LIFE CYCLE ASSESSMENT FOR BIO-BASED PRODUCTION

OF P-XYLENE

by

PRANEETH ANNAM

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Marianthi G. Ierapetritou

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ABSTRACT OF THE THESIS

Life Cycle Assessment for Bio-Based Production of p-Xylene

By PRANEETH ANNAM

Thesis Director:

Dr. Marianthi G. Ierapetritou

The importance of sustainable routes for the production of chemicals has increased over past few decades. The success of a biorefinery is based on its competitiveness with traditional refineries in terms of economics and process sustainability. This work aims to evaluate the environmental performance of cradle-to-gate production of p-Xylene from ligno-cellulosic biomass by a novel process involving the hydrolysis of biomass using Molten Salt Hydrates (MSH process) developed by Catalysis Center for Energy Innovation (CCEI) at University of Delaware and to compare with other existing hydrolysis processes including Dilute Acid (DA) and Concentrated Acid (CA) processes. The work is performed on ecoinvent database using ReCiPe and TRACI methods by a life cycle analysis software, SimaPro®. Noticeably, CA and MSH processes perform better in climate change, fossil depletion and ecotoxicity when compared to the DA process. The main contributions for the MSH process arise from the processing of high amount of steam and cultivation and processing of biomass. Sensitivity analysis indicates a significant variance in the MSH process for different kinds of biomass feedstock used and for various energy scenarios for the generation of steam. The uncertainties resulting from the assumptions and developing technologies are assessed by performing uncertainty analysis using Monte Carlo Analysis.

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1. Introduction

1.1 Motivation

Over the past few centuries, the energy is derived from fossil fuels all around the globe. A study by the US Department of Energy states that 85% of energy consumed by the United States is derived from fossil fuels. Unfortunately, the energy requirements are amplified to a much greater degree with time. Hence the depleting oil reservoirs, as well as the increasing environmental concerns impelled the development of renewable sources of energy over fossil fuels. Biomass is a rich source of several chemicals that are produced by petroleum resources. As the United States is fortunate to be endowed with abundant and diverse agricultural and forest resource, unused cropland and favorable climates, there is a huge scope to use these resources to augment our energy sources. The translation of importance from conventional refineries to bio-refineries is possible based on whether the bio-based products can successfully compete with petroleum-based products in terms of economics, reliability, and sustainability. According to a study, US Department of Energy has projected that bio-based fuels and chemicals in the year 2030 will contribute to 20% of US transportation fuel and 25% of the production of U.S. commodities, in comparison to 0.5% and 5% respectively in 2001.[1] Some of the top-value chemicals from the biomass mentioned by US Department of Energy, Energy Efficiency, and Renewable Energy are Ethanol, Formic acid, Furfural, Lactic acid, Glycerol, Malonic acid, Hydroxymethylfurfural (HMF) etc. The success of a biorefinery not only depends on the types of products but also its environmental performance. It is important to achieve better stasis between environmental impacts and the process economics. Bio-based production of p-Xylene has drawn interest of

several companies like Coca-Cola, H.J. Heinz Company, PepsiCo as p-Xylene is the main precursor to Polyester Polyethylene Terephthalate (PET) and high resin prices for petroleum derived p-Xylene. These factors have resulted in recent announcements [2, 3] by these companies to use plant based PET bottles. In our previous work [4-6], we have studied the Techno-Economic and the Life Cycle Analysis for the production of p-Xylene from starch. We found out that the minimum cost and the environmental impacts are higher than that of fossil-based p-Xylene. As the cost and the LCA results vary with different hydrolysis methods for the treatment of biomass, in our present work we studied a new hydrolysis process, Hydrolysis by Molten Salt Hydrates (MSH process) [7] developed by Catalysis Center for Energy Innovation (CCEI) at University of Delaware and compared its environmental impacts with other hydrolysis processes named Concentrated Acid Hydrolysis (CA process), and Dilute Acid Hydrolysis (DA process). [8]

1.2 Dilute Acid Hydrolysis

It is the most common used hydrolysis process to treat biomass, and is based on the work performed by Harris et al.[9] In our work we have taken the idea of the basic process and made small changes in the concentration of acid and steam for the production of sugars for different chemicals and fuels. It is a two-step hydrolysis process using dilute acids to hydrolyze the biomass to glucose and xylose.

1.2.1 Reaction pathway

Dilute Acid Process (DA process) is a two-stage process, wherein the first stage is the pretreatment of biomass; hemicellulose in the biomass is converted into xylose and in the second stage cellulose is broken down to glucose. We use Sulfuric acid (1.6 wt. % and liquid to solid ratio 1.35) for the process. The expected conversion

of hemicellulose is 85%. After the separation of Xylose, the solid stream enters the second stage of hydrolysis where glucose is formed with an expected yield of 57%. After this step, the unreacted solid which consists mostly of lignin filtered. Neutralization step is essential to prevent the buildup of acid in the downstream process.

1.2.2 Process description

The first stage is the prehydrolysis of hemicellulose to xylose and the second stage is hydrolysis of cellulose to glucose. The process flowsheet for DA process is shown in the figure 1. Stream 1, a composite of biomass, steam, and sulfuric acid is fed to the first stage reactor (R1) where hemicellulose is hydrolyzed to xylose. Liquid to Solid ratio (L/S) and the acid strength are maintained constant at 1.35 and 1.6 wt. % respectively. Reactor (R1) is maintained at 170 ^{0}C and a residence time averaging between 12-14 minutes. The conversion of hemicellulose is expected to be 85%. The product (Stream 2) is fed to a flash drum (V1), where steam is separated and recycled (Stream 3) to the reactor (R1). The stream exiting from the flash drum (Stream 4) is then washed with water and xylose and are separated using a filter (FIL 1). The outlet of the filter (Stream 5) is fed to another reactor (R2) where furthermore acid, steam, and water are added to maintain the acid strength at 0.8% and L/S ratio at 3. Reactor (R2) is maintained at 230 ^{0}C and a residence time of 4s. The expected yield of glucose is 57%. The product stream (Stream 6) is fed to a flash drum (V2) where steam is recycled (Stream 7). The stream exiting from flash drum (Stream 8) is washed with water and fed to a filter where lignin is separated. The outlet of the filter (Stream 9) is neutralized with lime in the reactor (R3). The neutralized residue is separated by a filter (FIL 2) and glucose is obtained as the product.

Figure 1: Process flowsheet for Dilute Acid Hydrolysis process

1.3 Concentrated Acid Hydrolysis

Concentrated Acid Hydrolysis (CA) process that was developed in the early 20th century as DA process but later discontinued due to its least economic viability for the high consumption of acids. However, the development of the effective acid recovery solutions for CA process, has gained the interest again in this process. Arkenol's [10] and Weyland's [11] processes are some of the concentrated acid patented processes that are extensively investigated and their technology is at pilot plant level. Arkenol's process is a two-stage hydrolysis process that uses sulfuric acid of 70-75 wt. % concentration. Whereas Weyland's process is also a two-stage hydrolysis process; it uses a mixture of sulfuric and phosphoric acid of 50-60 wt. % concentration and solvent to extract the acid from the products. We have used the Weyland's process in this paper considering the fact that Arkenol's process might be an expensive option due to involvement of chromatography separation for acid and sugars. Weyland's process is also a two-stage process that uses sulfuric acid of 70-75 wt. % concentration for the hydrolysis of biomass. Chromatography is used

to separate the products from the acid. This process also takes into consideration of combination of sulfuric and phosphoric acids at a concentration of 50-60%.

1.3.1 Reaction pathway

CA process is a two-stage process where in the first step the biomass carbohydrates are converted to oligosaccharides and in the second stage they are further converted into C_5 and C_6 sugars. In this process a combination of sulphuric acid and phosphoric acid is used for hydrolysis. The acid to biomass mass ratio and acid to water mass ratio is maintained at 3:1 and mass ratio of sulphuric acid to phosphoric acid is maintained at 2:1. The conversion of biomass to oligo-saccharides is expected to be 95%. We separate the acid and oligo-saccharides by extraction using dimethylether (DME) as the solvent. The mass ratio of hydrolysate to solvent is 3:8. The oligo-saccharides then enters the second stage where it is converted into mono-saccharides. The conversion of oligo-saccharides to glucose and xylose is expected to be 95%. A neutralization step is added to remove the acid as there is acid buildup in the downstream process.

1.3.2 Process description

The process flowsheet for CA process is shown in the figure 2. Biomass, acid and water (stream 1) is fed into the first stage reactor (R1). Reactor outlet stream (stream 2) is introduced into an extraction column (E1) with DME as the solvent. The organic stream (stream 3) containing solvent and acid is removed from the top and the aqueous phase (stream 4) containing oligo-saccharides and water is removed from the bottom. Organic stream is fed to an evaporator (V1) where the solvent is evaporated and acid is separated and recycled (stream 6). Vapor phase (stream 5) is fed to a separator (V2) where water is separated from the vapor solvent in vacuum.

Solvent (stream 7) is condensed in a condenser (V3) and recycled in the extraction column. The aqueous stream (stream 4) is washed with water and lignin is removed via a filter (FIL 1) and fed to the second stage reactor (R2). The product stream (stream 10) is neutralized with lime in reactor (R3). The neutralized residue is separated by a filter (FIL 2) and we get a mixture of C5 and C6 sugars.
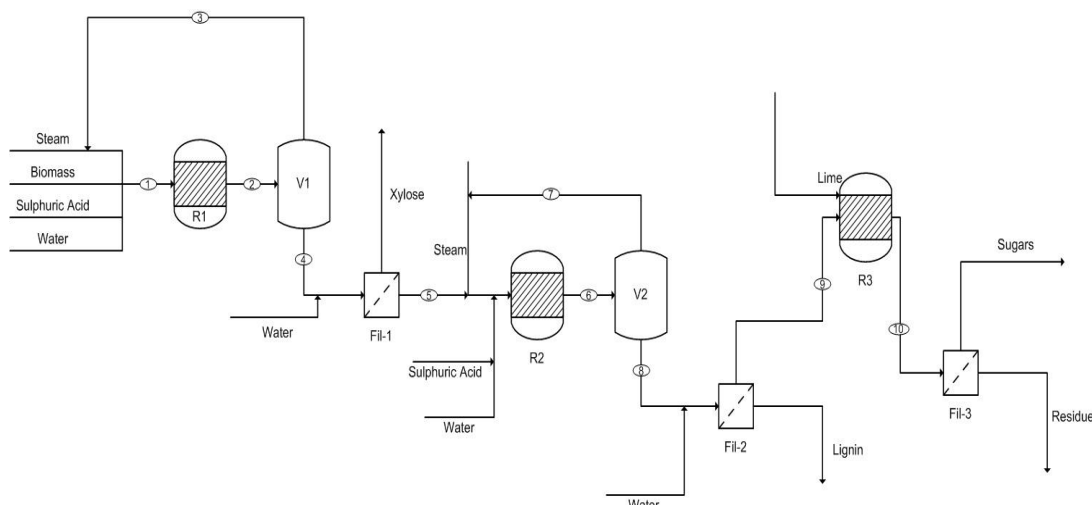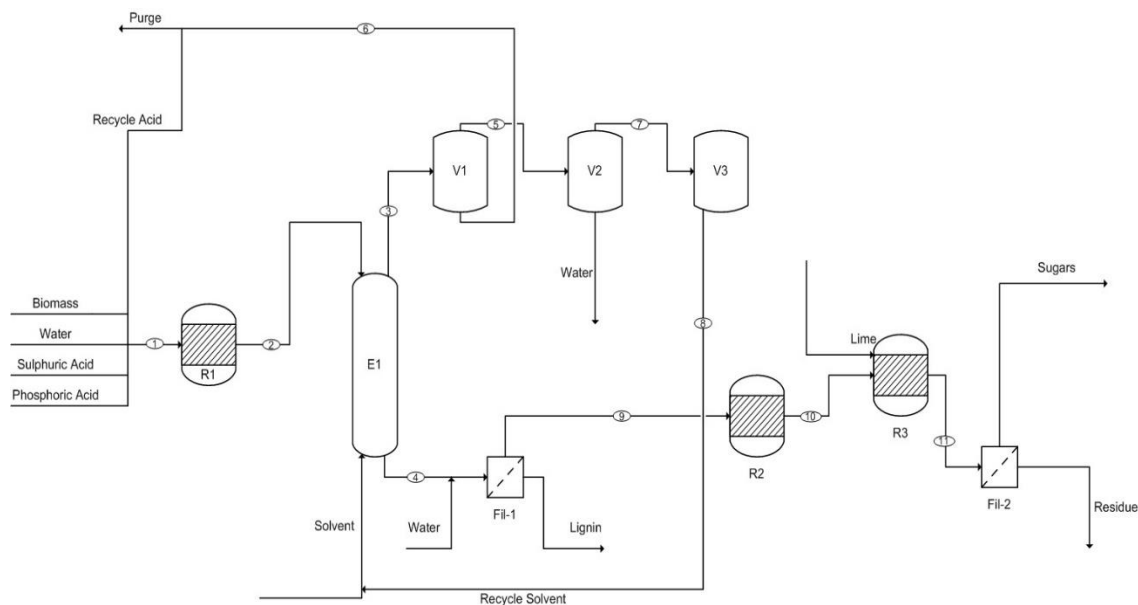

Figure 2: Process flowsheet for Concentrated Acid Hydrolysis Process

1.4 Hydrolysis by Molten Salt Hydrates

From our previous work on the economics and life cycle assessment for the production of p-Xylene from starch, it was found that the major contributors for both the categories were starch, solvent, and the catalyst, that were used in the conversion of starch to glucose. Hence our current work focuses on a novel process that produces glucose from biomass and integrating it with the downstream production of p-Xylene. This process is developed by Catalysis Center for Energy

Innovation (CCEI) at the University of Delaware. It uses molten salt hydrates for hydrolysis of biomass into C_5 and C_6 sugars.

