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

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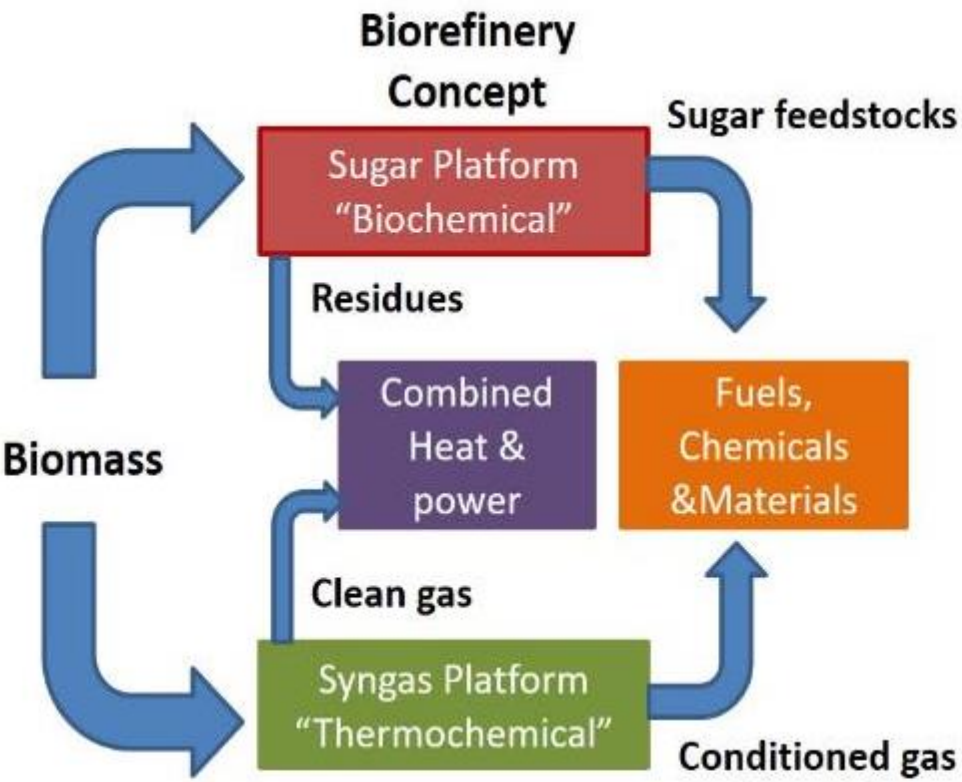
Laboratory for Optimization and Systems Analysis: From Left : Zilong Wang, Shu Yang, Shishir Vadodaria, Ravendra Singh, Praneeth Annam, Abhay Athaley, Nirupa Metta, Parham Farzan, Lisia Dias, Sebastian Escotet, Marianthi Ierapetritou, Charles Foster

Overview

- Motivation and process systems engineering tools.
- Phthalic Anhydride production from xylose solution.
- p-Xylene production from glucose/starch solutions
- p-Xylene production from biomass.
- Flowsheet Optimization.
- Summary and future work.

Introduction

- Biomass resources can be used to produce both high-volume and low-value fuels and high-value chemicals.
- Goal is to study the production of bio-based chemicals from the viewpoint of process systems engineering.

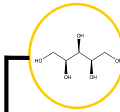
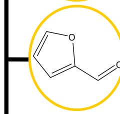
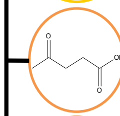
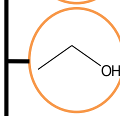
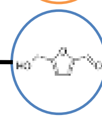
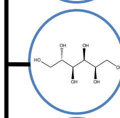
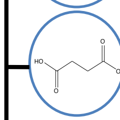
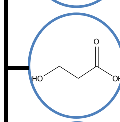
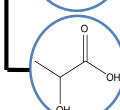
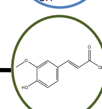


Source: http://www.nrel.gov/biomass/biorefinery.html

- To develop an integrated framework implementing process design, simulation, heat integration, life cycle assessment (LCA) and process optimization in order to achieve more economically and environmentally friendly production alternative.
- Work focuses on the development of efficient and economically sustainable routes for the production of bio-based platform chemicals and fuels.

Platform Chemicals

Biomass Pretreatment → Hemicellulose (Pentosans-Xylan), Cellulose (Hexosans-Glucan) → Sugars C5/C6 Sugars (xylose-Glucose); Lignin

Structure	Product	Direct Product Use	Product's Derivatives Use
	**Xylitol** Chemical pathway from pentoses	Non-nutritive sweetener Building block for Xylaric acid, glycols	Antifreeze, unsaturated polyester resins
	**Furfural** Chemical pathway from pentoses	Solvent in petrochemical refining, Building block for Tetrahydrofuran (THF), Nylon 6.6	Thermoplastic fibers, resins, solvents
	**Levulinic acid** Chemical pathway from hexoses/pentoses	Building block for Methyl tetrahydrofuran, butyrolactone, Diphenolic acid	Fuel oxygenates, pesticides, solvents, polycarbonate resins
	**Ethanol** Biotechnological pathway from hexoses/pentoses	Fuel for transport, Building block for Ethylterbutylether (ETBE), ethyl esters	Fuel, Fuel oxygenate
	**Hydroxymethylfurfural** Chemical pathway from hexoses	Building block for Diformylfuran, Dimethylfuran, Furandicarboxylic acid (FDCA)	PET like polymer, PET, solvents
	**Sorbitol** Chemical pathway from hexoses	Non-nutritive sweetener Building block for Isosorbide, propylene glycol	PET like polymers, antifreeze, water soluble polymers for water treatment
	**Succinic acid** Biotechnological pathway from hexoses	Building block for Butanediol (BDO), Tetrahydrofuran (THF), gamma-Butyrolactone (GBL), pyrrolidiones	Fibers such as Lycra, green solvents, water soluble polymers for water treatment
	**3-Hydroxypropionic acid** Biotechnological pathway from hexoses	Building block for 1,3 propane diol acrylates	Sorona Fiber, contact lenses, super adsorbent polymers (Diapers)
	**Lactic acid** Biotechnological pathway from hexoses	Building block for polylactides such as polylactide acid (PLA)	Biodegradable Polyethylene-like polymers
	**Ferulic acid** Biotechnological pathway from lignin by enzymatic depolymerization	Building block for vanillin, polymers	Flavouring agents, phenolic resins
	Sulfur-free solid fuel Pelletization of lignin rich solid residue	Fuel for heat and power generation	

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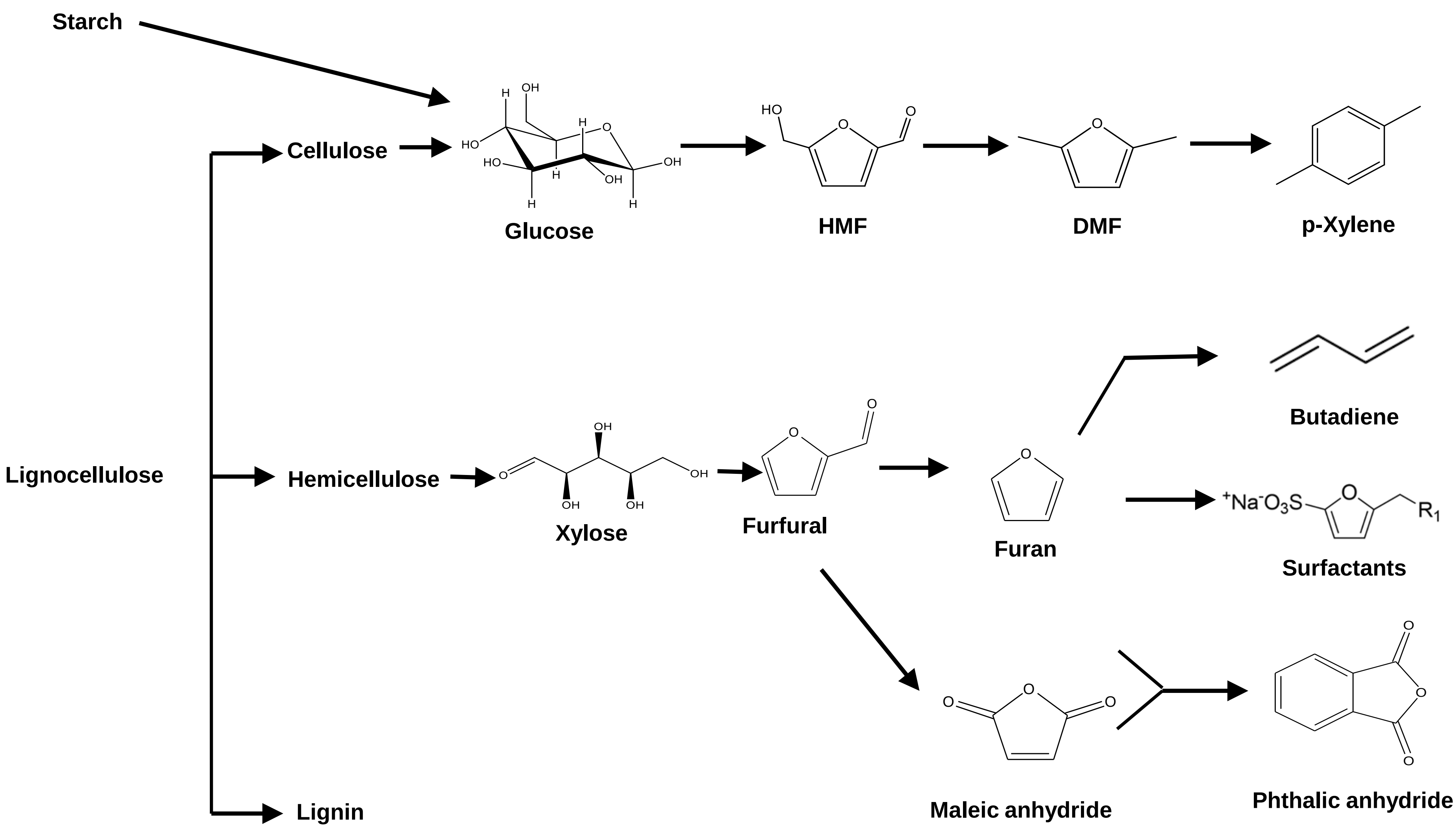
Selected Processes



Process Systems Engineering Tools

PSE tools are useful

- To facilitate the development of new process, to assess and compare different alternatives
- To determine the most important parameters that can be improved to promote commercialization
- To establish a sustainable production route to manufacture valuable chemicals

PSE tools	Usages
Techno-Economic Analysis	• Design process and evaluate economics • Identify promising alternatives.
Sensitivity Analysis	• Identify critical process parameters
Heat integration	• Reduce the energy consumption
Life cycle assessment	• Evaluate environmental impacts
Process Flowsheet Optimization	• Compare design alternatives • Select cost effective process design

Techno-Economic Analysis

- Economics is always a crucial for investors to assess the project's viability
- Techno-economic analysis (TEA) integrates conceptual process design and economic analysis
- TEA is an effective and efficient tool to eliminate unfavorable designs and identify promising alternatives.

- Simply design and simulate different production alternatives
- Roughly estimate economic feasibility

↓

- Design and simulate the detailed process flowsheet using process simulator

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- Perform economic analysis to calculate the capital and operating cost
- Determine the minimum product price

Heat Integration

The definition of HENS problem:

Given

- A set of hot process streams to be cooled and a set of cold streams to be heated
- The flowrates and of all the process streams
- The inlet and outlet temperatures and the heat capacities of all the process streams
- The available utilities and temperatures, and the units cost of the utilities,

the basic problem is to develop the heat exchanger network with the minimum annualized cost of equipment investment and operating cost.

Aspen Energy Analyzer uses a three-step procedure:

Step 1 LP — Simultaneously optimize heat exchange area and heat load for each utility to eliminate poor matches

Step 2 MILP
- Simultaneously optimize the number for heat exchanger units, heat exchanger area and heat loads on each utility

Step 3 MILP
- Each stream is divided into a given number of stages to generate an optimal network that simultaneously optimizes utility cost, the numbers of heat exchangers and selection of matches

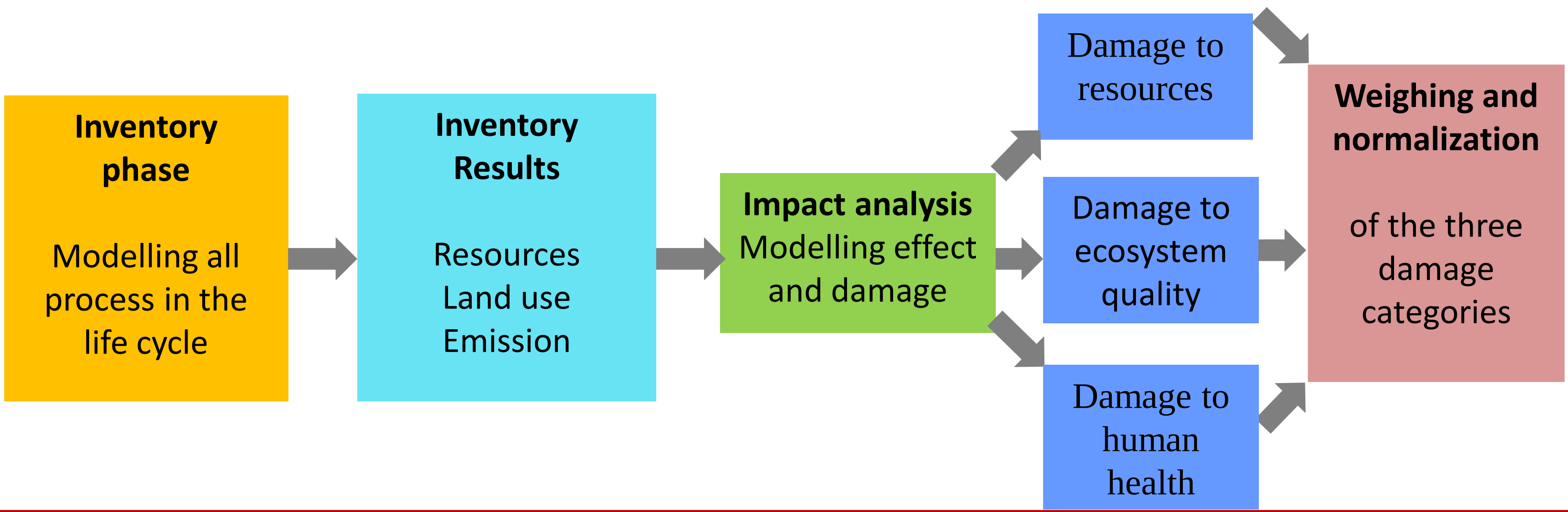
Life Cycle Analysis

- LCA is a tool to quantify the environmental performance of products by taking its complete life cycle into account
- LCA provides the quantitative and scientific basis for all the steps involved in the process

✓ SimaPro® is selected

- *A broad Life Cycle Database and a huge variety of impact assessment methods*

✓ ReCiPe midpoint, and Ecoindicator-99 methods are used



Methods Used in Life Cycle Analysis

Midpoint method

Considers the cause-effect chain of an impact category prior to the endpoints

Traditional approach with few uncertainties

It is a problem oriented method

ReCiPe method is used.

