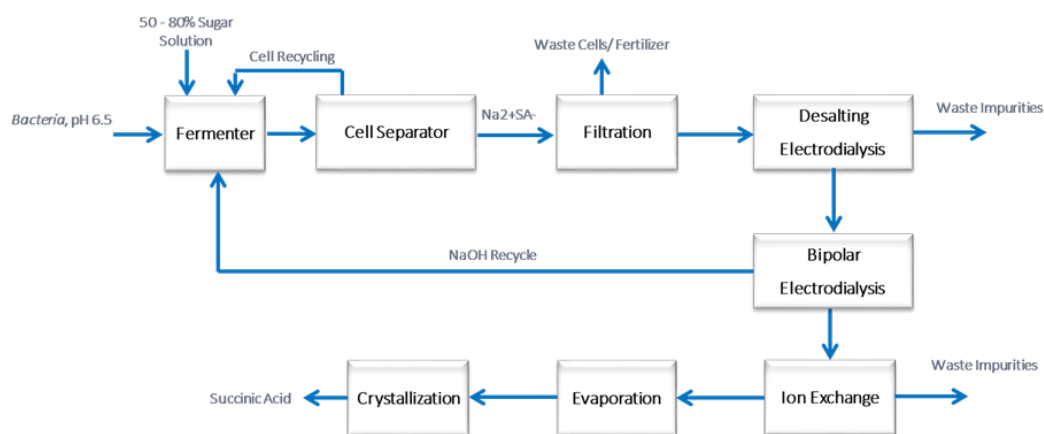


Figure 8-7: Purification of Succinic Acid by Electro dialysis

The removal of carboxylic acids from fermentation broth using reactive extraction was described by Kertes & King, 1985. Reactive extraction utilizes tertiary amines with high selectivity for the disassociated SA to improve yield. The resulting amine-acid complex is soluble in the organic phase of the extraction unit, and a back extractant is used in a stripping unit to regenerate amines and recover the purified H₂SA. The resulting H₂SA is then concentrated and crystallized. Song et al, 2007, suggested using trioctylamine with 1-octanol

for reactive extraction and were able to isolate succinic acid with a 99% yield. However, a lack of upstream processing suggests that residual mixed acids would lower the product purity. For this reason, Huh et al, 2006, pretreated the fermentation broth prior to reactive extraction and achieved an overall yield of 71% with 99% succinic acid purity. It should be noted that reactive extraction for the purification of succinic acid has not been demonstrated on the industrial scale, and its commercial viability depends largely on the ability to recover the tertiary amine and back extractant.

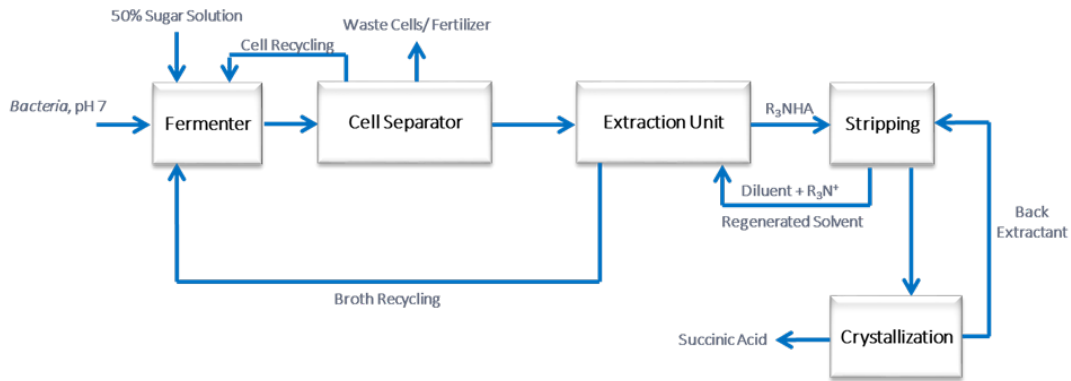


Figure 8-8: Purification of Succinic Acid by Reactive Extraction

Luque et al, 2009, described a succinct alternative to classic precipitation and electro dialysis with direct vacuum distillation and crystallization which requires limited reagents and generates fewer waste by-products. In this process, shown in Figure 8-9, pH can be controlled with either ammonia or magnesium carbonate added directly to the fermenter. After centrifugation and filtration, activated carbon is added directly to the recovered filtrate to remove trace contaminants and reduce color in the finished product. The filtrate can then

be sent directly to a low temperature, vacuum distillation unit where it is concentrated to one-fifth of its volume, prior to crystallization unit. In the crystallization unit, HCl is added directly to the solution to adjust the pH to 4.2 such that SA crystals can begin forming. The SA crystals are can then be separated from the solution and dried with hot air in fluidized bed or spray dryer. Luque et al reported SA crystal purity of 95% and an overall yield of 70%.

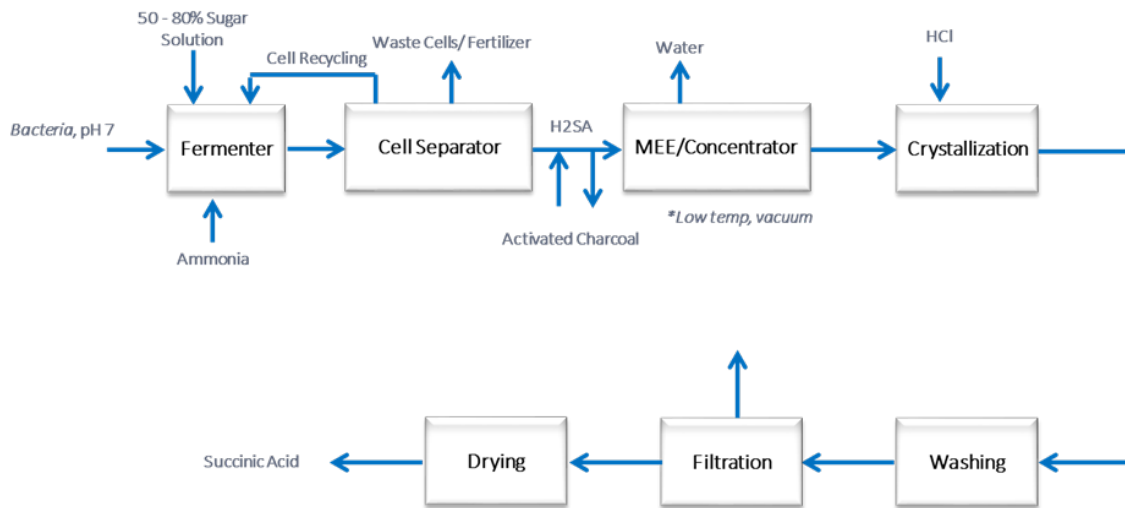


Figure 8-9: Direct Vacuum Distillation & Crystallization of Succinic Acid

As seen in Figure 8-10, the draft tube baffle (DTB) crystallizer receives the concentrated SA solution, and the SA slurry begins to form in the crystallizing zone of the unit. Baffles allow for a clarification zone where the SA crystal slurry is separated from the clear liquor. In some instances, the clear liquor is cooled with an adjacent heat exchanger and a portion of the stream is recycled to lower the overall operating temperature and promote crystallization. The SA crystal slurry is then removed, and the SA crystals are collected in a

process filter and washed with process water. One key advantage to the DTB crystallizer over a simple mixing tank is the ability to control SA crystal size distribution and avoid unwanted agglomeration of the SA crystals within the mixing tank. There is an alternative fluidized bed crystallizer as well but it's excessive cost and marginal differences in crystal shape are not suitable for SA production.

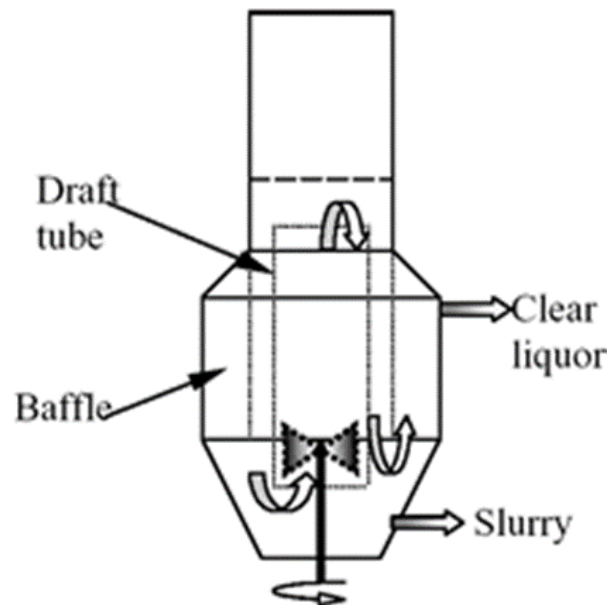


Figure 8-10: Draft Tube Crystallizer (GEA Process Engineering Inc, 2014)

8.4.5 Process Selection for Techno-Economic Analysis of Succinic Acid Production

A summary of the key process schema for purification of succinic acid is provided in Table 8-6. Overall, direct vacuum distillation and crystallization was considered to be the most promising of the process schema evaluated. While the average yield is only 70%, this cost burden is offset by simpler operation relative to the other routes evaluated and fewer by-

products generated as a result of purification. Precipitation was considered to be the least attractive of the processing routes considering the generation of hazardous waste and severe processing conditions (e.g. high temperature and acid consumption). Electrodialysis on the other hand, requires the least reagents and generates the fewest by-products, but this process suffers from high CAPEX and OPEX due to the operation of equipment required in addition to having the lowest yield. Lastly, reactive extraction is another route with a high potential yield of succinic acid product, but the use of solvents and solvent recovery contribute significantly to the CAPEX and OPEX.

Table 8-6: Summary of Purification Process Schema

Process Schema	Yield	Purity	Revenue Driver	Cost Driver	Sources
Classic Precipitation	60-70%	~99%	Simple	By-product generation, safety engineering	Datta et al, 2002
Ammonia Precipitation	80%	~99%	Improved yield, reagent recovery	Reagents, safety engineering, CAPEX	Berglund et al, 1999, Yedur et al, 2001
Electrodialysis	60%	~99%	Simple, fewer by-products	Poor yield, CAPEX	Zeikus et al, 1999
Reactive Extraction	71-99%	>99%	High yield	Solvents, solvent recovery, safety engineering	Kertes & King, 1985, Song et al, 2007
Direct Vacuum Distillation & Crystallization	70%	98%	Simple, fewer by-products	Average yield	Luque et al, 2009

For process modeling and techno-economic evaluation, direct vacuum distillation and crystallization with the fermentation provided by the micro-organism *E. coli* should be evaluated first. It is important to note that the yields stated are based on the total succinate available in the broth after fermentation is complete. It is not a yield based on starting sugars.

8.5 Case Scenarios

Multiple process case scenarios were explored in this study in order to determine an optimum commercialization path for biorefinery investments in the pulp and paper industry. Altogether, over 30 case scenarios were modeled for biosugar and biochemical production according to a variety of industrial contexts. Co-product valorization was also considered in order to examine its effect on process economics and product transfer price.

8.5.1 Bio-Sugars Produced from Mixed Southern Hardwoods

The production of mixed C5 and C6 bio-sugars from mixed southern hardwoods was modeled in order to establish a baseline in technoeconomic performance for the bio-refinery. For the cases shown in Table 8-7, three industrial contexts are considered: green fields investments, co-location investments, and pulp mill repurpose. These cases consider the utilization of existing pulp and paper industry assets in order to convert the glucan content of mixed southern hardwoods to industrial bio-sugars at 50% wt. solution. However, these cases are entirely hypothetical and it is acknowledged that there exists no market for mixed bio-sugars. The purpose of analyzing these cases was to determine the potential impact of industrial context assumptions on reducing the capital investment required for a commercial biorefinery process.

Table 8-7: Process Case Scenarios for Bio-Sugar Production

Legacy Feedstock	Product	Lignin Valorization	Context
Mixed Southern Hardwoods	Biosugar	Biomass Boiler	Greenfield
			Co-Location
			Repurpose

8.5.2 Bio-Chemicals Produced from Commodity Sugars

The value proposition for biorefining in the pulp and paper industry is largely based on two assumptions: first, that existing assets may be used in order to reduce the required capital investment, and second, that the biomass utilized in the process is cost-advantaged to current commodity, or “1st generation”, food-based sugars. Therefore, it was necessary to establish an additional baseline performance for producing bio-chemicals from hydrolyzed corn starch and then compare the economics an integrated bio-refinery, including the value of co-product from residue. For the cases shown in Table 8-8, the production of either succinic acid or 1,4 butanediol from starch was considered according to a greenfield investment. Opportunities for co-location with an existing corn wet mill were not considered.

Table 8-8: Process Case Scenarios for Bio-Chemical Production from Commodity Sugars

Legacy Feedstock	Product	Context
Hydrolyzed Starch	Succinic Acid	Greenfield
	1,4 Butanediol	

8.5.3 1,4 Butanediol Produced from Succinic Acid

It was assumed that the total market opportunity for succinic acid is small and that additional off-take to established chemical markets may be necessary in order to justify a bio-refinery producing succinic acid at commercial quantities. Therefore, it was necessary to examine the maximum transfer price of succinic acid to an independent 3rd party producing 1,4 butanediol. In these cases, as shown in Table 8-9, the MTP was calculated as the most an off-taker would be willing to pay for succinic acid in order to produce 1,4 butanediol at as assumed market price of \$2000/mt.

Table 8-9: Process Case Scenarios for 1,4 Butanediol Production from Succinic Acid

Legacy Feedstock	Product	Context
Succinic Acid	1,4 Butanediol	Greenfield
		Co-Location

8.5.4 Bio-Chemicals produced from Mixed Southern Hardwoods at an Integrated Bio-Refinery

Building upon the bio-sugar process, the production of succinic acid and 1,4 butanediol was modeled in order to determine the technoeconomic performance of a fully integrated bio-refinery. As shown in Table 8-10, these cases examine the production of either bio-chemical produced from mixed southern hardwoods according to a variety of industrial contexts. For the succinic acid cases, the bio-sugars are fermented by utilizing four different micro-organisms, and the yields and fermentation titer for each micro-organism was gathered from the literature. Succinic acid produced from fermentation was then purified and either sold as

a dry crystal for \$2400/mt or further converted into 1,4 butanediol and sold as a commodity chemical for \$2000/mt. For these cases, the lignin residue from enzymatic hydrolysis was consumed in order to meet process heat and power demands, and any additional process power (e.g. electricity) was exported to the grid at market prices.

Table 8-10: Process Case Scenarios for Bio-Chemicals from Mixed Southern Hardwoods

Legacy Feedstock	Product	Lignin Valorization	Context	Micro-Organism
Mixed Southern Hardwoods	Succinic Acid	Biomass Boiler	Greenfield	A. succinogenes
	1,4 Butanediol		Co-Location	M. succiniciproducens
			Repurpose	A. succiniciproducens
				E. coli

8.5.5 Valorization of Lignin Residue

Lastly, the valorization of lignin residue from the bio-refinery process was considered. As shown in Table 8-11, three co-product options were explored for the lignin. The first case scenario assumes the combustion of lignin in order to recover process heat and power. In this case scenario, additional power from the process may be sold back to the grid at market prices. The second scenario considers the drying and pelletization of the lignin in order to sell fuel pellets at \$156/mt (Fuel Pellets Institute), and this process requires additional capital investments towards a commercial pellet mill. The third scenario involves the chemical modification of the lignin, whereby the lignin is phenolated via acid catalysis of the lignin in the presence of excess phenol. The resulting phenolated lignin product may be used in wood adhesive formulations in order to reduce the amount of phenol required in phenol formaldehyde resins. The assumed price of \$1230/mt phenolated lignin was based on cost-in-

use assumptions for substituting reagents in PF resins with the product (ICIS Chemical). Significant capital investment was required in order to produce phenolated lignin, but the additional revenue received from the valorized lignin provides a significant contribution to the revenue such that transfer price pressure of the bio-chemical was reduced significantly.

Table 8-11: Process Case Scenarios for Bio-Refinery Lignin Valorization

Legacy Feedstock	Product	Lignin Valorization	Context
Mixed Southern Hardwoods	Succinic Acid	Biomass Boiler	Repurpose
	1,4 Butanediol	Pellets	
		Phenolation	

8.6 Results & Discussion

8.6.1 Life Cycle Inventory Analysis

As shown in Figure 8-11, the process for converting mixed southern hardwoods to mixed C5 and C6 sugars is predominantly a thermo-mechanical process. The biomass, as mixed southern hardwoods comprised mostly of *P. trichocarpa*, was assumed to have a composition consisting of 27% lignin (by mass), 49% glucan, 2% hexan, 17% xylan and 3% extractives. For the autohydrolysis step, the yield after pretreatment was assumed to be 98% (by mass) of the original lignin content, 43% of the glucan and hexan content, and 22% of the xylan content in order to accurately depict a pre-hydrolysis stage cook from a kraft pulping process (Smook et al 1992). During pre-hydrolysis, the “hot-water” cook hydrolyzes carboxylate groups on the hemicelluloses which produces an acetic acid by-product that helps to lower pH and further initiate an acid hydrolysis cook. During these conditions, the

hemicellulose content of the wood is hydrolyzed while the lignin and glucan is largely preserved. It was assumed that all of the extractives are solubilized during the autohydrolysis step.

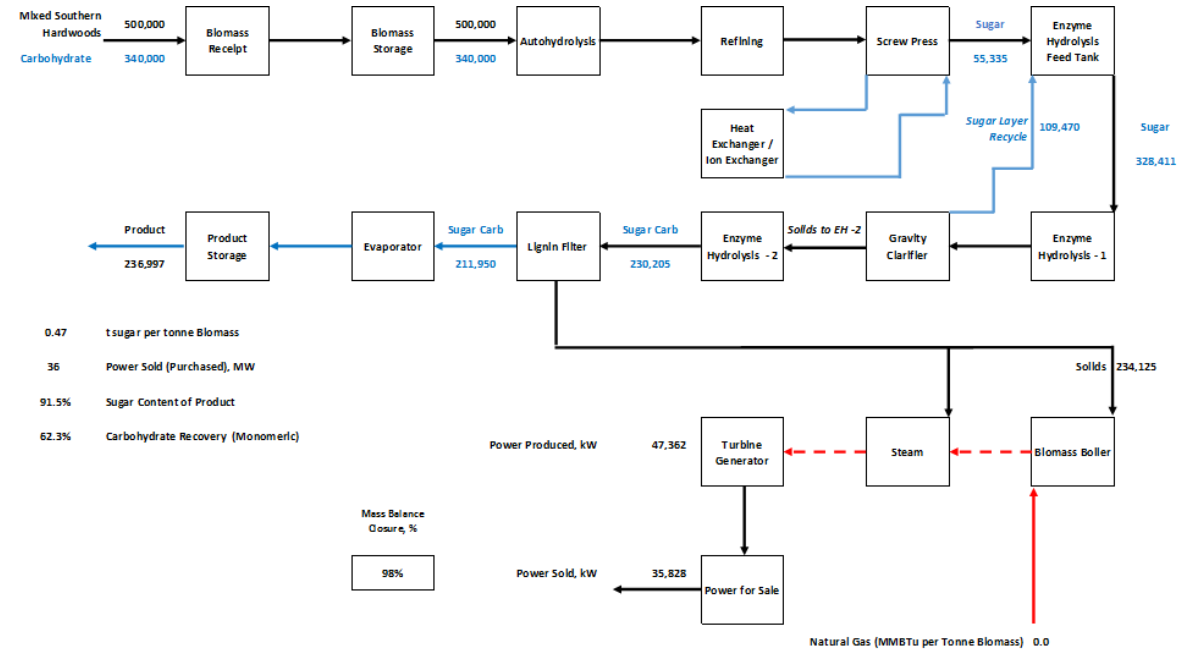


Figure 8-11: Bio-Sugar Production with Gross Material & Energy Balance *Units are mt/year unless otherwise noted

The pretreated biomass from autohydrolysis is then mechanically refined in order to increase the surface area of the substrate prior to enzymatic hydrolysis. After refining, the remaining solid biomass, or “pulp”, is pressed to 20% solids and the filtrate containing solubilized monomeric sugars from pre-treatment are subjected to ion-exchange in order to remove soluble inhibitors such as acetic acid and formic acid prior to being added back to the pretreated biomass. Exhausted ion exchange media and other consumables from the process

(e.g. refining plates) were not considered in the process model or captured in the life cycle inventory.

The remaining biomass is then saccharified using enzymes, assuming 84% carbohydrate conversion. Un-hydrolyzed carbohydrates remain with the lignin residue. Lastly, the lignin residue is filtered and pressed to 50% solids, washed once with 100% volume/volume process water, and then pressed again to 50% solids. The refining, pressing and washing unit operations are the largest power consumers for the process requiring approximately 150 kWhr per bdmt sugar product. The filtrate containing the soluble monomeric sugar product is concentrated to 50% solids in a multiple effect evaporator with a steam economy of 3 tons water evaporated per ton 10-bar steam. No additional purification of the soluble sugar product was considered. The lignin residue was assumed to have a heating value, HHV, of 10,000 BTU/lb (dry) and may be burned in a biomass boiler in order to generate an energy surplus for the process, unencumbered by chemical conversion unit operations (e.g. fermentation, purification, drying, hydrogenation, etc.). Any excess power produced from a back-pressure turbine operating at 10-bar may be sold back to the grid as an additional co-product.

At 500,000 bdmt/year biomass consumption, approximately 237,000 bdmt bio-sugar product is produced and 35 MW of surplus power may be sold back to the grid. Table 8-12 provides a complete list of the inventory items required by the aforementioned bio-sugar process. All items were normalized to the respective functional unit, 1 mt of dry biosugar. The thermo-mechanical process, autohydrolysis, is notable in that it requires little additional reagents in addition to the raw material. Furthermore, this is a proven technology employed

by many kraft pulp mills today that produces high purity kraft pulps (or pulps with a high cellulose content). The limited washing employed in this scheme minimizes water consumption and the energy required to concentrate the product to 50% solids. The limitation to this approach is the final 91.5% purity of the sugars which contains residual soluble lignin, acetic and formic acid. These impurities persist in subsequent chemical conversion and serve as a burden to required purification steps. It is noted that the purification necessary in order to achieve polymer-grade purity for chemical intermediates is a significant cost burden to the entire value chain proposed in this study.

Table 8-12: Life Cycle Inventory for Bio-Sugar Production

Inputs	Units	Per bdmt Product
Mixed Southern Hardwoods	bdmt	2.11
Enzymes	kg	11.49
Ammonia	kg	3.26
Water	mt	0.44
Outputs		
<i>Biosugar</i>	<i>bdmt</i>	<i>1.00</i>
Power Sold	MW hr	1.24

Succinic acid fermentation, separation, and purification is depicted in Figure 8-12. For the process diagram shown, 170,000 bdmt/year starch sugar was considered and is approximately equivalent to the glucose produced annually from bio-sugar production at 500,000 bdmt/year mixed southern hardwoods consumption. Approximately 140,000 mt/year of succinic acid may be produced at this scale. The succinic acid process generates two effluent streams that may be valorized as a fertilizer co-product. While this was not considered in the

technoeconomic analysis, the solids content from residual cell mass, proteins, process salts and lost succinic acid product were considered “cost-neutral” and are not recorded in the life cycle inventory.

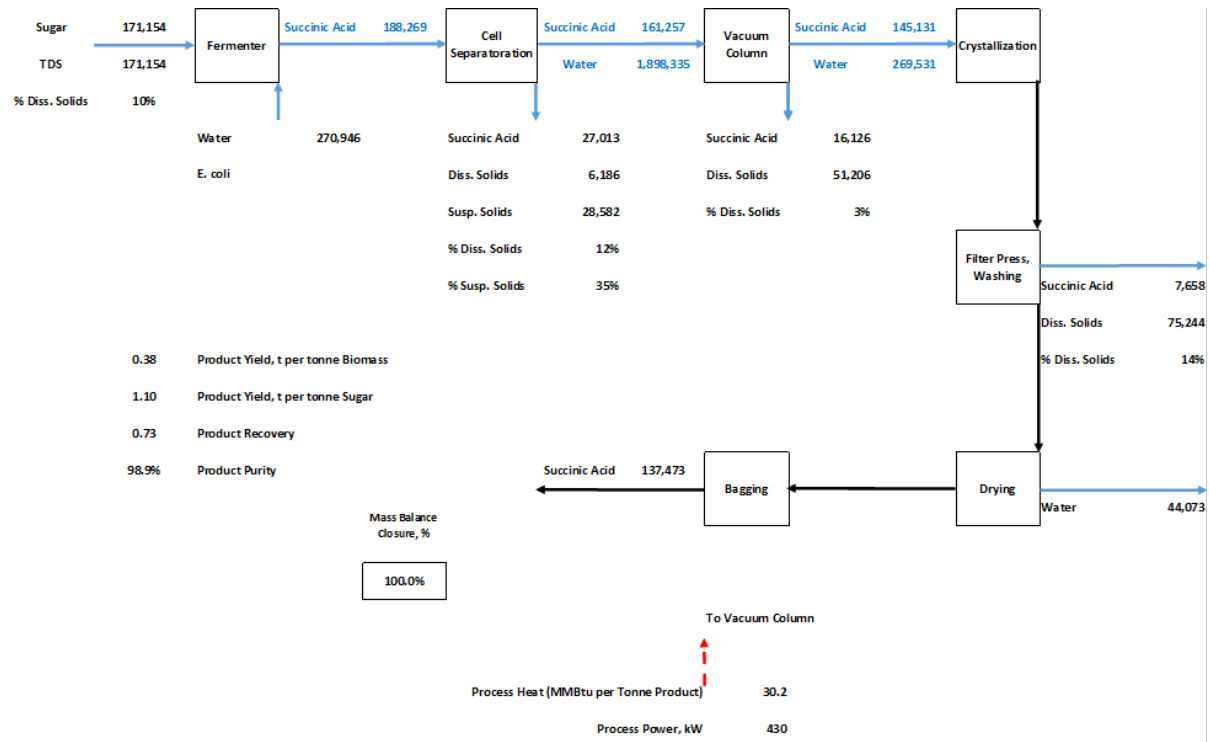


Figure 8-12: Succinic Acid Production with Gross Material & Energy Balance

Once purified, the dry succinic acid may be transferred to a subsequent conversion process for producing approximately 70,000 mt/year 1,4 butanediol via hydrogenation and hydrogenolysis. As shown in Figure 8-13, the hydrogenation reaction requires hydrogen, produced from an on-site steam methane reformer, in order to reduce the diacid to a diol product. Natural gas required for the production of hydrogen is reflected in the amount of

hydrogen recorded in the life cycle inventory and is not included in the natural gas requirement for process heat. As the reaction proceeds, additional hydrogenolysis produces valuable co-products such as tetrahydrofuran (THF) and gamma-butyrolactone (GBL). The co-product n-butanol, sharing an azeotrope with water, was considered too dilute to justify additional unit operations for its recovery. The THF may be removed easily by flashing the reactor from 10-bar to atmospheric pressure. However, the THF product contains residual impurities from the succinic acid process that must be removed via ion-exchange. As with the bio-sugar process, the consumption of ion-exchange resin was not considered.