1.4.1 Reaction pathway

Hydrolysis by Molten Salt Hydrates (MSH process) is a single stage process, based on a laboratory scale process. In this process, we use lithium bromide solution (59 wt. % LiBr + 0.5 wt. % H_2SO_4) for the hydrolysis of biomass. Hydrolysis is performed at 85 ^{0}C and yield of glucose and xylose is expected to be 89% and 95% respectively. At this stage, lithium bromide is not separated as it is very difficult and hence it is taken forward to dehydration step and then is recycled. It is observed that the molten salt hydrates do not affect the hydrolysis process.

1.4.2 Process description

The process flowsheet for MSH process is shown in the figure 3. Biomass, water, and molten salt hydrates (stream 1) are fed to a reactor (R1). The product stream (stream 2) that is coming out of the reactor is sent for filtration to separate lignin from the sugar mixture in a filter (FIL 1). We get a mixture of C_5 and C_6 sugars.
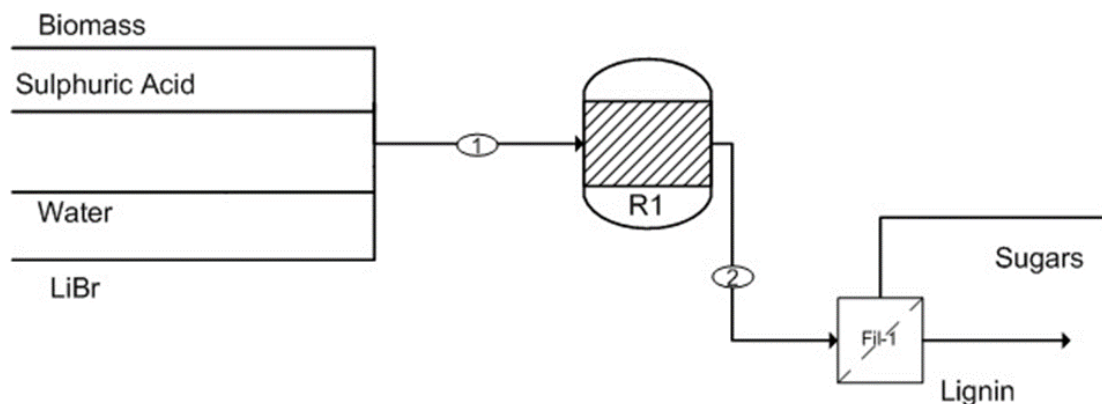
Figure 3: Process flowsheet for Hydrolysis by Molten Salt Hydrates

1.5 p-Xylene production

There are three important steps after the production of sugars by hydrolysis of biomass, which are production of HMF, DMF, and p-Xylene respectively. The process description for these three steps is explained below.

1.5.1 HMF/Furfural production

Sugar that is formed by the hydrolysis process is mixed with ethyl acetate and aluminum chloride and is fed to a biphasic reactor (R1). The organic phase (stream 2) containing the solvent, furfural, and HMF are then fed into a series of flash drums, where the solvent with furfural is separated from HMF (streams 2, 9, 11). The vapor phase is then sent to a distillation column (C1) where solvent and furfural streams are separated. Solvent stream (stream 15) is then recycled and furfural stream (stream 15) is further purified to take out HMF as a product. Another stream of solvent is introduced with the second extraction phase. The separation of solvent and aqueous phase is similar to the first stage where the solvent is recycled with HMF as the product and furfural as a by-product. The remaining aqueous phase (stream 5) is fed to a filter (FIL 1) to remove humins. The outlet from the filter (stream 6) is introduced into an evaporator (V1) where water produced from the dehydration reaction is separated. The outlet stream (stream 7) containing unreacted raw materials and catalyst is recycled.
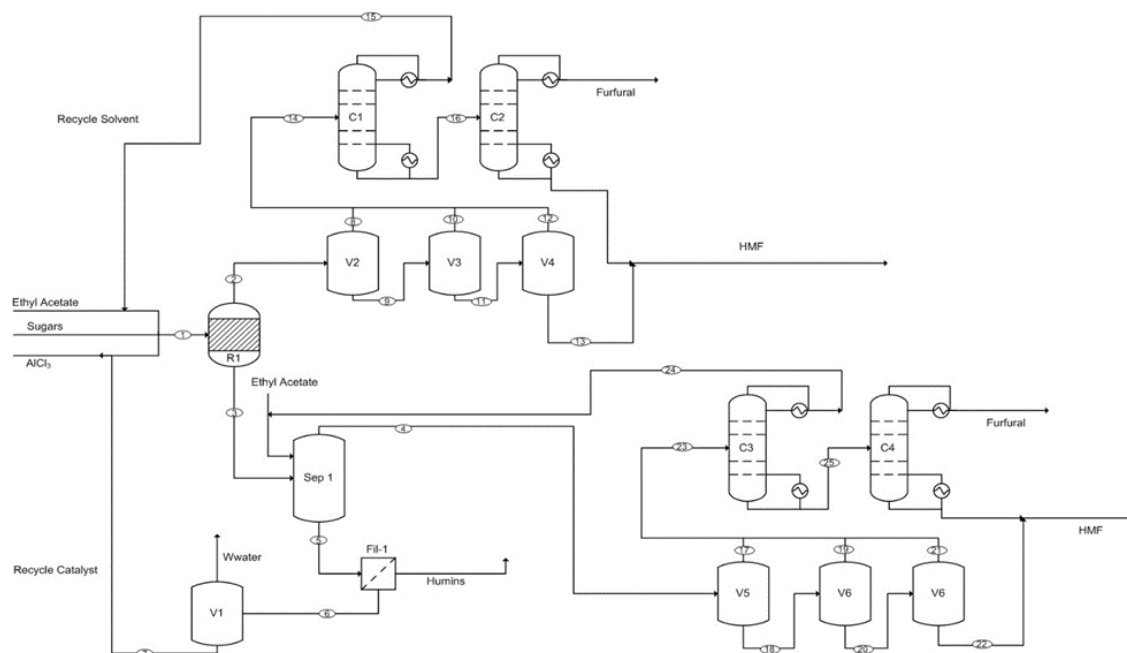
Figure 4: Process flowsheet for HMF/Furfural production

1.5.2 DMF production

HMF produced is evaporated and fed into a fluidized bed reactor (R1) with compressed hydrogen to form DMF (stream 2). Furfural present is converted to methylfuran. The product (stream 2) is fed to a flash drum to separate excess gas and water from DMF.
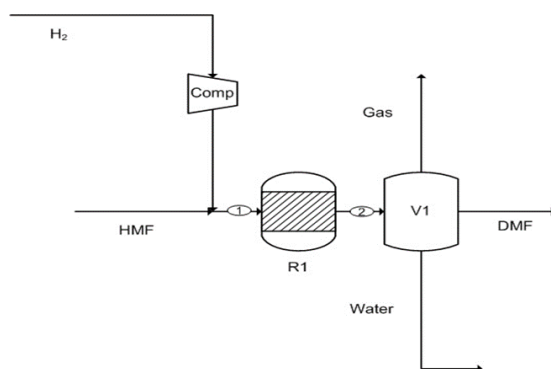
Figure 5: Process flowsheet for DMF production

1.5.3 p-Xylene production

DMF (stream 1) with heptane and compressed ethylene feed are fed to a CSTR (R1). A flash vessel in the latter step removes most of the water. The liquid organic stream (stream 3) is fed to a pump to increase the pressure to 5 MPa and is fed to a distillation column (C1) to remove most of the heptane which is then recycled back to the inlet of pump P1. 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 98%.
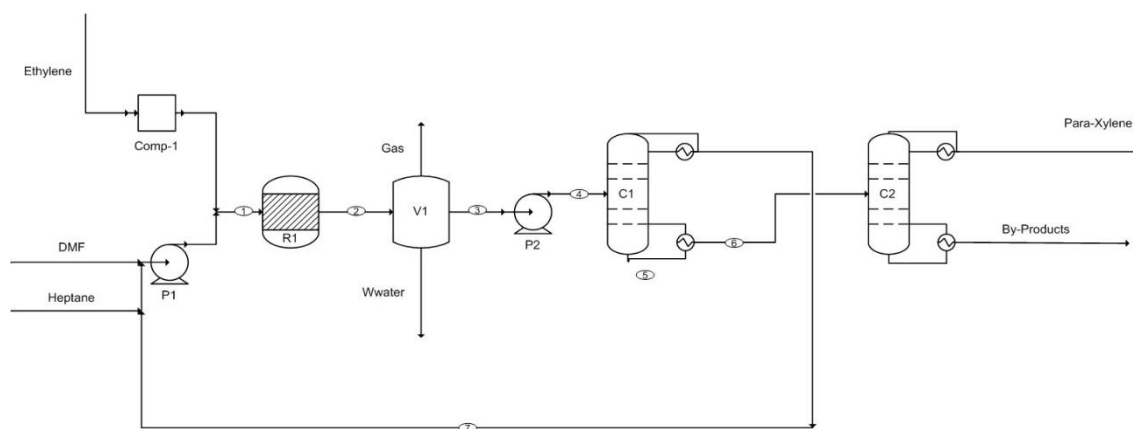
Figure 6: Process flowsheet for p-Xylene production

2. Life Cycle Assessment

2.1 Background

Environmental Life Cycle Analysis is the analytical framework to quantify the resources used and the impact to the environment 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.[12]

There are different variations to the fact of how the first LCA study is performed. It depends on who is telling it, but what is generally considered is a study for Coca-Cola conducted in 1969-70 by the Midwest Research Institute in the United States, when it was considering whether they should manufacture beverage cans and looking at a number of issues related to packaging: environmental consequences of packaging manufacture, alternatives to beverage cans, etc. The manager of the packaging function at Coca-Cola looked for an all-inclusive study that considered energy, material and environmental consequences of the entire packaging production, from raw material extraction to waste disposal. This work is never published because of the confidential nature of the work. One of the important outcomes was that the Coca-Cola Company gained comfort with the idea of switching from glass to plastic bottles.[13]

In its earlier phase, LCA was used as a tool for product comparisons, for example, in the comparison of environmental impacts of disposable and reusable products. But the scope of LCA has grown to a greater extent and in these days it is used in government policy-making, strategic planning, process improvement, product design etc. [14, 15] The great interest in LCA can be explained by a shift in the focus of environmental work in the industry when the idea- environmental protection should go beyond end-of-pipe strategies and emission control gained importance. As the result of LCA studies, the idea to quantitatively compare the alternatives to identify the eco-friendly option came into the picture. Moreover, it could deal with environmental issues in a structured way and it could handle several environmental issues at the same time. The interest in LCA was thereby converted into practice.

2.2 LCA methodology

The Life Cycle Assessment is a popular tool and a globally established method that uses several environmental impacts over the full life cycle of a product. It is generally carried out in four steps iteratively to allow for adjustments [16-18] (ISO standards 14040-14044). The network of the Life Cycle Analysis is shown in the figure 7.

1. **The Goal and Scope Definition phase:** which at first involves defining the objective/aim of the study; this defines the depth and breadth of LCA. According to ISO standard 14041, the goal definition "shall unambiguously state the intended application, the reason for carrying out the study and the intended audience." LCA may be carried out to support product development or strategic planning, or its intended use is marketing. The intended audience,

of course, varies between applications and may consist of product developers, top management, authorities, customers or a combination of these.

There are several choices that are essential to make in the scope of the LCA studies which includes functional unit (FU), definitions of temporal, geographical, and technology scopes system boundaries (natural systems, time etc.), principles of allocation (e.g. mass allocation, economic allocation, energy allocation, etc.) Each the above mentioned are related to perform the modeling.