Endpoint method

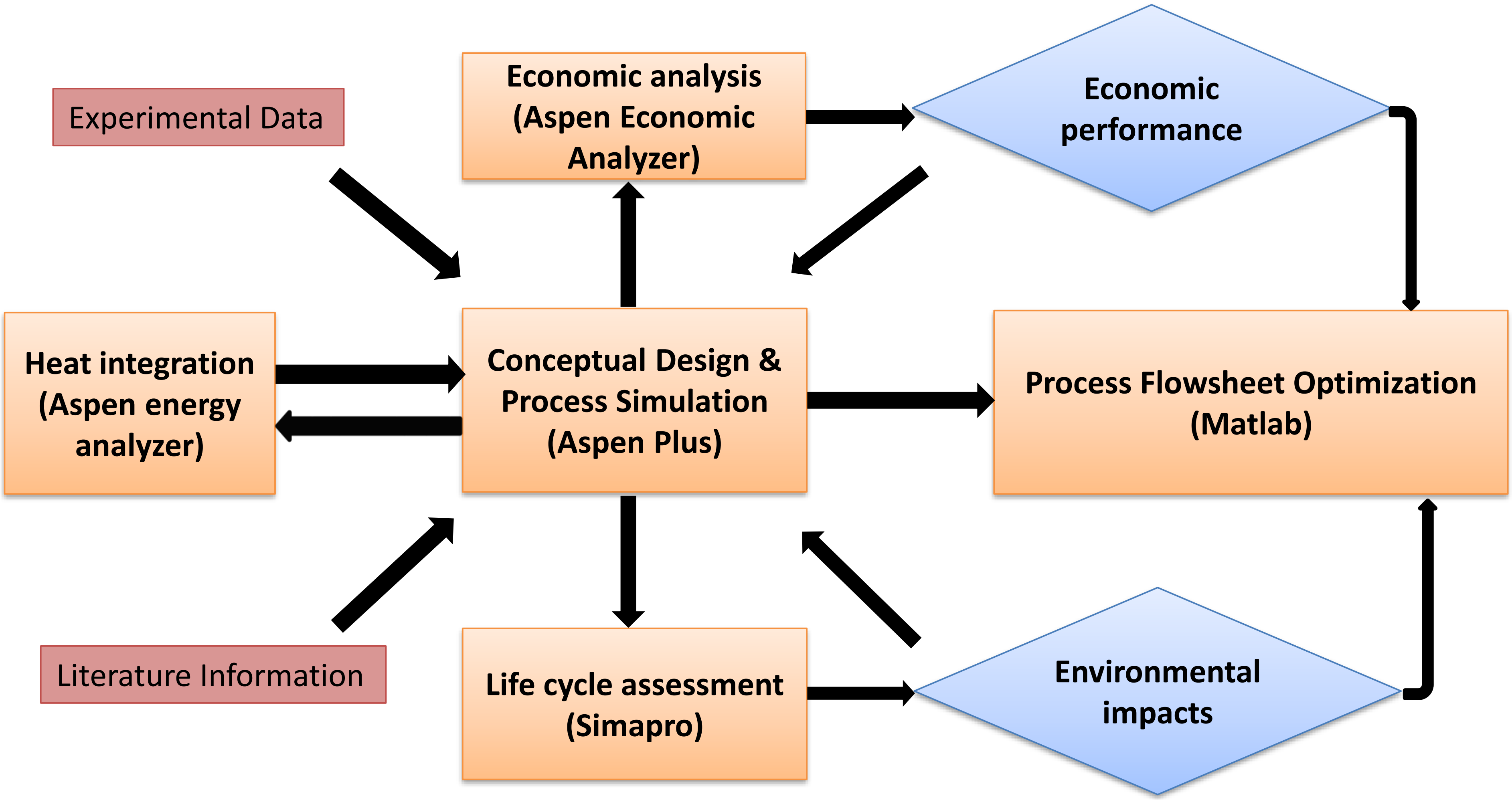
Characterization requires modeling all the way until the endpoint categories described by areas of protection

More assumptions and larger data uncertainties

It is a damage oriented method

Ecoindicator method is used.

General Framework



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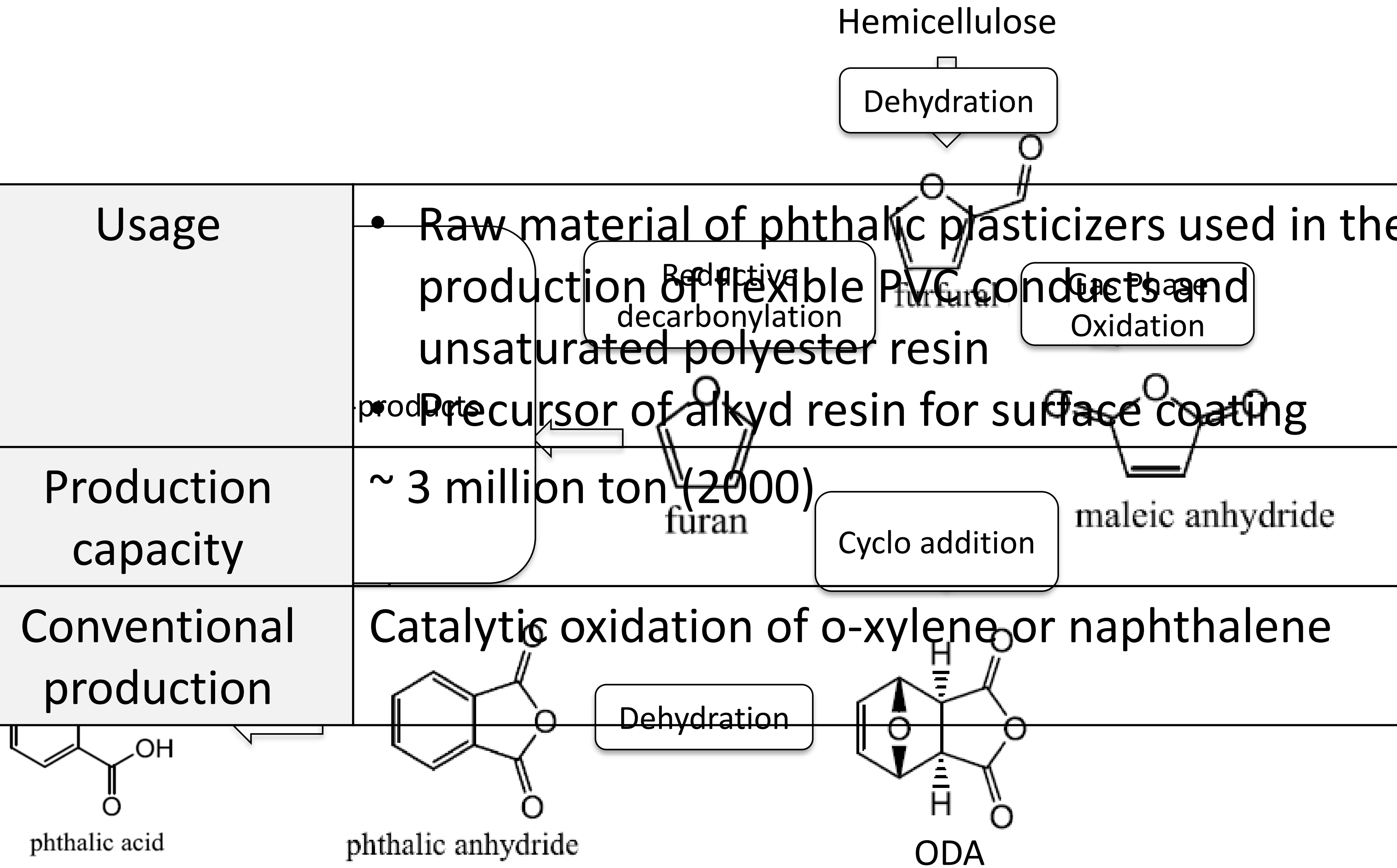
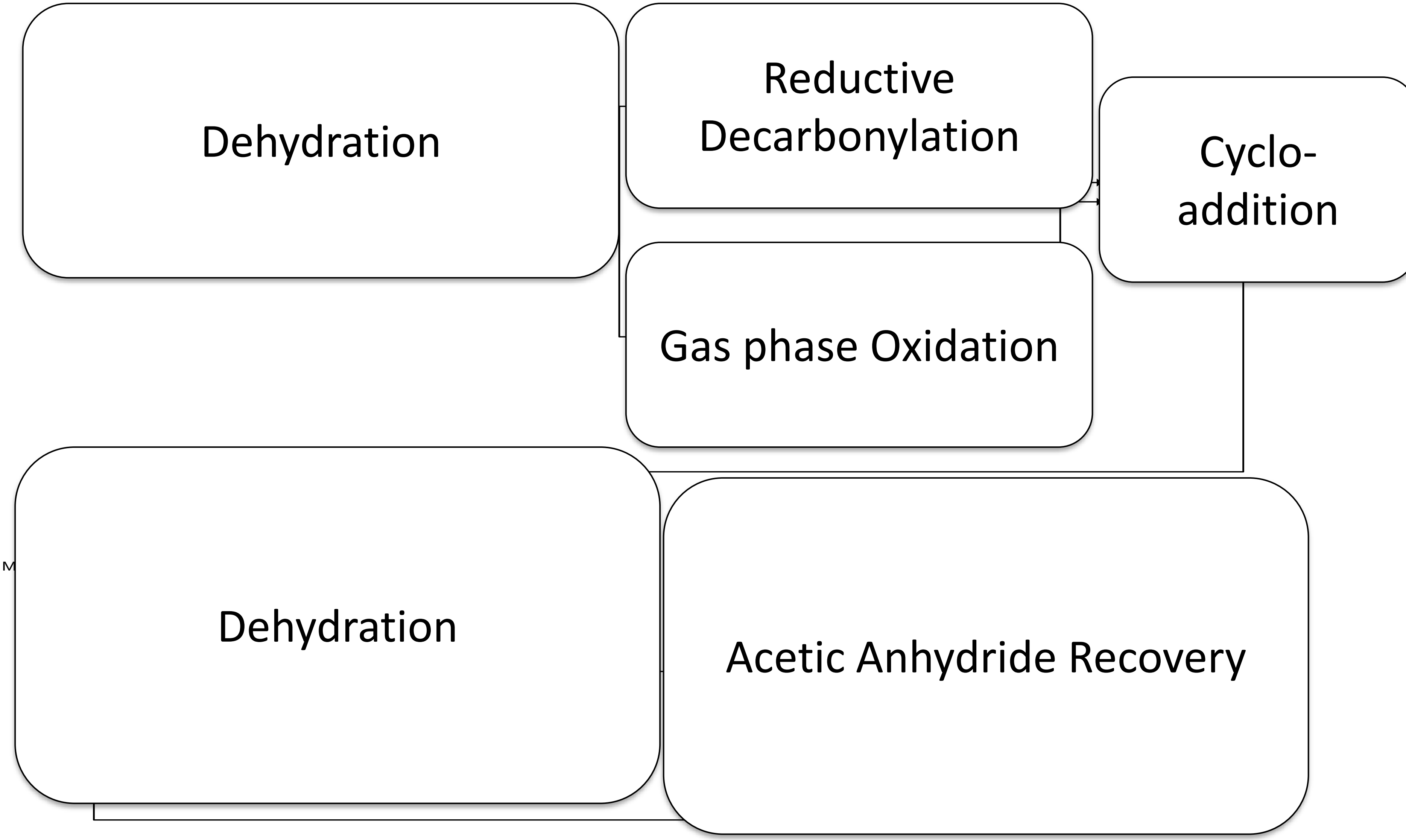
Phthalic Anhydride (PAN) Production

Phthalic Anhydride Production

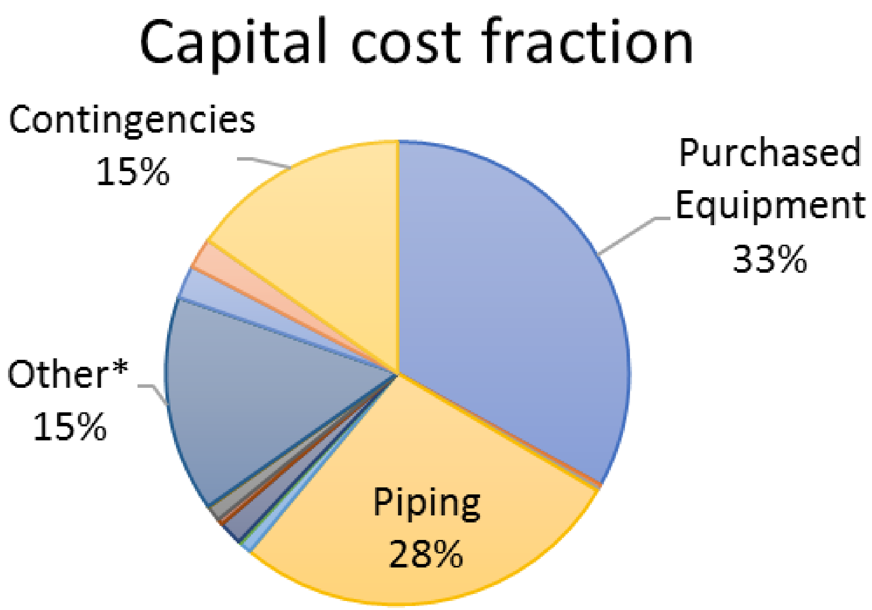


Usage	• Raw material of phthalic plasticizers used in the production of flexible PVC products and unsaturated polyester resin • Precursor of alkyd resin for surface coating
Production capacity	~ 3 million ton (2000)
Conventional production	Catalytic oxidation of o-xylene or naphthalene

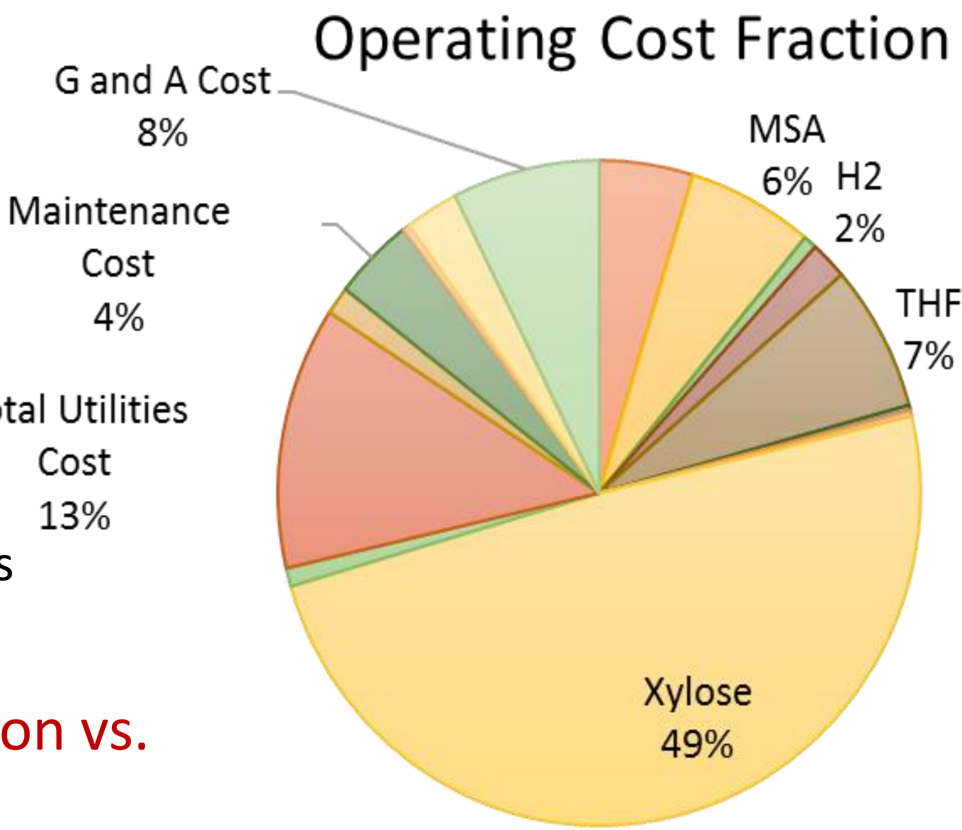
Phthalic Anhydride Production



TEA for PAN Production



- The total capital cost is $451.5 million
- The total operating cost is $151.3 million/yr



- The largest contribution is from heater exchangers.
- The second major equipment cost comes from xylose conversion to furfural.

