LIFE CYCLE ASSESSMENT AND DEVELOPMENT OF SUSTAINABLE PROCESSES FOR ALTERNATIVE FUEL DEVELOPMENT

By

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LIFE CYCLE ASSESSMENT AND DEVELOPMENT OF SUSTAINABLE PROCESSES FOR ALTERNATIVE FUEL DEVELOPMENT

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Abstract:

In recent years, search for alternative fuel sources has been the focus of tremendous effort and research in the United States and around the world. In 2007, the United States Congress passed the Energy Independence and Security (EISA) act that mandated the production of 21 billion gallons of advanced biofuels by the year 2022, 16 billion of which must come from lignocellulosic feed stocks and it required reduction in greenhouse gas (GHG) emissions. This study uses life cycle assessment (LCA), a technique for the quantification of potential environmental impacts throughout the life cycle of a process, to assess the environmental sustainability of different ethanol production processes. Using databases in SimaPro 8.0.0, impact assessment results were generated for select impact categories and the potential environmental impacts of the production of ethanol from sweet sorghum and eastern redcedar were quantified.

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CHAPTER I

INTRODUCTION

1.1. Background on life cycle assessment

Life cycle assessment (LCA) had its beginning in the 1960s and 1970s as a method of comparing the environmental impacts of products with similar uses. Before it was called LCA, it was also called: ecobalances, resource and environmental profile analysis (REPA), environmental profiles, and integral environmental analysis[1]. LCAs looked to answer the question, is product A better than product B, or is process A better than process B[2]. The first recognized LCA study was performed by the Coca-Cola company[3]; they wanted to know whether they should consider using aluminum beverage cans. Other alternatives were considered: glass bottles, disposable containers, and plastic bottles. The study included energy, material and environmental impacts of the production starting from raw material acquisition to waste disposal[1]. The results was never made public but Coca-Cola switched from glass to plastic bottles afterwards[3]. Most other early LCAs were performed by consultants for private companies and during this time, when LCA did not have a standard theoretical framework, it was mostly used by companies to reinforce marketing claims and this resulted in varying claims and conclusions on the same products[4].

1.2. Overview of life cycle assessment

Life cycle assessment (LCA) is a methodology of evaluating the potential environmental impacts of a process over its lifecycle chain [5]. An LCA study is systematic and it consists of four main components: goal and scope definition, inventory analysis, impact assessment and an interpretation of the results; an LCA framework diagram in Figure 1 shows the relationship between the different aspects of an LCA. An LCA can be used to inform decision makers and the general public about the environmental impacts of a certain process. It also can be used to identify areas of highest environmental impacts that can be targeted for improvement.