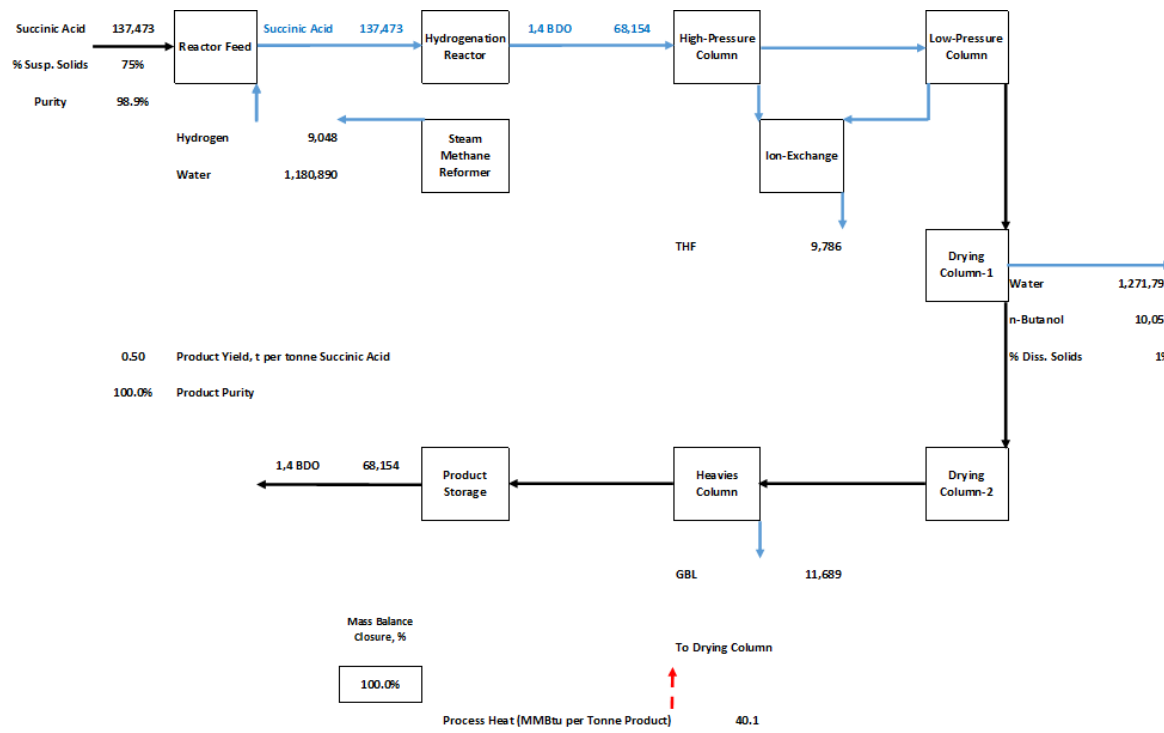


Figure 8-13: 1,4 Butanediol Production with Gross Material & Energy Balance

Table 8-13 provides the life cycle inventory results for non-integrated succinic acid and 1,4 butanediol chemical conversion processes. The succinic acid process requires a significant number of reagents. Fermentation requires corn steep liquor as nutrient addition to promote cell growth. Ammonia is required in order to adjust the pH during fermentation, and additional carbon dioxide must be added for the capnophilic micro-organism (*E. coli*) to achieve its potential yield reported in the literature (Song & Lee 2005). Hydrochloric acid addition is necessary for producing seed crystals during separation and purification. Most notably, each process possesses considerable energy requirements in order to separate and dry the products.

Table 8-13: Life Cycle Inventory for Non-Integrated Chemical Production

Inputs	Units	Per mt Succinic Acid	Per mt 1,4 Butanediol
Sugar or Succinic Acid	mt	1.25	2.02
Ammonia	mt	0.29	0.00
Hydrochloric Acid	mt	0.29	0.00
Corn Steep Liquor	mt	0.19	0.00
Natural Gas	MMBtu	37.62	49.74
Power	MWhr	0.08	0.16
Water	mt	0.60	1.35
Carbon Dioxide (Gas)	mt	0.22	0.00
Hydrogen	mt	0.00	0.13
Catalysts	kg	0.00	0.13
Outputs			
<i>Chemical Product</i>	<i>mt</i>	<i>1.00</i>	<i>1.00</i>
Tetrahydrofuran	mt	0.00	0.14
Gamma-butyrolactone	mt	0.00	0.17

Lastly, the individual processes reported above were integrated into one bio-refinery process and the life cycle inventory results are reported in Table 8-14. The valorization of the lignin has a notable impact on the life cycle inventory in that significant process heat and power is required to make up for the loss of energy that would otherwise have been produced from lignin combustion. In addition to the integrated heat demand for the chemical conversion processes, additional heat is required in order to dry the lignin prior to pelletization. Approximately 250,000 bdmt/year fuel pellets are produced from the pellet mill. For the phenolation cases, a substantial amount of energy is required in order to recover process solvents and reagents used in order to produce approximately 175,000 bdmt/year phenolated lignin.

Table 8-14: Life Cycle Inventory for Integrated Chemical Production

	<i>Lignin Valorization</i>	<i>Power</i>	<i>Pellets</i>	<i>Phenolated Lignin</i>	<i>Power</i>	<i>Pellets</i>	<i>Phenolated Lignin</i>
Inputs	Units	Per mt Succinic Acid	Per mt Succinic Acid	Per mt Succinic Acid	Per mt 1,4 Butanediol	Per mt 1,4 Butanediol	Per mt 1,4 Butanediol
Mixed Southern Hardwoods	bdmt	3.56	3.56	3.56	7.17	7.17	7.17
Enzymes	kg	19.39	19.39	19.39	39.07	39.07	39.07
Ammonia	mt	0.40	0.40	0.40	0.81	0.81	0.81
Hydrochloric Acid	mt	0.39	0.39	0.39	0.80	0.80	0.80
Corn Steep Liquor	mt	0.26	0.26	0.26	0.52	0.52	0.52
Gas	MMBtu	25.45	59.98	105.91	51.29	120.89	213.47
Power	MWhr	0.00	0.89	1.01	0.00	1.80	2.04
Water	mt	0.00	0.00	28.44	0.00	0.00	57.32
Landfill Costs	mt	0.00	0.00	0.91	0.00	0.00	1.84
Carbon Dioxide (Gas)	mt	0.21	0.21	0.21	0.43	0.43	0.43
Hydrogen	mt	0.00	0.00	0.00	0.13	0.13	0.13
Catalysts	kg	0.00	0.00	0.00	0.13	0.13	0.13

Table 8-14: Continued

	<i>Lignin Valorization</i>	<i>Power</i>	<i>Pellets</i>	<i>Phenolated Lignin</i>	<i>Power</i>	<i>Pellets</i>	<i>Phenolated Lignin</i>
Outputs	Units	Per mt Succinic Acid	Per mt Succinic Acid	Per mt Succinic Acid	Per mt 1,4 Butanediol	Per mt 1,4 Butanediol	Per mt 1,4 Butanediol
<i>Chemical Product</i>	<i>mt</i>	<i>1.00</i>	<i>1.00</i>	<i>1.00</i>	<i>1.00</i>	<i>1.00</i>	<i>1.00</i>
Lignin Co-Product	MW hr or mt	2.40	1.81	1.25	4.84	3.64	2.52
THF	mt	0.00	0.00	0.00	0.14	0.14	0.14
GBL	mt	0.00	0.00	0.00	0.17	0.17	0.17

8.6.2 Capital Expenditures (CAPEX)

First, Table 8-15, provides an overview of the capital investment required for the bio-sugar process at 500,000 bdmt/year mixed southern hardwoods. All costs shown represent the total installed costs. The greenfield context requires investments in the woodyard and biomass handling unit operations. Specifically, chip receiving, storage, and conveyance are the dominant wood yard costs. Wood chipping is not included and the biomass is received as wood chips suitable for autohydrolysis. Infrastructure costs reflect the land purchase, office space and waste water treatment assets. With the co-location and repurpose scenarios, a majority of these costs are provided from existing assets. However, the largest cost associated with a greenfield investment is the power system which includes the biomass boiler, high pressure turbine and power tie, and the greatest capital investment savings are realized by utilizing these existing assets with co-location and repurposing. The primary difference between co-location and repurpose is the ability to utilize pretreatment and materials storage assets. With co-location, some additional investment in material storage is required since it is assumed that these assets are still being utilized by the pulp mill. For the repurpose scenario, all of the solid product recovery system is accounted for with existing assets and only minor modifications are required for the pretreatment process. It is worth noting that for either co-location or repurpose scenarios there exists a valuation of existing assets based on current EBITDA from manufacturing kraft pulp. For the purposes of this study, the cost of acquiring said curtailed assets based on its potential value is considered a sunk cost and was not included with the total investment costs. This assumes that there is no additional cost to the asset holder for maintaining the curtailed equipment prior to investment in a bio-refinery conversion.

Table 8-15: Total Installed Cost for Bio-Sugar Production, \$ Millions

Area CAPEX, \$MM	Greenfield	Co-Location	Repurpose
Infrastructure	\$32.5	\$2.7	\$0.0
Biomass	\$45.2	\$0.0	\$0.0
Pretreatment	\$37.9	\$38.8	\$14.7
Enzymatic Hydrolysis	\$36.0	\$36.0	\$27.6
Product Recovery	\$35.2	\$32.7	\$31.8
Sugar System	\$11.0	\$11.0	\$10.3
Solid Product Recovery	\$11.4	\$11.4	\$0.0
Power System	\$78.8	\$0.0	\$0.0
Total Installed Cost	\$288	\$133	\$84

Table 8-16 provides an estimate for greenfield investments in the succinic acid and 1,4 butanediol plants. The succinic acid plant requires an ISBL (inside battery limits) investment of \$112 million and this investment remains constant for the assumed production capacity of 140,000 mt/year assumed for all cases. The 1,4 butanediol plant requires a \$107 million investment ISBL investment for the assumed production capacity of 70,000 mt/year. This includes the cost of a steam methane reformer for hydrogen production at \$58 million. When integrated with bio-sugar production, the OSBL (outside battery limits) items for infrastructure, materials storage and power are shared.

Table 8-16: Total Installed Cost for Non-Integrated Chemical Production, \$ Millions

Area CAPEX, \$MM	Succinic Acid		1,4 Butanediol	
Infrastructure	\$30.2		\$32.5	
Biomass	\$2.7		\$2.7	
Power System	\$13.3		\$11.0	
ISBL	\$112		\$108	
	<i>Fermentation</i>	<i>\$43.9</i>	<i>Hydrogenation Reactor</i>	<i>\$26.1</i>
	<i>Vacuum Column</i>	<i>\$12.2</i>	<i>High-Pressure Vessel</i>	<i>\$4.2</i>
	<i>3-Stage Steam Ejector</i>	<i>\$2.1</i>	<i>High-Pressure Column</i>	<i>\$4.6</i>
	<i>Mix Tank-1</i>	<i>\$3.2</i>	<i>Low-Pressure Column</i>	<i>\$3.5</i>
	<i>Mix Tank-2</i>	<i>\$3.2</i>	<i>Drying Column - 1</i>	<i>\$3.0</i>
	<i>Filter Press</i>	<i>\$3.5</i>	<i>Drying Column - 2</i>	<i>\$3.0</i>
	<i>Centrifuge</i>	<i>\$2.7</i>	<i>Heavies Column</i>	<i>\$1.0</i>
	<i>Rotary Dryer</i>	<i>\$3.5</i>	<i>Product Storage</i>	<i>\$1.7</i>
	<i>Draft Tube Crystallizer</i>	<i>\$18.9</i>	<i>Ion Exchange</i>	<i>\$1.6</i>
	<i>Product Storage</i>	<i>\$3.1</i>	<i>Hydrogen Plant</i>	<i>\$59.4</i>
	<i>Ultrafiltration</i>	<i>\$15.7</i>		
	<i>ISBL Total</i>	<i>\$112</i>	<i>ISBL Total</i>	<i>\$108</i>
Total Installed Cost	\$158		\$154	

Finally, Table 8-17 provides an overview of the total investment cost for the fully integrated greenfield biorefinery. When integrated, the bio-sugar and chemical conversion plants share the OSBL capital investment, and as noted previously, additional cost-savings opportunities may be applied when co-locating with or repurposing an existing kraft pulp mill. For the greenfield scenarios, the power option for consuming the lignin residue for process heat requires an \$81 million investment in the biomass boiler and steam turbine. This cost is slightly higher than the \$78 million investment required in the non-integrated bio-sugar process

because a larger steam turbine is needed in order to account for the additional heat demand from the chemical conversion processes. If the lignin is converted to fuel pellets, an additional \$28 million investment towards a pellet mill is required in the solid product recovery system, and the power system will require a \$17 million investment in a package gas boiler to provide process steam. An additional \$158 million investment is required in order to construct the lignin phenolation system, which involves reactors, solid and liquid separation systems, a solvent recovery system, product storage and additional waste water treatment.

Table 8-17: Total Installed Costs for Integrated Chemical Production, \$ Millions

Chemical Product	Succinic Acid	Succinic Acid	Succinic Acid	1,4 Butanediol	1,4 Butanediol	1,4 Butanediol
<i>Lignin Valorization</i>	<i>Power</i>	<i>Pellets</i>	<i>Phenolated Lignin</i>	<i>Power</i>	<i>Pellets</i>	<i>Phenolated Lignin</i>
Area CAPEX, \$MM						
Infrastructure	\$32.5	\$32.5	\$32.5	\$32.5	\$32.5	\$32.5
Biomass	\$45.2	\$45.2	\$45.2	\$45.2	\$45.2	\$45.2
Pretreatment	\$37.9	\$37.9	\$37.9	\$37.9	\$37.9	\$37.9
Enzymatic Hydrolysis	\$36.0	\$36.0	\$36.0	\$36.0	\$36.0	\$36.0
Product Recovery	\$35.2	\$35.2	\$35.2	\$35.2	\$35.2	\$35.2
Sugar System	\$11.0	\$11.0	\$11.0	\$11.0	\$11.0	\$11.0
Solid Product Recovery	\$11.4	\$39.9	\$11.4	\$11.4	\$39.9	\$11.4
Power System	\$81.4	\$17.2	\$23.8	\$81.4	\$17.2	\$23.8
Phenolation System	\$0	\$0	\$158	\$0	\$0	\$158
Succinic Acid System	\$126	\$126	\$126	\$126	\$126	\$126
1,4 Butanediol System	\$0	\$0	\$0	\$108	\$108	\$108
Total Installed Cost	\$416	\$381	\$517	\$524	\$489	\$625

8.6.3 Revenue Analysis

Table 8-18 provides an overview of the calculated revenues received from the production of bio-sugar and chemicals from 500,000 bdmt/year mixed southern hardwoods. At an assumed \$440/mt (NYMEX Sugar No. 11, 2016), bio-sugar sales results in \$126 million annual revenue, with \$17 million from power sales. Succinic acid generates approximately \$330 million in annual revenue from the conversion of bio-sugar produced at the bio-refinery, and 1,4 butanediol generates \$139 million, reflecting both a decrease in chemical price (from \$2,400 to \$2,000 per mt) and chemical production (from 140,000 to 70,000 mt/yr). Fuel pellet sales provide an additional \$40 million in annual revenue, roughly twice the revenue received from power sales. Phenolated lignin, however, provides a considerable increase in annual revenue of \$220 million assuming a product price of \$1,200/mt. When producing 1,4 butanediol, an additional \$70 million in annual co-product revenue may be received from the sale of THF and GBL at \$3,200/mt.

Table 8-18: Revenue Analysis for Integrated Chemical Production

<i>Lignin Valorization</i>	<i>Power</i>	<i>Power</i>	<i>Pellets</i>	<i>PL*</i>	<i>Power</i>	<i>Pellets</i>	<i>PL</i>
Revenue Item, \$ MM	Bio-Sugar	H2SA*	H2SA	H2SA	BDO*	BDO	BDO
Product	\$108	\$337	\$337	\$337	\$139	\$139	\$139
Pellets or Phenolated Lignin	\$0	\$0	\$40	\$221	\$0	\$40	\$221
Power	\$17	\$20	\$0	\$0	\$20	\$0	\$0
Tetrahydrofuran	\$0	\$0	\$0	\$0	\$32	\$32	\$32
Gamma-butyrolactone	\$0	\$0	\$0	\$0	\$38	\$38	\$38
Total Annual Revenue	\$126	\$357	\$378	\$558	\$229	\$250	\$431
\$ Per mt Product							
Product	\$440	\$2,400	\$2,400	\$2,400	\$2,000	\$2,000	\$2,000
THF	\$0	\$0	\$0	\$0	\$459	\$459	\$459
GBL	\$0	\$0	\$0	\$0	\$548	\$548	\$548
Lignin Co-Product	\$72	\$140	\$288	\$1,572	\$282	\$579	\$3,169
Total Per mt Product	\$512	\$2,540	\$2,688	\$3,972	\$3,289	\$3,587	\$6,177

*"H2SA" denotes succinic acid, "BDO" denotes 1,4 butanediol, "PL" denotes

phenolated lignin

8.6.4 Cost Analysis

Direct costs (i.e. variable costs) associated with production include the various raw materials, reagents and utility costs associated with bio-sugar and chemical conversion. These costs vary depending on production capacity. The indirect costs (i.e. fixed costs) were determined according to the size of the capital investment and include labor, maintenance, operating materials, overhead (e.g. sales & administrative costs), and depreciation costs. As shown in Table 8-19, the indirect costs may be reduced by up to \$30 million annually for the co-location and repurpose scenarios. This result primarily depends on the assumption of fixed cost allocation for the existing kraft pulp mill. That is, for a co-location and repurpose scenario the fixed costs for the existing kraft mill have been allocated to another division activity. For example, in the co-location scenario, the labor and maintenance associated with woodyard operations will remain constant regardless of whether or not the woodyard receives 1.5 million or 1 million bdmt/year in wood chips. It is noted that this assumption will vary depending on an organization's cost structure, and it is likely that any existing pulp mill operations would require a reallocation of fixed costs based on asset utilization by division activity (e.g. pulp mill production versus chemical production). However, for the purposes of this study, those fixed costs associated with the existing assets were considered sunk, with the exception of labor, and were not considered with this incremental analysis.

Table 8-19: Cost Analysis for Bio-Sugar & Non-Integrated Chemical Production

<i>Lignin Valorization</i>	<i>Power</i>	<i>Power</i>	<i>Power</i>		
Cost Item, \$ MM	Bio-Sugar-GF*	Bio-Sugar-CL*	Bio-Sugar-RP*	Succinic Acid	1,4 Butanediol
Direct Costs	\$55	\$55	\$55	\$153	\$379
Indirect Costs	\$59	\$32	\$28	\$40	\$37
Total Costs (Inc. Dep.)	\$114	\$87	\$83	\$193	\$416
Depreciation	\$26	\$13	\$9	\$13	\$13
\$ Per mt Product					
Biomass	\$153	\$153	\$153	\$570	\$5,033
Enzymes	\$77	\$77	\$77	\$0	\$0
Ammonia	\$3	\$3	\$3	\$240	\$0
Hydrochloric Acid	\$0	\$0	\$0	\$86	\$0
Corn Steep Liquor	\$0	\$0	\$0	\$11	\$0
Natural Gas	\$0	\$0	\$0	\$180	\$238
Power	\$0	\$0	\$0	\$5	\$10
Water	\$0	\$0	\$0	\$0	\$0
Landfill Costs	\$0	\$0	\$0	\$0	\$0
Carbon Dioxide (Gas)	\$0	\$0	\$0	\$23	\$0
Hydrogen	\$0	\$0	\$0	\$0	\$152
Catalysts	\$0	\$0	\$0	\$0	\$10
Phenolation	\$0	\$0	\$0	\$0	\$0
Total Direct	\$233	\$233	\$233	\$1,114	\$5,442
Labor (ex - Repair)	\$50	\$32	\$50	\$75	\$147
Maintenance and Repair	\$25	\$12	\$7	\$24	\$46
Operating Materials	\$25	\$12	\$7	\$24	\$46
Other Mill Fixed Costs	\$25	\$12	\$7	\$24	\$46
Overhead	\$11	\$11	\$11	\$48	\$60
Depreciation	\$112	\$57	\$37	\$97	\$181
Total Indirect	\$248	\$134	\$119	\$291	\$527
Total Cost Check	\$480	\$367	\$352	\$1,405	\$5,969

**"GF" denotes greenfield, "CL" denotes co-location, "RP" denotes repurpose

For the non-integrated succinic acid and 1,4 butanediol systems, the variable costs are considerably higher than bio-sugar production. For the succinic acid case, the feedstock cost for hydrolyzed corn starch or commodity sugar was assumed to be \$440/mt which results in a feedstock cost of \$570/mt succinic acid product. This reflects a noticeably higher yield of 0.8 mt product per mt feedstock when compared against bio-sugar utilization in the same non-integrated system with just 0.7 mt/mt. This is due to the higher purity feedstock resulting in fewer impurities in the succinic acid system which results in less washing (e.g. dilution water) and lower product losses from purification. Other significant costs include the ammonia for pH control and natural gas for process steam demand. For the 1,4 butanediol case, the feedstock for a non-integrated system is purified succinic acid, which was assumed to be \$2,400/mt. At this price, the feedstock costs are over \$5,000/mt of 1,4 butanediol produced, suggesting that succinic acid prices must be significantly lower in order to fulfill a commodity market where the price for 1,4 butanediol was assumed to be \$2,000/mt.

Similar to the capital estimate analysis, significant cost-savings may be realized by integrating the bio-sugar and chemical conversion processes as shown in Table 8-20. The most notable savings are with respect to labor and natural gas consumption. For example, the labor costs associated with manufacturing 1 mt of succinic acid for the non-integrated processes would be \$160/mt as opposed to \$105/mt when integrated (\$84 in labor to produce 1.6 bdmt bio-sugar and \$75/mt to produce 1 mt succinic acid). Similar logic applies to natural gas consumption when the separation and product drying unit operations are integrated and share process heat.

Table 8-20: Cost Analysis for Integrated Chemical Production

<i>Lignin Valorization</i>	<i>Power</i>	<i>Pellets</i>	<i>PL*</i>	<i>Power</i>	<i>Pellets</i>	<i>PL</i>
Cost Item, \$ MM	H2SA*	H2SA	H2SA	BDO*	BDO	BDO
Direct Costs	\$140	\$170	\$205	\$151	\$181	\$217
Indirect Costs	\$87	\$82	\$108	\$103	\$97	\$123
Total Costs (Inc. Dep.)	\$227	\$252	\$313	\$254	\$279	\$340
Depreciation	\$40	\$36	\$50	\$51	\$47	\$61
\$ Per mt Product						
Biomass	\$259	\$259	\$259	\$522	\$522	\$522
Enzymes	\$129	\$129	\$129	\$260	\$260	\$260
Ammonia	\$330	\$330	\$330	\$665	\$665	\$665
Hydrochloric Acid	\$117	\$117	\$117	\$236	\$236	\$236
Corn Steep Liquor	\$15	\$15	\$15	\$30	\$30	\$30
Natural Gas	\$122	\$287	\$507	\$245	\$578	\$1,021
Power	\$0	\$52	\$59	\$0	\$105	\$119
Water	\$0	\$0	\$0	\$0	\$0	\$1
Landfill Costs	\$0	\$0	\$9	\$0	\$0	\$18
Carbon Dioxide (Gas)	\$22	\$22	\$22	\$44	\$44	\$44
Hydrogen	\$0	\$0	\$0	\$152	\$152	\$152
Catalysts	\$0	\$0	\$0	\$10	\$10	\$10
Phenolation	\$0	\$0	\$15	\$0	\$0	\$29
Total Direct	\$994	\$1,211	\$1,462	\$2,164	\$2,602	\$3,108
Labor (ex - Repair)	\$104	\$104	\$104	\$210	\$210	\$210
Maintenance and Repair	\$62	\$56	\$77	\$156	\$146	\$187
Operating Materials	\$62	\$56	\$77	\$156	\$146	\$187
Other Mill Fixed Costs	\$62	\$56	\$77	\$156	\$146	\$187
Overhead	\$51	\$54	\$79	\$66	\$72	\$124
Depreciation	\$282	\$256	\$356	\$728	\$676	\$877
Total Indirect	\$622	\$583	\$769	\$1,474	\$1,395	\$1,771
Total Cost Check	\$1,616	\$1,794	\$2,231	\$3,638	\$3,997	\$4,878

*"H2SA" denotes succinic acid, "BDO" denotes 1,4 butanediol, "PL" denotes phenolated lignin

With respect to lignin residue valorization, the production of fuel pellets requires that additional power is purchased to make-up for the lost power that would have otherwise been produced by the biomass boiler. The incremental cost associated with exporting fuel pellets is an additional \$50/mt succinic acid for power and \$160/mt for natural gas. The incremental increase in power and natural gas costs is much more significant when incorporating the lignin phenolation system. Again, the process heat required to operate the phenolation system is considerable resulting in an additional cost of \$385/mt succinic acid. Other notable costs include phenolation reagents (e.g. sulfuric acid) and landfill costs for extra residue from the process which contribute an additional \$25/mt. Lastly, there is an additional \$25 million in annual indirect costs associated with maintaining the phenolation assets and selling the phenolated lignin product.

8.6.5 Total Mill Analysis & Discussion

The key performance indicators associated with bio-sugar production from mixed southern hardwoods are provided in Figure 8-14. Based on the assumptions used in this study, a greenfield investment to produce bio-sugars at \$440/bdmt from 500,000 bdmt mixed southern hardwoods per year results in 8% internal rate of return (IRR) and net present value (NPV) of negative \$130 million, with the lignin residue combusted for process heat and power. While EBITDA margins and free cash flow were comparable for the industrial contexts considered (30-40% and \$35 million annually), the investment cost-savings associated with co-location and repurposing offer significant improvement in project returns. When co-locating with an existing kraft pulp mill, the bio-sugar investment resulted in 23% IRR and

\$88 million NPV. The repurpose scenario offers additional improvement over co-location with 32% IRR and \$133 million NPV.

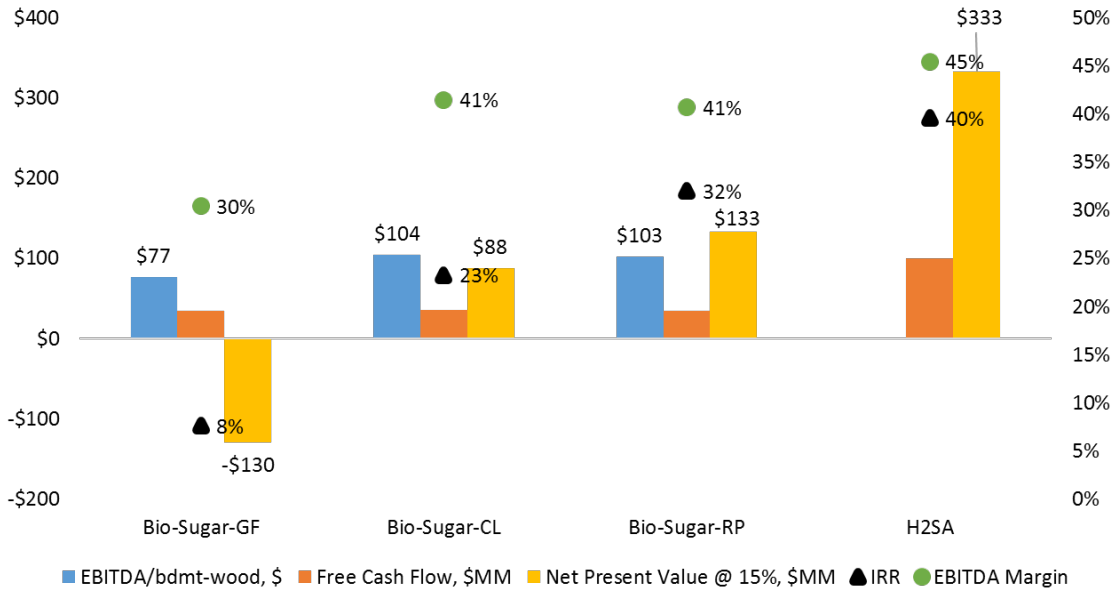


Figure 8-14: Key Financial Indicators for Non-Integrated Production

However, it should be noted that the \$440/bdmt bio-sugar price is a generous assumption for low purity, mixed C5 and C6 sugars, and the authors recognize that there is no existing market for a similar product with which to compare. Furthermore, as discussed in the cost analysis section, yields from chemical production are expected to receive a negative impact due to additional impurities in the system, brought in with the feedstock. For this reason, the minimum product revenue (MPR) necessary to achieve a 15% IRR offers additional insight to bio-refinery performance. A greenfield investment would require a \$560/bdmt bio-sugar MPR, and the co-location and repurpose scenarios reduce the MPR to \$355 and

\$310/bdmt, respectively. Based on these results, a non-integrated bio-sugar investment is likely not a promising venture, but the low MPRs for the co-location and repurpose scenario do suggest a significant opportunity to produce a cost-advantaged feedstock for fermentation and chemical production from monomeric sugars when compared with \$440/mt or more “1st generation”, food-based sugars.

The results for non-integrated succinic acid production reflect a feedstock cost of \$440/mt for hydrolyzed corn starch or commodity cane sugar. Again, a generous assumption for delivered glucose costs, where delivered costs may be substantially higher than market prices due to purity, purchase quantity and expected price volatility (USDA Economic Research - Sugar, NYMEX Sugar No. 11). The non-integrated succinic acid investment resulted in 40% IRR and \$130 million NPV. Of course, this assumes a current market price estimate of \$2,400/mt, and as stated previously, the market size for succinic acid is small, with limited immediate applications, suggesting a steep price elasticity of demand. Therefore, the future price for succinic acid at commercial quantities is largely unknown at this time. MPR results, however, suggests that \$1,750/mt is the minimum acceptable price assuming current process technology.