The bio-based PAN is **$810**/metric ton vs. oil-based PAN is **$1706**/metric ton

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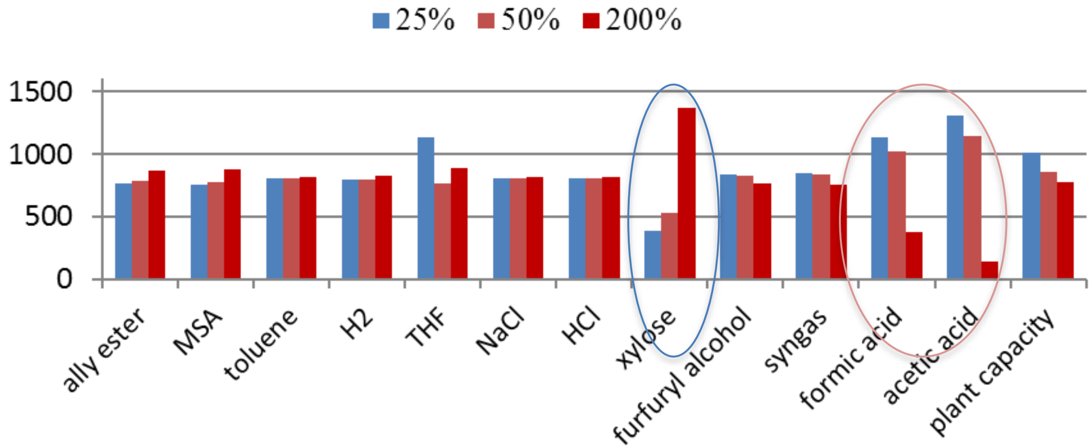
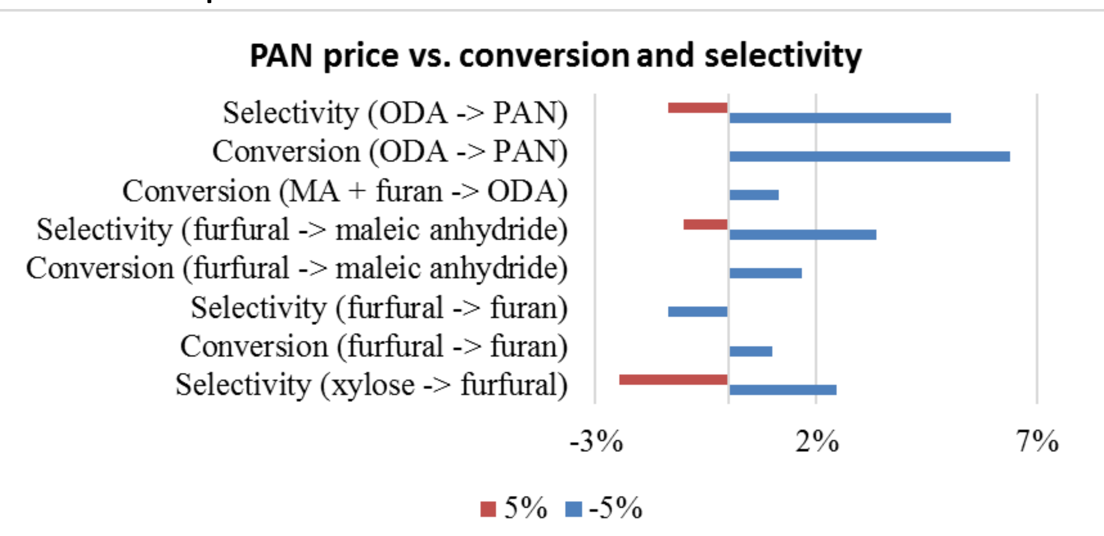
Sensitivity Analysis for PAN production

Raw material cost



- 100% increase of xylose price leads to 69% increase of PAN price.
- The PAN price is benefited from coproduction of high-valued products.
  - 25% increase of current Acetic Acid price results in 62% increase of PAN price
  - 25% increase of current Formic Acid price results in 40% increase of PAN price

Reaction parameter



- Selectivity has bigger impact than conversion varying from 2.5 to 6.4%
- Negative decrease has much higher impact than the positive variation due to increasing cost of separation

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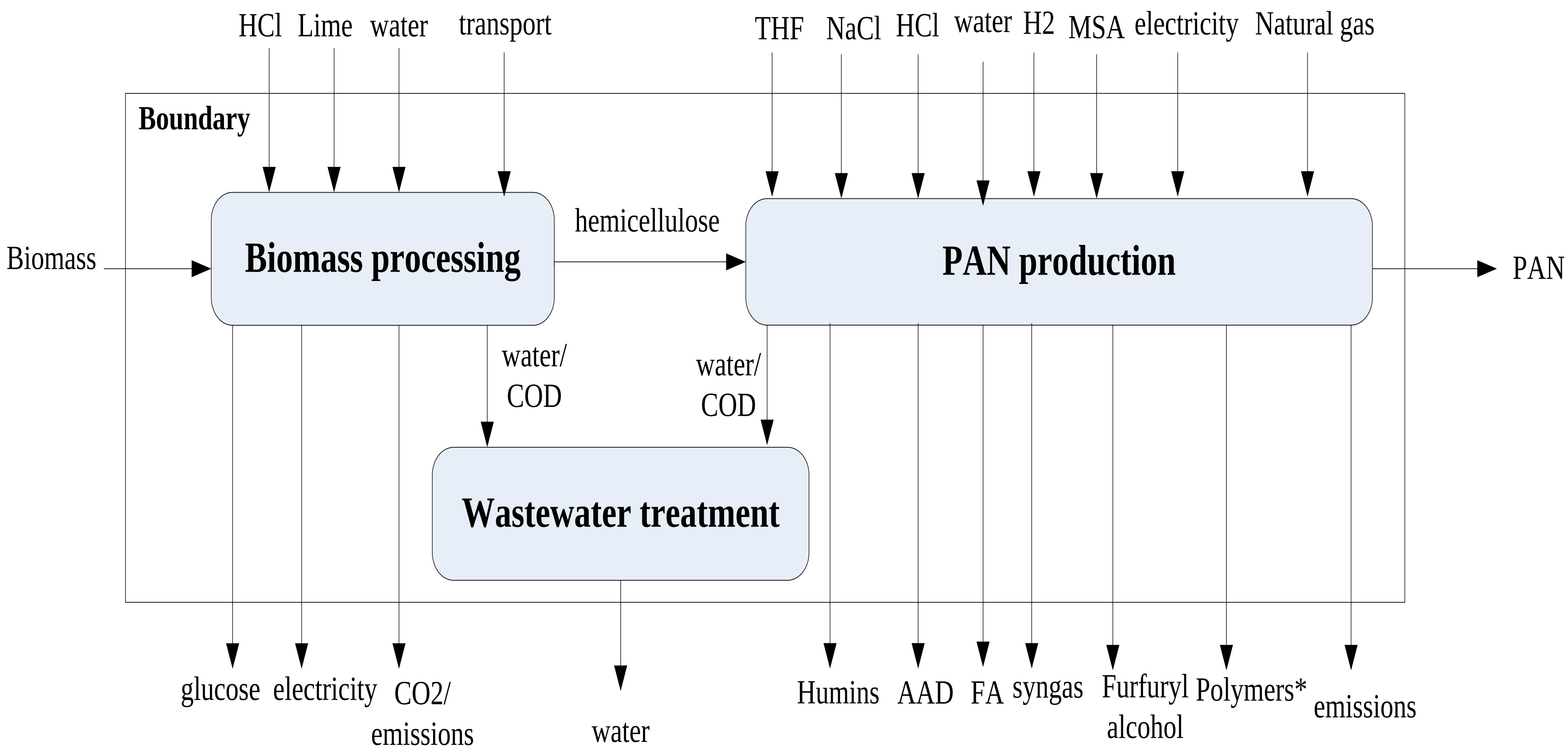
LCA for PAN Production

System boundaries: *Cradle-to-gate (Biomass → PAN)*

Functional unit: *1 metric ton PAN produced*



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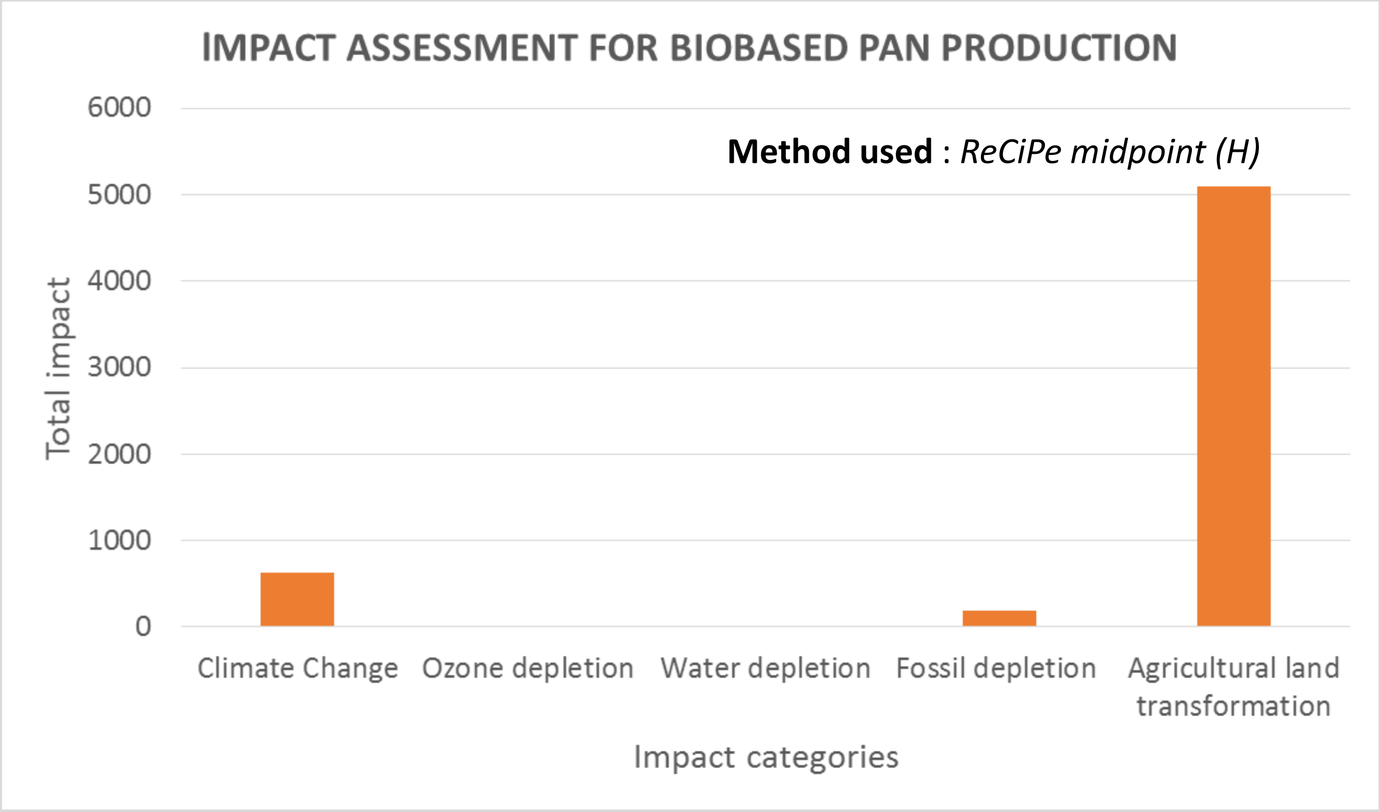
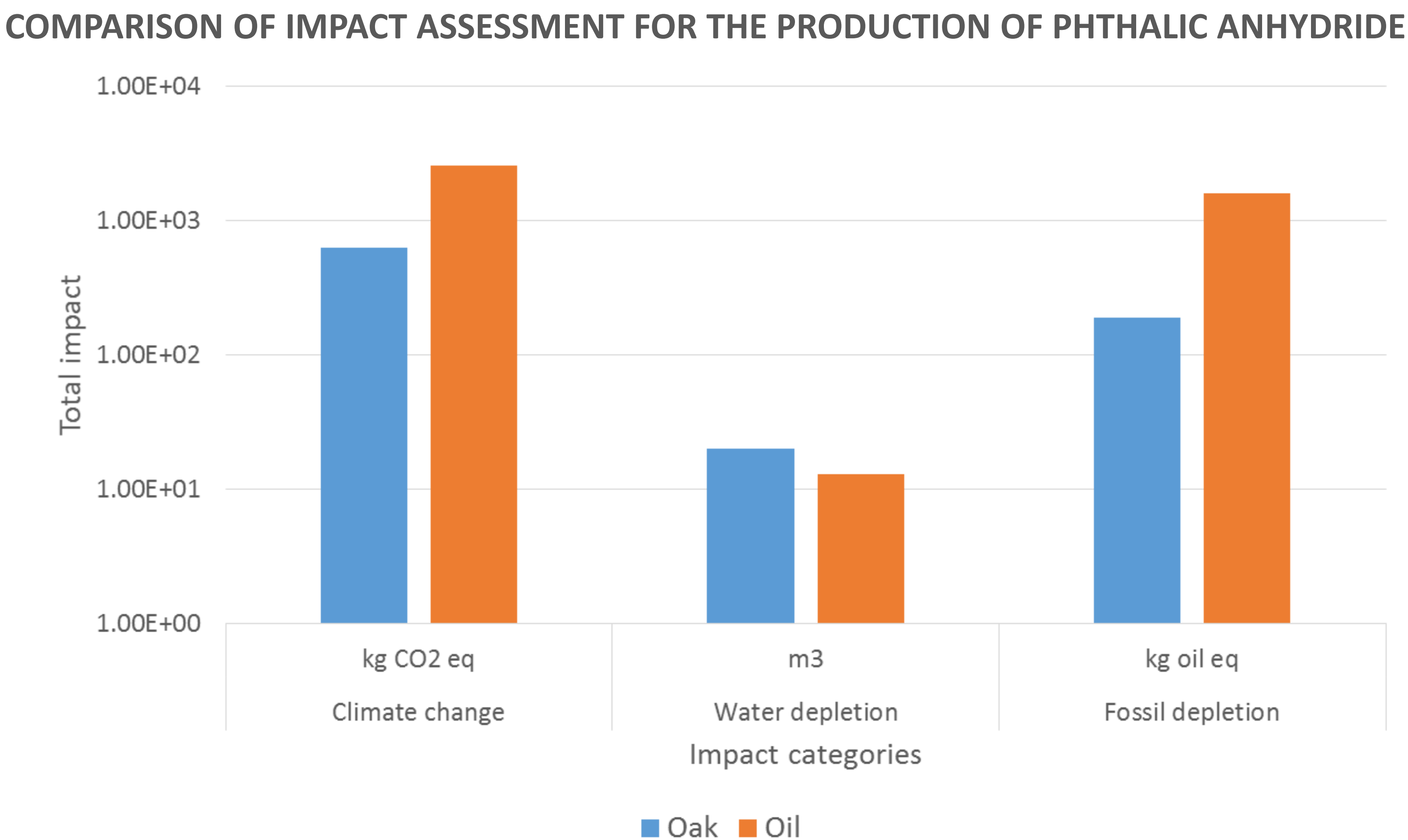
LCA of Phthalic Anhydride Production



- The climate changes mainly from CO_2, electricity and makeup solvent THF.
- The fossil fuel depletion is caused by the production of deionized water
- Processing of biomass has highest impact on Agricultural land occupation

