

INTEGRATED DESIGN, ANALYSIS AND OPTIMIZATION OF CHEMICAL
PRODUCTION FROM BIOMASS FEEDSTOCKS

by

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ABSTRACT OF THE DISSERTATION

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Biomass processing has been identified as a promising source of energy that can replace the use of fossil fuels in the near future. It can be used to produce both high-volume and low-value fuels and high-value but low volume chemicals. The priority for the development of variate fine chemicals from biomass feedstock stepped-up over the changing time. US Department of Energy has suggested some top-value platform chemicals derived from biomass which include levulinic acid, succinic acid, glycerol, furans, etc. The idea of bio-refinery has been proposed that uses different conversion technologies to produce multiple products. Bio-based product acceptance in the market depends on the competitiveness of economics and sustainability when compared to oil-based chemicals and products.

This work focuses on the development and design of economical routes for the production

of various chemicals by utilizing all the components of biomass by using different process systems engineering tools such as techno-economic and life cycle analysis. First, different hydrolysis processes are identified and compared using the tools mentioned above. Then, the hydrolysis process is integrated with the production of p-Xylene. Next, promising chemicals such as butadiene, surfactants, jet-fuels, and lubricants are designed, simulated, and integrated with the production of p-Xylene. Lignin produced is then used to produce high-value polymers, which is also integrated with the other processes to map a fully functional bio-refinery. Alternative biomass such as food waste is also explored for producing these chemicals and fuels. Finally, multi- objective optimization is used to develop an optimal bio-refinery configuration considering economic and environmental parameters with regards to supply, demand and process uncertainties.

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1 Introduction

1.1 Motivation

Today, readily available and everyday use chemicals and fuels are produced primarily from fossil fuels. Uncertainty of availability, price fluctuations and environmental concerns are some of the drawbacks of using fossil resources. The replacement of oil with biomass as raw material for fuel and chemical production is an interesting option and is the driving force for the development of bio-refinery complexes^[1]. The International Energy Agency Bioenergy Task 42 on bio-refineries has defined biorefining as the sustainable processing of biomass into a spectrum of bio-based products and bioenergy. A bio-refinery, like a petroleum refinery, can benefit from the exploitation of different components in biomass and maximize profit from biomass. The production of bio-based products could generate \$10-15 billion of revenue for the global chemical industry^[2]. First-generation biomass, which is derived from food crops such as grains, corn, sugarcane, etc. pose threats to the food supply, high water, and land usage and an increase in food prices. Ligno-cellulose biomass, which are second-generation biomass, are abundantly available on the earth and do not compete with food supply. Platform chemical derived from lingo-cellulose biomass provides notable opportunities to produce an array of derivatives to fulfill the societal needs of organic chemicals and polymers^[3]. US Department of Energy has suggested some top-value platform chemicals derived from biomass which include levulinic acid, succinic acid, glycerol, furans, etc.^[4]. In-depth studies have taken place for the production and conversion of furans esp. HMF and furfural, which is the main focus of this work.

1.2 Process System Engineering Tools

New chemistry and processes for the production of these platform chemicals are the focus

of current research work. New catalysts are discovered and prepared for the transformation of biomass to these highly specialized chemicals, which unfortunately, are not suitable for existing petroleum refineries. Hence, new processes and manufacturing are being investigated to produce these chemicals. Only a handful of these processes are in the commercialization phase and most of the work and analysis are still in the early stage of development. The chance of commercializing a new process is only about 1 to 3% at the experimental stage and increases to 10 to 25% at the development stage; and hence it is very important to evaluate the process at an early stage^[5]. Therefore, we need process system engineering tools to estimate and analyze the production process before it is commercialized, to minimize errors and production costs. Process system engineering utilizes various tools and methods to design, simulate, model and optimize various process used in chemical, agricultural, food and bio-based industries. The tools analyze, measures and compares different alternatives of a process, examine feasibility and provides parameters to study various bottlenecks of the process. In this study, the following systems engineering tools are utilized to develop, explore and model a bio-refinery.

Techno-economic analysis: Economics plays a very crucial role in a chemical industry. Techno-economic analysis combines process modelling and engineering design with economic evaluation^[6]. It is a tool to eliminate unfeasible design alternatives and explore favorable designs. This tool is used to eliminate bottlenecks in the process and can be used to aid the advancement of a new process to the commercialization stage. Specifically, all designs are modelled and simulated based on experimental and lab data. Different separation steps are integrated and simulated. After selecting all the designs, thorough economic analysis is performed by calculating capital and operating costs. Capital costs are

fixed costs, which consist of cost of equipment, construction and land and is not dependent on the output rate. Operating costs are divided into fixed and variable cost. Variable costs include cost of raw material, utility cost and catalyst costs. Fixed costs include operating labor, maintenance costs and general administration and research costs. Once all the costs have been calculated, minimum product price, which is defined as the price of the product at zero net present value with expected rate of return using discounted cash flow method^[7]. Uncertainty from different sources such as variation in cost of raw materials, solvent etc., and variability in process parameters can arise which can be evaluated by using sensitivity analysis.

Life cycle analysis: For a bio-refinery, the products may be acceptable in the market if the process is more environmentally sustainable even though the cost may be higher than oil based. Life cycle analysis is used to calculate the impacts of a process on the environment. Life cycle analysis is an analytical framework to quantify the resources used and the impact to the environmental and human health by a product service or system over its entire lifecycle by compiling an inventory of relevant inputs, outputs, and environmental releases. For most of the product systems, this means the period when raw materials are extracted from nature to the period when these materials are processed, as well as the manufacture of product system, the distribution of the user, the use and potential upgrade of the product, and the product's eventual land-filling, incineration or recycling^[8]. It is carried out in four steps^[9, 10]: 1) Goal and scope; involves defining the objective of the study, defining functional unit and system boundaries. 2) Inventory analysis; involves the collection of data of both the input, output as well as emissions to construct the system specified in the previous step. 3) Impact assessment; involves calculating the potential impact to the

environment by the input, output and the emissions identified by the previous step. 4) Interpretation; the results of the previous step are summarized and conclusions and recommendations are made based on the aim of the study.

1.3 Outline

The following section of this proposal is divided into four chapters. Chapter 2 describes the techno- economics and life cycle analysis of different types of hydrolysis process for the production of p- Xylene. Chapter 3 discusses production routes of different chemicals from furfural, which is integrated with p-Xylene production and techno-economic, and life cycle analysis is carried out of the process. Chapter 4 focuses on the production of polymers from lignin. Techno-economic analysis is carried out of a combined bio-refinery producing all the chemicals discussed above. Chapter 5 discusses optimal bio-refinery configurations considering economic and environmental aspects with supply, demand and process uncertainties.

2 Techno-Economic and Life Cycle Analysis of Different Types of Hydrolysis Process for the Production of p-Xylene

2.1 Introduction

Petroleum is currently the primary raw material for the production of fuels and chemicals. However, declining production of non-renewable petroleum resources, combined with increased demand for petroleum by emerging economies, and political and environmental concerns about fossil fuels, have stimulated an intensive effort to develop economical and energy-efficient processes for the sustainable production of fuels and chemicals from biomass^[11-13]. Bio-based p- xylene has drawn considerable attention because it is the main precursor for polyester polyethyleneterephthalate (PET), a polymer resin broadly used in the synthesis of fibers, films, and beverage containers^[14]. Several companies, such as Coca Cola, Pepsi, Avantium and Procter & Gamble have launched projects toward the utilization of bio-based PET^[15-17].

Thus, we investigated the production of p-Xylene from starch and the economics and environmental impact were studied and evaluated^[18]. The main cost factor to the price of p-Xylene was found out to be the cost of starch, solvent and the catalyst used for the dehydration reaction of 5-hydroxymethylfurfural (HMF) to 2-5 dimethylfuran (DMF). The initial cost of starch produced from lignocellulosic biomass (more expensive than biomass) and the isomerization of starch to glucose was the major contributor to the overall cost of p-Xylene. In order to further, minimize the costs we shift our focus on the production of glucose from lignocellulosic biomass instead of using starch as the primary raw material, and integrate it with the production of p-Xylene. A new one- step conversion method, developed by the Catalysis Center for Energy Innovation (CCEI) at the University of

Delaware, uses molten salt hydrate for the hydrolysis (MSH process) of non-food biomass into C5 and C6 sugars with a one pot depolymerization and saccharification process^[19]. Molten salt hydrates exhibit higher carbon efficiency for furan products when compared to non-salt systems and higher viscosity of the solution than water makes the separation of aqueous phase easy in the one pot reactor^[20]. The sugars are then dehydrated to produce furfural and HMF, respectively, in a biphasic reactor with a cheaper solvent and catalyst^[21]. The production of DMF and the subsequent production of p-Xylene from HMF are similar to our previous work utilizing the latest results that resulted in better conversion and yields of the products^[22-24].

p-Xylene produced from MSH process is then compared with different thermo-chemical hydrolysis processes, which are currently used/investigated in industries, i.e. dilute acid hydrolysis (DA) process, and concentrated acid hydrolysis (CA) process. Currently, change in concentration of acid and steam required have been made to the DA process to produce sugars, the basic process remains the same as reported by Harris et al.^[25]. The CA process, developed at the same time as DA process, has gained interest in recent years. There are a few patented hydrolysis processes which uses concentrated acid; Arkenol's process^[26] and Weyland's process^[27], which are currently in the pilot plant stage. We have used Weyland's process to compare with the MSH process as Arkenol's process is not practical for large-scale production due to involvement of chromatography separation for acid and sugars.

We have evaluated the techno-economic feasibility and life cycle sustainability of the p-Xylene production using the MSH process, estimate the minimum cost of p-Xylene, and compare it with the DA and CA processes. Lignocellulosic biomass is used as the starting

material for all the three-hydrolysis process with different initial loading. Sensitivity analysis is carried out to assess the impact of assumptions made in the simulation and various economic parameters such as cost of raw materials and the capacity of the plant. Detail analysis method and the process flowsheet of the three methods are described. An estimate of the minimum selling price of p-Xylene is calculated with and without the consideration of by-products and sensitivity analysis is performed to identify the significant cost factors. Finally, life cycle assessment including sensitivity analysis explaining the variations of the environmental impacts with different non-food biomass and process steam used in MSH process is carried out.

2.2 Methodology

Problem Definition

Conceptual design is a systematic procedure to successively add the layers of details to find the most economically feasible process flowsheet^[28]. Different separation alternatives are considered and assessed for a feasible design and hence flowsheet development is necessary as it identifies various bottlenecks in the process, which can be addressed, and a base case design is generated. Rigorous analysis is carried out by computing the mass and energy balance for each unit operation and for the entire flowsheet. Finally, economic and life cycle of the selected process is evaluated in terms of minimum and selling price and different environmental impacts for the required product specification.

It should be noticed that in order to perform such analysis the following steps should be carefully considered. First the all the materials required from raw materials to products should be carefully selected. Data regarding the material property and processing operating conditions should be collected from the available literature and in consultation with the

experimental experts. Moreover, it is very important to perform a very careful evaluation of the different thermodynamic packages used in the calculation of process performance since this plays a critical role especially in separation processes. Finally, different separation strategies should be considered to achieve the required product specifications. Table 1-2 shows the reaction conditions of different processes for the production of p-Xylene.

Table 1: The Specification of hydrolysis reactions

Process	DA		CA		MSH
Catalyst	Sulphuric Acid		Sulphuric and Phosphoric Acid		LiBr
Stages	I	II	I	II	I
T (K)	443	503	328	413	358
P (Kpa)	1500	4000	101.325	600	101.325
Conversion (%)	85	57	95	95	89,95

Table 2: The Specification of Reactions

Process	Glucose to HMF	HMF to DMF	DMF to p-Xylene
Catalyst	AlCl ₃	Cu-Ni (1:1)	HBEA - catalyst
T (K)	393	493	523
P (Kpa)	1700	680	6200
Conversion	84,85	99	97

Simulation based analysis

The simulation is performed using Aspen Plus V8.8. NRTL thermodynamic package is utilized to predict the liquid–liquid and liquid–vapor behavior. The Peng–Robinson method is exploited for the decanter that is used to separate DMF and water because it is found to produce more reliable results compatible with the solubility properties of DMF, which is known to be slightly soluble in water^[18]. Most of the components involved in the reactions are directly selected from the Aspen database, whereas some not included in the

database (i.e., lignin, hemi-cellulose etc.) are defined by the structures and properties taken from NREL^[29]. For the components with no specific molecular structure or complex structure such as humins and MSH, surrogates are used. Due to the unknown properties of lithium bromide, sodium chloride is used as a surrogate for this work. More studies should be carried out to validate this assumption. All the missing parameters are estimated by the molecular structures using the Unifac Model and Thermo Data Engine (TDE). TDE is a thermodynamic data correlation, evaluation, and prediction tool developed by the collaboration of Aspen plus and the National Institute of Standard and Technology. Since the detailed reaction mechanism is not known, the effect of solvent on conversion and selectivity of products for hydrodeoxygenation (HDO) of HMF to DMF and Diels-Alder cycloaddition of DMF to p-Xylene has not been considered in this study. The reactor pressure is determined by Aspen Plus simulation to satisfy the existence of a liquid-phase.

To enable the process simulation, the following assumptions are made:

1. Composition of biomass is assumed to have 40% cellulose, 30% hemicellulose and 30% lignin. Generally, hardwoods and softwoods contain around 40-50% cellulose, 25-30% hemicellulose, 18-25% lignin and <1% ash^[19]. For the base scenario, the assumption is satisfactory. Sensitivity analysis for the MSH process is carried out for different cellulose composition in biomass.
2. All the filtration processes are assumed to have 99% separation efficiency.
3. For the CA process, the reaction mechanism for the two stages as well as extraction mechanism is unknown. We assume that 90% of cellulose and hemicellulose is converted into oligo-saccharides and 90% to glucose and xylose. The solvent can extract most of the acid and the sugars.

4. In the biphasic reactor, it is assumed that the organic solvent extracts 95% of the furans. The solvent does not dissolve in the aqueous phase.
5. The by-products do not affect the conversion and selectivity of any reactions. No separation steps are considered before reaction.

Lignocellulose conversion processes

Dilute Acid process: DA process is a two-stage process^[25], in which the first stage is pretreatment of biomass where hemicellulose in the biomass is converted into xylose and in the second stage cellulose is broken down to glucose. Similar pre-treatment process is used by NREL in their report for the production of ethanol^[30]. Sulphuric acid strength is kept at 1.6 wt. % and the liquid to solid ratio is 1.35 before entering the reaction mass to the first stage reactor, which operates at 170 °C for 12-14 minutes. The conversion of hemicellulose is 85%. After the separation of xylose by filtration, the solid stream enters the second stage for cellulose hydrolysis, which operates at 230°C for a 40 s. The yield of glucose is 57%. After this step, the resultant solid consisting mostly lignin is filtered. Final step is acid neutralization to prevent the buildup of acid in the downstream process.

Concentrated acid process: CA process is a two-stage process^[27] where biomass carbohydrates is first converted into oligosaccharides and then converted into C5 and C6 sugars in the second stage. In this process, a combination of sulphuric acid and phosphoric acid is used for hydrolysis. The acid and water mixture to biomass mass ratio is kept at 2:1, acid and water mass ratio is 2:1:1. The first stage operates at 50 °C. The conversion of biomass to oligo-saccharides is 90%. To separate the acid and oligo-saccharides solvent extraction is used. The solvent used can be one or a combination of two solvents. For this analysis, dimethyl ether (DME) is used as the solvent. The mass ratio of hydrolysate to

solvent is 3:8. Extraction is carried out at higher pressure (8 bar) so that the solvent is in liquid phase. The organic phase containing solvent, acid and water is depressurized and cooled (20 °C) to separate solvent from the acid/water mixture. Water is evaporated from the acid at vacuum and the acid is recycled. The water stream is re-pressurized so that solvent present is evaporated and recycled. The oligo-saccharides then enters the second stage where it is converted into monosaccharides. This stage operates at 140 °C and 6 bar. The conversion of oligo-saccharides to glucose and xylose is 90%. A neutralization step is added to remove the acid to prevent buildup of acid in the downstream process.

MSH process: The analysis on the conversion of biomass in MSH is based on the laboratory-scale results^[19]. It is a single stage process in which lithium bromide solution (59 wt.% LiBr + 0.5 wt.% sulphuric acid) is used. Biomass loading is assumed as 10 wt.% in contrast to biomass loading in the DA and CA processes as 25% and 40% respectively. The reaction is carried out 85 °C and the yield of glucose and xylose are measured as 89% and 95%, respectively. Separation of lithium bromide is difficult at this stage and hence the product stream enters the dehydration stage directly without a separation step.

HMF/Furfural Production: In our previous work^[18], glucose was isomerized and dehydrated to HMF using Sn-beta as the isomerization catalyst and HCl as the dehydration catalyst. This reaction proceeds in a biphasic reactor in which it is saturated with NaCl salt and THF is used as the organic solvent/extractant. The solvent was a major contributor for the overall cost and thus alternative solvents were considered. According to Dutta et al^[21], ethyl acetate in the presence of AlCl₃ acting as the dehydration catalyst can be used as an alternative process which slightly reduces the operating cost and minimizes the inventory. The organic to aqueous volumetric ratio is 3:1 with 50 mol% catalyst. This process operates

at 120 °C and 120 min residence time. The conversion of glucose and xylose to HMF and furfural is 84% and 85% respectively. It is assumed that the extraction of HMF and furfural from the aqueous phase takes place in two stages. Flash drums can be used to separate the solvent and furfural from HMF although at high temperatures (~255 °C). More work is needed to find out other alternatives to this process as degradation of HMF can occur at this temperature. The purity of HMF is around 99% and for furfural is 99%. AlCl_3 is recycled back with the molten salt hydrate to the hydrolysis process.

DMF Production: Production of DMF from HMF proceeds in the vapor phase using a catalyst at 493K and 0.69 MPa^[31]. The older process^[22] uses copper-ruthenium-carbon (Cu-Ru/C) catalyst which gave a yield of ~81% DMF with main by-product as 2,5-dihydroxymethyltetrahydrofuran. A new catalyst^[32] which consists of copper-nickel-carbon (Cu-Ni/C) catalyst is used which is cheaper than the previous catalyst and gives a yield of ~99% DMF. As the yield is very high further purification is not necessary. Trace amount of furfural present is converted into 2-methylfuran in presence of Cu-N-/C catalyst.

p-Xylene Production: The process for p-Xylene production is similar to our previous work^[18] with some changes. Our reported process used HBEA zeolite in the presence of heptane and tridecane to convert DMF with ethylene to p-Xylene with a yield of ~89%. The competitive side reactions include the hydrolysis of DMF to 2,5-hexanedione and oligomerization or polymerization and alkylation of p-xylene. It is found that PBEA zeolite (prepared by incorporating P within the dealuminated BEA micropores by the calcination of H_3PO_4) can give a yield of ~97% p-Xylene in the presence of heptane which reduces the occurrence of the side reactions^[33].

Steam and power Generation: The process for steam and power generation is similar to

NREL's work^[30]. We assume that the pollutant from the flue gas is CO₂ only. The capacity of the system depends on the steam requirement of the process which is 281,000 kg/hr. for the DA process, 274,750 kg/hr. for the CA process and 370,000 kg/hr. for the MSH process at 454 °C and 900 psig with a boiler efficiency of 80%.

Process flowsheet and description

Dilute Acid Hydrolysis: Biomass, medium pressure steam (MP steam) and sulphuric acid (stream 1) are fed to the first stage reactor (R1) to hydrolyze hemi-cellulose to xylose. The product stream (stream 2) is fed to a flash drum (V1) where the stream is depressurized and cooled. The outlet of flash drum (stream 3) is washed with water and xylose is separated via a filter (FIL 1) and combined with stream 10. The outlet of filter (stream 4) is fed to the second stage reactor (R2). High pressure steam (HP steam), acid and water are added to keep the liquid to solid ratio as 3 and acid strength at 0.8 wt.%. The product stream (stream 5) is fed to two flash drums (V2 and V3) where water is separated and sent to power generation (Stream 6 and 8). The outlet of flash drum (stream 9) is washed with water and fed to a filter (FIL 3) where lignin is separated. The outlet of filter (stream 10) is mixed with xylose stream, which is neutralized with lime in reactor (R3). A filter (FIL 3) separates the neutralized residue. The aqueous solution from FIL 3 is introduced in an evaporator (V4) and we get combined sugars as the product stream.

Concentrated Acid Hydrolysis: Biomass, acid and water (stream 1) is fed into the first stage reactor (R1). Reactor outlet stream (stream 4) is introduced into an extraction column (E1) with DME as the solvent. DME is first compressed (COMP 1), cooled to a liquid state and introduced into E1. The organic stream (stream 6) containing solvent, acid and some amount of water is removed from the top and the aqueous phase (stream 7) containing oligo-

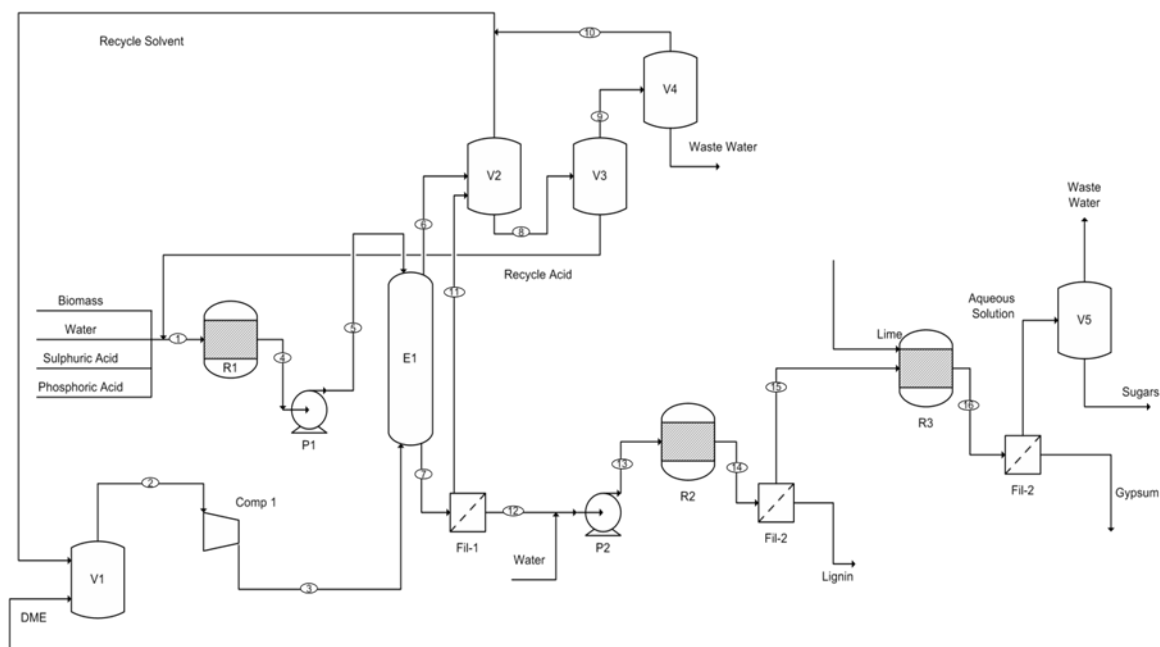


Figure 2: Process Diagram for Concentrated Acid Hydrolysis.

Molten Salt Hydrate hydrolysis: Biomass, water and MSH (stream 1) is fed to a reactor (R1). The product stream (stream 2) is fed to a filter (FIL 1) where lignin is separated from the sugar mixture. For MSH process, the catalyst from the dehydration step is recycled to reactor (R1).

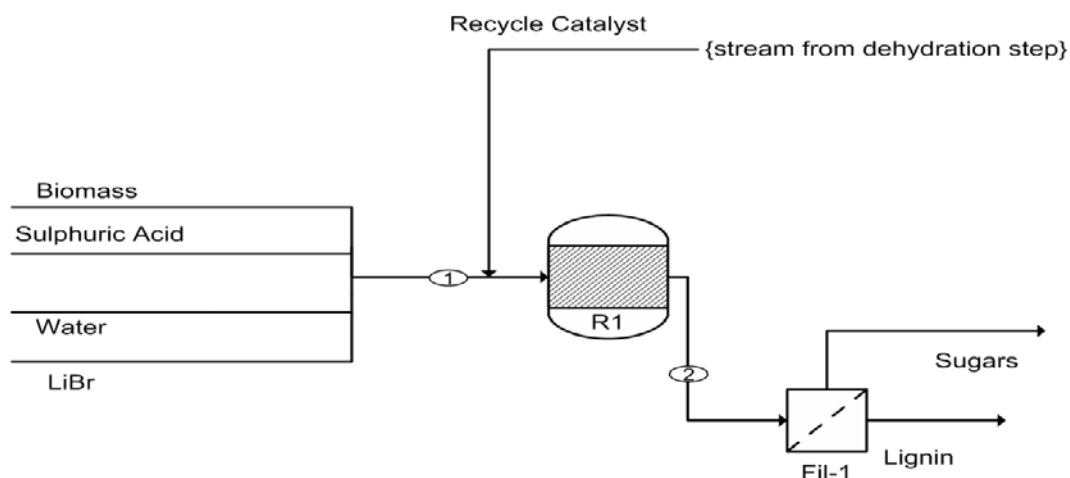


Figure 3: Process Diagram for Hydrolysis Using molten salt hydrates

HMF/Furfural Production: Sugar from the hydrolysis process is mixed with ethyl acetate and aluminum chloride and fed to biphasic reactor (R1). Another stream of solvent is introduced for the second extraction phase. The organic phase (stream 3 and 5) containing

solvent, HMF and furfural for both the stages are combined and fed to a distillation column (C1), where solvent and furfural are separated. Solvent stream (stream 7) is recycled. HMF is purified via distillation (C2) and we get furfural as a by-product. A filter (FIL 1) separates the humins from the aqueous phase (stream 6). The outlet stream from filter (stream 9) is introduced into an evaporator (V1) where excess water is separated. The outlet stream containing unreacted raw materials and catalyst is recycled.

DMF Production: HMF produced is fed into a fluidized bed reactor (R1) at 493 K and 0.69 MPa. Compressed hydrogen is also fed to the reactor (R1) to form DMF (Stream 2). The leftover furfural is converted into methyl-furan. The product (Stream 2) is fed to a flash drum where excess gas and water are separated from DMF. Excess gas containing hydrogen is recycled.

p-Xylene Production: DMF is mixed with heptane and is pumped to a CSTR (R1). Ethylene feed is compressed and added to R1. A flash vessel is used (V1) to remove most of the water. The liquid organic stream (stream 4) is introduced into a distillation column (C1) to remove most of the heptane. Heptane is condensed (V2) and recycled. The bottoms of the column C1 is fed to another distillation column to remove the by-products. The distillate is purified p-Xylene with a purity of 99%.

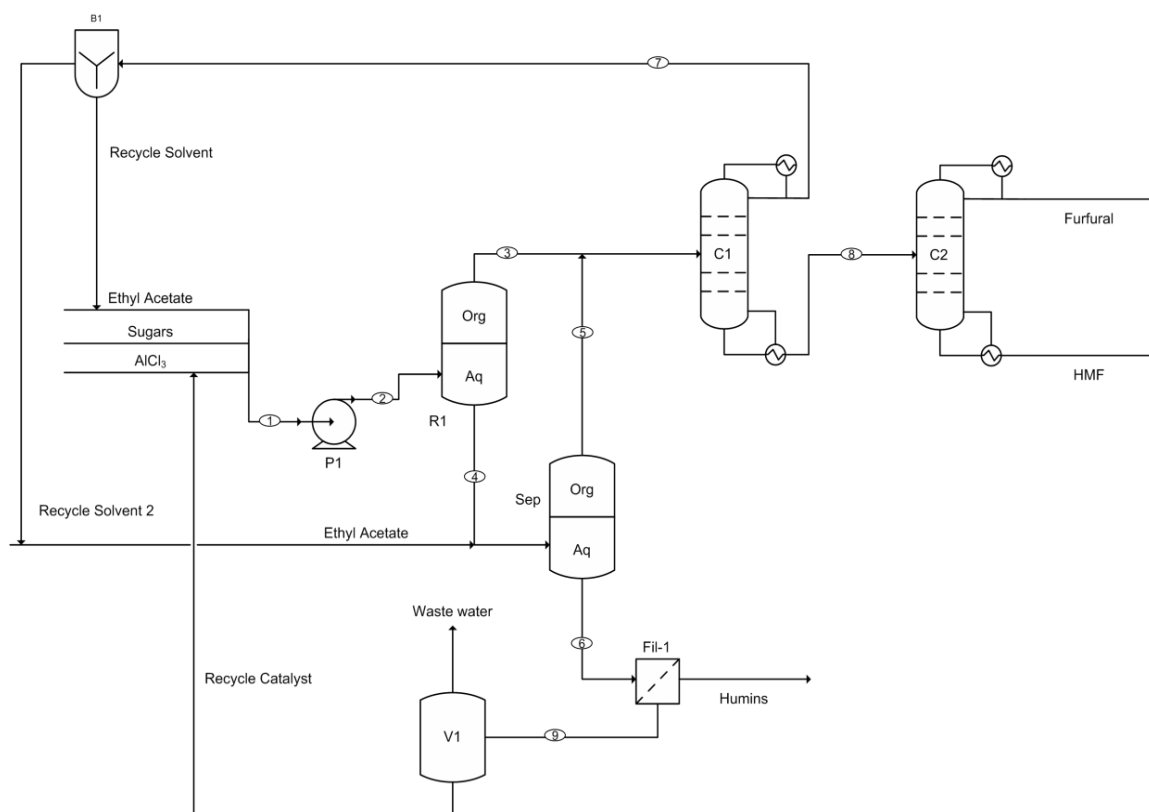


Figure 4: Process Diagram for HMF/Furfural Production

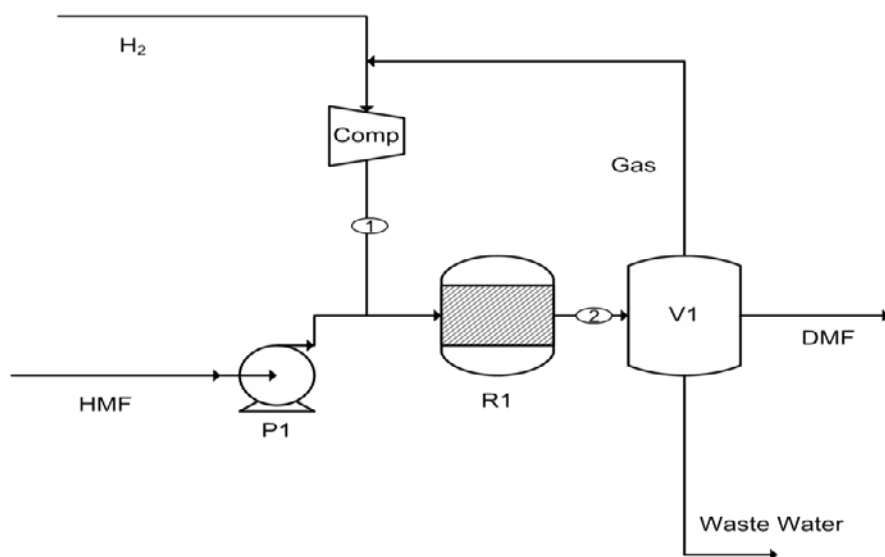


Figure 5: Process Diagram for DMF Production.

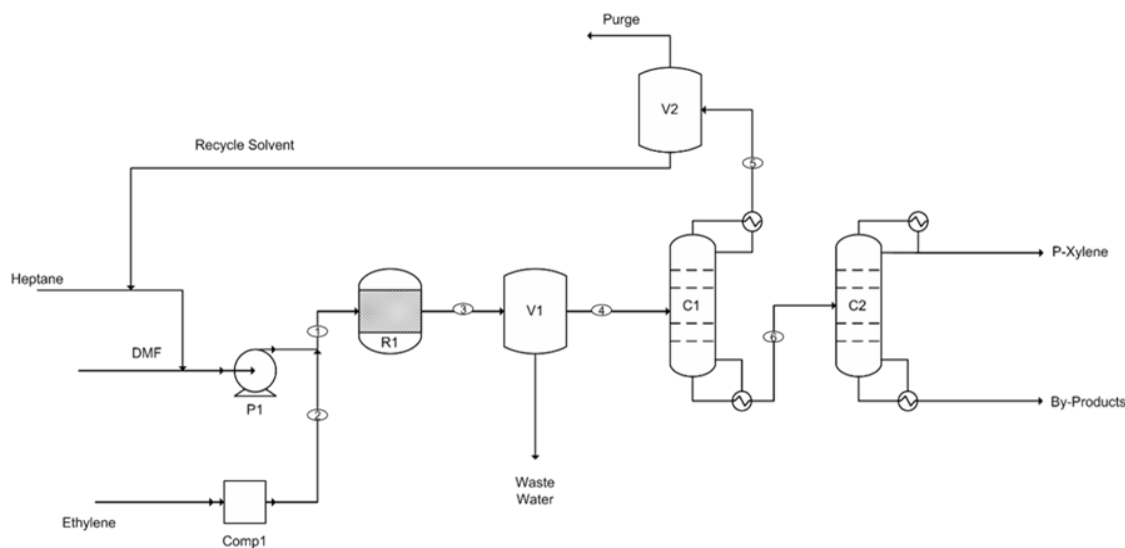


Figure 6: Process Diagram for p-Xylene Production.

Steam and Power Generation: Solids such as lignin and humins are burned in the boiler (R1) to produce steam at 454 °C and 64 bar. This steam is then introduced in a turbo-generator (turbine 1,2,3) with two extraction ports. HP steam is extracted at 40 bar pressure for feeding the process and BFW economizer (HX1). An additional steam is extracted at 18 bar for the process and BFW economizer (HX2). The remaining steam is used for the BFW economizer (HX 3) and for process consumption. The turbine shaft turns a generator to produce electricity. The generator efficiency is assumed to be 85%.

Techno-economic Analysis

Aspen Economic analyzer V8.8 is used to perform an economic assessment for the production of p-Xylene. Discounted cash flow analysis is used to perform the economic analysis for the different processes. The production cost of p-xylene is used to determine the minimum p-xylene cost, which is defined as the selling price of the product when the net present value (NPV) is zero^[7]. Some additional assumptions are necessary to perform the economic analysis as outlined below.

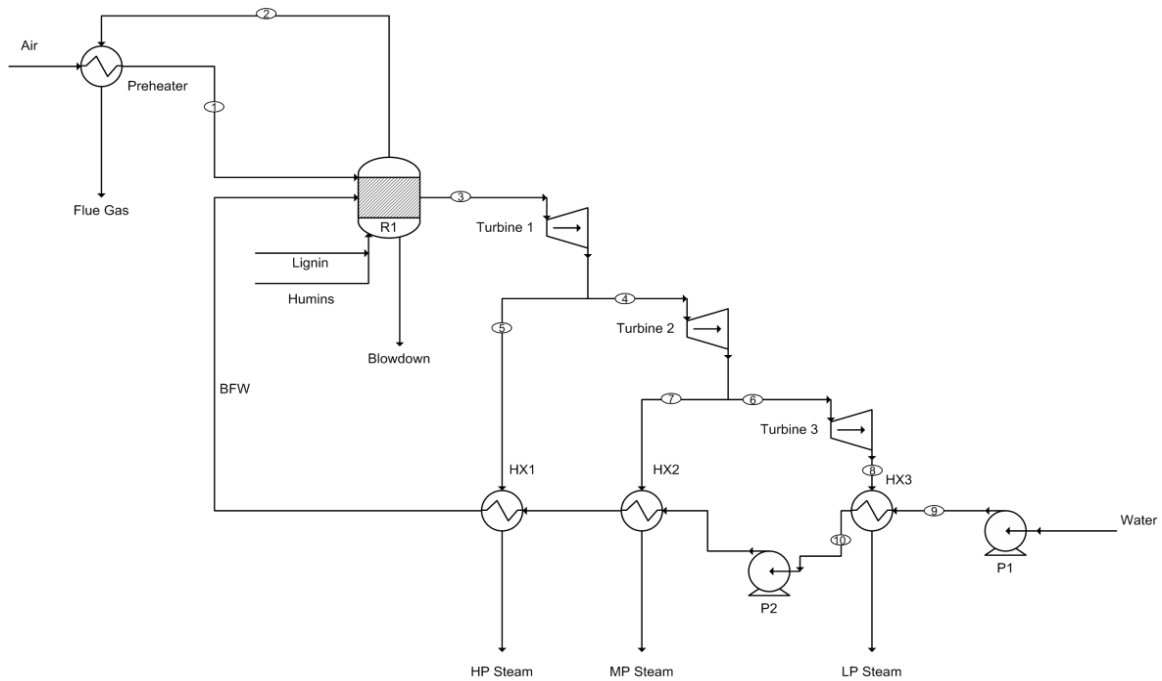


Figure 7: Process Diagram for Steam and power generation

1. All the equipment and operating costs estimated by Aspen Economic Analyzer V8.8 are based on the price of the first quarter in 2014. The filtration units are not explicitly designed and the design is based only on the flowrates.
2. Plant capacity is assumed as 50 metric tons per hour of biomass feedstock. The plant capacity assumed by NREL^[30] is ~85 metric tons per hour. In this work, in order to minimize the transportation cost for acquiring biomass feedstock we consider smaller capacity.
3. The cost of biomass is averaged to \$60 per ton^[34].
4. The plant operates in a continuous mode for 8000 h per year. The economic life of the project is assumed to be 20 years. The internal rate of return (ROR) on investment is assumed as 15%. 35% corporate tax is applied to the profits. The simplest depreciation method -- the straight-line method is applied as the salvage value is 10% of the original capital cost after 20 years. Recovery period is considered as 10 years.