Another approach towards determining a price for succinic acid and better understanding its opportunity, was to analyze what was assumed to be the largest foreseeable market opportunity for succinic acid: hydrogenation to 1,4 butanediol. For this example, an investment in a non-integrated system was considered uneconomical with respect to the assumed market prices for succinic acid and 1,4 butanediol. When assuming a succinic acid cost of \$2,400/mt, \$6,045/mt MPR is required for 1,4 butanediol. Alternatively, the MTP for

succinic acid used in this process scenario is \$695/mt if assuming \$2000/mt market prices for 1,4 butanediol. This is well below the \$1,750/mt MPR determined for the non-integrated succinic acid scenario. If the 1,4 butanediol plant is built near an existing steam methane reformer, or hydrogen gas pipeline, such that this and other OSBL investments can be avoided, a higher \$905/mt MTP may be required for succinic acid.

The key performance indicators greenfield investments in integrated chemical production from mixed southern hardwoods are provided in Figure 8-15. Again, the same input assumptions and 500,000 bdmt/year mixed southern hardwood consumption rates apply, and for both chemical process system options, the different lignin valorization scenarios are analyzed. At the \$2,400/mt price and 140,000 mt/yr succinic acid production capacity, the performance for the power scenario is 21% IRR and \$160 million NPV. Exporting the lignin for fuel pellet sales provides nearly identical results with 21% IRR and \$150 million NPV. However, when considering a co-location or repurpose context, the IRR and NPV for the power scenario provides an additional 5% IRR and \$90 million NPV over the pellet cases due to avoided costs associated with utilization of an existing biomass boiler. By comparison, the phenolation scenario provides a more promising 30% IRR and \$535 million NPV. The additional \$158 million capital investment required for the phenolation system increases the free cash flow from \$120 million annually to over \$200 million, and the EBITDA/bdmt-wood is \$590.

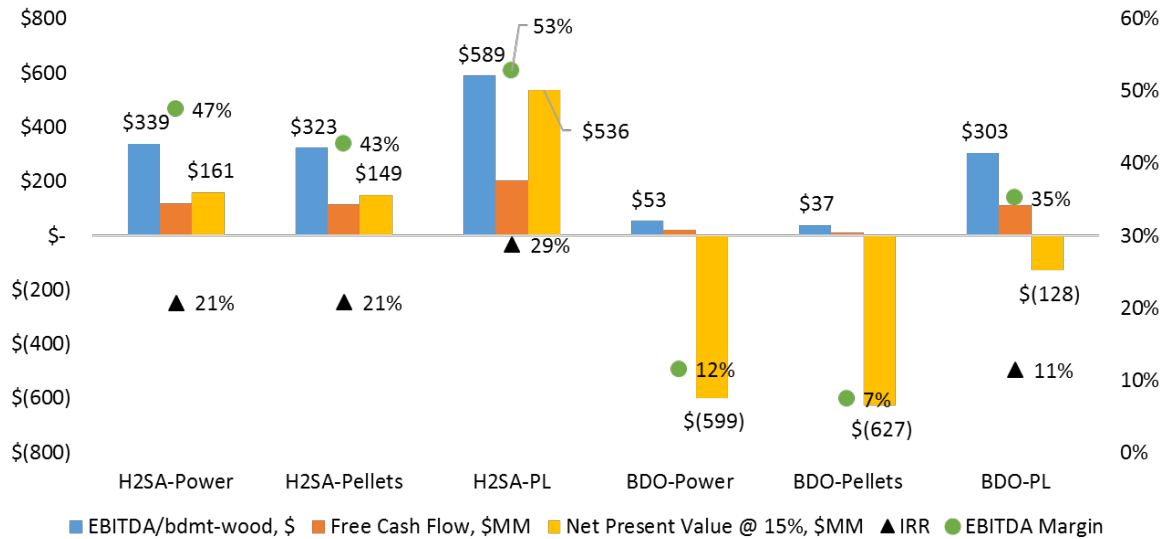


Figure 8-15: Key Performance Indicators for Greenfield Integrated Production

None of the greenfield 1,4 butanediol investment cases were determined to be economically feasible at an assumed market price of \$2,000/mt, although the additional free cash flow provided by phenolated lignin sales does result in 11% IRR. As shown in the Figure 8-16, the 1,4 butanediol-phenolated lignin scenario is improved significantly by applying the co-location and repurpose context assumptions, resulting in a 16% IRR - \$30 million NPV and 18% IRR - \$75 million NPV, respectively. On the other hand, the fuel pellet and power cases remained un-economical despite the same applied cost-savings. This suggests that an investment in a fully integrated 1,4 butanediol production system, co-located with a kraft pulp mill in order to use mixed southern hardwood as a feedstock, is likely not feasible for the assumed chemical prices, unless significant valorization of the lignin co-product can be realized. That is, combusting the lignin for process heat and power or even exporting it as a fuel pellet is not sufficient for the bio-refinery commercialization cases proposed in this study.

However, this does not suggest that higher value applications for the lignin, such as chemical modification, are absolutely necessary to justify bio-refinery investment, but lignin valorization most certainly will help to remove the price pressure from 1,4 butanediol sales. This provides a commercialization path for the proposed bio-refinery, where 1,4 butanediol can fulfill an immediate market need until the succinic acid market fully develops.

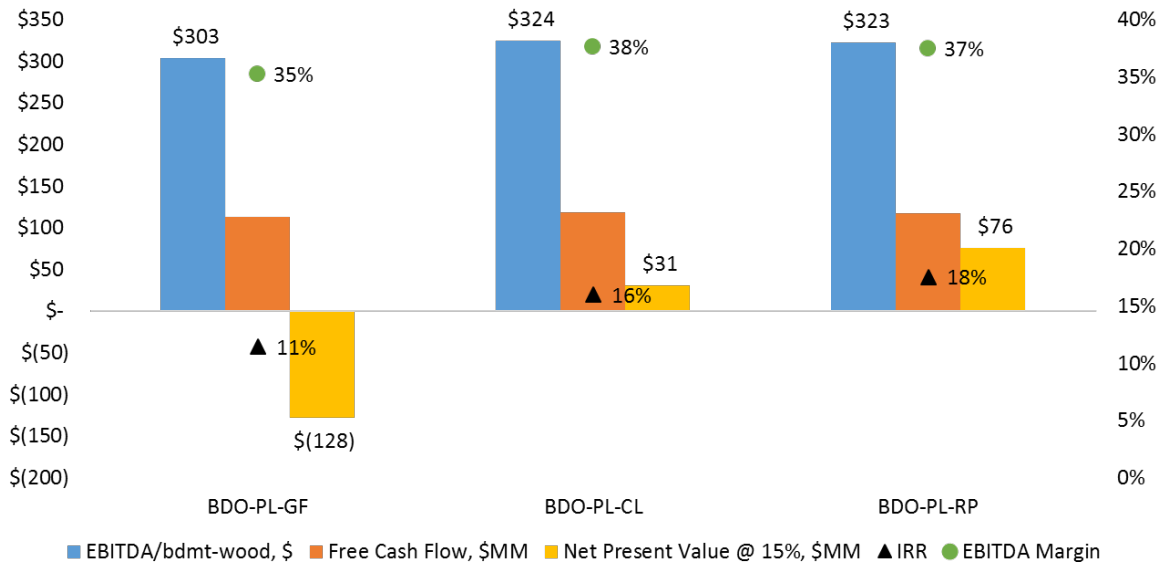


Figure 8-16: Key Performance Indicators for Integrated BDO-PL Production

As stated previously, the value proposition for an investment in a bio-refinery integrated with a kraft pulp mill presumes that the project will benefit from cost-advantaged mixed southern hardwoods with an established supply chain, opportunities for capital investment savings through utilization of existing assets, and opportunities for variable and fixed cost reduction through economies of scale (e.g. shared labor, utilities, etc.). Furthermore,

there may also be opportunities for receiving state and local incentives offered to avoid local unemployment with even a partial mill closure; as well as cost savings with respect to environmental permitting. This study determined that integrated bio-refinery investments may benefit from these assumptions, as shown in Table 8-21. Furthermore, the only commercially feasible scenario for cost-advantaged 1,4 butanediol was with an integrated bio-refinery where the lignin could be valorized with an additional phenolation system investment. MPR for these cases were determined to be lower than \$1900/mt. For the non-integrated 1,4 butanediol system, the MTP for succinic acid consumed was determined to be between \$695 to \$905/mt, significantly lower than a non-integrated succinic acid system's \$1,755/mt MPR. Lastly, an integrated bio-refinery producing succinic acid from mixed southern hardwoods exhibited MPR less than \$1,100/mt which is close to the \$905/mt MTP for succinic acid consumed by a non-integrated 1,4 butanediol system.

Table 8-21: MPR & MTP Results for Non-Integrated & Integrated Production

Non-Integrated Case Scenarios							
Product	Lignin Valorization	Context	IRR	NPV, \$MM	Market Price of Product	MPR @15%	Feedstock MTP @15%
Bio-Sugar	Power	GF	8%	-\$130	\$440	\$562	\$14
Bio-Sugar	Power	CL	23%	\$88	\$440	\$354	\$114
Bio-Sugar	Power	RP	32%	\$133	\$440	\$311	\$135
H2SA		GF	40%	\$333	\$2,400	\$1,755	\$880
H2SA		GF	15%	\$0	\$1,110	\$1,110	\$0
BDO		GF	--	-\$1,911	\$2,000	\$6,045	\$695
BDO		CL	--	-\$1,729	\$2,000	\$5,512	\$905
Integrated Case Scenarios							
H2SA	Power	GF	21%	\$161	\$2,400	\$2,068	\$160
H2SA	Power	CL	34%	\$387	\$2,400	\$1,669	\$265
H2SA	Power	RP	39%	\$430	\$2,400	\$1,594	\$285
H2SA	Pellets	GF	21%	\$149	\$2,400	\$2,088	\$155
H2SA	Pellets	CL	29%	\$294	\$2,400	\$1,834	\$222
H2SA	Pellets	RP	31%	\$321	\$2,400	\$1,786	\$234
H2SA	PL	GF	29%	\$536	\$2,400	\$1,376	\$342
H2SA	PL	CL	35%	\$689	\$2,400	\$1,107	\$413
H2SA	PL	RP	39%	\$733	\$2,400	\$1,031	\$433
BDO	Power	GF	--	-\$599	\$2,000	\$3,831	-\$167
BDO	Power	CL	-8%	-\$311	\$2,000	\$3,028	-\$62
BDO	Power	RP	-7%	-\$260	\$2,000	\$2,875	-\$42
BDO	Pellets	GF	--	-\$627	\$2,000	\$3,872	-\$172
BDO	Pellets	CL	--	-\$444	\$2,000	\$3,360	-\$105
BDO	Pellets	RP	--	-\$414	\$2,000	\$3,264	-\$93
BDO	PL	GF	11%	-\$128	\$2,000	\$2,437	\$15
BDO	PL	CL	16%	\$31	\$2,000	\$1,895	\$86
BDO	PL	RP	18%	\$76	\$2,000	\$1,741	\$106

8.6.6 Sensitivity Analysis

A simple sensitivity analysis was performed for the integrated bio-refinery producing succinic acid and phenolated lignin assuming a mill repurpose context. As shown in Figure 8-17, the process economics are most sensitive to succinic acid product price and yield. While it is tempting to surmise that decreases in product price may be offset with yield improvements, it is important to note that this study already assumes the best yields reported in the literature. Specifically, the 1.1 g/g substrate yield reported for *E. coli* requires additional CO₂ gas to boost the yield with CO₂ uptake which indicates the maximum carbon economy for the glucose substrate has been achieved. Any additional yields would require hydrogen gas as an additional hydrogen feedstock in order to redox balance the micro-organism for gas fermentation (Song & Lee 2005). This suggests that an upper limit has been achieved for glucose fermentation. Modification of the micro-organism in order to ferment xylose on the other hand remains a promising area of further research and development. Alternatively, the modeled carbohydrate conversion may be considered modest and due to the relatively insignificant impact from additional enzyme consumption, higher enzymes loading (e.g. 10 or 20 FPU/g substrate) may be warranted in order to maximize carbohydrate conversion of the mixed southern hardwood feedstock.

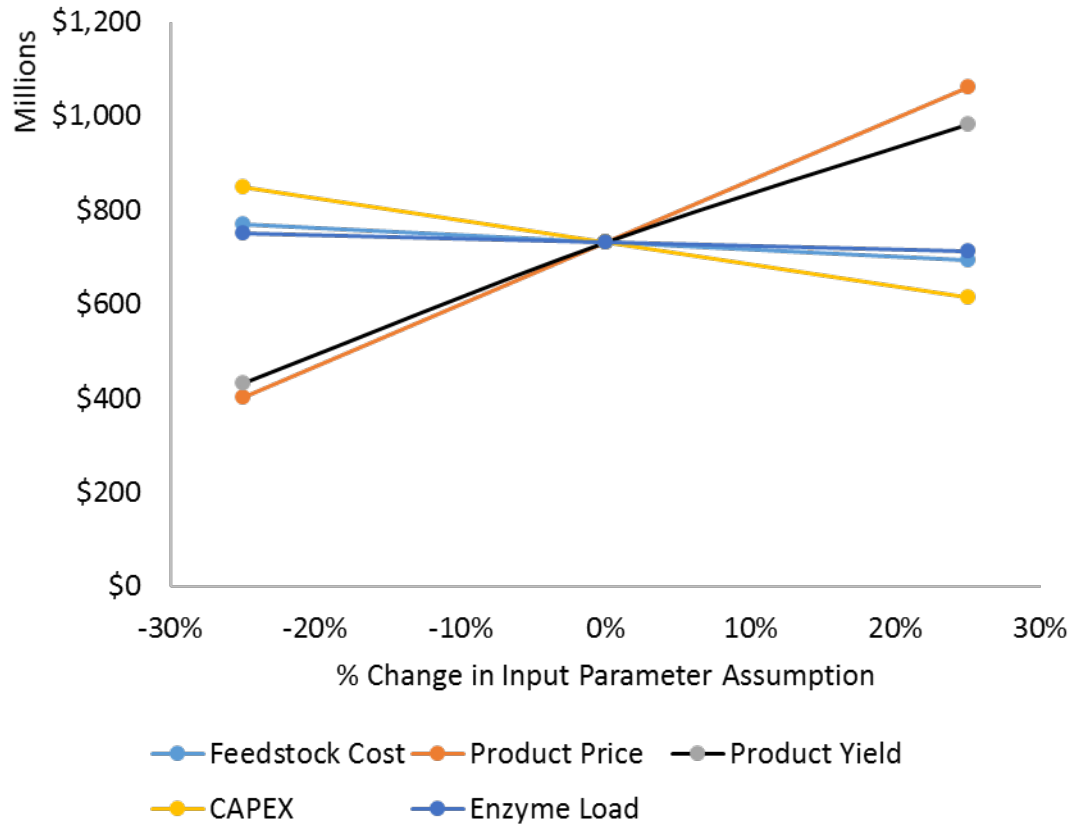


Figure 8-17: Sensitivity of Net Present Value (@15%) to % Changes in Input Parameters

The assumed market price for succinic acid of \$2,400/mt used in this study is not likely to see any price increases with commercialization since current market volumes are small (< 50,000 mt/yr), and the price may decrease well beyond 25%. Fortunately, the process economics were least sensitive to the capital investment and feedstock price and enzyme loading. This suggests that additional investments towards valorizing the lignin co-product may be worth the risk, especially if price volatility for succinic acid is anticipated. Also, additional investment towards the enzymatic hydrolysis and fermentation systems may be justified in order to further improve the process yields.

As shown in Figure 8-18, valorized lignin reduces the required price from bio-chemical sales for an equivalent project return. That is, in this example, the higher the sales price of phenolated lignin, the lower the required sales price from succinic acid and 1,4 butanediol. As suggested earlier, high elasticities of demand are anticipated for succinic acid sales at commercial scale considered in this analysis, which implies that prices for succinic acid may drop significantly as large quantities are brought to market. As this occurs, the valorization of lignin becomes imperative towards maintaining idea project returns. For example, if succinic acid sales drop from \$2400/mt to less than \$1000/mt, phenolated lignin must sell for at least \$1250/mt in order to maintain a 15% IRR. Similarly, if 1,4 butanediol prices were to drop below \$1000/mt, the phenolated lignin must sell for \$1500/mt or more.

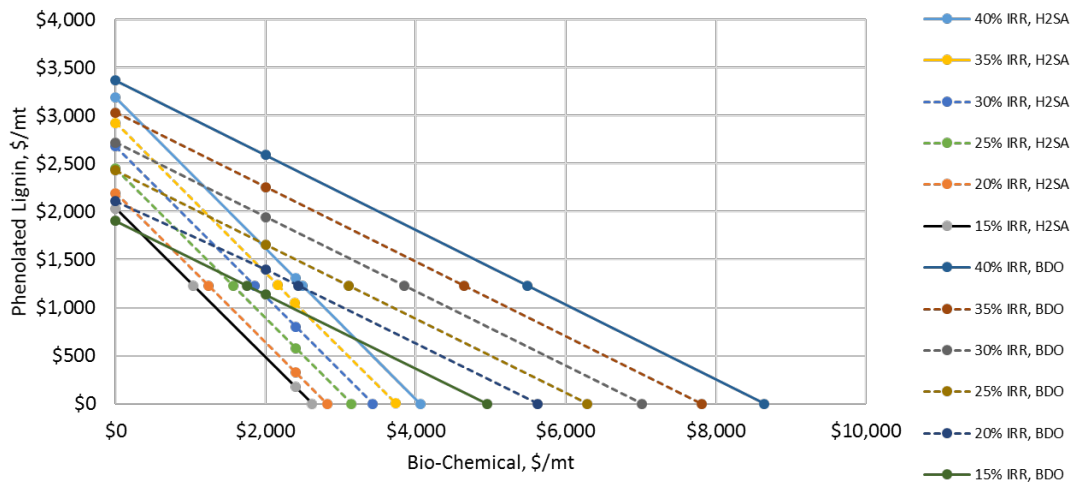


Figure 8-18: Integrated Bio-Refinery Parametric Chart

As stated previously, a significant item of the value-proposition for bio-refining in the pulp and paper industry maintains that the wood feedstock may be cost-advantaged to food-based sugars. Table 8-22 provides a summary of the impact historical price volatility may have on bio-chemical production from either feedstock. Again, an analysis of sugar futures (NYMEX, Sugar No.11) over the past 15 years exhibits an average sugar price of \$320/mt, with a standard deviation of \$140/mt, high of \$600/mt and an 80% probability of \$440/mt or less. By comparison, hardwoods exhibit an average price of \$70/bdmt, with a standard deviation of \$12/bdmt and an 80% probability of \$80/bdmt or less (RISI). While returns are favorable for the starch-based bio-refinery when considering a succinic acid price of \$2400/mt, the raw material price volatility of sugar has a significant effect on the MPR, and none of these cases achieve an MPR close to the \$1000/mt succinic acid transfer price required for a non-integrated 1,4 butanediol plant (as previously discussed). By comparison, the integrated pulp and paper bio-refinery that processes mixed southern hardwoods may experience significantly less variability with succinic acid MPR ranging from \$1030 to \$1110/mt. Furthermore, the total opportunity as measured by NPV is significantly higher for the integrated bio-refinery due to the co-product revenue from phenolated lignin (\$700 million as opposed to \$430 million with the non-integrated starch-based bio-refinery).

Table 8-22: Bio-Refinery Returns with Raw Material Price Volatility Considered

Context	Integrated Bio-Refinery, H2SA-PH-RP			Non-Integrated, H2SA-GF, from Sugar		
Feedstock Cost, \$/mt	\$70	\$82	\$58	\$320	\$460	\$180
IRR	39%	37%	39%	46%	39%	52%
Net Present Value @ 15%, \$MM	\$733	\$688	\$738	\$428	\$317	\$540
MPR @ 15%	\$1,031	\$1,112	\$1,020	\$1,579	\$1,784	\$1,374

Sensitivity to the maximum and minimum input parameter assumptions for the integrated bio-refinery producing succinic acid at a repurposed kraft pulp mill was considered. As shown in Figure 8-19, the importance of H₂SA and phenolated lignin price (i.e. lignin valorization) as key economic drivers are clearly indicated, and it is suggested that development efforts towards improving fermentation yields and lignin valorization may be important efforts towards offsetting the loss of returns due to succinic acid price reduction at commercial scale. Also, the negative impacts associated with cost overruns and delays in reaching production capacity are also important, and it is suggested that co-locating bio-refinery projects that leverage existing capabilities within the pulp and paper industry may help to significantly reduce time-to-revenue and improve project returns. Lastly, the bio-refinery project is only moderately impacted by dramatic fluctuations in feedstock price, which further underscores the value-proposition for utilizing abundant, sustainably forested North American wood feedstocks.

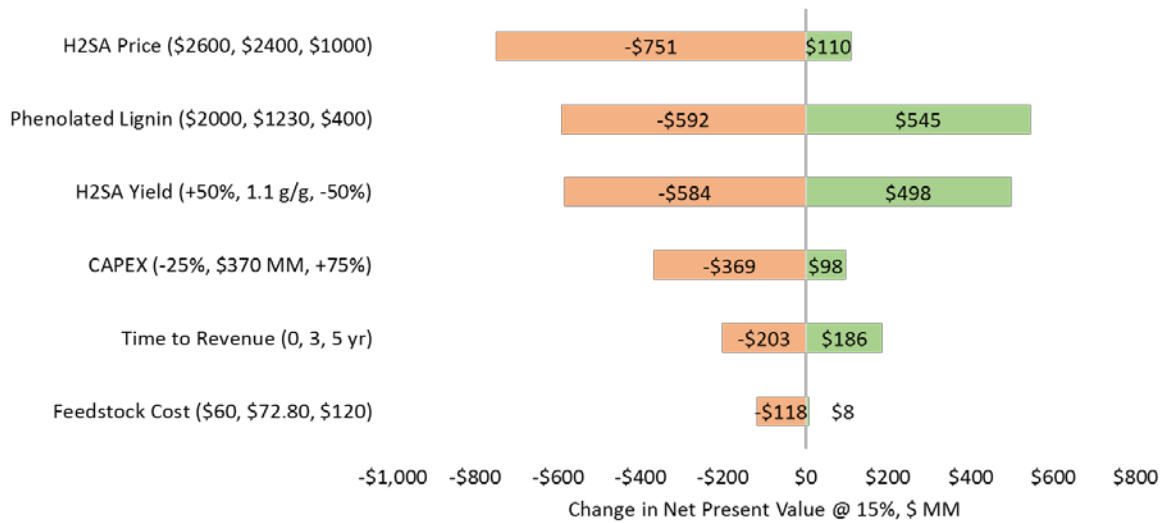


Figure 8-19: Sensitivity to Bio-Refinery Maximum & Minimum Input Parameters

8.7 Conclusions

The objective of this study was to explore the economic opportunity and feasibility of fermenting lignocellulosic, or “biorefinery”, sugars to succinic acid. Specifically, the proposed value proposition for biorefining in the pulp and paper industry was based on three assumptions: first, that existing assets may be used in order to reduce the required capital investment, second, that the biomass utilized in the process is cost-advantaged to current commodity, or “1st generation”, food-based sugars, and third, that there may be opportunities for variable and fixed cost reduction through economies of scale (e.g. shared labor, utilities, etc.). The scope of this analysis spanned the gate-to-gate production of succinic acid produced from wood chips, with mixed southern hardwood chips received and stored at the bio-refinery at a capacity of 500,000 “bone-dry” metric tons (bdmt) per year.

Using previously reported literature data and process modeling, this TEA study attempted to quantify the MPR, MTP and incremental EBITDA for succinic acid with respect to multiple, feasible process case scenarios. For the case scenarios identified, succinic acid can be manufactured and sold to an open market, or exported directly to a known off-taker with MPR as low as \$1,100/mt (e.g. towards 1,4 BDO production) when assuming a co-location or repurpose scenario. None of the greenfield 1,4 butanediol investment cases were determined to be economically feasible at an assumed market price of \$2,000/mt of 1,4 BDO, although the additional free cash flow provided by phenolated lignin sales does result in 11% IRR. Integrated production of 1,4 butanediol and phenolated lignin when co-located with or repurposing a pulp mill resulted in 16% IRR-\$31 million NPV and 18% IRR-\$76 million NPV. MPR for 1,4 butanediol produced with these assumptions was less than \$1,900/mt, or below the assumed market price.

Combusting the lignin for process heat and power or even exporting it as a fuel pellet was not considered sufficient for the bio-refinery commercialization cases proposed in this study. Investment in lignin valorization technology was suggested as a promising commercialization path for the proposed bio-refinery, where initial 1,4 butanediol sales are required to fulfill an immediate market need until the succinic acid market fully develops. Furthermore, additional investments towards valorizing the lignin co-product may be worth the risk, especially if price volatility for succinic acid is anticipated. Lastly, the literature suggests that an upper limit has been achieved for glucose fermentation to succinic acid at laboratory scale. Modification of the micro-organism in order to ferment xylose on the other hand remains a promising area of further research and development.

9 CONCLUSIONS

It is suggested that bio-refinery concepts that rely on the combustion, or fuel-value, of the lignin may not result in sufficient financial returns to justify the capital investment required for a proposed bio-refinery. Therefore, the first part of this research concerned the extraction, fractionation, characterization and valorization of kraft lignin and bio-refinery lignin residues. As indicated by the first four studies, a key advantage of bio-refining lignocellulosic feedstocks may be the opportunity to valorize the lignin co-product.

The second part of this research focuses on opportunities for integrating bio-refineries that produce value-added chemicals, as opposed to bio-fuels such as ethanol, from forest-based resources such as mixed southern hardwoods instead of 1st generation, food-based sugars and incorporates findings from the analysis of lignin extraction and valorization. The proposed value proposition for biorefining in the pulp and paper industry was based on three assumptions: first, that existing assets may be used in order to reduce the required capital investment required, second, that the biomass utilized in the process is cost-advantaged to current commodity, or “1st generation”, food-based sugars, and third, that there may be opportunities for variable and fixed cost reduction through economies of scale (e.g. shared labor, utilities, etc.). The scope of this work spanned the gate-to-gate production of extracted kraft lignin and succinic acid produced from wood chips, with mixed southern hardwood chips received and stored at the bio-refinery at a capacity of 500,000 “bone-dry” metric tons (bdmt) per year. The summary of this work, as shown in Table 9-1, quantifies the value proposition for bio-refining in the pulp and paper industry and identifies the context and economic drivers whereby commercial success (or profitability) may be achieved.

Table 9-1: Summary of Pulp & Paper Industry Bio-Refinery Project Key Financial Indicators

Product	Lignin Valorization	Context	IRR	NPV, \$MM	MPR @15%	EBITDA/mt-wood
Inc. SBSK	Pellets	CL	34%	\$34	\$74	\$192
Inc. SBHK	Pellets	CL	31%	\$27	\$104	\$184
Inc. 42 Lb. Liner	Pellets	CL	42%	\$60	-\$22	\$160
Bio-Sugar	Power	RP	32%	\$133	\$311	\$135
H2SA	Power	RP	39%	\$430	\$1,594	\$285
H2SA	Pellets	RP	31%	\$321	\$1,786	\$234
H2SA	PL	RP	39%	\$733	\$1,031	\$433
BDO	PL	RP	18%	\$76	\$1,741	\$106

9.1.1 TEA & LCA of Lignin Extraction in a Kraft Pulp Mill

Lignin extraction with a production capacity of 150 admt/day kraft lignin was determined to be a promising bio-refinery project, provided careful attention is given to the recovery boiler limiting assumptions. After the lignin is precipitated, the dilute black liquor is returned to the evaporators and additional inorganics solids loading may be experienced throughout the pulp mill chemical recovery loop. In all cases, lignin extraction without incremental pulp production resulted in negative project returns, and minimum product revenue (MPR) required for the lignin sales price was determined to be \$446 to \$471/admt for the fuel pellet scenarios. This suggests that significant valorization of the lignin may be necessary in order to justify a lignin extraction capital investment project without increases to incremental pulp production. The NPV for the various case scenarios were improved considerably with increases to pulp production, but the project returns were determined to be highly sensitive to the recovery boiler limiting assumptions which determines the amount of

increased pulp. For the SBSK case scenarios with lignin exported as fuel pellets, the project returns resulted in a favorable \$6 million and \$34 million NPV (16% and 34% IRR, respectively). For the SBHK and 42lb Liner case scenarios, only cases with a recovery boiler steam limiting assumption resulted in a positive project returns. For the SBHK cases, the project returns resulted in \$27 million NPV when the lignin was sold as a fuel pellet and \$24 million NPV when consumed on-site as lime kiln fuel (31% and 35% IRR, respectively). For the 42lb Liner case scenarios, the project returns resulted in \$60 million NPV when the lignin was sold as a fuel pellet and \$52 million NPV when consumed on-site as lime kiln fuel (42% and 46% IRR, respectively).