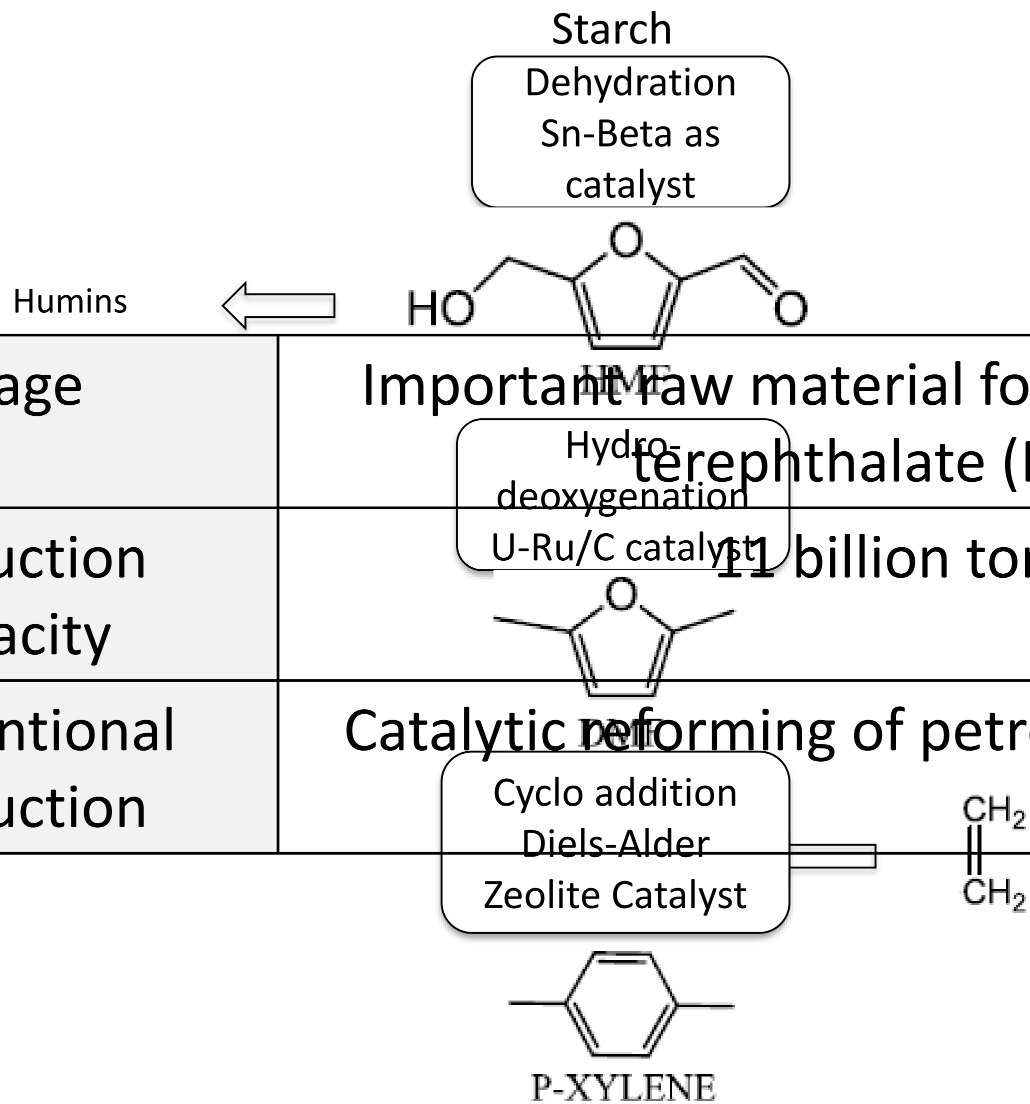
LCA of Phthalic Anhydride Production



- Oak-based PAN has better performance in terms of climate change and fossil depletion.
- Oak-based PAN requires more water usage.

p-Xylene Production

p-Xylene Production



Usage	Important raw material for polyethylene terephthalate (PET)
Production capacity	11 billion ton
Conventional production	Catalytic reforming of petroleum naphtha

p-Xylene Production

Dehydration

- First stage uses biphasic reactor to convert glucose to HMF
- The organic phase is fed to a flash to evaporate most of THF

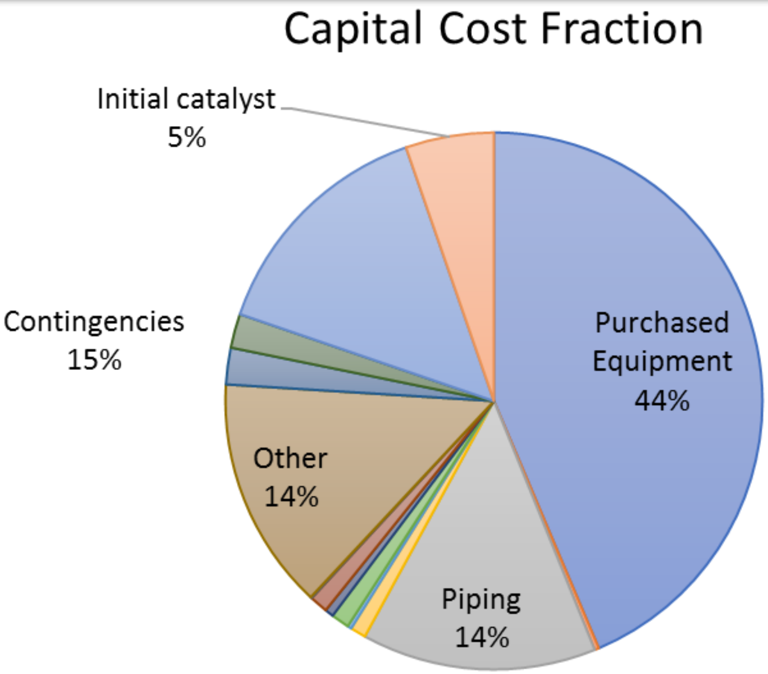
Hydro – deoxygenation

- HMF reacts with H2 to produce DMF
- A flash drum is used to remove low boiling point components and water
- DC to recycle THF
- Three more DCs are used to purify DMF and recycle intermediate

Cyclo – addition

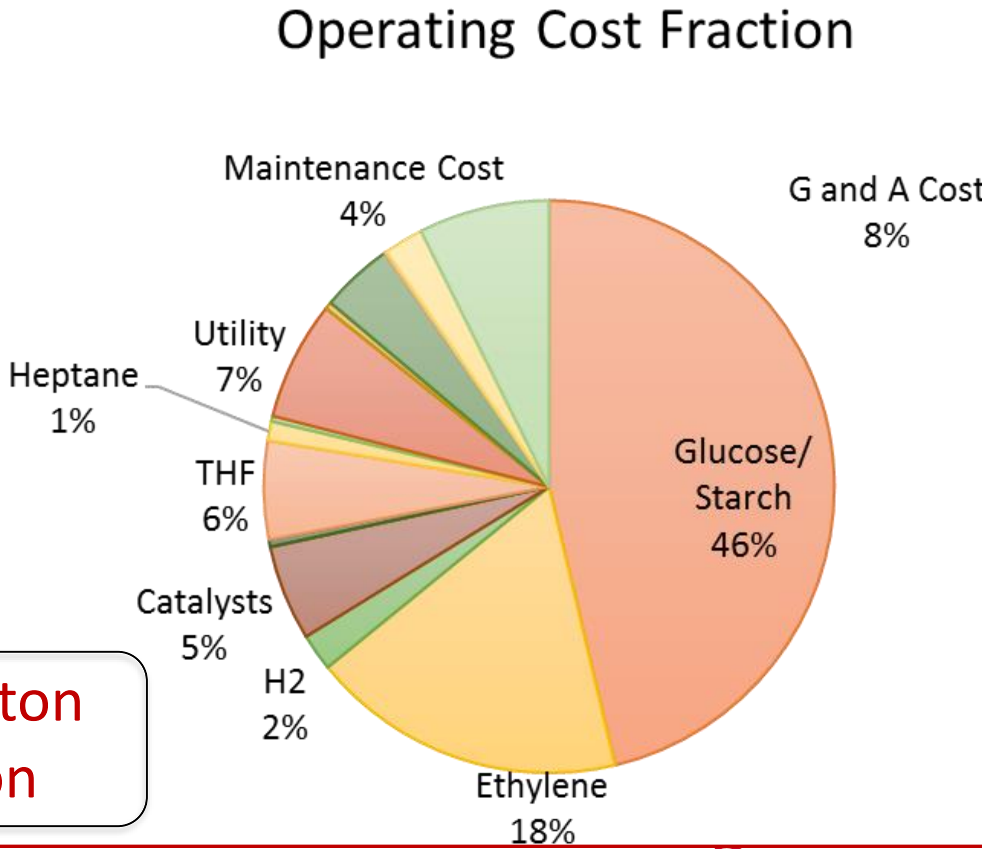
- DMF reacts with ethylene
- A decanter is used to remove water
- Two DC are used to recycle unreacted raw materials and solvents.
- One more DC is used to purify p-X

TEA of p-Xylene Production



- The total capital cost is $457.1 million
- The total operating cost is $388.9 million/yr

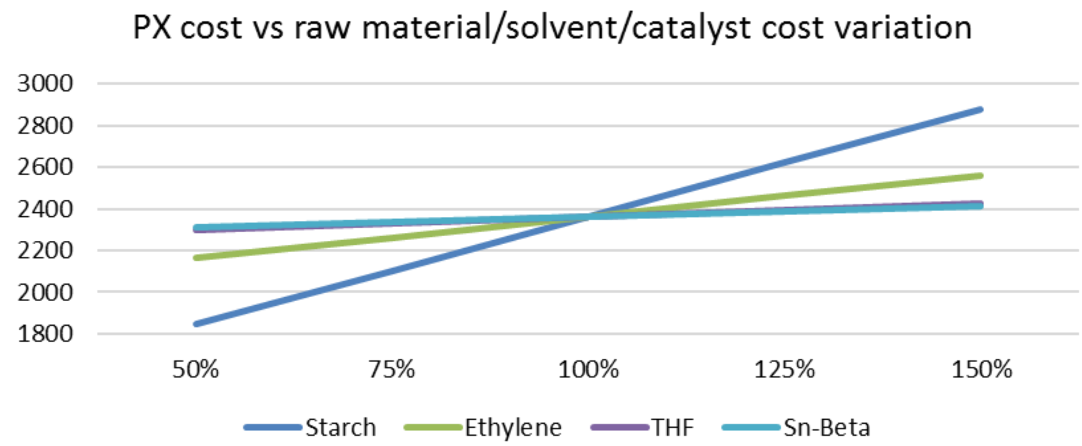
The equipment cost of glucose conversion to HMF is dominant



The bio-based PX is **$2120**/metric ton vs. oil-based PX is **$1650**/metric ton

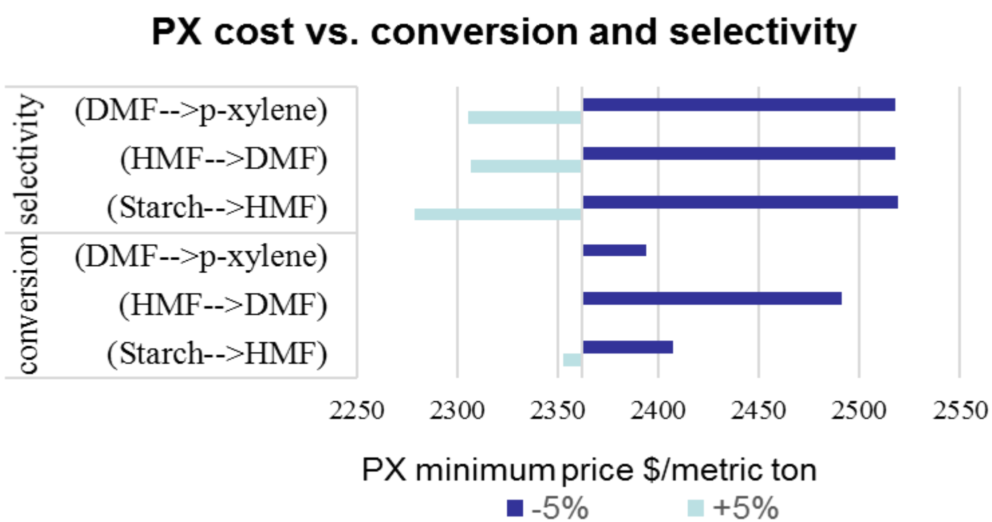
Sensitivity Analysis for p-Xylene production

Raw material cost



- 50% increase of starch/glucose cost leads to 22% increase of pX price
- 50% increase of ethylene price results in 7% increase of pX price

Reaction parameter



- Selectivity has bigger impact than conversion
- Selectivity decrease has much higher impact than the positive variation due to increasing cost of separation

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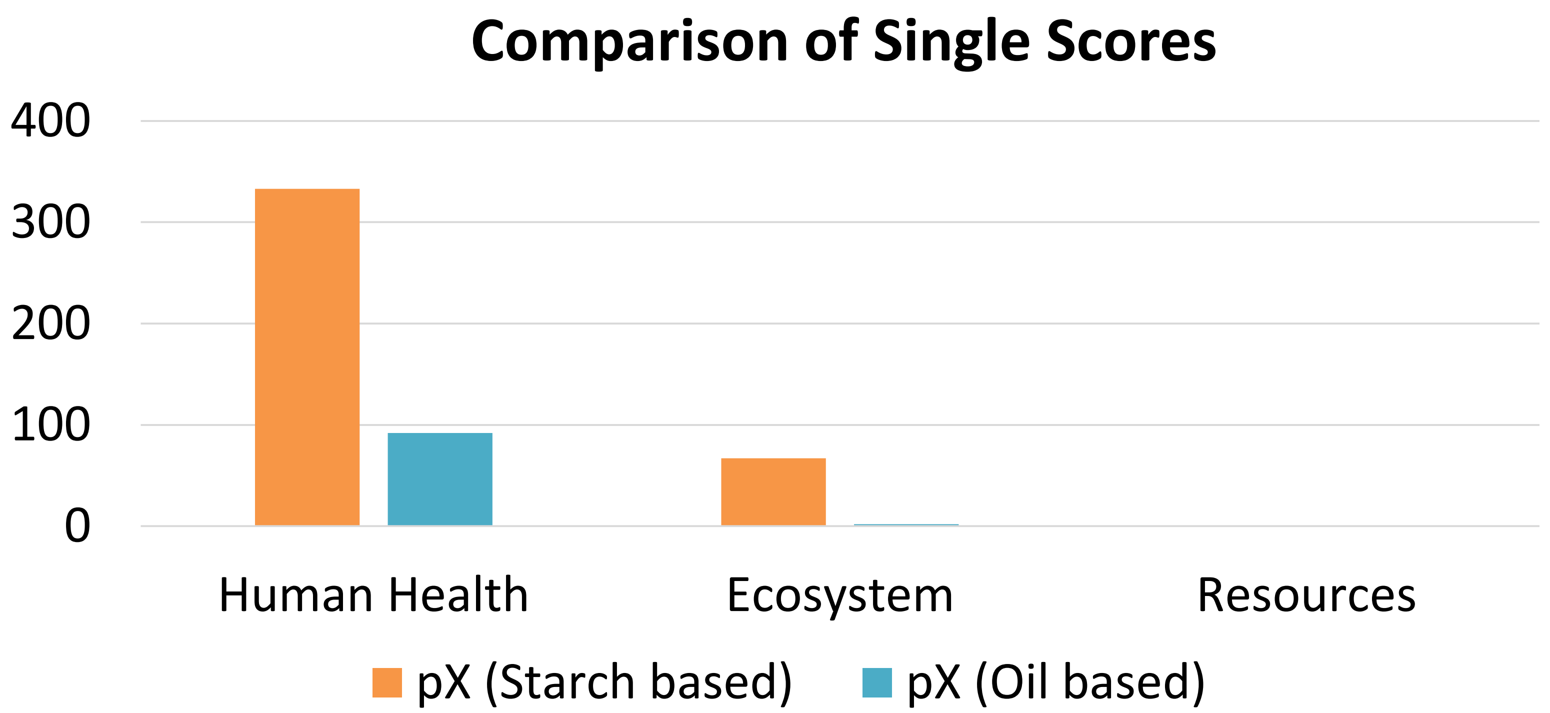
LCA of p-Xylene Production



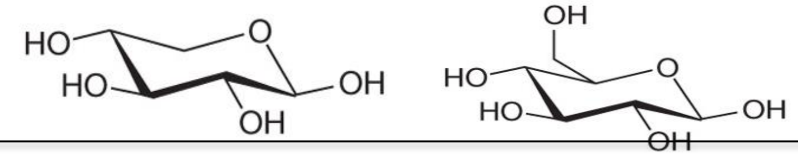
Label	pX (Starch based)	pX (Oil based)
Single Score (Pt)	401	94

p-Xylene from starch is has more adverse effects to the environment than oil based p-Xylene