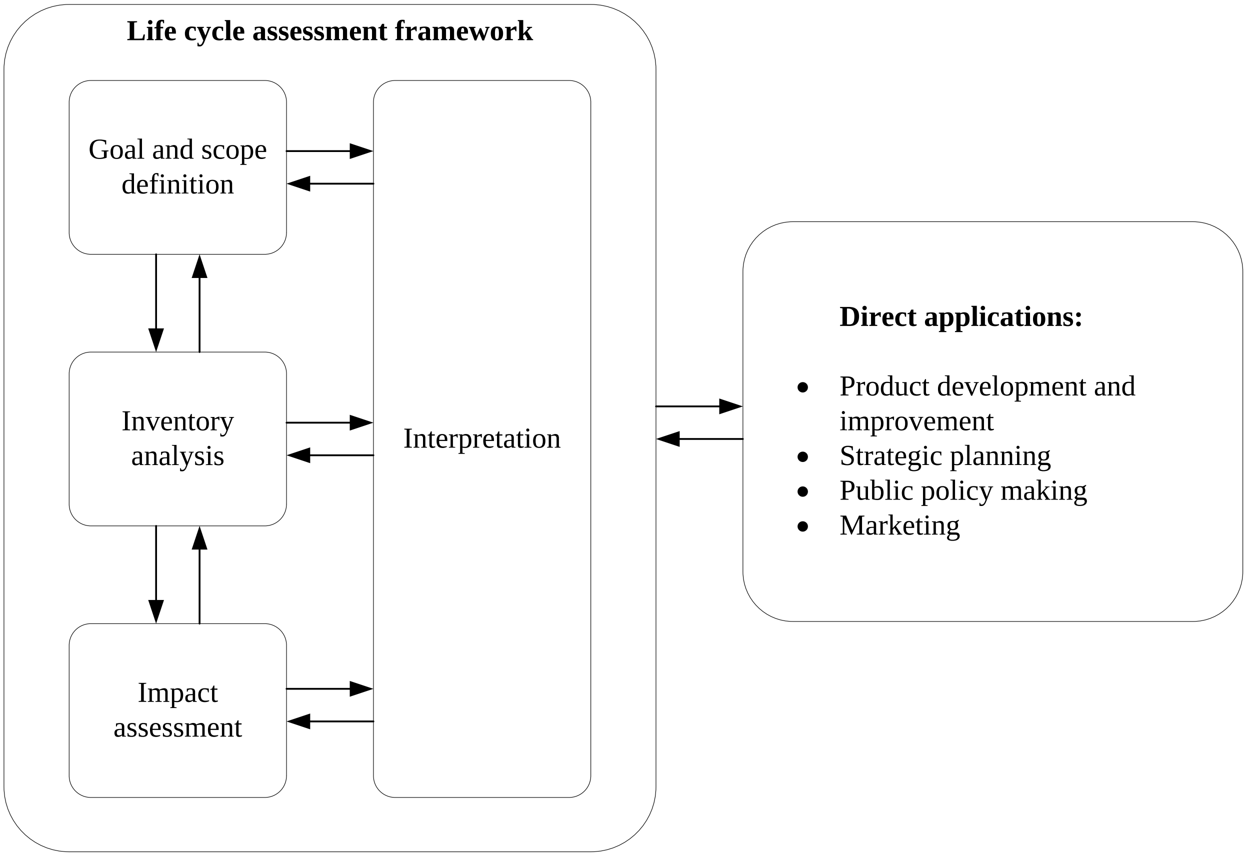

Figure 1.1: Life cycle assessment framework diagram. Based on ISO 14040:2006(E)[6]

1.2.1. Goal and scope definition

The goal and scope definition is the first part of the LCA and it is the foundation of the analysis, the depth and detail of the LCA is determined by the goal and scope definition. The goal of the LCA states the intended application, the reasons for carrying out the analysis, audience of the study, whether it is a comparative LCA and if the results will be disclosed to the public. The scope of the LCA includes the functional unit, reference flow, system boundary, product system that is being evaluated, function of the products, assumptions, impact categories, allocation procedures, data requirements, and allocation procedures[6]. ISO 14040 states “the scope should be sufficiently well defined to ensure that the breadth, depth and detail of the study are compatible and sufficient to address the stated goal”[6].

1.2.1.1. Functional unit

The functional unit in the LCA is a measurable quantity that defines the function of the product in the process that is being evaluated. The choice of a functional unit is important as it allows for comparison between two different processes, because of this, the functional unit has to be related to the function or use of the product that is in the analysis[7]. For example, products whose primary use is for energy will have functional units with units of energy, products whose primary use is for transportation, units of distance will be used for the functional unit.

1.2.1.2. System boundary

The system boundary in the LCA defines the unit processes that will included in the analysis and will be excluded, because of this, it is a crucial part of starting an LCA. The system boundary selection process is iterative, after an initial system boundary is chosen, it can be further refined as more information is available to the LCA practioner[8], a generic system boundary diagram can be seen in Figure 1.2. According to ISO 14040, when a system boundary is being developed, the following should be taken into consideration[6]:

- Raw material acquisition
- Inputs and output to the main production steps
- Transportation and distribution
- Use and production of electricity, fuel and heat
- Use and maintenance of products
- Disposal of waste and products
- Reuse, recycling and recovery of used products
- Construction, maintenance and decommissioning of capital equipment

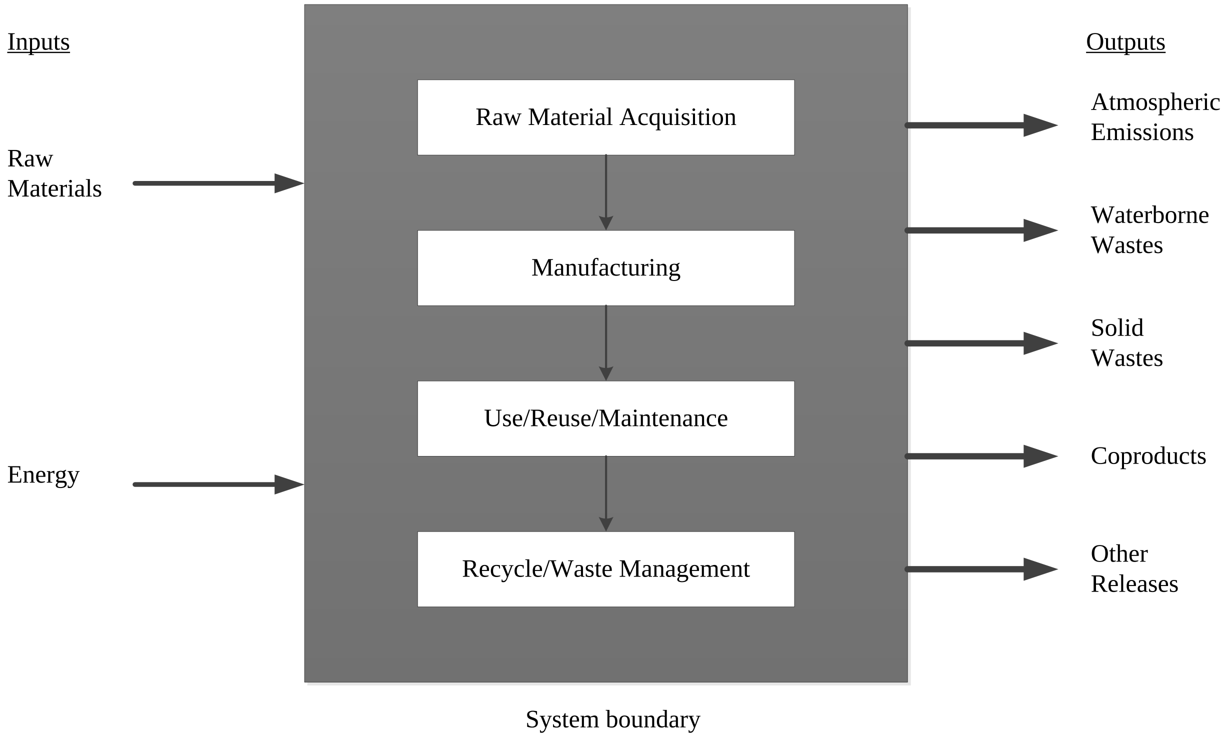

Figure 1.2: Generic system boundary diagram. Based on EPA 2006[9]