The project returns for lignin extraction were determined to be most sensitive to achievable incremental pulp production and the pulp market price, and by comparison, the key financial indicators were considerably less sensitive to the lignin sales price and capital investment required for lignin extraction. Furthermore, the maximum incremental EBITDA per mt-wood was determined to be between \$160 to \$190/bdmt. This suggests that additional capital investment towards improving production capacity may be warranted in order to achieve the incremental pulp production increases necessary for an adequate project return

The environmental impacts associated with lignin extraction were also considered and using system expansion, the simulated kraft pulp mill system was observed as having reduced environmental impact with the addition of a lignin co-product in part due to reduced stack emissions from the recovery boiler as a result of fewer combusted organics. Commercial lignin extraction was shown to have the potential to demonstrate marked improvement for the reduction of environmental impacts at the kraft pulp mill. From this study, it was determined

that this reduction with the addition of lignin extraction is achieved by reducing fossil fuel and raw material (chemical) consumption at the mill per unit of SBSK pulp produced.

The results for the environmental burdens of a lignin biopolymer produced from lignin extraction at a kraft pulp mill when using mass allocation were shown to be significantly less when compared with potential high value products such as phenolic resin or acrylonitrile monomers. This suggests that lignin is a sustainable bio-material. A hot spot analysis of the kraft pulp mill was also performed, and sodium chlorate used for chlorine dioxide generation and natural gas used in the lime kiln were shown to be significant contributors to overall mill environmental burdens. These were identified as key levers for reducing kraft pulp mill environmental burdens.

9.1.2 Fractionation, Modification & Valorization of Lignin

Both kraft lignin and “bio-refinery” lignin residue was analyzed for thermal properties with respect to molecular weight fractions. Thermal stability (as measured by mass loss and decomposition activation energies) was shown to decrease with decreasing molecular weight. Low molecular weight fractions of softwood kraft lignin exhibited the lowest glass transition temperatures between 69 to 86 °C, while maintaining good thermal stability up to 220 °C. Glass transition temperatures as low as 94 °C were observed for low molecular weight hardwood kraft lignin, while also maintaining good thermal stability. The “bio-refinery” lignin residue fractions showed only slight decreases in glass transition temperature, while suffering from poor thermal stability at temperature below 190 °C. Decomposition energies for both softwood and hardwood kraft lignin were shown to be similar at 40 kJ/mol, while bio-refinery lignin fractions were shown as having energies as low as 11 kJ/mol at 300 °C.

The whole lignin fractions appear to exhibit simple linear mixing rules for their constituent parts and only slight interactions resulting from thermally induced crosslinking were observed based on rise of glass transition temperatures upon subsequent reheating above the glass transition temperature, which suggests that small molecular weight fractions may impart some plasticizing effect to the whole lignin fraction. This is important when considering the design and operation of lignin processing unit operations.

For example, when phenolating the lignin via acid catalysis, careful attention must be given to the process parameters and capital equipment selection in order to avoid over-heating the lignin product. A conceptual lignin phenolation process based on acid catalysis of kraft lignin or bio-refinery lignin residue was modeled, and the goal of lignin phenolation is to improve its reactivity and ultimately improve product properties with increased lignin substitution of phenol in phenol formaldehyde (PF) resin systems. Again, the value proposition assumes that PF resin customers will pay an equivalent price (\$1200/mt), based on substituted phenol) for cost advantaged phenolated lignin, assuming no compromise to product performance is experienced, and at a reference capacity of 175,000 mt/yr phenolated lignin, the expected project returns may be \$48 million NPV and 18% IRR.

9.1.3 Screening Opportunities for Forest-Based Bio-Chemicals

An exhaustive literature review revealed over thirty potential bio-chemicals and conversion technologies which may be applied towards converting forest biomass to value-added products, and a simple new product development screening tool helped to determine which candidates justify commercialization. It was shown that bio-chemicals with potential revenue received for converting one unit of biomass that are less than the market price of the

raw material (assumed \$70 per bdmt for mixed hardwoods) can be removed from immediate consideration until the market price for the raw material plummets, the value of a specific chemical increases considerably, or microorganism or catalyst technology advances to allow an effective yield to approach or achieve the maximum theoretical yield. Fermentation technology for the efficient production of succinic acid was determined to be the most promising of bio-chemical candidates for commercialization over the short-term.

9.1.4 Sustainable Succinic Acid & Phenolated Lignin Production from a Bio-Refinery Integrated with an Existing Kraft Pulp Mill

For a bio-refinery co-located with an existing kraft pulp and paper mill, succinic acid can be manufactured and sold to an open market, or exported directly to a known off-taker with MPR as low as \$1,100/mt (e.g. towards 1,4 BDO production) when assuming a co-location or repurpose scenario. Integrated production of 1,4 butanediol and phenolated lignin when co-located with or repurposing a pulp mill resulted in 16% IRR-\$31 million NPV and 18% IRR-\$76 million NPV. MPR for 1,4 butanediol produced with these assumptions was less than \$1,900/mt, or below the assumed market price. The key levers for this bio-refinery process were the optimization of costs and capital investment reduction when co-locating with or repurposing the pulp and paper mill, and a critical element to this value-proposition was the price stability of North American biomass (e.g. mixed southern hardwoods) relative to 1st generation, or food-based, sugar feedstocks

Another important lever for implementing an economically feasible bio-refinery was the treatment of potentially valuable lignin residue co-products. Combusting the lignin for process heat and power or even exporting it as a fuel pellet was not considered sufficient for

the bio-refinery commercialization cases proposed in this study. Investment in lignin valorization technology was suggested as a promising commercialization path for the proposed bio-refinery, where initial 1,4 butanediol sales are required to fulfill an immediate market need until the succinic acid market fully develops. Furthermore, additional investments towards valorizing the lignin co-product may be worth the risk, especially if price volatility for succinic acid is anticipated.

10 FUTURE WORK

Two of the primary economic drivers for bio-refining projects in the pulp and paper industry identified in this work were the valorization of bio-refinery lignin residues and the fermentation of ligno-cellulosic sugars to value-added products. Therefore, additional research towards valorizing the lignin co-product is recommended, especially if price volatility for succinic acid is anticipated, and modification of micro-organisms in order to ferment xylose remains a promising area of further research and development.

Specifically, alkylation or esterification of the lignin towards stabilizing free-radical content responsible for thermally induced cross-linking may be of interest (Calvo-Flores 2010). For example, propoxylation has been shown to significantly improve thermoplasticity of the lignin (Glasser & Leitheiser 1984). Similar technologies that employ the use of this technique to modify and stabilize lignin, which is then blended with commodity polymers (e.g. polyethylene, polypropylene, etc.), has been shown to improve product performance and biodegradability (Cyclewood). It is believed that continued product and research development aimed towards meeting the enduring customer needs of superior product attributes and improved environmental life-cycle performance is imperative towards the successful commercialization of bio-refinery technology in the pulp and paper industry.

Separation and purification of xylose and other non-glucose monomeric sugars found in wood hemi-cellulose (e.g. mannose, etc) is another area of research and development worth considering, both for improved fermentation systems and commercialization of the sugars alone. While co-fermentation is feasible, it may be desirable to engineer and optimize micro-organisms to ferment xylose alone. The alternative is co-fermentation with a micro-organism

known to ferment wood hydrolysates, such as *M. succiniciproducens* (Song & Lee 2005), or fermentation with an engineered consortium (i.e. various, unique micro-organism that ferment specific substrates) that is optimized for the mixed sugar substrate (Xia et al 2012).

However, if the xylose is separated and purified to a “water-white” product, additional market opportunities may exist for a highly sought after sugar product that is currently unfulfilled. For example, xylose may be easily converted to xylitol, a well-known low calorie sweetener that does not compromise with respect to taste performance, and this product may see increasing demand given the recent announcement between S2G Biochem and Mondelez towards commercialization of xylitol and other bio-based glycols produced from lignocellulosic sugars (S2G Biochem).

To summarize, lignin valorization and purification of monomeric wood sugars are two areas of research and development that may greatly benefit bio-refining for the pulp and paper industry. Improvements with respect to each area provide additional levers whereby pressure may be applied to improve the competitiveness and economic feasibility of major bio-refining capital investment projects, the result of which may help to realize long-term and sustainable growth in the pulp and paper industry.

11 REFERENCES

1. Axelsson, E., Olsson, M. R., & Berntsson, T., “Increased capacity in kraft pulp mills: Lignin separation and reduced steam demand compared with recovery boiler upgrade”, *Nordic Pulp and Paper Research Journal*, 21(04), 485 – 492 (2006).
2. Wallmo, H., Richards, T., & Theliander, H., “An investigation of process parameters during lignin
3. precipitation from kraft black liquors: A step towards an optimised precipitation operation.” *Nordic Pulp and Paper Research Journal*, 24(02), 158-164 (2009).
4. Alen, R., Patja, P., & Sjostrom, E., “Carbon dioxide precipitation of lignin from pine kraft black liquor.” *Tappi*, 62(11), 108-110 (1979).
5. Whalen, D. M., “Simple method for precipitating easily filterable acid lignin from kraft black liquor.” *Tappi Journal*, 58(5), 110-112 (1975).
6. Perin-Levasseur, Z., Savulescu, L., & Benali, M., “Lignin production path assessment: Energy, water, and chemical integration perspective.” *Journal of Science and Technology for Forest Products and Processes*, 1(3), 25-30 (2011).
7. Moosavifar, A., Sedin, P., & Theliander, H., “Viscosity and boiling point elevation of black liquor: Consequences when lignin is extracted from the black liquor.” *Nordic Pulp & Paper Research Journal*, 21(2), 180-187 (2006).
8. Kannangara, M., Marinova, M., Fradette, L., & Paris, J., “Lignin recovery by acid precipitation in a kraft mill: An energy perspective.” Paper presented at the , 2. (4) pp. 28-32 (2012).

9. Olsson, M. R., Axelsson, E., & Berntsson, T., "Exporting lignin or power from heat-integrated kraft pulp mills: A techno-economic comparison using model mills." *Nordic Pulp and Paper Research Journal*, 21(04), 476-484 (2006).
10. Gullichsen, Symposium on the Recovery of Pulping Chemicals, Helsinki, May 13-17 (1968) 211-234
11. Maki, K., Holt-Hindle, P., Kouisni, L., & Paleologou, M., "The FPInnovations lignin demonstration plant: Process description and lignin products." Paper presented at the 2012 TAPPI PEERS Conference: Building a Sustainable Future, October 14, 2012 - October 18, pp. 707-715 (2012).
12. Kouisni, Lamfeddal, et al. "Kraft lignin recovery and its use in the preparation of lignin-based phenol formaldehyde resins for plywood." *Cellulose Chemistry and Technology* 45.7, 515 (2011).
13. Ulrich, G. D., "A guide to chemical engineering process design and economics" (VIII ed.). New York: Wiley (1984).
14. Kleppe, P. J. (1970). Kraft pulping. *Tappi*, 53(1), 35-47.
15. Valmet (2016). "LignoBoost-lignin from pulp mill black liquor." Retrieved from <http://www.valmet.com/products/pulping-and-fiber/chemical-recovery/lignin-separation/>
16. NORAM (2016). "LignoForce Process." Retrieved from <http://www.noram-eng.com/news-room/lignoforce.html>
17. Marshall & Swift, "Marshall & swift cost index." Unpublished manuscript (2013).

19. Phillips R. Lignin filter. Factored vendor quote. Confidential (2010).
20. Peters, Max Stone, et al. "Plant design and economics for chemical engineers." Vol. 4. New York: McGraw-Hill (1968).
21. Pirraglia, Adrian, Ronalds Gonzalez, and Daniel Saloni. "Techno-economical analysis of wood pellets production for US manufacturers." *BioResources* 5.4, 2374-2390 (2010).
22. ICIS Chemical Business (2014). Indicative Chemical Prices A-Z. Retrieved from <http://www.icis.com/chemicals/channel-info-chemicals-a-z/>.
23. U.S. Energy Information Administration (2014). Historical Natural Gas Futures. Retrieved from <http://www.eia.gov/dnav/ng/hist/rngc1d.htm>.
24. World Freight Rates (2014). Freight Calculator. Retrieved from <http://worldfreightrates.com/freight>.
25. Doty Energy (2011). Commercial CO2 Market Today. Retrieved from http://dotyenergy.com/Economics/Econ_Physical_CO2_Market.htm.
26. Pellet Fuels Institute (2014). Compare Fuel Costs. Retrieved from <http://pelletheat.org/pellets/compare-fuel-costs/>.
27. RISI's Pulp & Paper Week (2014). Price Watch. Retrieved from <http://www.risiinfo.com/pages/product/pulp-paper/market-prices.jsp>.
28. Axelsson, E., Olsson, M. R., & Berntsson, T. (2006). Increased capacity in kraft pulp mills: Lignin separation and reduced steam demand compared with recovery boiler upgrade *Nordic Pulp and Paper Research Journal*, 21(04), 485 - 492. doi:10.3183/NPPRJ-2006-21-04-p485-492

29. Baker, D. A., & Rials, T. G. (2013). Recent advances in low-cost carbon fiber manufacture from lignin. *Journal of Applied Polymer Science*, 130(2), 713-728. doi:10.1002/app.39273
30. Bernier, E., Lavigne, C., & Robidoux, P. (2013). Life cycle assessment of kraft lignin for polymer applications. *The International Journal of Life Cycle Assessment*, 18(2), 520-528. doi:10.1007/s11367-012-0503-y
31. Brander, M., & Wylie, C. (2011). The use of substitution in attributional life cycle assessment. *Greenhouse Gas Measurement & Management* 1 (3 – 4), 161-166
32. Daystar, J., Reeb, C., Venditti, R., Gonzalez, R., & Puettmann, M.E. (2012). Life-Cycle Assessment of Bioethanol from Pine Residues via Indirect Biomass Gasification to Mixed Alcohols. *Forest Products Journal* 62 (4), 314-325
33. Gaudreault, C. (2014). Pulp, kraft market, bleached, average production. NREL LCA Commons V2.0, www.lcacommons.gov
34. Gonzalez-Garcia, S., Hospido, A., Moreira, M.T., Romero, J., & Feijoo, G. (2009). Environmental impact assessment of total chlorine free pulp from *Eucalyptus globulus* in Spain. *Journal of Cleaner Production* 17, 1010-1016
35. Gullichsen (1968). Symposium on the Recovery of Pulping Chemicals, Helsinki, May 13-17 (1968) 211-234
36. ICIS Chemical Business (2014). Indicative Chemical Prices A-Z. Retrieved from <http://www.icis.com/chemicals/channel-info-chemicals-a-z/>.

37. Jungmeier, G., Werner, F., Jarnehammar, A., Hohenthal, C., & Richter, K. (2002). Allocation in LCA of Wood-based Products. *International Journal of LCA* 7 (5), 290 - 294
38. Kadla, J. F., Kubo, S., Venditti, R. A., & Gilbert, R. D. (2002). Novel hollow core fibers prepared from lignin polypropylene blends. *Journal of Applied Polymer Science*, 85(6), 1353-1355. doi:10.1002/app.10640
39. Kouisni, L., Fang, F., Paleologou, M., Ahvazi, B., Hawari, J., Zhang, Y., & Wang, X. (2011). Kraft lignin recovery and its use in the preparation of lignin-based phenol formaldehyde resins for plywood. *Cellulose Chemistry and Technology* 45(7), 515-520
40. Maki, K., Holt-Hindle, P., Kouisni, L., & Paleologou, M. (2012). The FPInnovations lignin demonstration plant: Process description and lignin products. Paper presented at the 2012 TAPPI PEERS Conference: Building a Sustainable Future, October 14, 2012 - October 18, pp. 707-715.
41. Nagy, M., Kosa, M., Theliander, H., & Ragauskas, A. J. (2010). Characterization of CO₂ precipitated kraft lignin to promote its utilization. *Green Chemistry*, 12(1), 31-34. doi:10.1039/B913602A
42. Pellet Fuels Institute (2014). Compare Fuel Costs. Retrieved from <http://pelletheat.org/pellets/compare-fuel-costs/>.
43. Rehnstrom, C. (2003). LCA of two chemical recovery processes in the pulp industry - a case study. *Nordic Pulp and Paper Research Journal*, 18(03), 344-354.
45. RISI's Pulp & Paper Week (2014). Price Watch. Retrieved from <http://www.risiinfo.com/pages/product/pulp-paper/market-prices.jsp>.

46. Weidema, B.P., Frees, N., & Nielsen, A., (1999). Marginal Production Technologies for Life Cycle Inventories. *International Journal of Life Cycle Assessment*, 4 (1), 48-56
47. Boerjan, W., Ralph, J., & Baucher, M. (2003). Lignin biosynthesis. *Annual review of plant biology*, 54(1), 519-546.
48. Heitner, C., Dimmel, D., & Schmidt, J. (Eds.). (2016). *Lignin and lignans: advances in chemistry*. CRC press.
49. Rødsrud, G., Lersch, M., & Sjöde, A. (2012). History and future of world's most advanced biorefinery in operation. *Biomass and bioenergy*, 46, 46-59.
50. Lindner, A., & Wegener, G. (1988). Characterization of lignins from organosolv pulping according to the organocell process PART 1. Elemental analysis, nonlignin portions and functional groups. *Journal of Wood Chemistry and Technology*, 8(3), 323-340.
51. Lora, J. H., & Aziz, S. (1985). Organosolv pulping: a versatile approach to wood refining. *Tappi;(United States)*, 68(8).
52. Humbird, D., Davis, R., Tao, L., Kinchin, C., Hsu, D., Aden, A., ... & Sexton, D. (2011). Process design and economics for biochemical conversion of lignocellulosic biomass to ethanol: dilute-acid pretreatment and enzymatic hydrolysis of corn stover (No. NREL/TP-5100-47764). National Renewable Energy Laboratory (NREL), Golden, CO.

53. Cui, C., Sadeghifar, H., Sen, S., & Argyropoulos, D. S. (2013). Toward thermoplastic lignin polymers; part II: thermal & polymer characteristics of kraft lignin & derivatives. *BioResources*, 8(1), 864-886.
54. Saito, T., Perkins, J. H., Vautard, F., Meyer, H. M., Messman, J. M., Tolnai, B., & Naskar, A. K. (2014). Methanol fractionation of softwood kraft lignin: Impact on the lignin properties. *ChemSusChem*, 7(1), 221-228.
55. Cui, C., Sun, R., & Argyropoulos, D. S. (2014). Fractional precipitation of softwood kraft lignin: isolation of narrow fractions common to a variety of lignins. *ACS Sustainable Chemistry & Engineering*, 2(4), 959-968.
56. Tolbert, A., Akinosho, H., Khunsupat, R., Naskar, A. K., & Ragauskas, A. J. (2014). Characterization and analysis of the molecular weight of lignin for biorefining studies. *Biofuels, Bioproducts and Biorefining*, 8(6), 836-856.
57. Leskinen, T., Kelley, S. S., & Argyropoulos, D. S. (2015). Refining of Ethanol Biorefinery Residues to Isolate Value Added Lignins. *ACS Sustainable Chemistry & Engineering*, 3(7), 1632-1641.
58. Moynihan, C. T., Easteal, A. J., Wilder, J., & Tucker, J. (1974). Dependence of the glass transition temperature on heating and cooling rate. *The journal of physical chemistry*, 78(26), 2673-2677.
59. Murugan, P., Mahinpey, N., Johnson, K. E., & Wilson, M. (2008). Kinetics of the pyrolysis of lignin using thermogravimetric and differential scanning calorimetry methods. *Energy & Fuels*, 22(4), 2720-2724.

60. Lu, X., & Weiss, R. A. (1992). Relationship between the glass transition temperature and the interaction parameter of miscible binary polymer blends. *Macromolecules*, 25(12), 3242-3246.
61. Ayoub, A., Venditti, R. A., Jameel, H., & Chang, H. M. (2014). Effect of irradiation on the composition and thermal properties of softwood kraft lignin and styrene grafted lignin. *Journal of Applied Polymer Science*, 131(1).
62. Venditti, R. A., & Gillham, J. K. (1997). A relationship between the glass transition temperature (T_g) and fractional conversion for thermosetting systems. *Journal of applied polymer science*, 64(1), 3-14.
63. Wang, C., & Venditti, R. A. (2015). UV Cross-Linkable Lignin Thermoplastic Graft Copolymers. *ACS Sustainable Chemistry & Engineering*, 3(8), 1839-1845.
64. Kadla, J. F., & Kubo, S. (2004). Lignin-based polymer blends: analysis of intermolecular interactions in lignin–synthetic polymer blends. *Composites Part A: Applied Science and Manufacturing*, 35(3), 395-400.
65. Wang, C., Kelley, S. S., & Venditti, R. A. (2016). Lignin-Based Thermoplastic Materials. *ChemSusChem*, 9(8), 770-783.
66. Smook, G. A., & Kocurek, M. J. (1982). *Handbook for pulp & paper technologists*. TAPPI; Canadian Pulp and Paper Association.
67. Li, H., & McDonald, A. G. (2014). Fractionation and characterization of industrial lignins. *Industrial Crops and Products*, 62, 67-76.
68. Schorr, D., Diouf, P. N., & Stevanovic, T. (2014). Evaluation of industrial lignins for biocomposites production. *Industrial Crops and Products*, 52, 65-73.

69. C. Rolando, B. Monties, C. Lapierre, in: S.Y. Lin, C.W. Dence (Eds.), *Methods in Lignin Chemistry*, Springer, Berlin, 1992, p. 334.
70. Lignin Chemistry, Springer, Berlin, 1992, p. 334.
71. G.M. Nicolaidis, PhD University of Waterloo, CAN, 1984.
72. Poursorkhabi, V., Misra, M., & Mohanty, A. K. (2013). Extraction of lignin from a coproduct of the cellulosic ethanol industry and its thermal characterization. *BioResources*, 8(4), 5083-5101.
73. Gordon, M., & Taylor, J. S. (1952). Ideal copolymers and the second-order transitions of synthetic rubbers. I. Non-crystalline copolymers. *Journal of Applied Chemistry*, 2(9), 493-500.
74. Pucciariello, R., Villani, V., Bonini, C., D'Auria, M., & Vetere, T. (2004). Physical properties of straw lignin-based polymer blends. *Polymer*, 45(12), 4159-4169.
75. Jeong, H., Park, J., Kim, S., Lee, J., Ahn, N., & Roh, H. G. (2013). Preparation and characterization of thermoplastic polyurethanes using partially acetylated kraft lignin. *Fibers and Polymers*, 14(7), 1082-1093.
76. Luong, N. D., Binh, N. T. T., Park, I. K., Lee, S. H., Kim, D. S., Lee, Y. S., ... & Yun, J. H. (2013). Chemical and rheological characteristics of thermally stable kraft lignin polycondensates analyzed by dielectric properties. *BioResources*, 8(3), 4518-4532.
77. Kubo, S., & Kadla, J. F. (2005). Hydrogen bonding in lignin: a Fourier transform infrared model compound study. *Biomacromolecules*, 6(5), 2815-2821.
78. Wisanrakkit, G., & Gillham, J. K. (1990). The glass transition temperature (T_g) as an index of chemical conversion for a high-T_g amine/epoxy system: chemical and

- diffusion-controlled reaction kinetics. *Journal of Applied Polymer Science*, 41(11-12), 2885-2929.
79. Brodin, I., Sjöholm, E., & Gellerstedt, G. (2010). The behavior of kraft lignin during thermal treatment. *Journal of Analytical and Applied Pyrolysis*, 87(1), 70-77.
80. Fenner, R. A., & Lephardt, J. O. (1981). Examination of the thermal decomposition of kraft pine lignin by Fourier transform infrared evolved gas analysis. *Journal of agricultural and food chemistry*, 29(4), 846-849.
81. Schuerch, C. (1952). The solvent properties of liquids and their relation to the solubility, swelling, isolation and fractionation of lignin. *Journal of the American Chemical Society*, 74(20), 5061-5067.
82. Hildebrand, J. H., & Scott, R. L. (1950). *Solubility of Nonelectrolytes* Reinhold Pub. Co., New York, 3.
83. Duval, A., Vilaplana, F., Crestini, C., & Lawoko, M. (2016). Solvent screening for the fractionation of industrial kraft lignin. *Holzforschung*, 70(1), 11-20.
84. Golden, J. S., & Handfield, R. B. (2014). Why Biobased? Opportunities in the Emerging Bioeconomy. *US Department of Agriculture, Office of Procurement and Property Management, Washington, DC, USA*, (<http://www.biopreferred.gov/files/WhyBiobased.pdf>).
85. De Jong, E., Higson, A., Walsh, P. & Wellisch, M. (2012) IEA Bioenergy, Task 42 Biorefinery, Bio based chemicals value added products from Biorefineries. Report. Retrieved from <http://www.ieabioenergy.com/wp-content/uploads/2013/10/Task-42-Biobased-Chemicals-value-added-products-from-biorefineries.pdf>

86. Peter Nelson, Elizabeth Hood, and Randall Powell (2010). *The Bioeconomy: A New Era of Products Derived from Renewable Plant-Based Feedstock*, Chapter-1, Plant Biomass Conversion, First Edition
87. USDA, U.S. Biobased Products: Market Potential and Projections through 2025, (2008). Report. Retrieved from www.USDA.gov/oce/reports/energy/BiobasedReport2008.pdf
88. Lipinsky, E. S. (1981). Chemicals from biomass: petrochemical substitution options. *Science*, 212(4502), 1465-1471.
89. Danner, H., & Braun, R. (1999). Biotechnology for the production of commodity chemicals from biomass. *Chem. Soc. Rev.*, 28(6), 395-405.
90. Hart, P. W., & Sommerfeld, J. T. (1997). Cost Estimation of Specialty Chemicals From Laboratory-Scale Priees. *Cost Engineering-Morgantown*, 39(3), 31-35.
91. Qi, W., Sathre, R., Morrow III, W. R., & Shehabi, A. (2015). Unit price scaling trends for chemical products.
92. Sigma Aldrich (2015). Online Catalog. Retrieved from <https://www.sigmaaldrich.com/united-states.html>
93. Ullmann's encyclopedia of industrial chemistry (2014). 7th Edition, Wiley-VCH, Weinheim
94. Chemical Engineering (2014). "Emerging Opportunity for Bio-Chemicals" Archived Article. Retrieved from www.chemengonline.com
95. Werpy, T., Petersen, G., Aden, A., Bozell, J., Holladay, J., White, J., & Jones, S. (2004). Top value added chemicals from biomass. Volume 1-Results of screening for

- potential candidates from sugars and synthesis gas (No. DOE/GO-102004-1992).
DEPARTMENT OF ENERGY WASHINGTON DC.
96. Holladay, J. E., et al. "Top value-added chemicals from biomass." DOE Report PNNL 16983 (2007).
97. Jang, Yu-Sin, et al. "Bio-based production of C2–C6 platform chemicals." *Biotechnology and bioengineering* 109.10 (2012): 2437-2459.
98. Kajaste, R. "Chemicals from biomass—managing greenhouse gas emissions in biorefinery production chains—a review." *Journal of Cleaner Production* 75 (2014): 1-10.
99. Dale, Bruce E. "‘Greening’ the chemical industry: research and development priorities for biobased industrial products." *Journal of Chemical Technology and Biotechnology* 78.10 (2003): 1093-1103.
100. Song H, Lee SY (2005) Production of succinic acid by bacterial fermentation. *Enzym Microbial Technol* 39:352–361
101. Kim DY, Yim SC, Lee PC, Lee WG, Lee SY, Chang HN. Batch and continuous fermentation of succinic acid from wood hydrolysate by *Mannheimia succiniciproducens* MBEL55E. *Enzyme Microb Technol* 2004;35:648–53
102. Hong SH, Kim JS, Lee SY, In YH, Choi SS, Rih JK, et al. The genome sequence of the capnophilic rumen bacterium *Mannheimia succiniciproducens*. *Nature Biotechnol* 2004;22:1275–81.