5. The market price of aluminum chloride is estimated as \$600/metric ton based on the prices reported at www.alibaba.com^[35]- a worldwide e-commerce market site originally from China. The price of chemicals may vary with many factors, such as season, location, producer, policy, etc.
6. The cost of ethylene is \$1300/metric ton and of ethyl acetate is \$910/metric ton^[36].
7. The catalyst costs are taken as the average of the prices as reported in the reference^[35]. Cu– Ru/C-catalyst loading and HZM-5 zeolite loading is assumed as 10 wt.% of the feed. The catalyst cost is estimated as the sum of precious metals cost which is \$6.73/kg plus \$11/kg of catalyst for support and manufacturing. The catalyst life is taken to be 6 months. It is assumed that the catalyst manufacturer will be able to recover 99% of the metals in the spent catalyst. Therefore, after every 6 months only the cost of the catalyst support, makeup metals and manufacturing cost would be required. The zeolite life is taken as 6 months and no recovery of the zeolite is possible. The cost of HZM-5 zeolite is \$5000/metric ton.
8. Other costs include raw materials, solvents and acids: cost of dimethyl ether is \$1000/metric ton and hydrogen is priced at \$653/metric ton^[31, 36]. The market price of sulphuric acid and phosphoric acid are \$250/metric ton and \$600/metric ton. The cost of lithium bromide is estimated to be \$1400/metric ton and lime as \$75/metric ton^[35].
9. In the base scenario the value of byproducts is not considered, even though the impact of considering their value is discussed.
10. Heat integration with steam and power generation from solid residue such as lignin and humins is considered in the simulation. Costing of the steam boiler and turbo-generator is taken from NREL's report with a scaling factor of 0.7^[30]. The selling price of

electricity is taken as \$0.085 per kWh.

11. Excess utilities such as hot oil, cooling water and refrigeration with wastewater treatment plants are not modeled explicitly, rather it is assumed instead that utilities are purchased and wastewater is treated by a third party at a fixed price per unit volume^[31].

Life Cycle Analysis

The goal of the LCA study is to evaluate and improve the environmental performance of bio-based production of p-Xylene and compare it with our previous process^[37]. The results of the LCA study (using SimaPro®^[38, 39]) are used to evaluate the bio-based p-Xylene from MSH process using sustainable criteria. The system boundaries are cradle-to-gate and are mentioned in detail in Figure 8. The solid lines determine the component streams that are consumed while the dashed lines represent the streams that are recycled. The red colored lines represent the DA process, blue the CA process, green represents the MSH process and black represents the streams that are common to all the hydrolysis processes. There are three stages involved in the process, first stage is the cultivation and hydrolysis of biomass; second stage is the dehydration of the sugars and the next stage is the p-Xylene production including hydro-deoxygenation and cycloaddition. One metric ton of p-Xylene produced is considered as the functional unit for the analysis and comparison of LCA results for different hydrolysis processes.

The important assumptions that are considered for LCA are:

1. The materials used in the manufacturing of p-Xylene are only considered. The materials used in the construction, other infrastructure, cooling water and catalysts are supposed to be recycled at the end of the process' life cycle and are not considered.
2. The feedstock is transported by a truck from the local biomass conversion facility, 100

- km away from the biorefinery facility.
- Electricity is supplied by medium voltage grid based on the average technology and total loss in US.
 - Heating is supplied by steam, among which 76% is generated by natural gas and the rest is generated by heavy oil fuel. Water input is not considered as heating since it is assumed to be a closed system.
 - Cooling is supplied by water, cooling, unspecified natural origin based on the assumption that 99.5% of the total is recycled and waste heat is emitted into atmosphere.
 - Flue gas from the power generation plant contains only CO₂.
 - Wastewater is connected to wastewater treatment units.

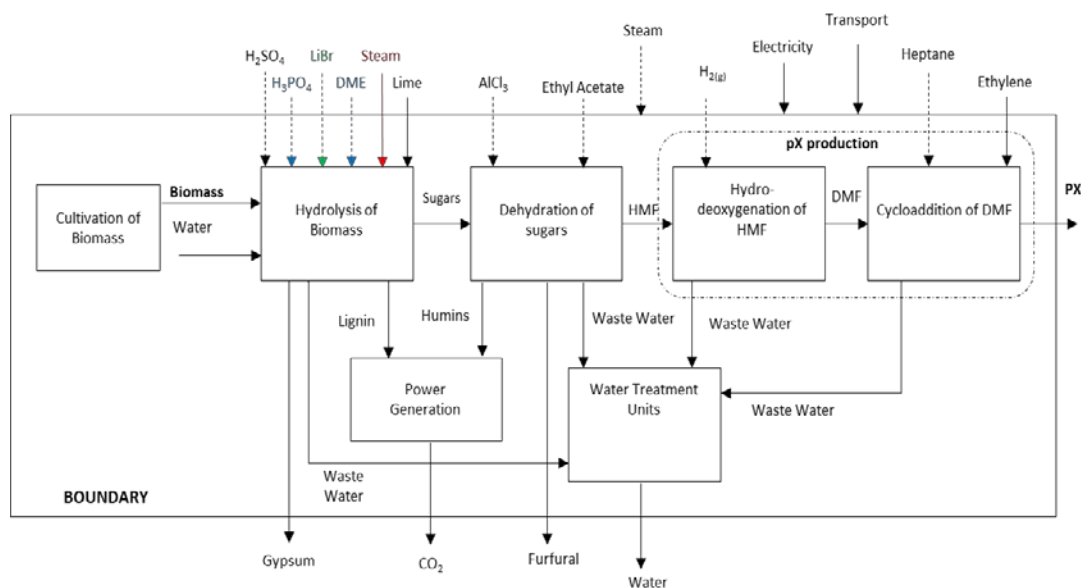


Figure 8: Scope definition of bio-based production of p-Xylene (DA (red), CA (blue), and MSH (green) processes

2.3 Results and Discussion

Simulation

The capacity of the three processes for the production of p-Xylene is based on processing 400,000 metric ton of biomass per year. The DA process produces 49,209 metric ton/year of p-Xylene, the CA process produces 71,341 metric ton/year of p-Xylene, and the MSH process produces 81,312 metric ton/year of p-Xylene.

All three hydrolysis processes produce lignin, furfural and electricity as the main by-products. Humins produced from the dehydration reaction of sugar can be used to produce high value products^[40, 41] but in this analysis we consider them as wastes with no value. Gypsum produced from DA and CA processes are also considered as wastes with no value. Large quantity of lignin is produced in all three processes, which along with humins are used for electricity and steam generation. HP steam (81,992 kg/hr. for DA process, 158,773 kg/hr. for CA process and 130,000 kg/hr. for MSH process), MP steam (115,964 kg/hr. for DA process and 188,900 kg/hr. for MSH process) and LP steam (74,614 kg/hr. for DA process, 107,735 kg/hr. for CA process and 40,000 kg/hr. for MSH process) are produced which is consumed in the process. A total of 22 MW, 19 MW and 26 MW of electricity is produced for DA, CA and MSH process, respectively. 5 MW, 22 MW and 7MW of electricity is consumed by DA, CA and MSH process, respectively. By-products such as 2,5-dihydroxymethyltetrahydrofuran (DHMTHF), 2,5-hexanedione (HEXANED), and 1-ethyl-2,5-dimethylbenzene (ETHLYPXY) are produced in very small quantity and hence purifying and selling them is not a viable option. Mass balance for all the three processes is given in table 3-5.

Table 3: Mass Balance for DA process.

Kg/hr.	Hydrolysis Section							
	Glucose	Xylose	H ₂ SO ₄	Water	Furfural	Biomass	CaO	CaSO ₄
MP Steam	0	0	0	26,500	0	0	0	0
Biomass	0	0	0	0	0	50,000	0	0
Sulphuric acid	0	0	850	0	0	0	0	0
Water	0	0	0	50,000	0	0	0	0
1	0	0	850	76,500	0	50,000	0	0
2/3	0	14,054	850	74,918	278	50,000	0	0
Water	0	0	0	35,500	0	0	0	0
Xylose	0	13,070	791	102,689	259	1,863	0	0
4	0	984	60	7,729	19	35,388	0	0
Hp steam	0	0	0	36,375	0	0	0	0
Sulphuric acid	0	0	750	0	0	0	0	0
Water	0	0	0	55,500	0	0	0	0
5	13,722	984	810	98,232	19	23,038	0	0
6	0	0	1	39,947	13	0	0	0

7	13,722	984	808	58,285	6	23,038	0	0
8	0	0	0	29,961	5	0	0	0
9	13,722	984	808	28,324	23,038	0	0	0
Water	0	0	0	603,512	0	0	0	0
10	12,761	915	752	587,607	1	1,152	0	0
Lignin	961	69	57	44,228	0	21,886	0	0
Lime	0	0	0	0	0	0	1,000	0
10	12,761	13,985	0	690,579	260	3,014	118	2,141
Aqueous solution	12,749	13,971	0	689,888	259	30	1	21
Gypsum	13	14	0	691	0	2,984	117	2,119
Waste water	0	1	0	658,196	256	0	0	0
Sugars	12,749	13,970	0	31,693	4	30	1	21

Dehydration Section

Kg/hr.	Glucose	Xylose	AlCl ₃	Ethyl	Water	HMF	Furfural	Biomass	Humins	CaO	CaSO ₄
Ethyl Acetate	0	0	0	28	0	0	0	0	0	0	0
Ethyl Acetate 1	0	0	0	28	0	0	0	0	0	0	0

Sugars	12,749	13,970	0	0	31,693	0	4	30	0	1	21
AlCl ₃	0	0	1,409	0	0	0	0	0	0	0	0
1/2	12,749	13,970	10,934	275,692	69,414	397	63	30	20	1	21
3	0	0	0	275,692	0	3,991	3,831	0	0	0	0
5	0	0	0	275,692	0	3,592	3,448	0	0	0	0
7	0	0	0	551,329	0	0	0	0	0	0	0
8	0	0	0	55	0	7,583	7,280	0	0	0	0
Recycle Solvent	0	0	0	275,664	0	0	0	0	0	0	0
Recycle solvent 2	0	0	0	275,664	0	0	0	0	0	0	0
Furfural	0	0	0	55	0	16	7,267	0	0	0	0
HMF	0	0	0	0	0	7,567	13	0	0	0	0
4	0	0	10,934	0	76,940	3,991	3,831	30	4,028	1	22
6	0	0	10,934	0	76,940	399	383	30	4,028	1	22
Humins	0	0	55	0	385	2	2	30	4,008	1	21
9	0	0	10,879	0	76,555	397	381	0	20	0	0
Waste water	0	0	1,354	0	38,833	0	322	0	0	0	0
Recycle catalyst	0	0	9,525	0	37,722	397	59	0	20	0	0

Hydroxy-deoxygenation section

Kg/hr.	Water	HMF	DMF	H ₂	Furfural	DHMTF	Mefuran
H ₂	0	0	0	364	0	0	0
1	1	0	13	379	0	0	0
HMF	0	7,567	0	0	13	0	0
2	2,144	0	5,723	16	0	79	11
Gas	1	0	13	15	0	0	0
DMF	53	0	5,710	0	0	79	11
Waste Water	2,089	0	0	0	0	0	0

Cyclo-Addition Section

Kg/hr.	Water	DMF	Furfural	DHMTF	Ethylene	Heptane	p- Xylene	Hexaned	Ethylpxy	Me-furan
Heptane	0	0	0	0	0	48	0	0	0	0
DMF	53	5,710	0	79	0	0	0	0	0	11
Ethylene/2	0	0	0	0	1,711	0	0	0	0	0
1	55	5,710	0	79	1,715	2,005	85	0	0	25
3	1,104	0	0	79	31	2,005	6,202	68	159	25
4	5	0	0	47	19	2,005	6,202	40	95	15
Waste water	1,099	0	0	32	13	0	1	27	65	10

5	5	0	0	0	19	1,974	85	0	0	15
Purge	3	0	0	0	15	17	0	0	0	0
Recycle solvent	2	0	0	0	3	1,957	85	0	0	15
6	0	0	0	47	0	31	6,117	40	95	0
p-Xylene	0	0	0	0	0	31	6,109	12	0	0
By-products	0	0	0	47	0	0	8	28	95	0

Table 4: Mass Balance for CA process.

Hydrolysis Section											
Kg/hr.	Glucose	Xylose	H ₂ SO ₄	H ₃ PO ₄	Water	Oligo-saccharides	DME	Biomass	CaO	CaSO ₄	Ca ₃ PO ₄
Biomass	0	0	0	0	0	0	0	50,000	0	0	0
Water	0	0	0	0	16,642	0	0	0	0	0	0
Sulphuric Acid	0	0	751	0	0	0	0	0	0	0	0
Phosphoric Acid	0	0	0	375	0	0	0	0	0	0	0
1	0	0	50,000	25,000	25,000	35	164	50,019	0	0	0
4/5	0	0	50,000	25,000	21,159	35,380	164	18,515	0	0	0
DME	0	0	0	0	0	0	714	0	0	0	0

2/3	0	0	0	0	6,193	0	309,757	0	0	0	0
6	0	0	47,500	23,750	13,676	0	309,921	0	0	0	0
Recycle Solvent	0	0	0	0	1,329	0	288,193	0	0	0	0
8	0	0	49,250	24,625	21,920	35	21,728	19	0	0	0
9	0	0	1	0	13,562	0	21,564	0	0	0	0
Recycle acid	0	0	49,249	24,625	8,358	35	164	19	0	0	0
10	0	0	0	0	4,864	0	20,850	0	0	0	0
Waste water	0	0	1	0	8,699	0	714	0	0	0	0
7	0	0	2,500	1,250	13,676	35,380	0	18,515	0	0	0
11	0	0	1,750	875	9,573	35	0	19	0	0	0
12	0	0	750	375	4,103	35,344	0	18,497	0	0	0
Water	0	0	0	0	95,000	0	0	0	0	0	0
13	0	0	750	375	99,103	35,344	0	18,497	0	0	0
14	18,002	13,808	750	375	99,103	3,534	0	18,497	0	0	0
15	17,984	13,794	749	375	99,004	35	0	185	0	0	0

Lignin	18	14	1	0	99	3,499	0	18,312	0	0	0
Lime	0	0	0	0	0	0	0	0	1,000	0	0
16	17,984	13,794	0	0	99,245	35	0	185	250	1,040	593
Aqueous solution	17,804	13,656	0	0	98,252	0	0	0	0	0	0
Gypsum	180	138	0	0	992	35	0	185	250	1,040	593
Waste water	0	0	0	0	71,170	0	0	0	0	0	0
Sugars	17,804	13,656	0	0	27,082	0	0	0	0	0	0

Dehydration Section

Kg/hr.	Glucose	Xylose	AlCl ₃	Ethyl	Water	HMF	Furfural	Biomass	Humins
Ethyl Acetate	0	0	0	35	0	0	0	0	0
Ethyl Acetate 1	0	0	0	35	0	0	0	0	0
Sugars	17,804	13,656	0	0	27,082	0	0	30	0
AlCl ₃	0	0	953	0	0	0	0	0	24
1/2	17,804	13,656	12,667	351,672	91,285	554	89	30	0
3	0	0	0	351,672	0	5,574	3,759	0	0
5	0	0	0	351,672	0	5,017	3,383	0	0
7	0	0	0	703,273	0	0	0	0	0

8	0	0	0	71	0	10,590	7,142	0	0
Recycle Solvent	0	0	0	351,637	0	0	0	0	0
Recycle solvent 2	0	0	0	351,637	0	0	0	0	0
Furfural	0	0	0	71	0	59	7,097	0	0
HMF	0	0	0	0	0	10,532	45	0	
4	0	0	12,667	0	100,003	5,574	3,759	0	4,743
6	0	0	12,667	0	100,003	557	376	0	4,743
Humins	0	0	63	0	500	3	2	0	4,719
9	0	0	12,604	0	99,503	555	374	0	24
Waste water	0	0	889	0	35,301	0	285	0	0
Recycle catalyst	0	0	11,715	0	64,202	554	89	0	24

Hydroxy-deoxygenation section

Kg/hr.	Water	HMF	DMF	H ₂	Furfural	DHMTF	Mefuran
H ₂	0	0	0	507	0	0	0
1	1	0	15	526	0	0	0
HMF	0	10,532	0	0	45	0	0
2	2,989	0	7,963	19	0	110	38

Gas	1	0	15	19	0	0	0
DMF	74	0	7,948	0	0	110	38
Waste Water	2,913	0	0	0	0	0	0

Cyclo-Addition Section

Kg/hr.	Water	DMF	Furfural	DHMTTHF	Ethylene	Heptane	p- Xylene	Hexaned	Ethylpxy	Me-furan
Heptane	0	0	0	0	0	597	0	0	0	0
DMF	74	7,948	0	110	0	0	0	0	0	38
Ethylene/2	0	0	0	0	2,805	0	0	0	0	0
1	75	7,948	1	110	2,811	2,801	583	0	0	73
3	1,535	0	1	110	469	2,801	9,097	94	222	73
4	16	0	1	67	285	2,799	9,092	57	135	45
Waste water	1,519	0	0	43	184	2	5	37	87	29
5	16	0	0	0	285	2,399	597	0	0	45
Purge	16	0	0	0	279	195	14	0	0	9
Recycle solvent	1	0	0	0	6	2,204	583	0	0	35
6	0	0	0	67	0	401	8,495	57	135	0
p- Xylene	0	0	0	0	0	401	8,495	22	0	0

By- products	0	0	0	67	0	0	0	36	135	0
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Table 5: Mass Balance for MSH process.

Hydrolysis Section										
Kg/hr.	Glucose	Xylose	H ₂ SO ₄	LiBr	AlCl ₃	Water	HMF	Furfural	Humins	Biomass
Biomass	0	0	0	0	0	0	0	0	0	50,000
Sulphuric Acid	0	0	4	0	0	0	0	0	0	0
Water	0	0	0	0	0	1,155	0	0	0	0
LiBr	0	0	0	1,769	0	0	0	0	0	0
1	0	0	735	295,000	14,378	154,250	657	421	27	50,000
Recycle Catalyst	0	0	731	293,232	14,378	153,095	657	421	27	1
2	21,111	21,090	735	294,705	14,363	150,168	657	421	27	17,651
Sugars	21,090	15,155	734	294,705	14,363	150,168	656	421	0	177
Lignin	21	15	1	295	14	150	1	0	27	17,475

Dehydration Section											
Kg/hr.	Glucose	Xylose	H ₂ SO ₄	LiBr	AlCl ₃	Ethyl	Water	HMF	Furfural	Biomass	Humins
Ethyl Acetate	0	0	0	0	0	8	0	0	0	0	0
Ethyl	0	0	0	0	0	8	0	0	0	0	0

Acetate 1											
Sugars	21,090	15,155	734	294,705	14,363	0	150,168	656	421	177	0
AlCl ₃	0	0	0	0	171	0	0	0	0	0	0
1/2	21,090	15,155	734	294,705	14,534	809,785	150,168	656	421	177	0
3	0	0	0	0	0	809,785	0	6,602	4,333	0	0
5	0	0	0	0	0	809,785	0	5,942	3,899	0	0
7	0	0	0	0	0	1,619,550	0	0	0	0	0
8	0	0	0	0	0	17	0	12,545	8,232	0	0
Recycle Solvent	0	0	0	0	0	809,777	0	0	0	0	0
Recycle solvent 2	0	0	0	0	0	809,777	0	0	0	0	0
Furfural	0	0	0	0	0	17	0	38	8,172	0	0
HMF	0	0	0	0	0	17	0	12,477	60	0	0
4	0	0	734	294,705	14,534	0	160,183	6,608	4,333	177	5,437
6	0	0	734	294,705	14,534	0	160,183	660	433	177	5,437
Humins	0	0	4	1,474	79	0	801	3	2	176	5,410
9	0	0	731	293,232	14,461	0	159,383	657	431	1	27
Waste water	0	0	0	0	84	0	6,288	0	10	0	0

Recycle catalyst	0	0	731	293,232	14,378	0	153,095	657	421	1	27
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Hydroxy-deoxygenation section

Kg/hr.	Water	HMF	DMF	H ₂	Furfural	DHMTTHF	Mefuran
H ₂	0	0	0	601	0	0	0
1	1	0	18	623	0	0	0
HMF	0	12,477	0	0	60	0	0
2	3,542	0	9,433	22	1	131	51
Gas	1	0	18	22	0	0	0
DMF	88	0	9,415	0	1	131	50
Waste Water	3,452	0	0	0	0	0	0

Cyclo-Addition Section

Kg/hr.	Water	DMF	Furfural	DHMTTHF	Ethylene	Heptane	p- Xylene	Hexaned	Ethylpxy	Me-furan
Heptane	0	0	0	0	0	92	0	0	0	0
DMF	88	9,415	1	131	0	0	0	0	0	50
Ethylene/2	0	0	0	0	2,805	0	0	0	0	0
1	92	9,415	1	131	2,810	3,318	134	0	0	121
3	1,821	0	1	131	35	3,318	10,221	112	263	121
4	8	0	1	78	21	3,318	10,220	66	156	72

Waste water	1,814	0	0	53	14	0	1	45	107	49
5	8	0	0	0	21	3,246	134	0	0	72
Purge	4	0	0	0	16	20	0	0	0	1
Recycle solvent	4	0	0	0	5	3,226	134	0	0	71
6	0	0	1	78	0	72	10,086	66	156	0
p- Xylene	0	0	1	0	0	72	10,072	19	0	0
By- products	0	0	0	78	0	0	14	47	156	0

Economics

The capital and operating cost of all the three processes to produce p-Xylene are listed in Table 6-8. The capital cost of the DA process is estimated at \$174.2 million and the operating cost is estimated as \$95.08 million. The capital cost for CA process is estimated as \$236.7 million and the operating cost as \$93.5 million. For MSH process, the capital cost is estimated as \$200.65 million and the operating cost as \$97.05 million. Equipment details for DA, CA and MSH process is given in table 9-11 and the total utility consumption is given in table 12.

Table 6: Summary of the Capital and Operating Cost of the DA Process.

Item	Cost (Million \$)	Item	Cost per year (Million \$)
Purchased Equipment	123.7	Total Catalyst Cost	0.03
Other	19.6	Total Raw Materials Cost	59.3
General and Administrative Overheads	4	Total Utilities Cost	21.7
Contract Fee	4.3	Operating Labor Cost	1.6
Contingencies	14.3	Maintenance Cost	3
Working Capital	8.3	Operating Charges	0.4
Total Capital Cost	174.2	Plant Overhead	2.3
		General and Administrative Cost	6.75
		Total Operating Cost	95.08

Table 7: Summary of the Capital and Operating Cost of the CA Process.

Item	Cost (Million \$)	Item	Cost per year (Million \$)
Purchased Equipment	164.6	Total Catalyst Cost	0.04
Other	30	Total Raw Materials Cost	75.7

General and Administrative Overheads	5.45	Total Utilities Cost	3.7
Contract Fee	5.8	Operating Labor Cost	1.6
Contingencies	19.5	Maintenance Cost	3
Working Capital	11.3	Operating Charges	0.4
Total Capital Cost	236.7	Plant Overhead	2.3
		General and Administrative Cost	6.75
		Total Operating Cost	93.5

Table 8: Summary of the Capital and Operating Cost of the MSH Process.

Item	Cost (Million \$)	Item	Cost per year (Million \$)
Purchased Equipment	139.6	Total Catalyst Cost	0.05
Other	25.4	Total Raw Materials Cost	79.65
General and Administrative Overheads	4.6	Total Utilities Cost	3.3
Contract Fee	4.95	Operating Labor Cost	1.6
Contingencies	16.5	Maintenance Cost	3
Working Capital	9.6	Operating Charges	0.4
Total Capital Cost	200.65	Plant Overhead	2.3
		General and Administrative Cost	6.75
		Total Operating Cost	97.05

Table 9: Equipment Details for DA process.

Component Name	Component Type	Total Direct Cost (\$)	Equipment Cost (\$)
Hydrolysis Section			
R1	DAT Reactor	420,500	238,000
V1	DVT Cylinder	160,900	36,700
Fil 1	DF Roty Drum	883,100	619,400

P1	DCP Centrif	73,300	30,100
R2	DAT Reactor	413,000	231,500
V2	DVT Cylinder	203,300	57,000
V3	DVT Cylinder	156,900	28,800
Fil 2	DF Roty Drum	423,900	286,500
P2	DCP Centrif	142,700	86,100
R3	DAT Reactor	689,100	446,800
Fil 3	DF Roty Drum	249,900	145,600
V4	DVT Cylinder	1,412,300	669,500
Dehydration Section			
R1	DAT Reactor	8,440,000	7,300,900
Sep1	DVT Cylinder	255,000	90,100
V1	DVT Cylinder	201,500	40,400
C1 – cond acc	DHT Horiz Drum	278,900	71,900
C1 – reflux pump	DCP Centrif	137,600	48,000
C1 – tower	DTW Tower	4,115,700	2,555,400
C2 – cond acc	DHT Horiz Drum	86,400	11,900
C2 – reflux pump	DCP Centrif	39,100	5,200
C2 – tower	DTW Tower	394,800	163,500
Fil 1	DF Roty Drum	36,700	21,500
P1	DCP Centrif	230,600	123,300
Hydroxy-deoxygenation section			
R1	DAT Reactor	3,510,800	2,911,300
V1	DVT Cylinder	89,800	16,800

Comp	DGC Centrif	1,622,200	1,482,200
P1	DCP Centrif	40,300	5,400
Cyclo-Addition Section			
R1	DAT Reactor	13,208,900	11,781,600
V1	DVT Cylinder	116,600	33,700
V2	DVT Cylinder	112,500	14,900
C1 – cond acc	DHT Horiz Drum	102,100	14,600
C1 – reflux pump	DCP Centrif	32,200	4,400
C1 – tower	DTW Tower	515,500	264,300
C2 – cond acc	DHT Horiz Drum	86,900	11,400
C2 – reflux pump	DCP Centrif	39,200	5,300
C2 – tower	DTW Tower	717,000	425,300
Comp	DGC Recip Motr	1,061,000	953,100
P1	DCP Centrif	119,800	77,700
Steam and Power Generation Section			
Pretreatment	-	1,453,508	-
Boiler	-	60,154,822	-
Turbine	-	12,517,718	-
Heat Exchangers			
HX-1	DHE Tema Exch	15,587	-
HX-2	DHE Tema Exch	12,173	-
HX-3	DHE Tema Exch	24,651	-
HX-4	DHE Tema Exch	10,839	-
HX-5	DHE Tema Exch	22,830	-
HX-6	DHE Tema Exch	663,195	-

HX-7	DHE Tema Exch	21,670	-
HX-8	DHE Tema Exch	13,150	-
HX-9	DHE Tema Exch	13,228	-
HX-10	DHE Tema Exch	140,826	-
HX-11	DHE Tema Exch	31,836	-
HX-12	DHE Tema Exch	10,068	-
HX-13	DHE Tema Exch	1,022,033	-
HX-14	DHE Tema Exch	28,149	-
HX-15	DHE Tema Exch	171,403	-
HX-16	DHE Tema Exch	88,045	-
HX-17	DHE Tema Exch	16,659	-
HX-18	DHE Tema Exch	82,852	-
HX-19	DHE Tema Exch	14,530	-
HX-20	DHE Tema Exch	171,548	-
HX-21	DHE Tema Exch	17,268	-
HX-22	DHE Tema Exch	27,153	-
HX-23	DHE Tema Exch	395,338	-
HX-24	DHE Tema Exch	1,258,672	-
HX-25	DHE Tema Exch	1,570,561	-
HX-26	DHE Tema Exch	17,249	-
HX-27	DHE Tema Exch	2,487,857	-
HX-28	DHE Tema Exch	205,356	-
HX-29	DHE Tema Exch	10,261	-
HX-30	DHE Tema Exch	31,732	-
HX-31	DHE Tema Exch	43,326	-
HX-32	DHE Tema Exch	37,385	-

HX-33	DHE Tema Exch	14,468	-
HX-34	DHE Tema Exch	12,392	-
HX-35	DHE Tema Exch	12,395	-

Table 10: Equipment Details for CA process.

Component Name	Component Type	Total Direct Cost (\$)	Equipment Cost (\$)
Hydrolysis Section			
R1	DAT Reactor	9,825,400	7,129,800
P1	DCP Centrif	90,800	15,200
E1	DVT Cylinder	569,300	162,300
V1	DVT Cylinder	748,000	341,500
V2	DVT Cylinder	781,600	185,300
V3	DVT Cylinder	410,100	85,100
V4	DVT Cylinder	292,800	100,700
Comp	DGC Centrif	21,652,400	20,735,100
Fil 1	DF Roty Drum	857,000	619,400
Fil 2	DF Roty Drum	386,700	273,600
Fil 3	DF Roty Drum	174,600	100,700
P2	DCP Centrif	70,300	12,700
R2	DAT Reactor	1,124,300	773,000
R3	DAT Reactor	361,800	190,900
V5	DVT Cylinder	409,900	73,700
Dehydration Section			
R1	DAT Reactor	8,475,800	7,316,000
Sep1	DVT Cylinder	295,800	107,900

V1	DVT Cylinder	209,000	42,400
C1 – cond acc	DHT Horiz Drum	314,400	87,900
C1 – reflux pump	DCP Centrif	201,000	70,700
C1 – tower	DTW Tower	5,238,600	3,003,500
C2 – cond acc	DHT Horiz Drum	86,400	11,900
C2 – reflux pump	DCP Centrif	39,100	5,200
C2 – tower	DTW Tower	394,800	163,500
Fil 1	DF Roty Drum	222,000	141,500
P1	DCP Centrif	275,800	167,100
Hydroxy-deoxygenation section			
R1	DAT Reactor	3,510,800	2,911,300
V1	DVT Cylinder	93,100	16,800
Comp	DGC Centrif	1,574,900	1,442,300
Comp-2	DGC Centrif	1,574,900	1,442,300
P1	DCP Centrif	40,300	5,400
Cyclo-Addition Section			
R1	DAT Reactor	13,208,900	11,781,600
V1	DVT Cylinder	116,600	33,700
V2	DVT Cylinder	118,500	17,300
C1 – cond acc	DHT Horiz Drum	103,000	14,600
C1 – reflux pump	DCP Centrif	32,200	4,400
C1 – tower	DTW Tower	523,600	265,300
C2 – cond acc	DHT Horiz Drum	103,700	12,900
C2 – reflux pump	DCP Centrif	39,400	5,700
C2 – tower	DTW Tower	748,300	433,000

Comp	DGC Recip Motr	1,238,000	1,123,500
P1	DCP Centrif	123,000	80,300
Steam and Power Generation Section			
Pretreatment	-	1,310,797	-
Boiler	-	59,348,435	-
Turbine	-	11,440,372	-
Heat Exchangers			
HX-1	DHE Tema Exch	21,826	-
HX-2	DHE Tema Exch	18,824	-
HX-3	DHE Tema Exch	81,145	-
HX-4	DHE Tema Exch	87,641	-
HX-5	DHE Tema Exch	84,499	-
HX-6	DHE Tema Exch	146,175	-
HX-7	DHE Tema Exch	877,373	-
HX-8	DHE Tema Exch	55,688	-
HX-9	DHE Tema Exch	78,800	-
HX-10	DHE Tema Exch	386,794	-
HX-11	DHE Tema Exch	804,302	-
HX-12	DHE Tema Exch	859,042	-
HX-13	DHE Tema Exch	110,962	-
HX-14	DHE Tema Exch	171,338	-
HX-15	DHE Tema Exch	17,516	-
HX-16	DHE Tema Exch	11,075	-
HX-17	DHE Tema Exch	14,871	-

HX-18	DHE Tema Exch	10,321	-
HX-19	DHE Tema Exch	41,297	-
HX-20	DHE Tema Exch	1,579,973	-
HX-21	DHE Tema Exch	25,460	-
HX-22	DHE Tema Exch	27,750	-
HX-23	DHE Tema Exch	40,317	-
HX-24	DHE Tema Exch	487,165	-
HX-25	DHE Tema Exch	46,048	-
HX-26	DHE Tema Exch	27,897	-
HX-27	DHE Tema Exch	1,361,745	-
HX-28	DHE Tema Exch	300,159	-
HX-29	DHE Tema Exch	2,824,964	-
HX-30	DHE Tema Exch	342,843	-
HX-31	DHE Tema Exch	16,371	-
HX-32	DHE Tema Exch	52,007	-
HX-33	DHE Tema Exch	17,643	-
HX-34	DHE Tema Exch	280,050	-
HX-35	DHE Tema Exch	11,332	-
HX-36	DHE Tema Exch	82,278	-
HX-37	DHE Tema Exch	98,338	-
HX-38	DHE Tema Exch	14,451	-
HX-39	DHE Tema Exch	21,072	-
HX-40	DHE Tema Exch	10,800	-
HX-41	DHE Tema Exch	29,708	-

HX-42	DHE Tema Exch	569,121	-
HX-43	DHE Tema Exch	188,548	-
HX-44	DHE Tema Exch	63,198	-
HX-45	DHE Tema Exch	2,914,115	-
HX-46	DHE Tema Exch	13,142	-
HX-47	DHE Tema Exch	10,257	-
HX-48	DHE Tema Exch	160,343	-
HX-49	DHE Tema Exch	16,829	-
HX-50	DHE Tema Exch	20,069	-
HX-51	DHE Tema Exch	324,010	-

Table 11: Equipment Details for MSH process.