2. **The Life Cycle Inventory Analysis phase:** It is an inventory of input/output data with regard to the system being studied, it involves the collection of the data required to meet the goals of the defined study. In other words, making an inventory analysis is to construct a flow model of a technical system.
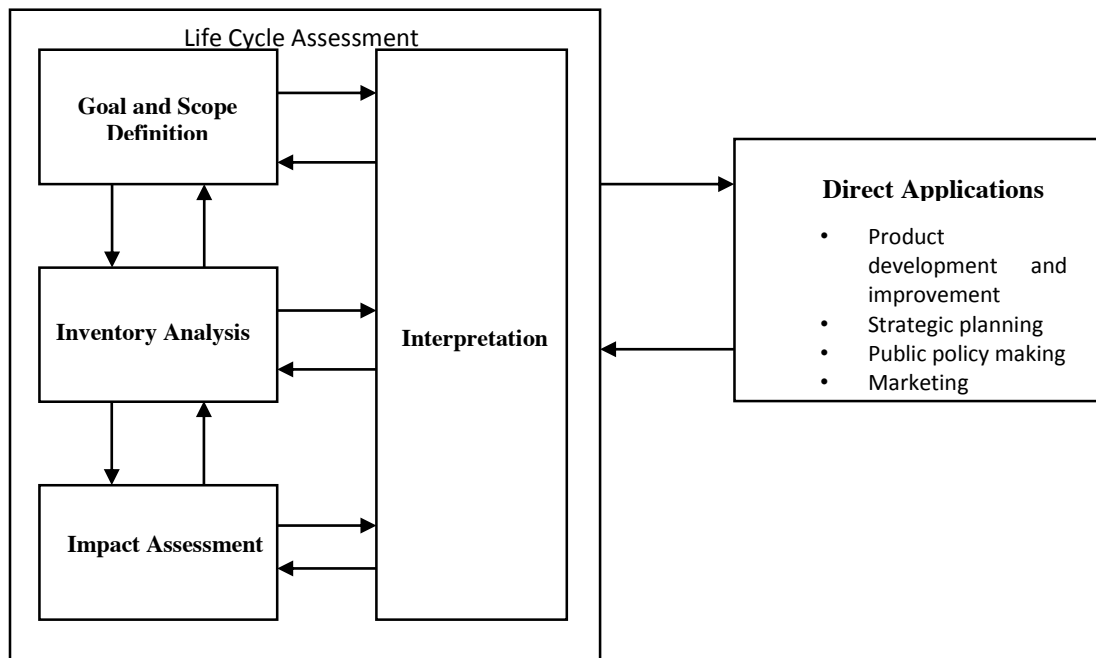
Figure 7: Methodological framework for LCA (ISO 14040 and 14044)

Generally, the activities of the life cycle inventory analysis (LCI) include:

1. Construction of the flowchart according to the system boundaries decided on in the goal and scope definition

2. Data collection for all the activities in the product system followed by documentation of collected data

3. Calculation of the environmental loads (resource use and pollutant emissions) of the system in relation to the functional unit

It is either a cumulative or even in some cases, an iterative effort. There is a necessity to make some changes in the goal and scope definition as the data gets collected and we study more about the system.

There are different databases from several countries to compute the life cycle inventory like US LCI, ELCD, US Input Output, EU and Danish Input Output, Swiss Input Output etc.

3. **The Life Cycle Impact Assessment phase:** It is the third step of LCA which is used to provide an additional information to help assess a product system's LCI results so as to better understand their environmental significance. It involves calculating the potential impacts created by the identified inputs and emissions.

Impact assessment is a vital phase of LCA. An impact assessment is used to interpret the emissions and resource consumption with the stages of (a.) classification which involves sorting of all substances into classes according to the effect they have on environment, (b.) characterization which involves multiplication of all the substances by a factor that reflects their relative contribution to environmental impact, (c.) normalization, which involves the comparison of the quantified impact to a certain reference value and (d.)

weighting which involves assigning different value choices to impact categories to generate a single score.

For each substance, a schematic cause-response pathway needs to be developed that describes the environmental mechanism of the substance emitted. Along with this environmental mechanism, an impact category indicator result can be chosen either at midpoint or endpoint level. Midpoint level indicators are considered to reflect the links in the cause-effect chain prior to endpoints, from the activities causing environmental stressors to environmental effects whilst endpoint indicators are the scale to quantify the final end effects. Traditionally midpoint indicators are grouped into 18 categories like ozone depletion, climate change, eutrophication etc. (it might vary with the method used) and endpoint indicators are grouped into three areas of protection, human health, ecosystem diversity and resource availability.

4. **The Interpretation phase:** It is the final phase of the LCA procedure, in which the results of an LCI or an LCIA, or both, are summarized and discussed as a basis for conclusions, recommendations, and decision-making in accordance with the goal and scope definition to help make a more informed decision. This phase includes uncertainty and sensitivity analysis (it deals with the effect of critical or imprecise data on the results), dominance analysis (investigation of the parts of LCA that yields dominant environmental impact), contribution analysis (identifying environmental loads that contribute to the overall environmental impact) etc.

2.3 Life Cycle Impact Assessment Calculations

The main objective of the environmental science is to understand the effects of human activities on our ecology. LCA associates these effects or impacts to these specific activities or products. These activities lead several chemicals enter to our eco-system and affect natural processes and their environment including human health, environmental health, and resource depletion. Impact assessment connects emissions of these activities/products (that are mentioned in inventory) to the variations in the aforementioned categories. Developing an impact assessment model is important yet a vital step to proceed with performing LCA. These models give characterization factors for different impact assessment methods to calculate the overall magnitude of the impact.

The first step to get these characterization factors is by environmental sampling and measurement methods which is followed by environmental fate and transport models which explain the motion of chemicals through the environment. The final step is to study the effects of these chemicals on humans and organisms (that come in contact with them), through exposure and effect modeling.

Impact assessment considers the changes in the environment and the potential damages that occur to our environment over the product's life cycle. These changes in the environment are calculated via measurement of concentrations of substances in various media. This is a complex task than it seemed to be; this is because of various reasons like the substances' properties, very low concentrations in the media, and importantly the complexity of measuring concentrations everywhere, everything and every time. So, it uses the previously developed environmental protocols for sampling, and then extrapolate the samples to a large scale. In many cases, it is efficient to measure the overall changes in the environment rather than

measuring for each chemical. These are called direct indicators of impacts. (E.g. pH is a direct indicator for acidification, dissolved oxygen (D.O.) is a direct indicator for eutrophication)

Impact assessment depends on the characterization factors that convert emissions to impacts which rely on the fate of a substance in the environment and its potency for a receptor. For example, in USEtox model the characterization factor (CF) is a function of fate factor (FF), exposure factor (XF), and effect factor (EF), which is given by:

$$CF = FF * XF * EF$$

The indicator result (I) is given as a function of characterization factor, Q(i) that connects intervention with impact category and the magnitude of the intervention, m(i).

$$I = \sum_i Q(i)m(i)$$

There are different models and methodologies of Life Cycle Impact Assessment to assess the environmental impact of a system, which are used in LCA software to quantify the impact results.

2.4 Life Cycle Impact Assessment Methods

There are several impact assessment methods to solve the complexity of environmental problems. The main reason behind the concept of having several LCIA methods are the widely diverging views of humans on nature and the ways to control the society. These different methods represent, more or less, various solutions to these problems. The final decision will have to be made by the decision-

maker irrespective of whatever the method is used. There are several types of LCIA methods for different regions of the world and for different functions such as US' TRACI method, Japan's LIME method, Netherlands' ReCiPe method etc.

LCIA methods are evaluated either at midpoint or endpoint level. Midpoints are considered to be links in the cause-effect chain of an impact category, prior to endpoints, whilst endpoint method further normalizes and weighs these impact categories data to interpret the values as single indicator scores. For example, the midpoint indicator for ozone layer depletion is decreased ozone potential whereas the endpoint indicator is skin cancer for humans. Figure 8 shows the general framework for LCIA.[19] For our analysis, we chose ReCiPe and TRACI method to analyze the p-Xylene produced.
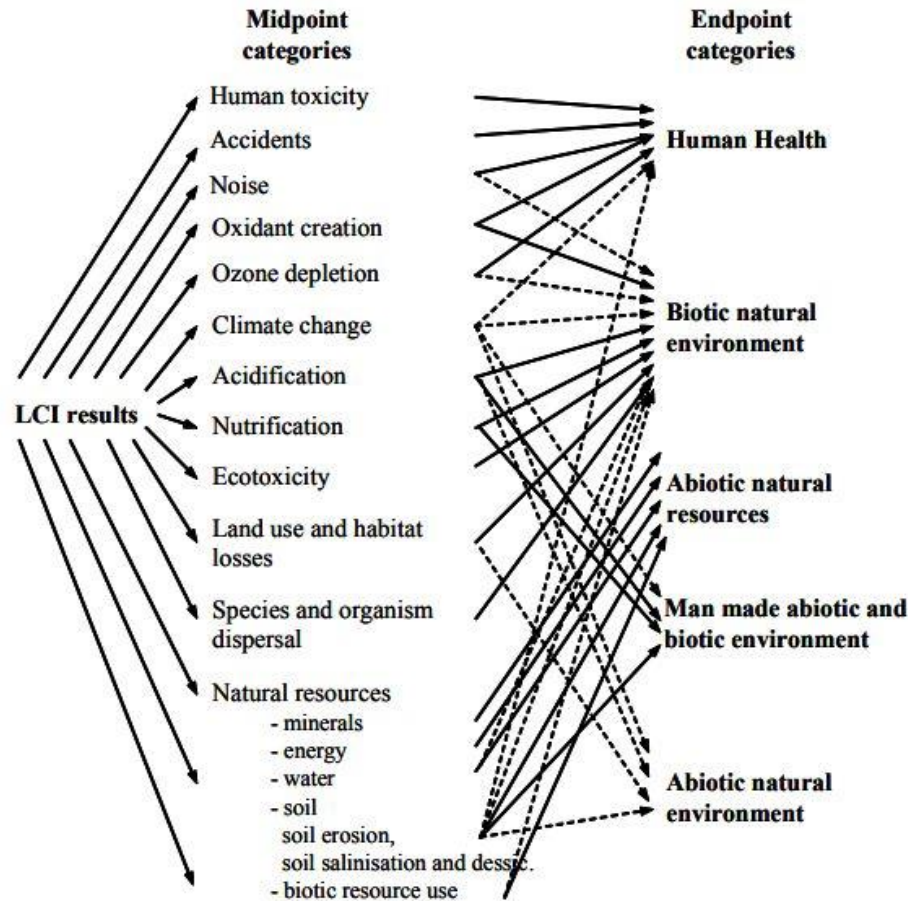
Figure 8: General structure of LCIA framework

+Dotted arrows: The present information available between midpoint and damage levels is uncertain by the preliminary analyses

2.4.1 ReCiPe method

ReCiPe method [20] was first developed in Netherlands focused on LCA for Europe region, which later on increased its scope to a global level. ReCiPe 2008 method is a recent midpoint-endpoint method built on Eco-indicator 99 [21] and the CML Handbook on LCA. It consists two sets of impact categories i.e. for midpoint and endpoint with their respective characterization factors. There are 18 impact

categories at midpoint level: climate change, ozone depletion, terrestrial acidification, freshwater and marine eutrophication, human toxicity, photochemical oxidant formation, particulate matter formation, terrestrial ecotoxicity, freshwater and marine ecotoxicity, ionizing radiation, agricultural and urban land transformation, natural land transformation, water depletion, mineral resource and fossil fuel depletion. These impact categories are further normalized and weighted into three endpoint categories: damage to human health, damage to ecosystem diversity, damage to resource availability. In this work we calculate the impacts of climate change (GHG emissions), land occupation, water depletion, and fossil depletion. Table 1 shows the characterization factors associated with the aforementioned impact categories.

Impact category name	Abbr.	Indicator name	unit
Climate Change	CC	Infrared radiative forcing	$W*yr./m^2$
Land Occupation	LO	Occupation	$m^2*yr.$
Water Depletion	WD	Amount of water	m^3
Fossil Depletion	FD	Lower heating value	MJ

Table 1: Overview of selected midpoint categories and their indicators

Climate change (GHG emissions):

Climate change which occurs as a result of emission of GHG gases leads to adverse effects on our ecosystem. These gases form a layer that acts as a blanket in our atmosphere and reflects the IR radiation back to the surface of Earth thus increasing the temperature. Every greenhouse gas has a property in common which helps in

characterization modeling, called radiation forcing in the atmosphere. Radiative forcing is the capacity of a gas to absorb IR radiation or effectively heat of the atmosphere. Every greenhouse gas cause climate change, the significant contribution of a gas to climate change is given by its global warming potential (GWP). GWP of a substance is the ratio between the increased IR absorption it causes and the increased absorption caused by 1 kg CO_2.

$$GWP_{T,i} = \frac{\int a_i c_i(t)dt}{\int a_{CO_2} c_{CO_2}(t)dt}$$

Where a_i is the radiative forcing per unit concentration increase of GHG (W/m^{2}kg), $c_i(t)$ is the concentration of GHG i at time T after release (kg/m^3) and t is the time over which the integration is formed (yr.) This is dependent on the timeframe considered as greenhouse gases have different lifespans in the atmosphere. If a substance has a lifespan comparable to that of CO_2, the factor is relatively insensitive to the timeframe. It varies significantly for the ones with higher or lower lifetime. The GWPs used in LCA were developed by the UN Intergovernmental Panel on Climate Change (IPCC) and are updated regularly.

Land occupation:

There is a huge loss to our environment due to the excessive land usage for several man-made purposes. This impact category calculates the damage to ecosystems due to the effects of land occupation and transformation. There is a heavy loss of biodiversity with the way the land is used (which is dealt in the endpoint method). For the midpoint characterization deals with the land metrics of how much land is either occupied or transformed and competition approach has been chosen, the same way it is used in CML methodology. The unit of the occupation LCI parameter is m^2*yr. It gives the amount of land occupied in a certain amount of time. This

approach cumulates all the types of land uses and includes LCI parameters defined as m^2*yr. There are two midpoint categories to improve this method, as shown in the table 2.

Midpoint impact category	CF	LCI	With:
Agricultural Land Occupation	$CF_{agr}=1$	$A_{o(agr)}.t$	$A_{o(agr)}$: amount of agricultural area occupied (m^2) t: time of occupation in years
Urban Land Occupation	$CF_{urban}=1$	$A_{o(urban)}.t$	$A_{o(urban)}$: amount of urban area occupied (m^2) t: time of occupation in years

Table 2: Midpoint characterization factors for two midpoint impact categories on land occupation

At midpoint level, we take only the amount of area occupied or transformed (m^2*yr.) into consideration and there is no differentiation made to the land use types.

Water depletion:

Water is an important resource that is abundant in many parts of the world and at the same time, is scarce in other parts of the world. We cannot assure a global market for a global distribution of water, unlike other resources. At midpoint level characterization, the indicator gives the total amount of water that is used for a

process. Extracting water from a dry area could cause a critical damage to the ecosystem and human health. There are no models to quantify them and hence making it difficult to express the damage on endpoint level.