103. Bechthold I, Bretz K, Kabasci S, Kopitzky R, Springer A(2008) Succinic acid: a new platform chemical for biobased polymers from renewable resources. *Chem Eng Technol* 5:647–654
104. Zeikus, J. G., M. K. Jain, and P. Elankovan. "Biotechnology of succinic acid production and markets for derived industrial products." *Applied Microbiology and Biotechnology* 51.5 (1999): 545-552.
105. Minh, Doan Pham, et al. "Aqueous-phase hydrogenation of biomass-based succinic acid to 1, 4-butanediol over supported bimetallic catalysts." *Topics in Catalysis* 53.15-18 (2010): 1270-1273.
106. Gallezot, Pierre. "Conversion of biomass to selected chemical products." *Chemical Society Reviews* 41.4 (2012): 1538-1558.
107. Patel, Martin, et al. Techno-economic feasibility of large-scale production of bio-based polymers in Europe. IPTS Technical Report EUR 22103 EN, Seville, 2005.
108. Sauer, Michael, et al. "Microbial production of organic acids: expanding the markets." *Trends in biotechnology* 26.2 (2008): 100-108.
109. Xiu, Zhi-Long, and An-Ping Zeng. "Present state and perspective of downstream processing of biologically produced 1, 3-propanediol and 2, 3-butanediol." *Applied Microbiology and Biotechnology* 78.6 (2008): 917-926.
110. Tao, Ling, and Andy Aden. "The economics of current and future biofuels." In *Vitro Cellular & Developmental Biology-Plant* 45.3 (2009): 199-217.
111. Wang, Zhengxiang, et al. "Glycerol production by microbial fermentation: a review." *Biotechnology Advances* 19.3 (2001): 201-223.

112. Abdel-Rahman, Mohamed Ali, Yukihiro Tashiro, and Kenji Sonomoto. "Lactic acid production from lignocellulose-derived sugars using lactic acid bacteria: overview and limits." *Journal of biotechnology* 156.4 (2011): 286-301.
113. Pal, Parimal, et al. "Process intensification in lactic acid production: A review of membrane based processes." *Chemical Engineering and Processing: Process Intensification* 48.11 (2009): 1549-1559.
114. Hayes, Daniel J., et al. "The Biofine process-Production of levulinic acid, furfural, and formic acid from lignocellulosic feedstocks." *Biorefineries—Industrial Processes and Product 1* (2006): 139-164.
115. Huber, George W., and Avelino Corma. "Synergies between Bio-and Oil Refineries for the Production of Fuels from Biomass." *Angewandte Chemie International Edition* 46.38 (2007): 7184-7201.
116. Bozell, Joseph J. "Feedstocks for the future—biorefinery production of chemicals from renewable carbon." *CLEAN—Soil, Air, Water* 36.8 (2008): 641-647.
117. Lange, Jean-Paul. "Sustainable chemical manufacturing: a matter of resources, wastes, hazards, and costs." *ChemSusChem* 2.6 (2009): 587-592.
118. Zakrzewska, Małgorzata E., Ewa Bogel-Łukasik, and Rafał Bogel-Łukasik. "Ionic liquid-mediated formation of 5-hydroxymethylfurfural □ A promising biomass-derived building block." *Chemical reviews* 111.2 (2010): 397-417.
119. Tong, Xinli, Yang Ma, and Yongdan Li. "Biomass into chemicals: conversion of sugars to furan derivatives by catalytic processes." *Applied Catalysis A: General* 385.1 (2010): 1-13.

120. Thananatthanachon, Todsapon, and Thomas B. Rauchfuss. "Efficient route to hydroxymethylfurans from sugars via transfer hydrogenation." *ChemSusChem* 3.10 (2010): 1139-1141.
121. Tachibana, Yuya, et al. "Chemical synthesis of fully biomass-based poly (butylene succinate) from inedible-biomass-based furfural and evaluation of its biomass carbon ratio." *Biomacromolecules* 11.10 (2010): 2760-2765.
122. Okano, Kenji, et al. "Biotechnological production of enantiomeric pure lactic acid from renewable resources: recent achievements, perspectives, and limits." *Applied microbiology and biotechnology* 85.3 (2010): 413-423.
123. Zhang A, Yang ST. 2009. Engineering *Propionibacterium acidipropionici* for enhanced propionic acid tolerance and fermentation. *Biotechnol Bioeng* 104:766–773.
124. Wang L, Zhao B, Li F, Xu K, Ma C, Tao F, Li Q, Xu P. 2011a. Highly efficient production of D-lactate by *Sporolactobacillus* sp. CASD with simultaneous enzymatic hydrolysis of peanut meal. *Appl Microbiol Biotechnol* 89:1009–1017.
125. Nakamura CE, Whited GM. 2003. Metabolic engineering for the microbial production of 1,3-propanediol. *Curr Opin Biotechnol* 14:454–459.
126. Clomburg JM, Gonzalez R. 2011. Metabolic engineering of *Escherichia coli* for the production of 1,2-propanediol from glycerol. *Biotechnol Bioeng* 108:867–879.
127. Pal, Parimal, et al. "Process intensification in lactic acid production: A review of membrane based processes." *Chemical Engineering and Processing: Process Intensification* 48.11 (2009): 1549-1559.

128. Jiang L, Wang J, Liang S, Cai J, Xu Z, Cen P, Yang S, Li S. 2011. Enhanced butyric acid tolerance and bioproduction by *Clostridium tyrobutyricum* immobilized in a fibrous bed bioreactor. *Biotechnol Bioeng* 108:31–40.
129. Zhang X, Wang X, Shanmugam KT, Ingram LO. 2011. L-Malate production by metabolically engineered *Escherichia coli*. *Appl Environ Microbiol* 77:427–434.
130. Kenealy W, Zaady E, du Preez JC, Stieglitz B, Goldberg I. 1986. Bio-chemical aspects of fumaric acid accumulation by *Rhizopus arrhizus*. *Appl Environ Microbiol* 52:128–133.
131. Yim H, Haselbeck R, Niu W, Pujol-Baxley C, Burgard A, Boldt J, Khandurina J, Trawick JD, Osterhout RE, Stephen R, et al. 2011. Metabolic engineering of *Escherichia coli* for direct production of 1,4-butanediol. *Nat Chem Biol* 7:445–452.
132. Liao JC, Chang P, Industrial Technology Research Institute, Assignee. (2010). Genetically modified microorganisms for producing itaconic acid with high yields. United States patent US 2010/0285546 A1.
133. Zhang K, Sawaya MR, Eisenberg DS, Liao JC. (2008). Expanding metabolism for biosynthesis of nonnatural alcohols. *Proc Natl Acad Sci USA* 105:20653–20658.
134. Granstrom TB, Izumori K, Leisola M. (2007). A rare sugar xylitol. Part II: Biotechnological production and future applications of xylitol. *Appl Microbiol Biotechnol* 74:273–276.
135. Cirino PC, Chin JW, Ingram LO. 2006. Engineering *Escherichia coli* for xylitol production from glucose–xylose mixtures. *Biotechnol Bioeng* 95:1167–1176.

136. Moon TS, Dueber JE, Shiue E, Prather KL. 2010. Use of modular, synthetic scaffolds for improved production of glucaric acid in engineered E. coli. *Metab Eng* 12:298–305
137. Stuart, P. R., & El-Halwagi, M. M. (Eds.). (2012). *Integrated biorefineries: design, analysis, and optimization*. CRC Press.
138. Baek, J., Kim, T. Y., Kim, W., Lee, H. J., & Yi, J. (2014). Selective production of 1, 3-butadiene using glucose fermentation liquor. *Green Chemistry*, 16(7), 3501-3507.
139. Yi, G., Teong, S. P., & Zhang, Y. (2015). The Direct Conversion of Sugars into 2, 5-Furandicarboxylic Acid in a Triphasic System. *ChemSusChem*, 8(7), 1151-1155.
140. Ait Rass, H., Essayem, N., & Besson, M. (2015). Selective Aerobic Oxidation of 5-HMF into 2, 5-Furandicarboxylic Acid with Pt Catalysts Supported on TiO₂-and ZrO₂-Based Supports. *ChemSusChem*, 8(7), 1206-1217.
141. Shen, Y., Sun, J., Yi, Y., Wang, B., Xu, F., & Sun, R. (2014). 5-Hydroxymethylfurfural and levulinic acid derived from monosaccharides dehydration promoted by InCl₃ in aqueous medium. *Journal of Molecular Catalysis A: Chemical*, 394, 114-120.
142. Hu, L., Sun, Y., & Lin, L. (2012). Efficient conversion of glucose into 5-hydroxymethylfurfural by chromium (III) chloride in inexpensive ionic liquid. *Industrial & Engineering Chemistry Research*, 51(3), 1099-1104.

143. Chidambaram, M., & Bell, A. T. (2010). A two-step approach for the catalytic conversion of glucose to 2, 5-dimethylfuran in ionic liquids. *Green Chemistry*,*12*(7), 1253-1262.
144. Adreas et al “Fermentative Production of Fumaric Acid by *Candida Blankii*”
WO 2013120924, DE 102012101153
145. Gu, C., Zhou, Y., Liu, L., Tan, T., & Deng, L. (2013). Production of fumaric acid by immobilized *Rhizopus arrhizus* on net. *Bioresource technology*, *131*, 303-307.
146. Zhang, B., Skory, C. D., & Yang, S. T. (2012). Metabolic engineering of *Rhizopus oryzae*: effects of overexpressing *pyc* and *pepc* genes on fumaric acid biosynthesis from glucose. *Metabolic engineering*, *14*(5), 512-520.
147. Biebl, H., Menzel, K., Zeng, A. P., & Deckwer, W. D. (1999). Microbial production of 1, 3-propanediol. *Applied Microbiology and Biotechnology*,*52*(3), 289-297.
148. Haas, T., Jaeger, B., Weber, R., Mitchell, S. F., & King, C. F. (2005). New diol processes: 1, 3-propanediol and 1, 4-butanediol. *Applied Catalysis A: General*, *280*(1), 83-88.
149. González-Pajuelo, M., Meynial-Salles, I., Mendes, F., Andrade, J. C., Vasconcelos, I., & Soucaille, P. (2005). Metabolic engineering of *Clostridium acetobutylicum* for the industrial production of 1, 3-propanediol from glycerol. *Metabolic Engineering*, *7*(5), 329-336.

150. Nakamura, C. E., & Whited, G. M. (2003). Metabolic engineering for the microbial production of 1, 3-propanediol. *Current opinion in biotechnology*, 14(5), 454-459.
151. Wang, Z., Zhuge, J., Fang, H., & Prior, B. A. (2001). Glycerol production by microbial fermentation: a review. *Biotechnology Advances*, 19(3), 201-223.
152. Yim, H., Haselbeck, R., Niu, W., Pujol-Baxley, C., Burgard, A., Boldt, J., ... & Estadilla, J. (2011). Metabolic engineering of Escherichia coli for direct production of 1, 4-butanediol. *Nature chemical biology*, 7(7), 445-452. Metabolic engineering of e. coli allows for direct fermentation of glucose to 1,4 BDO
153. Minh, D. P., Besson, M., Pinel, C., Fuertes, P., & Petitjean, C. (2010). Aqueous-phase hydrogenation of biomass-based succinic acid to 1, 4-butanediol over supported bimetallic catalysts. *Topics in Catalysis*, 53(15-18), 1270-1273.
154. Kumar, V., Ashok, S., & Park, S. (2013). Recent advances in biological production of 3-hydroxypropionic acid. *Biotechnology advances*, 31(6), 945-961.
155. Zhou, S., Catherine, C., Rathnasingh, C., Somasundar, A., & Park, S. (2013). Production of 3-hydroxypropionic acid from glycerol by recombinant Pseudomonas denitrificans. *Biotechnology and bioengineering*, 110(12), 3177-3187.
156. Horikawa H. (2013). "Method for producing 3-hydroxypropionic acid"
WO2013137277 A1
157. Lynch M. (2011). "Method for producing 3-hydroxypropionic acid and other products" WO2011038364 A1

158. Le Nôtre, J., Scott, E. L., Franssen, M. C., & Sanders, J. P. (2011). Biobased synthesis of acrylonitrile from glutamic acid. *Green Chemistry*, *13*(4), 807-809.
159. Kang, M. S., Han, S. S., Kim, M. Y., Kim, B. Y., Huh, J. P., Kim, H. S., & Lee, J. H. (2014). High-level expression in *Corynebacterium glutamicum* of nitrile hydratase from *Rhodococcus rhodochrous* for acrylamide production. *Applied microbiology and biotechnology*, *98*(10), 4379-4387.
160. Lange, JP WO2014108417 A1 "Production of Acrylic Acid"
161. Sato, S., Akiyama, M., Takahashi, R., Hara, T., Inui, K., & Yokota, M. (2008). Vapor-phase reaction of polyols over copper catalysts. *Applied Catalysis A: General*, *347*(2), 186-191.
162. Straathof, A. J., Sie, S., Franco, T. T., & Van der Wielen, L. A. (2005). Feasibility of acrylic acid production by fermentation. *Applied microbiology and biotechnology*, *67*(6), 727-734.
163. Humbird, D., Davis, R., Tao, L., Kinchin, C., Hsu, D., Aden, A., & Sexton, D. (2011). Process design and economics for bio-chemical conversion of lignocellulosic biomass to ethanol: dilute-acid pretreatment and enzymatic hydrolysis of corn stover. National Renewable Energy Laboratory.
164. Kalinowski, J., Bathe, B., Bartels, D., Bischoff, N., Bott, M., Burkovski, A., ... & Goesmann, A. (2003). The complete *Corynebacterium glutamicum* ATCC 13032 genome sequence and its impact on the production of L-aspartate-derived amino acids and vitamins. *Journal of biotechnology*, *104*(1), 5-25

165. Delaunay, S., Uy, D., Baucher, M. F., Engasser, J. M., Guyonvarch, A., & Goergen, J. L. (1999). Importance of phosphoenolpyruvate carboxylase of *Corynebacterium glutamicum* during the temperature triggered glutamic acid fermentation. *Metabolic engineering*, 1(4), 334-343.
166. Hermann, T. (2003). Industrial production of amino acids by coryneform bacteria. *Journal of biotechnology*, 104(1), 155-172.
167. Peters-Wendisch, P. G., Schiel, B., Wendisch, V. F., Katsoulidis, E., Mockel, B., Sahm, H., & Eikmanns, B. J. (2001). Pyruvate carboxylase is a major bottleneck for glutamate and lysine production by *Corynebacterium glutamicum*. *Journal of molecular microbiology and biotechnology*, 3(2), 295-300.
168. Biella, S., Prati, L., & Rossi, M. (2002). Selective oxidation of D-glucose on gold catalyst. *Journal of catalysis*, 206(2), 242-247.
169. Kiely, D.E., Hash, K.R., US7692041B2 "Method of Oxidation Using Nitric Acid"
170. DeGuzman, Doris (2014). "Q&A: Rivertop Renewables on Glucaric Acid" Web log post. Retrieved from <http://greenchemicalsblog.com/2014/05/01/qa-rivertop-renewables-on-glucaric-acid/>
171. Boussie, T.R., Dias, E.L., Fresco, Z.M., Murphy, V.J., Shoemaker, J., Archer, R., & Jiang, H. US8669397 B2 "Production of Adipic Acid and Derivatives from Carbohydrate-containing Materials." 2014.
172. Niu, W., Draths, K. M., & Frost, J. W. (2002). Benzene-Free Synthesis of Adipic Acid. *Biotechnology progress*, 18(2), 201-211.

173. G. Paris, L. Berlinguet, R. Gaudry, J. English, Jr. and J. E. Dayan (1963). "Glutaric Acid and Glutaramide". *Org. Synth.;Coll. Vol. 4*, p. 496
174. Gokarn et al, 2007. "3HP & Other Organic Compounds" US7186541 B2
175. Lee, E.K., Baek, Y.H., 2008. "Production of Tetrahydrofuran from 1,4 Butanediol." US7465816 B2
176. Jong, E., Higson, A., Walsh, P., & Wellisch, M. (2012). Product developments in the bio-based chemicals arena. *Biofuels, Bioproducts and Biorefining*, 6(6), 606-624.
177. Shen, L., Haufe, J., & Patel, M. K. (2009). Product overview and market projection of emerging bio-based plastics PRO-BIP 2009. *Report for European Polysaccharide Network of Excellence (EPNOE) and European Bioplastics*, 243.
178. Cooper, R. G., Edgett, S. J., & Kleinschmidt, E. J. (1997). Portfolio management in new product development: Lessons from the leaders--I. *Research Technology Management*, 40(5), 16.
179. Zondervan, E., Nawaz, M., de Haan, A. B., Woodley, J. M., & Gani, R. (2011). Optimal design of a multi-product biorefinery system. *Computers & Chemical Engineering*, 35(9), 1752-1766.
180. Tang, M. C., Chin, M. W., Lim, K. M., San Mun, Y., Ng, R. T., Tay, D. H., & Ng, D. K. (2013). Systematic approach for conceptual design of an integrated biorefinery with uncertainties. *Clean Technologies and Environmental Policy*, 15(5), 783-799.

181. Sharma, P., Sarker, B. R., & Romagnoli, J. A. (2011). A decision support tool for strategic planning of sustainable biorefineries. *Computers & Chemical Engineering*, *35*(9), 1767-1781.
182. Sammons, N. E., Yuan, W., Eden, M. R., Aksoy, B., & Cullinan, H. T. (2008). Optimal biorefinery product allocation by combining process and economic modeling. *Chemical Engineering Research and Design*, *86*(7), 800-808.
183. Bozell, J. J., & Petersen, G. R. (2010). Technology development for the production of biobased products from biorefinery carbohydrates—the US Department of Energy’s “top 10” revisited. *Green Chemistry*, *12*(4), 539-554.
184. Kim, S. J., Seo, S. O., Jin, Y. S., & Seo, J. H. (2013). Production of 2, 3-butanediol by engineered *Saccharomyces cerevisiae*. *Bioresource technology*, *146*, 274-281.
185. Nan, H., Seo, S. O., Oh, E. J., Seo, J. H., Cate, J. H., & Jin, Y. S. (2014). 2, 3-Butanediol production from cellobiose by engineered *Saccharomyces cerevisiae*. *Applied microbiology and biotechnology*, *98*(12), 5757-5764.
186. Othmer, D. F., Bergen, W. S., Shlechter, N., & Bruins, P. F. (1945). Liquid-Liquid Extraction Data. *Industrial & Engineering Chemistry*, *37*(9), 890-894.
187. Othmer, D. F., Marshak, S., & Schlecter, N. (1945). Esterification of 2, 3-Butylene Glycol with Acetic Acid. *Industrial & Engineering Chemistry*, *37*(9), 900-905.

188. Shlechter, N., Othmer, D. F., & Brand, R. (1945). PYROLYSIS OF 2, 3-BUTYLENE GLYCOL DIACETATE TO BUTADIENE. *INDUSTRIAL AND ENGINEERING CHEMISTRY*, 37(9), 905-908.
189. Brenner, K., You, L., & Arnold, F. H. (2008). Engineering microbial consortia: a new frontier in synthetic biology. *Trends in biotechnology*, 26(9), 483-489.
190. International Rubber Study Group (2011) "Latest Rubber Bulletin". Retrieved from <http://www.rubberstudy.com/>.
191. Lee, K., & Ni, S. (2002). On the dynamic effects of oil price shocks: a study using industry level data. *Journal of Monetary Economics*, 49(4), 823-852.
- Kannegiesser, M., Günther, H. O., Van Beek, P., Grunow, M., & Habla, C. (2009). *Value chain management for commodities: a case study from the chemical industry* (pp. 1-31). Springer Berlin Heidelberg.
192. Mosier, N., Wyman, C., Dale, B., Elander, R., Lee, Y. Y., Holtzapple, M., & Ladisch, M. (2005). Features of promising technologies for pretreatment of lignocellulosic biomass. *Bioresource technology*, 96(6), 673-686.
193. Wear, D., Abt, R., Alavalapati, J., Comatas, G., Countess, M., & McDow, W. (2010). The south's outlook for sustainable forest bioenergy and biofuels production. Treesearch.fs.fed.us
194. Raunekar, R., Buongiorno, J., Turner, J. A., & Zhu, S. (2010). Global outlook for wood and forests with the bioenergy demand implied by scenarios of the Intergovernmental Panel on Climate Change. *Forest Policy and Economics*, 12(1), 48-56.

195. Carle, J., & Holmgren, P. (2008). Wood from planted forests: a global outlook 2005-2030. *Forest Products Journal*, 58(12), 6.
196. Marion, T. J., & Meyer, M. H. (2011). Applying Industrial Design and Cost Engineering to New Product Development in Early-Stage Firms. *Journal of Product Innovation Management*, 28(5), 773-786.
197. Cooper, R. G., & Kleinschmidt, E. J. (1991). New product processes at leading industrial firms. *Industrial Marketing Management*, 20(2), 137-147.
198. Straathof, A. J. (2013). Transformation of biomass into commodity chemicals using enzymes or cells. *Chemical reviews*, 114(3), 1871-1908.
199. DuPont Tate & Lyle (2006). DuPont Tate & Lyle Bio Products being Bio-PDO production in Tennessee. Announcement. Retrieved from http://www.duponttateandlyle.com/news_112706
200. Tunc, M. S., & van Heiningen, A. R. (2008). Hemicellulose extraction of mixed southern hardwood with water at 150 C: Effect of time. *Industrial & Engineering Chemistry Research*, 47(18), 7031-7037.
201. Leonard-Barton, D. (1992). Core capabilities and core rigidities: A paradox in managing new product development. *Strategic management journal*, 13(S1), 111-125.
202. Baker, J. (2016). Bio-Succinic Acid - Platform Chemical Goes to Market. ICIS Special Supplement. Published by ICIS, of Reed Business Information. Retrieved from <https://www.bio-amber.com/bioamber/en/news/2016/icis-publishes-special-supplement-on-bioamber>

203. Myriant (2013). Myriant Achieves Major Milestone: Successful Start-Up At Flagship Bio-Succinic Acid Plant in Lake Providence, LA. Announcement. Retrieved from <http://www.myriant.com/media/press-releases/myriant-achieves-successful-start-up-at-lake-providence-la-plant.cfm>
204. Song H, Lee SY (2005) Production of succinic acid by bacterial fermentation. *Enzym Microbial Technol* 39:352–361
205. Raab, Andreas M., et al. "Metabolic engineering of *Saccharomyces cerevisiae* for the biotechnological production of succinic acid." *Metabolic engineering* 12.6 (2010): 518-525.
206. Guettler MV, Jain MK, Rumler D. Method for making succinic acid, bacterial variants for use in the process, and methods for obtaining variants. US Patent 5,573,931; 1996.
207. Van der Werf MJ, Guettler MV, Jain MK, Zeikus JG. Environmental and physiological factors affecting the succinate product ratio during carbohydrate fermentation by *Actinobacillus* sp. 130Z. *Arch Microbiol* 1997;168:332–42.
208. Guettler MV, Jain MK, Soni BK. Process for making succinic acid, microorganisms for use in the process and methods for obtaining the microorganisms. US Patent 5,504,004; 1996.
209. Kim DY, Yim SC, Lee PC, Lee WG, Lee SY, Chang HN. Batch and continuous fermentation of succinic acid from wood hydrolysate by *Mannheimia succiniciproducens* MBEL55E. *Enzyme Microb Technol* 2004;35:648–53.

210. Lee PC, Lee SY, Hong SH, Chang HN. Batch and continuous cultures of *Mannheimia succiniciproducens* MBEL55E for the production of succinic acid from whey and corn steep liquor. *Bioprocess Biosyst Eng* 2003;26:63–7.
211. Hong SH, Kim JS, Lee SY, In YH, Choi SS, Rih JK, et al. The genome sequence of the capnophilic rumen bacterium *Mannheimia succiniciproducens*. *Nature Biotechnol* 2004;22:1275–81.
212. Lee PC, Lee WG, Lee SY, Chang HN. Succinic acid production with reduced by-product formation in the fermentation of *Anaerobiospirillum succiniciproducens* using glycerol as a carbon source. *Biotechnol Bioeng* 2001;72:41–8.
213. Lee PC, Lee SY, Hong SH, Chang HN, Park SC. Biological conversion of wood hydrolysate to succinic acid by *Anaerobiospirillum succiniciproducens*. *Biotechnol Lett* 2003;25:111–4.
214. Lee PC, Lee WG, Kwon S, Lee SY, Chang HN. Succinic acid production by *Anaerobiospirillum succiniciproducens*: effects of the H₂/CO₂ supply and glucose concentration. *Enzyme Microb Technol* 1999;24:549–54.
215. Hong SH, Moon SY, Lee SY. Prediction of maximum yields of metabolites and optimal pathways for their production by metabolic flux analysis. *J Microbiol Biotechnol* 2003;13:571–7.
216. Stols L, Donnelly MI. Production of succinic acid through overexpression of NAD⁺-dependent malic enzyme in an *Escherichia coli* mutant. *Appl Environ Microbiol* 1997;63:2695–701.

217. Lin H, Bennett GN, San K-Y. Metabolic engineering of aerobic succinate production systems in *Escherichia coli* to improve process productivity and achieve the maximum theoretical succinate yield. *Metab Eng* 2005;7:116–27.
218. Bechthold I, Bretz K, Kabasci S, Kopitzky R, Springer A(2008) Succinic acid: a new platform chemical for biobased polymers from renewable resources. *Chem Eng Technol* 5:647–654
219. Humbird D, Davis R, Tao L, Kinchin C, Hsu D, Aden A, et al. Process design and economics for biochemical conversion of lignocellulosic biomass to ethanol. NREL. NREL/TP-5100-47764; 2011.
220. GNC Centrifuge, 2014
221. Datta R, Glassner DA, Jain MK, Vicky Roy JR (1992) Fermentation and purification process for succinic acid. US patent 5,168,055
222. Berglund KA, Yedur S, Dunuwila D (1999) Succinic acid production and purification. US patent 5,958,744
223. Yedur S, Berglung KS, Dunuwila DD (2001) Succinic acid production and purification. US patent 6,265,190
224. Zeikus, J. G., M. K. Jain, and P. Elankovan. "Biotechnology of succinic acid production and markets for derived industrial products." *Applied Microbiology and Biotechnology* 51.5 (1999): 545-552.
225. Kertes AS, King CJ (1985) Extraction chemistry of fermentation product carboxylic acids. *Biotechnol Bioeng* 28:269

226. Song H, Huh YS, Lee SY, Hong WH, Hong YK (2007) Recovery of succinic acid produced by fermentation of a metabolically engineered *Mannheimia succiniciproducens* strain. *J Biotechnol* 132:445–452
227. Huh YS, Jun Y-S, Kong YK, Song H, Lee SY, Hong WH (2006) Effective purification of succinic acid from fermentation broth produced by *Mannheimia succiniciproducens*. *Proc Biochem* 41:1461–1465
228. Luque, Rafael, et al. "Chemical transformations of succinic acid recovered from fermentation broths by a novel direct vacuum distillation-crystallisation method." *Green Chemistry* 11.2 (2009): 193-200.
229. GEA Process Engineering Inc, 2014,
http://www.niroinc.com/evaporators_crystallizers/crystallization_theory_dtb.asp
230. Ulrich, G. D., "A guide to chemical engineering process design and economics" (VIII ed.). New York: Wiley (1984).
231. Reuters Fact Sheet, Myriant, September 2014
232. <http://www.biofuelsdigest.com/bdigest/2014/03/10/myriant-biofuels-digests-2014-5-minute-guide/>
233. Progressive Media, Succinity, March 2014
234. <http://www.succinity.com/news/140303.htm>
235. <http://www.reverdia.com/technology/commercial-plants/>
236. <http://www.reverdia.com/press-releases/reverdia-aims-tap-chinese-plastics-market-pbs-2/>
237. http://www.bio-amber.com/bioamber/en/company/manufacturing_facilities

238. Baker, J. (2016). Bio-Succinic Acid - Platform Chemical Goes to Market. ICIS Special Supplement. Published by ICIS, of Reed Business Information. Retrieved from <https://www.bio-amber.com/bioamber/en/news/2016/icis-publishes-special-supplement-on-bioamber>
239. <http://www.genomatica.com/manufacturing/commercialization/>
240. Global Data, Genomatica. September 2014
241. Hong, U. G., Lee, J., Hwang, S., & Song, I. K. (2011). Hydrogenation of Succinic Acid to γ -Butyrolactone (GBL) Over Palladium-Alumina Composite Catalyst Prepared by a Single-Step Sol–Gel Method. *Catalysis letters*, 141(2), 332-338. *Hydrogenolysis by-products*
242. Minh, D. P., Besson, M., Pinel, C., Fuertes, P., & Petitjean, C. (2010). Aqueous-phase hydrogenation of biomass-based succinic acid to 1, 4-butanediol over supported bimetallic catalysts. *Topics in Catalysis*, 53(15-18), 1270-1273.
243. Marshall & Swift, “Marshall & swift cost index.” Unpublished manuscript (2015).
244. Phillips R. Lignin filter. Factored vendor quote. Confidential (2010).
245. Peters, Max Stone, et al. “Plant design and economics for chemical engineers.” Vol. 4. New York: McGraw-Hill (1968).
246. Pirraglia, Adrian, Ronalds Gonzalez, and Daniel Saloni. "Techno-economical analysis of wood pellets production for US manufacturers." *BioResources* 5.4, 2374-2390 (2010).
247. Couper et al “Selecting Chemical Process Equipment”

248. ICIS Chemical Business (2015). Indicative Chemical Prices A-Z. Retrieved from <http://www.icis.com/chemicals/channel-info-chemicals-a-z/>.
249. U.S. Energy Information Administration (2015). Historical Natural Gas Futures. Retrieved from <http://www.eia.gov/dnav/ng/hist/rngc1d.htm>.
250. World Freight Rates (2015). Freight Calculator. Retrieved from <http://worldfreightrates.com/freight>.
251. <https://apps.catalysts.basf.com/apps/eibprices/mp/> Catalyst reagent costs for rare earth metals. Retrieved from BASF on Nov 6 2016
252. Park, S. W., Kim, S. H., Choi, H. S., & Cho, H. H. (2010). Preparation and physical properties of biodegradable polybutylene succinate/polybutylene adipate-co-terephthalate blend monofilament by melt spinning. *Journal of the Korean society of Fisheries Technology*, 46(3), 257-264.
253. Fujimaki, T. (1998). Processability and properties of aliphatic polyesters, 'BIONOLLE', synthesized by polycondensation reaction. *Polymer degradation and stability*, 59(1), 209-214.
254. Ek, M. (Ed.). (2009). *Pulping chemistry and technology* (Vol. 2). Walter de Gruyter.
255. Young, R. A., & Akhtar, M. (1998). *Environmentally friendly technologies for the pulp and paper industry*. John Wiley & Sons.
256. Glasser, W. G., & Leitheiser, R. H. (1984). Engineering plastics from lignin. *Polymer Bulletin*, 12(1), 1-5.
257. <http://cyclewood.com/technology/>

258. Xia, T., Eiteman, M. A., & Altman, E. (2012). Simultaneous utilization of glucose, xylose and arabinose in the presence of acetate by a consortium of *Escherichia coli* strains. *Microbial cell factories*, 11(1), 1.
259. <http://www.s2gbiochem.com/>
260. Podschun, J., Saake, B., & Lehnen, R. (2015). Reactivity enhancement of organosolv lignin by phenolation for improved bio-based thermosets. *European Polymer Journal*, 67, 1-11.