Component Name	Component Type	Total Direct Cost (\$)	Equipment Cost (\$)
Hydrolysis Section			
R1	DAT Reactor	1,665,000	1,310,200
Fil 1	DF Roty Drum	376,600	260,500
Dehydration Section			
R1	DAT Reactor	8,920,900	7,522,900
Sep1	DVT Cylinder	427,900	175,000
V1	DVT Cylinder	255,700	84,300
C1 – cond acc	DHT Horiz Drum	477,100	177,900
C1 – reflux pump	DCP Centrif	343,100	157,100
C1 – tower	DTW Tower	9,373,300	5,416,500
C2 – cond acc	DHT Horiz Drum	85,800	10,900
C2 – reflux pump	DCP Centrif	39,100	5,200
C2 – tower	DTW Tower	408,100	172,100

Fil 1	DF Roty Drum	101,100	52,000
P1	DCP Centrif	436,300	282,000
Hydroxy-deoxygenation section			
R1	DAT Reactor	3,510,800	2,911,300
V1	DVT Cylinder	95,500	18,100
Comp	DGC Centrif	1,597,500	1,462,400
Comp – 2	DGC Centrif	1,596,800	1,461,700
P1	DCP Centrif	40,400	5,500
Cyclo-Addition Section			
R1	DAT Reactor	12,303,600	10,964,400
V1	DVT Cylinder	117,300	34,400
V2	DVT Cylinder	117,200	17,300
C1 – cond acc	DHT Horiz Drum	103,000	14,600
C1 – reflux pump	DCP Centrif	32,800	5,000
C1 – tower	DTW Tower	554,900	279,700
C2 – cond acc	DHT Horiz Drum	108,700	16,700
C2 – reflux pump	DCP Centrif	39,700	5,800
C2 – tower	DTW Tower	747,400	432,200
Comp	DGC Recip Motr	123,800	1,123,500
P1	DCP Centrif	123,200	80,500
Steam and Power Generation Section			
Pretreatment	-	2,034,300	-
Boiler	-	70,952,497	-
Turbine	-	13,617,044	-
Heat Exchangers			

HX-1	DHE Tema Exch	1,200,562	-
HX-2	DHE Tema Exch	27,282	-
HX-3	DHE Tema Exch	622,581	-
HX-4	DHE Tema Exch	25,344	-
HX-5	DHE Tema Exch	16,947	-
HX-6	DHE Tema Exch	13,268	-
HX-7	DHE Tema Exch	14,237	-
HX-8	DHE Tema Exch	75,498	-
HX-9	DHE Tema Exch	19,161	-
HX-10	DHE Tema Exch	12,341	-
HX-11	DHE Tema Exch	27,896	-
HX-12	DHE Tema Exch	101,556	-
HX-13	DHE Tema Exch	18,176	-
HX-14	DHE Tema Exch	4,305,161	-
HX-15	DHE Tema Exch	98,126	-
HX-16	DHE Tema Exch	28,304	-
HX-17	DHE Tema Exch	13,459	-
HX-18	DHE Tema Exch	493,003	-
HX-19	DHE Tema Exch	41,312	-
HX-20	DHE Tema Exch	97,496	-
HX-21	DHE Tema Exch	105,394	-
HX-22	DHE Tema Exch	16,933	-
HX-23	DHE Tema Exch	40,396	-
HX-24	DHE Tema Exch	11,716	-

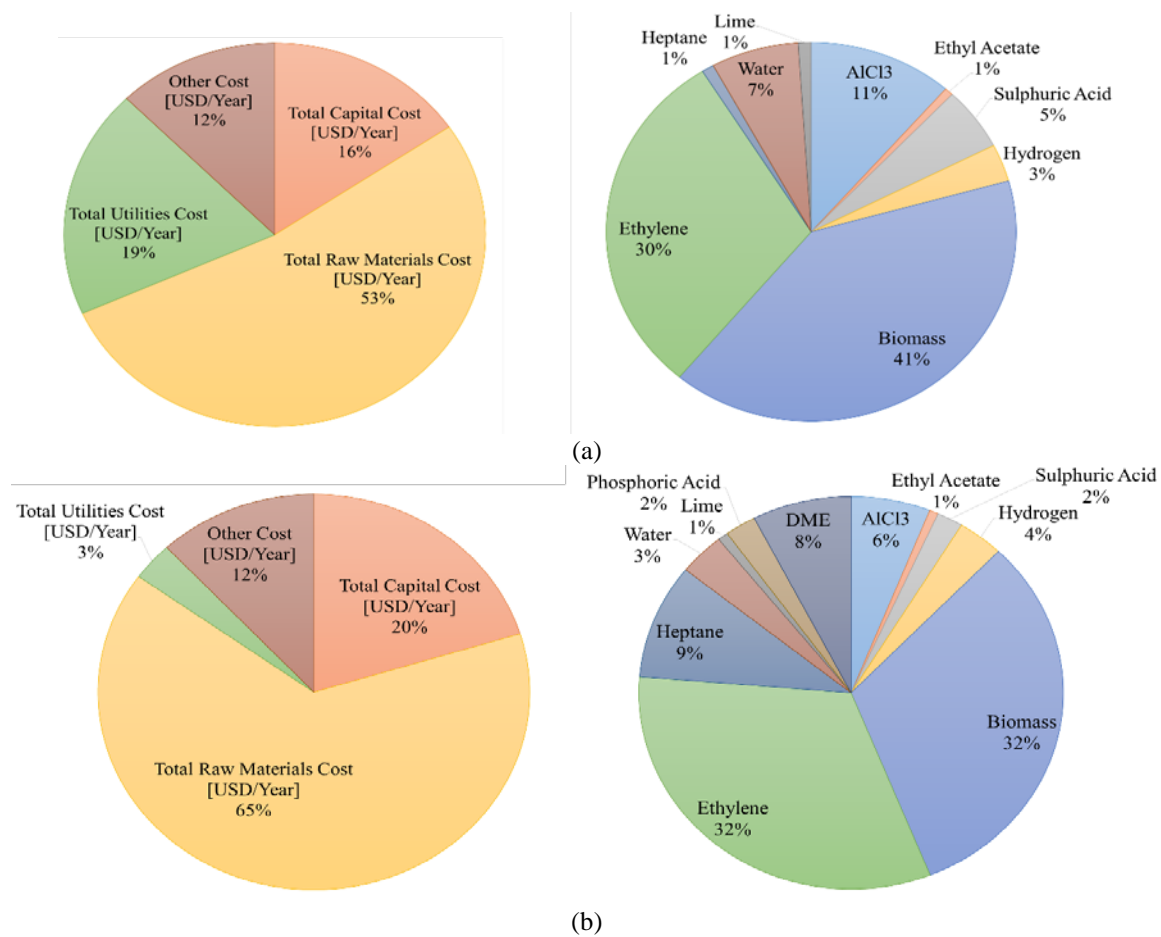
HX-25	DHE Tema Exch	55,272	-
HX-26	DHE Tema Exch	20,199	-
HX-27	DHE Tema Exch	21,880	-
HX-28	DHE Tema Exch	278,522	-

Table 12: Utility Consumption.

Utility	Consumption (KJ/hr.)
DA Process	
Electricity (kWh)	4979
Cooling Water	1.97E+08
Hot Oil	1.00E+07
LP Steam	1.39E+09
CA Process	
Electricity (kWh)	21787
Cooling Water	3.90E+08
Hot Oil	1.00E+07
Refrigerant	4.00E+07
MSH Process	
Electricity (kWh)	8.00E+08
Cooling Water	1.00E+07
MP Steam	9.00E+07

Capital cost for CA process is the highest as it uses special materials such as glass lined CS or Teflon coated CS for handling the concentrated acids. In terms of operating costs, the main contributor for all the three processes is the cost of raw materials at 53%, 65% and 68% for DA, CA and MSH process, respectively. In particular, the fraction of raw

materials can be further decomposed: 41% from biomass and 30% from ethylene for the DA process, 32% from biomass and 32% from ethylene for CA process and 30% from biomass and 37% from ethylene for MSH process. The detailed fractions are given in Figure 9.



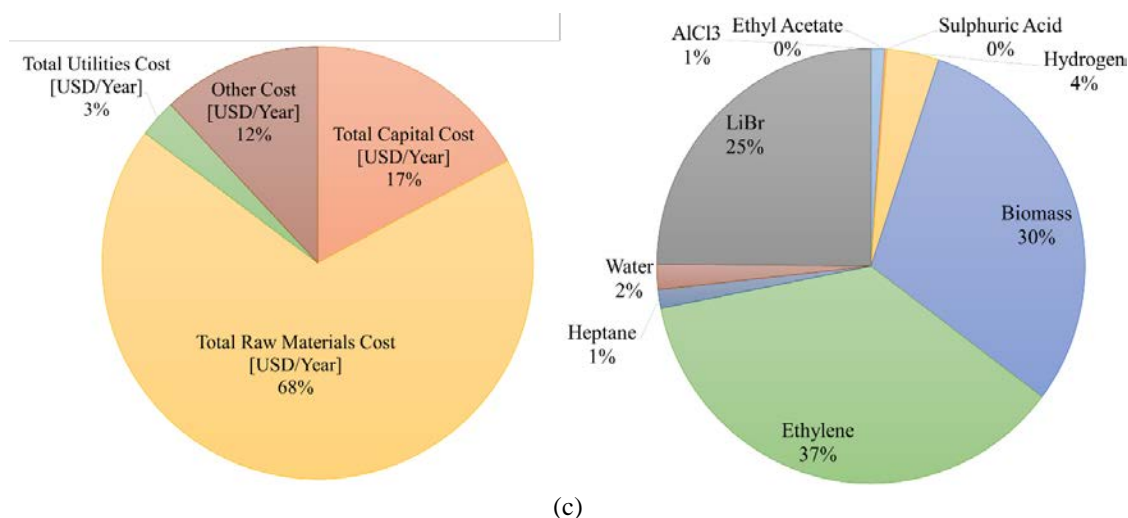


Figure 9: Overview of cost and impact of raw materials on selling price of p-Xylene a) Dilute Acid Hydrolysis b) Concentrated Acid Hydrolysis and c) Hydrolysis using molten salt hydrate.

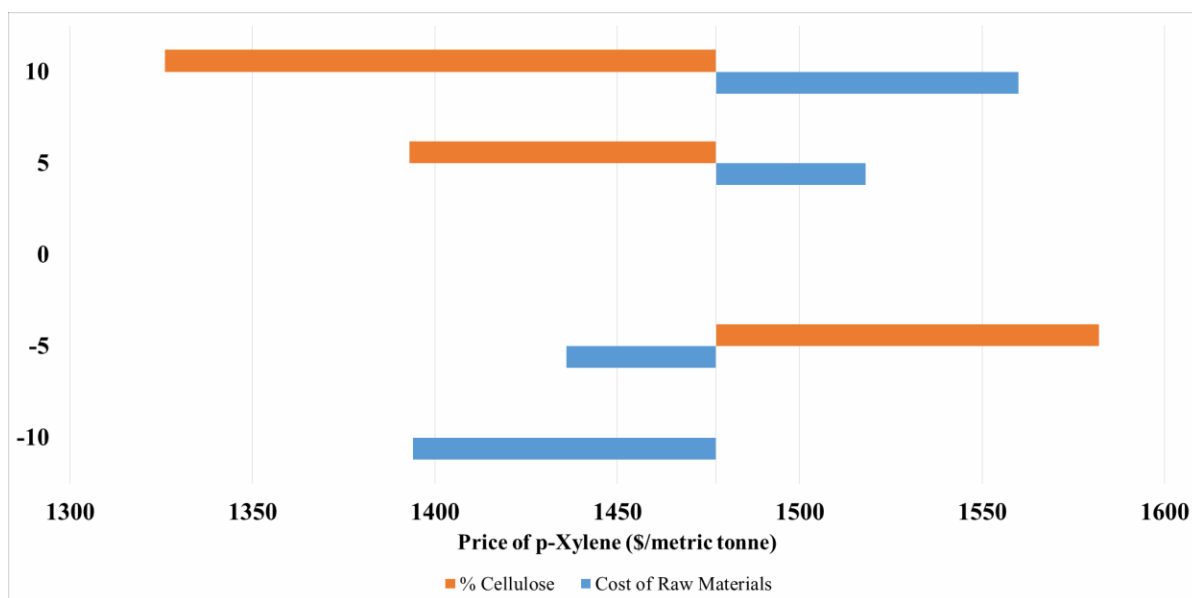
Although the MSH process is a one-stage process, it requires a large amount of solvent for the extraction of HMF/furfural when compared with the other two processes. A 10% biomass loading is used initially based on experimental data. The use of higher concentrations of biomass can be achieved, but since there are no data regarding the impact of initial biomass concentration on the conversion and selectivity, 10% is used in this analysis, in contrast to higher biomass loading in the other two processes. A 3:1 volumetric ratio of organic to aqueous phase is used in the experiment to achieve better phase partition and high selectivity of HMF and furfural. This results in large amount of solvent and higher need of utilities to separate the solvent from HMF and furfural and thus increases the capital cost for MSH process when compared with the DA process.

In the base case scenario, where only electricity produced and no byproducts value is considered, the minimum price of p-Xylene, for DA, CA and MSH process is \$2,322/metric ton, \$1,898/metric ton, and \$1,477/metric ton, respectively. If the value of furfural at \$1,000/metric ton^[35] is considered, then the economics are substantially improved. The minimum selling price for p-Xylene is calculated to be \$1,265/metric ton, \$1,215/metric

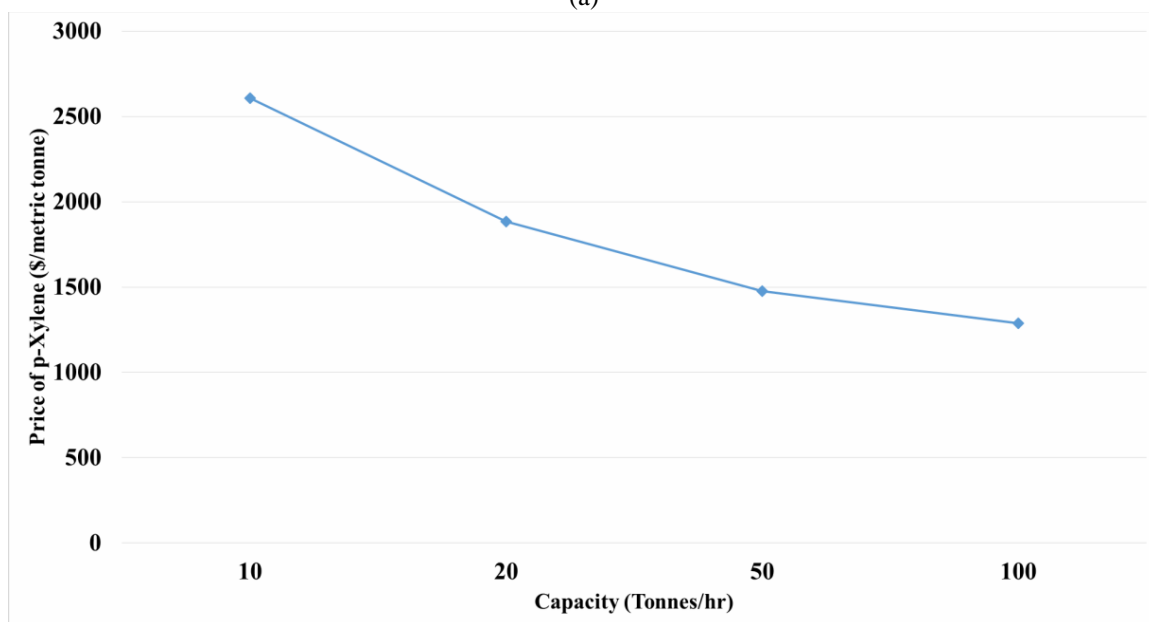
ton and \$760/metric ton for the DA, CA and MSH process, respectively. The lower price is because large quantities of furfural are produced (~85% of xylose is converted to furfural). However, even though large quantity of furfural is produced, we assume the price of furfural in the market remains constant and hence reduces the overall minimum selling price of p-Xylene. The 2014 market price of p-Xylene fluctuated between \$1350-\$1500^[42]. When compared the prices of MSH process is comparable with oil-based p-Xylene process. Sensitivity analysis is carried out to assess the impact of cost of raw materials and capacity of the plant, and is shown in Figure 10. As MSH process is the most promising alternative, sensitivity analysis is carried out for this process. Raw material cost is the most significant factor of p-Xylene price. The cost of raw materials changes significantly based on geography and source. By changing the price of materials by $\pm 10\%$, the price of p-Xylene changes by $\pm 5.6\%$. Among raw materials biomass and ethylene are the major contributors. Biomass feedstock price varies significantly based on the choice of biomass and its source. It is found that a 50% increase of biomass feedstock cost raises the minimum cost of p-xylene by 10.55%, while a 50% increase of ethylene increases the minimum cost of p-xylene by 12.8%. Although bio-based ethylene can be produced via dehydration of ethanol which is obtained from fermentation of biomass^[43], in this analysis, a petroleum-based ethylene price is used. We have also assumed that all the solvents are not solvable in water; thus, no solvent is wasted. If 2.5% of ethyl acetate is mixed with the aqueous phase in each stage, we find a 61% increase in the price of p-Xylene because of high quantity of solvent needed for extraction. As this is a significant increase, more studies should be carried out to investigate the actual partition coefficients of the solvent with water as well as any other method suitable for the removal of HMF/furfural from the aqueous phase. Similarly, we

have also studied the impact of 99% separation efficiency of the filtration system to the minimum selling price of p- Xylene. A decrease of 1% efficiency of the filtration system increases the minimum selling price of p-Xylene by 26.4%. This is a significant increase as reducing the separation efficiency increases the cost of raw materials specially the cost of the lithium bromide as some amount of it comes out with the humins as waste. More studies have to be carried out for the design of filtration system to decrease the price of p-Xylene. To simulate the process, we have assumed that the cellulose content of biomass is 40%. We have also studied the change in the cellulose content of the biomass. The higher the cellulose content, the lower the minimum cost of p-Xylene. Increasing the cellulose content to 50% decreases the minimum selling price of p-Xylene by 10.2%, whereas decreasing the cellulose content to 35% increases the minimum selling price of p-Xylene by 7%. Hence, different types of biomass can change the overall price of p-Xylene. The graph of the results from the sensitivity analysis is given in Figure 10a

As this process is in its early stage of development, the effect of change in capacity of the plant is also investigated. The lower the capacity of the plant, the higher the cost of p-Xylene. Lowering the capacity of the plant from 50 T/hr. of biomass feedstock to 10 T/hr. of biomass feedstock results in a 76.5% increase in the price of p-Xylene whereas increasing the capacity to 100T/hr. of biomass feedstock results in a 12.8% decrease in the price of p-Xylene. Thus, higher capacity is always preferred. However, as the capacity of the plant increases, biomass supply and collection become a major limitation in the overall operation of the plant (Figure 10b).



(a)



(b)

Figure 10: Sensitivity Analysis for MSH process a) cost of p-Xylene when raw materials. b) cost of p-Xylene when plant capacity changes.

Life Cycle Analysis

The characterization results for CA, DA, and MSH processes are calculated by ReCiPe midpoint method^[44]. Mass allocation is applied for the distribution of environmental impacts among co-products, which is shown in Table 13. Impact categories including

climate change, water depletion, land occupation, ecotoxicity, and fossil depletion are considered in our analysis due to their significant normalized impacts.

Table 13: Allocation fraction for different products for (a) DA process (b) CA process and (c) MSH process.

Products	DA	CA	MSH
p-Xylene	45.60%	55.24%	55.18%
Furfural	54.40%	44.76%	44.82%

MSH process performed better in all impact categories except for climate change and fossil depletion, while DA process performs the worst in all impact categories. CA process performs better than MSH and DA process in climate and fossil depletion. MSH process offers a benefit of 44% and 7.5% for water depletion, 83% and 25% for ecotoxicity, 27% and 12% for land occupation over DA and CA process, respectively, whereas CA process offers a benefit of 77% and 8% for climate change, 87% and 22% for fossil depletion over DA and MSH process, respectively. The detailed environmental performance of the three processes is shown in Figure 11. Contribution of raw materials to the environmental impact for MSH process is shown in Figure 12. MSH process is the main contributor to climate change and water depletion due to burning of solid residues and steam production. LiBr is the main contributor to ecotoxicity, usage of oil-based ethylene is the main contributor to fossil depletion and usage of woody biomass is the main contributor for land occupation.

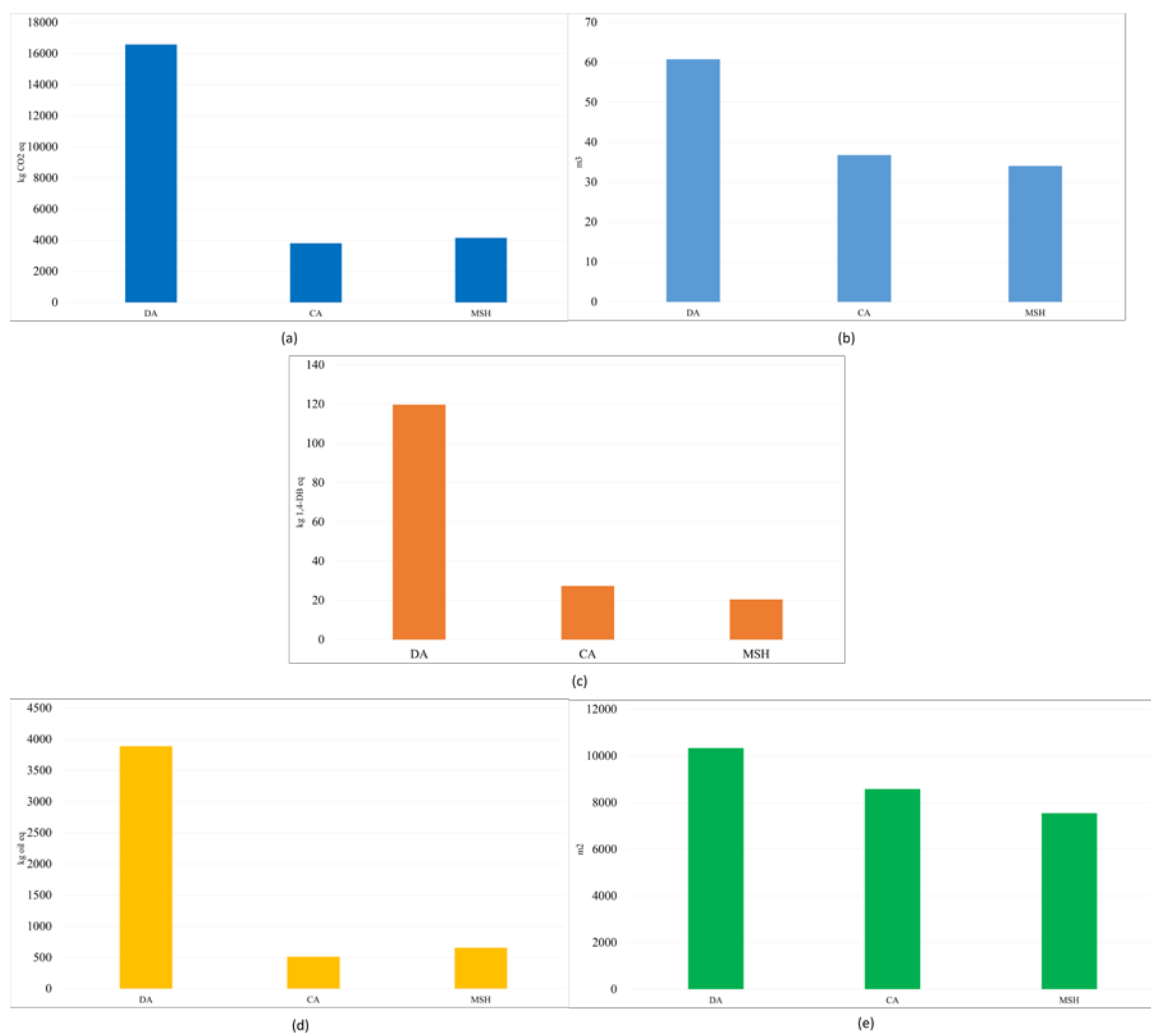


Figure 11: Characterization results (ReCiPe midpoint method) of three processes for a) Climate change b) Fossil depletion c) Ecotoxicity d) Water depletion e) Land occupation.

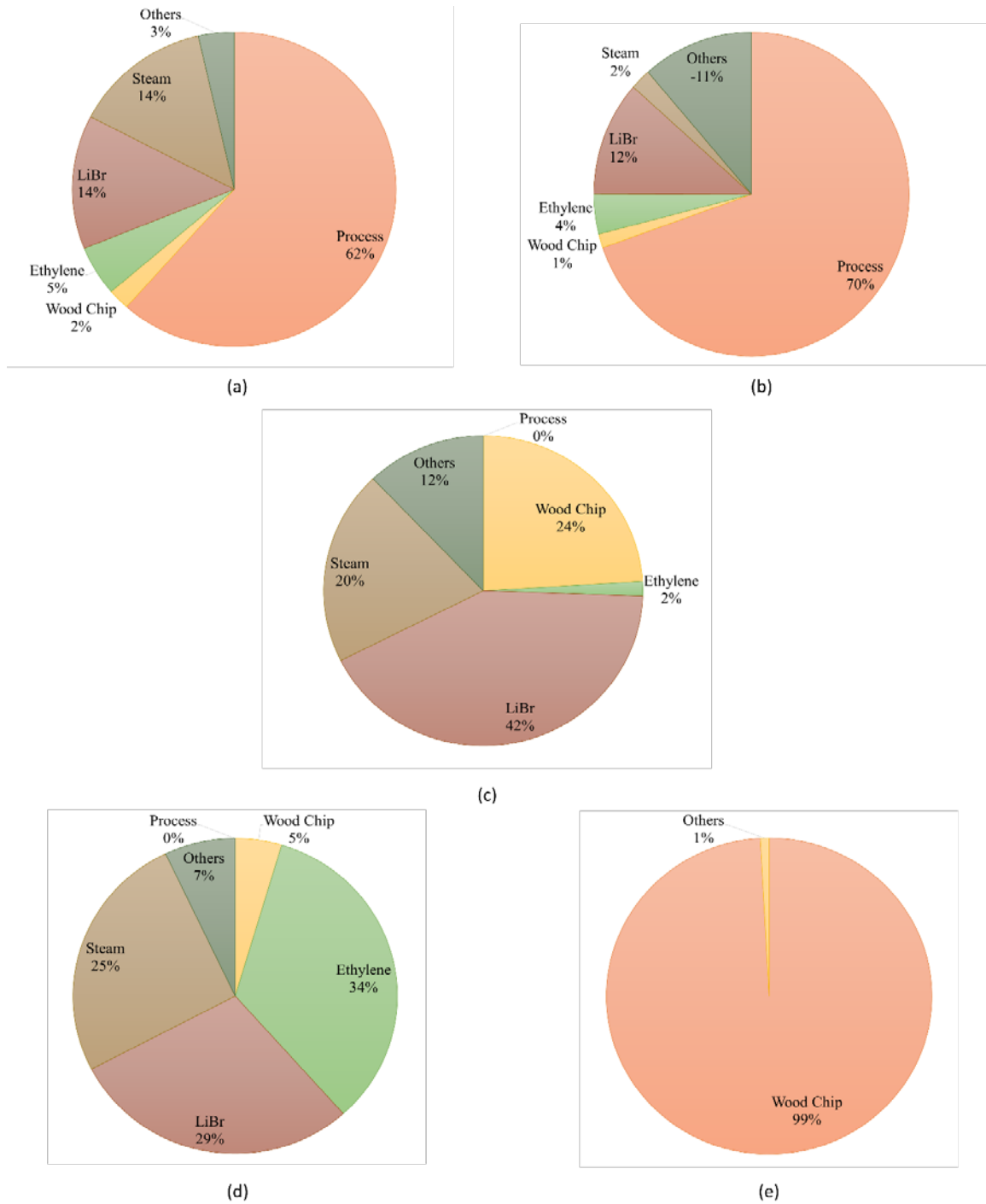


Figure 12: Contribution of raw materials of MSH processes for a) Climate change b) Water depletion c) Ecotoxicity d) Fossil depletion e) Land occupation.

The biomass concentration changes significantly for different biomass feedstock^[25, 45], since the cellulose's composition varies from 12 to 93% while hemicellulose varies from 0 to 66% and lignin from 0 to 54% . We have considered four different biomass feedstocks

namely red oak, grass, rye straw, and newspaper. The single scores of p-Xylene formed by MSH process from different biomass feedstock are shown in Figure 6. Newspaper is considered as waste in this work, hence the environmental load of its production is not included in our calculations. p-Xylene from rye straw and grass are unfavorable due to the environmental impact involved in their cultivation and processing. The p-Xylene from newspaper has better environmental impact when compared to p-Xylene from other biomass feedstock. This is because of the high cellulosic content in the newspaper. However, the loading and processing of heavy weights of newspaper can make the process infeasible. It should be noted that the environmental impacts vary with different biomass feedstock mainly due to their cultivation and processing.

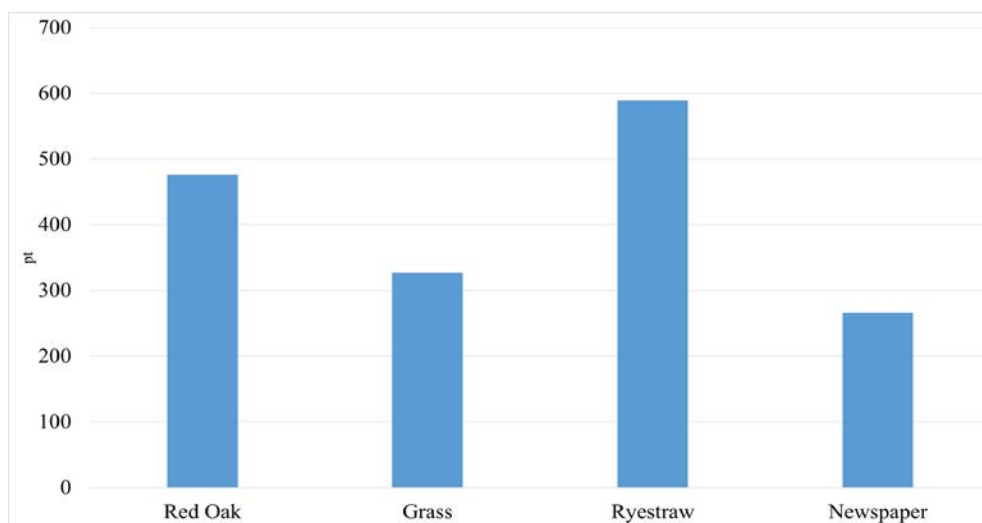


Figure 13: Single indicator scores for different biomass feedstock.

2.4 ZnBr₂ as Molten Salt Hydrate

As stated above LiBr as MSH, was effective to depolymerize and saccharify a variety of untreated lignocellulosic biomass in one-step reaction. While techno-economic analysis suggested favorable process economics of the LiBr-AMSH system in comparison with commercially relevant dilute and concentrated acid processes, high cost of LiBr was still a drawback. In addition, the process derived lignin was highly condensed with very little C-O linkages, having similar characteristics as biorefinery technical lignin. Hence, for the next step in our work, we use ZnBr₂ MSH medium, without any added acid, which is as effective as the LiBr AMSH solution for one-step depolymerization and saccharification of biomass into soluble sugars with high yield at 85 °C. The acidified MSH system, referred hereto as ZnBr₂ AMSH, achieves comparable yield of glucose at a comparable production rate as that of ZnBr₂ MSH without any added acid^[46].

Using our experimental glucose yield from the ZnBr₂ AMSH and ZnBr₂ MSH processes and HMF recovery results from glucose dehydration following our prior work we performed a techno- economic analysis (TEA) for HMF production using Aspen Economic analyzer V8.8, and NRTL thermodynamic package to predict the liquid–liquid and liquid–vapor behavior [47]. The process flowsheets and assumption for the proposed process is the same as above. The analysis suggests that the ZnBr₂ AMSH process produces 103,478, 67,803 and 134,074 metric ton of HMF, furfural and lignin, respectively, per year, whereas these values from the ZnBr₂ MSH process are 95,038, 64,038 and 152,671 metric ton per year. The purity of HMF and furfural from both the processes is 99%. The purity of isolated lignin from the AMSH and MSH processes are 85% and 77%, respectively. For the base case scenario, we assumed electricity production from both processes by burning lignin.

The capital and operating costs of the AMSH process are estimated at \$176 million and \$51.5 million, respectively. These values of the MSH process are \$182 million and \$53 million, respectively and is shown in table 14 and 15.

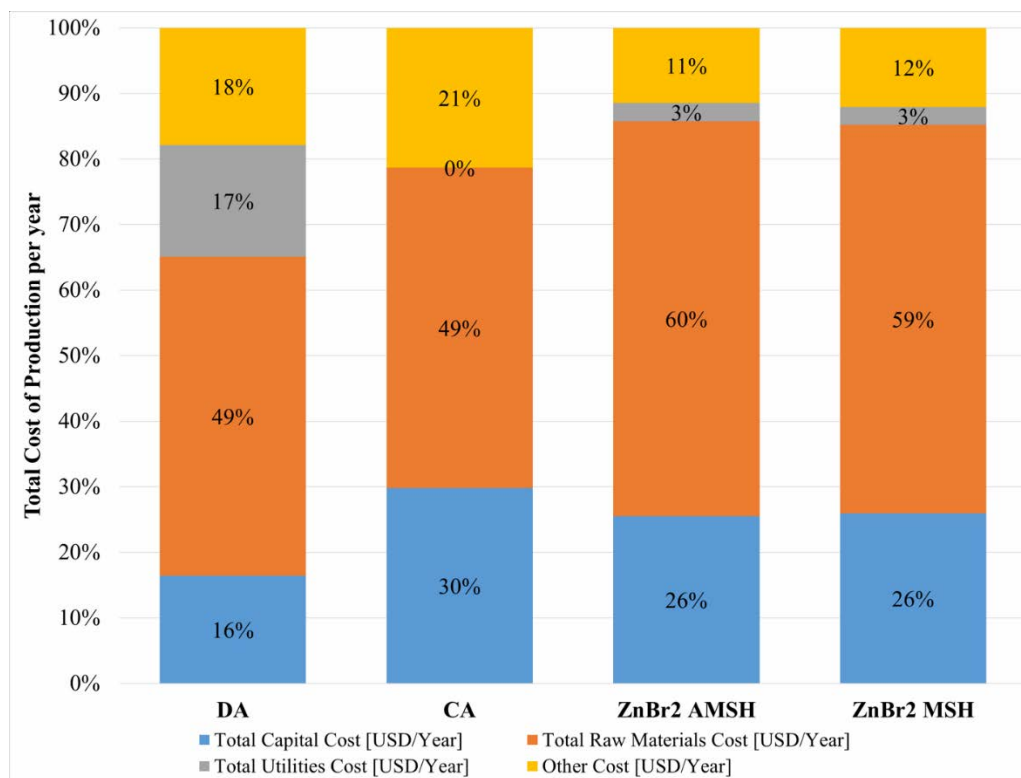
Table 14: Summary of the Capital and Operating Cost of the AMSH Process.

Item	Cost (Million \$)	Item	Cost per year (Million \$)
Purchased Equipment	132	Total Raw Materials Cost	41.6
Other	13	Total Utilities Cost	1.9
General and Administrative Overheads	4	Operating Labor Cost	0.8
Contract Fee	4	Maintenance Cost	1.9
Contingencies	14.5	Operating Charges	0.2
Working Capital	8.4	Plant Overhead	1.3
Total Capital Cost	176	General and Administrative Cost	3.8
		Total Operating Cost	51.5

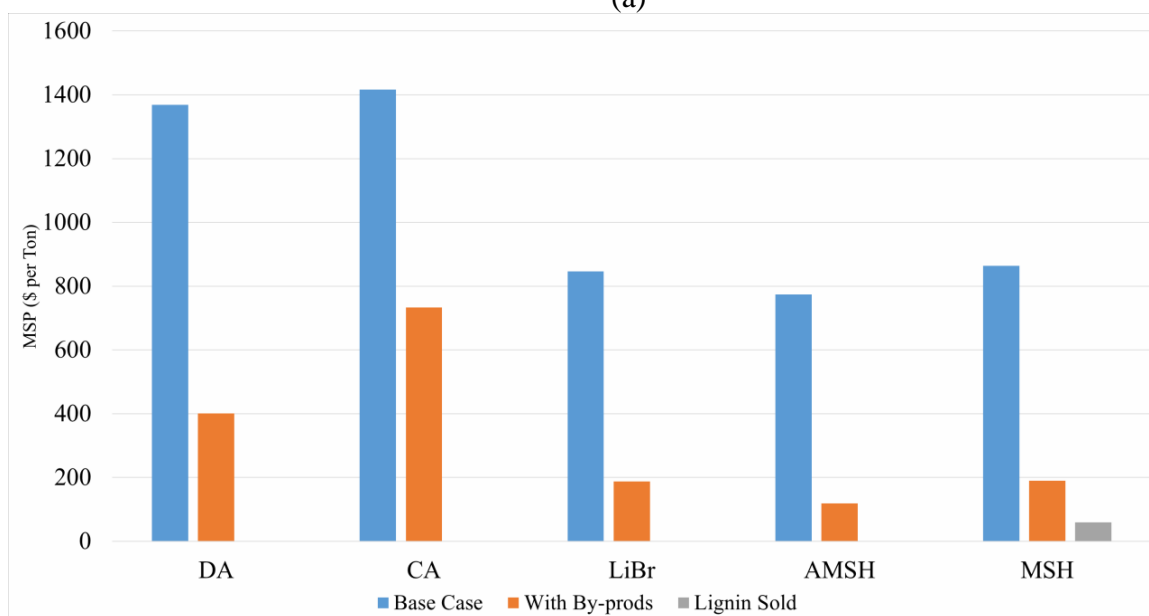
Table 15: Summary of the Capital and Operating Cost of the MSH Process.

Item	Cost (Million \$)	Item	Cost per year (Million \$)
Purchased Equipment	136	Total Raw Materials Cost	41.5
Other	14	Total Utilities Cost	2.5
General and Administrative Overheads	4	Operating Labor Cost	0.8
Contract Fee	4.5	Maintenance Cost	2.2
Contingencies	15	Operating Charges	0.2
Working Capital	8.6	Plant Overhead	1.5
Total Capital Cost	182	General and Administrative Cost	3.9
		Total Operating Cost	53

Higher reaction time of the MSH process contributed to a slightly higher capital cost for it when compared with the AMSH process. The operating cost for both processes is similar. The minimum selling prices of HMF from ZnBr_2 AMSH and ZnBr_2 MSH were compared with the DA and CA processes (shown in figure 14a and 14b) and it shows that when furfural value is considered and lignin is assumed to generate electricity, the minimum price of HMF is \$774 per metric ton for the ZnBr_2 AMSH process, and \$863 per metric ton for the ZnBr_2 MSH process. When the price of furfural is considered as \$1,000 per metric ton, the minimum price of HMF decreased to \$119 per metric ton for the ZnBr_2 AMSH process, and \$190 per metric ton for the ZnBr_2 MSH process. If the price of lignin from the MSH process is considered to be \$100 per metric ton and no electricity is produced, the minimum price of HMF from the ZnBr_2 MSH process further decreased to \$59 per metric ton. The minimum price of HMF from the ZnBr_2 AMSH process is slightly lower than that of the ZnBr_2 MSH for all scenarios, which is due to the longer reaction time of the ZnBr_2 AMSH process in the absence of any external acid. However, these calculations did not consider the higher quality and higher value of lignin produced from the ZnBr_2 AMSH process and the implication of the added acid to the potential corrosion of the processing equipment.