Cut-off criteria can be used in a system boundary selection, these are used for inclusions of inputs and output into the analysis and all assumptions used in selecting the cutoff criteria must be described. ISO 14044 allows for cut-off criteria using mass, energy and environmental significance[10]. The previous two are more commonly used while the latter, environmental significance is less applicable in practice since it would require evaluating the environmental significance of each input and output before the LCA is performed[11, 12]. Attempts to refine system boundary selection, especially cut-off criteria by Raynolds et al[11, 12] resulted in a system boundary selection method that takes into account mass, energy and replaces environmental significance with economic value. This system boundary selection method, called the relative mass-energy-economic

(RMEE) method was designed specifically for LCA studies on energy system and was developed to produce repeatable and equivalent system boundaries[11].

1.2.2. Inventory analysis

Inventory analysis, also called life cycle inventory analysis involves the data collection step of the LCA. This is another iterative process, as more data is collected and more is known about the process, new data requirements or limitations may arise that would require a change in data collection, this could also results in requiring a change to the goal and scope of the LCA[6]. During this step, the LCA practitioner collects data on the consumption of raw materials, resources, and emissions throughout the entire life cycle of the product. This data is not confined to one location because the consumption of resource and generation of waste is likely to occur at multiple locations[13]. Data for each unit process will fall into one of the following categories[6]:

- Energy inputs, raw material inputs, supplemental inputs, and other physical inputs
- Products, co-products, and waste
- Emissions (air, water, soil)
- Other environmental aspects

When a process has more than one product, the environmental impacts must be attributed to each co-product through an allocation procedure. According to ISO 14044[10], when possible, allocation should be avoided by:

1) Dividing the unit process that requires allocation into two or more sub unit processes and collected input and output data related only to each individual sub unit process, or

2) Expanding the system boundary to include additional functions or use of the related co-products

If avoiding allocation is not possible then the inputs and outputs of the system should be divided in a way that reflects the physical relationships between the different products. If that is not possible, then allocation of inputs and outputs can be performed based on the economic value of the co-products. The procedure for inventory analysis as defined by ISO 14044 can be seen in Figure 1.3.