12 APPENDICES

12.1 Appendix A: Supplemental Lignin Extraction TEA & LCA Data

Table A1: Complete Sodium (Na) and Sulfur (S) Balance

Na (kg/hr)				S (kg/hr)			
Inputs	BC	LE-P	SOL-P	Inputs	BC	LE-P	SOL-P
Fresh NaOH in O2 Reactors	254	254	267	R-10 Saltcake	274	274	288
R-10 Saltcake	367	367	386	Lignin Extraction H2SO4	0	123	123
Fresh NaOH in for WL Adjustment	128	336	342				
Total	749	957	995	Total	274	397	411
Outputs	BC	LE-P	SOL-P	Outputs	BC	LE-P	SOL-P
Brown Stock Screening	16	16	16	Brown Stock Screening	2	2	2
Carryover to Bleach Plant	205	205	216	Carryover to Bleach Plant	6	6	7
Soap Skimming	109	98	103	Black Liquor Flash Tanks	35	35	36
Recovery Boiler Precipitator Loss	84	84	89	Soap Skimming	22	21	22
Recovery Boiler Catch Purge	266	467	482	Recovery Boiler Precipitator Loss	48	49	52
Green Liquor Clarifier Dregs	16	16	16	Recovery Boiler Catch Purge	154	274	282
Slaker Grits	16	15	16	Green Liquor Clarifier Dregs	3	3	3
Kiln Dust	38	38	40	Slaker Grits	3	3	3
Lignin Cake	0	6	6	Kiln Dust	0	0	0
				Lignin Cake	0	4	4
Total	750	944	983	Total	274	397	412
% Difference Inputs to Outputs	0%	-1%	-1%	% Difference Inputs to Outputs	0%	0%	0%

Table A2: Relative Contribution of Process Inventory to Environmental Impact Categories. Data is based on the BC & SOL-P scenarios.

Base Case	NaOH, 50%	CaO	H2O2, 50%	H2SO4	NaClO3	CH3OH	CO2 (gas)	Nat. Gas	Emissions	Soft.W.	Solid Residue	Transport	Transport, F.	Power
Global Warming	7%	5%	2%	0%	19%	0%	0%	70%	660%	-654%	0%	1%	6%	-16%
Acidification	4%	1%	1%	6%	10%	1%	0%	68%	1%	20%	0%	1%	5%	-16%
Carcinogenics	8%	0%	5%	1%	45%	1%	0%	32%	0%	3%	12%	0%	1%	-7%
Non carcinogenics	3%	0%	6%	1%	52%	1%	0%	46%	0%	2%	0%	0%	0%	-11%
Respiratory effects	6%	1%	1%	7%	16%	1%	0%	77%	0%	6%	0%	0%	3%	-18%
Eutrophication	8%	1%	2%	2%	18%	0%	0%	14%	0%	15%	37%	1%	5%	-3%
Ozone depletion	8%	7%	5%	1%	20%	1%	0%	50%	0%	0%	1%	2%	18%	-12%
Ecotoxicity	15%	1%	13%	1%	55%	0%	0%	11%	0%	3%	1%	0%	1%	-3%
Smog	3%	1%	1%	1%	9%	0%	0%	22%	0%	54%	0%	2%	12%	-5%

SOL-P	NaOH, 50%	CaO	H2O2, 50%	H2SO4	NaClO3	CH3OH	CO2 (gas)	Nat. Gas	Emissions	Soft.W.	Solid Residue	Transport	Transport, F.	Power
Global Warming	10%	6%	3%	1%	22%	0%	4%	84%	722%	-759%	0%	1%	7%	0%
Acidification	4%	0%	1%	6%	8%	1%	1%	58%	1%	16%	0%	1%	4%	0%
Carcinogenics	9%	0%	4%	2%	39%	0%	3%	28%	0%	2%	11%	0%	1%	0%
Non carcinogenics	3%	0%	5%	1%	46%	1%	1%	42%	0%	1%	0%	0%	0%	0%
Respiratory effects	6%	1%	1%	7%	13%	1%	1%	63%	0%	5%	0%	0%	2%	0%
Eutrophication	9%	1%	2%	2%	16%	0%	3%	13%	0%	14%	35%	1%	4%	0%
Ozone depletion	8%	5%	4%	1%	16%	1%	4%	43%	0%	0%	1%	2%	15%	0%
Ecotoxicity	18%	1%	12%	1%	50%	0%	3%	10%	0%	3%	1%	0%	1%	0%
Smog	4%	1%	1%	1%	8%	0%	1%	21%	0%	50%	0%	2%	12%	0%

Table A3: Simple Carbon Balance (as Global Warming Potential, kg CO₂ eq per ADmt SBSK or ADmt Lignin) for all case scenarios

Life Cycle Inventory	System Expansion			Mass Allocation		
	BC	LE-P	SOL-P	BC	LE-P	SOL-P
NaOH, 50%	4.80E+01	6.38E+01	6.26E+01	4.67E+01	5.57E+01	5.49E+01
CaO	3.68E+01	3.62E+01	3.62E+01	3.58E+01	3.16E+01	3.18E+01
H ₂ O ₂ , 50%	1.66E+01	1.66E+01	1.66E+01	1.61E+01	1.45E+01	1.45E+01
H ₂ SO ₄	3.24E+00	4.18E+00	4.13E+00	3.15E+00	3.65E+00	3.63E+00
NaClO ₃	1.38E+02	1.38E+02	1.38E+02	1.34E+02	1.20E+02	1.21E+02
CH ₃ OH	2.51E+00	2.51E+00	2.51E+00	2.44E+00	2.19E+00	2.20E+00
CO ₂ (gas)	0.00E+00	2.63E+01	2.50E+01	0.00E+00	2.29E+01	2.19E+01
NG	5.09E+02	5.24E+02	5.24E+02	4.94E+02	4.58E+02	4.60E+02
DE	4.77E+03	4.58E+03	4.50E+03	4.63E+03	4.00E+03	3.95E+03
		-	-		-	-
SW	-4.73E+03	4.73E+03	4.73E+03	-4.60E+03	4.13E+03	4.15E+03
Solid Residue	1.10E+00	1.19E+00	1.19E+00	1.07E+00	1.04E+00	1.04E+00
Transport	5.31E+00	5.94E+00	5.90E+00	5.16E+00	5.19E+00	5.18E+00
Transport, Feedstock	4.09E+01	4.10E+01	4.10E+01	3.98E+01	3.58E+01	3.60E+01
		-	-		-	-
Power	-1.18E+02	1.94E+01	2.03E+00	-1.15E+02	1.70E+01	1.78E+00
		-	-		-	-
Lignin Credit	0.00E+00	4.55E+02	4.33E+02	NA	NA	NA
Total GWP	7.22E+02	2.34E+02	1.94E+02	7.02E+02	6.02E+02	5.50E+02

Table A4: Life Cycle Inventory Impact Assessment Characterization Results for the Base Case, BC, with System Expansion

System Expansion, per 1 ADmt SBSK (92 wt%)									
Life Cycle Inventory	GW	AD	CG	NCG	RE	EU	OD	EC	SM
NaOH, 50%	4.80E+01	1.17E+01	2.18E-01	1.74E+03	7.20E-02	4.15E-02	2.94E-06	1.57E+02	8.67E-02
CaO	3.68E+01	1.87E+00	8.13E-03	1.00E+02	1.26E-02	3.00E-03	2.54E-06	1.48E+01	2.74E-02
H2O2, 50%	1.66E+01	2.55E+00	1.43E-01	3.43E+03	1.45E-02	1.26E-02	1.70E-06	1.40E+02	2.05E-02
H2SO4	3.24E+00	1.81E+01	4.07E-02	3.66E+02	8.48E-02	8.93E-03	3.32E-07	1.22E+01	2.06E-02
NaClO3	1.38E+02	3.21E+01	1.25E+00	3.01E+04	2.00E-01	9.51E-02	7.44E-06	5.74E+02	2.34E-01
CH3OH	2.51E+00	3.62E+00	1.59E-02	4.83E+02	1.69E-02	9.56E-04	2.79E-07	2.05E+00	4.12E-03
CO2 (gas)	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Natural Gas	5.09E+02	2.19E+02	8.85E-01	2.66E+04	9.75E-01	7.44E-02	1.89E-05	1.15E+02	5.69E-01
Direct Emissions	4.77E+03	3.10E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Softwood	-4.73E+03	6.37E+01	7.96E-02	9.53E+02	7.96E-02	7.96E-02	0.00E+00	3.40E+01	1.43E+00
Solid Residue	1.10E+00	4.13E-01	3.33E-01	2.48E+01	1.34E-03	1.90E-01	4.00E-07	6.34E+00	8.46E-03
Transport	5.31E+00	1.98E+00	4.27E-03	1.73E+01	5.05E-03	3.01E-03	8.73E-07	8.22E-01	4.27E-02
Transport, Feedstock	4.09E+01	1.53E+01	3.29E-02	1.33E+02	3.89E-02	2.32E-02	6.72E-06	6.33E+00	3.29E-01
Power	-1.18E+02	-5.10E+01	-2.06E-01	-6.18E+03	-2.27E-01	-1.73E-02	-4.39E-06	-2.68E+01	-1.32E-01
Lignin Credit	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Total	7.22E+02	3.23E+02	2.80E+00	5.78E+04	1.27E+00	5.14E-01	3.77E-05	1.04E+03	2.64E+00

Table A5: Life Cycle Inventory Impact Assessment Characterization Results for the Base Case, BC, with Mass Allocation

Mass Allocation, per 1 ADmt SBSK (92 wt%), 1 ADmt Lignin (95 wt%) or 1 mt Soap									
Life Cycle Inventory	GW	AD	CG	NCG	RE	EU	OD	EC	SM
NaOH, 50%	4.67E+01	1.13E+01	2.12E-01	1.69E+03	7.00E-02	4.04E-02	2.86E-06	1.53E+02	8.43E-02
CaO	3.58E+01	1.81E+00	7.90E-03	9.76E+01	1.23E-02	2.91E-03	2.47E-06	1.43E+01	2.66E-02
H2O2, 50%	1.61E+01	2.48E+00	1.39E-01	3.33E+03	1.41E-02	1.23E-02	1.65E-06	1.36E+02	1.99E-02
H2SO4	3.15E+00	1.76E+01	3.96E-02	3.55E+02	8.24E-02	8.67E-03	3.23E-07	1.18E+01	2.00E-02
NaClO3	1.34E+02	3.12E+01	1.21E+00	2.93E+04	1.95E-01	9.24E-02	7.23E-06	5.58E+02	2.28E-01
CH3OH	2.44E+00	3.52E+00	1.54E-02	4.70E+02	1.64E-02	9.29E-04	2.71E-07	1.99E+00	4.00E-03
CO2 (gas)	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Natural Gas	4.94E+02	2.13E+02	8.60E-01	2.58E+04	9.48E-01	7.23E-02	1.84E-05	1.12E+02	5.53E-01
Direct Emissions	4.63E+03	3.01E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Softwood	-4.60E+03	6.19E+01	7.74E-02	9.26E+02	7.74E-02	7.74E-02	0.00E+00	3.30E+01	1.39E+00
Solid Residue	1.07E+00	4.01E-01	3.24E-01	2.41E+01	1.30E-03	1.84E-01	3.89E-07	6.16E+00	8.22E-03
Transport	5.16E+00	1.93E+00	4.15E-03	1.68E+01	4.91E-03	2.92E-03	8.49E-07	7.99E-01	4.15E-02
Transport, Feedstock	3.98E+01	1.48E+01	3.20E-02	1.29E+02	3.78E-02	2.25E-02	6.54E-06	6.16E+00	3.20E-01
Power	-1.15E+02	-4.95E+01	-2.00E-01	-	-2.20E-01	-1.68E-02	-4.27E-06	-2.61E+01	-1.28E-01
Lignin Credit			01	6.01E+03		02			01
Total	7.02E+02	3.14E+02	2.73E+00	5.61E+04	1.24E+00	5.00E-01	3.67E-05	1.01E+03	2.57E+00

Table A6: Life Cycle Inventory Impact Assessment Characterization Results for the Base Case, BC, with Economic Allocation for SBSK
Economic Allocation, per 1 ADmt SBSK (92 wt%)

Life Cycle Inventory	GW	AD	CG	NCG	RE	EU	OD	EC	SM
NaOH, 50%	4.78E+01	1.16E+01	2.17E-01	1.73E+03	7.17E-02	4.14E-02	2.93E-06	1.56E+02	8.64E-02
CaO	3.67E+01	1.86E+00	8.10E-03	1.00E+02	1.26E-02	2.99E-03	2.53E-06	1.47E+01	2.73E-02
H2O2, 50%	1.65E+01	2.54E+00	1.42E-01	3.42E+03	1.45E-02	1.26E-02	1.69E-06	1.39E+02	2.04E-02
H2SO4	3.23E+00	1.80E+01	4.06E-02	3.64E+02	8.44E-02	8.89E-03	3.31E-07	1.21E+01	2.05E-02
NaClO3	1.37E+02	3.19E+01	1.24E+00	3.00E+04	1.99E-01	9.47E-02	7.41E-06	5.72E+02	2.33E-01
CH3OH	2.50E+00	3.61E+00	1.58E-02	4.81E+02	1.68E-02	9.52E-04	2.78E-07	2.04E+00	4.10E-03
CO2 (gas)	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Natural Gas	5.07E+02	2.18E+02	8.82E-01	2.65E+04	9.71E-01	7.41E-02	1.88E-05	1.15E+02	5.67E-01
Direct Emissions	4.75E+03	3.08E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
-	-	-	-	-	-	-	-	-	-
Softwood	4.71E+03	6.34E+01	7.93E-02	9.49E+02	7.93E-02	7.93E-02	0.00E+00	3.38E+01	1.43E+00
Solid Residue	1.10E+00	4.11E-01	3.32E-01	2.47E+01	1.34E-03	1.89E-01	3.98E-07	6.31E+00	8.43E-03
Transport	5.29E+00	1.97E+00	4.25E-03	1.72E+01	5.03E-03	2.99E-03	8.70E-07	8.19E-01	4.25E-02
Transport, Feedstock	4.08E+01	1.52E+01	3.28E-02	1.33E+02	3.87E-02	2.31E-02	6.70E-06	6.31E+00	3.28E-01
-	-	-	-2.05E-	-	-2.26E-	-1.72E-	-4.38E-	-	-1.32E-
Power	1.18E+02	5.08E+01	01	6.16E+03	01	02	06	-2.67E+01	01
Lignin Credit									
Total	7.20E+02	3.21E+02	2.79E+00	5.75E+04	1.27E+00	5.12E-01	3.76E-05	1.03E+03	2.63E+00

Table A7: Life Cycle Inventory Impact Assessment Characterization Results for the Base Case, BC, with Economic Allocation for Soap
Economic Allocation, per 1 mt Soap

Life Cycle Inventory	GW	AD	CG	NCG	RE	EU	OD	EC	SM
NaOH, 50%	6.60E+00	1.60E+00	3.00E-02	2.38E+02	9.89E-03	5.70E-03	4.04E-07	2.16E+01	1.19E-02
CaO	5.06E+00	2.56E-01	1.12E-03	1.38E+01	1.73E-03	4.12E-04	3.48E-07	2.03E+00	3.76E-03
H2O2, 50%	2.28E+00	3.50E-01	1.96E-02	4.71E+02	1.99E-03	1.73E-03	2.33E-07	1.92E+01	2.81E-03
H2SO4	4.45E-01	2.49E+00	5.59E-03	5.02E+01	1.16E-02	1.23E-03	4.56E-08	1.67E+00	2.83E-03
NaClO3	1.89E+01	4.40E+00	1.72E-01	4.14E+03	2.75E-02	1.31E-02	1.02E-06	7.89E+01	3.22E-02
CH3OH	3.44E-01	4.97E-01	2.18E-03	6.64E+01	2.31E-03	1.31E-04	3.83E-08	2.82E-01	5.65E-04
CO2 (gas)	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Natural Gas	6.98E+01	3.01E+01	1.22E-01	3.65E+03	1.34E-01	1.02E-02	2.60E-06	1.58E+01	7.81E-02
Direct Emissions	6.55E+02	4.25E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Softwood	-6.49E+02	8.75E+00	1.09E-02	1.31E+02	1.09E-02	1.09E-02	0.00E+00	4.66E+00	1.97E-01
Solid Residue	1.51E-01	5.67E-02	4.57E-02	3.41E+00	1.84E-04	2.60E-02	5.49E-08	8.70E-01	1.16E-03
Transport	7.30E-01	2.72E-01	5.87E-04	2.37E+00	6.93E-04	4.13E-04	1.20E-07	1.13E-01	5.87E-03
Transport, Feedstock	5.62E+00	2.10E+00	4.52E-03	1.83E+01	5.34E-03	3.18E-03	9.23E-07	8.70E-01	4.52E-02
Power	-1.62E+01	-7.00E+00	-2.83E-02	-8.49E+02	-3.11E-02	-2.37E-03	-6.03E-07	-	-1.82E-02
Lignin Credit			02	02	03			3.68E+00	02
Total	9.92E+01	4.43E+01	3.85E-01	7.93E+03	1.75E-01	7.07E-02	5.18E-06	1.42E+02	3.63E-01

Table A8: Life Cycle Inventory Impact Assessment Characterization Results for the Alternative Case, LE-P, with System Expansion

System Expansion, per 1 ADmt SBSK (92 wt%)									
Life Cycle Inventory	GW	AD	CG	NCG	RE	EU	OD	EC	SM
NaOH, 50%	6.38E+01	1.55E+01	2.90E-01	2.31E+03	9.57E-02	5.52E-02	3.91E-06	2.09E+02	1.15E-01
CaO	3.62E+01	1.83E+00	7.99E-03	9.87E+01	1.24E-02	2.95E-03	2.49E-06	1.45E+01	2.69E-02
H2O2, 50%	1.66E+01	2.55E+00	1.43E-01	3.43E+03	1.45E-02	1.26E-02	1.70E-06	1.40E+02	2.05E-02
H2SO4	4.18E+00	2.33E+01	5.24E-02	4.71E+02	1.09E-01	1.15E-02	4.28E-07	1.57E+01	2.65E-02
NaClO3	1.38E+02	3.21E+01	1.25E+00	3.01E+04	2.00E-01	9.51E-02	7.44E-06	5.74E+02	2.34E-01
CH3OH	2.51E+00	3.62E+00	1.59E-02	4.83E+02	1.69E-02	9.56E-04	2.79E-07	2.05E+00	4.12E-03
CO2 (gas)	2.63E+01	3.35E+00	9.75E-02	5.50E+02	1.95E-02	1.97E-02	1.77E-06	3.91E+01	2.64E-02
Natural Gas	5.24E+02	2.26E+02	9.12E-01	2.74E+04	1.00E+00	7.67E-02	1.95E-05	1.19E+02	5.86E-01
Direct Emissions	4.58E+03	3.12E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Softwood	-4.73E+03	6.37E+01	7.96E-02	9.53E+02	7.96E-02	7.96E-02	0.00E+00	3.40E+01	1.43E+00
Solid Residue	1.19E+00	4.45E-01	3.59E-01	2.68E+01	1.45E-03	2.05E-01	4.32E-07	6.84E+00	9.14E-03
Transport	5.94E+00	2.22E+00	4.78E-03	1.93E+01	5.64E-03	3.36E-03	9.76E-07	9.19E-01	4.78E-02
Transport, Feedstock	4.10E+01	1.53E+01	3.30E-02	1.34E+02	3.90E-02	2.32E-02	6.75E-06	6.35E+00	3.30E-01
Power	-1.94E+01	-8.37E+00	-3.38E-02	-1.02E+03	-3.72E-02	-2.84E-03	-7.22E-07	-4.40E+00	-2.17E-02
Lignin Credit	-4.55E+02	-7.62E+01	-	-7.76E+03	-3.73E-01	-6.97E-01	-1.51E-05	-5.07E+02	-1.38E+00
Total	2.34E+02	3.08E+02	1.54E+00	5.72E+04	1.19E+00	01	2.99E-05	6.50E+02	1.46E+00

Table A9: Life Cycle Inventory Impact Assessment Characterization Results for the Alternative Case, LE-P, with Mass Allocation

Mass Allocation, per 1 ADmt SBSK (92 wt%), 1 ADmt Lignin (95 wt%) or 1 mt Soap									
Life Cycle Inventory	GW	AD	CG	NCG	RE	EU	OD	EC	SM
NaOH, 50%	5.57E+01	1.35E+01	2.53E-01	2.01E+03	8.35E-02	4.82E-02	3.41E-06	1.82E+02	1.01E-01
CaO	3.16E+01	1.60E+00	6.98E-03	8.62E+01	1.08E-02	2.57E-03	2.18E-06	1.27E+01	2.35E-02
H2O2, 50%	1.45E+01	2.23E+00	1.25E-01	3.00E+03	1.27E-02	1.10E-02	1.48E-06	1.22E+02	1.79E-02
H2SO4	3.65E+00	2.04E+01	4.58E-02	4.11E+02	9.53E-02	1.00E-02	3.74E-07	1.37E+01	2.31E-02
NaClO3	1.20E+02	2.80E+01	1.09E+00	2.63E+04	1.75E-01	8.30E-02	6.50E-06	5.02E+02	2.05E-01
CH3OH	2.19E+00	3.16E+00	1.39E-02	4.22E+02	1.47E-02	8.35E-04	2.44E-07	1.79E+00	3.59E-03
CO2 (gas)	2.29E+01	2.92E+00	8.51E-02	4.80E+02	1.71E-02	1.72E-02	1.55E-06	3.41E+01	2.30E-02
Natural Gas	4.58E+02	1.97E+02	7.97E-01	2.39E+04	8.78E-01	6.69E-02	1.70E-05	1.04E+02	5.12E-01
Direct Emissions	4.00E+03	2.73E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
-	-	-	-	-	-	-	-	-	-
Softwood	4.13E+03	5.56E+01	6.95E-02	8.32E+02	6.95E-02	6.95E-02	0.00E+00	2.97E+01	1.25E+00
Solid Residue	1.04E+00	3.89E-01	3.14E-01	2.34E+01	1.26E-03	1.79E-01	3.77E-07	5.97E+00	7.98E-03
Transport	5.19E+00	1.93E+00	4.17E-03	1.69E+01	4.93E-03	2.94E-03	8.52E-07	8.03E-01	4.17E-02
Transport, Feedstock	3.58E+01	1.34E+01	2.88E-02	1.17E+02	3.41E-02	2.03E-02	5.89E-06	5.55E+00	2.88E-01
-	-	-	-2.95E-	-	-3.25E-	-2.48E-	-6.30E-	-	-1.90E-
Power	1.70E+01	7.31E+00	02	8.87E+02	02	03	07	-3.85E+00	02
Lignin Credit									
Total	6.02E+02	3.36E+02	2.80E+00	5.67E+04	1.36E+00	5.09E-01	3.92E-05	1.01E+03	2.48E+00

Table A10: Life Cycle Inventory Impact Assessment Characterization Results for the Alternative Case, LE-P, with Economic Allocation for SBSK

Economic Allocation, per 1 ADmt SBSK (92 wt%)									
Life Cycle Inventory	GW	AD	CG	NCG	RE	EU	OD	EC	SM
NaOH, 50%	6.15E+01	1.49E+01	2.79E-01	2.22E+03	9.22E-02	5.32E-02	3.77E-06	2.01E+02	1.11E-01
CaO	3.49E+01	1.77E+00	7.70E-03	9.52E+01	1.20E-02	2.84E-03	2.40E-06	1.40E+01	2.60E-02
H2O2, 50%	1.60E+01	2.46E+00	1.38E-01	3.31E+03	1.40E-02	1.22E-02	1.64E-06	1.35E+02	1.97E-02
H2SO4	4.02E+00	2.25E+01	5.05E-02	4.54E+02	1.05E-01	1.11E-02	4.12E-07	1.51E+01	2.55E-02
NaClO3	1.33E+02	3.09E+01	1.20E+00	2.90E+04	1.93E-01	9.16E-02	7.17E-06	5.54E+02	2.26E-01
CH3OH	2.42E+00	3.49E+00	1.53E-02	4.66E+02	1.62E-02	9.22E-04	2.69E-07	1.98E+00	3.97E-03
CO2 (gas)	2.53E+01	3.23E+00	9.40E-02	5.30E+02	1.88E-02	1.90E-02	1.71E-06	3.77E+01	2.54E-02
Natural Gas	5.05E+02	2.18E+02	8.79E-01	2.64E+04	9.69E-01	7.39E-02	1.88E-05	1.15E+02	5.65E-01
Direct Emissions	4.41E+03	3.01E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
-	-	-	-	-	-	-	-	-	-
Softwood	4.56E+03	6.14E+01	7.67E-02	9.18E+02	7.67E-02	7.67E-02	0.00E+00	3.27E+01	1.38E+00
Solid Residue	1.15E+00	4.29E-01	3.46E-01	2.58E+01	1.39E-03	1.97E-01	4.16E-07	6.59E+00	8.80E-03
Transport	5.72E+00	2.14E+00	4.60E-03	1.86E+01	5.44E-03	3.24E-03	9.41E-07	8.86E-01	4.60E-02
Transport, Feedstock	3.96E+01	1.48E+01	3.18E-02	1.29E+02	3.76E-02	2.24E-02	6.50E-06	6.13E+00	3.18E-01
-	-	-	-	-	-	-2.74E-	-6.96E-	-	-2.09E-
Power	1.87E+01	8.07E+00	-3.26E-02	9.79E+02	-3.59E-02	03	07	-4.24E+00	02
Lignin Credit									
Total	6.64E+02	3.71E+02	3.09E+00	6.26E+04	1.51E+00	5.61E-01	4.33E-05	1.11E+03	2.74E+00

Table A11: Life Cycle Inventory Impact Assessment Characterization Results for the Alternative Case, LE-P, with Economic Allocation for Lignin