(a)



(b)

Figure 14: Comparison of a) capex and variable costs for HMF production from biomass from dilute acid (DA), concentrated acid (CA), ZnBr₂ AMSH and ZnBr₂ MSH processes and b) minimum price of HMF/metric ton from these four processes.

3 Process Intensification for Furfural-Based Chemical Production Using Techno-Economic and Life Cycle Analysis

3.1 Introduction

Biomass, a renewable carbon source, has the potential to replace traditional fossil fuel, as it is abundant and can significantly reduce CO₂ emissions. In recent years, great attention has been given to it, as it is a promising option for a green and sustainable production of fuels and chemicals^[48]. A bio-refinery, like a petroleum refinery, can benefit from utilizing the various components in biomass to maximize profit. The three large obstacles to profitable biomass bio-refineries are (1) high processing costs, (2) huge capital investment, and (3) a narrow margin between feedstock and product prices^[49]. A lot of work in terms of conceptual design, optimization and other design methodologies have performed to tackle these obstacles and to increase the viability of biorefineries to an industrial scale. Methodologies considering techno-economics is one way of designing a conceptual bio-refinery. Using different types of biomass can lead to feasible designs with favorable economics. Moncada et al. propose a sugarcane-based bio-refinery producing sugar, ethanol and other chemicals^[50]. Amidon et al.^[51], and Liu et al.^[52] propose a wood-based bio-refinery which segregates the components of the biomass focusing on pre-treatment and separation technology which can be utilized to produce high volume fuels and high price chemicals. Lam et al. propose an algae based multi-product bio-refinery but do state that the costs are still high due to lack of processing technologies^[53]. Moncada et al. proposes a design which integrates first, second and third generation biomass to make the economics more favorable^[54]. Alonso et al. proposes a multi-product bio-refinery, which produces intermediate products such as furfural and cellulosic pulp that can be

commercialized^[55]. Cheali et al.^[56] suggests of upgrading the bio-ethanol to more value-added chemicals such as butadiene and di-ethyl ether to improve the economic performance of bio-refinery by using an optimization-based decision supporting tool. Moncada et al.^[54] presents a biorefinery design approach based on the idea of integrating multiple technologies, include different raw materials and follow a strategy based on the concepts of hierarchy, sequencing, and integration. Sammons et al.^[57] provide an interesting framework where multiple alternatives can be analyzed considering experimental and simulation data and mathematical models.

Furfural was the main by-product from the production of p-Xylene using MSH hydrolysis. Furfural was the main by-product from this process. Furfural is a promising platform compound, which can be used to produce high quality fuel and valuable chemicals. Hence, in this study, we focus on production of different chemicals from furfural, especially, butadiene, surfactants, jet-fuels with lubricants and integrated it with the production of p-Xylene.

Butadiene is a key monomer in the production of synthetic rubber^[58]. Roughly 12 million tons of butadiene are produced worldwide from either dehydrogenation of n-butane^[59] or naphtha cracking alongside the production of numerous coproducts which includes ethylene and propylene^[60]. Butadiene production from renewable source such as lignocellulosic biomass remains a major goal for the chemical industry. Different pathways for the production of butadiene from biomass have been proposed mainly through ethanol or four-carbon alcohols^[61]. An alternative thermochemical pathway for butadiene production is proposed where initially a five-carbon sugars such as xylose is converted to furfural^[20], followed by decarbonylation^[62] and hydrogenation to tetrahydrofuran

(THF)^[63]. Selective dehydration and ring opening of (THF) is carried out using phosphorus- containing siliceous zeolites to produce butadiene^[64].

Surfactants are ever-present in both industry and in households and are used as a cleaning product, personal care product and in the manufacturing processes in many industries^[65]. In 1997, two major markets (household and industrial and institutional cleaning products) consumed more than 60% of the 5.14 billion pounds of surfactants produced in the U.S^[66]. All major surfactants are produced from fossil fuels and thus it is necessary to produce surfactants from renewable source whose performance, if not better, is identical to fossil based ones. Production of bio-based surfactants is proposed where the benzene ring in the surfactant is replaced by biomass-derived furan. Combined anhydride formation and furan acylation is carried out of furan with a fatty acid^[67]. Hydrogenation is carried out to form the precursor of the surfactant. Finally, sulphonation/neutralization of precursor is carried out to form the surfactant^[68].

Utilization of lignocellulosic biomass for liquid fuels have received increased attention because of its natural abundance and sustainability^[69, 70]. Substantial research is taking place for the production of high carbon branched and long chain alkanes for jet (C8-15) or diesel (C12-22) ranged fuels in recent years because of the goal set by US Federal Aviation Administration (FAA) for the US aviation industry to consume renewable jet fuel from 2018^[71]. The thermochemical processing of lignocellulose-to-jet fuels via pyrolysis or gasification, followed by the catalytic upgrading of the resulting bio-oils or syngas has previously been reported^[72]. Direct conversion of carbohydrates to fuels has a drawback as low carbon sugar units (C5/C6) in biomass is unsuited for jet fuels. Hence, polysaccharides are first converted to furanic platforms (furfural) via hydrolysis and dehydration. The

intermediates are coupled via aldol-condensation or hydroxyalkylation/alkylation (HAA) reactions to form precursors of the desired carbon chain length^[73]. Subsequent hydrogenation, ring opening (RO), and deoxygenation of the resulting molecules over heterogeneous catalysts can produce alkanes of desired carbon numbers^[74]. Oil-based lubricants are used widely in automobiles, aviation, refrigeration etc. and represent over \$60 billion global chemical enterprise^[75, 76]. Bio-based lubricants are produced using natural oils such as animal fats and vegetable oils which currently have poor economics and high catalyst consumption. A novel strategy is proposed by using 2-alkylfurans and aldehydes obtained from non-food biomass. First, the furan and aldehydes are converted to condensed furans (CF) via HAA. Following, HDO reaction is carried out of the CFs to produce the desired lubricant^[77].

The aim of this work is to evaluate the techno-economic feasibility of producing butadiene, surfactants, jet-fuels and lubricants coupled with production of p-Xylene and estimate the minimum cost of each chemical. Furfural, produced from the p-Xylene process, is used as the starting material for all the four process. Minimum selling price of the chemicals are calculated keeping the price of p-Xylene, calculated from previous work, constant. The rest of the manuscript is structured as follows: Reaction and production pathways are introduced and assumptions required to perform process simulation and economic analysis is discussed. Flowsheets of the production routes are discussed in detail. Finally, simulation and economic results are discussed for the four processes.

3.2 Methodology

A lot of effort has gone into the advancement of bio-based chemical production, however, designing an integrated process combining process path for different chemical production

have rarely been dealt with. In this paper, we use process system engineering tools such as techno- economic and life cycle analysis, to facilitate the development of the bio-refinery and determine the important parameters that can be improved to promote commercialization of the process. First, detailed reaction pathways and conditions are analyzed from the literature. All the raw materials need is identified and thermodynamic properties of these materials are collected either from laboratory experiments or from existing literature. Next, detailed process flowsheet is developed and designed including the selection of various separation steps to achieve the required product specifications. Heat integration is carried out to the process to make it more economically viable and bottlenecks of the process are identified and accordingly changes are made to get a base case design. Finally, techno-economic and life cycle analysis is carried out to identify important parameters which can help in the commercialization of the designed process.

Reaction Path

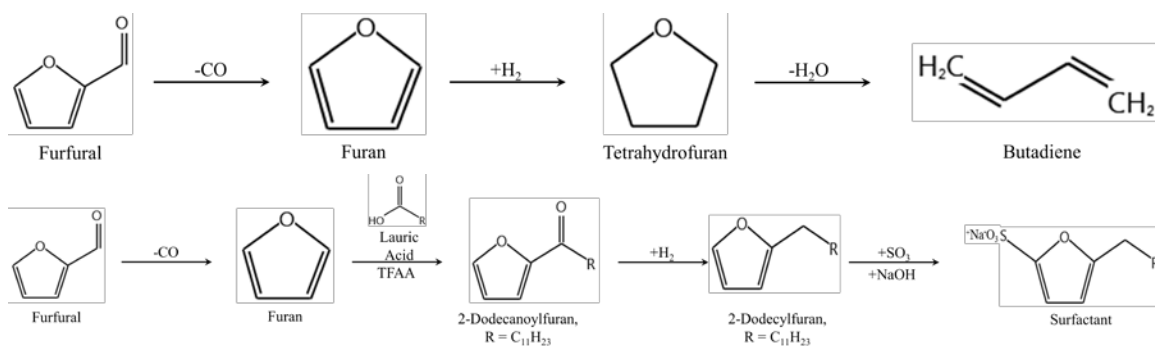
The reaction pathways to produce butadiene, jet-fuels and surfactants are shown below. For the production of butadiene, first furfural from the p-Xylene process is converted to furan by reductive decarbonylation reaction by using low H_2 to furfural ratios^[62]. Subsequently, furan is hydrogenated to tetrahydrofuran with palladium (Pd) catalyst^[63]. Finally, dehydration and ring –opening of THF is carried out to produce butadiene with phosphorus-containing self-pillared pentasil (P-SPP) catalyst^[64].

Surfactant production starts with the production of furan from furfural by the same process discussed above. Combined anhydride formation and furan acylation is carried out with a fatty acid in the presence of trifluoroacetic anhydride (TFAA) and a solvent. %. Fatty acid used can be lauric acid, myristic acid or stearic acid depending on the number of carbon

atoms. Hydrogenation reaction is carried out on copper chromite. The pre-cursor formed after hydrogenation is sulphonated via air/Sulphur trioxide (SO_3) mixture and neutralized with caustic soda to form surfactant^[67].

To produce jet-fuel, furfural is first converted to methylfuran. Methylfuran and furfural are then reacted together to form a C-15 fuel precursor which is transformed to C-15 branched alkane, used as jet-fuel. Methylfuran and furfural are coupled via aldol-condensation or hydroxyalkylation/alkylation (HAA) reaction. Improved graphene oxide (IGO) is used as the catalyst in the literature. It was seen that recovery and costing of IGO is difficult. Hence, Amberlyst-15 catalyst is used in this paper for HAA reaction. Final step includes the hydrodeoxygenation (HDO) of the fuel precursor with supported palladium catalyst and hafnium triflate promoter in the presence of cyclohexane solvent^[74].

Production of lubricants starts with the production of furan from furfural by the same process discussed above. Combined anhydride formation and furan acylation is carried out with a fatty acid in the presence of TFAA and a solvent. For this study, valeric acid is used. Hydrogenation reaction is carried out on copper chromite to produce the desired alkyl furan. HAA reaction is carried out using P-SiO₂ catalyst to produce CF. CF undergoes HDO reaction in the presence of Ir-ReO_x/SiO₂ catalyst to produce condensed furan alkane (lubricant)^[78].



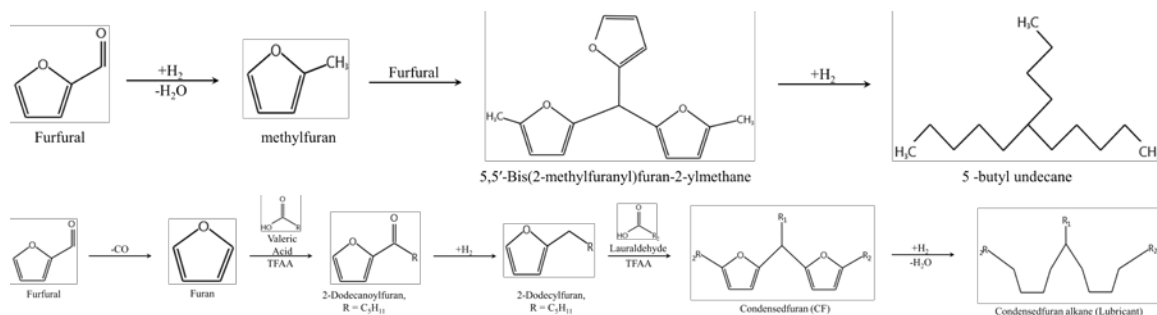


Figure 15: Reaction route for butadiene, jet-fuel, surfactant and lubricant production.

Simulation, Economics and Life cycle analysis

Simulation: The simulation is performed using Aspen Plus V8.8. NRTL thermodynamic package is utilized to predict the liquid–liquid and liquid–vapor behavior. Most of the components involved in the reactions are directly selected from the Aspen database, whereas some not included in the database (i.e., fuel precursor, jet-fuel, surfactants etc.) are defined by their molecular structures. All the missing parameters are estimated by the molecular structures using the Unifac Model and Thermo Data Engine (TDE). TDE is a thermodynamic data correlation, evaluation, and prediction tool developed by the collaboration of Aspen plus and the National Institute of Standard and Technology.

To enable the process simulation, the following assumptions are made:

1. The yield and reaction conditions of all the reactions are shown in table 16-19. Furfural flowrate and purity are taken as same from our previous study of p-Xylene production^[79].
2. The by-products do not affect the conversion and selectivity of any reactions. No separation steps are considered before reaction.
3. The sulphonation process using air/SO₃ mixture is a well-known process and has specialized equipment designed with rigorous control system for it which cannot be designed in Aspen plus. Simplified equipment is used for the sulphonation process and

hence the capital cost for the process is underestimated than the actual cost of the equipment.

4. Continuous regeneration of catalyst is a well-known process and uses specialized equipment which cannot be designed in Aspen plus and therefore, continuous regeneration of catalyst is not included in the calculation. Hence, the capital cost for the process is underestimated than the actual cost of the equipment.

Table 16: The Specification of reactions for production of Butadiene.

Process	Decarbonylation	Hydrogenation	Dehydra-Decyclization
Catalyst	Pd/Aluminate	Pd/C	PSPP
T (°C)	250	100	400
P (bar)	5	55	1
Yield	91	100	73

Table 17: The Specification of reactions for production of Surfactants.

Process	Decarbonylation	Acylation	Hydrogenation	Sulphonation
Catalyst	Pd/Aluminate	-	Copper Chromite	-
T (°C)	250	30	220	30
P (bar)	5	1	7	1
Yield	91	95	92	99

Table 18: The Specification of reactions for production of Lubricants.

Process	Decarbonylation	Acylation	HAA	HDO
Catalyst	Pd/Aluminate	-		Ir-ReO _x /SiO ₂
T (°C)	250	30	65	170
P (bar)	5	1	1	50
Yield	91	95	85	86

Table 19: The Specification of reactions for production of Jet-Fuel.

Process	HDO	HAA	HDO
Catalyst	Ni-Cu/C	Amberlyst-15	Pd/C
T (°C)	220	60	200
P (bar)	7	1	50
Yield	99	95	96

Economics: Aspen Economic analyzer V8.8 is used to perform an economic assessment for the bio-refinery. Discounted cash flow analysis is used to perform the economic

analysis for the different processes. The production cost of the chemicals is used to determine the minimum selling price, which is defined as the selling price of the product when the net present value (NPV) is zero^[7]. As furfural is a by-product from the p-Xylene process, we need to consider selling of p-Xylene to calculate the minimum selling price of each chemical produced. The selling price of p- Xylene is taken as \$1,477 per ton, which is calculated in our previous study^[79]. Some additional assumptions are necessary to perform the economic analysis as outlined below.

1. All the equipment and operating costs estimated by Aspen Economic Analyzer V8.8 are based on the price of the first quarter in 2014.
2. Furfural flowrate is taken as the same, calculated from our previous study, which had a plant capacity of 50 metric tons per hour of biomass feedstock. The market price of furfural is taken as \$1,000/metric ton^[35].
3. The plant operates in a continuous mode for 8000 h per year. The economic life of the project is assumed to be 20 years and the recovery period is assumed as 10 years. The internal rate of return (ROR) on investment is assumed as 15%. 35% corporate tax is applied to the profits. The simplest depreciation method -- the straight-line method is applied as the salvage value is 10% of the original capital cost after 20 years.
4. The market price of heptane and cyclohexane are estimated as \$1,500/metric ton and \$1,400/metric ton^[36].
5. The cost of trifluoroacetic anhydride is \$1,000/metric ton and of lauric acid is \$3,300/metric ton based on the prices reported at www.alibaba.com^[35]- a worldwide e-commerce market site originally from China. The price of chemicals may vary with many factors, such as season, location, producer, policy, etc. The cost of lauraldehyde

- is assumed as \$2,500/metric ton.
6. The catalyst cost for butadiene production is estimated as precious metal cost plus \$11000/ton of supported catalyst and catalyst manufacturing^[31]. Unit price of palladium (Pd) is \$23262/kg^[80]. Pd/Li-aluminate catalyst that is used in the conversion of furfural to furan consists of 0.5 wt.% of Pd leading to a price of \$127,255/metric ton whereas for hydrogenation the catalyst contains 5 wt.% Pd leading to a price of \$1,173,550/metric ton. The catalyst life is taken to be 6 months. It is assumed that the catalyst manufacturer will be able to recover 99% of the metals in the spent catalyst. Therefore, after every 6 months only the cost of the catalyst support, makeup metals and manufacturing cost would be required. The zeolite life is taken as 6 months and no recovery of the zeolite is possible. The cost of PSPP zeolite is \$5000/metric ton.
 7. Catalyst cost for jet-fuel production is estimated similar to butadiene production. Unit price of Ni-Cu is taken as \$6.73/kg^[35]. Ni-Cu catalyst used for hydro-deoxygenation reaction of furfural consists of 10 wt.% of Ni-Cu leading to a price of \$10,573/metric ton. Production of fuel precursor uses Amberlyst -15 which is priced at \$153/kg^[81]. For the hydro- deoxygenation of the pre-cursor to jet fuel, 10wt % Pd catalyst with hafnium triflate promoter is used. The unit cost of Pd is taken as above and hence the cost is \$2,336,100/metric ton. The price of hafnium triflate is taken as \$16.4/gram^[82]. Catalyst life and make-up assumption is taken as above.
 8. The cost of copper chromite catalyst is \$110,000/metric ton^[35].

9. Catalyst for lubricants is calculated similarly. Ir-ReO_x/SiO₂ catalyst cost is estimated as precious metal cost plus cost of supported catalyst and catalyst manufacturing. Unit price of Ir and Re are \$45,819/kg and \$2,844/kg^[80]. Ir-ReO_x/SiO₂ catalyst of 4 wt.% of Ir and molar ratio of Ir:Re is 2, leading to a price of \$2,062,856/metric ton. The catalyst life is taken to be 12 months. Cost of P-SiO₂ catalyst is \$5,000/metric ton^[35].
10. Other costs includes: Cost of Sulphur is \$110/metric ton, cost of caustic soda is \$498/metric ton^[35]. Cost of hydrogen is \$653/metric ton^[31].
11. Utilities and wastewater treatment plants are not modeled explicitly, rather it is assumed instead that utilities are purchased and wastewater is treated by a third party at a fixed price per unit volume^[31].

Life Cycle Analysis: Life cycle analysis (LCA) is used to assess and improve the impact of the bio- refinery to the environment and make the process more sustainable. SimaPro®^[38, 39] is used to evaluate the bio-refinery using sustainable criteria. Cradle-to-gate system boundary is chosen and is shown in figure 16. Solid lines are the component streams which are consumed in the process while the dashed lines represent the streams which are recycled. Furfural, from the p-Xylene production is the starting material for all the three process. In this work, a functional unit of one metric ton of product is considered for LCA. Furthermore, some assumptions are made to perform LCA including:

1. The materials used in the manufacturing of p-Xylene are only considered. The materials used in the construction, other infrastructure, cooling water and catalysts are supposed to be recycled at the end of the process' life cycle and are not considered.
2. The feedstock for production is produced in the same bio-refinery facility.

3. For surfactants production, we assume recycled and used lauric acid as the main raw material, which reduces the overall environmental impact.
4. Lauric acids, valeric acids and lauraldehyde are not available in the inventory for life cycle analysis. A generic fatty acid is assumed from vegetable oil is assumed.
5. Electricity is supplied by medium voltage grid based on the average technology and total loss in US.
6. Heating is supplied by steam, among which 76% is generated by natural gas and the rest is generated by heavy oil fuel.
7. Cooling is supplied by water, cooling, unspecified natural origin based on the assumption that 99.5% of the total is recycled and waste heat is emitted into atmosphere.

Process Flowsheet

The process flow diagrams for all the four processes are shown in Figures 17 to 20.

Butadiene Production: Butadiene production starts from furfural as the main raw material obtained from p-Xylene process. Furfural and pressurized hydrogen at 5 bar (stream 1) is fed to reactor(B- R1) containing catalyst at 250 °C. Decarbonylation takes place of furfural to produce furan and syngas (stream 2), and is introduced into a flash drum (B-V1) at -30 °C. Syngas is separated which is used for the electricity generation. The liquid stream (stream 3) is fed to another flash drum(B- V2) and then introduced to column (B-C1) to purify furan from water and other by-products (furfuryl alcohol and methylfuran). Furan is then pressurized to 55 bar and is hydrogenated to form tetrahydrofuran (THF) (stream 8) in reactor (B-R2) at 100 °C with the help of Pd/C catalyst. Product stream is then introduced to another flash drum (B-V3) to separate the gas from liquid phase. THF is then heated in

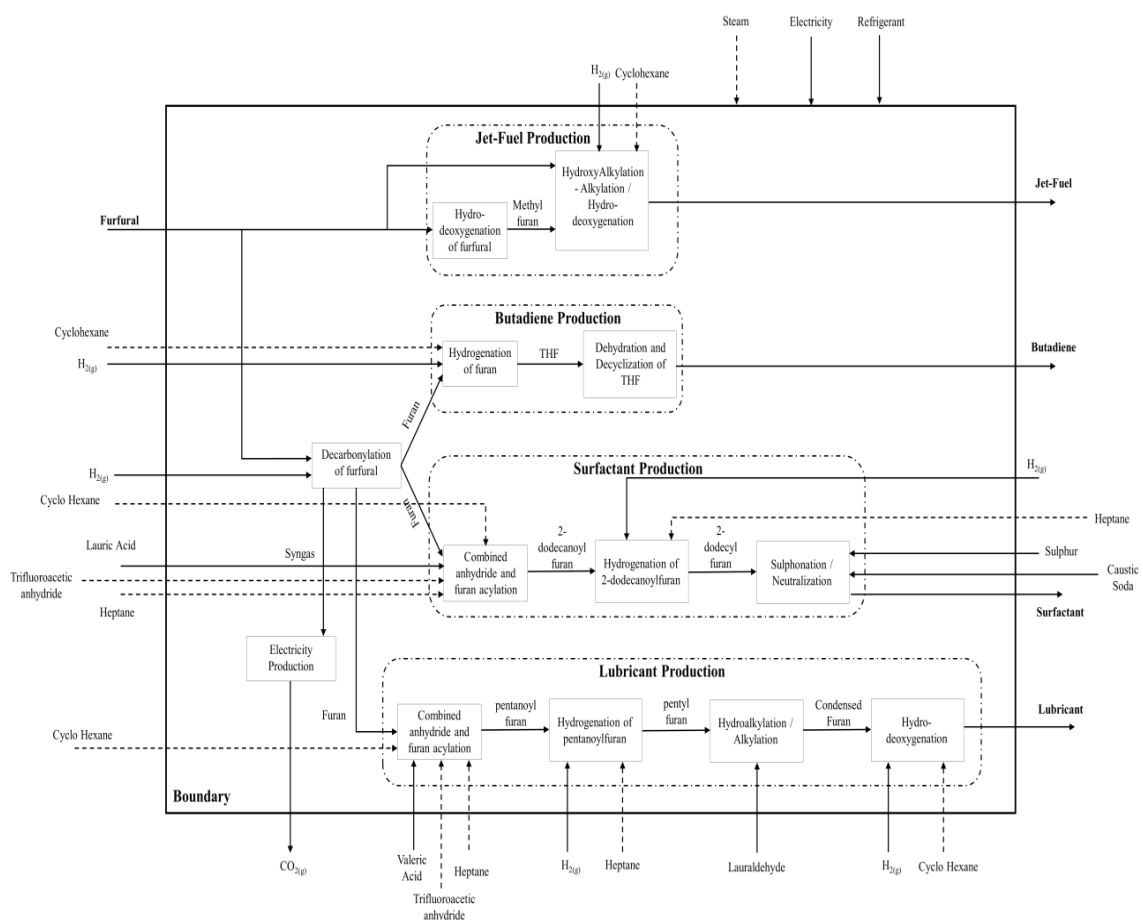


Figure 16: Scope definition of bio-based chemical production.

a heater (B-H1) to 400 °C and fed to reactor (B-R3) where decyclization and dehydration reaction takes place at atmospheric pressure. Water is separated in flash drum (B-V4). The gaseous phase (stream 11) as well as liquid phase (stream 12) is then pressurized, mixed with each other in a flash drum (B-V5) and send to a distillation column (B-C2) where butadiene is separated from the unreacted components (stream 16) which is recycled back to increase the overall yield of the reaction. The purity of butadiene is ~99%.

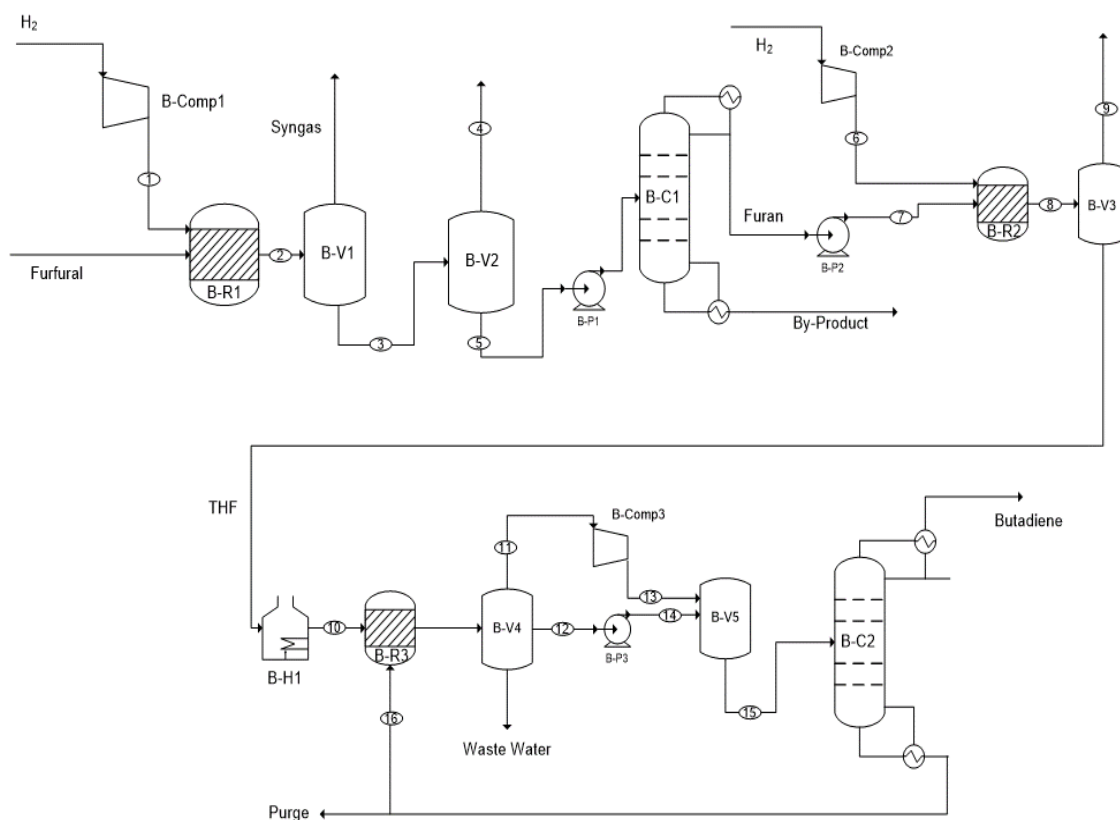


Figure 17: Process Diagram for Butadiene Production.

Surfactants Production: Furan needed for the combined acylation process is produced by decarbonylation process, which is described above. Furan is acylated with lauric acid with the help of trifluoroacetic anhydride (TFAA) in heptane in reactor (S-R2). In the literature, hexane is used as the solvent for the reaction. Hexane in large quantity is difficult to handle as it is too volatile and thus heptane is used as the solvent as the boiling point is higher than hexane and thus easier to handle. Product stream (stream 5) containing 2-dodecanoylfuran, TFAA and heptane is fed to a flash drum (S-V3) to remove the volatile component (TFAA, heptane and water) (stream 7). The volatile component is then introduced in a decanter (S-V5) as heptane is insoluble in water. Most of the TFAA is present in the heptane stream (Recycle) which is recycled. Some of the TFAA is still dissolved in the water stream, which must be separated to decrease the cost of raw materials. Cyclo-hexane is used to separate

TFAA from the water stream. Another decanter (S-V7) is used to separate cyclo-hexane and water. Cyclo-hexane/TFAA mixture is separated in a distillation column (S-C2) and recycled. 2-dodecanoylfuran from S-V3 is hydrogenated in the presence of heptane and copper chromite catalyst at 220 °C and 7 bar to form 2-dodecylfuran. Product stream (stream 15) is fed to a series of flash drum (S-V9, S-V10) and a distillation column (S-C3) to purify 2-dodecylfuran. Heptane and water are separated via a decanter (S-V11) and the heptane is recycled. 2-dodecylfuran is sulphonated with the help of air/SO₃ mixture. Combustion of Sulphur is carried out with the help of dry air to generate Sulphur dioxide (SO₂) in a reactor (S-R4). SO₂ is delivered to reactor (S-R5) containing vanadium pentoxide to convert it to Sulphur trioxide (SO₃). The yield of the above process is 99.5%. SO₃ is injected into a reactor (S-R6) simultaneously with 2-dodecylfuran to form sulphonic acid. The acid formed is neutralized with the help of 50 wt.% caustic soda in reactor (S-R7) and the resultant product is the surfactant desired with a purity of ~94%.

Jet-Fuel Production: Furfural from the p-Xylene process is first split in 7:3 ratio. The higher ratio stream is used to produce methylfuran. Furfural is hydro-deoxygenated with the help of hydrogen and Cu-Ni/C catalysts at 220 °C and 7 bar in a reactor (J-R1). The product stream (stream 1) containing mainly methylfuran, is fed to a flash drum (J-V1) to separate the unreacted gas and water formed during the reaction. HAA reaction of methylfuran with remaining furfural is carried out in reactor (J-R2) at 60 °C with the help of Amberlyst 15 catalyst. The fuel intermediate formed is flashed in a vessel (J-V2). The vapor stream is distilled (J-C1) to remove wastewater and the liquid stream is purified. The fuel intermediate is hydro-deoxygenated in the presence of cyclohexane at 200 °C and 50 bar pressure with the help of Pd/C catalyst and hafnium triflate promoter. The branched

alkane formed (stream 4) is fed to a series of flash drum (J-V3, J-V4) and vacuum distillation columns (J-C3, J-C4) to get the desired jet fuel at 99% purity. The gaseous

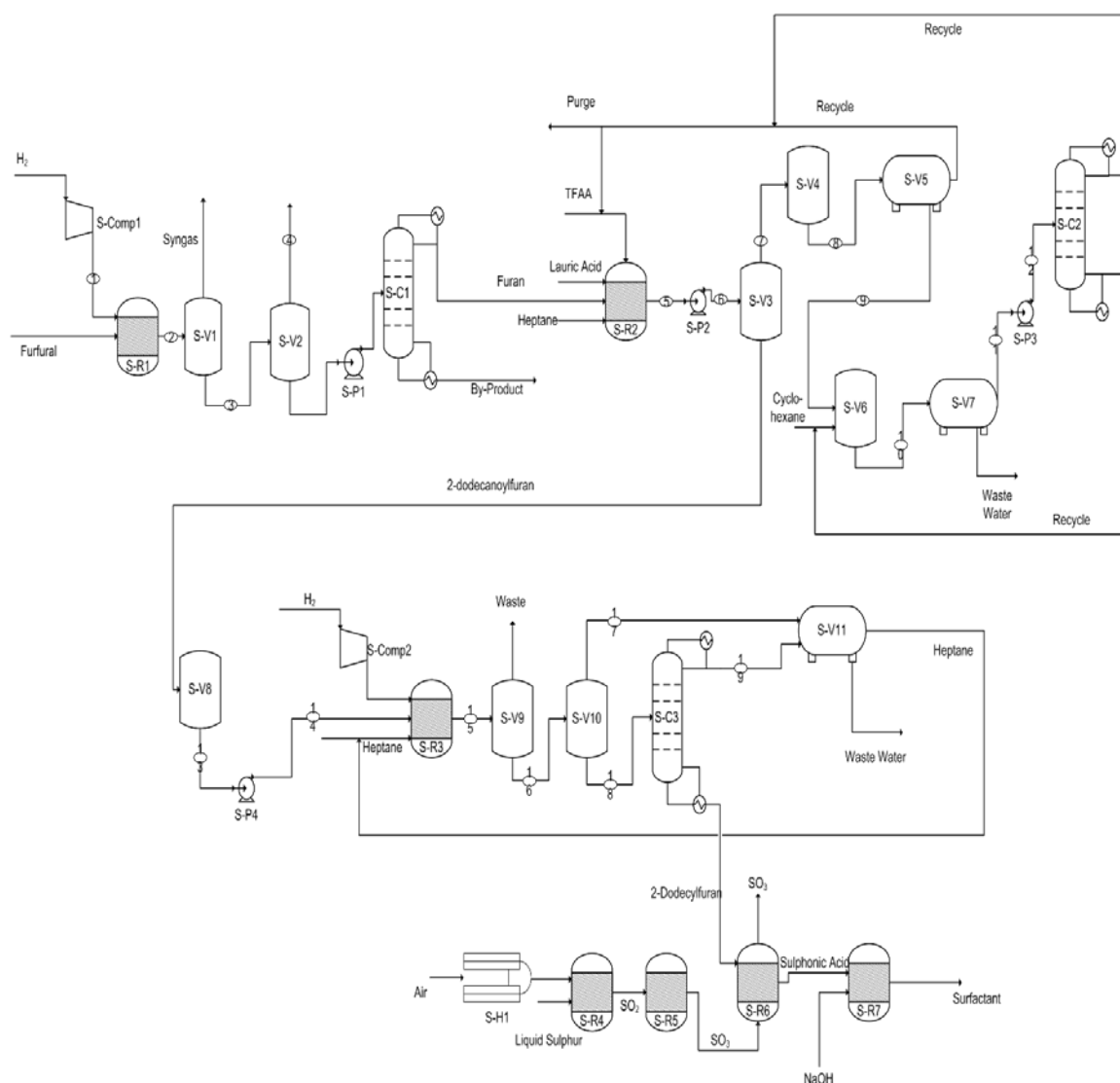
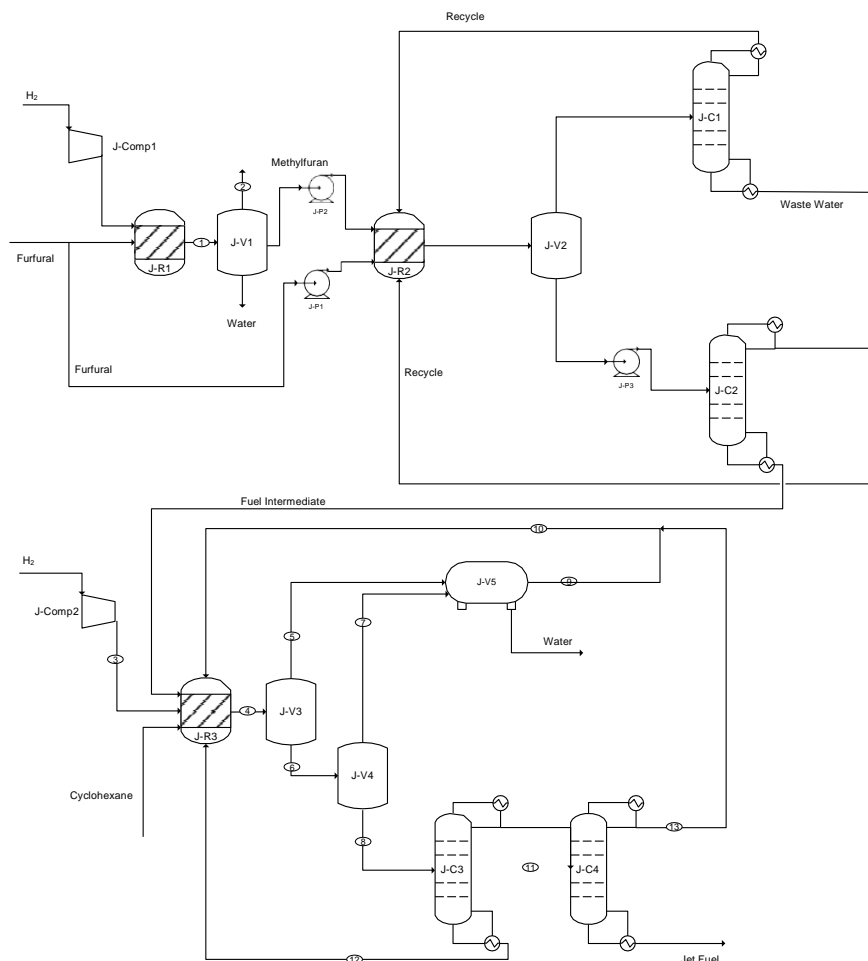


Figure 18: Process Diagram for Surfactant Production.

phase (stream 5, 7) from the flash drum contains a small amount of water. Water and heptane are separated with the help of a decanter (J-V5) and the heptane is recycled.