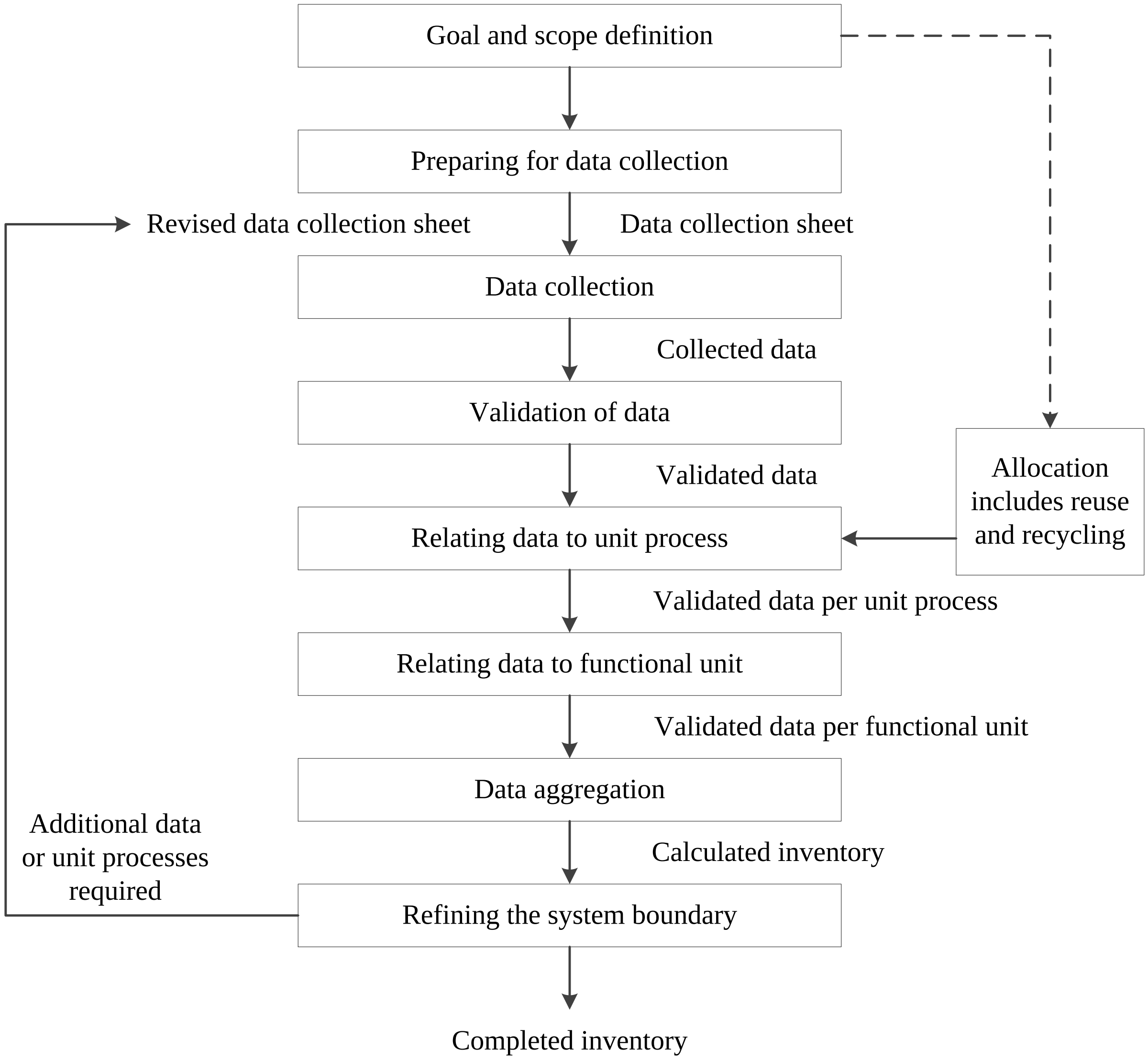

Figure 1.3: Simplified procedures for inventory analysis. Based on ISO 14044:2006(E)[10]

1.2.3. Impact assessment

The life cycle impact assessment (LCIA) step of an LCA includes the evaluation of potential environmental and human health impacts based on the chosen impact categories. These impacts categories are usually related to ecological, human health effects, and resource depletion. An LCIA links data collected in the inventory analysis to each impact category and also establishes a link between the products and their environmental impacts[9]. In SimaPro 8.0.0, a life cycle assessment software developed by PRé, the following impact assessment methods are available:

- European
    - CML-IA (Center of Environmental Science of Leiden University)
    - Ecological scarcity 2013
    - EDIP 2003
    - EPD (2013)
    - EPS 2000 (Environmental Priority Strategies)
    - IMPACT 2002+ (IMpact Assessment of Chemical Toxics)
    - ReCiPe
    - ILCD 2011 Midpoint
- North American
    - BEES (Building for Environmental and Economic Sustainability)
    - TRACI 2.1 (Tool for the Reduction and Assessment of Chemical and other environmental Impacts)

Within each impact assessment method, there are different impact categories, the impact categories in the IMPACT 2002+ impact assessment method are the midpoint categories in Figure 1.4.