Economic Allocation, per 1 ADmt Lignin (95 wt%)									
Life Cycle Inventory	GW	AD	CG	NCG	RE	EU	OD	EC	SM
NaOH, 50%	1.77E+01	4.30E+00	8.05E-02	6.41E+02	2.66E-02	1.53E-02	1.09E-06	5.80E+01	3.20E-02
CaO	1.01E+01	5.10E-01	2.22E-03	2.74E+01	3.45E-03	8.19E-04	6.93E-07	4.03E+00	7.48E-03
H2O2, 50%	4.60E+00	7.09E-01	3.97E-02	9.53E+02	4.03E-03	3.50E-03	4.72E-07	3.88E+01	5.68E-03
H2SO4	1.16E+00	6.48E+00	1.46E-02	1.31E+02	3.03E-02	3.19E-03	1.19E-07	4.35E+00	7.36E-03
NaClO3	3.82E+01	8.91E+00	3.47E-01	8.37E+03	5.56E-02	2.64E-02	2.07E-06	1.60E+02	6.51E-02
CH3OH	6.97E-01	1.01E+00	4.42E-03	1.34E+02	4.68E-03	2.66E-04	7.76E-08	5.70E-01	1.14E-03
CO2 (gas)	7.29E+00	9.30E-01	2.71E-02	1.53E+02	5.43E-03	5.46E-03	4.92E-07	1.09E+01	7.32E-03
Natural Gas	1.46E+02	6.28E+01	2.53E-01	7.61E+03	2.79E-01	2.13E-02	5.41E-06	3.30E+01	1.63E-01
Direct Emissions	1.27E+03	8.68E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
-	-	-	-	-	-	-	-	-	-
Softwood	1.31E+03	1.77E+01	2.21E-02	2.65E+02	2.21E-02	2.21E-02	0.00E+00	9.44E+00	3.98E-01
Solid Residue	3.30E-01	1.24E-01	9.98E-02	7.44E+00	4.02E-04	5.69E-02	1.20E-07	1.90E+00	2.54E-03
Transport	1.65E+00	6.16E-01	1.33E-03	5.37E+00	1.57E-03	9.34E-04	2.71E-07	2.55E-01	1.33E-02
Transport, Feedstock	1.14E+01	4.25E+00	9.17E-03	3.71E+01	1.08E-02	6.45E-03	1.87E-06	1.77E+00	9.17E-02
-	-	-	-	-	-	-7.89E-	-2.01E-	-	-6.03E-
Power	5.39E+00	2.33E+00	-9.39E-03	2.82E+02	-1.03E-02	04	07	-1.22E+00	03
Lignin Credit									
Total	1.91E+02	1.07E+02	8.92E-01	1.80E+04	4.34E-01	1.62E-01	1.25E-05	3.21E+02	7.89E-01

Table A12: Life Cycle Inventory Impact Assessment Characterization Results for the Alternative Case, LE-P, with Economic Allocation for Soap

Economic Allocation, per 1 mt Soap									
Life Cycle Inventory	GW	AD	CG	NCG	RE	EU	OD	EC	SM
NaOH, 50%	8.48E+00	2.06E+00	3.85E-02	3.06E+02	1.27E-02	7.33E-03	5.20E-07	2.77E+01	1.53E-02
CaO	4.81E+00	2.44E-01	1.06E-03	1.31E+01	1.65E-03	3.92E-04	3.31E-07	1.93E+00	3.58E-03
H2O2, 50%	2.20E+00	3.39E-01	1.90E-02	4.56E+02	1.93E-03	1.68E-03	2.26E-07	1.86E+01	2.72E-03
H2SO4	5.55E-01	3.10E+00	6.97E-03	6.26E+01	1.45E-02	1.53E-03	5.69E-08	2.08E+00	3.52E-03
NaClO3	1.83E+01	4.26E+00	1.66E-01	4.00E+03	2.66E-02	1.26E-02	9.89E-07	7.63E+01	3.11E-02
CH3OH	3.33E-01	4.81E-01	2.11E-03	6.42E+01	2.24E-03	1.27E-04	3.71E-08	2.73E-01	5.47E-04
CO2 (gas)	3.49E+00	4.45E-01	1.30E-02	7.30E+01	2.60E-03	2.61E-03	2.36E-07	5.20E+00	3.50E-03
Natural Gas	6.97E+01	3.00E+01	1.21E-01	3.64E+03	1.34E-01	1.02E-02	2.59E-06	1.58E+01	7.79E-02
Direct Emissions	6.08E+02	4.15E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Softwood	-6.28E+02	8.46E+00	1.06E-02	1.27E+02	1.06E-02	1.06E-02	0.00E+00	4.51E+00	1.90E-01
Solid Residue	1.58E-01	5.92E-02	4.78E-02	3.56E+00	1.92E-04	2.72E-02	5.74E-08	9.09E-01	1.21E-03
Transport	7.89E-01	2.94E-01	6.35E-04	2.57E+00	7.50E-04	4.47E-04	1.30E-07	1.22E-01	6.35E-03
Transport, Feedstock	5.46E+00	2.04E+00	4.39E-03	1.78E+01	5.18E-03	3.09E-03	8.97E-07	8.45E-01	4.39E-02
Power Lignin Credit	-2.58E+00	-1.11E+00	-4.49E-03	-1.35E+02	-4.95E-03	-3.77E-04	-9.59E-08	-5.85E-01	-2.89E-03
Total	9.15E+01	5.11E+01	4.27E-01	8.63E+03	2.08E-01	7.74E-02	5.97E-06	1.54E+02	3.77E-01

Table A13: Life Cycle Inventory Impact Assessment Characterization Results for the Alternative Case, SOL-P, with System Expansion

System Expansion, per 1 ADmt SBSK (92 wt%)									
Life Cycle Inventory	GW	AD	CG	NCG	RE	EU	OD	EC	SM
NaOH, 50%	6.26E+01	1.52E+01	2.84E-01	2.26E+03	9.38E-02	5.41E-02	3.83E-06	2.05E+02	1.13E-01
CaO	3.62E+01	1.84E+00	8.00E-03	9.88E+01	1.24E-02	2.95E-03	2.50E-06	1.45E+01	2.70E-02
H2O2, 50%	1.66E+01	2.55E+00	1.43E-01	3.43E+03	1.45E-02	1.26E-02	1.70E-06	1.40E+02	2.05E-02
H2SO4	4.13E+00	2.31E+01	5.19E-02	4.66E+02	1.08E-01	1.14E-02	4.23E-07	1.55E+01	2.62E-02
NaClO3	1.38E+02	3.21E+01	1.25E+00	3.01E+04	2.00E-01	9.51E-02	7.44E-06	5.74E+02	2.34E-01
CH3OH	2.51E+00	3.62E+00	1.59E-02	4.83E+02	1.69E-02	9.56E-04	2.79E-07	2.05E+00	4.12E-03
CO2 (gas)	2.50E+01	3.18E+00	9.27E-02	5.22E+02	1.86E-02	1.87E-02	1.68E-06	3.72E+01	2.51E-02
Natural Gas	5.24E+02	2.26E+02	9.12E-01	2.74E+04	1.00E+00	7.67E-02	1.95E-05	1.19E+02	5.86E-01
Direct Emissions	4.50E+03	3.03E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Softwood	-4.73E+03	6.37E+01	7.96E-02	9.53E+02	7.96E-02	7.96E-02	0.00E+00	3.40E+01	1.43E+00
Solid Residue	1.19E+00	4.44E-01	3.58E-01	2.67E+01	1.44E-03	2.04E-01	4.30E-07	6.82E+00	9.11E-03
Transport	5.90E+00	2.20E+00	4.74E-03	1.92E+01	5.60E-03	3.34E-03	9.69E-07	9.13E-01	4.74E-02
Transport, Feedstock	4.10E+01	1.53E+01	3.30E-02	1.34E+02	3.90E-02	2.32E-02	6.75E-06	6.35E+00	3.30E-01
Power	2.03E+00	8.75E-01	3.53E-03	1.06E+02	3.89E-03	2.97E-04	7.54E-08	4.60E-01	2.27E-03
Lignin Credit	-4.33E+02	-7.24E+01	-1.59E+00	-7.38E+03	-3.54E-01	-6.63E-01	-1.43E-05	-4.82E+02	-1.31E+00
Total	1.94E+02	3.21E+02	1.65E+00	5.86E+04	1.24E+00	02	3.12E-05	6.74E+02	1.55E+00

Table A14: Life Cycle Inventory Impact Assessment Characterization Results for the Alternative Case, SOL-P, with Mass Allocation

Mass Allocation, per 1 ADmt SBSK (92 wt%), 1 ADmt Lignin (95 wt%) or 1 mt Soap									
Life Cycle Inventory	GW	AD	CG	NCG	RE	EU	OD	EC	SM
NaOH, 50%	5.49E+01	1.33E+01	2.49E-01	1.98E+03	8.24E-02	4.75E-02	3.37E-06	1.80E+02	9.92E-02
CaO	3.18E+01	1.61E+00	7.02E-03	8.68E+01	1.09E-02	2.59E-03	2.19E-06	1.27E+01	2.37E-02
H2O2, 50%	1.45E+01	2.24E+00	1.25E-01	3.01E+03	1.27E-02	1.11E-02	1.49E-06	1.23E+02	1.80E-02
H2SO4	3.63E+00	2.03E+01	4.56E-02	4.09E+02	9.48E-02	9.99E-03	3.72E-07	1.36E+01	2.30E-02
NaClO3	1.21E+02	2.82E+01	1.10E+00	2.64E+04	1.76E-01	8.35E-02	6.54E-06	5.04E+02	2.06E-01
CH3OH	2.20E+00	3.18E+00	1.40E-02	4.24E+02	1.48E-02	8.39E-04	2.45E-07	1.80E+00	3.61E-03
CO2 (gas)	2.19E+01	2.79E+00	8.13E-02	4.59E+02	1.63E-02	1.64E-02	1.48E-06	3.26E+01	2.20E-02
Natural Gas	4.60E+02	1.98E+02	8.01E-01	2.41E+04	8.82E-01	6.73E-02	1.71E-05	1.04E+02	5.15E-01
Direct Emissions	3.95E+03	2.66E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	-								
Softwood	4.15E+03	5.59E+01	6.99E-02	8.36E+02	6.99E-02	6.99E-02	0.00E+00	2.98E+01	1.26E+00
Solid Residue	1.04E+00	3.90E-01	3.14E-01	2.34E+01	1.27E-03	1.79E-01	3.78E-07	5.99E+00	7.99E-03
Transport	5.18E+00	1.93E+00	4.16E-03	1.68E+01	4.92E-03	2.93E-03	8.51E-07	8.01E-01	4.16E-02
Transport, Feedstock	3.60E+01	1.34E+01	2.90E-02	1.17E+02	3.42E-02	2.04E-02	5.92E-06	5.58E+00	2.90E-01
Power	1.78E+00	7.68E-01	3.10E-03	9.32E+01	3.42E-03	2.61E-04	6.62E-08	4.04E-01	1.99E-03
Lignin Credit									
Total	5.50E+02	3.45E+02	2.84E+00	5.80E+04	1.40E+00	5.12E-01	4.00E-05	1.01E+03	2.51E+00

Table A15: Life Cycle Inventory Impact Assessment Characterization Results for the Alternative Case, SOL-P, with Economic Allocation for SBSK

Economic Allocation, per 1 ADmt SBSK (92 wt%)									
Life Cycle Inventory	GW	AD	CG	NCG	RE	EU	OD	EC	SM
NaOH, 50%	6.03E+01	1.46E+01	2.74E-01	2.18E+03	9.04E-02	5.21E-02	3.70E-06	1.97E+02	1.09E-01
CaO	3.49E+01	1.77E+00	7.71E-03	9.52E+01	1.20E-02	2.84E-03	2.41E-06	1.40E+01	2.60E-02
H2O2, 50%	1.60E+01	2.46E+00	1.38E-01	3.31E+03	1.40E-02	1.22E-02	1.64E-06	1.35E+02	1.97E-02
H2SO4	3.98E+00	2.22E+01	5.00E-02	4.49E+02	1.04E-01	1.10E-02	4.08E-07	1.49E+01	2.53E-02
NaClO3	1.33E+02	3.09E+01	1.20E+00	2.90E+04	1.93E-01	9.16E-02	7.17E-06	5.54E+02	2.26E-01
CH3OH	2.42E+00	3.49E+00	1.53E-02	4.66E+02	1.62E-02	9.21E-04	2.69E-07	1.98E+00	3.97E-03
CO2 (gas)	2.40E+01	3.07E+00	8.93E-02	5.03E+02	1.79E-02	1.80E-02	1.62E-06	3.58E+01	2.41E-02
Natural Gas	5.05E+02	2.18E+02	8.79E-01	2.64E+04	9.68E-01	7.39E-02	1.88E-05	1.15E+02	5.65E-01
Direct Emissions	4.33E+03	2.92E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
-	-	-	-	-	-	-	-	-	-
Softwood	4.56E+03	6.14E+01	7.67E-02	9.18E+02	7.67E-02	7.67E-02	0.00E+00	3.27E+01	1.38E+00
Solid Residue	1.14E+00	4.28E-01	3.45E-01	2.57E+01	1.39E-03	1.97E-01	4.15E-07	6.57E+00	8.78E-03
Transport	5.68E+00	2.12E+00	4.57E-03	1.85E+01	5.40E-03	3.22E-03	9.34E-07	8.80E-01	4.57E-02
Transport, Feedstock	3.96E+01	1.48E+01	3.18E-02	1.29E+02	3.76E-02	2.24E-02	6.50E-06	6.12E+00	3.18E-01
Power	1.96E+00	8.43E-01	3.40E-03	1.02E+02	3.75E-03	2.86E-04	7.27E-08	4.44E-01	2.19E-03
Lignin Credit									
Total	6.04E+02	3.79E+02	3.12E+00	6.36E+04	1.54E+00	5.62E-01	4.39E-05	1.11E+03	2.75E+00

Table A16: Life Cycle Inventory Impact Assessment Characterization Results for the Alternative Case, SOL-P, with Economic Allocation for Lignin

Economic Allocation, per 1 ADmt Lignin (95 wt%)									
Life Cycle Inventory	GW	AD	CG	NCG	RE	EU	OD	EC	SM
NaOH, 50%	1.83E+01	4.44E+00	8.30E-02	6.61E+02	2.74E-02	1.58E-02	1.12E-06	5.98E+01	3.30E-02
CaO	1.06E+01	5.37E-01	2.34E-03	2.89E+01	3.63E-03	8.62E-04	7.30E-07	4.24E+00	7.88E-03
H2O2, 50%	4.84E+00	7.46E-01	4.17E-02	1.00E+03	4.24E-03	3.69E-03	4.97E-07	4.09E+01	5.98E-03
H2SO4	1.21E+00	6.74E+00	1.52E-02	1.36E+02	3.16E-02	3.32E-03	1.24E-07	4.53E+00	7.66E-03
NaClO3	4.02E+01	9.37E+00	3.65E-01	8.80E+03	5.85E-02	2.78E-02	2.18E-06	1.68E+02	6.85E-02
CH3OH	7.33E-01	1.06E+00	4.64E-03	1.41E+02	4.93E-03	2.79E-04	8.16E-08	6.00E-01	1.20E-03
CO2 (gas)	7.29E+00	9.30E-01	2.71E-02	1.53E+02	5.43E-03	5.46E-03	4.92E-07	1.09E+01	7.32E-03
Natural Gas	1.53E+02	6.61E+01	2.67E-01	8.01E+03	2.94E-01	2.24E-02	5.69E-06	3.47E+01	1.71E-01
Direct Emissions	1.31E+03	8.84E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
-	-	-	-	-	-	-	-	-	-
Softwood	1.38E+03	1.86E+01	2.33E-02	2.78E+02	2.33E-02	2.33E-02	0.00E+00	9.93E+00	4.19E-01
Solid Residue	3.46E-01	1.30E-01	1.05E-01	7.80E+00	4.22E-04	5.96E-02	1.26E-07	1.99E+00	2.66E-03
Transport	1.72E+00	6.43E-01	1.39E-03	5.61E+00	1.64E-03	9.75E-04	2.83E-07	2.67E-01	1.39E-02
Transport, Feedstock	1.20E+01	4.47E+00	9.64E-03	3.90E+01	1.14E-02	6.79E-03	1.97E-06	1.86E+00	9.64E-02
Power	5.93E-01	2.56E-01	1.03E-03	3.10E+01	1.14E-03	8.67E-05	2.20E-08	1.35E-01	6.63E-04
Lignin Credit									
Total	1.83E+02	1.15E+02	9.46E-01	1.93E+04	4.67E-01	1.70E-01	1.33E-05	3.38E+02	8.35E-01

Table A17: Life Cycle Inventory Impact Assessment Characterization Results for the Alternative Case, SOL-P, with Economic Allocation for Soap

Economic Allocation, per 1 mt Soap									
Life Cycle Inventory	GW	AD	CG	NCG	RE	EU	OD	EC	SM
NaOH, 50%	8.75E+00	2.12E+00	3.97E-02	3.16E+02	1.31E-02	7.56E-03	5.36E-07	2.86E+01	1.58E-02
CaO	5.07E+00	2.57E-01	1.12E-03	1.38E+01	1.74E-03	4.12E-04	3.49E-07	2.03E+00	3.77E-03
H2O2, 50%	2.32E+00	3.57E-01	2.00E-02	4.80E+02	2.03E-03	1.76E-03	2.38E-07	1.95E+01	2.86E-03
H2SO4	5.78E-01	3.23E+00	7.26E-03	6.51E+01	1.51E-02	1.59E-03	5.92E-08	2.17E+00	3.67E-03
NaClO3	1.92E+01	4.48E+00	1.75E-01	4.21E+03	2.80E-02	1.33E-02	1.04E-06	8.03E+01	3.28E-02
CH3OH	3.51E-01	5.06E-01	2.22E-03	6.75E+01	2.36E-03	1.34E-04	3.90E-08	2.87E-01	5.75E-04
CO2 (gas)	3.49E+00	4.45E-01	1.30E-02	7.30E+01	2.60E-03	2.61E-03	2.36E-07	5.19E+00	3.50E-03
Natural Gas	7.33E+01	3.16E+01	1.28E-01	3.83E+03	1.40E-01	1.07E-02	2.72E-06	1.66E+01	8.20E-02
Direct Emissions	6.29E+02	4.23E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
-	-	-	-	-	-	-	-	-	-
Softwood	6.61E+02	8.90E+00	1.11E-02	1.33E+02	1.11E-02	1.11E-02	0.00E+00	4.75E+00	2.00E-01
Solid Residue	1.66E-01	6.21E-02	5.01E-02	3.73E+00	2.02E-04	2.85E-02	6.02E-08	9.53E-01	1.27E-03
Transport	8.24E-01	3.08E-01	6.63E-04	2.68E+00	7.83E-04	4.67E-04	1.35E-07	1.28E-01	6.63E-03
Transport, Feedstock	5.74E+00	2.14E+00	4.61E-03	1.87E+01	5.45E-03	3.25E-03	9.43E-07	8.88E-01	4.61E-02
Power	2.84E-01	1.22E-01	4.94E-04	1.48E+01	5.44E-04	4.15E-05	1.05E-08	6.43E-02	3.17E-04
Lignin Credit									
Total	8.76E+01	5.50E+01	4.52E-01	9.23E+03	2.24E-01	8.15E-02	6.37E-06	1.62E+02	4.00E-01

Table A18: Sensitivity to the Production Capacity of Commercial Lignin Extraction, with System Expansion (shown left) and Mass Allocation (shown right) for the SOL-P Case

Total Emissions	Per admt Lignin	System Expansion			Mass Allocation		
		SOL-P	SOL-P, -25%	SOL-P, +25%	SOL-P	SOL-P, -25%	SOL-P, +25%
Global Warming	kg CO2 eq	1.94E+02	3.20E+02	6.26E+01	5.50E+02	5.80E+02	5.17E+02
Acidification	H+ moles eq	3.21E+02	3.26E+02	3.14E+02	3.45E+02	3.43E+02	3.47E+02
Carcinogenics	kg benzen eq	1.65E+00	1.95E+00	1.33E+00	2.84E+00	2.83E+00	2.85E+00
Non carcinogenics	kg toluen eq	5.86E+04	5.91E+04	5.81E+04	5.80E+04	5.81E+04	5.77E+04
Respiratory effects	kg PM2.5 eq	1.24E+00	1.28E+00	1.21E+00	1.40E+00	1.39E+00	1.42E+00
Eutrophication	kg N eq	-7.98E-02	6.97E-02	-2.29E-01	5.12E-01	5.11E-01	5.13E-01
Ozone depletion	kg CFC-11 eq	3.12E-05	3.33E-05	2.91E-05	4.00E-05	3.97E-05	4.03E-05
Ecotoxicity	kg 2,4-D eq	6.74E+02	7.67E+02	5.81E+02	1.01E+03	1.02E+03	1.01E+03
Smog	kg NOx eq	1.55E+00	1.83E+00	1.26E+00	2.51E+00	2.54E+00	2.48E+00