Lubricant Production: Furan needed for the combined acylation process is produced by decarbonylation process, which is described above. Furan is acylated with valeric acid with the help of trifluoroacetic anhydride (TFAA) in heptane in reactor (L-R2) at atmospheric temperature and pressure. Water is produced as a by-product. Product stream (stream 5)



separate intermediate and the unreacted valeric acid. TFAA-Heptane-water mixture is then introduced in a decanter (L- V4) as heptane is insoluble in water. Most of the TFAA is present in the heptane stream (stream 8) which is recycled. Some of the TFAA is still dissolved in the water stream, which must be separated to decrease the cost of raw materials. Cyclo-hexane is used to separate TFAA from the water stream. Another decanter (L-V6) is used to separate cyclo-hexane and water. Cyclo- hexane/TFAA mixture is separated in column (L-C3) and recycled. The intermediate formed is hydrogenated to form 2-pentylfuran. Product stream (stream 15) is fed to a series of flash drum (L-V7, L-V8), a

decanter to separate heptane and water and a distillation column (L-C4) to purify 2-pentylfuran. The purified heptane is recycled. HAA of 2-pentylfuran and lauraldehyde is carried out at 60 °C in the presence of P-SiO₂ in reactor (L-R4). CF produced is hydrogenated in reactor (L-R5) in the presence Ir-ReOx/SiO₂ catalyst and cyclohexane. The product produced is flashed in a series of flash drum (L-V11, L-V12, and L-V13) to separate cyclohexane and water formed. Cyclohexane and water are immiscible and hence a decanter (L-V14) is used for separating them and the purified cyclohexane is then recycled. Lubricant produced is then purified in a vacuum distillation column (L-C5) with a purity of 90%.

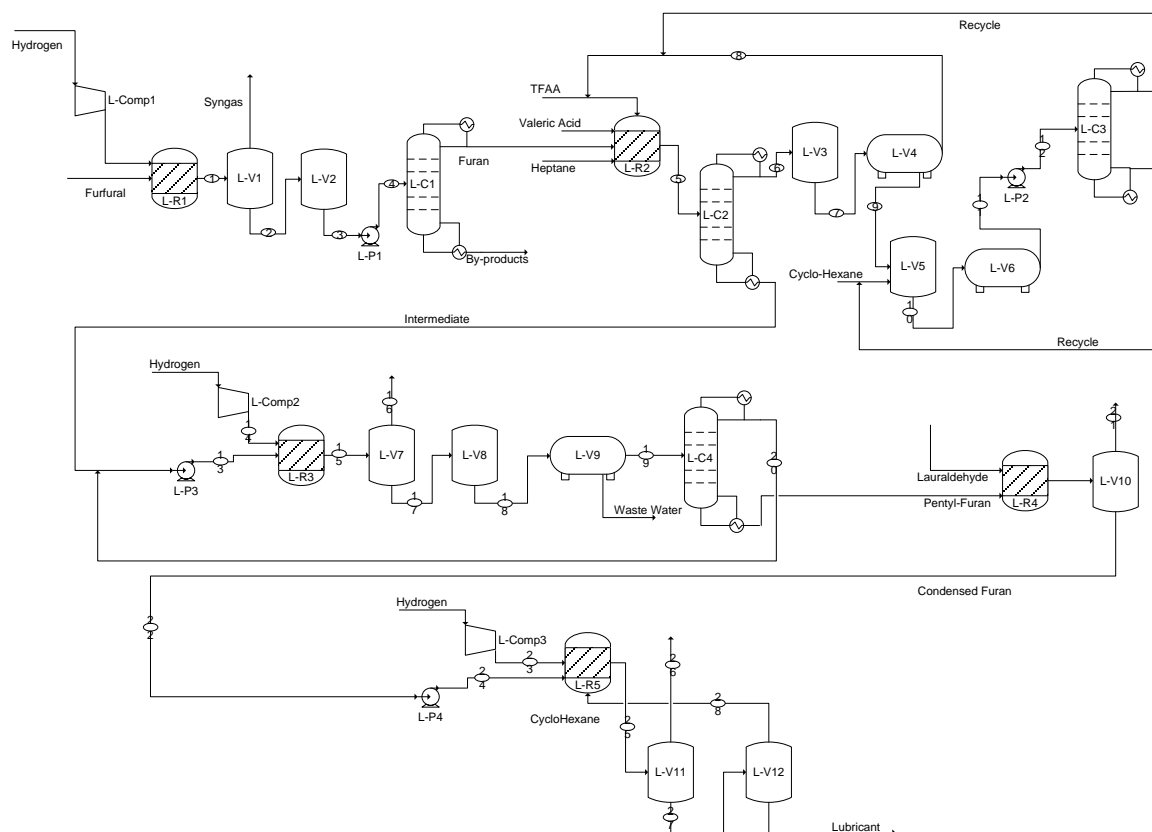


Figure 20: Process Diagram for Lubricant Production.

3.3 Results and Discussion

Simulation: The capacity of the four process is based on the flow rate of furfural, which is 65,380 metric ton per year. Total products produced are calculated for individual process as well as for combined process. Individually, 27,205 metric ton of butadiene, 175,875 metric ton of surfactants, 14,001,034 gallons of jet fuels and 98,945 metric ton of lubricants are produced per year. For the combined process – where all products are produced simultaneously with p-Xylene, 6,495 metric ton of butadiene, 43,969 metric ton of surfactants, 3,637,928 gallons of jet fuels and 23,485 metric ton of lubricants are produced. Syngas, which is produced during decarbonylation of furan is the only by-product produced. 37,083,489 kWh/yr. is produced for butadiene, surfactant and lubricant process. No electricity is produced for jet-fuel process.

Economics: The detailed capital and operating cost of all the individual processes are listed in table 20-23. The capital cost to produce butadiene is estimated at \$86.76 million and the operating cost is estimated as \$8.6 million. The capital cost for surfactant production is estimated at \$148.4 million and the operating cost is estimated as \$404.2 million. For Jet-Fuels, the capital cost is estimated at \$78.8 million and the operating cost is estimated as \$21.8 million. Capital and operating cost for producing lubricants are \$162.6 million and \$361 million respectively. When combined with p-Xylene process, the capital cost for butadiene, surfactant, jet-fuel and lubricants is \$287.45 million, \$349.1 million, \$279.5 million and \$363.3 million respectively, whereas the operating cost is \$105.5 million, \$501.1million, \$118.7 million and \$458 respectively. For the combined process the capital cost is estimated at \$456.6 million and the operating cost is estimated as \$302 million.

Table 20: Summary of the Capital and Operating Cost of the Butadiene Process.

Item	Cost (Million \$)	Item	Cost per year (Million \$)
Purchased Equipment	55.1	Total Catalyst Cost	1.3
Other	16.3	Total Raw Materials Cost	3.2
General and Administrative Overheads	2.0	Total Utilities Cost	1.25
Contract Fee	2.1	Operating Labor Cost	1.1
Contingencies	7.1	Maintenance Cost	0.3
Working Capital	4.1	Operating Charges	0.28
Total Capital Cost	86.76	Plant Overhead	0.7
		General and Administrative Cost	0.5
		Total Operating Cost	8.6

Table 21: Summary of the Capital and Operating Cost of the Surfactants Process.

Item	Cost (Million \$)	Item	Cost per year (Million \$)
Purchased Equipment	67.03	Total Catalyst Cost	0.69
Other	55.03	Total Raw Materials Cost	386.55
General and Administrative Overheads	3.42	Total Utilities Cost	3.01
Contract Fee	3.66	Operating Labor Cost	1.56
Contingencies	12.20	Maintenance Cost	2.96
Working Capital	7.06	Operating Charges	0.39
Total Capital Cost	148.4	Plant Overhead	2.29
		General and Administrative Cost	6.75
		Total Operating Cost	404.2

Table 22: Summary of the Capital and Operating Cost of the Jet-fuel Process.

Item	Cost (Million \$)	Item	Cost per year (Million \$)
Purchased Equipment	50.2	Total Catalyst Cost	1.3
Other	14.6	Total Raw Materials Cost	6.75
General and Administrative Overheads	1.8	Total Utilities Cost	5
Contract Fee	1.9	Operating Labor Cost	1.24
Contingencies	6.5	Maintenance Cost	3.4
Working Capital	3.75	Operating Charges	0.3
Total Capital Cost	78.8	Plant Overhead	2.3
		General and Administrative Cost	1.4
		Total Operating Cost	21.8

Table 23: Summary of the Capital and Operating Cost of Lubricants Process.

Item	Cost (Million \$)	Item	Cost per year (Million \$)
Purchased Equipment	103.6	Total Catalyst Cost	3.23
Other	30.1	Total Raw Materials Cost	313.75
General and Administrative Overheads	3.74	Total Utilities Cost	6.41
Contract Fee	4.01	Operating Labor Cost	1.24
Contingencies	13.37	Maintenance Cost	6.38
Working Capital	7.74	Operating Charges	0.31
Total Capital Cost	162.6	Plant Overhead	3.81
		General and Administrative Cost	25.95
		Total Operating Cost	361.08

Capital cost for lubricants production is the highest and comparable with surfactant production when compared to other processes. Use of enormous quantity of solvent for the acylation and hydrogenation process dictates the use of bigger size equipment, which increases the capital cost. Although the capital cost for lubricant production is higher, the cost of surfactants may be higher as use of specialized equipment for the sulphonation process are not modelled and simulated. Use of high costing raw materials such as valeric acid, lauraldehyde and lauric acid increases the operating cost, which dictates highest operating costs for lubricant and surfactant production. The main contributor for the operating cost for all the four processes combined with p-Xylene process is the cost of raw materials at 69%, 90%, 65% and 83% for butadiene, surfactants, jet-fuels and lubricants respectively. Fraction of raw material can be further decomposed: 34% from ethylene and 28% from biomass for butadiene process, 75% from lauric acid and 6% from ethylene for surfactant process, 33% from ethylene and 27% from biomass for jet-fuel process and 44% valeric acid and 30% lauraldehyde for lubricant production process. The total utility cost contributes 4%, 1%, 6% and 1% of the overall cost for butadiene, surfactants, jet-fuels and

lubricant production. The detailed fractions are given in Figure 21 and 22. Detailed equipment details is given in table 24-27 .

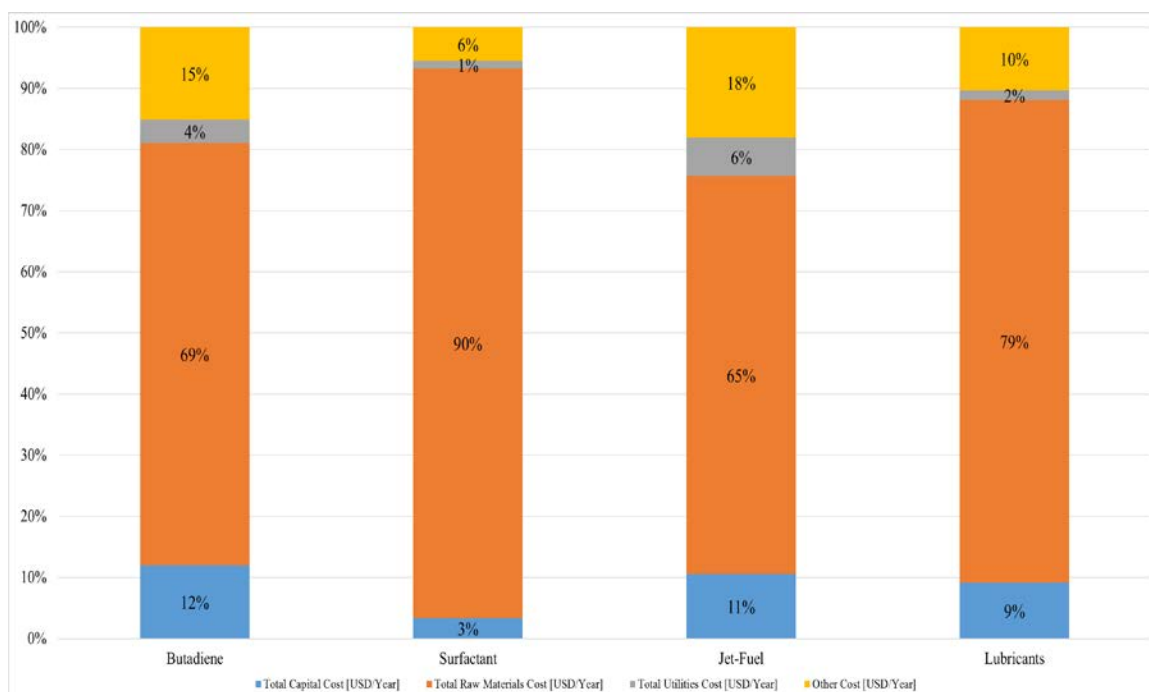
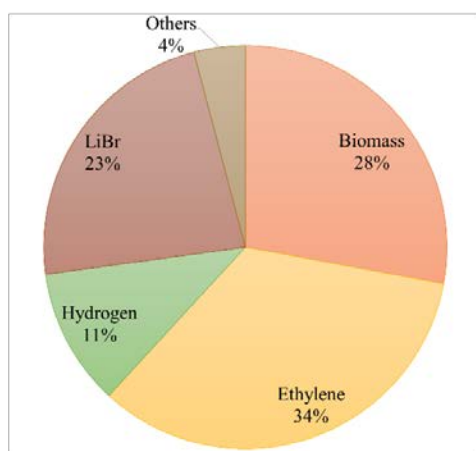
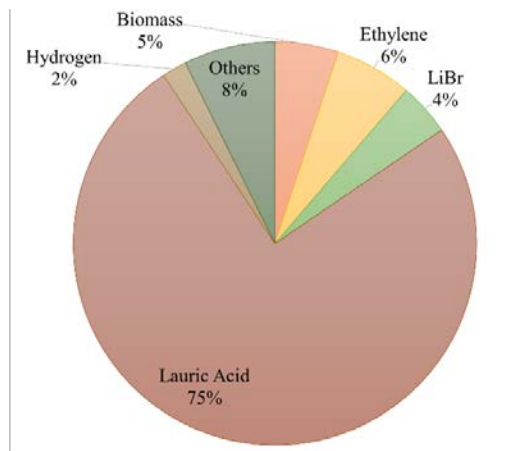


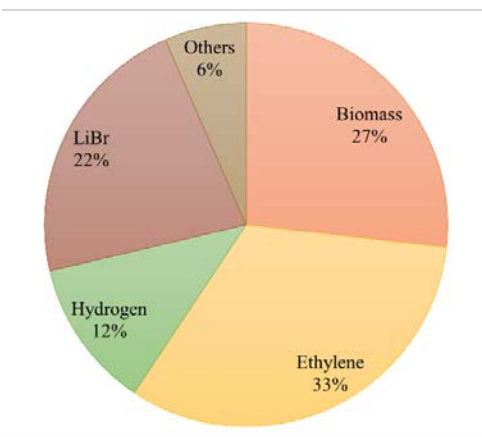
Figure 21: Overview of cost on selling price of chemicals.



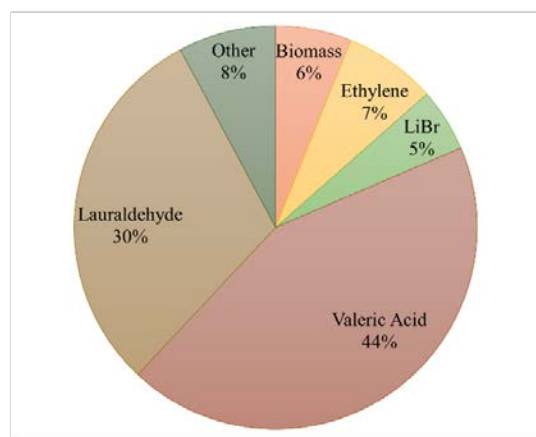
(a)



(b)



(c)



(d)

Figure 22: Contributions of raw materials on selling price of chemicals a) Butadiene process b) Surfactant process c) Jet-fuel process and (d) lubricants process.

Table 24: Equipment Details for Butadiene process.

Component Name	Component Type	ASPEN Model	Total Direct Cost (million \$)	Equipment Cost (million \$)
Furan Production Section				
B-C1 – cond acc	DHT Horiz Drum	N/A	75,600	11,800

B-C1 – reflux pump	DCP Centrif	N/A	25,900	4,400
B-C1 – tower	DTW Tower	RadFrac Stages – 40 Reflux Ratio – 0.04 Pressure – 2 bar	496,200	272,900
B-P1	DCP Centrif	Pump Pressure – 2 bar	32,200	4,500
B-R1	DAT Reactor	RStoic Temperature – 250 °C Pressure – 1 bar	39,561,000	36,200,000
B-V1	DVT Cylinder	Flash2 Temperature – -30 °C Pressure – 1 bar	150,700	17,300
B-V2	DVT Cylinder	Flash2 Temperature – 30 °C Pressure – 1 bar	108,700	17,300
THF Production Section				
B-Comp1	DGC Centrif	Compr Pressure – 55 bar	1,960,500	1,823,300
B-P2	DCP Centrif	Pump Pressure – 55 bar	91,800	57,800
B-R2	DAT Reactor	RStoic Temperature – 100 °C Pressure – 55 bar	217,900	74,800
B-V	DVT Cylinder	Flash2 Temperature – 27 °C Pressure – 1 bar	96,100	16,900

B-V3	DVT Cylinder	Flash2 Temperature – 30 °C Pressure – 1 bar	110,600	28,500
Butadiene Production Section				
B-R3	DAT Reactor	RStoic Temperature – 400 °C Pressure – 1 bar	1,372,500	1,034,500
B-C2 – cond acc	DHT Horiz Drum	N/A	77,500	11,800
B-C2 – reflux pump	DCP Centrif	N/A	27,500	4,400
B-C2 – tower	DTW Tower	RadFrac Stages – 35 Reflux Ratio – 0.167 Pressure – 3 bar	422,600	220,100
B-Comp2	DGC Centrif	Compr Pressure – 3 bar	713,000	585,900
B-P3	DCP Centrif	Pump Pressure – 3 bar	29,300	4,500
Heat Exchangers				
H1	DHE Tema Exch	N/A	16,643	
H2	DHE Tema Exch	N/A	15,484	
H3	DHE Tema Exch	N/A	26,322	
H4	DHE Tema Exch	N/A	20,590	
H5	DHE Tema Exch	N/A	10,976	
H6	DHE Tema Exch	N/A	21,930	
H7	DHE Tema Exch	N/A	76,747	
H8	DHE Tema Exch	N/A	11,575	

H9	DHE Tema Exch	N/A	38,620
H10	DHE Tema Exch	N/A	11,508
H11	DHE Tema Exch	N/A	14,430
H12	DHE Tema Exch	N/A	10,013
H13	DHE Tema Exch	N/A	25,139
H14	DHE Tema Exch	N/A	65,457
H15	DHE Tema Exch	N/A	31,823
H16	DHE Tema Exch	N/A	34,482
H17	DHE Tema Exch	N/A	12,642
H18	DHE Tema Exch	N/A	42,958
H19	DHE Tema Exch	N/A	10,418
H20	DHE Tema Exch	N/A	32,240
H21	DHE Tema Exch	N/A	12,785
H22	DHE Tema Exch	N/A	40,902
H23	DHE Tema Exch	N/A	17,385
H24	DHE Tema Exch	N/A	12,762
H25	DHE Tema Exch	N/A	38,377
H26	DHE Tema Exch	N/A	10,394
H27	DHE Tema Exch	N/A	19,130
H28	DHE Tema Exch	N/A	33,929

Table 25: Equipment Details for Surfactants process.

Component Name	Component Type	ASPEN Model	Total Direct Cost (million \$)	Equipment Cost (million \$)
Furan Production Section				
S-C1 – cond acc	DHT Horiz Drum	N/A	75,600	11,800
S-C1 – reflux pump	DCP Centrif	N/A	25,900	4,400
S-C1 – tower	DTW Tower	RadFrac Stages – 40 Reflux Ratio – 0.04 Pressure – 2 bar	496,200	272,900
S-P1	DCP Centrif	Pump Pressure – 2 bar	32,200	4,500
S-R1	DAT Reactor	RStoic Temperature – 250 °C Pressure – 1 bar	39,561,000	36,200,000
S-V1	DVT Cylinder	Flash2 Temperature – -30 °C Pressure – 1 bar	150,700	17,300
S-V2	DVT Cylinder	Flash2 Temperature – 30 °C Pressure – 1 bar	108,700	17,300
Acylation Process Section				
S-C2 – cond acc	DHT Horiz Drum	N/A	67,300	12,000
S-C2 – reflux pump	DCP Centrif	N/A	19,200	5,100

S-C2 – tower	DTW Tower	RadFrac Stages – 45 Reflux Ratio – 2 Pressure – 2 bar	681,800	390,400
S-C3 – cond acc	DHT Horiz Drum	N/A	52,400	12,000
S-C3 – reflux pump	DCP Centrif	N/A	15,400	5,100
S-C3 – tower	DTW Tower	RadFrac Stages – 30 Reflux Ratio – 0.012 Pressure – 1 bar	311,800	165,500
S-Comp2	DGC Centrif	Compr Pressure – 7 bar	1,582,400	1,449,600
S-P2	DCP Centrif	Pump Pressure – 0.1 bar	33,500	9,100
S-P3	DCP Centrif	Pump Pressure – 2 bar	30,500	7,100
S-P4	DCP Centrif	Pump Pressure – 3 bar	50,600	18,900
S-R2	DAT Reactor	RStoic Temperature – 30 °C Pressure – 1 bar	735,300	527,600
S-R3	DAT Reactor	RStoic Temperature – 220 °C Pressure – 7 bar	4,343,500	3,704,900
S-V3	DVT Cylinder	Flash2	334,800	81,100

		Temperature – 120 °C Pressure – 0.1 bar		
S-V11	DVT Cylinder	Decanter Temperature – 30 °C Pressure – 1 bar	172,600	45,800
S-V4	DVT Cylinder	Flash2 Temperature – 67 °C Pressure – 1 bar	301,200	51,500
S-V5	DVT Cylinder	Decanter Temperature – 30 °C Pressure – 1 bar	145,200	29,500
S-V6	DVT Cylinder	Flash2 Temperature – 49 °C Pressure – 1 bar	143,500	33,800
S-V7	DVT Cylinder	Decanter Temperature – 30 °C Pressure – 1 bar	143,300	33,700
S-V8	DVT Cylinder	Flash2 Temperature – 30 °C Pressure – 1 bar	104,900	18,500
S-V9	DVT Cylinder	Flash2 Temperature – 73 °C Pressure – 1 bar	185,900	45,500
S-V10	DVT Cylinder	Flash2 Temperature – 120 °C Pressure – 1 bar	191,800	51,000

S-V	DVT Cylinder	Flash2 Temperature – 50 °C Pressure – 1 bar	200,800	52,300
Sulphonation Process				
S-R4	DAT Reactor	RGibbs Temperature– 750 °C Pressure – 1 bar	785,100	536,400
S-R5	DAT Reactor	RStoic Temperature– 420 °C Pressure – 1 bar	568,100	497,300
S-R6	DAT Reactor	RStoic Temperature – 30 °C Pressure – 1 bar	30,500	12,400
S-R7	DAT Reactor	RStoic Temperature – 30 °C Pressure – 1 bar	50,600	9,500
Heat Exchangers				
H1	DHE Tema Exch	N/A	145,783	
H2	DHE Tema Exch	N/A	517,982	
H3	DHE Tema Exch	N/A	160,944	
H4	DHE Tema Exch	N/A	136,522	
H5	DHE Tema Exch	N/A	26,146	
H6	DHE Tema Exch	N/A	12,413	
H7	DHE Tema Exch	N/A	22,207	
H8	DHE Tema Exch	N/A	25,509	

H9	DHE Tema Exch	N/A	344,480
H10	DHE Tema Exch	N/A	162,367
H11	DHE Tema Exch	N/A	31,946
H12	DHE Tema Exch	N/A	64,213
H13	DHE Tema Exch	N/A	148,902
H14	DHE Tema Exch	N/A	2,283,204
H15	DHE Tema Exch	N/A	51,680
H16	DHE Tema Exch	N/A	13,986
H17	DHE Tema Exch	N/A	34,541
H18	DHE Tema Exch	N/A	850,714
H19	DHE Tema Exch	N/A	84,671
H20	DHE Tema Exch	N/A	30,547
H21	DHE Tema Exch	N/A	43,838
H22	DHE Tema Exch	N/A	116,272
H23	DHE Tema Exch	N/A	37,870
H24	DHE Tema Exch	N/A	18,709
H25	DHE Tema Exch	N/A	391,315
H26	DHE Tema Exch	N/A	226,668
H27	DHE Tema Exch	N/A	435,714
H28	DHE Tema Exch	N/A	53,505
H29	DHE Tema Exch	N/A	13,226
H30	DHE Tema Exch	N/A	143,191
H31	DHE Tema Exch	N/A	220,442
H32	DHE Tema Exch	N/A	62,823

H33	DHE Tema Exch	N/A	34,062
H34	DHE Tema Exch	N/A	67,333

Table 26: Equipment Details for Jet-Fuel process.

Component Name	Component Type	ASPEN Model	Total Direct Cost (million \$)	Equipment Cost (million \$)
Methyl-Furan Production Section				
J-Comp1	DGC Centrif	Compr Pressure – 7 bar	1,561,300	1,433,700
J-P	DCP Centrif	Pump Pressure – 7 bar	34,200	5,200
J-R1	DAT Reactor	RStoic Temperature–220 °C Pressure – 6.89 bar	4,240,900	3,317,200
J-V1	DVT Cylinder	Flash3 Temperature – 35 °C Pressure – 6.5 bar	104,300	16,800
Intermediate Production Section				
J-C1 – cond acc	DHT Horiz Drum	N/A	80,400	11,000
J-C1 – reflux pump	DCP Centrif	N/A	38,200	5,200
J-C1 – tower	DTW Tower	RadFrac Stages – 75 Reflux Ratio – 5.87 Pressure – 1 bar	1,734,100	1,353,600
J-C2 – cond acc	DHT Horiz Drum	N/A	89,800	14,800

J-C2 – reflux pump	DCP Centrif	N/A	25,900	4,400
J-C2 – tower	DTW Tower	RadFrac Stages – 25 Reflux Ratio – 0.02 Pressure – 0.1 bar	481,300	151,100
J-P1	DCP Centrif	Pump Pressure – 10 bar	44,200	15,600
J-P2	DCP Centrif	Pump Pressure – 10 bar	33,800	4,800
J-P3	DCP Centrif	Pump Pressure – 0.1 bar	34,000	4,800
J-P	DCP Centrif	Pump Pressure – 10 bar	26,200	4,600
J-R2	DAT Reactor	RStoic Temperature – 60 °C Pressure – 10 bar	654,700	430,200
J-V2	DVT Cylinder	Flash2 Temperature – 240 °C Pressure – 1 bar	109,900	17,400
J-V	DVT Cylinder	Flash2 Temperature – 94 °C Pressure – 1 bar	106,100	14,900
J-V	DVT Cylinder	Flash2 Temperature – 30 °C Pressure – 1 bar	106,300	15,000

Jet-Fuel Production Section				
J-C3 – cond acc	DHT Horiz Drum	N/A	103,000	12,900
J-C3 – reflux pump	DCP Centrif	N/A	38,500	5,500
J-C3 – tower	DTW Tower	RadFrac Stages – 30 Reflux Ratio – 0.015 Pressure – 1 bar	565,200	251,100
J-C4 – cond acc	DHT Horiz Drum	N/A	85,000	11,000
J-C4 – reflux pump	DCP Centrif	N/A	38,600	5,100
J-C4 – tower	DTW Tower	RadFrac Stages – 30 Reflux Ratio – 0.4 Pressure – 0.1 bar	623,000	262,600
J-Comp2	DGC Centrif	MCompr Stages – 4 Pressure – 50 bar	1,813,400	1,790,300
J-P	DCP Centrif	Pump Pressure – 50 bar	351,100	215,800
J-P	DCP Centrif	Pump Pressure – 0.1 bar	353,00	5,200
J-R3	DAT Reactor	RStoic Temperature– 200 °C Pressure – 50 bar	27,43,900	24,929,200
J-V3	DVT Cylinder	Flash2 Temperature – 30 °C	247,800	70,500

		Pressure – 1 bar		
J-V4	DVT Cylinder	Flash2 Temperature – 81 °C Pressure – 1 bar	364,400	172,600
J-V5	DVT Cylinder	Decanter Temperature – 60 °C Pressure – 1 bar	275,800	81,100
J-V	DVT Cylinder	Flash2 Temperature – 43 °C Pressure – 1 bar	148,100	27,000
J-V	DVT Cylinder	Flash2 Temperature – 25 °C Pressure – 1 bar	294,500	89,900
J-V	DVT Cylinder	Flash2 Temperature – 30 °C Pressure – 1 bar	247,800	70,500
Heat Exchangers				
H1	DHE Tema Exch	N/A	64,041	
H2	DHE Tema Exch	N/A	70,446	
H3	DHE Tema Exch	N/A	74,170	
H4	DHE Tema Exch	N/A	94,723	
H5	DHE Tema Exch	N/A	10,886	
H6	DHE Tema Exch	N/A	237,770	
H7	DHE Tema Exch	N/A	11,423	
H8	DHE Tema Exch	N/A	10,200	

H9	DHE Tema Exch	N/A	20,852
H10	DHE Tema Exch	N/A	11,856
H11	DHE Tema Exch	N/A	43,472
H12	DHE Tema Exch	N/A	11,664
H13	DHE Tema Exch	N/A	112,581
H14	DHE Tema Exch	N/A	33,033
H15	DHE Tema Exch	N/A	58,669
H16	DHE Tema Exch	N/A	639,804
H17	DHE Tema Exch	N/A	631,071
H18	DHE Tema Exch	N/A	41,672
H19	DHE Tema Exch	N/A	13,575
H20	DHE Tema Exch	N/A	49,781
H21	DHE Tema Exch	N/A	10,067
H22	DHE Tema Exch	N/A	31,814
H23	DHE Tema Exch	N/A	23,965
H24	DHE Tema Exch	N/A	17,965
H25	DHE Tema Exch	N/A	34,240
H26	DHE Tema Exch	N/A	10,180
H27	DHE Tema Exch	N/A	24,178
H28	DHE Tema Exch	N/A	39,741
H29	DHE Tema Exch	N/A	548,694
H30	DHE Tema Exch	N/A	1,142,393
H31	DHE Tema Exch	N/A	1,217,571
H32	DHE Tema Exch	N/A	27,851

H33	DHE Tema Exch	N/A	24,787
H34	DHE Tema Exch	N/A	10,295
H35	DHE Tema Exch	N/A	90,056
H36	DHE Tema Exch	N/A	29,178
H37	DHE Tema Exch	N/A	27,961
H38	DHE Tema Exch	N/A	2,002,326
H39	DHE Tema Exch	N/A	460,602
H40	DHE Tema Exch	N/A	12,683
H41	DHE Tema Exch	N/A	10,144

Table 27: Equipment Details for Lubricant process.

Component Name	Component Type	ASPEN Model	Total Direct Cost (million \$)	Equipment Cost (million \$)
Furan Production Section				
L-C1 – cond acc	DHT Horiz Drum	N/A	75,600	11,800
L-C1 – reflux pump	DCP Centrif	N/A	25,900	4,400
L-C1 – tower	DTW Tower	RadFrac Stages – 40 Reflux Ratio – 0.04 Pressure – 2 bar	496,200	272,900
L-P1	DCP Centrif	Pump Pressure – 2 bar	32,200	4,500
L-R1	DAT Reactor	RStoic Temperature – 250°C	39,561,000	36,200,000

		Pressure – 1 bar		
L-V1	DVT Cylinder	Flash2 Temperature – -30 °C Pressure – 1 bar	150,700	17,300
L-V2	DVT Cylinder	Flash2 Temperature – 30 °C Pressure – 1 bar	108,700	17,300
Acylation Process Section				
L-V	DVT Cylinder	Flash2 Temperature – 30 °C Pressure – 1 bar	205,600	36,000
L-C2 - cond acc	DHT Horiz Drum	N/A	153,000	27,900
L-C2 - reflux pump	DCP Centrif	N/A	59,400	10,400
L-C2 - tower	DTW Tower	RadFrac Stages – 35 Reflux Ratio – .035 Pressure – 1 bar	1,391,000	809,200
L-C3 - cond acc	DHT Horiz Drum	N/A	99,600	21,000
L-C3 - reflux pump	DCP Centrif	N/A	49,100	6,700
L-C3 - tower	DTW Tower	RadFrac Stages – 50 Reflux Ratio – 10.4 Pressure – 15 bar	1,317,100	834,800
L-C4 - cond acc	DHT Horiz Drum	N/A	74,500	18,000

L-C4 - reflux pump	DCP Centrif	N/A	27,800	4,100
L-C4 - tower	DTW Tower	RadFrac Stages – 30 Reflux Ratio – 0.205 Pressure – 3 bar	460,700	212,000
L-COMP2	DGC Centrif	Compr Pressure – 7 bar	1,584,500	1,451,500
L-P2	DCP Centrif	Pump Pressure – 15 bar	113,500	58,700
L-P3	DCP Centrif	Pump Pressure – 7 bar	78,100	19,000
L-R2	DAT Reactor	RStoic Temperature – 30 °C Pressure – 1 bar	770,400	524,300
L-R3	DAT Reactor	RStoic Temperature – 220 °C Pressure – 7 bar	9,763,000	8,470,100
L-V9	DVT Cylinder	Decanter Temperature – 30 °C Pressure – 1 bar	205,600	47,000
L-V3	DVT Cylinder	Flash2 Temperature – 43 °C Pressure – 1 bar	169,100	29,700
L-V4	DVT Cylinder	Decanter Temperature – 30 °C Pressure – 1 bar	169,100	29,700

L-V5	DVT Cylinder	Flash2 Temperature – 46 °C Pressure – 1 bar	174,700	33,700
L-V6	DVT Cylinder	Decanter Temperature – 30 °C Pressure – 1 bar	170,200	30,500
L-V	DVT Cylinder	Flash2 Temperature–230 °C Pressure – 1 bar	136,800	18,500
L-V7	DVT Cylinder	Flash2 Temperature – 81 °C Pressure – 1 bar	207,500	45,500
L-V8	DVT Cylinder	Flash2 Temperature – 30 °C Pressure – 1 bar	214,900	46,600
HydroxyAlkylation/Alkylation Process				
L-R4	DAT Reactor	RStoic Temperature – 65 °C Pressure – 1 bar	1,014,400	748,500
L-V10	DVT Cylinder	Flash2 Temperature–260 °C Pressure – 0.1 bar	200,600	22,200
Hydroxy-deoxygenation Process				

L-V	DVT Cylinder	Flash2 Temperature – 30 °C Pressure – 1 bar	295,200	86,300
L-Comp3	DGC Centrif	Compr Pressure – 60 bar	1,933,600	1,797,800
L-P4	DCP Centrif	Pump Pressure – 60 bar	343,800	231,600
L-R5	DAT Reactor	RStoic Temperature – 60 °C Pressure – 60 bar	22,143,400	19,645,100
L-V11	DVT Cylinder	Flash2 Temperature – 30 °C Pressure – 1 bar	173,100	22,400
L-V12	DVT Cylinder	Flash2 Temperature–150°C Pressure – 1 bar	292,300	151,900
L-V	DVT Cylinder	Flash2 Temperature – 75 °C Pressure – 1 bar	375,300	158,800
Heat Exchangers				
H1	DHE Tema Exch	N/A	29,540	
H2	DHE Tema Exch	N/A	72,752	
H3	DHE Tema Exch	N/A	73,630	
H4	DHE Tema Exch	N/A	42,914	
H5	DHE Tema Exch	N/A	85,135	

H6	DHE Tema Exch	N/A	19,618
H7	DHE Tema Exch	N/A	83,346
H8	DHE Tema Exch	N/A	544,893
H9	DHE Tema Exch	N/A	57,898
H10	DHE Tema Exch	N/A	634,128
H11	DHE Tema Exch	N/A	112,537
H12	DHE Tema Exch	N/A	10,685
H13	DHE Tema Exch	N/A	77,745
H14	DHE Tema Exch	N/A	75,337
H15	DHE Tema Exch	N/A	122,795
H16	DHE Tema Exch	N/A	53,763
H17	DHE Tema Exch	N/A	138,782
H18	DHE Tema Exch	N/A	1,020,009
H19	DHE Tema Exch	N/A	68,928
H20	DHE Tema Exch	N/A	986,589
H21	DHE Tema Exch	N/A	14,576
H22	DHE Tema Exch	N/A	412,857
H23	DHE Tema Exch	N/A	39,591
H24	DHE Tema Exch	N/A	27,055
H25	DHE Tema Exch	N/A	139,998
H26	DHE Tema Exch	N/A	1,945,882
H27	DHE Tema Exch	N/A	106,569
H28	DHE Tema Exch	N/A	856,618
H29	DHE Tema Exch	N/A	30,097

H30	DHE Tema Exch	N/A	12,137
H31	DHE Tema Exch	N/A	17,251
H32	DHE Tema Exch	N/A	31,970
H33	DHE Tema Exch	N/A	14,906
H34	DHE Tema Exch	N/A	14,848
H35	DHE Tema Exch	N/A	54,375
H36	DHE Tema Exch	N/A	70,158
H37	DHE Tema Exch	N/A	327,787
H38	DHE Tema Exch	N/A	46,517
H39	DHE Tema Exch	N/A	13,384
H40	DHE Tema Exch	N/A	10,072
H41	DHE Tema Exch	N/A	1,313,204
H42	DHE Tema Exch	N/A	12,951
H43	DHE Tema Exch	N/A	1,71,358
H44	DHE Tema Exch	N/A	32,531
H45	DHE Tema Exch	N/A	53,658
H46	DHE Tema Exch	N/A	34,074
H47	DHE Tema Exch	N/A	10,010

In the base case scenario, where p-Xylene production is coupled with each of the four processes individually, the minimum selling price of butadiene is \$1,228/metric ton, surfactants is \$2,502/metric ton, \$3.45/gallon for jet fuel and \$4,037/metric ton for lubricants. The price of oil-based butadiene is ~\$2,500-\$3,500 per metric ton, surfactants is ~\$2,500-\$2,800 per metric ton, ~\$1.9-\$2.5 per gallon of jet fuel and ~\$4,000-\$4,500 per metric ton of surfactants^[35, 36]. For the combined process we calculate the contribution

margin for each product. The variable cost for individual production process is \$315 per ton for butadiene, \$2298 per ton for surfactants, \$1.55 per gallon for jet fuel and \$3649 per ton for lubricants and the contribution margins keeping the selling price as above is \$913 per ton for butadiene, \$204 per ton for surfactants, \$1.9 per gallon for jet fuel and \$388 per ton for lubricants. Producing butadiene is the most profitable while producing surfactants is the least profitable. For the combined process the variable cost is \$591 per ton for butadiene, \$2502 per ton for surfactants, \$2.54 per gallon for jet-fuels and \$3677 per ton for lubricants. The contribution margin then for the products keeping the selling price as above stated is \$637 per ton for butadiene, \$260 per ton for surfactants, \$0.90 per gallon for jet fuel and \$360 per ton for lubricants. The variable cost per product produced because of increase in the cost of utilities per product produced. The contribution margins decrease while the minimum selling price of each product for the combined process increase because if multiple products are produced simultaneously, the profits gained by producing one chemical is divided over the production costs of all products and/or we are not producing enough of the most profitable product.