It is an important issue to determine which type of water usage leads to water shortage. For example, if water is evaporated or consumed in a production process, we could assume that water is lost from an area and if water is consumed and is released near the source of consumption, one could argue that water is not lost. In such cases, water usage doesn't lead to water shortage. Table 3 shows different water types used in the ecoinvent data that should be used as default in many cases. But it is recommended that an LCA practitioner should assess case by case basis to proceed with water depletion.

Resources	$CF_{midpoint}$ (m^3/m^3)	$CF_{endpoint}$
Water, lake	1	NA*
Water, river	1	NA
Water, well, in ground	1	NA
Water, unspecified natural origin	1	NA

Table 3: Midpoint characterization factors for the midpoint impact category freshwater depletion

*NA = not available

Fossil depletion:

The term fossil fuel takes back to 300 million years (late Jurassic, Cretaceous, Permian ages) back where huge amounts of oil, gas, and coal were formed from

animal and plant depositions under the surface of the earth. Fossil fuel refers to the resources that contain hydrocarbons (volatile matter like methane, to liquid petrol, to non-volatile matter like anthracite coal). Over the past few centuries, there is been heavy exploitation of fossil fuels for various reasons like transportation, production processes etc.

While extracting the conventional oil and gas, they flow out of the well without any external energy until a certain point. Once it is reached, they could be only extracted by increasing the production energy requirement which in turn increases the production cost. This could mean that the increase in costs and energy is not only because of gradual decrease of resource quality but also because of resources' depletion. In this method, we use energy content as midpoint characterization factor and the marginal cost increase as endpoint characterization factor.

The midpoint characterization factor is a dimensionless quantity that is based on energy content (lower heating value):

$$CF_{midpoint,i} = \frac{CED_i}{CED_{ref}}$$

Where $CF_{midpoint,i}$ is the midpoint characterization factor for the non-renewable resource i (in kg oil-equivalents/unit of resource i), CED_i is the cumulative energy demand indicator of non-renewable resource i (in MJ/unit of resource i) and CED_{ref} is the cumulative energy demand indicator of the reference oil resource (in MJ/kg oil).

2.4.2 TRACI method

TRACI [22, 23] (The Tool for Reduction and Assessment of Chemical and other environmental Impacts), is a tool to allow a level of sophistication,

comprehensiveness, and applicability to LCIA, originally developed by the US EPA as a midpoint method that represents the environmental conditions in the United States. TRACI 2.1 is the latest version of this impact method and it has 10 impact categories at midpoint level: climate change, ozone depletion, ecotoxicity, human health toxicity (carcinogenic, and non-carcinogenic), particulate matter respiratory effects, photochemical smog formation, acidification, eutrophication, and fossil fuel depletion. In this work we deal with climate change and fossil fuel depletion and compare the trend with ReCiPe method, to validate if the trend in the US is similar to that of EU. Table 4 shows the TRACI portfolio of impact assessment with its midpoint units.

Impact category	Methodology	Midpoint units
Climate Change	Intergovernmental Panel on Climate Change 2007 (revised 2011) (Solomon et al. 2011)	kg CO_2 eq
Fossil fuel Depletion	US EPA (Bare et al. 2003) and Eco-indicator 99 (Goedkoop and Spriensma 2001)	MJ Surplus

Table 4: TRACI portfolio of impact assessment methodologies

Climate change:

US EPA uses the same approach to assess climate change as EC (e.g. ReCiPe method). It is based on the measurement of GWPs of greenhouse gases emitted, relative to CO_2. The important greenhouse gases that are identified by Kyoto

Protocol are carbon dioxide, methane, nitrous oxide, hydrofluorocarbons, perfluorocarbons, and sulfur hexafluoride. The GWP method used is recognized globally and is developed by IPCC to measure the radiative forcing of various greenhouse gases.

Fossil fuel depletion:

TRACI 2.1 method uses the concept that the continuous extraction of fossil fuels tends to the early consumption of the economically recoverable reserves, and hence the continuous extraction will become more energy intensive in the future (assuming no change in the technology). The characterization factors (developed and introduced by Muller-Wenk 1998) for individual fuel type (e.g. coal, oil etc.) predicts the energy required for extraction of these fuels at a point in future where the total consumption is five times the present scenario's total consumption. The increase in unit energy requirement per unit consumption of each fuel gives an estimate of the incremental energy input cost per unit of consumption (MJ/MJ).

2.5 Uncertainty and Sensitivity Analysis

Uncertainty analysis deals with the effect of inaccurate data on the life cycle results. Data could be considered inaccurate might be because of the assumptions considered in the process and hence, the data for a material could range over an interval. The interval in which the data varies could be an important piece of information for a comparison. In order to perform uncertainty analysis, it is important to collect all the data that is varying and we could establish the interval and the distribution.

Uncertain data could be also studied without performing uncertainty analysis. It is performed by sensitivity analysis which could be done by changing the system's input parameters. These could lead to a variation in results, for example like selection of allocation principle might vary the LCA, choice for the source of electricity etc. The need for the accurate data for these parameters is high.

3. Life Cycle Assessment for bio-based p-Xylene production

The Life Cycle Assessment for the bio-based production of p-Xylene from three processes (DA, CA, and MSH) that are simulated using Aspen Plus ® is performed and the detailed systematic procedure is explained. It involves 4 steps, goal and scope definition, inventory analysis, impact assessment and interpretation.

3.1 Framework of LCA

3.1.1 Goal and Scope definition

The definite goal of our LCA study is to evaluate and improve the environmental performance of the bio-based production of p-Xylene. The results of the LCA study are used to evaluate the environmental performance bio-based p-Xylene, and to compare the three different hydrolysis processes (DA, CA, and MSH) with conventional oil-based p-Xylene production. The system boundaries are cradle-to-gate and are mentioned in detail in the scope definition that is shown in the figure 9 for DA, CA, and MSH processes respectively. The solid lines determine that the component streams are consumed whereas the dashed lines represent the component streams are recycled. There are 3 steps involved in all 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 the comparison of the LCA results.
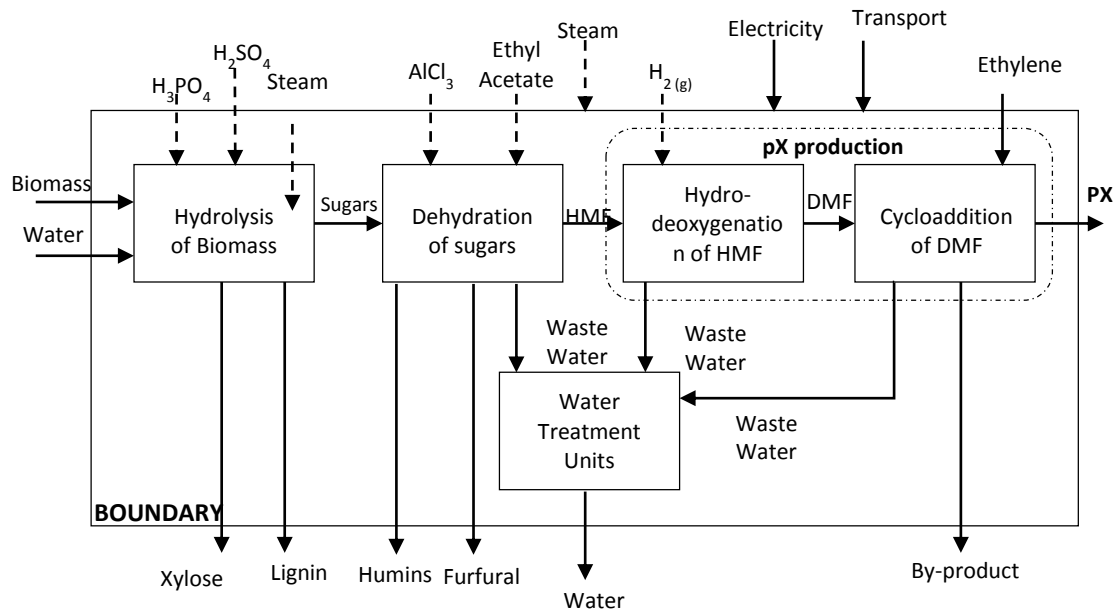
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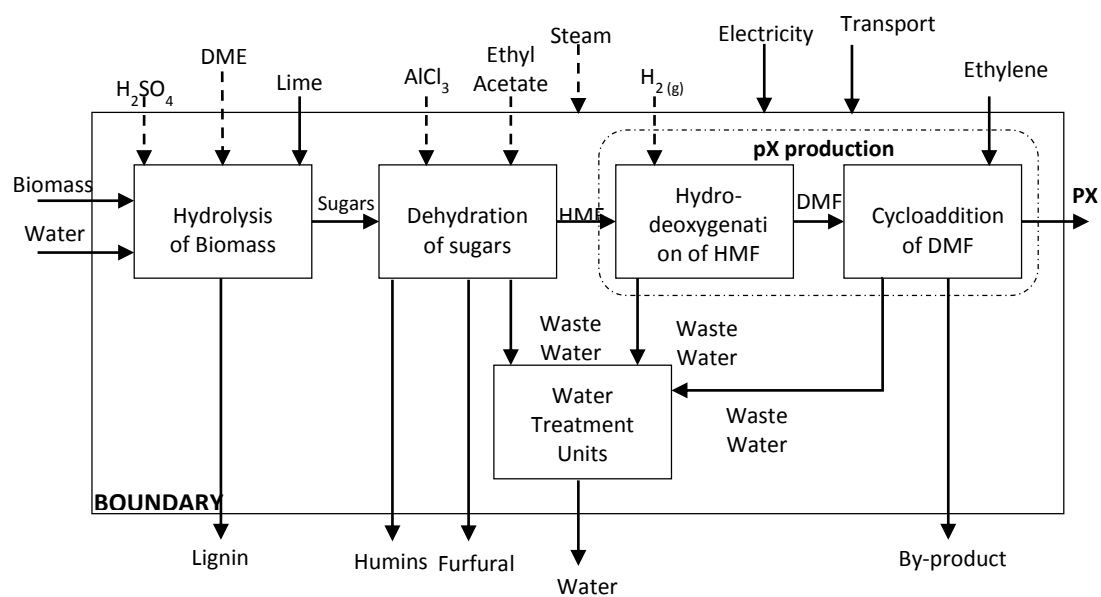
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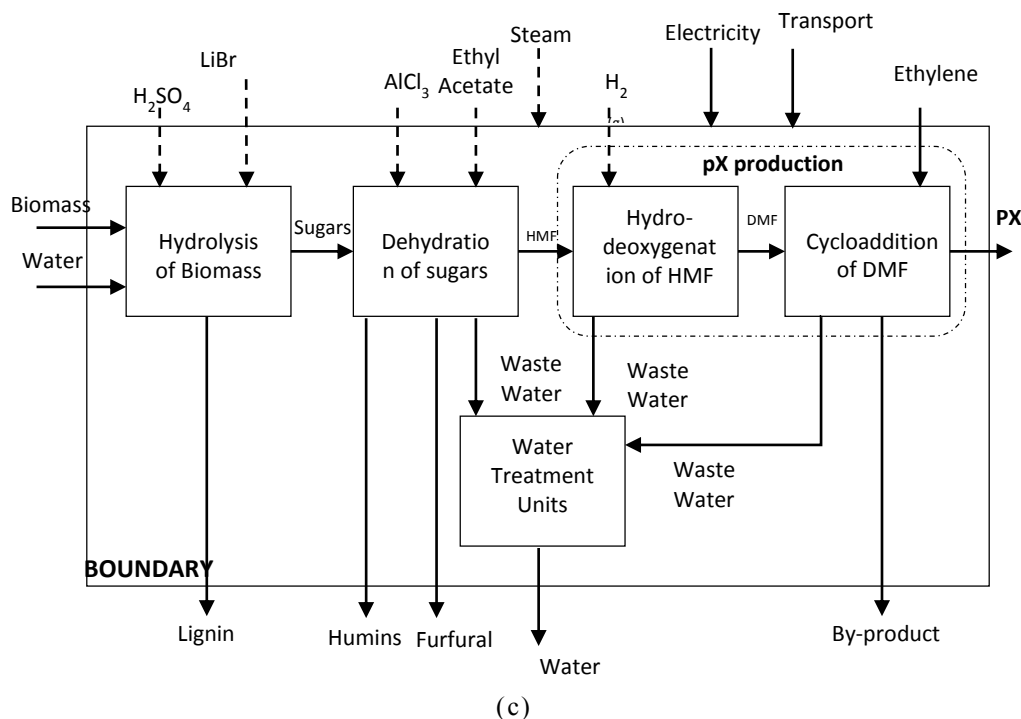
Figure 9: Scope definition for pX production using (a) DA process (b) CA process and (c) MSH process

3.1.2 Life Cycle Inventory Analysis

The most important stage in LCA is data collection. We have several databases to calculate the Life Cycle Inventory (LCI) such as Ecoinvent, US LCI, ECLD, US Input Output, EU and Danish Input Output, Swiss Input Output, etc. The different databases have different LCI for their differences in location, technology, emission level, etc. For example, the impact result for categories such as fossil depletion, water depletion, and agricultural land occupation is given zero. But these categories have some results when we use the other databases like Ecoinvent. For our work, we used Ecoinvent® v3.3 for its large database and that is has been undergone a review and validation with the consideration of uncertainties. In the earlier versions of Ecoinvent®, most of the components were limited to European data (technologies,

emission level etc.) which are now developed to global data in the latest version of Ecoinvent®.