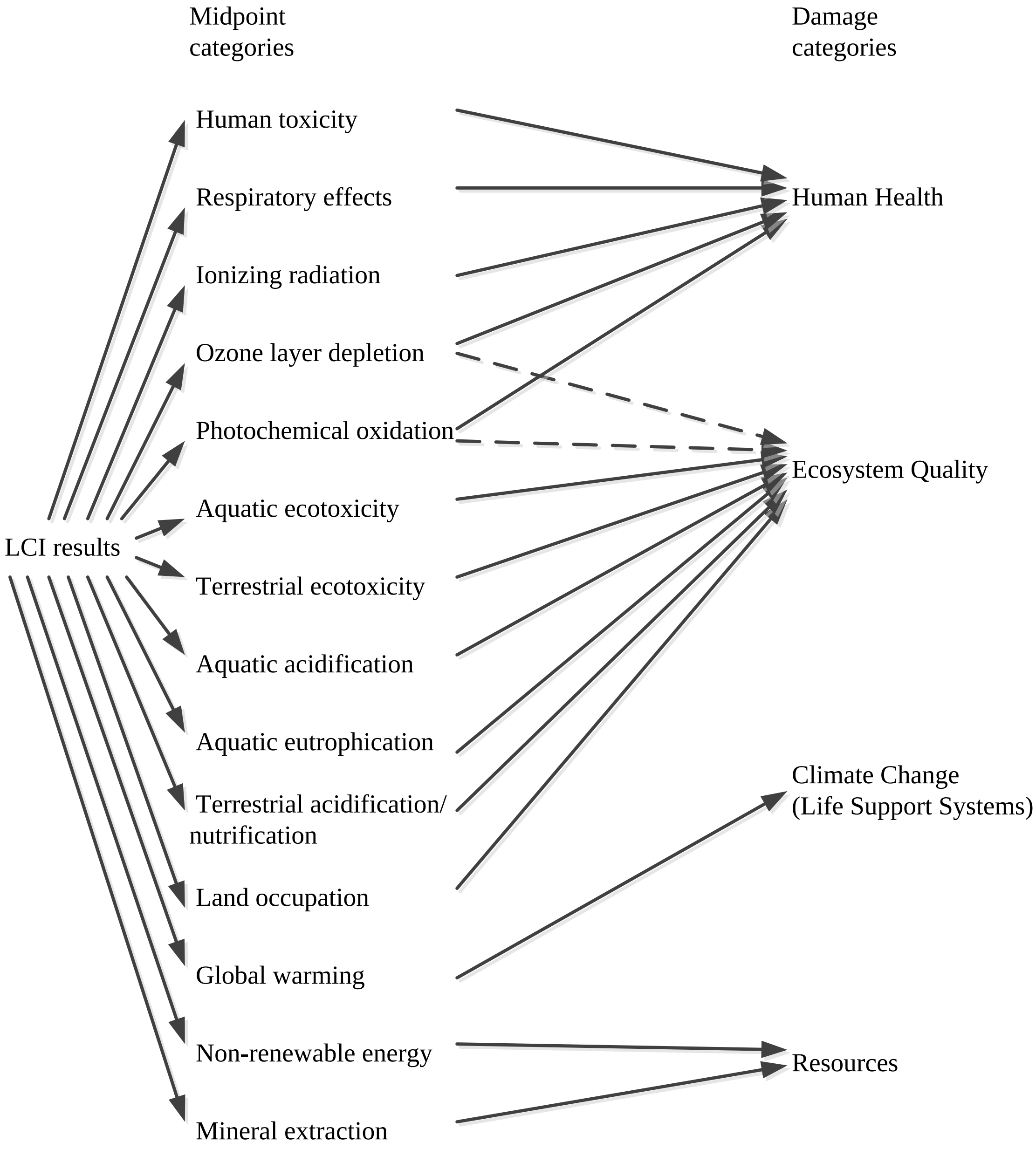

Figure 1.4: Schematic of IMPACT 2002+ framework linking LCI results to midpoint categories and midpoint categories to damage categories, human toxicity include carcinogens and non-carcinogens. Based on Jolliet et al. 2003[14]

1.2.4. Interpretation

This step requires identifying areas of significant issues based on the impact assessment results, it also includes sensitivity analysis, conclusions, limitations and recommendations. The results of the impact assessment step must be interpreted in a way that relates to the goal and scope of the study[10]. It is important to refine the results from the impact assessment step and present it in a way that the most important impacts can be made known to the target audience[1]. Like other categories of an LCA, as more information is known, the interpretation phase may involve reviewing and revising the goal and scope of the LCA[6].

1.3. Limitations

LCA is purely an environmental assessment tool, it is only able to quantify the possible environmental burdens of a process during its entire life cycle. Because of this, it doesn’t offer much insight into social and economic factors[15]. Also, since the inventory analysis, impact assessment and interpretation are related to the goal and scope, environmental impacts that are not considered in the scope of the study might be overlooked[6]. System boundary selection in LCAs greatly affects the results and conclusions that are drawn, comparative LCAs often lead to conflicting conclusions and LCAs on the same process can produce varying results[16]. Another limitation of LCA is its dependence and requirement of quality inventory data. Since an LCA seeks to account for environmental impacts of a product or process throughout its entire life cycle, this results in large data requirements. Data availability is not guaranteed and LCA practitioners may have to rely on estimates to fill gaps in data with contributes to greater uncertainties in results. There are growing databases with life cycle inventories for unit processes, some of these include: Evoinvent, USLCI, ELCD, and EU & DK Input Output databases.

1.4. Why perform an LCA?

One of the main strengths of an LCA is that it studies the entire product life cycle, from raw material acquisition to product end use and it allows the results to be related to the function of the product[1]. It can also allow room for innovation because not only does it provide information on the product life cycle impacts, but also on different production stages and in doing so, more efforts can be directed in areas where environmental impacts need to be reduced. It can also provide data that can help with compliance with environmental regulations or government initiatives. In 2007, the energy independence and security act (EISA) of 2007 was passed by the United States Congress and it mandated the production of 21 billion gallons of advanced biofuels by the year 2022, 16 billion of which must come from lignocellulosic feed stocks[17]. It required 20% reduction in greenhouse gas (GHG) emissions from corn ethanol production, 60% reduction in GHG emissions from lignocellulosic biomass ethanol, and 50% reduction in advanced biofuels when compared to gasoline[17]. LCA allows alternative energy researchers to test fuel production processes and see if they meet the standards set by the EISA act and to also test various configurations so that the environmental impacts of their processes can be minimized.

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CHAPTER II

LITERATURE REVIEW

2.1. Life cycle assessment of sugar feed stocks for energy production

The most common sugar based feed stock for fuel production is sugarcane; Brazil was a pioneer for the production of ethanol from sugarcane in the 1970s. The production begins with the cultivation of sugarcane, the crop is irrigated, and fertilizer and plant protection is also used. The harvested crop is transported to a sugar cane mill where it is washed and the raw juice is extracted. The left over biomass from this process, called the bagasse, is used for electricity cogeneration. Using sulphur, limestone and polyacrylamide, the juice is clarified and then fermented. The fermented ethanol is distilled and dehydrated to produce anhydrous ethanol[1]. Numerous life cycle assessments (LCA) have been performed on sugarcane ethanol production[1-3]. Renouf et al. performed a comparison with Australian sugarcane to UK sugar beets to US corn but only investigated production of sugars for fermentation. That study considered the following impact categories: fossil energy input, greenhouse gas (GHG) emissions, acidification potential, eutrophication potential, and water use. On a per kg of monosaccharide produced basis, sugarcane was best in two of the five impact categories: fossil energy input, and GHG emissions[4].