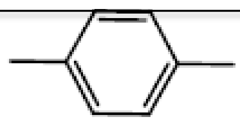
p-Xylene Production from Biomass

p-Xylene Production from Biomass

Biomass → Hydrolysis →



- A new hydrolysis process is investigated to further reduce the price of p-Xylene.
- Hydrolysis using molten salt hydrate (MSH process) is developed by Catalysis Center for Energy Innovation, University of Delaware and compared with two other hydrolysis processes – Dilute acid hydrolysis (DA) and Concentrated acid hydrolysis (CA).
- We also incorporate the increase in selectivity and conversion for DMF and p-Xylene by using different but cheaper catalyst.
- Capacity is also reduced to model a more realistic bio-refinery.



p-Xylene Production- DA process

1st Stage

Hemi-cellulose from the biomass is converted into xylose (Sulphuric Acid)

2nd Stage

Cellulose is converted into glucose (yield =57%)

Neutralization

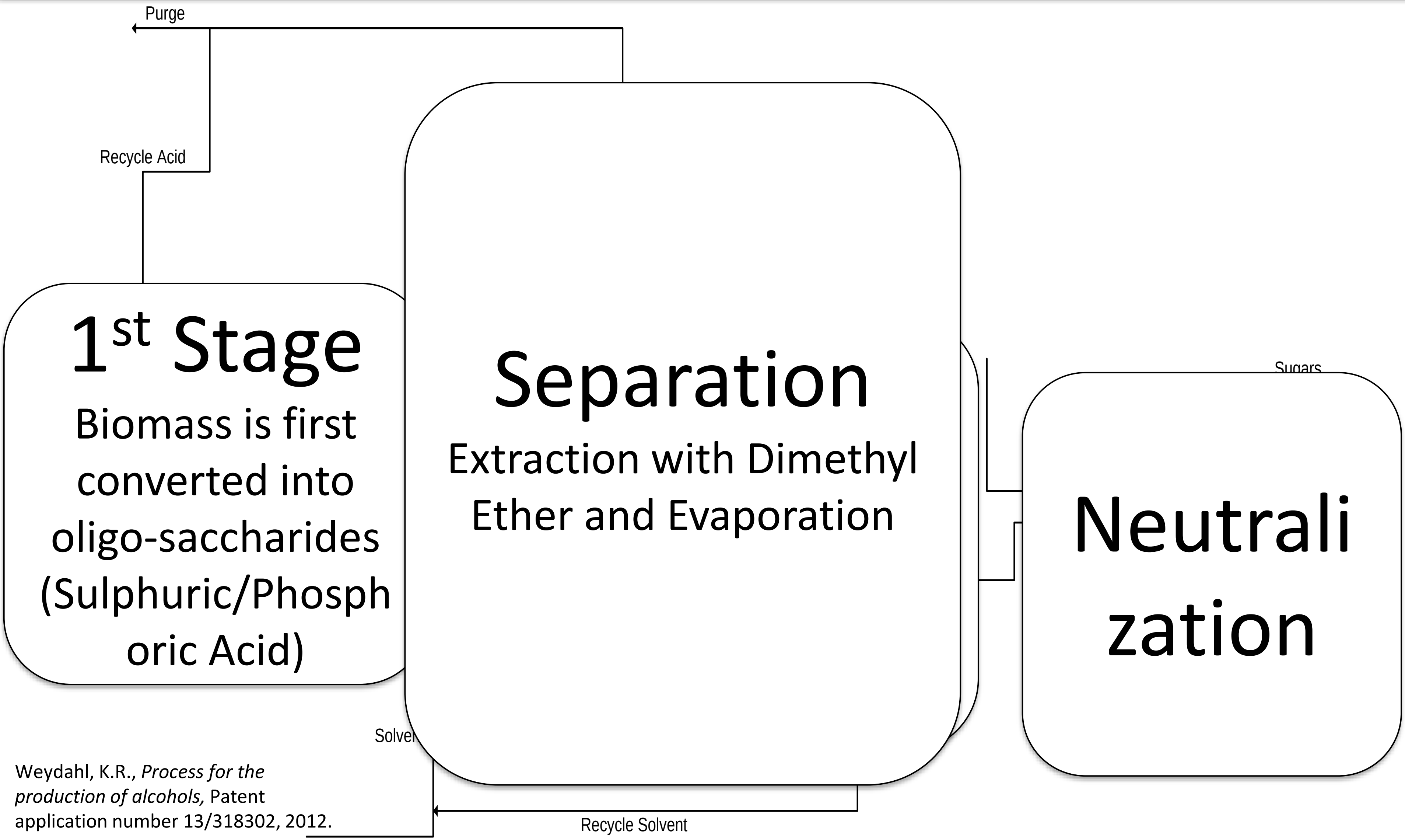
Residue

Lignin

Water

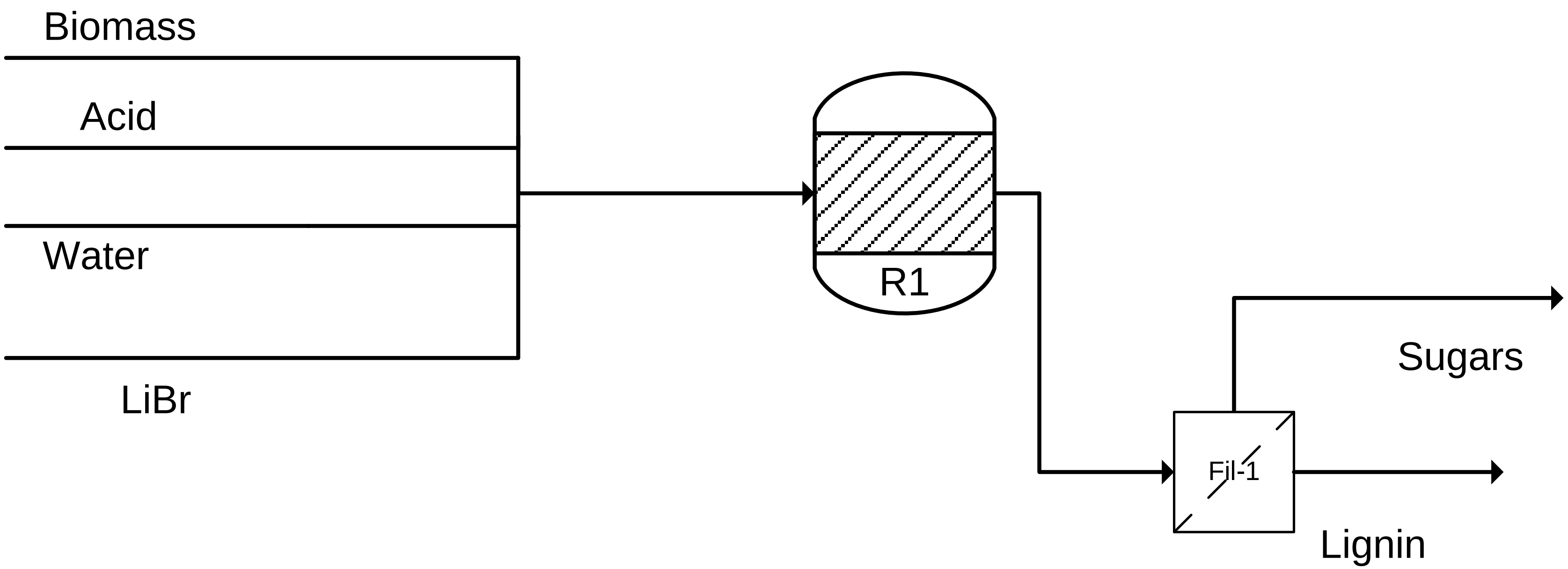
Harris, J.F.a.F.P.L., *Two-stage, dilute sulfuric acid hydrolysis of wood: an investigation of fundamentals*, F.S. U.S. Dept. of Agriculture, Forest Products Laboratory., Editor. 1985.

p-Xylene Production- CA process



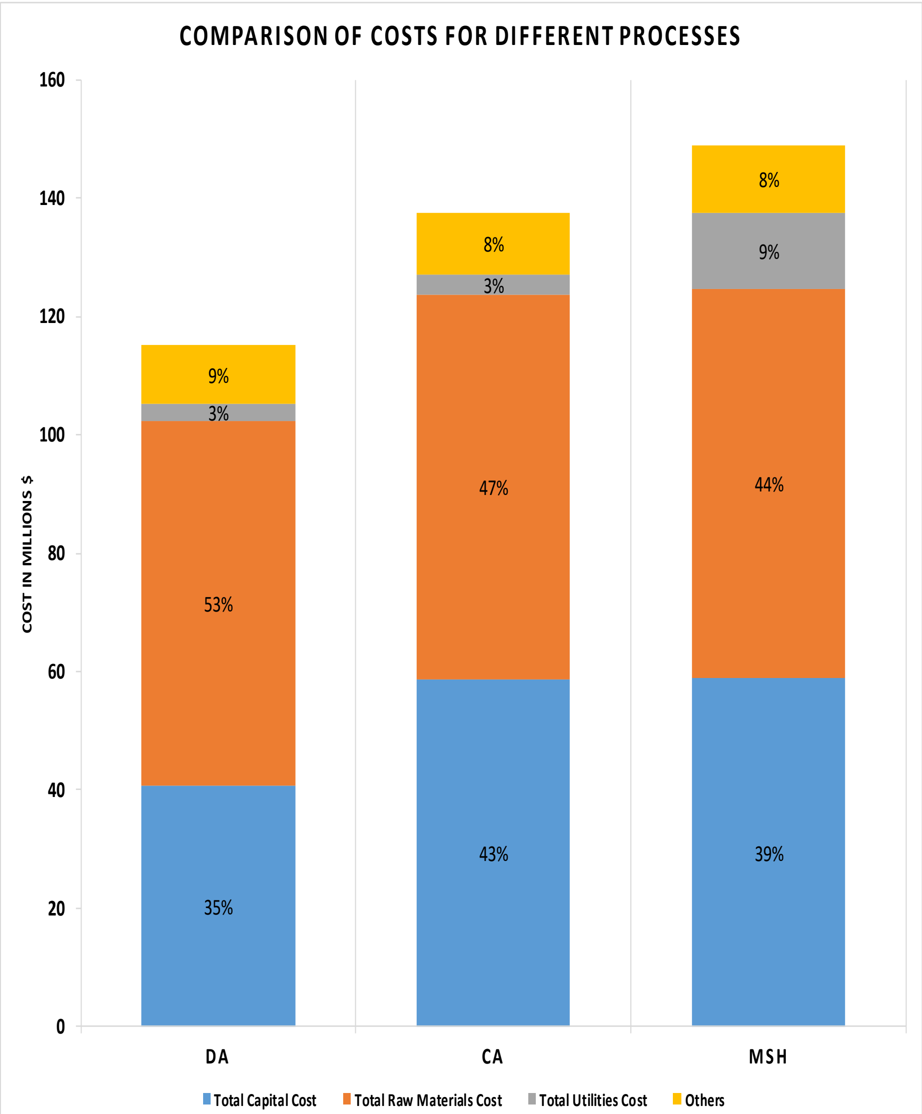
Weydahl, K.R., *Process for the production of alcohols,* Patent application number 13/318302, 2012.

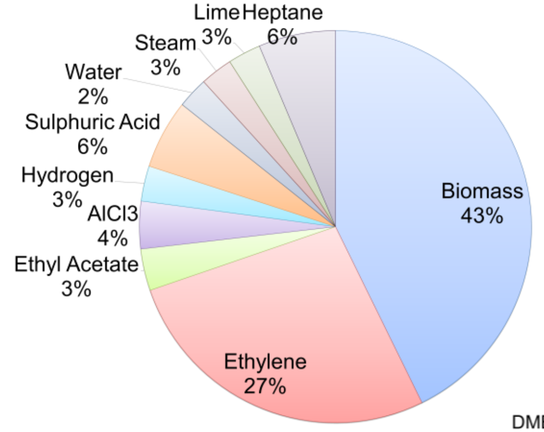
p-Xylene Production- MSH process



- It is a single stage hydrolysis process.
- Biomass, sulphuric acid, water and molten salt hydrate (LiBr) is fed to a reactor (R1).
- Biomass loading is assumed as 10 wt% with 59 wt.% LiBr. The strength of acid is 0.05 wt%.
- The yield of glucose and xylose is expected to be 83% and 89%, respectively.

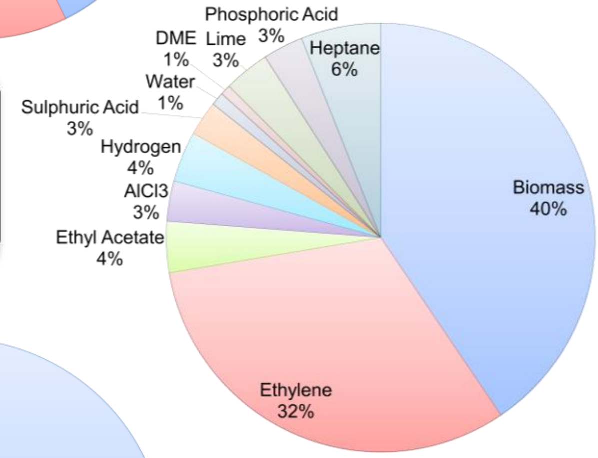
TEA of p-Xylene Production from Biomass

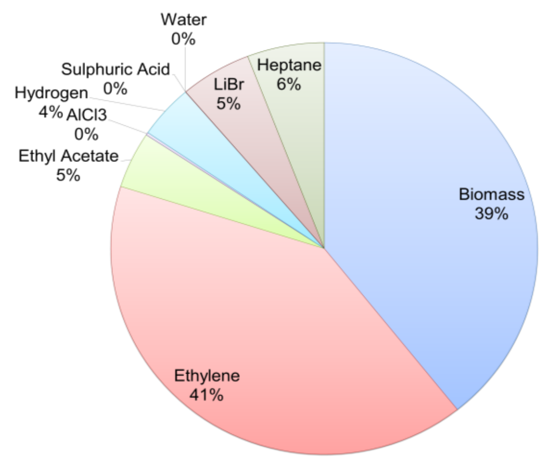




The minimum selling price of p-Xylene from **DA process** is **$1967**.

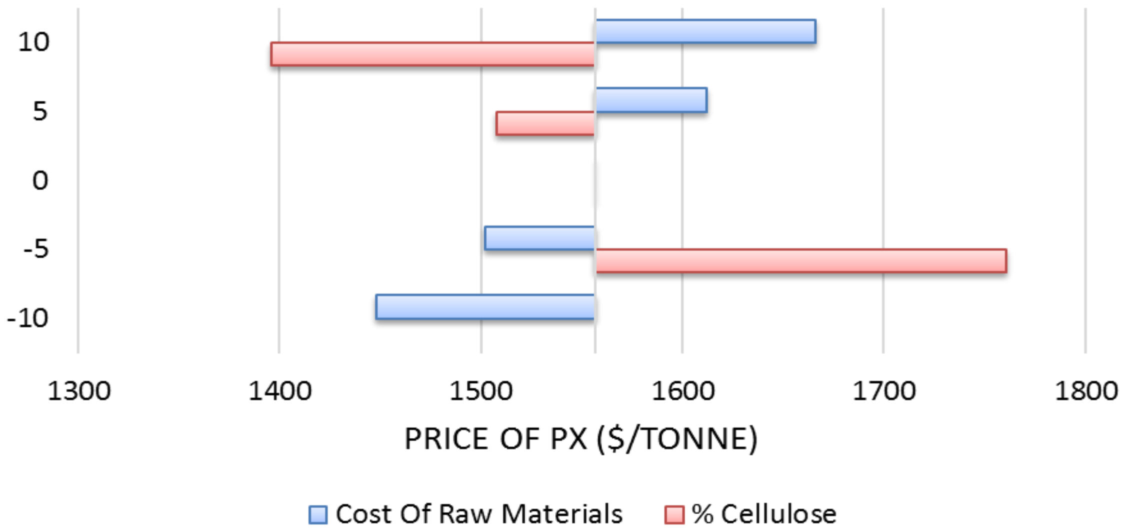
The minimum selling price of p-Xylene from **CA process** is **$1589**.