Red oak is used as the biomass in our work. The LCI for the cultivation and processing of Red oak is directly selected from Ecoinvent® v3.3 [24, 25] which involves processes like seed germination and stand establishment, tending, young growth tending, cleaning, maintenance of forest road, thinning and final harvest. The process of converting lignocellulose to p-Xylene is given in the above sections and the LCI is derived from the simulations based on Aspen Plus®. The inventory data for mass and energy flows in our work for the production of 1 metric ton of p-Xylene is shown in the table 5 for DA, CA, and MSH processes.

COMPONENTS/ENERGY		kip/GJ	COMPONENTS		ton
INPUT			**OUTPUT**		
Materials	Woodchips	**110.229**	**PRODUCTS**	p-XYLENE	6.156
	Sulfuric acid	3.527		Furfural	0.609
	Ethylene	4.329		Xylose	13.474
	Ethyl acetate	0.496			
	Aluminum Chloride	1.010			
	Hydrogen	0.888			
	Steam	59.150			
	Heptane	1.069			
	Water	394.621			

	Lime	5.621			
Utility	Cooling water	-0.016*	**Emissions**	Waste water	201.4
	Electricity (kW)	1691.4			
	Steam	5.9			
	Hot oil	0.075			

(a)

COMPONENTS/ENERGY		ton/GJ	COMPONENTS		ton
INPUT			**OUTPUT**		
Materials	Woodchips	**110.229**	**PRODUCTS**	p-XYLENE	8.671
	Sulfuric acid	1.713		Furfural	7.072
	Ethylene	5.566			
	Ethyl acetate	0.388			
	Aluminum Chloride	0.825			
	Hydrogen	1.155			
	Dimethyl ether	0.126			
	Heptane	0.571			
	Water	163.7			
Utility	Cooling water	-0.0028*	**Emissions**	Waste water	75.5

	Electricity (kW)	15836			
	Steam	0.69			
	Hot oil	0.18			

(b)

COMPONENTS/ENERGY		ton/GJ	COMPONENTS		ton
INPUT			**OUTPUT**		
Materials	Woodchips	**110.229**	**PRODUCTS**	p-XYLENE	9.968
	Sulfuric acid	0.00106		Furfural	8.319
	Ethylene	6.184			
	Ethyl acetate	0.902			
	Aluminum Chloride	0.0804			
	Hydrogen	1.373			
	Lithium Bromide	0.65			
	Heptane	0.608			
	Water	2.461			
Utility	Cooling water	-0.046*	**Emissions**	Waste water	12.9
	Electricity (kW)	3171.335			
	Steam	4.8			

	Hot oil	0.2			

(c)

Table 5: Life Cycle Inventory for bio-based p-Xylene production by (a) DA process (b) CA process (c) MSH process

negative value represents the cooling utility usage

The important assumptions that are considered in our work are:

1. Red oak is considered as the biomass for the analysis

2. 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 from the scope

3. The feedstock is transported by a truck from the local biomass conversion facility- 100 km away from the biorefinery facility

4. Electricity is supplied by medium voltage grid based on the average technology and total loss in US

5. Heating is supplied by steam, among which 76% is generated by natural gas and rest is generated by heavy oil fuel, water input is not considered as heating is a closed system

6. 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

7. Wastewater is connected to wastewater treatment units

3.1.3 Life Cycle Impact Assessment

Impact assessment is a vital phase of LCA. An impact assessment is used to interpret the emissions and resource consumption with the stages of (a.) classification which involves sorting of all substances into classes according to the effect they have on environment, (b.) characterization which involves multiplication of all the substances by a factor that reflects their relative contribution to environmental impact, (c.) normalization, which involves the comparison of the quantified impact to a certain reference value and (d.) weighting which involves assigning different value choices to impact categories to generate a single score. For our work we have used an LCA software – SimaPro® v 8.4.0 for its large number of impact assessment methods and broad international scope life cycle inventory databases.

For each substance, a schematic cause-response pathway needs to be developed that describes the environmental mechanism of the substance emitted. Along this environmental mechanism, an impact category indicator result can be chosen either at midpoint or endpoint level. Midpoint (CML etc.) and endpoint (Eco-indicator) methods are the commonly used approaches. Midpoint impact categories take into consideration the cause-effect chain of an impact category prior to the endpoints, whereas the endpoint method further normalizes and weights these impact data to present the results as single indicator scores. Endpoint method results have a higher level of uncertainty compared to that of midpoint results because of the larger uncertainties introduced at the stages of the normalization and weighting. Endpoint results despite having larger uncertainties they are easier to understand by decision makers to design an eco-friendly alternative because of their single metric. We have used ReCiPe midpoint and endpoint methods for our analysis. ReCiPe midpoint

method comprises of 18 impact categories. Climate Change, Ozone Depletion, Terrestrial Acidification, Freshwater Eutrophication, Marine Eutrophication, Human Toxicity, Photochemical Oxidant Formation, Terrestrial Ecotoxicity, Freshwater Ecotoxicity, Marine Ecotoxicity, Ionizing Radiation, Agricultural land Occupation, Urban Land Occupation, Natural Land Transformation, Water Depletion, Mineral Resource Depletion, and Fossil Fuel Depletion. Whereas we have used the endpoint method to calculate the environmental single scores (pt) for compare the environmental performances of p-Xylene that is produced in various scenarios. All these methods are built on three different perspectives, with subjective changes on time horizon, manageability etc., identified by names: (1.) Individualist (I) – short-term interest, undisputed impact types, (2.) Hierarchist (H) – timeframe and other issues are based on most common policy principles, and (3.) Egalitarian (E) – longest time frame, but impact types that are not fully established but for which some indication is applicable. We have assumed Hierarchist perspective in our process.

Considering the high volumes of by-products in our process along with p-Xylene, allocation is applied to distribute the environmental impacts amongst them. There are two types of allocation economic allocation and mass allocation. Mass allocation is considered in our work in seeing that the economic allocation being biased for different prices in different scenarios. For example, the petroleum-based p-Xylene is produced with several high-priced by-products which in turn leads to a cheaper p-Xylene resulting in lesser allocation. The allocations for DA, CA, and MSH processes are shown in the table 6.

Products	Mass allocation
p-Xylene	30.41%
Furfural	3.02%
Xylose	66.57%

(a)

Products	Mass allocation
p-Xylene	54.76%
Furfural	45.24%

(b)

Products	Mass allocation
p-Xylene	54.51%
Furfural	45.49%

(c)

Table 6: Allocation fraction for different products for (a) DA process (b) CA process (c) MSH process

3.2 Results and Discussions

3.2.1 Environmental impacts using ReCiPe midpoint method

The characterization results of all the three DA, CA, MSH processes are calculated by ReCiPe midpoint method. We have considered climate change, land occupation, ecotoxicity, water and fossil depletion in the analysis as they have significantly high values for their impact categories.

The CA process performed remarkably better for impact categories like climate change, fossil depletion, and ecotoxicity while DA process showed highest environmental impact. Whereas the MSH process performs slightly better than DA process for the aforementioned impact categories. The largest difference between these processes comes because of process steam required for heating. DA process performs better in land occupation and water depletion when compared to other processes. The detailed environmental performance of the three processes is shown in figure 10.
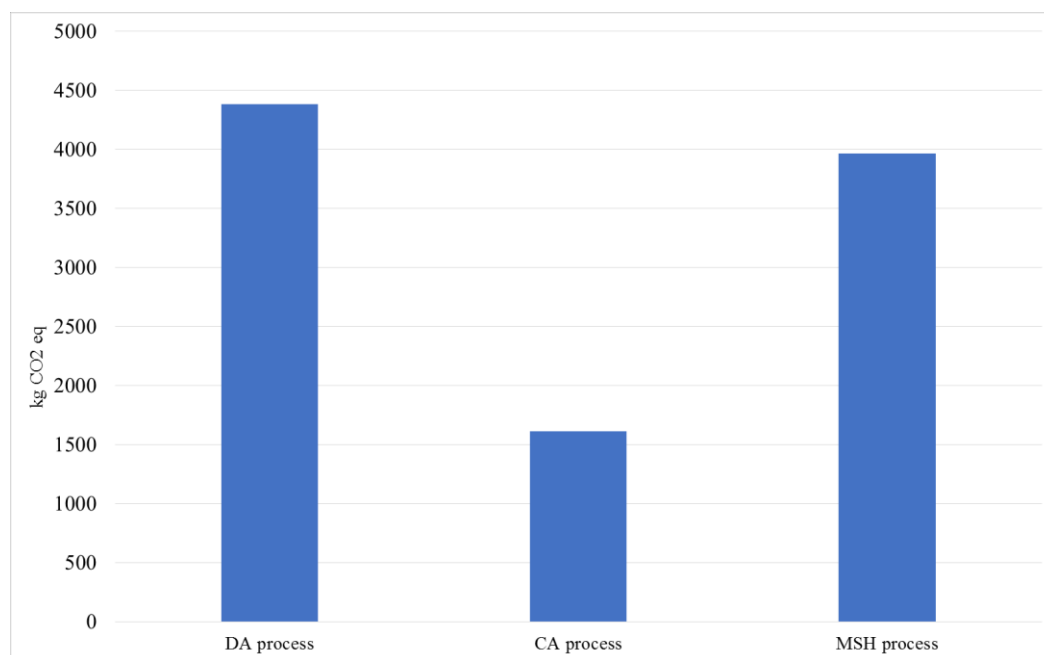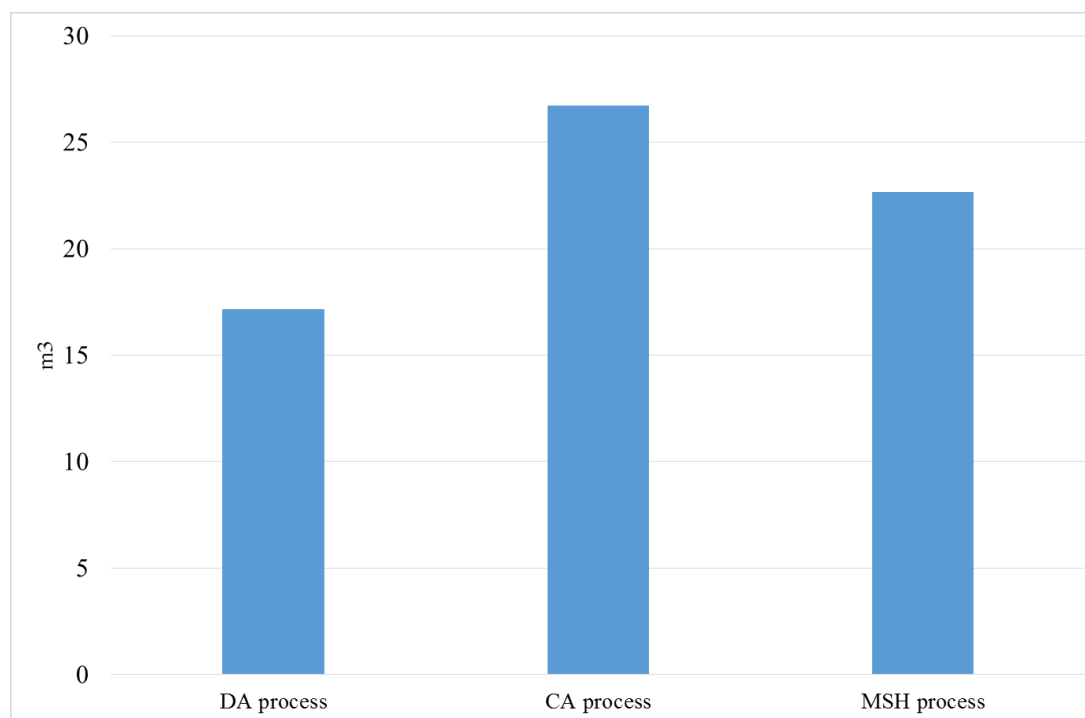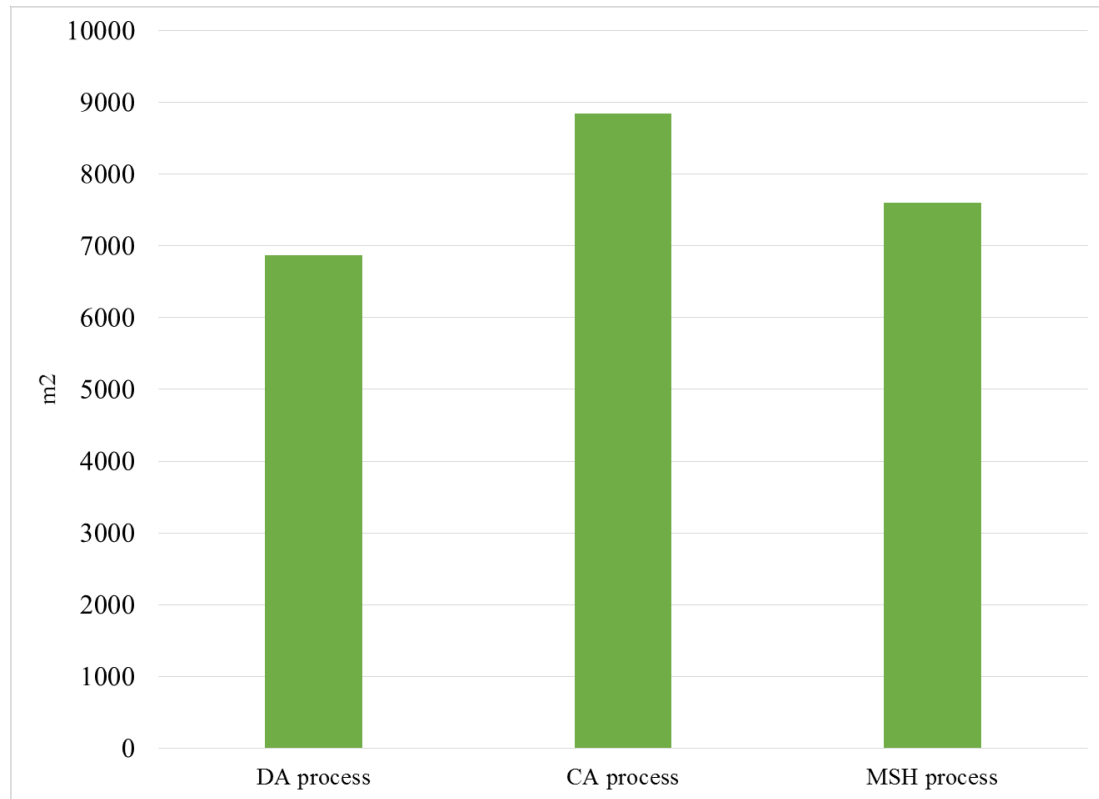
(a)
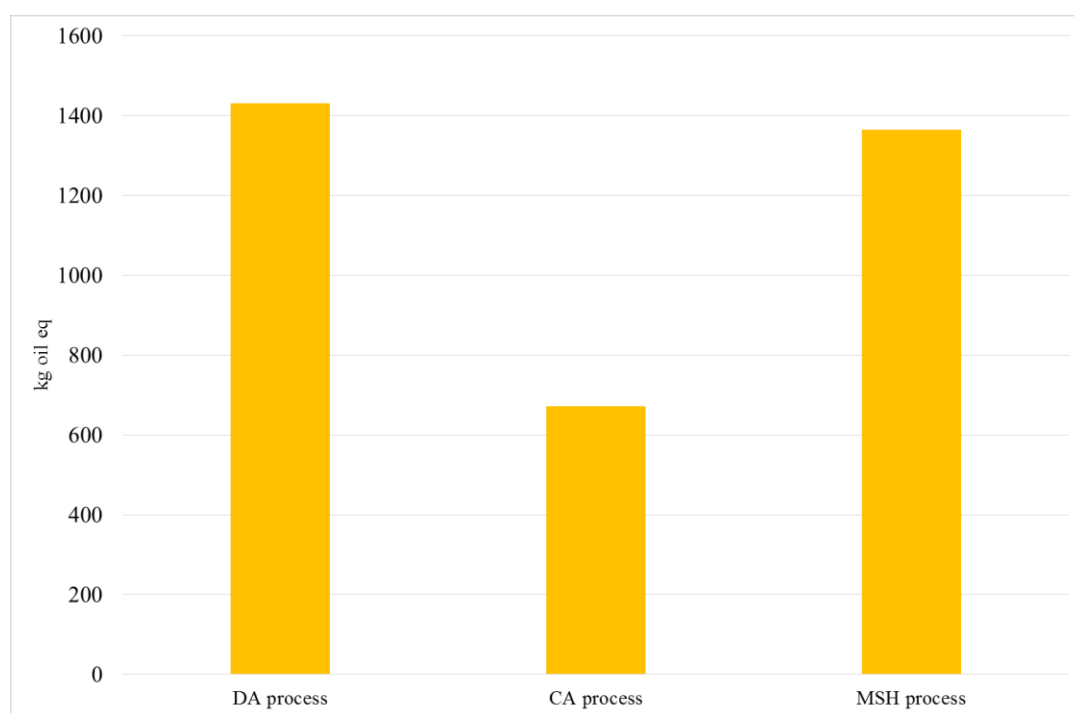
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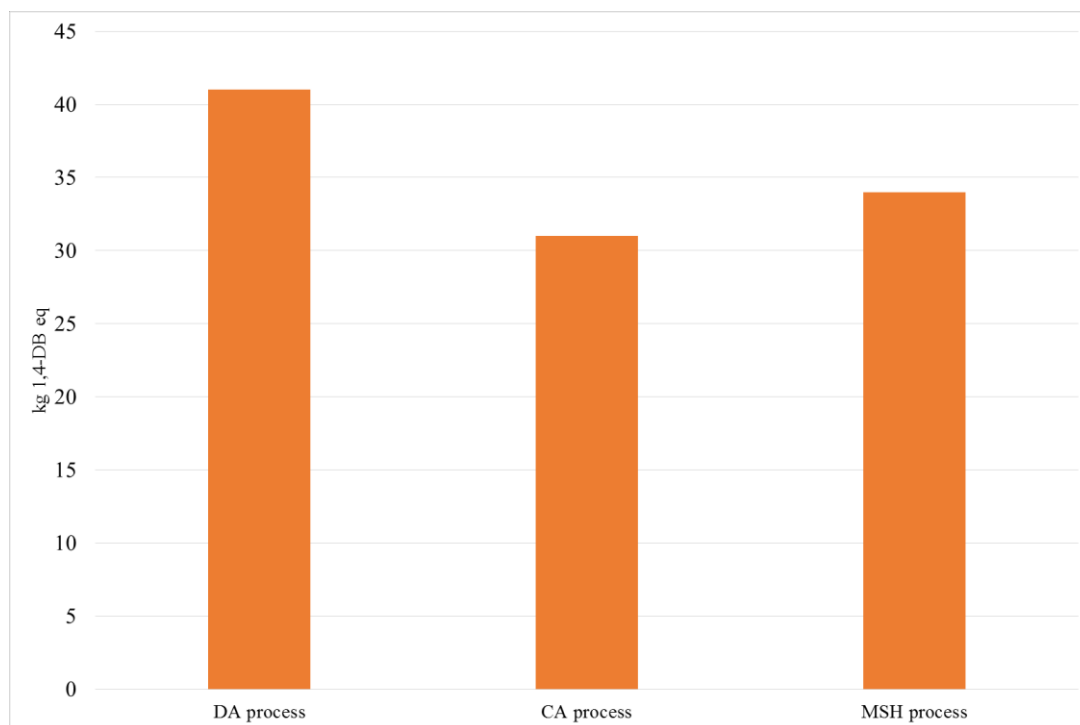
(c)