Ometto et al. did not perform a comparative LCA but instead focused on fuel ethanol production in Brazil, and their findings showed that the main contributing factor to impact potential when normalization was performed was nutrient application, burning that occurs while the sugar cane is harvested, and diesel usage[2]. Luo et al. performed a cradle-to-grave analysis, meaning that the environmental use of the ethanol as fuel was taken into consideration. The study evaluated ethanol production in Brazil with sugarcane as the feed stock and a comparison was made to gasoline. Three options were available for the end use of the ethanol produced, E10 (10% ethanol, 90% gasoline), E85 (85% ethanol, 15% gasoline), and E100 (100% ethanol). Results indicated that replacing gasoline powered car with E85 powered cars reduced GHG emissions by 81% and natural resource depletion by 83%[1]. A study in England that evaluated carbon and energy balances for different biofuel options compared the life cycle impacts of ethanol production from sugar beets to the production of gasoline from crude oil and showed that per MJ of fuel, sugar beets as a feed stock resulted in 0.04 kg of equivalent CO_2 while gasoline resulted in 0.08 kg of equivalent CO_2, a 50% decrease. When energy requirement was also evaluated, 0.5MJ of energy was required to produce 1MJ of ethanol from sugar beets while 1.19MJ of energy was required to produce 1 MJ of gasoline from crude oil[5].

2.2. Life cycle assessment of lignocellulosic feedstocks for energy production

Production of ethanol from lignocellulosic feedstocks begins with a pretreatment step followed by an enzymatic hydrolysis and fermentation step[6]. The pretreatment step breaks down the lignin structure and prepares the biomass for the enzymatic hydrolysis and fermentation. Lignin fraction that is removed in the pretreatment step along with nondigested cellulose and hemicellulose can be used as fuel for other parts of the process, resulting in lower fossil energy requirements[7]. A study performed by Sparati et al. on the environmental impacts of switchgrass and corn stover derived ethanol fueled automobiles compared the cradle-to-grave impacts of low-sulfur reformulated gasoline to switchgrass ethanol to corn stover ethanol. The results show that GHG emissions are 57% lower for an E85 switchgrass ethanol vehicle and 65% lower for an E85 corn stover ethanol vehicle[8]. When emissions for SO_x were evaluated, the E85 powered vehicles resulted in higher emissions, gasoline powered vehicle emitted 0.09g/km, switchgrass E85 ethanol vehicle emitted 0.54g/km, and corn stover E85 ethanol vehicle emitted 0.53g/km. The same was present when particulate matter emissions were evaluated, gasoline powered vehicle emitted 0.02 g/km, and switchgrass and corn stover E85 ethanol vehicles both emitted 0.07g/km[8]. Another study performed an LCA on the production of ethanol from wood and agricultural wastes with four scenarios: cultivated feed stock with the fossil electric grid as the process energy source, waste biomass feed stock with the fossil electric grid as the process energy source, cultivated feed stock with waste biomass as the process energy source, and waste biomass feed stock with waste biomass as the process energy source. The cradle-to-grave comparison is made between E10 vehicles and 100% gasoline vehicles in Canada. The results show that when the E10 scenarios using the fossil electric grid as the process energy source were matched up against gasoline, both resulted in higher GHG emissions, 256 g/km for the cultivated feedstock and 255 g/km for the waste biomass feedstock while gasoline emissions were 252 g/km. The comparison for the E10 scenarios with waste biomass as the process energy source resulted in lower GHG emissions when compared to gasoline powered vehicles, 245 g/km for the cultivated feedstock and 243 g/km for the waste biomass feedstock[9].

2.3. Life cycle assessment of corn grain as a feedstock for energy production

Several studies have been performed on the environmental impacts of corn ethanol[10-14] and many show that the replacement of gasoline with corn ethanol in the transportation sector results in lower GHG emissions. Corn ethanol production plants are divided into two categories: wet milling and dry milling plants. In a wet milling process, corn grain are soaked in water with sulfur dioxide (SO_2) so that the kernels can be soften and the hulls can be loosened. The kernels are then degermed and oils are extracted from the separated germs, the kernels are ground, and the starch is separated from the gluten for use in the ethanol production[14]. In a dry milling process, the kernels are ground without soaking in water and SO_2, the milled kernels are fermented where the starch is turned into ethanol. The unfermented parts become distiller grains and solubles (DGS) and are sold as animal feed[14]. Wang et al. performed an analysis on GHG emissions impacts on different corn ethanol plants, mainly focusing on the process fuel source and whether the co-product, wet DGS was produced. A summary of their results for six corn ethanol plant types are present in Table 2.1. Their results show the importance of co-product credits and fuel source. Configurations with fossil energy as the process fuel source resulted in less GHG emissions reduction than those that were fueled with DGS and wood chips. The maximum reduction from coal fueled facility was 18%, 39% for a natural gas fuel facility, and 52% for a wood chips fueled facility[14]. Co-product allocation was also very important, the coal powered facility went from no GHG emissions reduction to an 18% reduction when the environmental benefits of producing wet DGS and feeding it to cattle were included in the analysis, for natural gas, the inclusion of wet DGS improved GHG emissions reduction from 28% to 39%.