The above calculations are performed in an integrated flowsheet model combined with the production of p-Xylene. A scenario where the minimum selling price of the products is calculated when furfural is bought directly from the market rather than producing it from biomass is considered. The minimum selling price of butadiene, surfactants, jet-fuels and lubricants is \$3,170/metric ton, \$2,802/metric ton, \$7.22/gallon and \$4,570/metric ton, respectively. It should be noticed that there is an increase of 158%, 12%, 109.3% and 13.2% in the minimum selling price. For both butadiene and jet-fuel, cost of furfural is the major factor in the operating cost instead of biomass and hence there is a decrease in selling

price, as it contributes 95% and 91% to the overall raw material cost.

Few assumptions have been taken for the techno-economic analysis. Sensitivity analysis is carried out for various scenarios for different processes. For butadiene production, THF needed for the ring opening process is identified as the most crucial parameter. A change of $\pm 10\%$ in capital cost and a change of $\pm 10\%$ in operating cost changes the minimum price of butadiene by $\pm 15.3\%$ and $\pm 31.6\%$ respectively. For the surfactant production, the sulphonation process uses specialized equipment. A change of $\pm 10\%$ in capital cost changes the minimum price of surfactants by $\pm 1.6\%$. A change of $\pm 10\%$ in operating cost changes the minimum price by $\pm 11.4\%$. For jet fuel production, Amberlyst-15 catalyst is used instead of IGO, which decreases the yield of process. An increase in 10% yield, decreases the minimum selling price of jet fuel by 9%. For lubricant production, regeneration of the catalysts has not been designed and simulated. A change of $\pm 10\%$ in capital cost and operating cost changes the minimum price of lubricants by $\pm 1.6\%$ and $\pm 11.5\%$ respectively. The price and availability of lauraldehyde is not available and thus we have assumed its market price. A change of $\pm 10\%$ in the price of lauraldehyde changes the minimum price of lubricants by $\pm 3\%$. Finally, the prices of all the chemicals depend on the selling price of p-Xylene. An increase of 10% in the selling price of p-Xylene decreases the selling price of butadiene by 36%, surfactant by 2.75%, and jet-fuel by 24.7% and lubricant by 3% and vice a versa.

Life Cycle: The characterization results for butadiene, surfactant, jet-fuel and lubricants production processes are calculated using ReCiPe midpoint method^[44]. Impact categories including climate change, water depletion, land occupation and fossil depletion are considered in our analysis due to their significant normalized impacts. Surfactants process

overall performs better than butadiene, jet-fuels and lubricants process in all the impact categories except for water depletion. High quantity of products is produced in the case of surfactants production, which decreases the overall environmental impacts of the process. Butadiene production environmental indicators are worse in all categories except for water depletion. This is because the quantity of butadiene produced is very low when compared to other processes which means greater amount of raw materials and utilities are required for the production of one metric ton of butadiene when compared with the other processes. The detailed environmental performance of all the processes is shown in Figure 23.

Contribution of raw materials for individual process combined with p-Xylene process is also taken into consideration. Production of furfural from p-Xylene process is the main contributor for all the impact categories for the case of butadiene production. Similarly, for the production of jet-fuels, production of furfural from p-Xylene production is the main contributor for the impact categories. For the case of surfactants and lubricant production, main contributor for CO₂ emission and water depletion is furfural whereas, production of fatty acid is the main contributor for fossil depletion and land occupation. Contribution of raw materials is shown in the figure 24-27. More sustainable sources of furfural should be explored to make the production process more ecological and competitive with oil-based sources.

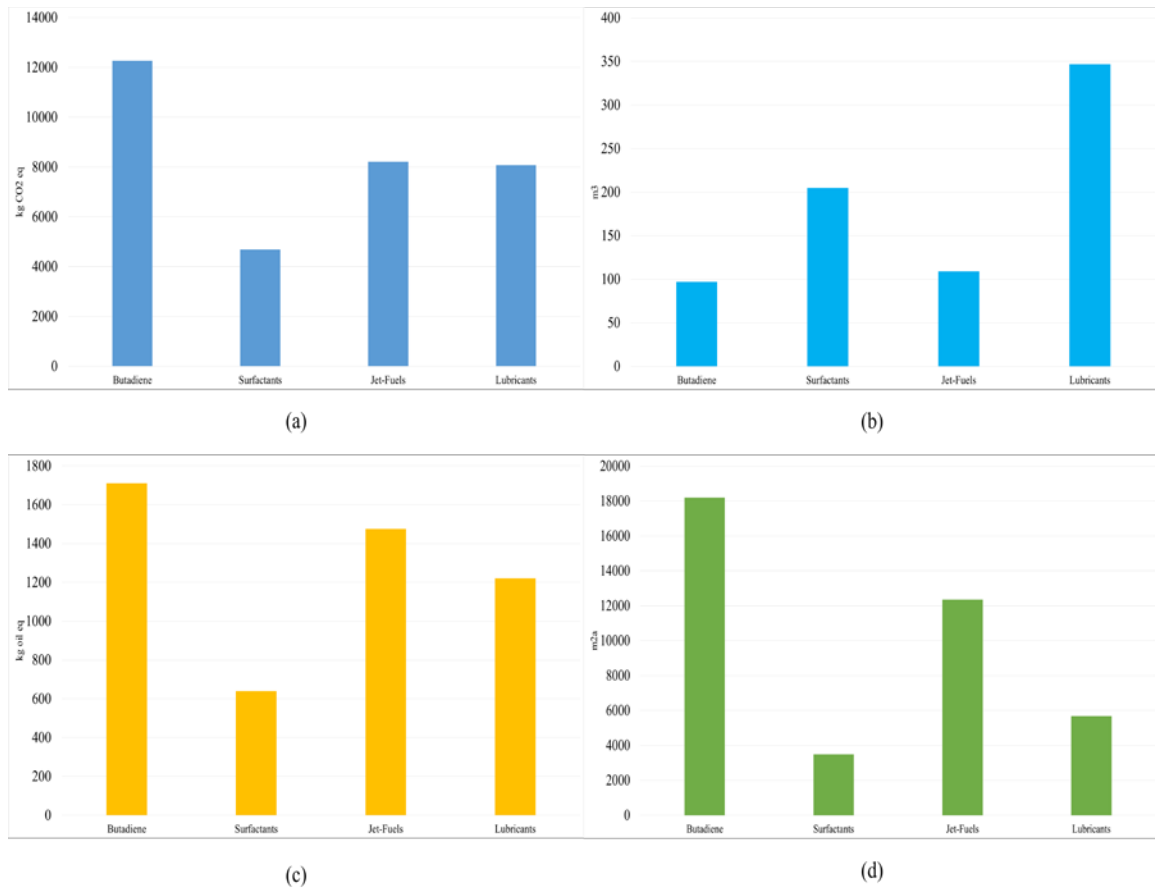


Figure 23: Characterization results (ReCiPe midpoint method) of three processes for a) Climate change b) Water depletion c) Fossil depletion d) Land occupation.

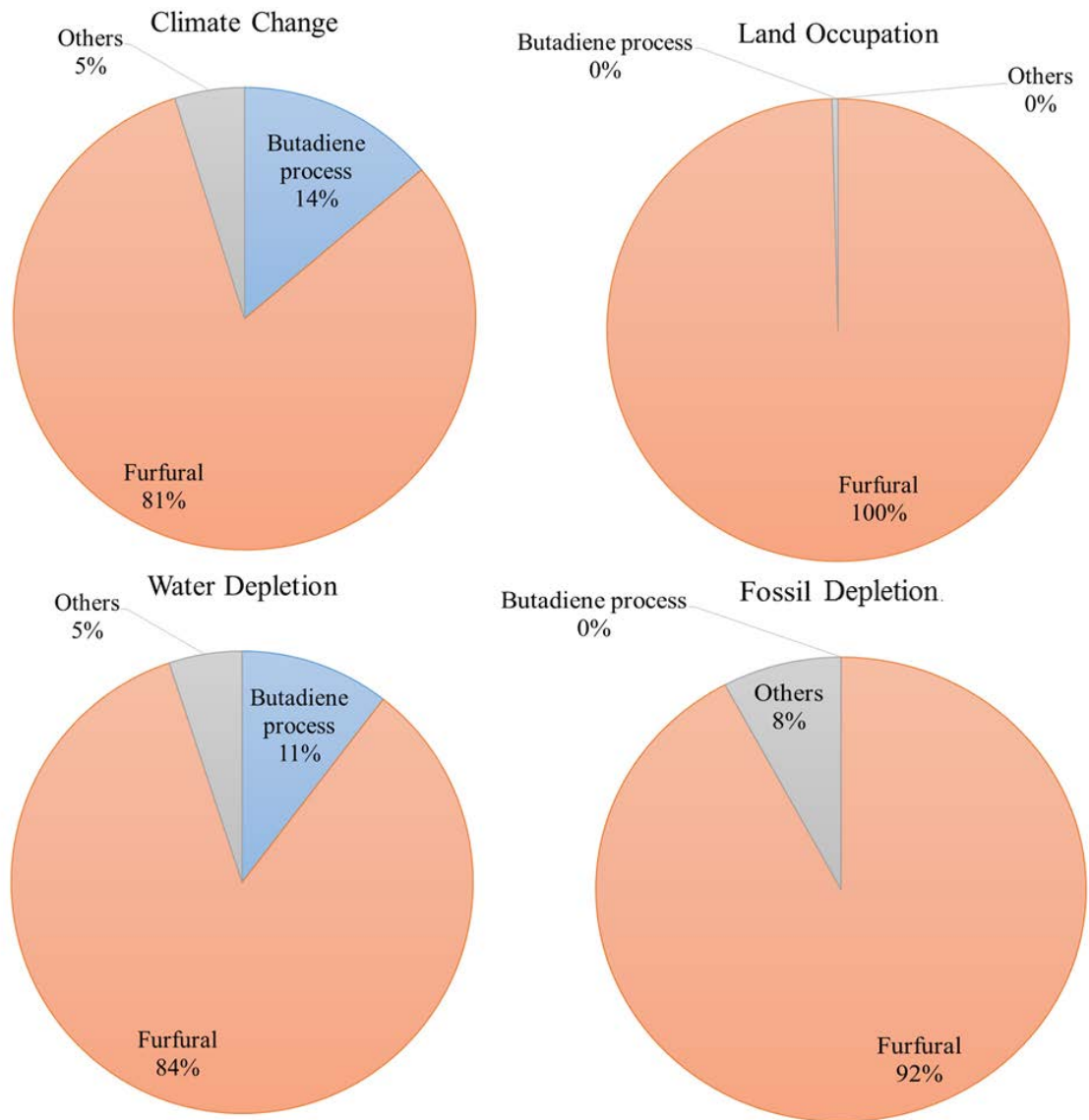


Figure 24: Raw Material contribution for Butadiene process.

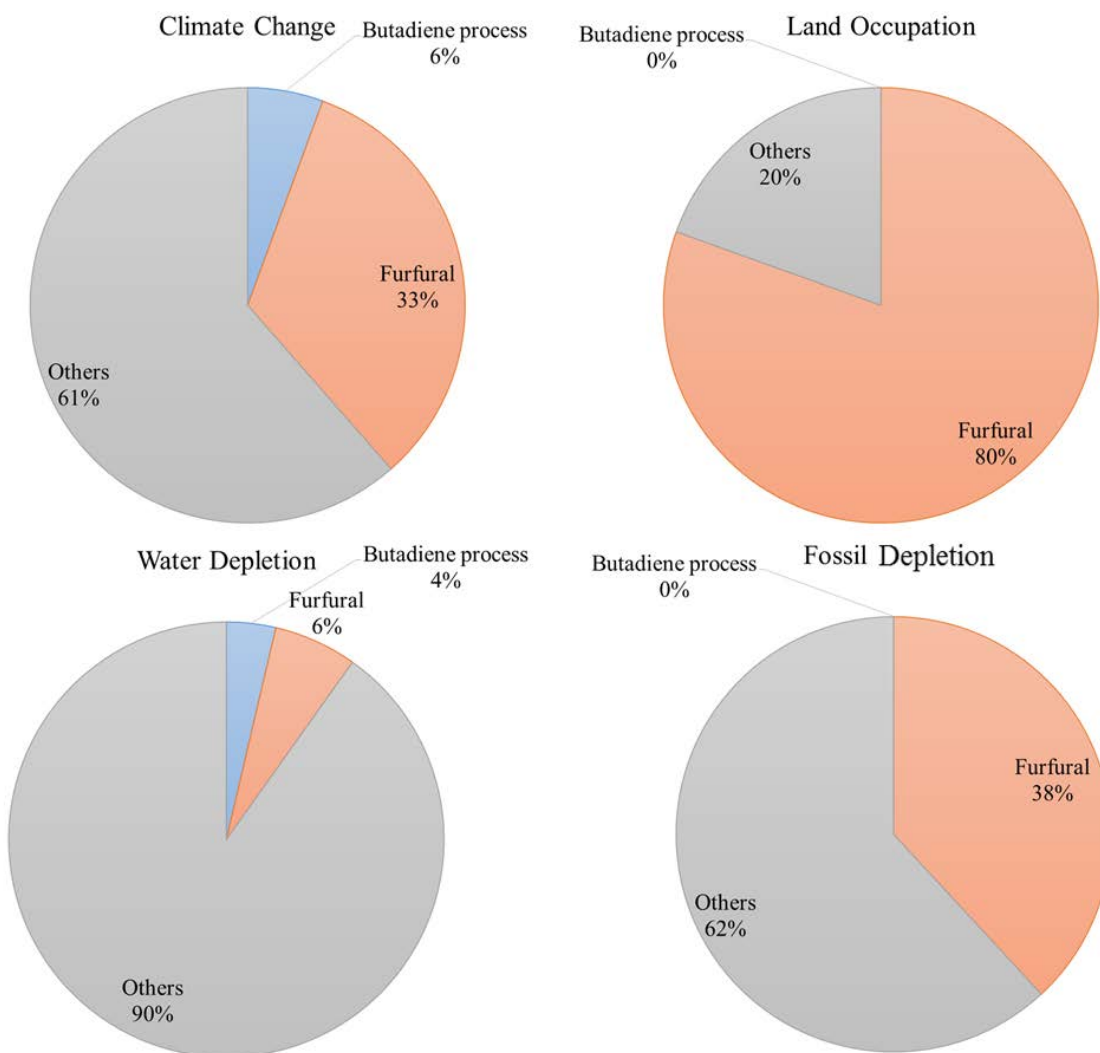


Figure 25: Raw Material contribution for Surfactants process.

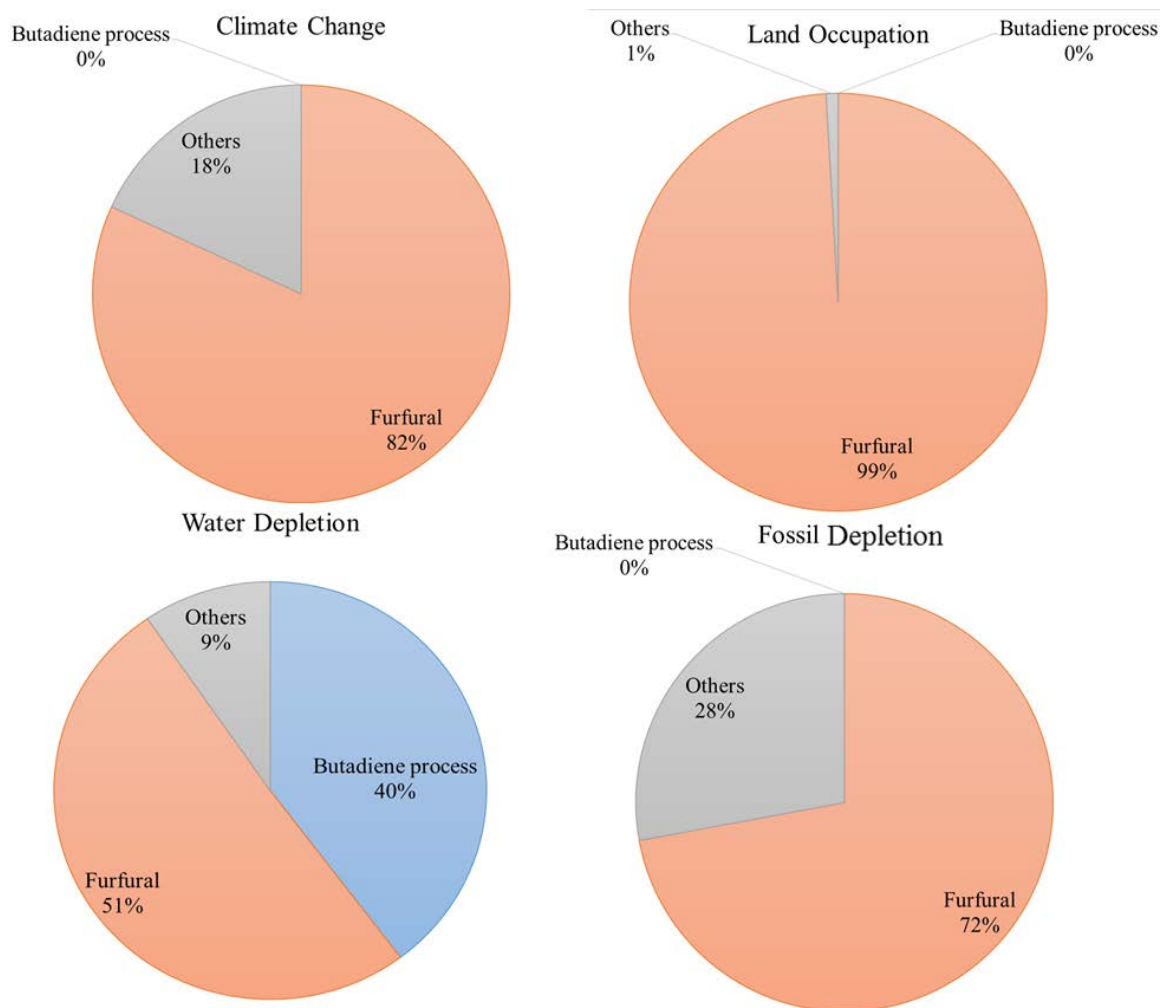


Figure 26: Raw Material contribution for Jet-Fuels process.

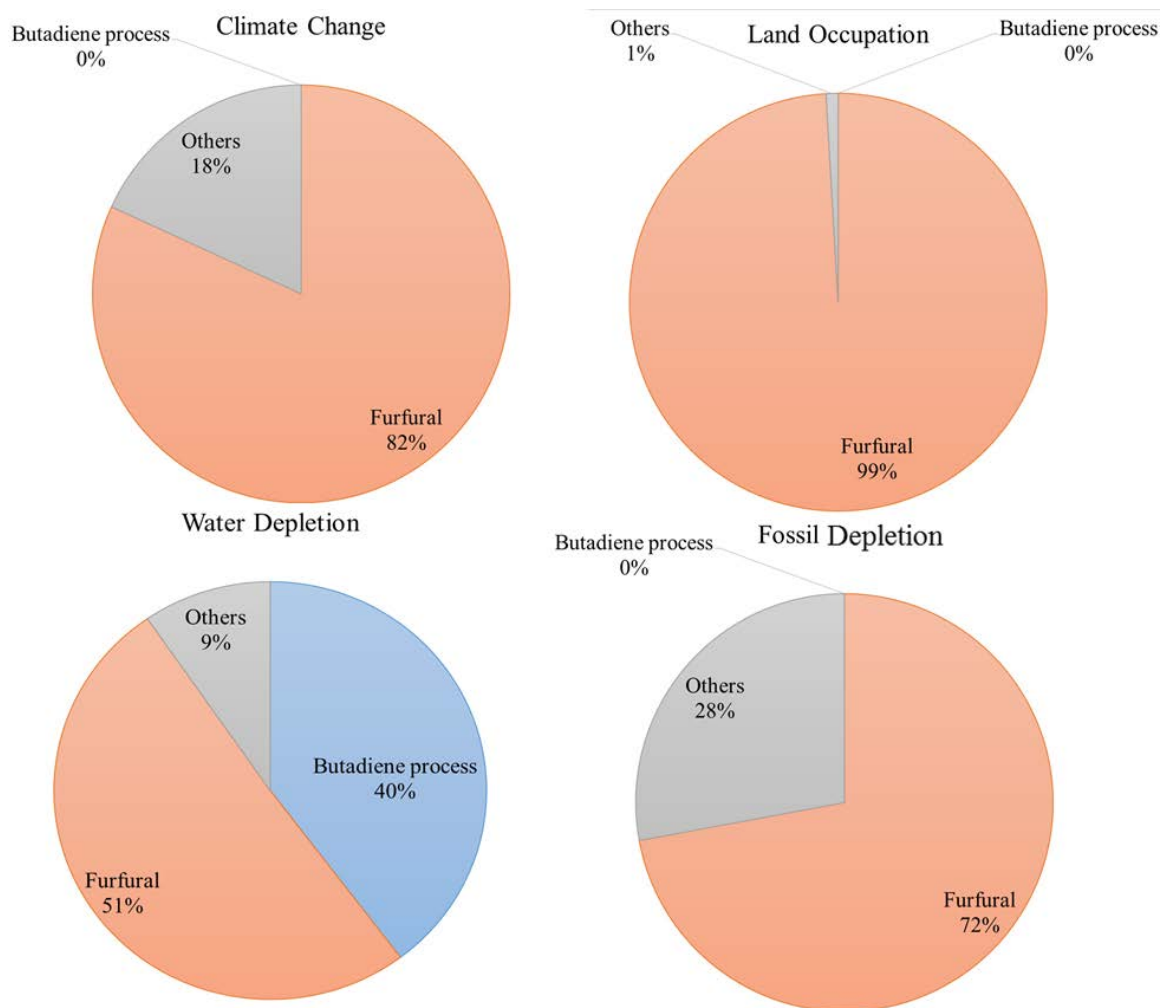


Figure 27: Raw Material contribution for Lubricants process.

4 Lignin Based Chemical Production and Integration of a Bio-refinery

4.1 Introduction

Lignin is the most abundant source of aromatic building blocks in nature and is a major component in lignocellulosic biomass^[83]. The pulp and paper industry estimated that 50 million tons of lignin were extracted in 2010, but only 2% has been commercialized for the formulation of dispersants, adhesives, and surfactants or as antioxidants in plastics and rubbers. Commonly, lignin formed, is treated as waste and is used to produce electricity. Lignin are linked by a robust C-C and C-O bonds^[84] and hence depolymerization can generate a complex mixture of compounds. Although there are a number of studies showing profitable ways to valorize lignin by the production of various monomeric phenolic compounds, they face difficulties regarding the fractionation/isolation of pure compounds from the complex mixtures resulting from lignin depolymerization^[85]. In this work, a novel production path to produce pressure sensitive adhesive (PSA) from biomass depolymerization at high purity and yield is discussed^[86].

PSA are a family of adhesives that adhere to a surface after a small external pressure is applied. No heat or solvent is required for the activation of adhesive. PSA's are used extensively in day to day scenario esp. in packaging, sticky notes, plastic wraps etc. The global market for PSA is expected to reach \$13 billion by 2023^[87]. Acrylate based polymers such as poly(methyl methacrylate) (PMMA) exhibit good adhesion and without any additives^[88]. A novel method of replacing the oil-based polymer with biomass-based polymer is proposed.

In this work, we evaluate the techno-economic feasibility of producing PSA from lignin, which is first depolymerized from biomass. The unreacted wood is then used for producing

p-Xylene production. Minimum selling price of the PSA is then calculated keeping the price of p-Xylene constant. First, the reaction pathways and assumptions to perform the simulation is discussed. The economic results are then calculated and discussed. Finally, we have integrated the production of different chemicals from the furfural produced to simulate the bio-refinery. Techno-economic analysis of the combined process is carried out the minimum selling price of all the chemicals is calculated.

4.2 Methodology

Reaction Path

The reaction path for the production of PSA is shown in Figure 28. First, biomass is depolymerized with the help of hydrogen in the presence of methanol and commercially available Ru/C catalyst at 250 °C and 40 bar. The monomers; 4-propylsyringol (4pS) and 4-propylguaiacol (4pG) are obtained after the depolymerization step with relative mass fractions of 0.6 and 0.4 respectively at a total yield of 10 wt.% on the basis of dry poplar wood. Cyclohexane is used to extract the monomers from the methanol mixture. The unreacted wood containing cellulose and hemi-cellulose is sent to the hydrolysis process for the production of p-Xylene. Next, the monomer mixture is acrylated with acryloyl chloride in the presence of triethylamine and dichloromethane at 0°C. The residence time is 8hrs. The product obtained is a co-polymer of 4-propylsyringyl acrylate (4pSA) and 4-propylguaiacyl acrylate (4PGA). The co-polymer acts as a monomer (co- monomer) for the PSA. SaBSa triblock polymer (PSA) is synthesized in a two-step RAFT polymerization. First, poly n-butyl acrylate (PBA) is synthesized in the presence of mixture of anisole with 5 wt.% N,N-dimethylformamide (DMF) at 70 °C. 2,2'-azobis(isobutyronitrile) (AIBN) is used as the initiator with 3,5-bis(2-dodecyl-

thiocarbonothioylthio-1- oxopropoxy)benzoic acid (BTCBA) as the chain transfer agent. Next, PBA is chain extended by adding the co-monomer to make the SaBSa triblock polymer at 72 °C. Typical reaction time is 6- 7 hrs. SaBSa is then precipitated in the presence of tetrahydrofuran (THF) and methanol at 0 °C^[86].

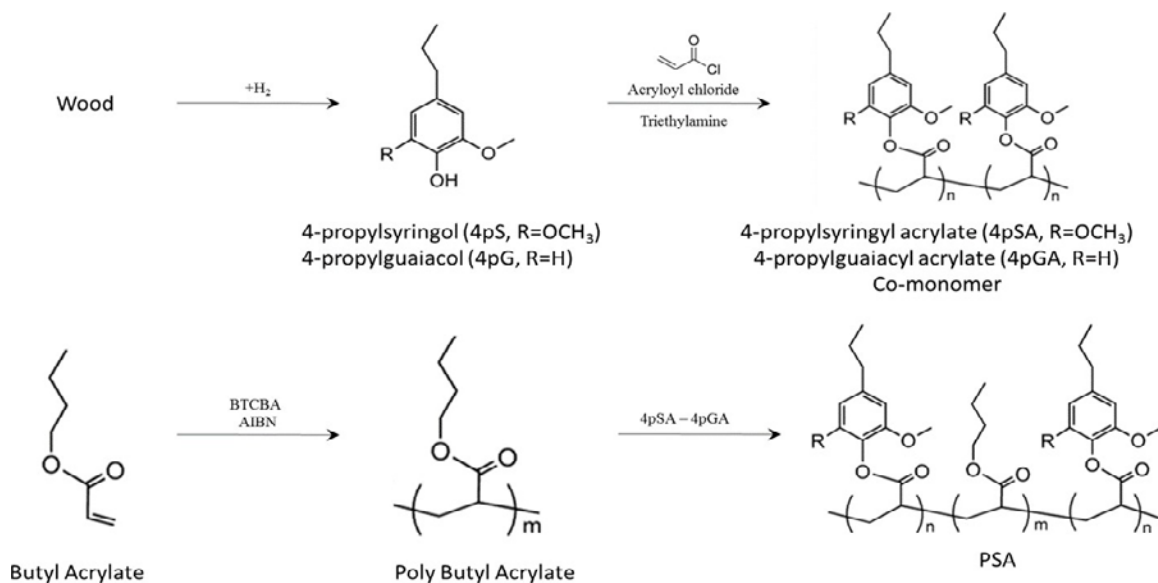


Figure 28: Reaction route for pressure sensitive adhesive (PSA) production.

Simulation and Economics

Simulation: Aspen Economic Analyzer® V8.8.2 is used to simulate the production process of pressure sensitive adhesive. Poly-NRTL method is utilized to predict the liquid-liquid and liquid- vapor behavior. Most of components involved in the reactions are directly selected from Aspen database, whereas some not included in the database (i.e. lignin and xylan) are defined by the structures and the properties used by NREL^[29]. All the missing parameters are estimated by the molecular structures using the UNIFAC Model and Thermo Data Engine (TDE) especially for aromatic methoxyphenol, co-monomers as well as SaBSa polymers.

To enable the process simulation, the following assumptions are made:

1. Composition of biomass is assumed to have 40% cellulose, 30% hemicellulose and 30% lignin. Generally, hardwoods and softwoods contain around 40-50% cellulose, 25-30% hemicellulose, 18-25% lignin and <1% ash^[19]. For the base scenario, the assumption is satisfactory. Sensitivity analysis for the MSH process is carried out for different cellulose composition in biomass.
2. The yield and reaction conditions of all the reactions are shown in table 28.
3. The by-products do not affect the conversion and selectivity of any reactions. No separation steps are considered before reaction.
4. Although BTCBA is used as the chain transfer agent, key data regarding the structure and parameters is not available. Hence, it was not included in the simulation.
5. The kinetics of the co-monomer production is available but have not been implemented currently. Hence, heat integration of the process is not carried out.
6. For the combined process, where all the processes are integrated, we have assumed that flowrate of furfural is split into 2:1:1:1 ratio of jet-fuel, butadiene, surfactants and lubricants respectively.

Table 28: The Specification of reactions for the production of PSA.

Process	Depolymerization of Biomass	Monomer Production	Polymer Production
T (K)	523	273	345
P (Kpa)	4000	101.325	101.325
Conversion(%)	10	100	80

Economics: Aspen Economic analyzer V8.8 is used to perform an economic assessment for the bio-refinery. Discounted cash flow analysis is used to perform the economic analysis for the different processes. As the production of p-Xylene is coupled with PSA

production, we need to consider selling of p-Xylene to calculate the minimum selling price of PSA. The selling price of the p-Xylene is taken as \$1,477 per ton, which has been calculated in the previous chapters. Some additional assumptions are necessary to perform the economics analysis as outline below:

1. All the equipment and operating costs estimated by Aspen Economic Analyzer V8.8 are based on the price of the first quarter in 2014.
2. The capacity of base scenario is assumed 50 metric ton/year of dried biomass. The cost of biomass is averaged to (\$60/metric ton) based on the data of 2011 from NREL^[30].
3. The plant operates in a continuous mode for 8000 h per year. The economic life of the project is assumed 20 years and the recovery period is assumed as 10 years. The internal rate of return (ROR) on investment is assumed as 15%. 35% corporate tax is applied to the profits. The simplest depreciation method -- the straight-line method is applied, as the salvage value is 10% of the original capital cost after 20 years.
4. The market price of methanol is estimated as \$500/metric ton and for acryloyl chloride is \$10,000/metric ton.
5. The cost of cyclohexane is \$1,400/metric ton, hydrogen is \$653/metric ton, DCM is \$550/metric ton, Anisole is \$3,500/metric ton and of BA is \$1,500/metric ton.
6. The cost of DMF is \$1000/metric ton, THF is \$1500/metric ton, AIBN is \$6000/metric ton and for triethylamine is \$2,000/metric ton.
7. The catalyst cost for butadiene production is estimated as precious metal cost plus \$11000/ton of supported catalyst and catalyst manufacturing^[31]. Unit price of RU is taken as \$1867/kg^[80]. Ru/C catalyst is used for the depolymerization reaction consists of 5 wt.% leading to a price of \$103,800/metric ton. The catalyst life is taken to be 6 months. It is assumed that the catalyst manufacturer will be able to recover 99% of the metals in the

spent catalyst. Therefore, after every 6 months only the cost of the catalyst support, makeup metals and manufacturing cost would be required.

8. Utilities and wastewater treatment plants are not modeled explicitly, rather it is assumed instead that utilities are purchased and wastewater is treated by a third party at a fixed price per unit volume^[31].

Process Flowsheet

Production of PSA starts with the depolymerization of biomass and is shown in figure 29. Biomass, dissolved in methanol is mixed with pressurized hydrogen (40 bar) in reactor (R1), which contains catalyst at 250 °C. The product stream is then fed to flash drum (V1) and excess hydrogen is separated and recycled. Cyclohexane is introduced in the extraction column (E1) which separates the monomers of lignin. Methanol stream containing unreacted wood is then fed to a dryer to evaporate the methanol, which is recycled. The unreacted wood is used for the production of p- Xylene. Cyclohexane stream is also separated by evaporating it in flash drum (V2) and recycled back. The monomers are mixed with acryloyl chloride and trimethylamine in the presence of dichloromethane (DCM) at 0°C. HCl is produced as a byproduct which is neutralized by triethylamine. The salts produced is separated out by filter (Fil 1). The liquid stream is dried in another flash drum (V5) to separate out DCM, which is recycled. For the polymerization step, first butyl acrylate is polymerized with AIBN in the presence of anisole and DMF mixture. The co-monomer is introduced in the reactor (R4) to form SaBSa triblock polymer. The polymer is precipitated in the presence of cold methanol and THF mixture. The remaining liquid mixture is distilled to separate the polymerization solvent and methanol-THF mixture. The PSA formed can be further dried if needed.