(d)

(e)

Figure 10: Characterization results (ReCiPe midpoint method) of three processes for a. climate change b. Fossil depletion c. ecotoxicity d. water depletion e. land occupation

CA process offers a benefit of 59% and 63% for climate change, 51% and 53% for fossil depletion, 9% and 24% for ecotoxicity over MSH and DA processes respectively. Heating steam is a major contributor and it accounts for more than 50% of the total environmental impact for the each impact category excluding land occupation in MSH process. The cultivation and processing of woodchips is the immediate contributor that accounts for more than 25% for all the impact categories. The detailed contributions for the environmental impacts for MSH process is shown in figure 11.
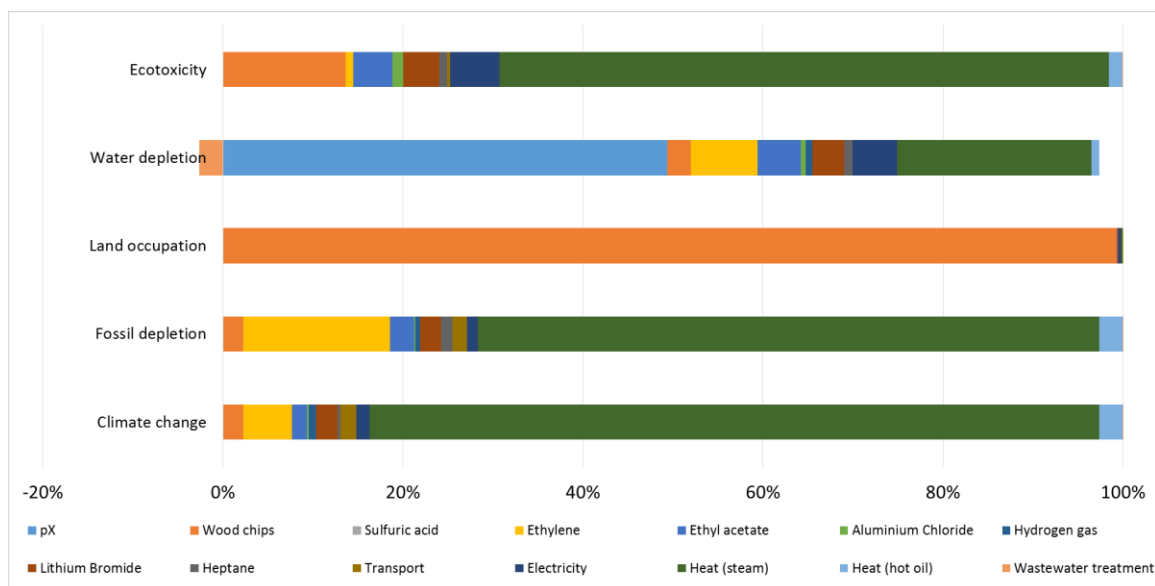
Figure 11: Detailed contributions for selected impact categories for MSH process

3.2.2 Environmental impacts using TRACI method

We calculated the characterization results for climate change, fossil depletion, and ecotoxicity using TRACI method for all the three processes to check the consistency in the trend of environmental impacts observed in ReCiPe midpoint method. Water depletion and land occupation are not considered for this case because the environmental impacts for these categories in ReCiPe midpoint method is represented as a cumulated amount of resources used, and it remains same for any method used. It could be observed from figure 12 that CA process is performing better of all the processes in all the three impact categories. At the same time MSH process performs slightly better than the DA process for each impact category considered. This is similar to the trend that is observed in ReCiPe midpoint method.

(a)

(b)