12.2 Appendix B: Supplemental Differential Scanning Calorimetry Data

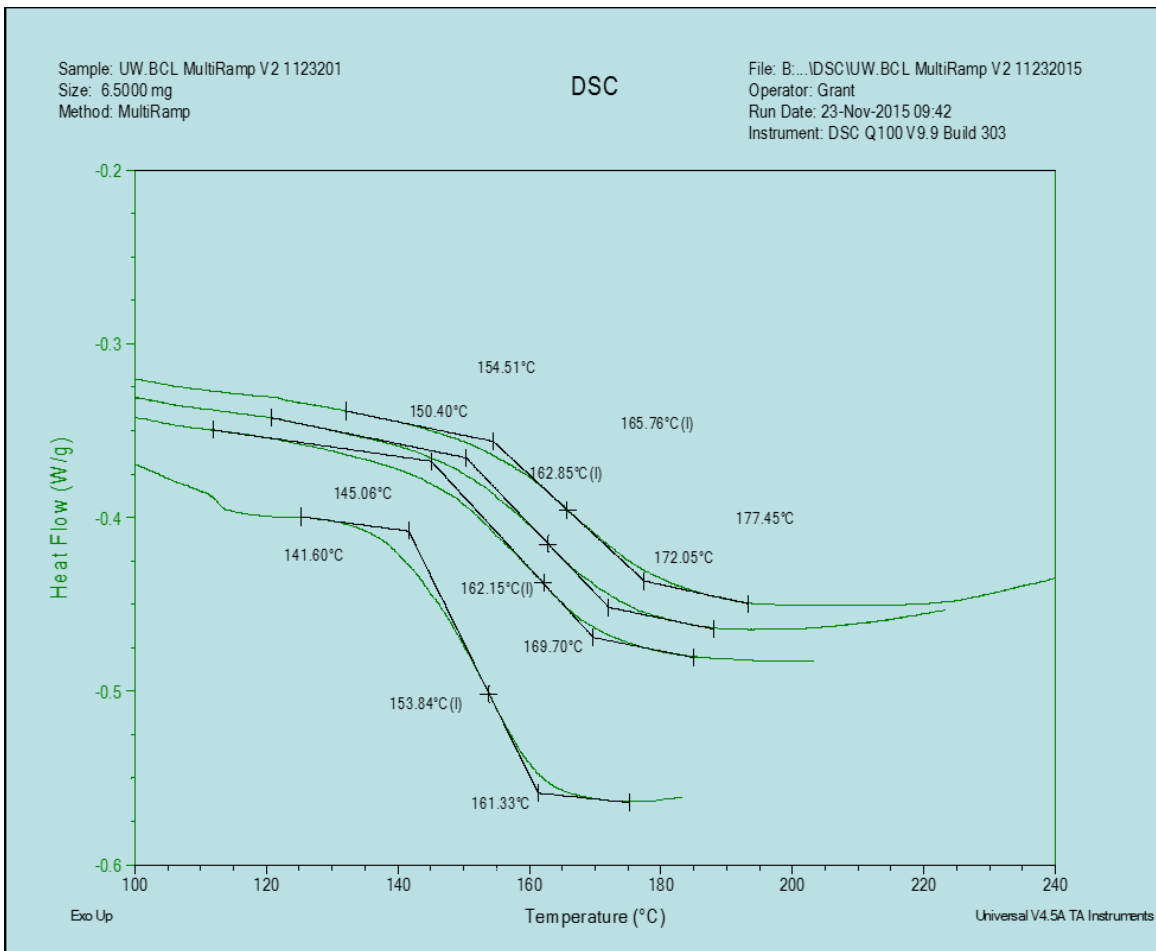


Figure B1: SWKL Differential Scanning Calorimetry

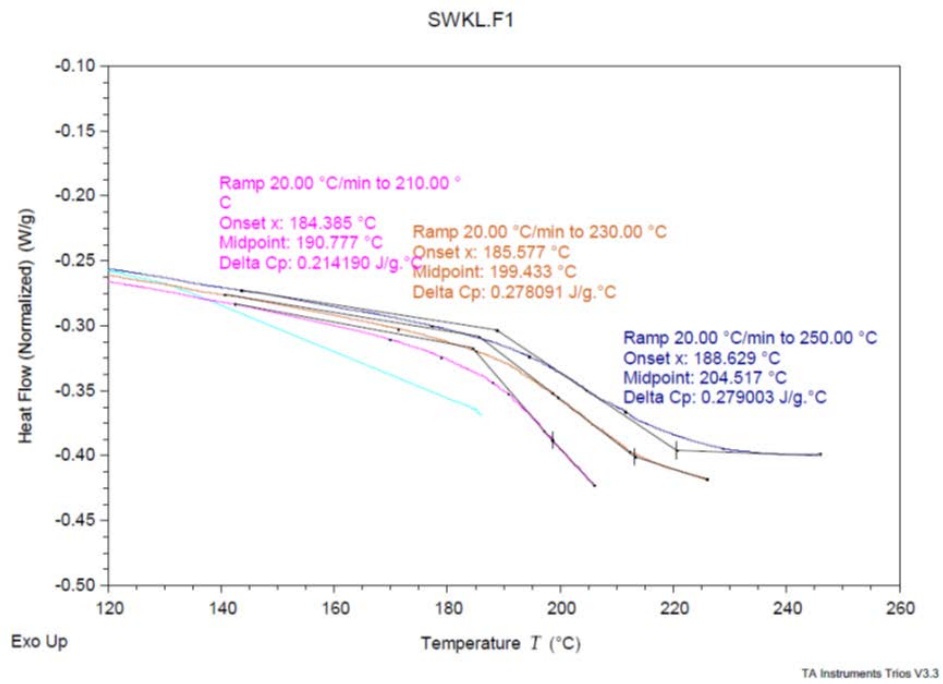


Figure B2: SWKL.F1 Differential Scanning Calorimetry

SWKL.F2

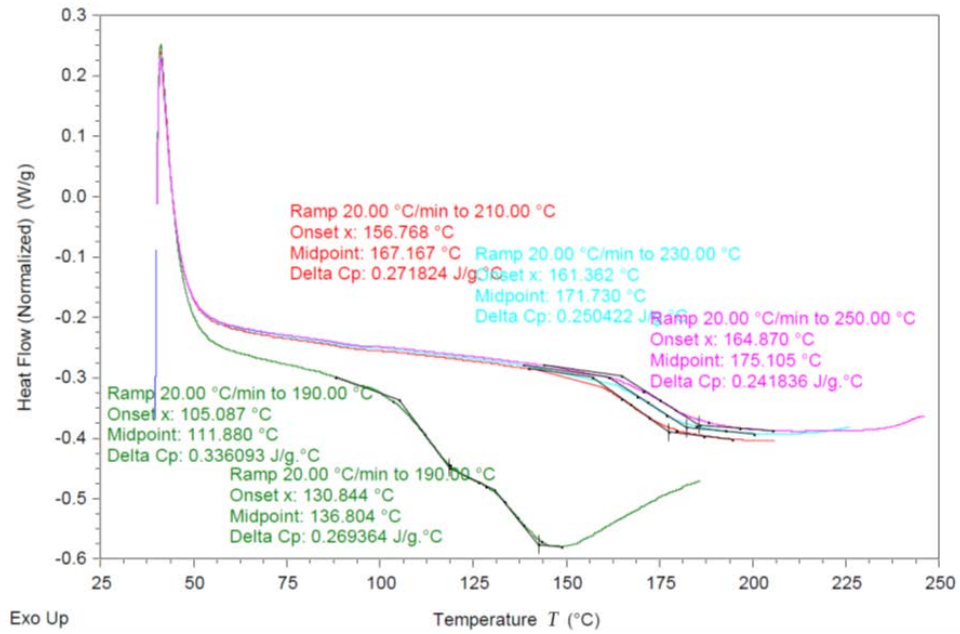


Figure B3: SWKL.F2 Differential Scanning Calorimetry

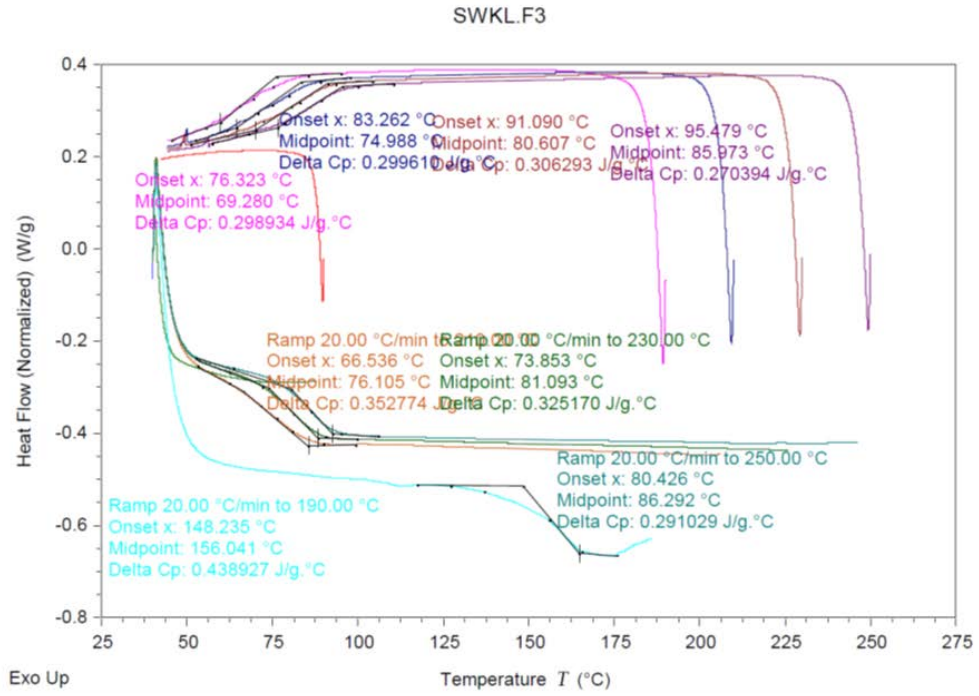


Figure B4: SWKL.F3 Differential Scanning Calorimetry

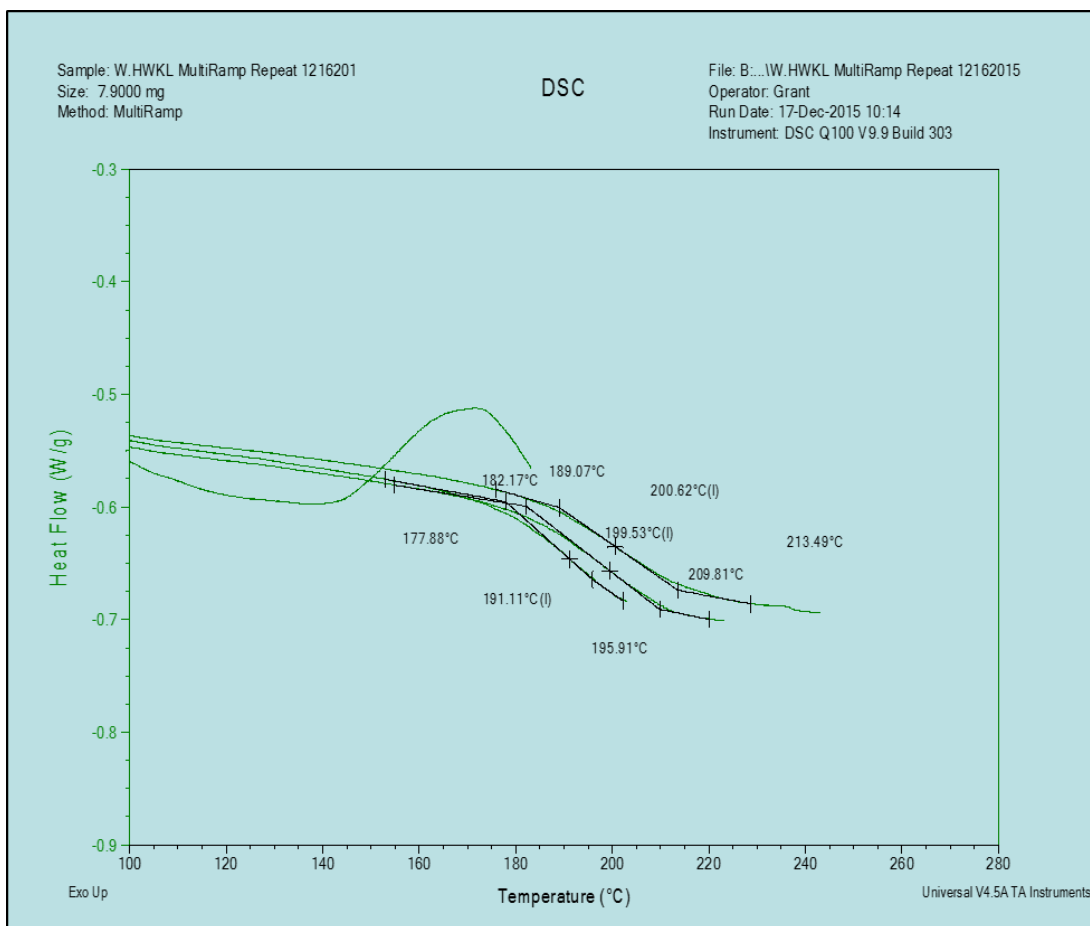


Figure B5: HWKL Differential Scanning Calorimetry

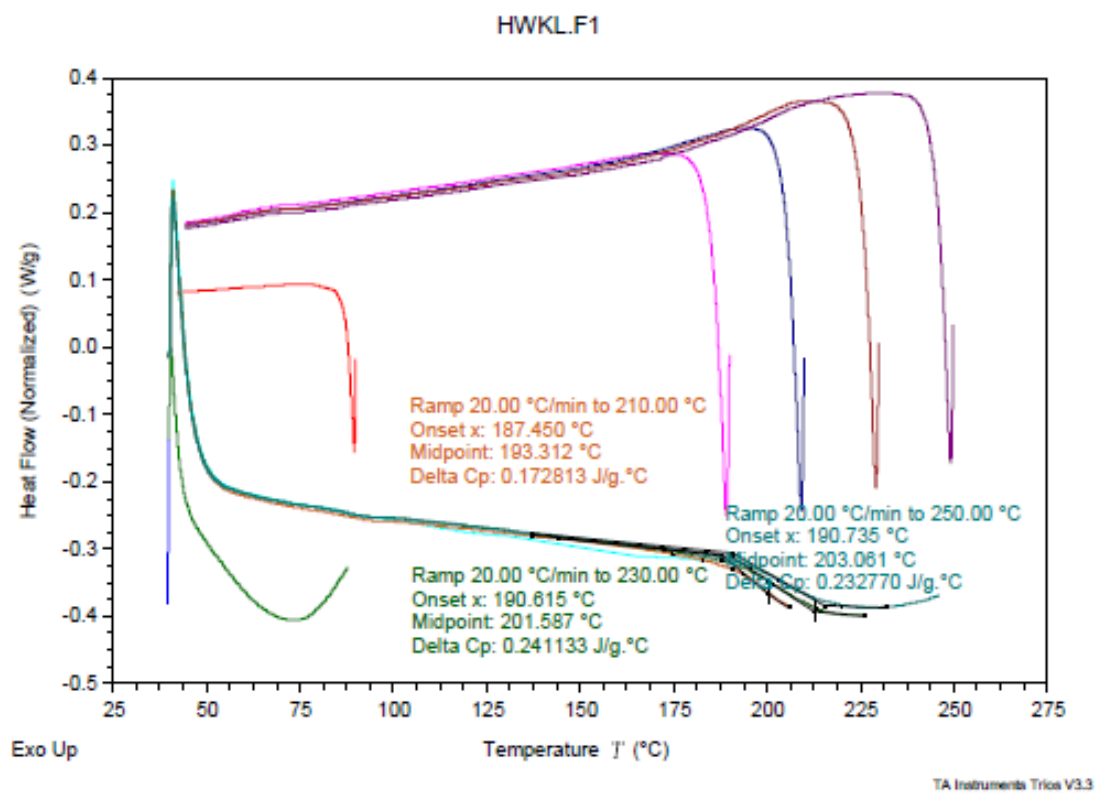


Figure B6: HWKLF1 Differential Scanning Calorimetry

HWKL.F2

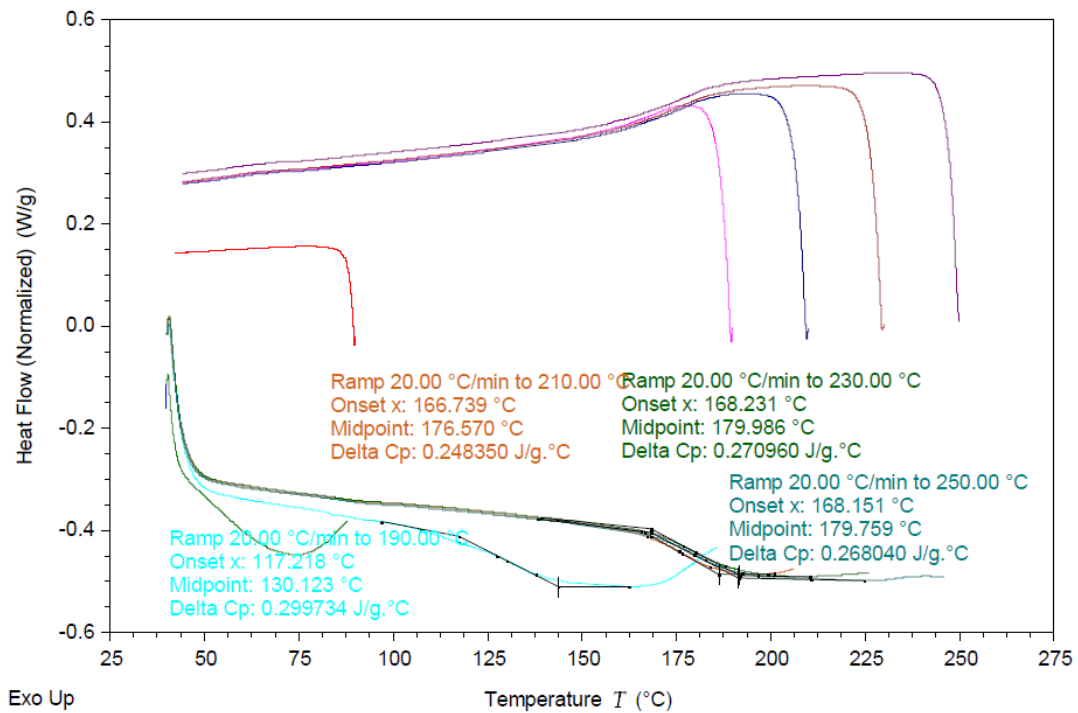


Figure B7: HWKL.F2 Differential Scanning Calorimetry

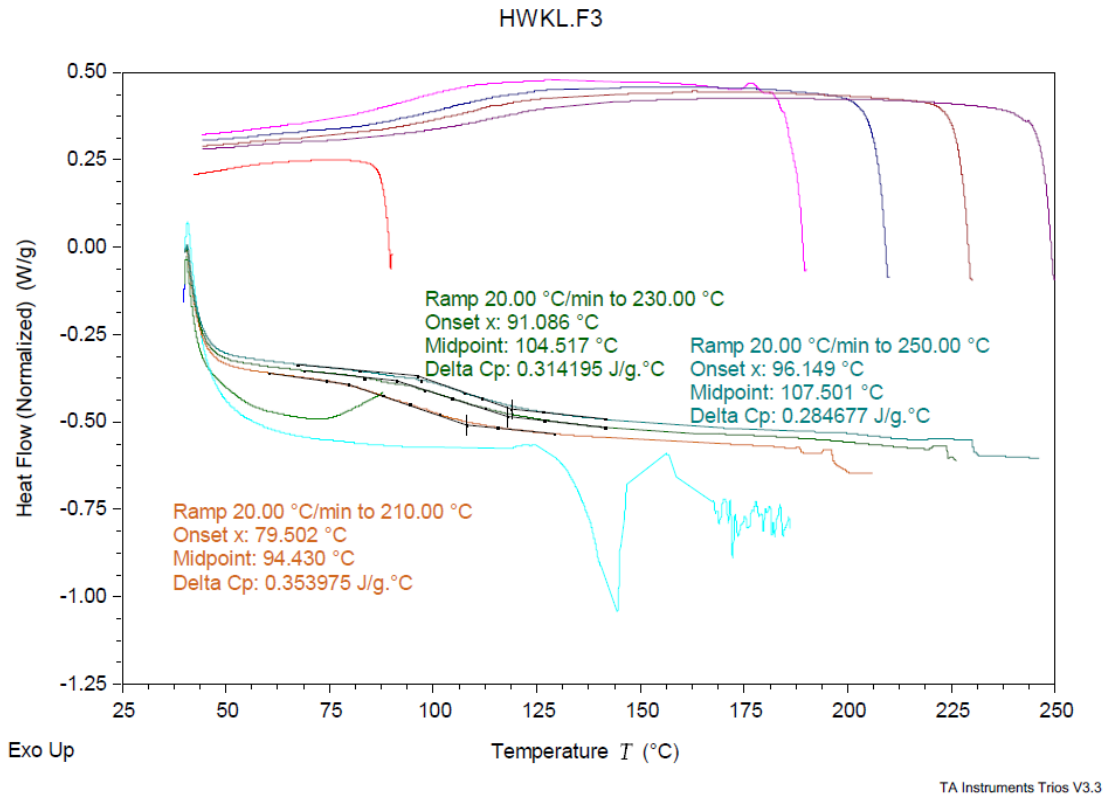


Figure B8: HWKL.F3 Differential Scanning Calorimetry

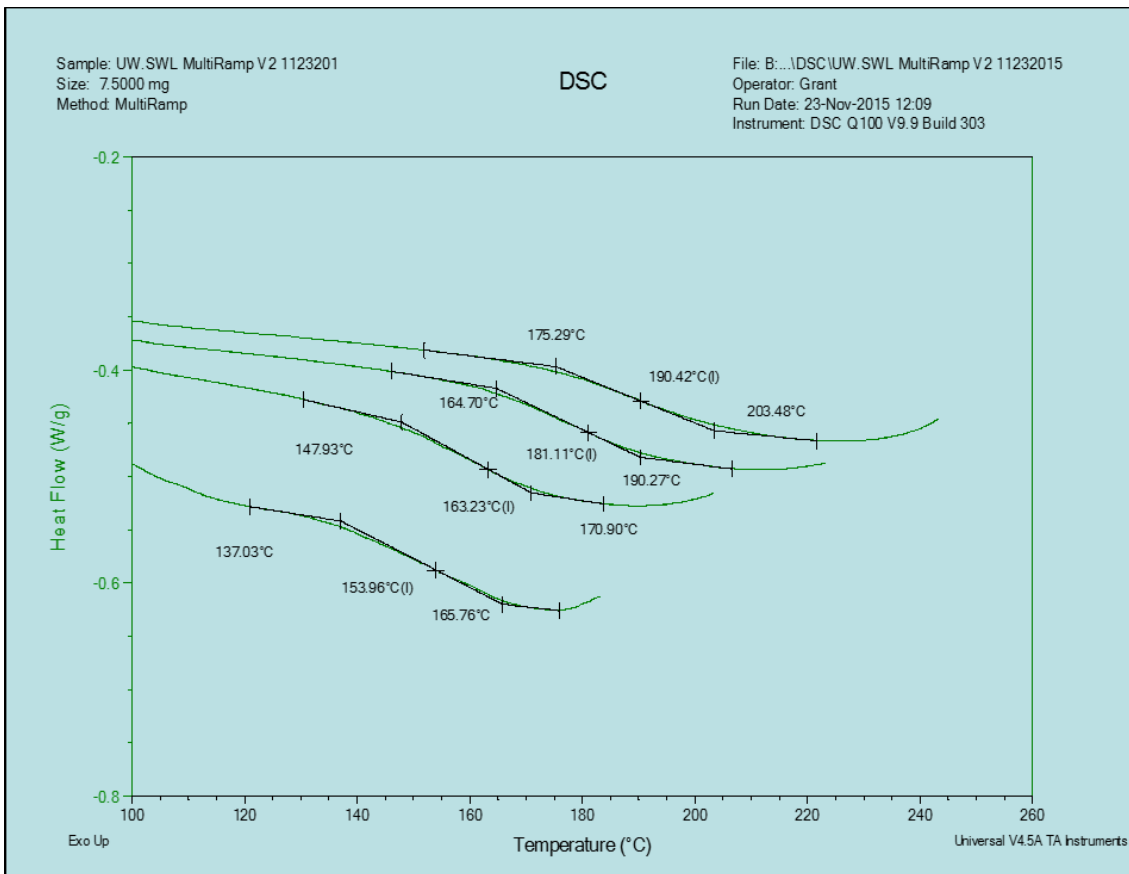


Figure B9: DAHL Differential Scanning Calorimetry

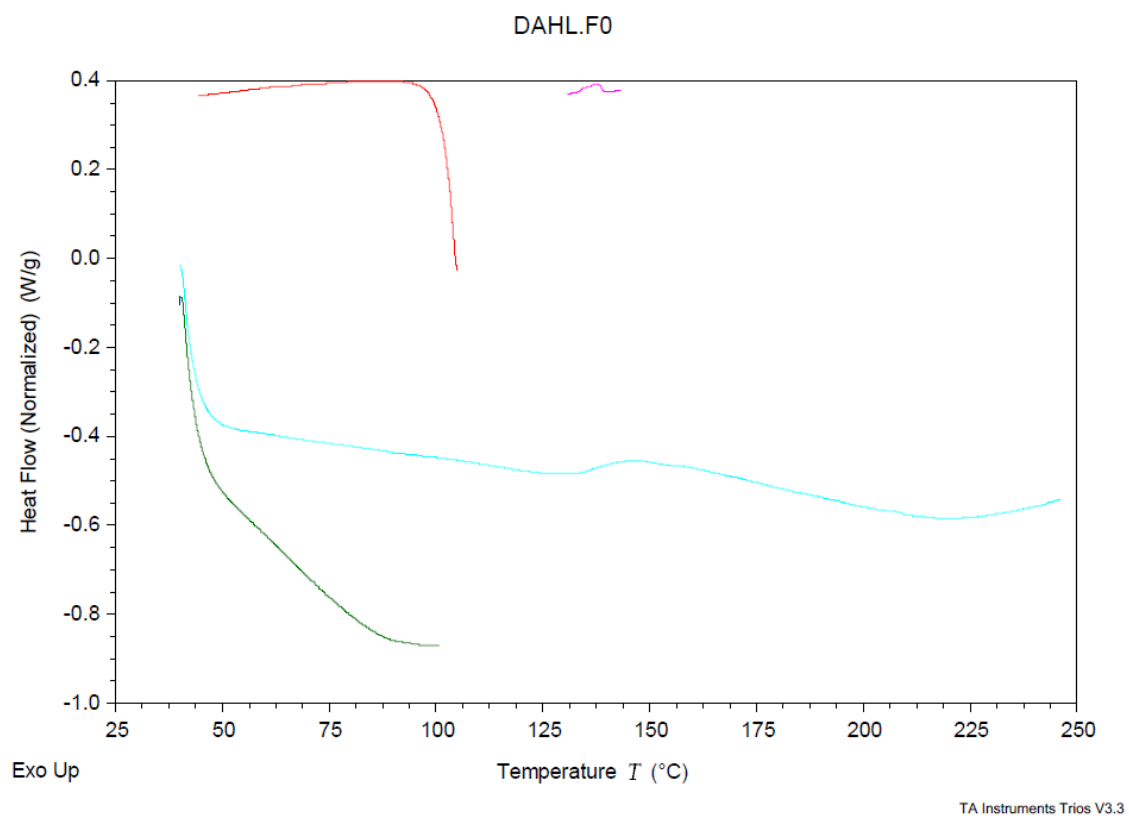


Figure B10: DAHL.F0 Differential Scanning Calorimetry

DAHL.F1

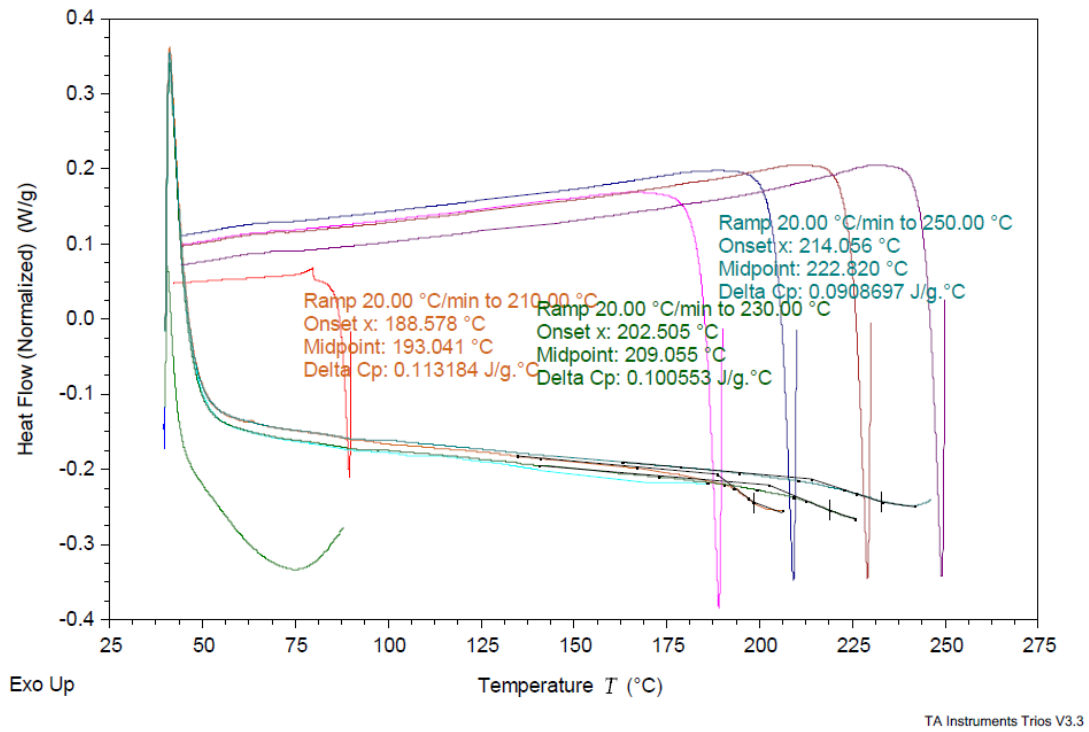
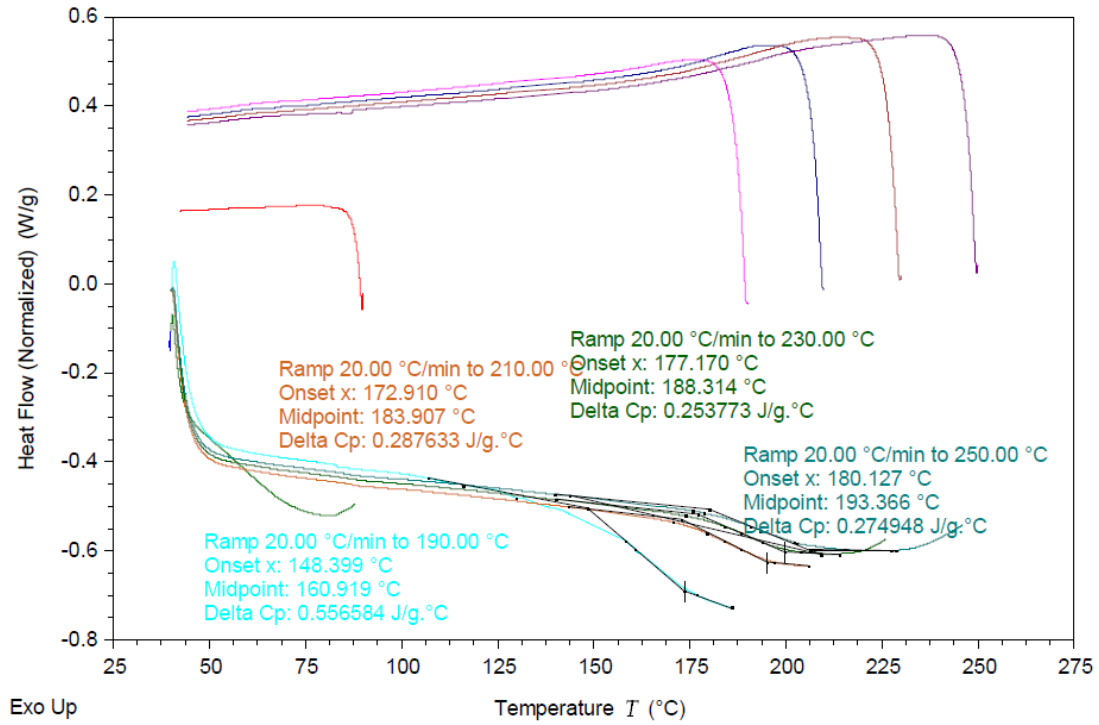


Figure B11: DAHL.F1 Differential Scanning Calorimetry

DAHL.F2



TA Instruments Trios V3.3

Figure B12: DAHL.F2 Differential Scanning Calorimetry

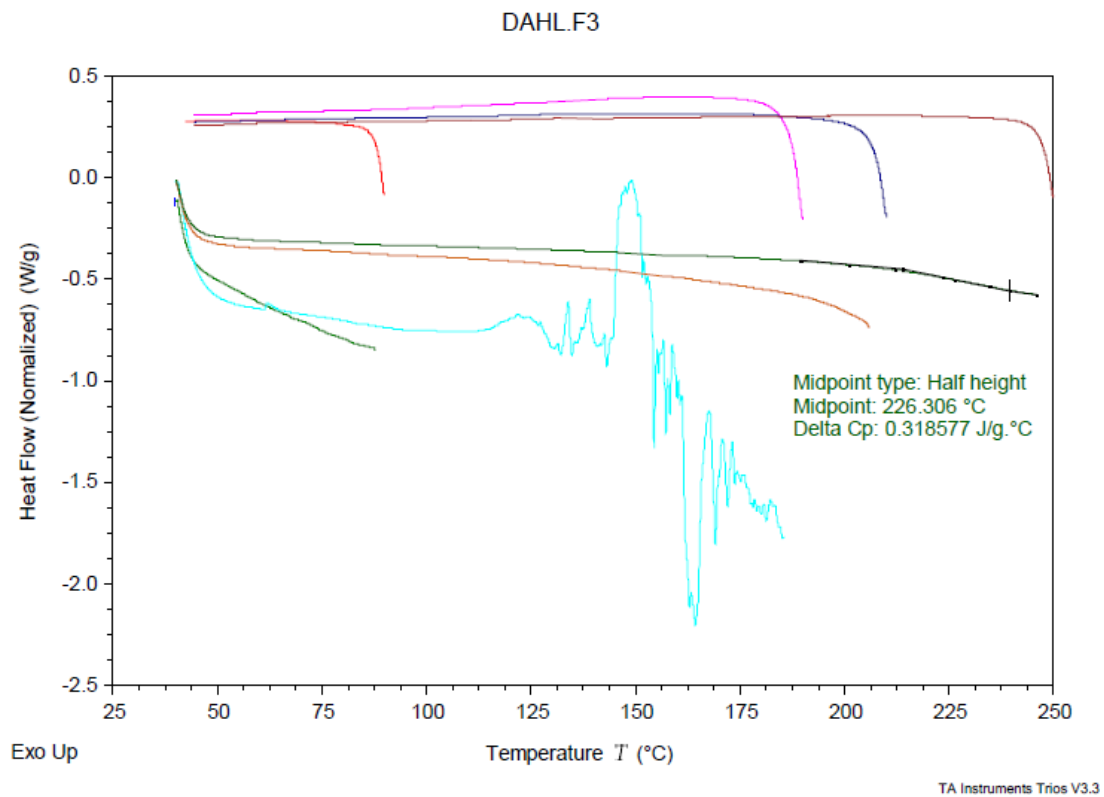


Figure B13: DAHL.F3 Differential Scanning Calorimetry