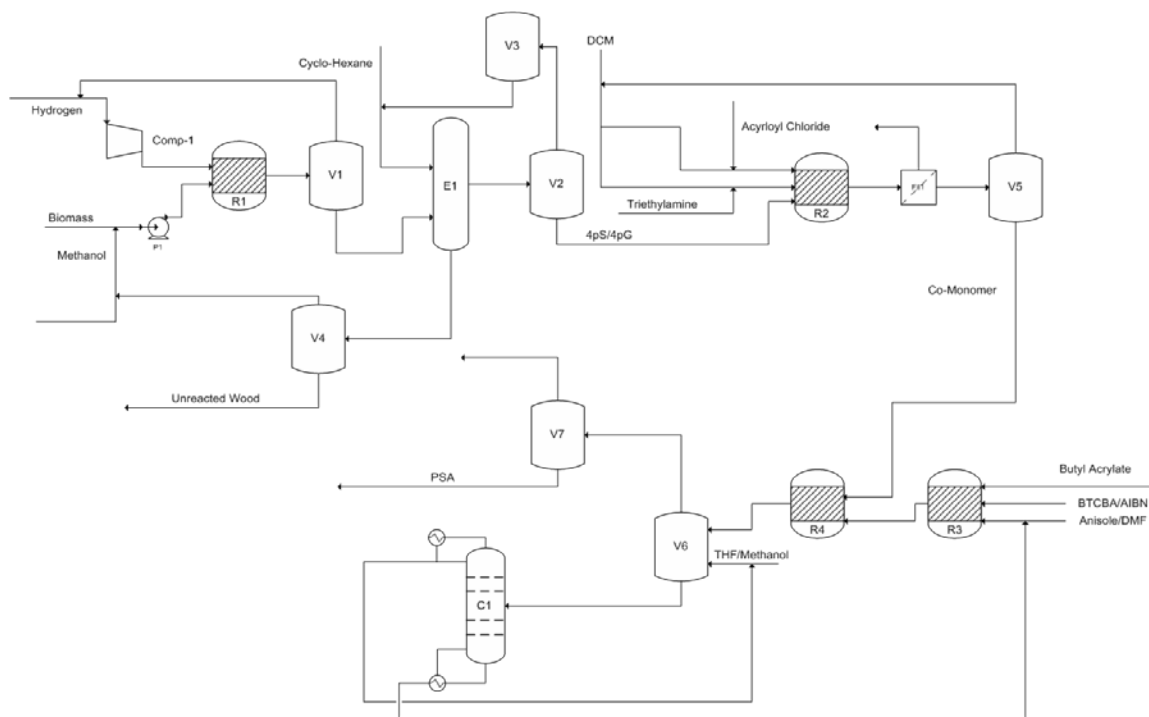


Figure 29: Process Diagram for PSA Production.

4.3 Results and Discussion

Simulation: The capacity of the process is based on the processing 400,000 metric ton of biomass per year. The process produces 35,200 metric ton/year. The unreacted wood is used for the production of p-Xylene which produces 81,312 metric ton/year of p-Xylene. As lignin is used PSA production, no electricity is produced from the p-Xylene production. Furfural produced from the p-Xylene process is the only by-product which is produced at 66056 metric ton/year. By-products such as 2,5-dihydroxymethyltetrahydrofuran, 2,5-hexanedione, and 1-ethyl-2,5- dimethylbenzene have are produced in very small quantity and hence purifying and selling them is not a viable option.

Economics: The detailed capital and operating cost of the individual process is listed in table 29. The capital cost for the production of PSA is estimated at \$27.05 million and the operating cost is estimated as \$287.11 million. When combined with p-Xylene process, the capital cost is \$122.44 and the operating cost is \$399.41 million.

Capital cost for PSA process is low as compared to other process, as the solvents are easy to separate. Use of high costing raw materials such as acryloyl chloride and triethylamine increases the operating cost for PSA process. The main contributor for the operating cost for the combined process or PSA and p-Xylene process is the cost of raw materials at 69%. In particular, fraction of raw materials can be further decomposed: 45% from acryloyl chloride and 12% from triethylamine. The total utility cost contributes 17% to the overall cost for PSA production. As heat integration is not applied the cost of utility is high as compared to other processes. The detailed fractions are given in figure 30.

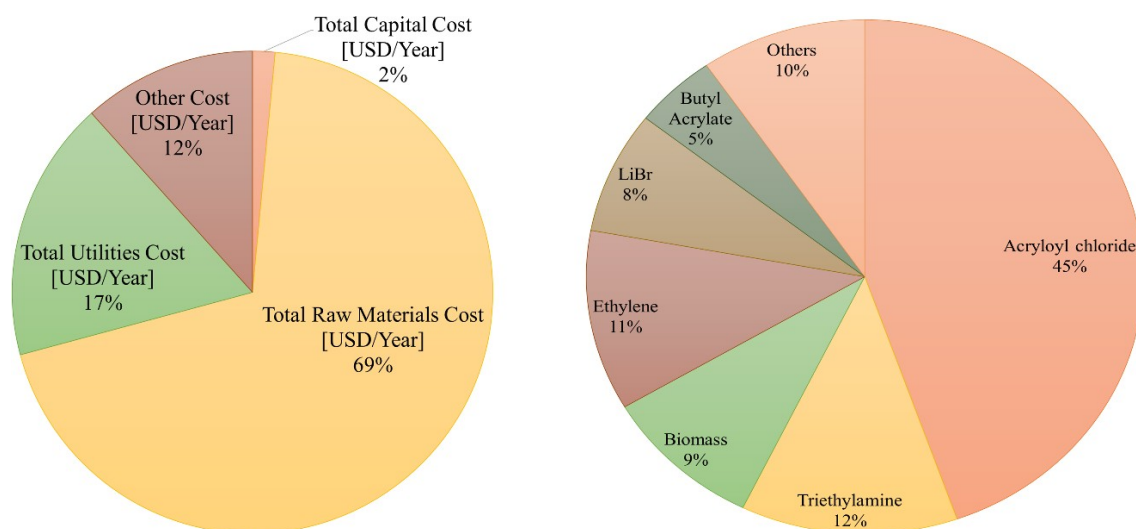


Figure 30: Overview of cost and impact of raw materials on selling price of chemicals a) Butadiene process b) Surfactant process c) Jet-fuel process and (d) Lubricants process.

In the base case scenario, where only the individual process is taken, the minimum selling price of PSA is \$8,293/metric ton. If p-Xylene process is coupled, the minimum selling price of PSA increases to \$8,554/metric ton which is an increase of 3%. If the value of furfural at \$1,000/metric ton is considered, then the economics are substantially improved. The minimum selling price of PSA is calculated to be \$6,654/metric ton which is a decrease of 19.76%.

Table 29: Summary of the Capital and Operating Cost of the PSA Process.

Item	Cost (Million \$)	Item	Cost per year (Million \$)
Purchased Equipment	62.05	Total Catalyst Cost	10.12
Other	38.65	Total Raw Materials Cost	251.1
General and Administrative Overheads	2.82	Total Utilities Cost	70.98
Contract Fee	3.02	Operating Labor Cost	2.57
Contingencies	10.07	Maintenance Cost	3.18
Working Capital	5.83	Operating Charges	0.64
Total Capital Cost	122.44	Plant Overhead	2.87
		General and Administrative Cost	27.95
		Total Operating Cost	399.41

Integrated Process: We have also carried out techno-economic analysis of an integrated bio- refinery where all the process has been combined. Figure 31 shows the map of bio-refinery proposed. In the above figure, the biomass is first depolymerized to separate lignin and cellulose/hemi-cellulose. Lignin is used for PSA production and the cellulose/hemi-cellulose is used for production of p-Xylene. Furfural produced is used to produce different chemicals such as butadiene, surfactants, jet-fuels and lubricants. The flowrate of furfural is divided into 1:1:2:1 ratio to butadiene, surfactants, jet-fuels and lubricants respectively. The capacity of the process is considered the same which is 400,000 metric ton of biomass per

year. The integrated bio-refinery produces 35,200 metric ton of lubricants per year, 81,312 metric ton of p-Xylene per year, 5,441 metric ton of butadiene per year, 5,600,414 gallons of jet-fuels per year, 22,134 metric ton surfactants per year and 15,659 metric ton of lubricants per year. Syngas, the only by-product formed, is used for electricity production. 1,831,258 kWh/yr. of electricity is produced from syngas. The capital and operating cost for the bio-refinery is \$194.45 million and \$512.61 million. The detailed costing is given in table 30.

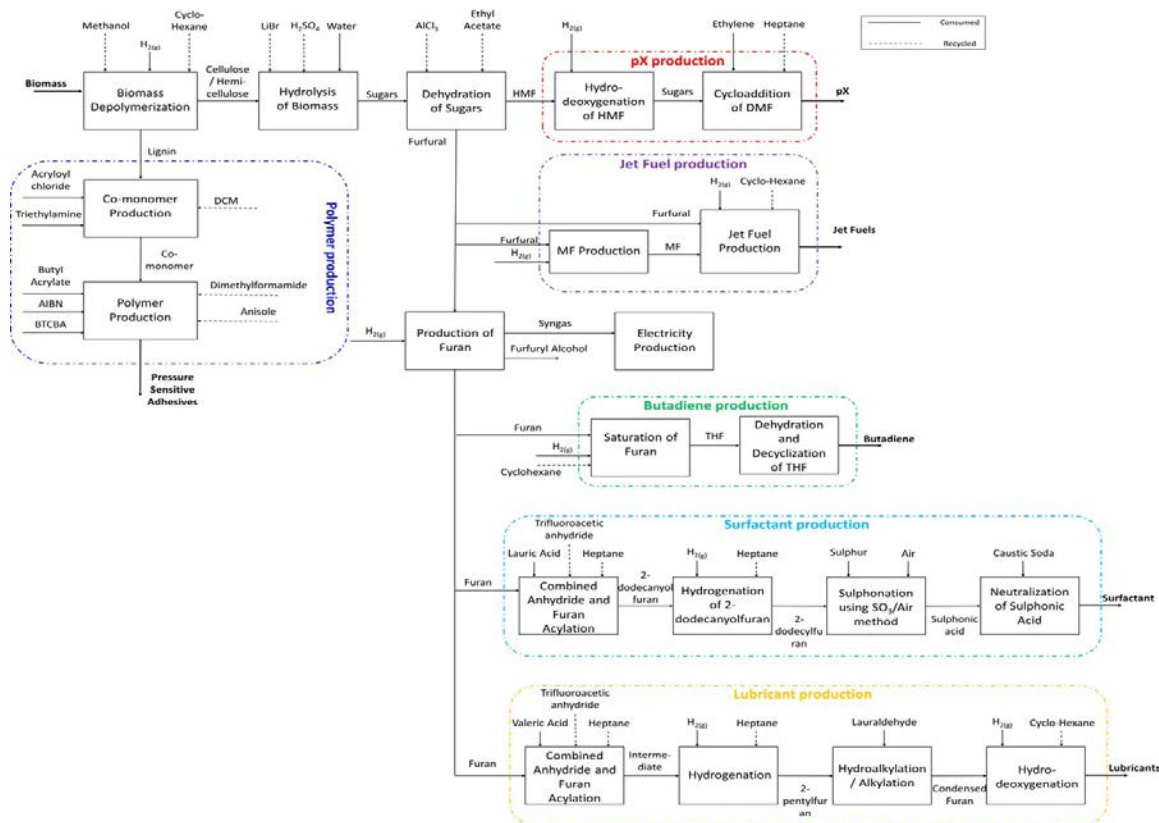


Figure 31: Bio-refinery map.

For calculating the minimum selling price of a product, we assume that the selling price of p- Xylene is kept constant, which is \$1,477/metric ton, as well as, we have to assume the cost of all the remaining products, which is calculated in the above chapters. The minimum selling price of butadiene is negative, which states that butadiene does not have a minimum

selling price and can be sold at any price. Similarly, the cost of surfactants, jet-fuels, lubricants and PSA are \$1,120/metric ton, \$2.52/gallon \$4,480/metric ton and \$8,405/metric ton respectively.

Table 30: Summary of the Capital and Operating Cost for the bio-refinery.

Item	Cost (Million \$)	Item	Cost per year (Million \$)
Purchased Equipment	129.03	Total Catalyst Cost	11.32
Other	30.89	Total Raw Materials Cost	374.07
General and Administrative Overheads	4.48	Total Utilities Cost	80.34
Contract Fee	4.80	Operating Labor Cost	3.96
Contingencies	15.99	Maintenance Cost	6.24
Working Capital	9.26	Operating Charges	0.99
Total Capital Cost	194.45	Plant Overhead	4.95
		General and Administrative Cost	30.73
		Total Operating Cost	512.61

5 Repurposing of food waste to an integrated bio-refinery

5.1 Introduction

Global food waste (FW) is currently estimated to be 1.3 billion tons annually^[89], roughly one-third of global food production. With increasing global population, the estimated number of FW will definitely increase in the future. Approx. 1 trillion worth of food with an energy content of 26 ExaJoules is wasted annually^[90]. FW is the third largest contributor to greenhouse gas if it was considered a country, behind China and United States^[89]. Recently, the United States Department of Agriculture (USDA), the Environmental Protection Agency (EPA), and the Food and Drug administration (FDA) signed a federal interagency strategy to reduce and redirect food waste away from landfills^[91]. According to the United State Department of Energy^[92], “An expanding bioenergy industry must be sustainable, addressing environmental, social, and economic aspects of sustainability along the entire bioenergy supply chain”. Together with lignocellulosic biomass and FW resources, a bio- refinery can produce both low value fuels as well as high value chemicals, which can boost global economies^[11, 93]. Therefore, repurposing FW into chemicals can have tremendous environmental, economic, and ecological impact.

In this work, we evaluate the economics of producing chemicals esp. HMF from waste potato peels(PPW). We develop a multi-conversion process step: PPW extraction to recover extractives for antioxidants’ production, hydrolysis combined with simultaneous glucose dehydration into 5- hydroxymethyl furfural (HMF) and pyrolysis of the residual lignin into biochar for treating pesticide contaminated water. This introduces a new strategy for repurposing FW in an integrated biorefinery where FW and lignocellulose can be (co-)processed to produce a slate of products analogous to a conventional refinery.

Assumptions to perform the simulation and results from TEA are discussed are then calculated and discussed.

5.2 Methodology

Simulation and Economics

Simulation: Aspen Economic Analyzer® V8.8.2 is used to simulate the production process of pressure sensitive adhesive. NRTL method is utilized to predict the liquid-liquid and liquid-vapor behavior. Most of components involved in the reactions are directly selected from Aspen database, whereas some not included in the database (i.e. components of biomass and humins) are defined by the structures and the properties used by NREL^[30]. All the missing parameters are estimated by the molecular structures using the UNIFAC Model and Thermo Data Engine (TDE). TDE is a thermodynamic data correlation, evaluation, and prediction tool developed by the collaboration of Aspen plus and the National Institute of Standard and Technology^[18]. To enable the process simulation, the following assumptions are made:

1. Composition of PPW is assumed and is shown in table 31.

Table 31: Composition of PPW.

Components	Amount in wt. %
Ash	9
Extractives	25
Starch	35
Glucan	15.5
Xylan	1
Galactan	2

Acetate	0.5
Lignin	12

2. Filtration processes to separate extractives and carbohydrates and unreacted biomass from the combined hydrolysis and dehydration process are assumed to have 99% separation efficiency.
3. The by-products do not affect the conversion and selectivity of any reactions. No separation steps are considered before hydrolysis reaction.
4. We assume that there is no mixing between the organic and aqueous phase in the one pot reactor.
5. The yield and reaction conditions of all the reactions are shown in table 32.

Table 32: The Specification of reactions for repurposing PPW.

Process	Hydrolysis	Dehydration	Pyrolysis
Catalyst	LiBr + H ₂ SO ₄	AlCl ₃	N/A
T (°C)	160	160	1000
P (bar)	20	20	1
Conversion(%)	85	40	-

Economics: Aspen Economic analyzer V8.8 is used to perform an economic assessment for the bio-refinery. Some additional assumptions are necessary to perform the economics analysis as outline below:

1. Plant capacity is assumed as 100 metric tons per hour of potato peels feedstock.
2. All the equipment and operating costs estimated by Aspen Economic Analyzer V8.8 are based on the price of the first quarter in 2014. The filtration units are not explicitly designed, and the design is based only on the flowrates.

3. The cost of the peels is taken as zero.
4. The plant operates in a continuous mode for 8,000 hr. per year. The economic life of the project is assumed to be 20 years. 15% per year interest rate is applied to the capital cost. 35% corporate tax is applied to the profits. The simplest depreciation method – the straight-line method is applied as the salvage value – is 10% of the original capital cost after 20 years. The recovery period is considered as 10 years.
5. The market price of the raw materials is given in Table 33.

Table 33: Market price of raw materials.

Components	Cost (\$ per ton)
Methanol	504 ^[94]
Aluminium Chloride	600 ^[35]
2-butanol	988 ^[35]
LiBr	1400 ^[35]
Sulphuric Acid	250 ^[55]

6. The market price of the products is given in Table 34.

Table 34: Market price of products.

Components	Cost (\$ per ton)
Extractives	35,000 ^[55]
HMF	1,000 ^[95]
Bio-Char	2,580 ^[96]

7. The cost of ultrasonic mixer is taken as that of the cost of a static mixer. Costing of the pyrolysis reactor is taken as 20% of the equipment cost (not including the cost of heat exchangers).
8. Heat integration is carried out using the Aspen Energy Analyzer® V8.8.2, which uses

- the pinch analysis method for heat integration. The lowest operating cost scenario is considered for heat integration. All the utilities are purchased, and wastewater is treated by a third party at a fixed price per unit volume^[31].
9. Three profitability metrics were calculated (Equations 1 – 6)^[97] to evaluate the feasibility of the biorefinery: return on Investment (ROI), payback time, and breakeven.
 10. The ROI is the ratio of gains to cost and it measures (in %), per period, the rate of return on money invested in the biorefinery. A positive ROI means that the investment gains compare favorably to the costs; the larger the ROI, the better. The payback time is the time needed for the gains from the investment to equal the costs, i.e., for an investment to pay for itself. The smaller the payback time, the better. Breakeven refers to the specific period in which it's the profits from an investment equal its total costs and its net income will be zero.

$$ROI = \frac{\text{Annual Net Profit}}{\text{Total Capital Investment}} \quad (1)$$

$$\text{Payback Time} = \frac{\text{Total Capital Investment}}{\text{Annual Net Profit}} \quad (2)$$

$$\text{Break Even (units)} = \frac{\text{Fixed Costs}}{\left(\frac{\text{Price}}{\text{Unit}} - \frac{\text{Variable Cost}}{\text{Unit}} \right)} \quad (3)$$

$$\text{Depreciation} = \frac{(\text{Capital Cost} - \text{Salvage Value})}{\text{Recovery Period}} \quad (4)$$

$$\text{Net Profit} = \text{Revenue} - (\text{Corporate Tax} + \text{Depreciation} + \text{Interest} + \text{Operating Costs}) \quad (5)$$

$$\text{Fixed Cost} = \text{Utilities Cost} + \text{Depreciation} + \text{Interest} \quad (6)$$

Process Flowsheet

The biorefinery process (Figure 32) starts with the separation of extractives from the carbohydrates and lignin using a water-methanol mixture. The mixture is mixed using an ultrasonic mixer for 15 minutes at room temperature. The outlet stream from the mixer is introduced to a filter to remove the extractant and the solid mixture. A series of flash drums is used to separate methanol and to dry the extractives for a purity of 99%. The solid mixture is first dried and then mixed with water containing LiBr, AlCl_3 and H_2SO_4 and then introduced to a reactor for hydrolysis at a temperature of 140 °C for a residence time of 1 hr. After hydrolysis, the product mixture is mixed with a 2- butanol and introduced in a “one-pot” reactor where simultaneous dehydration reaction and separation of HMF occurs at 160 °C and 20 bar for a residence time of 3 hrs. 80% of the HMF is extracted by the organic phase and is sent to a distillation column for purification. The solvent is recycled. The aqueous phase is filtered to remove the unreacted solids and humins. The liquid phase is then flashed to remove excess water and the liquid is recycled back to the dehydration reactor. The solid phase is used to produce bio-char by pyrolyzing it at 1000 °C. Pyrolysis was simulated as close to possible as literature data and the pyrolysis gasses consist of mostly CO and H_2 with trace amount of CH_4 , CO_2 and C_2H_2 and biochar as the main product. The gas is then used to generate electricity and both the capital costs and the operating costs are included. The cost of pollutant control is assumed in the total cost of pyrolysis reactor. The gas after electricity production consists of CO_2 and H_2O .

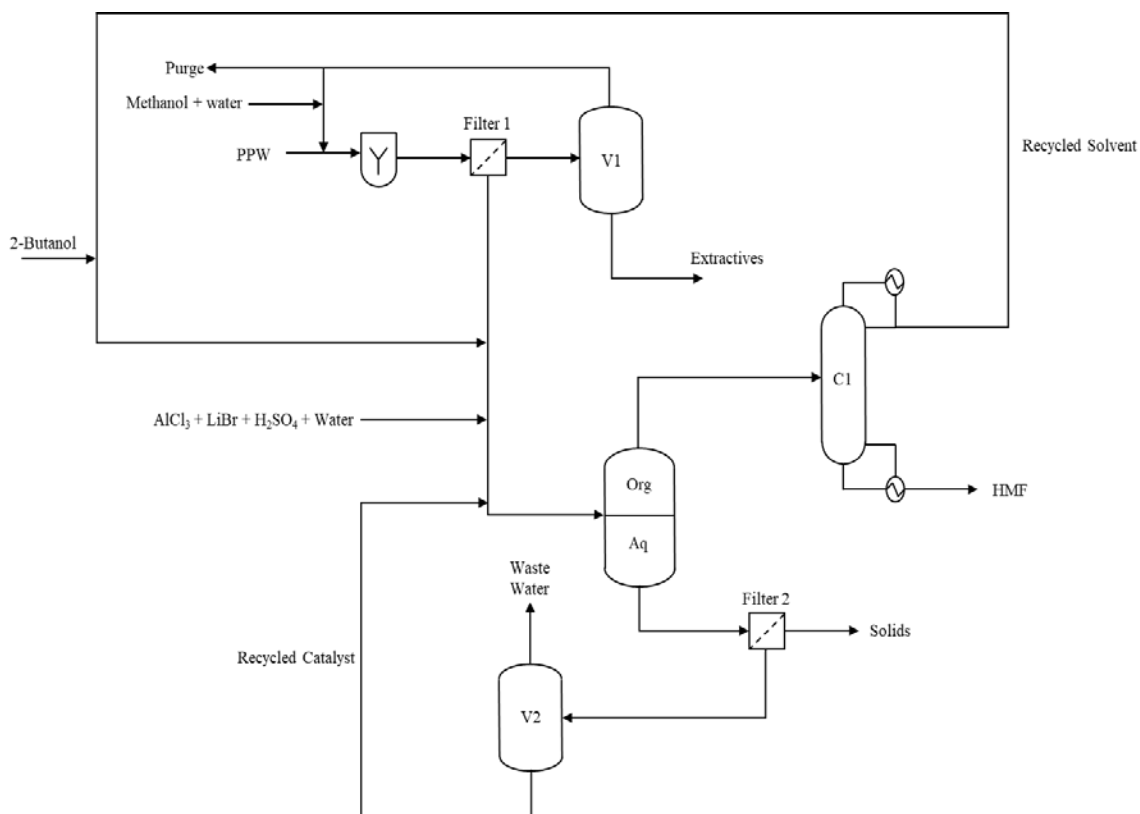


Figure 32: Process Diagram for HMF Production from PPW.

5.3 Results and Discussion

According to the proposed process, 1 MT of dry PPW can be converted to 240 kg of extractives, 130 kg of HMF, and 80 kg of biochar (Fig. 33a). These yields are significantly higher than those obtained by other technologies, such as the production of ethanol (348 kg of ethanol per MT PPW or 34.8 wt. % yield)^[98] or of lactic acid (250 kg of lactic acid per MT PPW or 25 wt. % yield)^[99]. Mass balances and utility consumption are given in Tables 35 and 36, respectively. The capital and operating cost is given in Table 37 and depicted in Figure 34, with breakdown costs in Table 38.

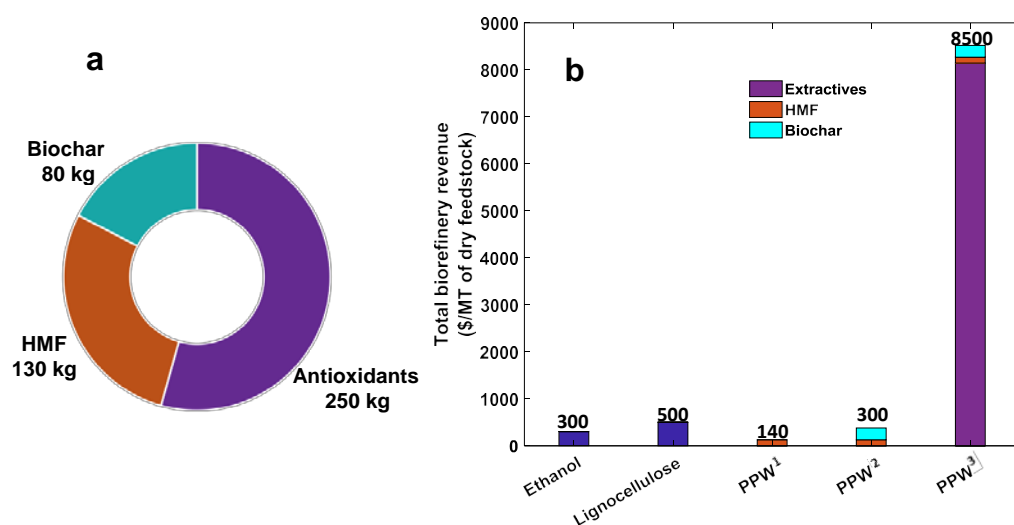


Figure 33: Results of techno-economic analysis. a, Product distribution from PPW biorefinery. b, Economic comparison of different integrated biorefineries. PPW¹ assumes HMF is the only product, PPW² assumes HMF and biochar are the only products, PPW³ assumes production of extractives, HMF and biochar.

Table 35: Material Balance.

Process Step	Stream Name	Mass Flow (kg/hr.)
Extraction	Methanol + Water	1,776,069
	PPW	100,000
	Filter Outlet – Liquid	166,449
	Filter Outlet – Solid	218,336
	Dried Solid	76,336
	V1 – Vapor	1,775,708
	V1 – Liquid	24,027
	Purge	18
Combined hydrolysis and dehydration	LiBr + AlCl ₃ Mixture	2,286,250
	2-butanol	5,464,180
	Reactor - Organic Phase	5,476,470
	Reactor – Aqueous Phase	2,552,064

	Filter 2 – Solids	83,031
	Filter 2 – Liquids	2,469,027
	Recycled Solvent	5,463,630
	HMF	12,839
	Waste Water	1,860
	Recycled Catalyst	2,467,167

Table 36: Utility Consumption.

Utility	Load (KJ/hr.)
Cooling Water	22,405,714,843
LP Steam	1,189,941,795
MP Steam	1,370,113,257
HP Steam	2,130,434,781
Fired Heater	136,822,812
Electricity	11289.57 KW

Table 37: Summary of the capital and operating costs of the HMF process.

Item	Cost (Million \$)	Item	Cost per year (Million \$)
Purchased Equipment	434	Total Raw Materials Cost	71.6
Other	27.6	Total Utilities Cost	136.7
General and Administrative Overheads	12.9	Operating Labor Cost	0.9
Contract Fee	13.9	Maintenance Cost	11.1
Contingencies	46.2	Operating Charges	0.2
Working Capital	26.7	Plant Overhead	6.0
Total Capital Cost	561.3	General and Administrative Cost	8.0

		Total Operating Cost	234.6
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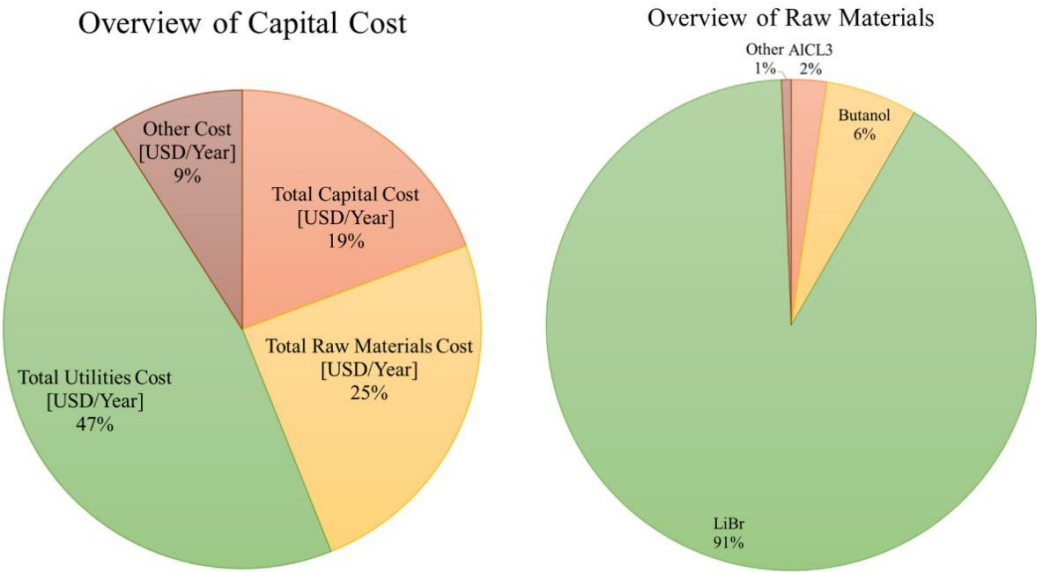


Figure 34: Figure 34: Overview of cost and impact of raw materials.

Table 38: Breakdown of Costs.

Process Step	Capital Cost (MM\$)	Operating Cost (MM\$)
Extraction Step	1.95	0.17
Combined Hydrolysis and dehydration step	105.5	71.46
Pyrolysis	26.7	
Heat exchangers	264	
Electricity Production	9.58	
Utilities		136.7
Total Equipment Cost	398.15	
Total Capital Cost	561.3	
Total Operating Cost		234.6

Around 60% of the capital cost is attributed to heat exchangers. Utility costs (primarily for heating reactors and biochar manufacture via pyrolysis) account for 59% of the operating cost. A lower pyrolysis temperature will result in less energy requirement and lower utility cost. Among processing steps, the hydrolysis and dehydration are the highest contributors to the operating and annualized capital costs. The capital costs can be reduced by better heat and energy integration within the plant.

We further compare the energy requirements for different biorefineries (Table 39 and Table 40). The energy requirements for biochemical based biorefineries, leading to ethanol^[100, 101] and biogas^[102, 103], are much lower than biorefineries involving thermochemical transformations in the proposed FW-based and lignocellulose-based biorefineries^[55] leading to more diverse bioproducts. The use of low fermentation temperatures (30 – 45 °C) and ambient pressure reduces utility costs. However, ethanol and biogas are high volume but low value products^[104], whereas molecules like furans and their derivatives, e.g., lubricants, are much more complex, lower volume/higher value products. Furthermore, biochemical transformations are inherently slow, requiring large reactors whereas thermochemical transformations of biomass can be very fast^[105] and thus amenable to mobile processing. We use the ratio of revenue to energy input (REI) to compare these different refineries. This provides a fair comparison between the value of biorefinery products and energy required to make the products. Our FW biorefinery has a high REI ratio (Table 39) across the different biorefineries (almost three times that of a lignocellulose based biorefinery). This shows that high energy inputs (Table 40) required to manufacture high value products can be justified by the revenue made from sales. Efforts towards lower energy production of high value bioproducts should be a target for further biorefinery

development.

Table 39: REI ratios for different biorefineries.

Biorefinery Type	$\frac{Revenue}{E_{Input}}$ (REI) \$/MJ
Food Waste	0.0310
Lignocellulose	0.0104
Cellulosic Ethanol	0.0173
Anaerobic Digestion	0.0191

Table 40: Parameters used in computing REI ratios.

	Energy Input	Product	Unit price of product	Product Yield	Basis
Lignocellulose	1,116,000 KJ/s ^[55]	Cellulose pulp, furfural, lignin	\$ 700/ton ^[55]	700 kg/ ton feedstock ^[55]	0.0232 ton feedstock/s ^[55]
Ethanol	81,090 KJ/gal ^[100]	Ethanol	\$ 1.4/gal ^[106]	112 gal/ ton feedstock ^[100]	0.01 ton of feedstock ^[103]
Anaerobic Digestion	59,400 KJ/ ton feedstock ^[103]	Biomethane	\$ 2.3/1000 ft ^[107]	492 ft ³ / ton feedstock ^[103]	1 ton feedstock ^[103]

The overall revenue of the process is \$6,779 million per year, equivalent to \$8,470 per metric ton of dry PPW and results in a return on investment (ROI) of 5.8. Other economic profitability indices reveal a payback period and break-even time of 0.17 and 0.15 years, respectively, making the technology very attractive for investment. The best-case scenario uses an antioxidant market price of \$35/kg. For a worst-case scenario, the minimum extractive price (MEP) for net profit > 0 was calculated to be \$8/kg. Payback period was calculated for various values of MEP (Fig 35). From the figure, there is a transition from high to low price sensitivity (observing the change in slope) around a MEP of \$9.5 suggesting that as a good extractive selling price. At a MEP OF \$12, the payback period equals 1 year (annual net profit = total capital investment). While current economic estimations are made at current market price for antioxidants, there is a likelihood of price reduction driven by a glut effect from bio-based antioxidants flooding the market.

Therefore, two scenarios excluding the extractive fraction are evaluated. In the first scenario, HMF is taken as the only product and in the second scenario, HMF and biochar are the only products. With the biorefinery operating under these scenarios, the economics still compares favorably with other biorefinery processes. For the scenario including extractives production, the crude as obtain extractives yield is used in the TEA and economic calculations. Depending on the final application (dietary supplements, cosmetics, lubricants or polymers), further purification of the extractive product will increase the operating cost, reduce the overall revenue and increase the ROI. Therefore, a TEA on a pilot-scale of the technology would help substantiate these preliminary estimates. Reducing the extract selling price by 50% lowers the ROI to 2.1 and increases the payback period to 0.5 years. Including a “cost” for PPW, at a price of \$100 per MT of PPW, indicates that the total cost of raw materials doubles (increases by 112%), with the PPW cost being the main contribution, while the net profit reduces by only 2% and the payback period increases from 0.13 to 0.14 years. These results indicate that the predictions are robust and independent of whether PPW is free of charge or not. The operating cost increases by 12.4% by accounting for 1% mixing of the organic phase into the aqueous phase. In order to enhance the overall revenue of the biorefinery, increasing the HMF yield (Figure 36) would be a more attractive, rather than an equivalent increase in glucose yield.

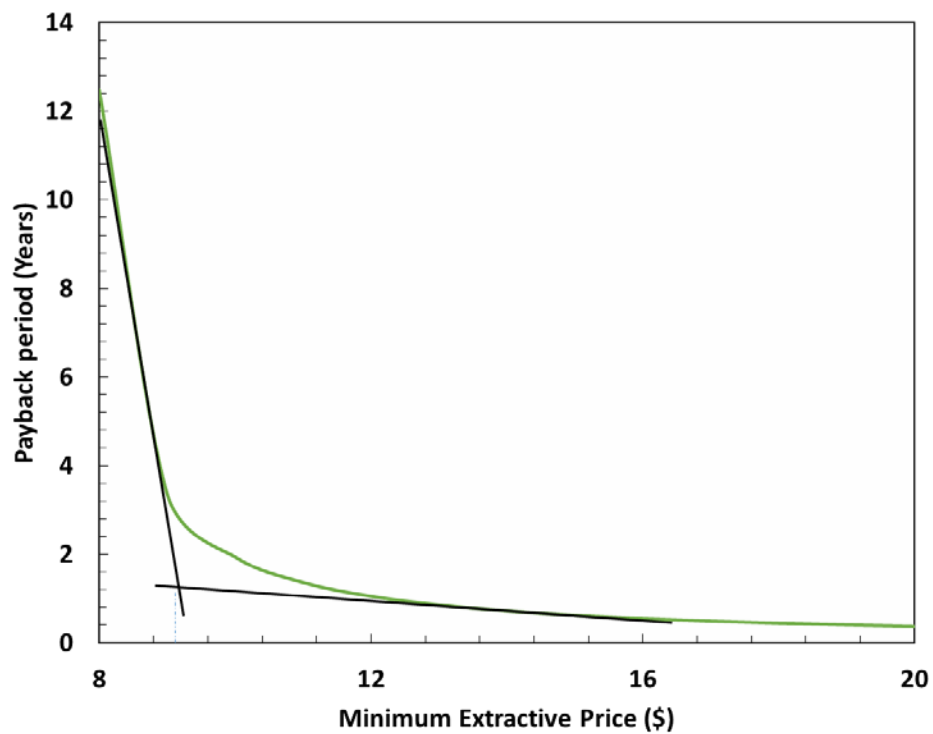


Figure 35: Variation in payback period duration as a function of minimum extractive price.