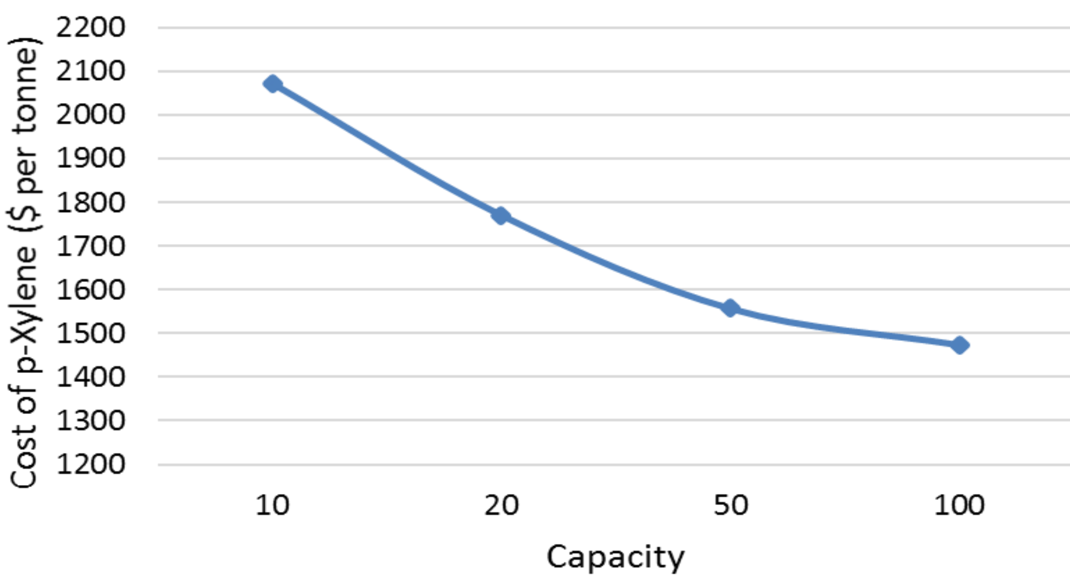




The minimum selling price of p-Xylene from **MSH process** is **$1557**.

Sensitivity Analysis: p-Xylene production from Biomass



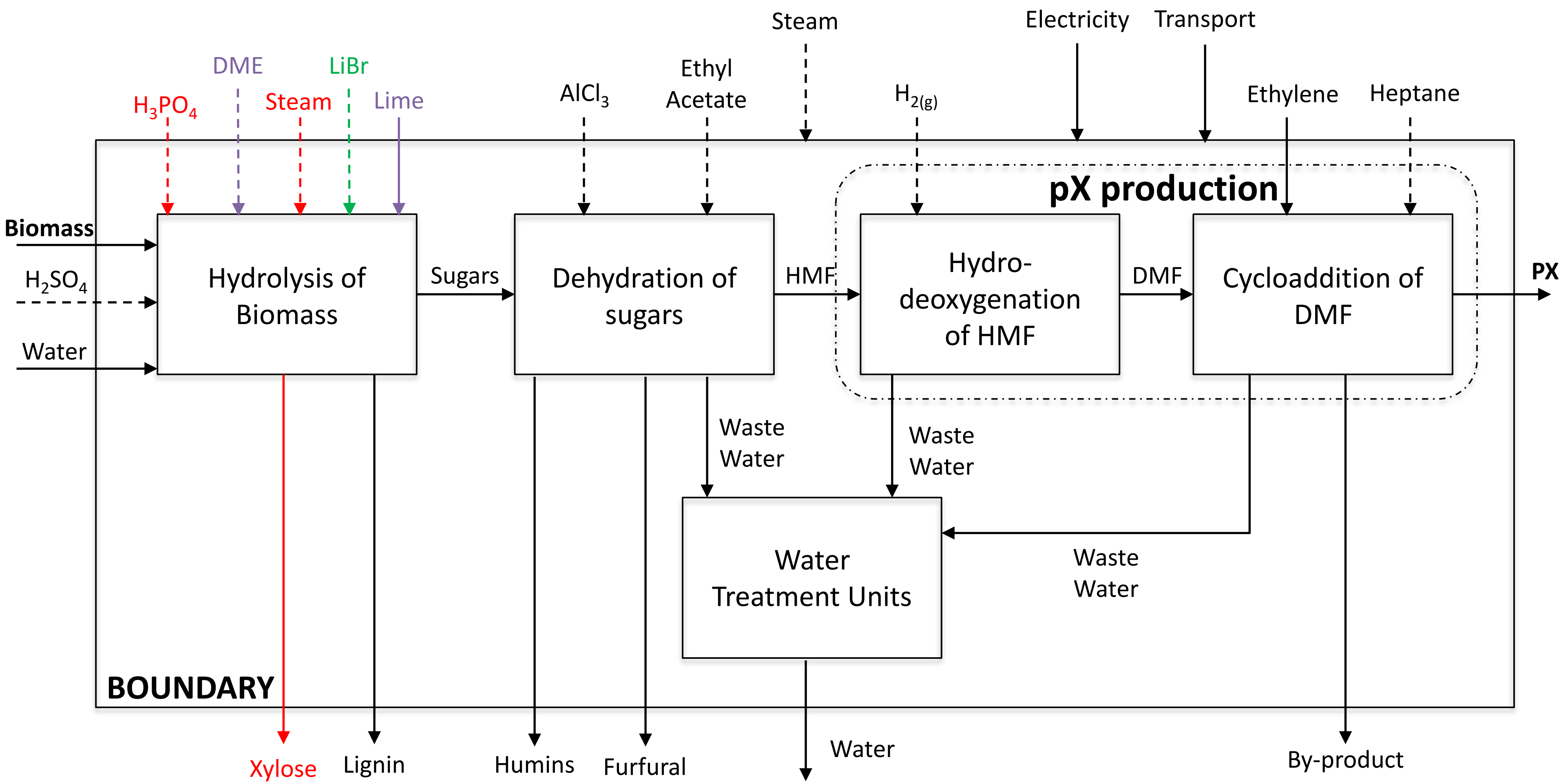


- Changing the price of raw materials by ±10%, the price of p-Xylene changes by ±7%.
- 50% increase of biomass feedstock cost raises the minimum cost of p-xylene by 14%.
- 50% increase of ethylene increases the minimum cost of p-xylene by 14.45%.
- Increasing the cellulose content to 50% decreases the minimum selling of p-Xylene by 10.37%.
- Change in biomass loading to 40% decreases the price of p-Xylene by 18.77%

LCA of p-Xylene production

Functional unit: *1 metric ton p-Xylene produced*

System boundaries: *Cradle-to-gate (Biomass → pX)*



LCA of p-Xylene production

ReCiPe midpoint method

Four major impact categories are considered in the LCA analysis

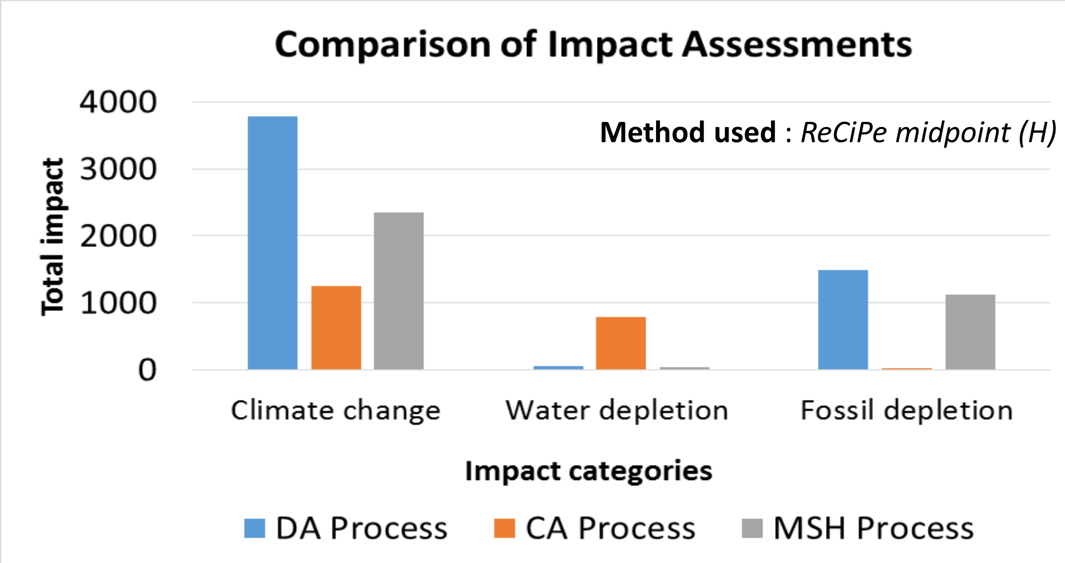
- Climate Change
- *Fossil Depletion*
- *Water Depletion*
- *Agricultural Land Occupation*

Ecoindicator method

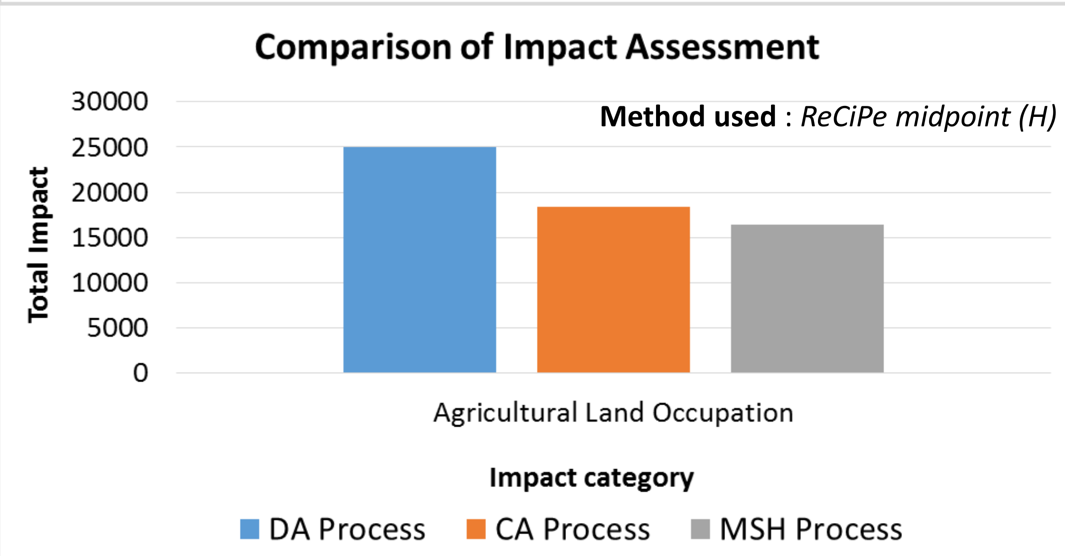
Three major impact categories are considered in the LCA analysis:

- Human Health
- Ecosystem Quality
- Resources

LCA of p-Xylene production

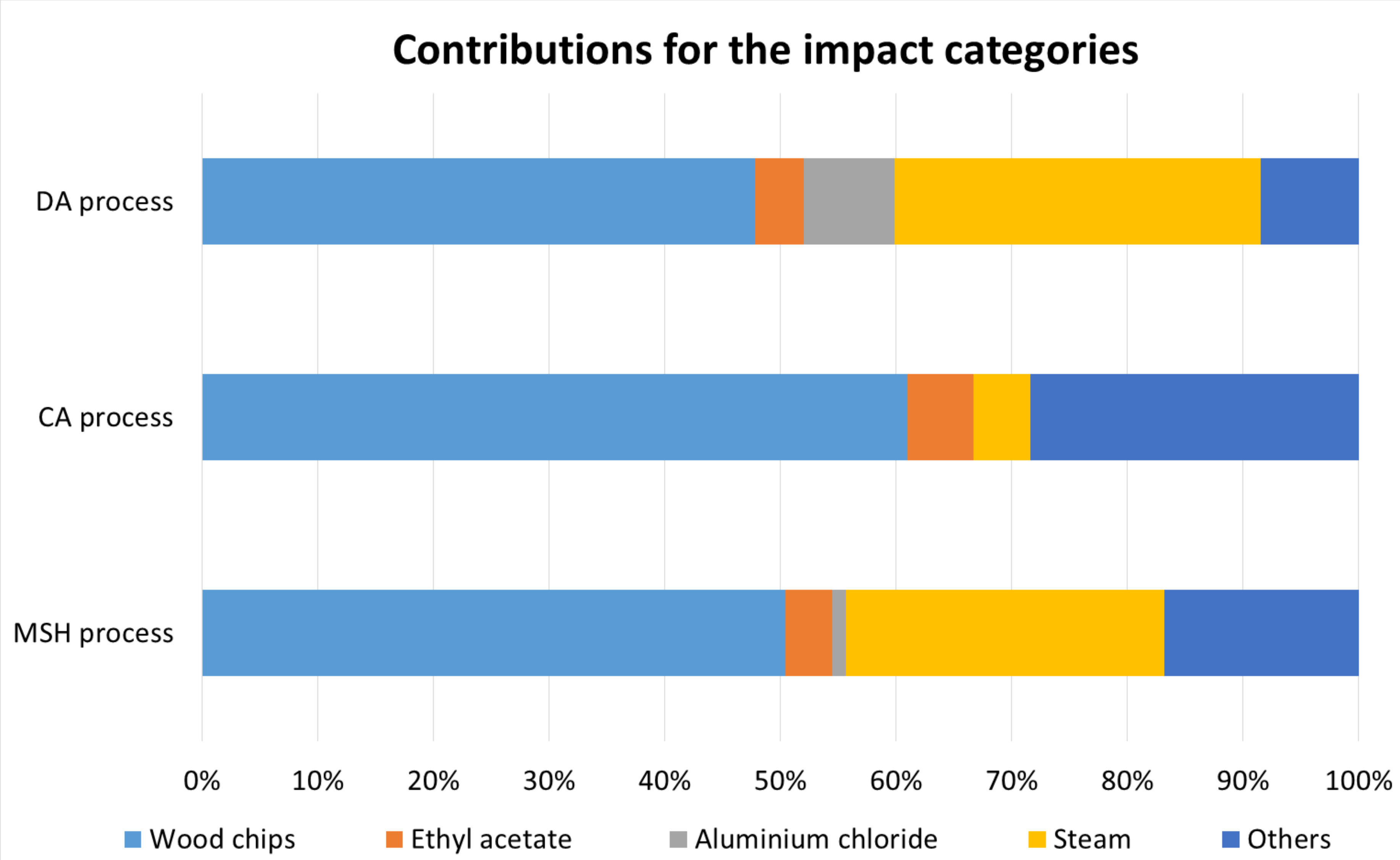


- Steam is the primary contributor in climate change due to energy requirements
- Ethylene plays a major role in fossil depletion – DA high requirement