(c)
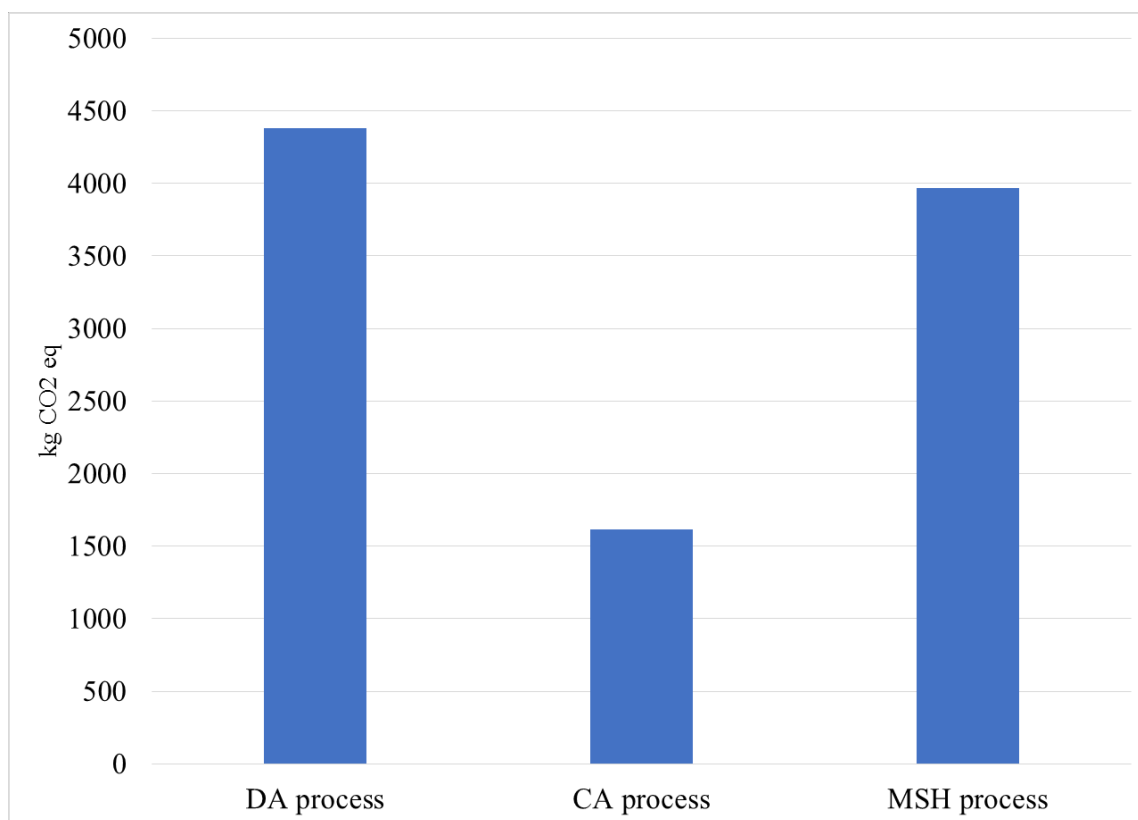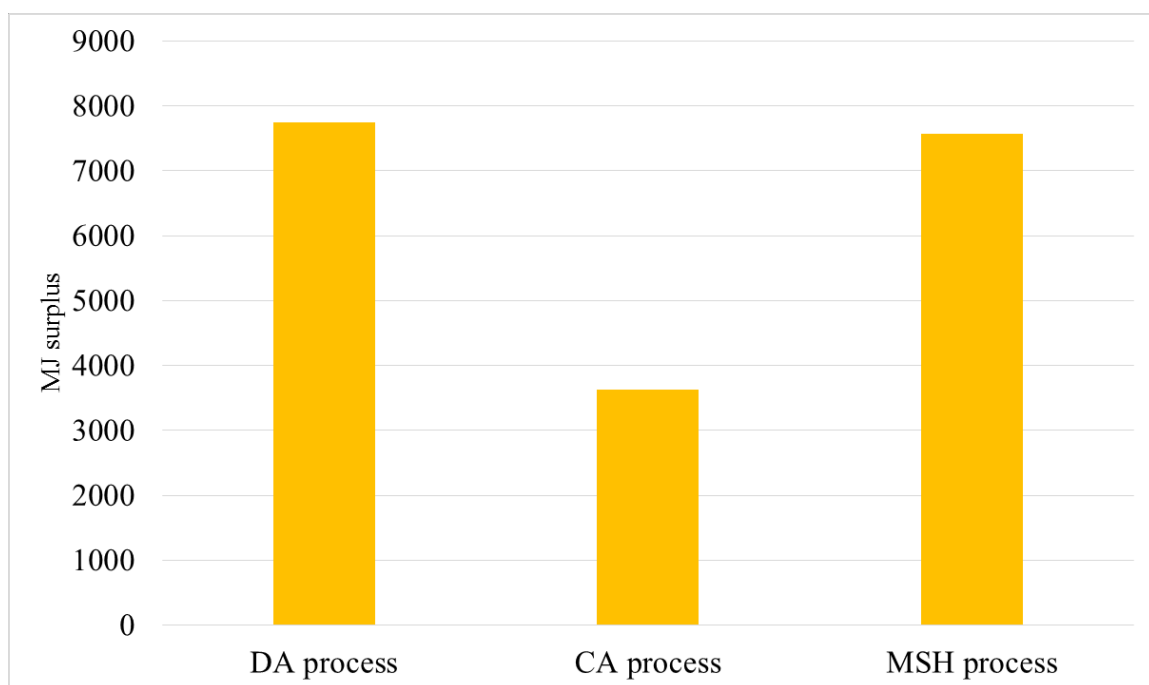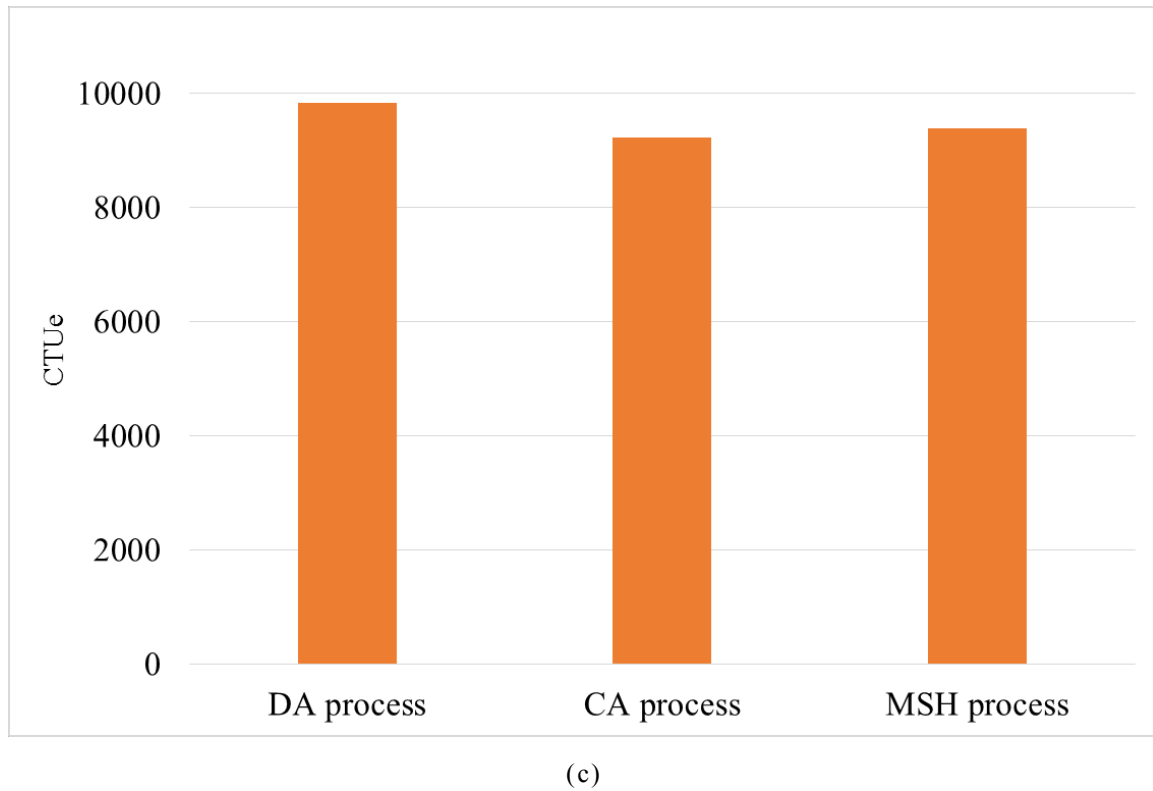
Figure 12: Characterization results (TRACI) of three processes for a. climate change b.

fossil depletion c. ecotoxicity

CA process offers a benefit of 59% and 63% for climate change, 52% and 53% for fossil depletion, 2% and 6% for ecotoxicity over MSH and DA processes respectively.

3.2.3 Sensitivity Analysis

Biomass feedstock:

The biomass concentration varies for different feedstock [9, 26], more specifically the component of interest, cellulose's composition varies from 12 to 93% whereas the components like hemicellulose from 0 to 66% and lignin from 0 to 54% We have considered four different biomass feedstock namely red oak, grass, rye straw, and newspaper whose compositions are mentioned in table 7. The single scores of p-

Xylene formed by MSH process from different biomass feedstock is shown in figure 13. Newspaper is considered as waste in our work, hence the environmental load of its production is not involved in our calculation. The newspaper based p-Xylene has the best environmental impact among all of them for its highest cellulosic content. But loading and processing heavy weights of newspaper is quite unfeasible. Rye straw based p-Xylene has the worst performance particularly in terms of eco-toxicity, land occupation and fossil depletion. We could observe that the environmental impacts vary with different biomass feedstock mainly due to cultivation and processing but ligno-cellulosic p-Xylene but the environmental impacts are comparable for all the different biomass used.

Compositions,%	Red oak	Grass	Rye straw	Newspaper
Extractives	6.63	0	11	
Cellulose	43.07	34.2	44.41	76.28
Hemicellulose	28.45	44.7	26.34	10.64
Lignin	21.85	21.1	18.25	13.08

Table 7: The normalized compositions for different biomass feedstock (dried)
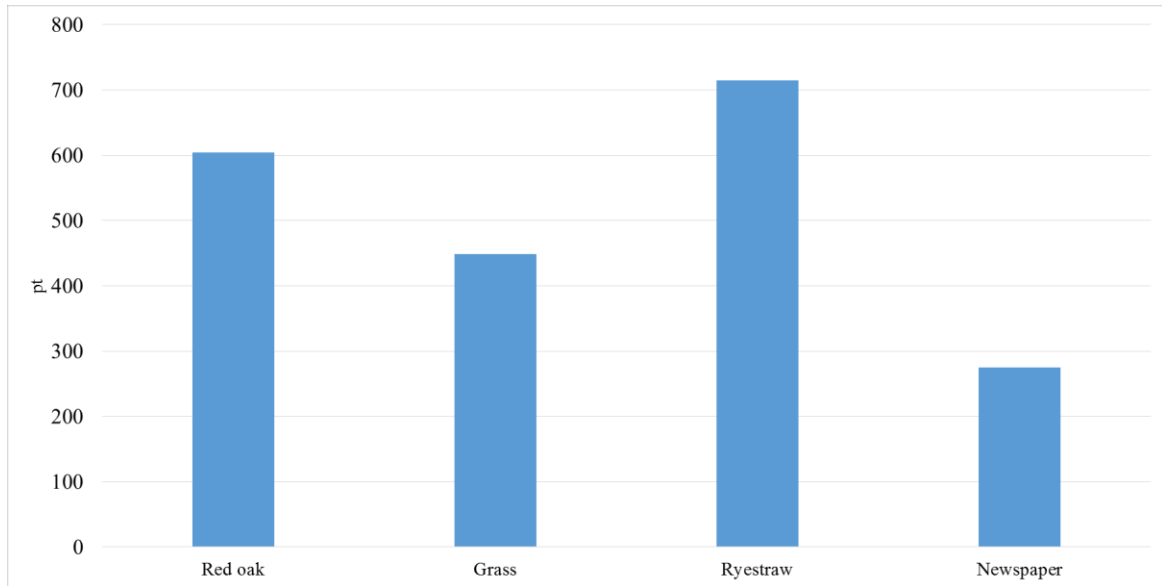
Figure 13: Single indicator scores for different biomass feedstock

Heating steam:

Heating steam is the major contributor for the overall environmental impact categories, we studied the changes in the total load by varying the types of steam that are produced from different processes. Our process is modeled based on the assumption that the water input is excluded from steam generation as it is being used in a closed system. In this analysis we compare this type with a scenario where the steam production considers water input. The environmental impact of steam with water is higher by a scale of 100 when compared to steam that doesn't consider water input. The single scores for these two processes are shown in figure 14. The largest difference between these two choices comes in water depletion, eutrophication and natural land transformation.
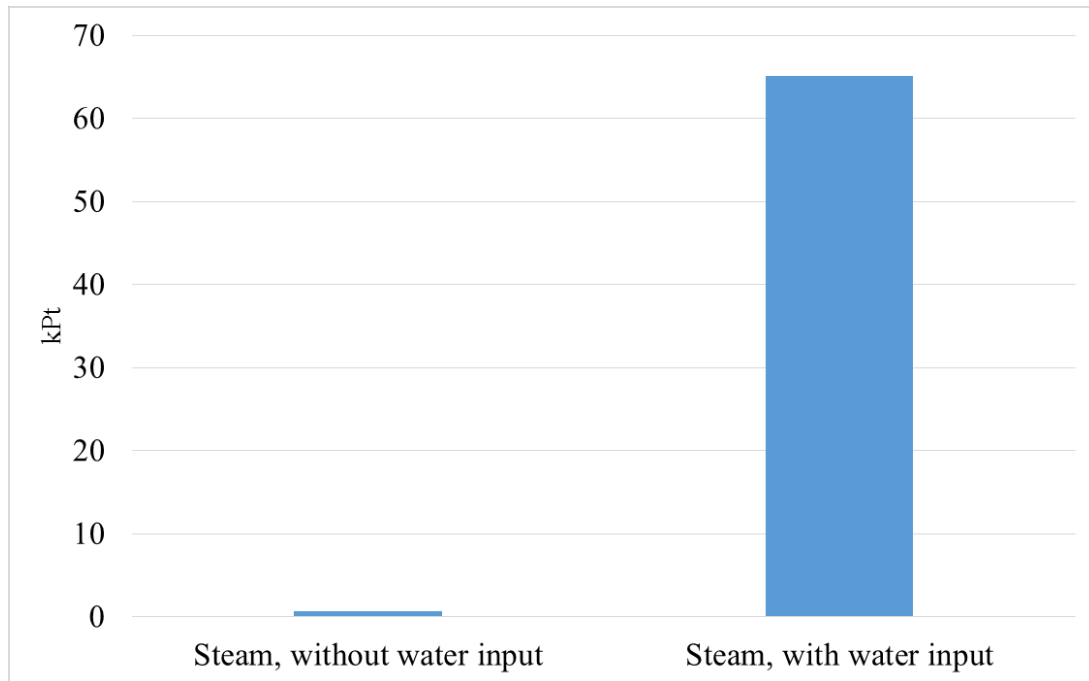
Figure 14: Single indicator scores for different types of steam used (with and without water input)