Table 2.1: Summary of select results from Wang et al.[14]

Process fuel source	Wet DGS produced?	GHG emissions reduction
Coal	No	-
Coal	Yes	18%
Natural gas	No	28%
Natural gas	Yes	39%
DGS	No	39%
Biomass (wood chips)	No	52%

A study by Liska et al. investigated improvements in the energy efficiency and GHG emissions of corn ethanol production. The study evaluates corn ethanol production for different regions and with different primary fuel sources. The regions include: the Midwest, Iowa, and Nebraska. The results in Table 2.2 show a relationship between the primary fuel sources and the GHG emissions reduction, plants that used coal as the primary source of process energy had lower GHG emissions than those that used natural gas[15], this same trend was observed in Wang et al. The study also stresses the importance of data sources, particularly for the cultivation of corn and energy usage of corn ethanol bio refineries. They stated that most LCAs are performing an analysis on the entire

United States corn ethanol industry which requires the use of aggregate data on average crop yields and bio refinery performances, some of which is outdated[15].

Table 2.2: Performance of different corn ethanol configurations in different regions, adapted from Liska et al.[15] MW=Midwest, IA=Iowa, NE=Nebraska, HYP=High yield progressive, NG=Natural gas, NNG=New natural gas, NGW=Natural gas with wet DGS only, CL=Closed-loop facility with anaerobic digestion

	MW-NG	**MW-NNG**	**IA-NG**	**NE-NG**	**NE-NGW**	**NE-CL**	**NE-coal**	**HYP-NG**
Dry DGS (%)	35	66	22	32	0	0	100	32
Modified DGS (%)	30	31	23	32	0	0	0	32
Wet DGS (%)	35	3	55	36	100	100	0	36
GHG emissions (g CO_2/ MJ ethanol)	45.1	45.0	42.0	48.1	37.5	30.6	76.0	43.8
GHG emissions reduction (%)	51	51	54	48	59	67	17	52

2.4. Sweet sorghum as a feedstock for ethanol production

Sweet sorghum, a C_4 crop in the grass family belonging to the genus *Sorghum bicolor* L. has the potential to be a renewable energy feedstock and is a viable candidate for ethanol production[16]. Sweet sorghum also had high photosynthetic efficiency and is able to be grown in a variety of climates with or without irrigation[16], it is also an attractive feedstock because it has been identified as a crop with low input costs[17]. Different pathways for producing ethanol from sweet sorghum exist, they include: extraction and fermentation of sweet sorghum juice[16], solid state fermentation[18], pretreatment and enzymatic hydrolysis of sweet sorghum bagasse[19]. A composition analysis for sweet sorghum can be seen in Table 2.3 and sweet sorghum juice composition is available in Table 2.4.

Table 2.3: Composition of sweet sorghum crop as percentage of dry weight, 70% moisture content[20]

	Composition (%)
Cellulose	12.4
Hemicellulose	10.2
Lignin	4.8
Sucrose	55.0
Glucose	3.2
Ash	0.3

Table 2.4: Sweet sorghum juice composition, adapted from Yu et al.

	Composition of concentrated sweet sorghum juice (g/L)
Glucose	45.5 ± 0.2
Fructose	34.9 ± 0.1
Sucrose	99.6 ± 0.3
Total nitrogen	0.07 ± 0.01
Total phosphorus	0.325 ± 0.01

Process that utilize only the sorghum juice for the production of ethanol separate the juice by pressing the stem in a mechanical roller and then fermenting the juice using dry yeast (S. cerevisiae)[16]. A study carried out by Kundiyana et al. performed fermentation experiments in 3.8L polyethlyene tetraphthalate vessels, a 14-gauge blunt edge syringe along with a rubber stopper was used for liquid sample collection. Temperature inside the fermentation vessels was monited using a temperature logger, pHs of 4.3 and 5.4 were evaluated, 0.05% w/v of fermenation volume of dry yeast (Fermax or Superstart) was used, and for certain treatments, 200 ppm of urea was added[16]. The results showed that Fermax yeast produced higher ethanol levels, higher sugar conversion efficiency and required less time to do so. It also showed that a reduction in pH or the addition of urea does not improve ethanol productivity or fermentation rate[16].

A study by Zipos et al. investigates the use of sweet sorghum juice and sweet sorghum bagasse for ethanol production. In the process schematic in Figure 2.5, crushed sweet sorghum is sent through mechanical rollers where the sweet sorghum juice is extracted and sent to an ethanol fermentation process. The bagasse from the juice extraction step is then sent to a steam pretreated step after with the slurry is separated into a fiber fraction and a liquid fraction. The liquid fraction undergoes one of two options, pentose fermentation to produce ethanol or cellulase production. The fiber fraction undergoes enzymatic hydrolysis and is then fermented to produce ethanol.