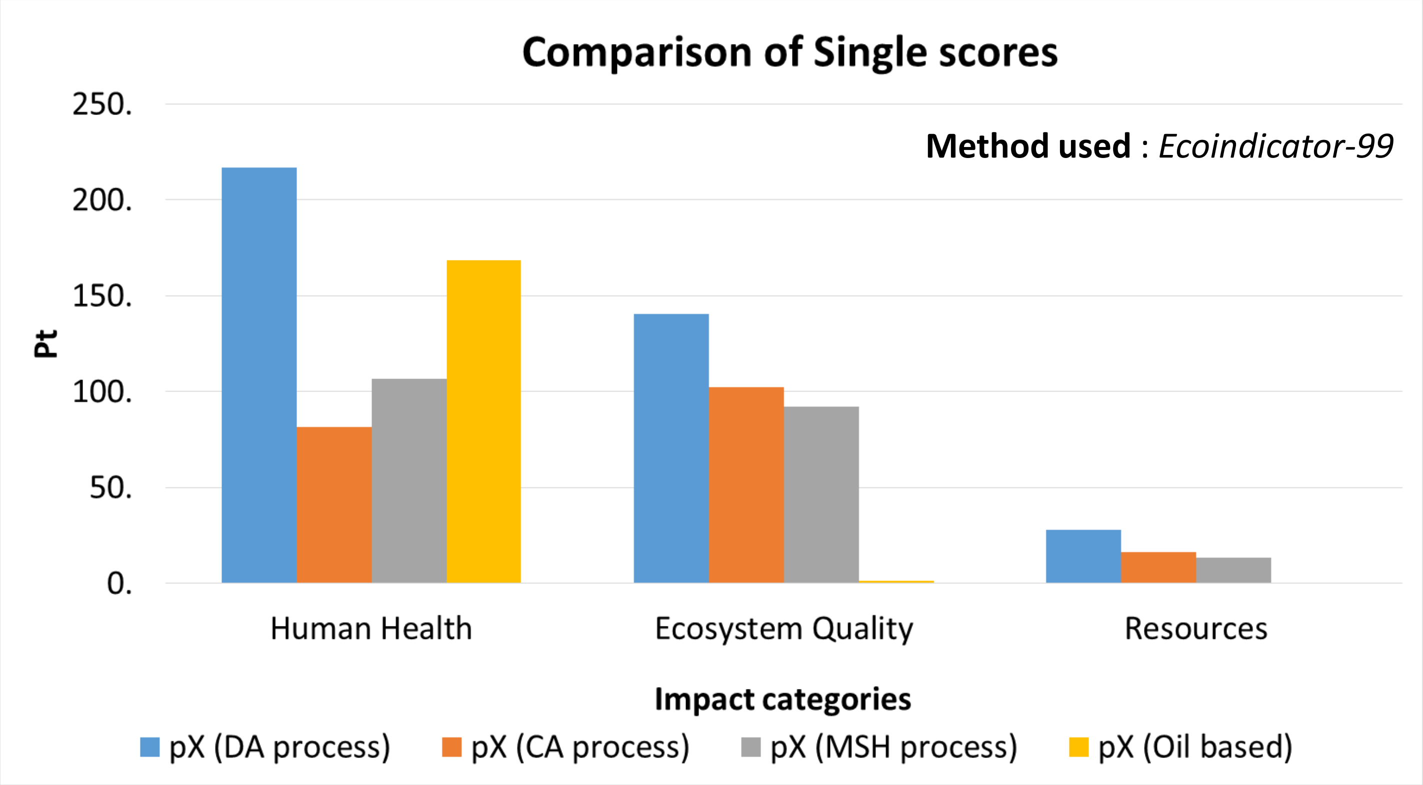


- Processing of biomass has highest impact on agricultural land occupation

LCA of p-Xylene production

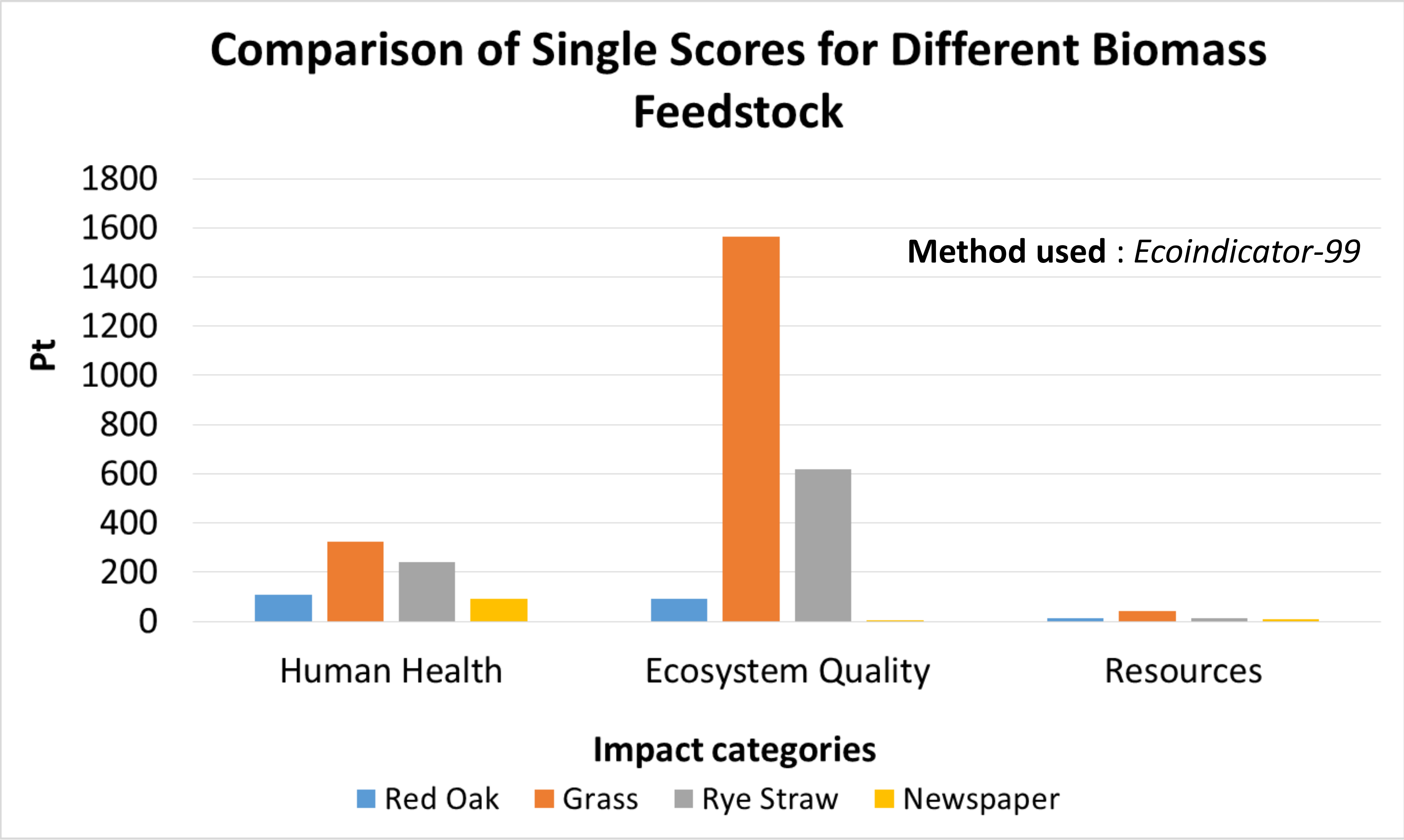


LCA of p-Xylene production



Label	Single score (pt)
pX (DA process)	385
pX (CA process)	200
pX (MSH process)	212
pX (Oil based)	170

LCA of p-Xylene production



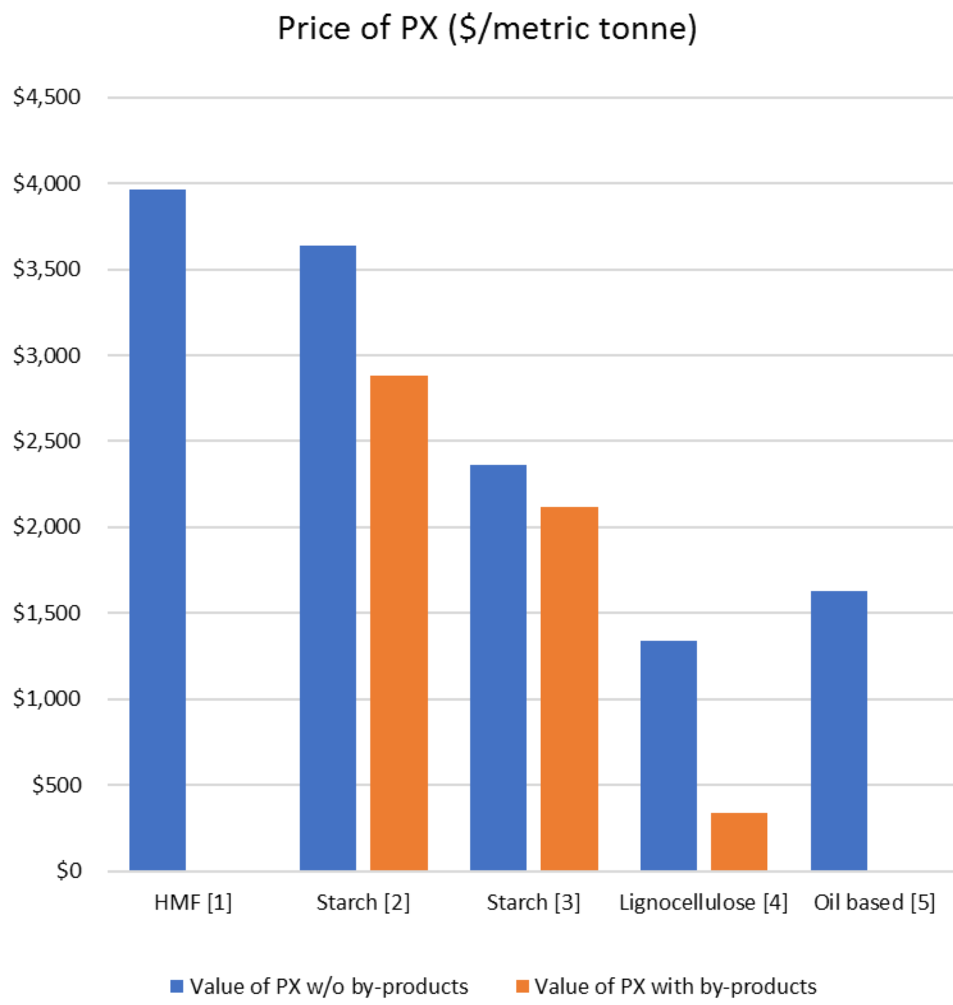
Feedstock	Red Oak	Grass	Rye Straw	Newspaper
Single Score	212	1930	872	104

Discussion: MSH Process

- Use of dilute solutions
    - Increasing the sugar concentration from ~10% to ~40% can reduce the overall impact.
- Use of non – biobased feedstocks. The replacement of ethyl acetate, ethylene and etc. may be useful to further decrease the minimum price as well as environmental impacts
- Incorporating Heat Integration and use of better heat exchangers.
- Decreasing the amount of solvent required for the extraction of HMF which reduces the cost of utilities.

Price of p-Xylene predicted over the years

- HMF as the starting material which is the main contributor of cost of PX.
- Starch as the starting material with conversion to glucose in one reactor and dehydration in another reactor and thus the cost of PX reduces.
- Starch as starting material but the isomerization and the dehydration step are carried out in one biphasic reactor which reduces the cost significantly.
- Start from lignocellulose, which reduces the cost of raw materials.
- Due to better catalyst activity we increase the conversion and selectivity of the HMF to DMF reaction as well as DMF to PX reaction



[1] Lin, Z., M. Ierapetritou, and V. Nikolakis, *Aromatics from Lignocellulosic Biomass: Economic Analysis of the Production of p-Xylene from 5- Hydroxymethylfurfural.* AIChE Journal, 2013. **59**(6): p. 2079-2087.
[2] Lin, Z., V. Nikolakis, and M. Ierapetritou, *Alternative Approaches for p-Xylene Production from Starch: Techno-Economic Analysis.* Industrial & Engineering Chemistry Research, 2014. **53**(26): p. 10688-10699.
[3] Lin, Z., Integrated Design, Evaluation and Optimization of Biomass Conversion to Chemicals, Ph.D. thesis, 2015.
[4] Current Research
[5] ICIS pricing. Available from: www.icispricing.com (accessed May 18, 2013) subjected to change based on crude oil prices.

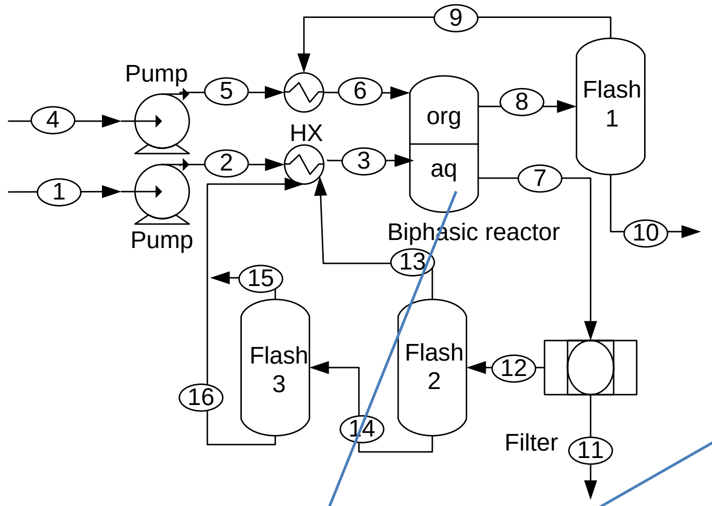
Flowsheet Optimization

Process Flowsheet Optimization

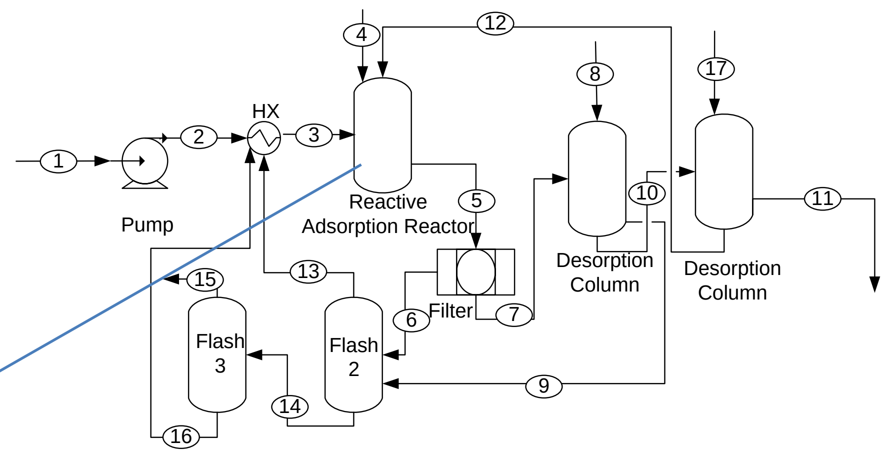
- To achieve better accuracy, the unit models are simulated by detailed models or simulators.
- Deterministic optimization solvers cannot be directly applied in such cases where the simulation is expensive to evaluate for the approximation of derivatives, or the derivatives of the original functions are inaccessible or cannot be accurately estimated due to noise.
- Derivative-free optimization (DFO) methods, specifically surrogate-based optimization, will herein be applied.
- Surrogate-based optimization is that, the original model is used as a source of “computational experiments” to generate data points and then a simpler model is built with these data points.