The steam considered with water depletion is produced by 76% by natural gas and the remaining by heavy fuel oil. We have considered several scenarios by varying the energy distributions for producing the steam as shown in the figure 15. The environmental impacts for case i is better than other cases, and it could be clearly observed from figure 15 that the difference in the scores is because of the usage of higher amounts of heavy fuel oil. Using 100% of natural gas for heating reduces the single score by more than 7% of total score for the composition we have considered. But it is not economically feasible to use 100% of natural gas to generate steam from water.
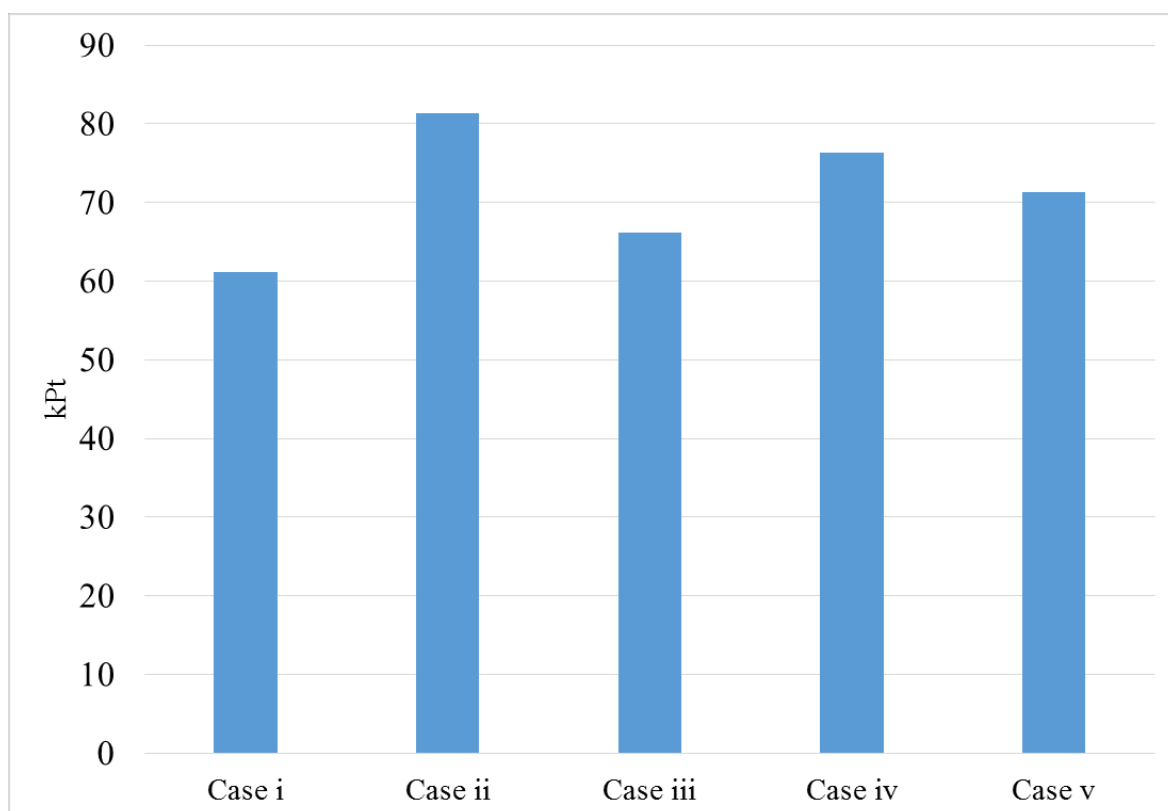
Figure 15: Single indicator scores for different scenarios of energy used for steam produced i. 100% natural gas ii. 100% heavy fuel oil iii. 75% natural gas and 25% heavy fuel oil iv. 25% natural gas and 75% heavy fuel oil and v. 50% of natural gas and 50% of heavy fuel oil

Economic allocation:

LCIA results vary for the different allocation principles used. There is a discussion on how economic allocation yields better results when compared to other principles. For the sensitivity analysis we have chosen economic allocation principle to study the variations in the LCIA results for the MSH process. The cost of biomass (dried) is $80/metric ton. The price of bio-based p-Xylene (MSH process) is fixed at

$1320/metric ton, furfural at $1000/metric ton. The allocation fraction for the products is shown in table 8.

Product	Allocation
p-Xylene	61.3%
Furfural	38.7%

Table 8: Economic allocation fraction for different products in MSH process

There is an increase of environmental impact scores of all the selected impact categories. We could observe an increase of 11% for climate change, fossil depletion, land occupation, 10% for water depletion and 13% increase for ecotoxicity when compared to the results obtained from mass allocation. Table 9 shows the comparison of characterization results for MSH process using mass and economic allocation.

Impact category	Mass allocation	Economic allocation
Climate change	3966	4460
Fossil depletion	1365	1535
Land occupation	7598	8544
Water depletion	22.6	25.5
Ecotoxicity	34	39.3

Table 9: Comparison of characterization results using mass and economic allocations

3.2.4 Uncertainty analysis

From our prior knowledge, we understand that the production of chemicals from biomass is in its nascent stages and it involves assumptions in the impact assessment calculations. These variations in the data could be explained by performing uncertainty analysis. It gives a distribution, expressed as a standard deviation. In SimaPro® we perform Monte-Carlo uncertainty analysis consisting of 1000 runs to investigate the impact of variance of input parameters. The standard deviation (SD) is estimated by a pedigree matrix [27, 28] including six indicators: reliability referring acquisition methods and verification procedures, completeness relating to the statistical properties, temporal correlation representing the time correlation of the data age, geographical correlation illustrating the correlation between the defined area and the obtained data, further technological correlation, and sample size, to handle the uncertainties and calculate the data uncertainty in the results. The score of each indicator selected for MSH process is shown in the table 8. The SD calculated is 2.16 for MSH process which is calculated by the following formula.

$$\sigma^2 = \exp\{\sqrt{(ln\ U_1)^2 + (ln\ U_2)^2 + (ln\ U_3)^2 + (ln\ U_4)^2 + (ln\ U_5)^2 + (ln\ U_6)^2}\ \}$$

	Score	Description	Uncertainty factors	Selection
U_1 = Reliability	1	Verified data based on measurement	1.00	

	2	Verified data partly based on assumptions or non-verified data based on measurements	1.05	
	3	Non-verified data partly based on qualified estimates	1.10	√
	4	Qualified estimate based on data derived from theoretical information	1.20	
	5	Non-qualified estimate	1.50	
U_2 = Completeness	1	Representative data from all sited relevant for the market considered, over an adequate period even out normal fluctuations	1.00	
	2	Representative data from >50% of the sites relevant for the market considered, over an adequate period even out normal fluctuations	1.02	

	3	Representative data from only some sited (≤50%) relevant for the market considered or >50% of sites but from shorter periods	1.05	
	4	Representative data from only one site relevant for the market considered or some sites but from shorter periods	1.10	
	5	Representativeness unknown or data from a small number of sites and from shorter periods	1.20	√
U_3 = Temporal correlation	1	Less than 3 years of difference to the time periods of the dataset	1.00	
	2	Less than 6 years of difference to the time periods of the dataset	1.03	

	3	Less than 10 years of difference to the time periods of the dataset	1.10	√
	4	Less than 15 years of difference to the time periods of the dataset	1.20	
	5	Age of data unknown or more than 15 years of difference to the time period of the dataset	1.50	
U_4 = Geographical correlation	1	Data from area under study	1.00	
	2	Average data from larger area in which the area under study is included	1.01	
	3	Data from area with similar production conditions	1.02	
	4	Data from area with slightly similar production conditions		

|	5	Data from unknown or distinctly different area	1.10	√
U$_5$ = Further technological correlation	1	Data from enterprises, processes and materials under study (i.e. identical technology)	1.00	
	2			
	3	Data on related processes or materials but same technology, OR Data from processes and materials under study but from different technology	1.20	
	4	Data on related processes or materials but different technology, OR data on laboratory scale processes and same technology	1.50	
	5	Data on related processes or materials but on laboratory scale of different technology	2.00	√

U_6 = Sample size	1	>100, continuous measurement, balance of purchased products	1.00	
	2	>20	1.02	
	3	>10	1.05	
	4	≥ 3	1.1	
	5	Unknown	1.2	√

Table 10: The selection of pedigree matrix indicator

Monte Carlo analysis confirmed the results obtained for DA, CA, and MSH processes with a great probability that CA process has the lowest impact whereas DA having the highest environmental impact in the selected categories. For fossil depletion and climate change CA has the higher impact for all the runs. DA process performs better than MSH process in 83% of the runs for ecotoxicity. There is a great uncertainty for the water depletion where MSH process performed better than DA process in 42% of the runs and CA process performed better than MSH process in 54% of the runs. The detailed comparison of these processes is shown in figure 16. Nonetheless with the uncertainties in water depletion and land occupation we could observe that CA process has lower environment impacts when compared to other processes.
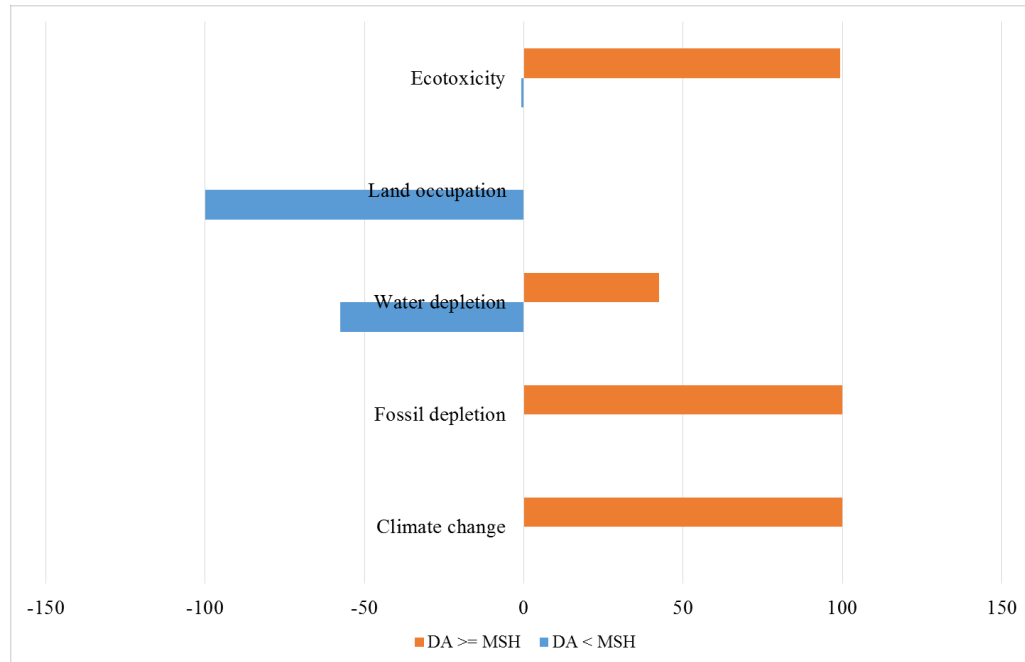
(a)
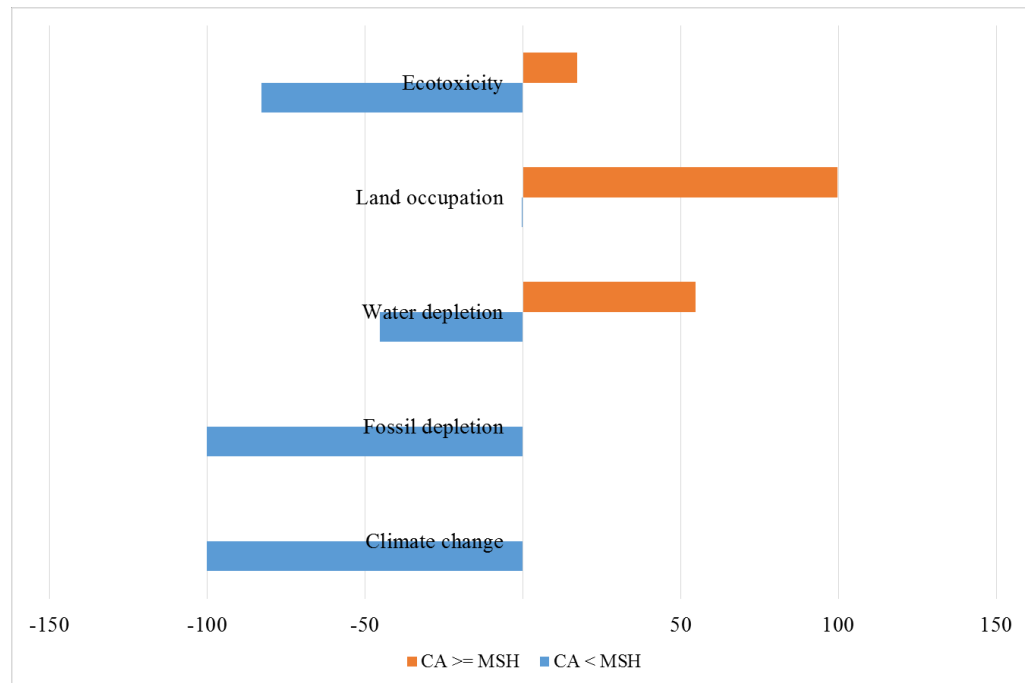
(b)

Figure 16: Uncertainty analysis for (a) DA and MSH process (b) CA and MSH process. The probability of each process having greater/lower environmental impact is shown in the figure

4. Conclusion and Future Work

4.1 Conclusion

This study has focused on the cradle-to-gate life cycle assessment to demonstrate the sustainability of bio-based p-Xylene production. Since there is a significant change in LCA for different hydrolysis processes, a novel process (MSH process) developed by Catalysis Center for Energy Innovation (CCEI), University of Delaware is compared to other existing hydrolysis processes (DA and CA processes). CA process performs better than other two processes but the MSH process is comparable to it. DA process is not as eco-friendly as comparable to others. High usage of steam, cultivation and processing of biomass are the major contributors for the environmental impact categories.

Sensitivity Analysis shows that the LCA results vary extensively for different types of biomass and scenarios of heating steam used. The integrated bio-refinery technology is still developing, so for them to well compete with traditional refineries in terms of cost efficiency, and environmental impacts, several technological aspects must be improved.

4.2 Future work

There is a great opportunity for future work to extend the scope of this study. Firstly, we could study the life cycle analysis for MSH process with an extended system boundary, such as grave-to-grave, cradle-to-grave etc. There is a scope to study the

optimization of biomass input for production of p-Xylene. This could increase the production of p-Xylene with less loading of biomass.

Finally, we could increase the scope of this study by conducting life cycle analysis for the production of several other specialty chemicals like jet fuels, surfactants, and butadiene from the heavy amounts of furfural that is being co-produced in the process.

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Several sections of this thesis work have been published or are being under the review for publication. They are acknowledged below:

Several sections of chapter 1 is being prepared for publication under the citation:

1.   Athaley, A., et al., *Techno-economic and life cycle analysis of different types of hydrolysis process for the prodcution of p-Xylene*. 2017.

Several sections of chapter 1 is published under the citation:

2.   Athaley, A., B. Saha, and M. Ierapetritou, *Techno-economic Analysis of Different Types of Hydrolysis Process for the Production of p-Xylene*. 2017.

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