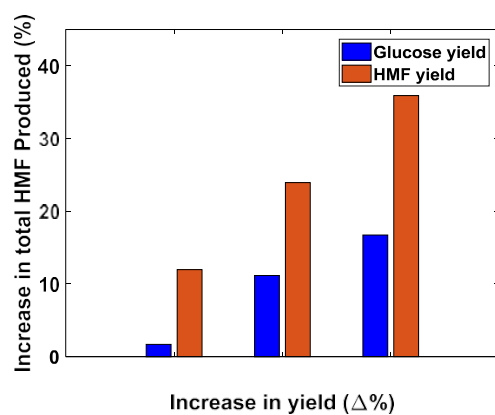


Figure 36: Sensitivity Analysis (SA) for change in yield of glucose and HMF.

6 Optimal Bio-refinery Configuration Considering Economic and Environmental Aspects with Supply, Demand and Process Uncertainties using Multi-objective Optimization

6.1 Introduction

In previous chapters, we developed a bio-refinery map for the production of different chemicals and fuels and carried out techno-economic analysis to calculate the minimum selling price. As different chemicals are being produced, it is difficult to calculate the minimum price of each chemicals and have to assume the price of some chemicals to calculate a price of a given chemicals. Moreover, as various chemicals are being produced, the selling price can be changed to maximize the total profits keeping the impacts of environmental impacts to a minimum. Hence, we propose an optimization problem to tackle the given problem using multi-objective optimization.

Multi-objective optimization is used to solve optimization problem which involves more than one objective function to be optimized simultaneously. Multi-objective optimization is an area of multiple criteria decision making, that is concerned with mathematical optimization problems involving more than one objective function to be optimized simultaneously^[108]. This tool gives a set of solutions that gives a best trade-off between the two objectives. A pareto-optimal front is obtained which is a boundary defined by the set of all points in a feasible decision space. For this problem, two objectives; minimizing the minimum selling price to maximize the profit and minimizing the environmental impacts for the above designed bio-refinery.

From an economic point of view, extensive work has been carried out. Selection of different biomass feedstock is a critical factor in the viability of bio-based chemical

production. A study developed a systematic procedure for scheduling and operation of flexible biodiesel plants accommodating a variety of feedstocks^[109]. Another study introduces a shortcut method for the synthesis and screening of integrated biorefineries^[110]. Additionally, a study proposed a systematic approach for the optimal production planning and facility placement of a biorefinery^[111]. Azapagic and Clift introduced a decision-making process whereby a system is simultaneously optimized on a number of environmental objective functions, defined and quantified through the LCA approach^[112]. Another study presented a mathematical programming-based methodology for the explicit inclusion of life cycle assessment (LCA) criteria as part of the strategic investment decisions related to the design and planning of supply chain networks^[113].

We can see that all of the above studies have not considered simultaneously minimization of the overall environmental impact and maximization of the total annual profit. A novel optimization model through a mathematical programming formulation for the optimal selection of feedstocks, processing technology and a set of products is proposed^[114] where simultaneous consideration of maximization of profit and minimization of environmental impact in the objective function. The economic objective function considers the availability of bioresources, processing limits, and demands of the products in a specific region as well as the costs of feedstocks, products, and processing routes, while environmental assessment includes the overall environmental impact measured through life cycle analysis methodology using Recipe midpoint method.

6.2 Methodology

The problem can be described as given a set of available feedstocks, which can be converted into different products through different processing routes, where there is not

necessarily a single option to obtain the required products. Thus, each processing route is associated to an efficiency of feedstocks to products and an efficiency for feedstocks to byproducts identified as conversion factors (α , β and γ). The superstructure for problem specifically for our bio-refinery design is presented in Figure 37. The indexes used in the model formulation is described below: m is the type of feedstock, $r1$ is the intermediate processing route, $k1$ is the intermediate with $k11$ and $k12$ as the by-product, $r2$ is the final processing route and $k2$ is the final product and $r21$ is the final processing route for the by-product intermediates and $k21$ is the final product from the by-product intermediate.

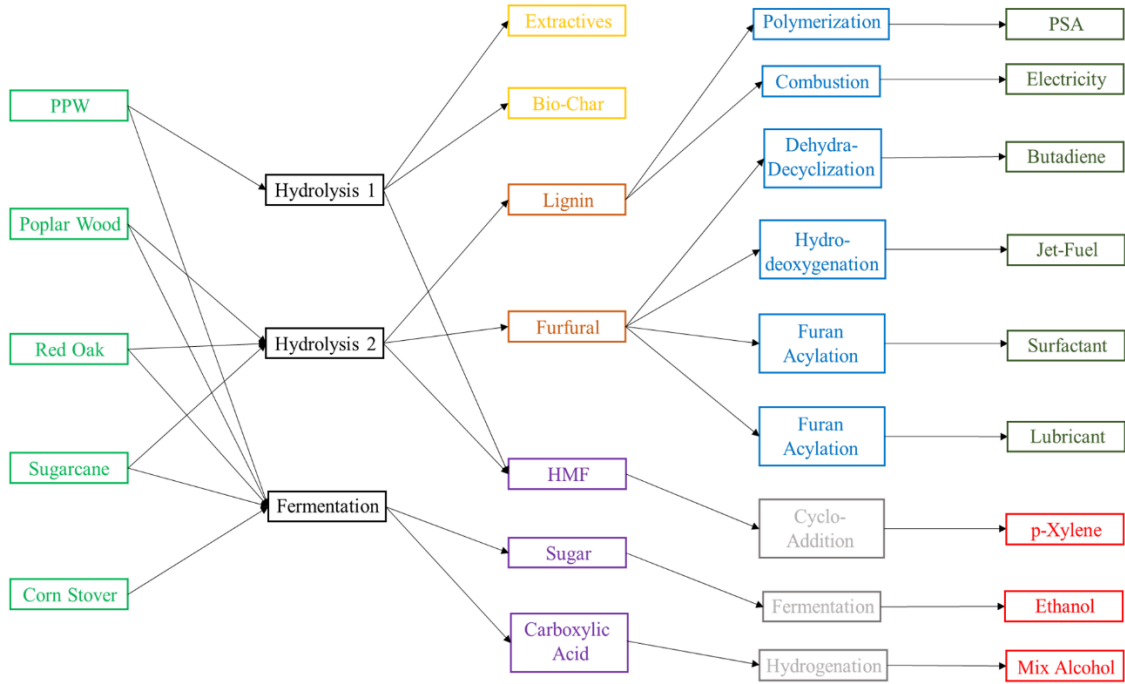


Figure 37: Superstructure for optimal planning of bio-refinery map.

For the intermediate product $k1$ produced from the raw material m through route $r1$, the mass balance can be stated as follows

$$P_{k1}^1 = \sum_m \sum_{r1} F_{k1mr1}^{bio} * \alpha_{k1mr1}^1, \forall k1$$

Where P is the formation of intermediate/product, F is the flowrate of biomass and α is the conversion factor. Similarly, for the intermediates by-products $k11$ and $k12$ through route $r1$, the mass balance is as follows

$$P_{k11}^{11} = P_{HMF}^1 * \beta_{k11mr1}^1, \quad \forall k11$$

$$P_{k12}^{12} = P_{HMFHyd1}^1 * \gamma_{k12mr1}^1, \quad \forall k12$$

Where β and γ are the conversion factor. For the intermediates, we can either further process it to produce more valuable end products or sell it directly to the market which can be shown as follows

$$P_{k1}^1 = \sum_{k2} \sum_{r2} F_{k2k1r2}^2 + F_{k1}^3, \quad \forall k1$$

$$P_{k11}^1 = \sum_{k21} \sum_{r21} F_{k21k11r21}^4 + F_{k11}^5, \quad \forall k11$$

$$F_{k1}^3 \leq P_{k1}^1, \quad \forall k1$$

$$F_{k11}^5 \leq P_{k11}^1, \quad \forall k11$$

Where $F3$ and $F5$ are the flow of intermediates which can be sold to the market. The mass balance for the end product produced from the intermediate product is given as

$$P_{k2}^2 = \sum_{k1} \sum_{r2} F_{k2k1r2}^2 * \alpha_{k2k1r2}^2, \quad \forall k2$$

$$P_{k21}^{21} = \sum_{k11} \sum_{r21} F_{k21k11r21}^4 * \beta_{k21k11r21}^2, \quad \forall k21$$

Besides the mass balance, some constraints have to be considered for

- 1) Maximum Available Raw Materials: The availability of the raw materials is region specific and is different for different feedstock. The maximum availability constraints can be stated as the sum of the quantities of the feedstock used in the manufacture of each product through each processing route, and it must be lower than the total amount of the feedstock

available. These constraints are stated as follows

$$F_m^{max} \geq \sum_{k1} \sum_{r1} F_{k1mr1}^{bio}, \forall m$$

Where, F_m^{max} is the maximum amount available for biomass feedstock m and is a parameter known prior to the optimization process.

- 2) Maximum Products Demand. Another constraint considers the product demand to prevent higher production rates than necessary to avoid waste of sources and to guarantee its consumption

$$P_{k2}^2 \leq Pp_{k2}^{max}, \forall k2$$

$$P_{k21}^2 \leq Pp_{k21}^{max2}, \forall k21$$

Where, Pp_{k2}^{max} and Pp_{k21}^{max2} is a parameter that represents the maximum demand from product k2 and k21.

- 3) Maximum Processing Limits. Finally, further constraints involve processing feedstock limits associated with a processing route and, as a consequence, to specific equipment. These constraints are only for upper limits which are the maximum amount of feedstock for each processing technology

$$P_{k1mr1}^{max} \geq F_{k1mr1}^{bio} * \alpha_{k1mr1}^1, \forall k1$$

Where, P_{k1mr1}^{max} is the maximum amount of intermediate product k1 that can be produced from biomass feedstock m through technology r1.

- 4) We also have a constraint that the minimum amount of each biomass used is atleast 1 t/h or 8000 t/y.

As stated above, the objective function should consider simultaneously maximization of the total profit and minimization of the overall environmental impact.

$$objective\ function = [\max profit; \min EI]$$

Where profit is the total profit generated by the sale of products minus the capital and operating costs, whereas EI is the total environmental impact of the intermediate and final products. The capital and operating costs is taken from above work for the specified chemicals produced through techno-economic analysis and the environmental impact is calculated via life cycle analysis.

Economic Objective. The economic objective function is formulated in terms of the total annual profit. This function considers the costs of feedstocks, products, byproducts, and processing routes and is stated as follows

$$\begin{aligned}
 Profit = & \sum_{k2} P_{k12}^{12} * C_{k12}^{p12} + \sum_{k1} F_{k1}^3 * C_{k1}^{I1} + \sum_{k1} F_{k11}^5 * C_{k11}^{I11} + \sum_{k2} P_{k2}^2 * C_{k2}^{p2} \\
 & + \sum_{k21} P_{k21}^{21} * C_{k21}^{p21} - \sum_{k1} \sum_m \sum_{r1} F_m^{bio} * C_m^{bio} - \sum_{k2} \sum_{k1} \sum_{r2} P_{k2}^2 * C_{k2k1r2}^{Pro2} \\
 & - \sum_{k21} \sum_{k11} \sum_{r21} P_{k21}^{21} * C_{k21k11r21}^{Pro21}
 \end{aligned}$$

Where, C^p is the market price of final product, C^I is the market price of intermediate product, C^{bio} is the market cost of biomass, C^{Pro} is the processing cost of intermediate/final product.

Environmental Objective. The environmental objective function is formulated in terms of social cost of carbon emission and water depletion and is given as

$$\begin{aligned}
 E.I. = & \left(\sum_{k1} F_{k1}^3 + \sum_{k11} F_{k11}^5 + \sum_{k12} P_{k12}^{12} + \sum_{k2} P_{k2}^2 + \sum_{k21} P_{k21}^{21} \right) * SC \\
 & + \left(\sum_{k1} F_{k1}^3 + \sum_{k11} F_{k11}^5 + \sum_{k12} P_{k12}^{12} + \sum_{k2} P_{k2}^2 + \sum_{k21} P_{k21}^{21} \right) * WC
 \end{aligned}$$

Where, SC is the social cost of carbon emission and WC is the social cost of for water depletion

To solve the objective function, ϵ -constraint method is used. ϵ -constraint method keeps one

of the objectives and restrict the other objective with specified values. For this work, we restrict the EI objective to a specific value. To get the values of ε , we first solve minimization problem to obtain a limit for the pareto curve. Next, we solve the maximization problem to obtain another limit of the curve. Once the extreme solutions are found we can obtain the pareto curve by solving the equation below for different values of ε .

6.3 Results and Discussion

The problem stated is solved using multi-objective optimization and the pareto curve obtained is shown in figure 38. The two extreme points are designated as scenario A, where we have zero annual profits and minimum environmental impact, and scenario C, where we have maximum profit and maximum environmental impact. We also consider a midway point called scenario B, where we have intermediate annual point and intermediate environmental impact. Figure 39-41 shows the bio-refinery configuration for all the three scenarios.

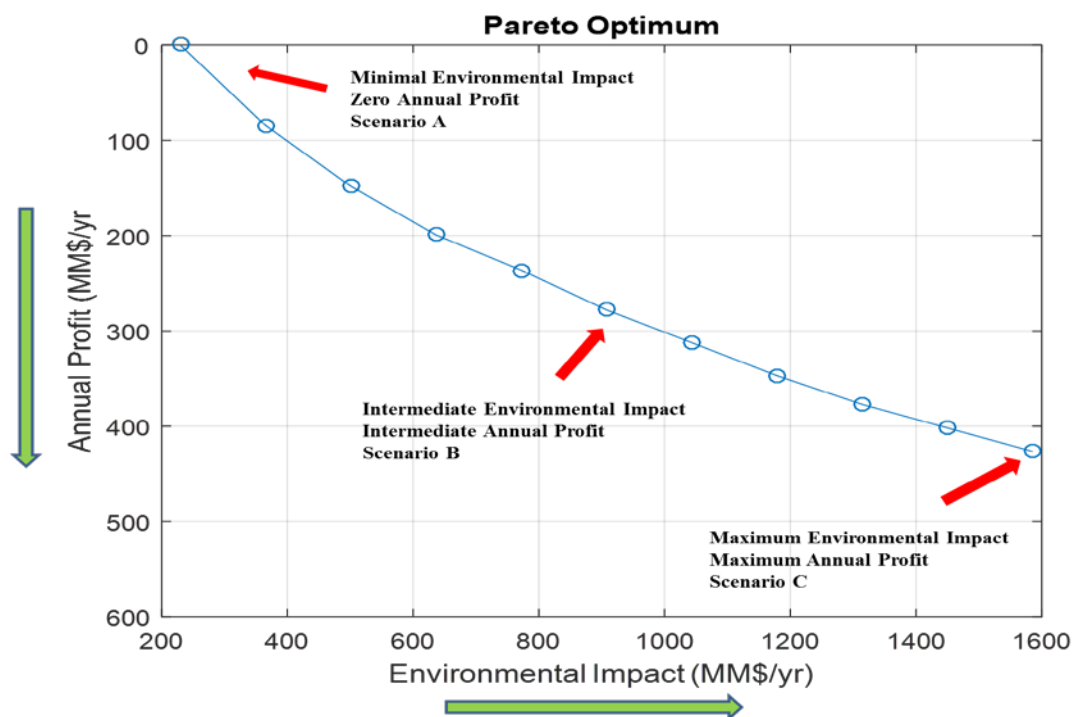


Figure 38: Pareto Optimum curve.

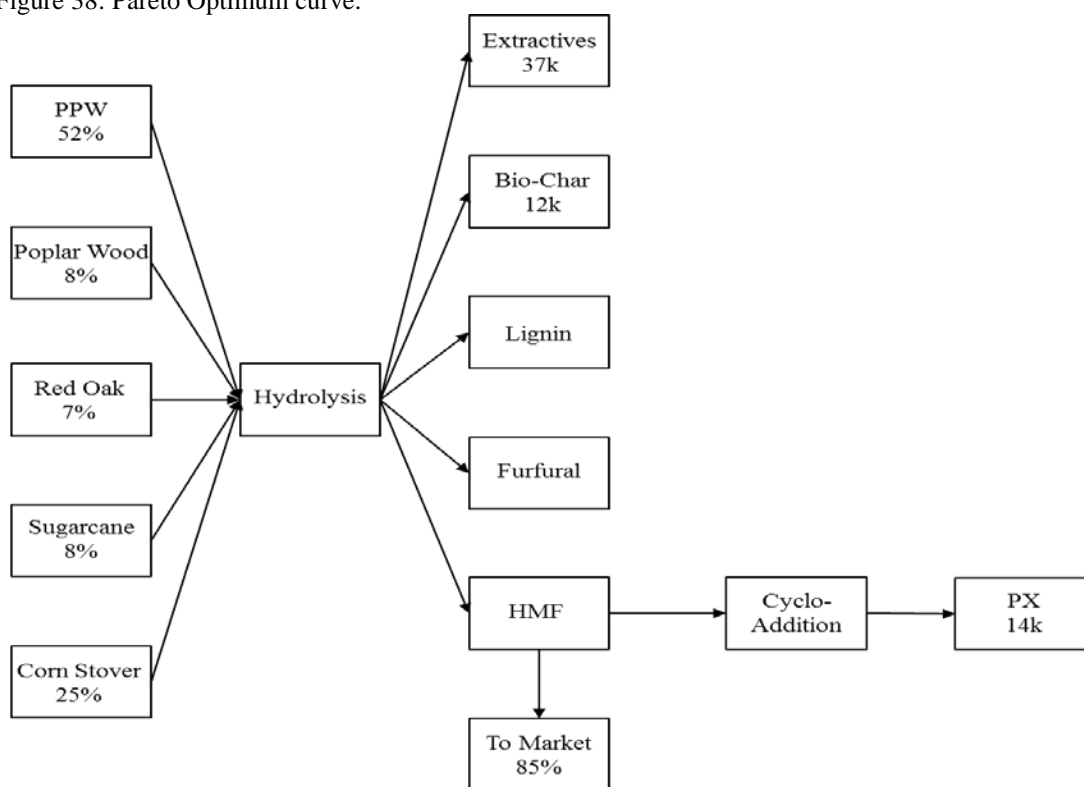


Figure 39: Bio-refinery Configuration for the scenario A.

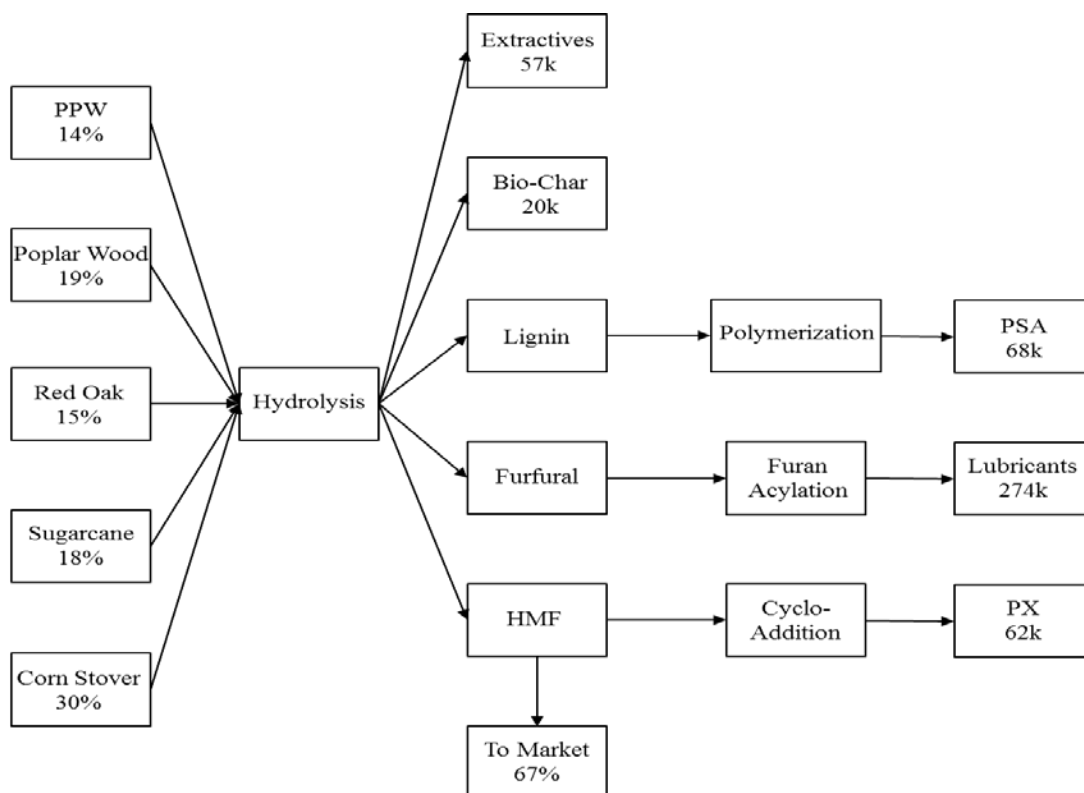


Figure 40: Bio-refinery Configuration for the scenario B.

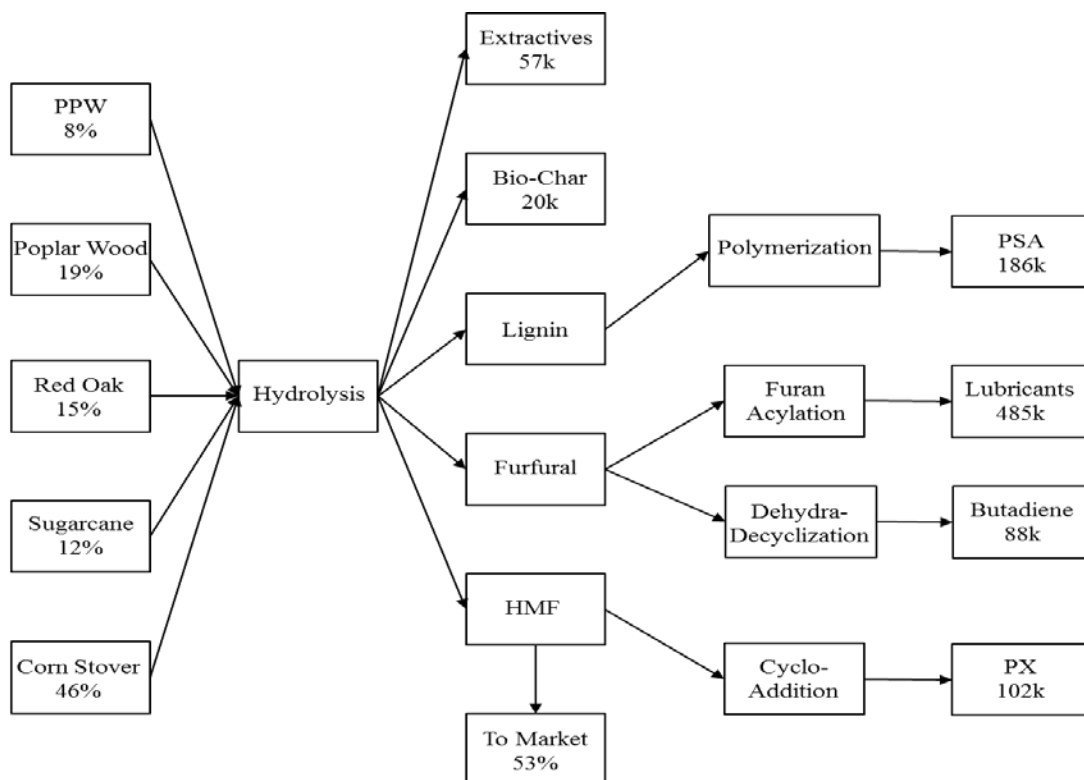


Figure 41: Bio-refinery Configuration for the scenario C.

The capacity is relatively low to keep the impacts to a minimum. For scenario C, the capacity is the highest when compared to all the three scenarios. Aside from extractives, PSA and butadiene are the most profitable and hence the problem produces both these chemicals.

Corn Stover is the most available biomass and hence the problem maximizes the usage of it. For scenario B, the capacity is between the two extremes. We are producing PSA although the quantity is less when compared to scenario C. Butadiene has the highest impacts on the environment, thus, we are not producing it. Corn Stover is still the highest contributor to the overall biomass.

Table 41: Scenario Analysis result.

	Base (Scenario C)	Increase in cost of corn by 50%	Increase in sugarcane supply by 50%	Decrease in extractives market price by 25%
Capacity (MT/y)	3.56	2.13	3.84	3.1
PPW	8%	18%	6%	8%
Poplar Wood	19%	20%	18%	19%
Red Oak	15%	18%	16%	15%
Sugarcane Bagasse	12%	20%	21%	13%
Corn Stover	46%	24%	39%	45%
Profit	426	282	446	392
EI	1586	987	1674	1372

Table 42: Scenario Analysis result.

	Base (Scenario C)	Increase in cost of potato peels by 50%	No Potato peels available	No Demand of Extractives
Capacity (MT/y)	3.56	3.2	2.3	2.8
PPW	8%	7%	0%	1%
Poplar Wood	19%	15%	15%	20%
Red Oak	15%	18%	14%	16%
Sugarcane Bagasse	12%	20%	20%	18%
Corn Stover	46%	40%	51%	45%
Profit	426	392	280	292
EI	1586	1385	1245	1141

We have carried out scenario analysis and compared it with scenario C to find which parameters affect the configuration of the bio-refinery and is shown in table 41 and 42. For the scenarios where there is uncertainty in availability of potato peels or extractives, the problem decreases the capacity of the bio-refinery which decreases the profits as well as environmental impacts. Corn Stover is still the highest contributor to the total biomass even in the case where the cost increases by 50%. Ethanol and mixed alcohols are never produced as the profit gained from them is far less than specialized chemicals we are producing. We also see that no matter what scenario we analyse, the environmental impact is much higher than the profits indicating that more research has to be conducted in optimizing the processes to be competitive with oil based chemical production. From the above analysis, we see that uncertainties in raw material availability, raw material prices product

demand and conversion can change the configuration and thus change the economics and sustainability significantly. Hence, we carry out a worst-case analysis scenario which can deal with all the uncertainties stated above and still gives us a decent profit with decent environmental impacts. We take the worst-case scenario for all raw material availability decreased by 50%, all raw material price increased by 120%, conversion of biomass to intermediates decreased by 5% and product demand decreased by 50%. The configuration for this scenario (worst case scenario) is shown in figure 42 and compared it with scenario C (Base case) in table 43. The capacity of worst-case scenario is reduced by a large amount when compared to scenario C. Production of extractives is still the most profitable even with for the worst case and the problem tends to produce it the most and thus PPW is the highest contributor to the overall biomass. HMF produced is used to produce lubricants and p-Xylene with 15% of it being sold directly to market

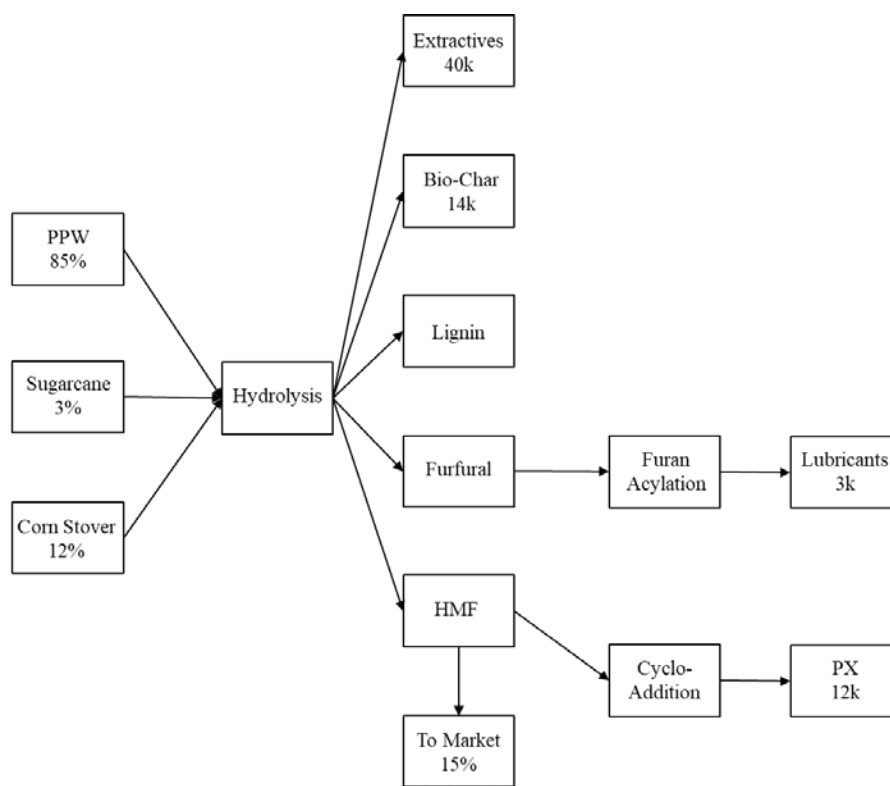


Figure 42: Bio-refinery Configuration for worst case scenario

Table 43: Worst case scenario Analysis result.

	Base (Scenario C)	Worst Case Scenario
Capacity (MT/y)	3.56	1.8
PPW	8%	85%
Poplar Wood	19%	0%
Red Oak	15%	0%
Sugarcane Bagasse	12%	3%
Corn Stover	46%	12%
Profit	426	295
EI	1586	956

Usually for product demand, the uncertainty can be predicted based on previous demands and hence a probability distribution can be obtained to predict the product demand. Two stage stochastic optimization is used where the uncertainties can be obtained by a probability distribution. For the first stage, our main variable is the capacity of the plant and for the second stage our main variable is product volume based on the demand. For this optimization, we assume that the product demand has normal distribution with low standard of deviation. We have two cases: 1) combine with Scenario C 2) combine with worst case scenario. For both the cases, we see almost no change in optimal configuration which suggests that the configuration obtained is fairly stable for the current probability distribution with low standard of deviation as shown in table 43. Only change appears where the probability distribution has significant standard of deviation esp. where there is huge deviation in demand of extractives and demand of PSA, which have the highest

contributor to profits.

Table 44: Two stage stochastic optimization result.

	Base Scenario with 2- Stage	Worst Case Scenario with 2 stage
Capacity (MT/y)	3.42	1.65
PPW	8%	82%
Poplar Wood	19%	0%
Red Oak	15%	0%
Sugarcane Bagasse	12%	6%
Corn Stover	46%	12%
Profit	420	289
EI	1523	914

7 Conclusion and Future work

7.1 Conclusion

With the increasing attention on bio-based chemicals, it is of great importance to assess alternative production routes from a process viewpoint leading to the development of biorefinery, where a general framework is applied implementing process design, simulation, heat integration, life cycle assessment and process optimization which has led to sustained efforts for cost reduction. To lower the price of bio-based p-Xylene, this work integrates the hydrolysis of biomass to the overall process for the production of p-Xylene. A novel process of hydrolysis using molten salt hydrate is investigated and is compared to other hydrolysis process and techno-economic and life cycle analysis is carried out for all the three process. For the base case scenario, the minimum price of p-Xylene, for DA, CA and MSH process is \$2,320/metric ton, \$1,900/metric ton, and \$1,480/metric ton, respectively. Although the prices of bio-based p-Xylene is comparable with oil-based p-Xylene, the price is much lower when the price of by-products are considered i.e. \$1,270/metric ton, \$1,220/metric ton and \$760/metric ton for the DA, CA and MSH process, respectively. Based on sensitivity analysis, it was found that the cost of p-Xylene depends on the cost of raw materials specially cost of biomass and ethylene, capacity of the plant and composition of biomass. It was also found that the price of p-Xylene depends on the extraction of HMF and furfural from the aqueous phase by ethyl acetate. More studies are necessary to further understand the phenomenon of the extraction process and the effects of different solvents to reduce the overall cost of p-Xylene. From life cycle analysis, MSH process' environmental performance is better than DA but comparable to CA process. Type of biomass used significantly affects the life cycle results. Techno-economic analysis

shows beneficial process economics of the ZnBr_2 process when compared with other biomass saccharification processes commonly used by cellulosic biorefineries.

Next, to further improve economics and sustainability, furfural and lignin, which is a by-product produced from p-Xylene production is used to produce butadiene, surfactants, jet-fuels and lubricants from furfural and PSA from lignin to maximize the profit potential of the bio-refinery. Techno-economic and life cycle analysis is carried out for all the five processes. For the individual process combined with p-Xylene process, the minimum selling price of butadiene is \$1,228/metric ton, surfactants is \$2,502 /metric ton, \$3.45/gallon for jet fuel, \$4,037/metric ton for lubricants and \$8,293/metric ton for PSA, making the prices calculated comparable with oil-based chemicals. From life cycle analysis, surfactants process performs better than butadiene, jet-fuels and lubricants process in all the impact categories except water depletion. On the other hand, production of butadiene has the worse environmental performance in all categories but water depletion. The results highlighted the reduce in minimum selling price of bio-based chemicals when compared to oil-based chemicals. The bio-refinery still depends on oil-based resources such as hydrogen, different acids and aldehydes and all the solvents, which increases the environmental emissions, and thus more work should be carried out to reduce the dependency. Better optimization of the heat networks and utilities should be carried out to reduce the overall economics and increase the sustainability of the bio-refinery. Long residence time and requirement of huge volume of solvent are some of the bottlenecks in the process, which increases the capital and operating costs. For the production of polymers, solvent recyclability is the most important step to make the costs economical. Bio based production is at the early stage development of technology; hence with the integration of biomass conversion to fuels, chemicals,

electricity, etc., it will become more environmentally friendly.

Utilization of FW feedstocks is one of the most important steps toward economic feasibility and technology commercialization of a multi-product biorefinery and represents a step toward commercialization of integrated biorefineries where FW and lignocellulose-plant material can be used symbiotically. Moreover, this technology provides a novel waste management approach, effectively diverting FW from landfills and reducing its environmental impact while creating commodity products that can penetrate existing and new markets. With extractives, carbohydrates, and lignin components possessing different structures and reactivities, we effectively separate each component and process it into distinct renewable products. Excitingly, the high-value products result in an overall revenue of \$8,500/MT of dry feedstock, which is much higher than that of a cellulosic ethanol facility or a lignocellulose based biorefinery. The favorable economics is driven by the high yield of PPE, coupled with the high value of the antioxidant product. PPW manufacturing industries could generate revenues of ~\$8,500 per ton of PPW, compared to ~\$100 per ton of PPW when used for animal feed or incurring a landfill disposal cost of ~\$400 per ton of PPW¹⁴. This provides an opportunity for successful translation of our technology to an economically profitable industry. Comparison of the revenue to energy input for biorefineries utilizing different feedstocks underscores the tremendous potential impact FW can play in the bioenergy economy.

Final Chapter presents a multi-objective optimization problem to find the optimal configuration for a bio-refinery which uses multiple biomasses to produce different intermediates and end products. A pareto optimum pareto solution gives a combination with highest benefits from both economic and environmental perspective. We also apply

scenario analysis, robust optimization as well as two stage stochastic optimization to analyze uncertainty in raw material availability, raw material price and product demand. Generally, the problem tends to maximize the production of extractives from PPW as they are the most profitable with low environmental impacts which makes PPW as the highest contributor to biomass.

7.2 Future work

With the increasing attention on bio-based chemicals, it is of great importance to assess alternative production or to further improve the production processes for all the chemicals and fuels produced in this study. Some of the assumptions used to model and simulate the processes should be evaluated and validated. For example, treatment of waste water consisting of aluminium chloride and lithium bromide should be added, which can give us more realistic calculations for capital and operating costs. Besides, the different nature of bio-based derived feedstocks and the compounds involved in the bio based conversion are often relatively new and less studied so that the physical properties of them are lacking in the database and sometimes it is even difficult to find in the literatures. The relating studies to explore the physical properties will be useful to build a more accurate model. Future work should also concentrate on the study of reducing solvent and better design of catalyst. More chemicals and fuels are being investigated which can further increase the economics of the bio-refinery. The technology of repurposing food wastes can be extended to other types of FW and a larger range of bioproducts for the commodity market.

Finally, the framework of finding optimal configuration of a multi-product bio-refinery can be extended to include more different types of biomasses such as various food wastes as well as different types of algae (third generation of biomass). More products from lignin

as well as from cellulose can also be considered. Adding different life cycle analysis parameters such as fossil depletion and land occupation to the optimization model can lead to more realistic models for environmental impact.

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