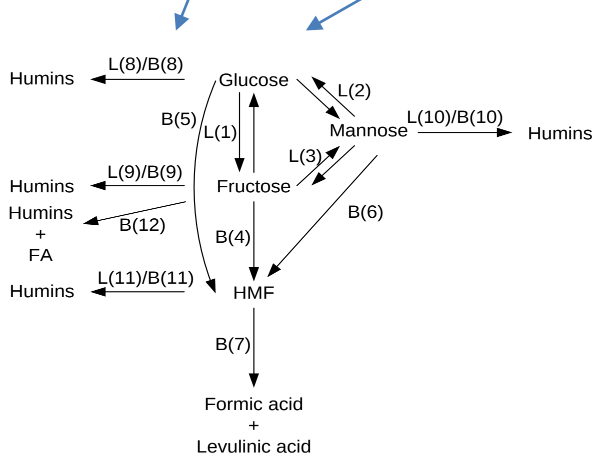
Problem Statement

Reactive extraction



Reactive adsorption





- Reaction and flash units are represented by kriging models

$$F_i^{out} = \hat{f}_R^F(F_{Glu}^{in}, F_{Man}^{in}, F_{Fru}^{in}, F_{HMF}^{in}, F_{LA}^{in}, F_{FA}^{in}, F_{water}^{in}, F_{CrOH^{2+}}^{in}, F_{H^+}^{in}, T_R, \tau, m^*)$$

$*$: m is amount of actived carbon that is used in reactive adsorption

$$F_i^{out} = \hat{f}_{FL}^F(F_i^{in}, P_{FL}, Vf_{FL}, T_{feed})$$

$$Q_{FL} = \hat{f}_{FL}^T(F_i^{in}, P_{FL}, Vf_{FL}, T_{feed})$$

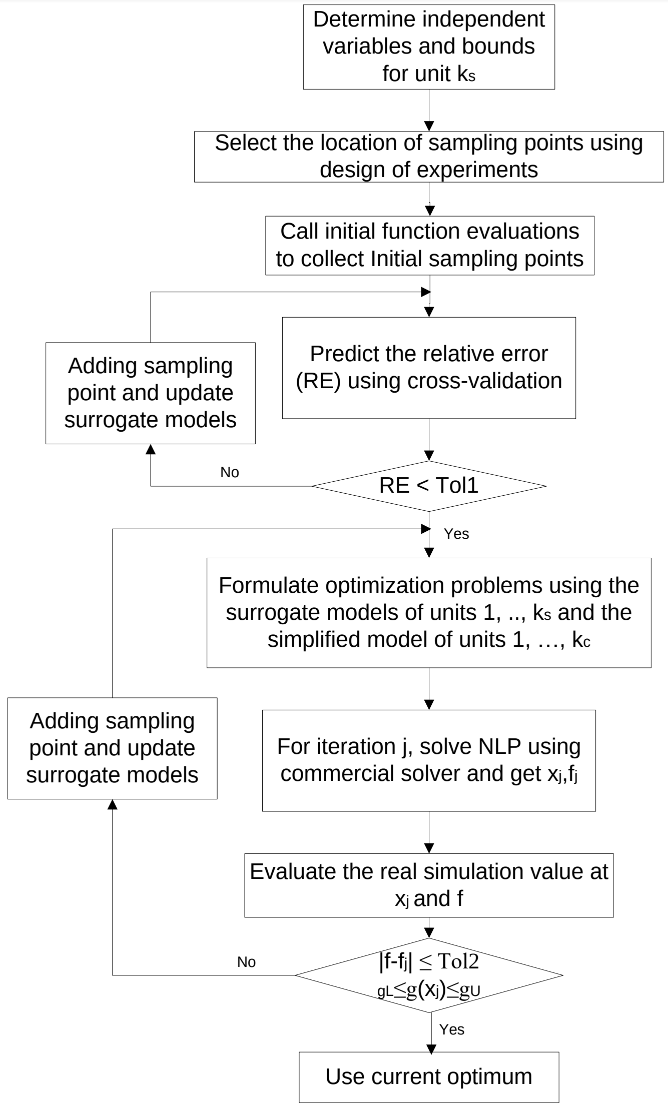
- The other units use simplified models
- Obj: $\dfrac{\sum_k R_k C_k^R + \sum_j Q_j C_j^Q + ATCC}{\sum_i P_i}$

$$ATCC = \frac{TCC}{\text{project life}} = \frac{TDC + TIC + WC}{\text{project life}} \qquad TDC = \sum_u TDC_u \left(\frac{CAP_u^r}{CAP_u^b}\right)^{sf}$$

Optimization Framework

Model construction

Process flowsheet optimization

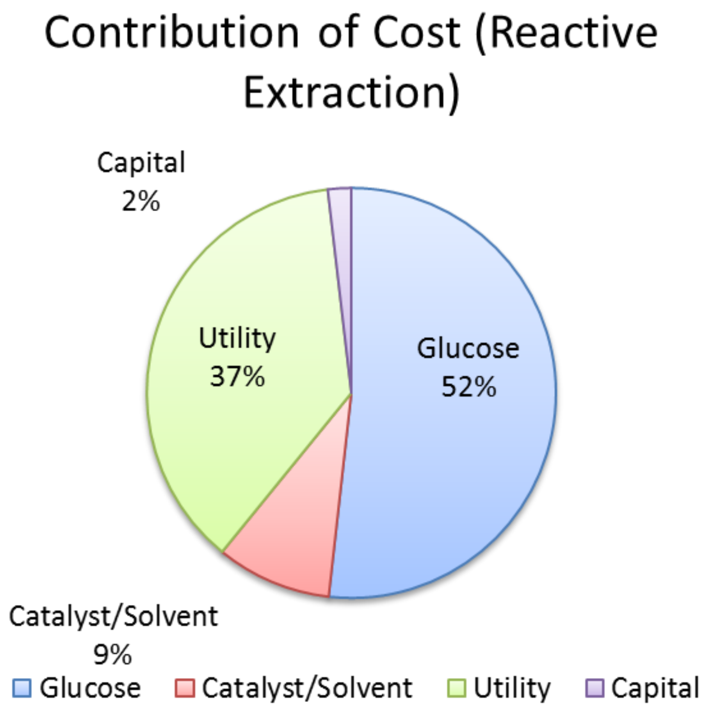


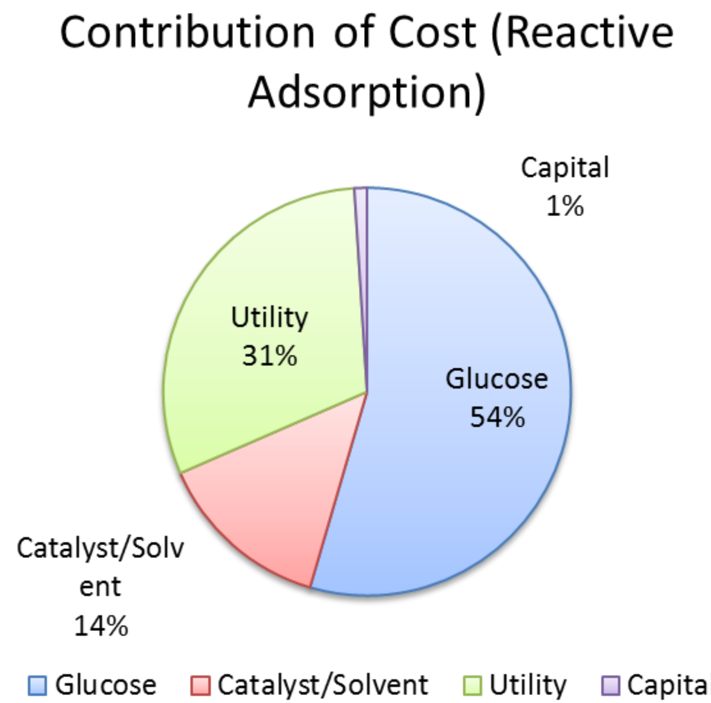
- Derivative - free optimization (DFO) methods, specifically surrogate - based optimization, will herein be applied.
- Surrogate - based model replace each complex unit model. Remaining units are represented with simplified units.

Lin, Z., Wang, J., Nikolakis, V., Ierapetritou, M., *Process Flowsheet Optimization of Chemicals Production from Biomass Derived Glucose Solutions.*, Computers and Chemical Engineering. DOI: 10.1016/j.compchemeng.2016.09.012

Flowsheet Optimization

- Relatively high reaction temperature and short residence time are favored.
- Higher capacity is favored.
- The minimum unit production cost of HMF at 30% glucose loading for reactive extraction is $833/metric ton whereas for reactive adsorption it is $896/metric ton.
- **Glucose** is the primary contributor for the cost of producing PX in both the cases.





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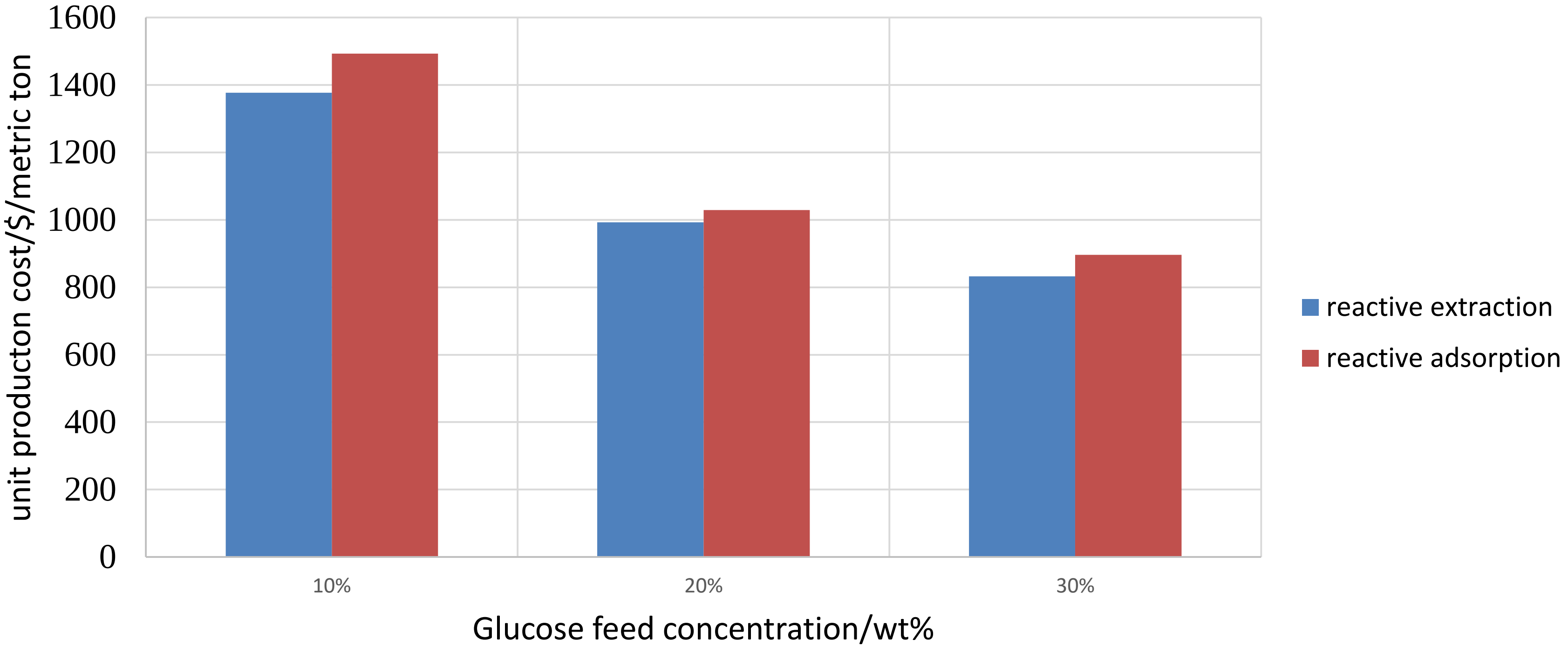
Impacts of Feed Concentration

- The concentration of glucose are considered from 10 wt% to 30 wt%

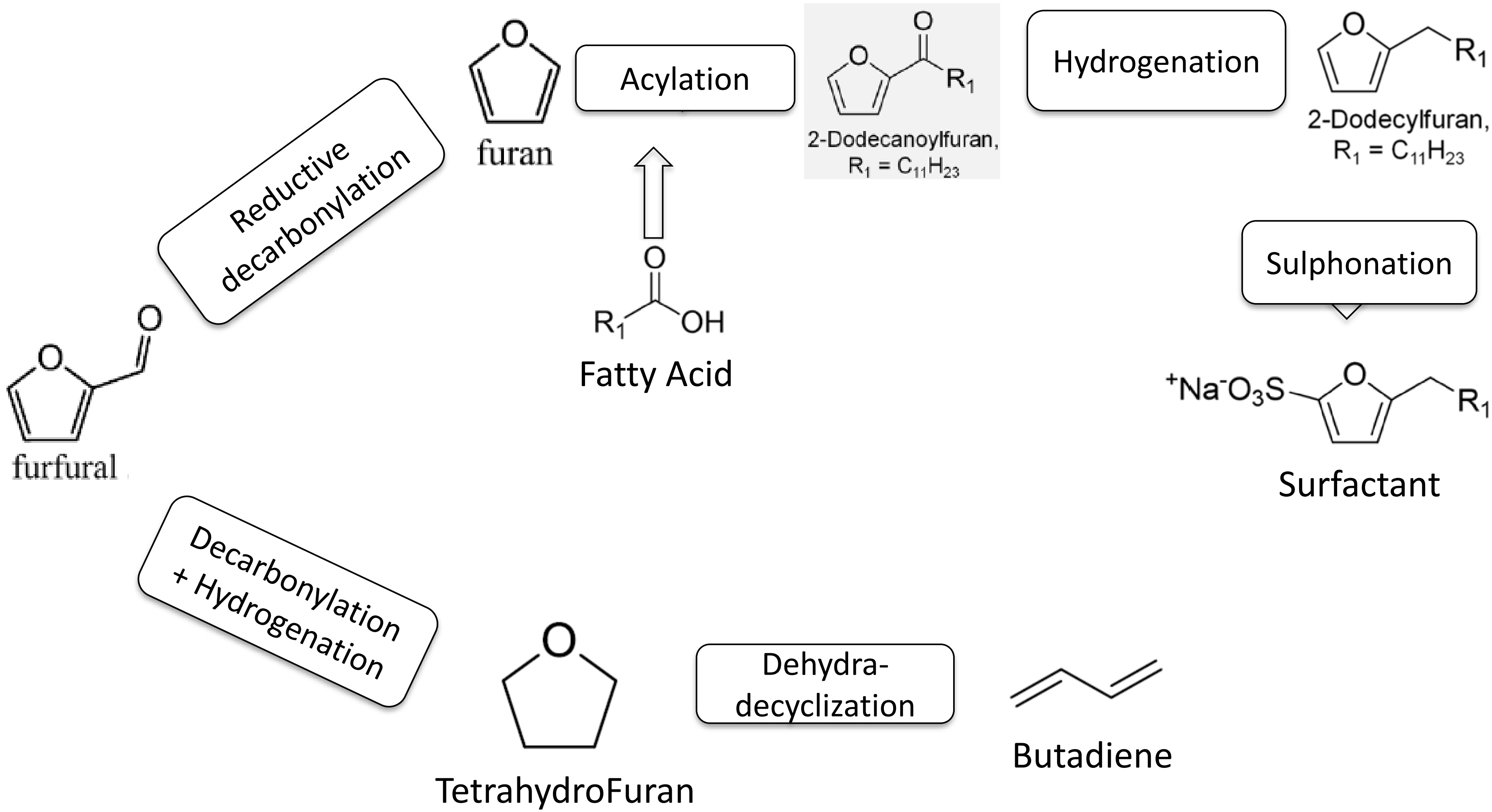


- Higher concentration is preferred since it leads to lower energy consumptions and solvent requirement as well as resulting in higher yields.

Summary

- The pX production from hydrolysis of biomass feedstocks is studied.
- Techno-Economic and life cycle analysis are carried out for three different types of hydrolysis process.
- MSH process gives the best result for economic analysis out of the three processes.
- The dilute acid hydrolysis process is least eco-friendly in the production of bio-based pX.
- Oil based PX process is still better environmentally than bio-based PX process.
- The large requirements of non-renewable chemicals have large contributions to the environmental impact
- The variation of LCA results starting from different types of biomass feedstock is extensive.

Current Work for production of different chemicals



Current and Future Work

1. To find the optimized operating conditions for the MSH process using multi-criteria surrogate based optimization.

2. Integration of the production of a variety of products including surfactants and butadiene from furfural.

3. Integrating chemicals produced from biomass into one flowsheet to simulate a working bio-refinery.

4. Optimizing the production process of the bio-refinery according to market’s need and demand.

Acknowledgements

Financial support

The Catalysis Center for Energy Innovation, an Energy Frontier Research Center in University of Delaware, funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0001004

National Science Foundation under the grant number NSF CBET 1434548.