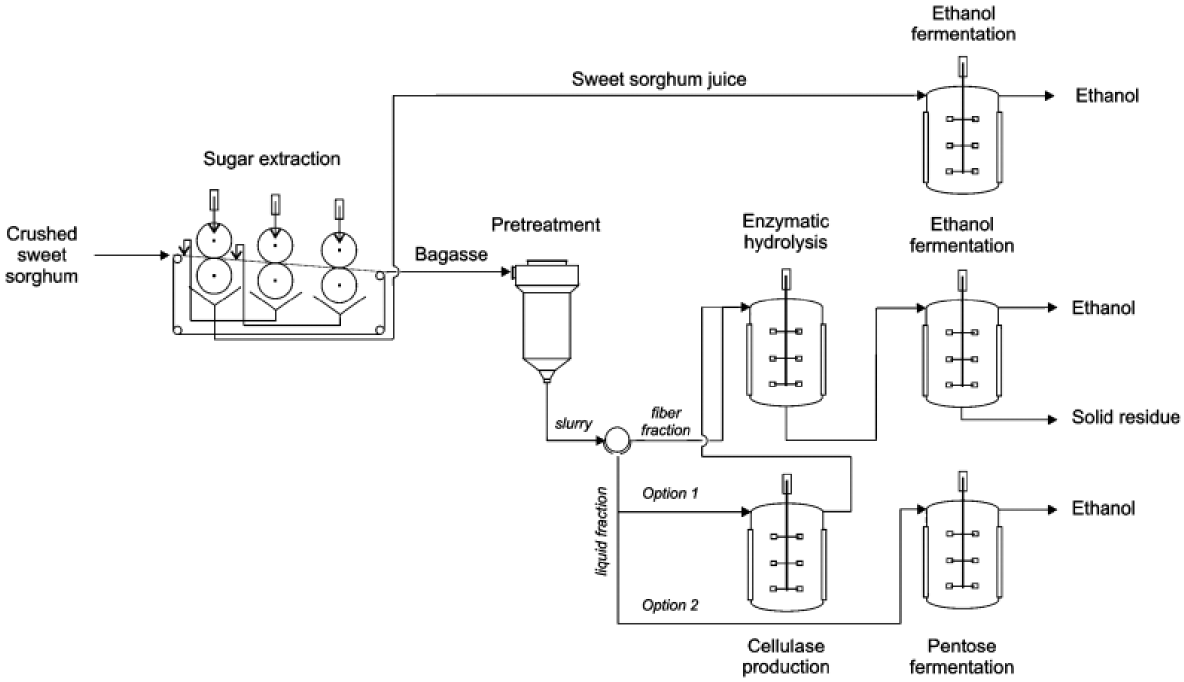

Figure 2.5: Process schematic of the production of ethanol from sorghum, utilizing sorghum juice and sorghum bagasse, adapted from Zipos et al.[19]

Their results showed that up to 92% conversion of the separated fiber fraction could be realized at pretreatment conditions of 200°C and 5 minutes because the digestibility of the biomass was improved and 80-90% glucose to ethanol yields were observed with *S. cerevisiae*[19].

2.5. Eastern redcedar as a feedstock for ethanol production

Eastern redcedar (*Juniperus virginiana* L.) is a softwood that is a member of the cypress family common found in the central and eastern United States and is currently being investigated as a potential feed stock for the production of ethanol[21]. Lignocellulosic biomass, like redcedar are composed of cellulose, hemicellulose and lignin, Table 2.5 shows the breakdown for eastern redcedar. Using pretreatment and enzymatic hydrolysis steps, the cellulose and hemicellulose in the biomass are broken down into sugars that can be fermented, producing ethanol [8]. Other lignocellulosic biomass feed stocks include: corn stover, wheat straw, switchgrass (herbaceous crops), salix, yellow poplar, eucalyptus (hardwoods), spruce, and douglas fir(softwoods) [22]. In the chemical conversion of redcedar into ethanol, pretreatment is the first step. This increases digestibility and fermentable sugar yield without producing too many toxic or inhibitory compounds that will be present in subsequent steps [23]. Various pretreatment techniques include: acid hydrolysis, concentrated acid, dilute acid, steam explosion, lime and NaOH, ammonia fiber explosion (AFEX), ammonia recycling percolation (ARP) [24] and sulfite pretreatment to overcome recalcitrance of lignocellulose (SPORL) [25]. Effective pretreatment can improve enzymatic hydrolysis by making cellulose more accessible to enzymes [23]. Enzymatic hydrolysis involves taking the pretreated biomass and hydrolyzing its polysaccharides into monomeric sugars carried out by cellulase and hemicellulase enzymes. Substrates, enzyme activity and reactor conditions have an impact on the effectiveness of enzymatic hydrolysis [26]. The presence of redcedar oil in this step has been shown to be an inhibitor to the hydrolysis of cellulose, its inhibitory effects become greater as the concentration of redcedar oil increases[27] Fermentation involves conversion of sugars (pentoses and hexoses) into alcohols using yeast (naturally occurring & recombinant), and/or bacteria (naturally occurring & recombinant). The efficiency of this process can be affected by the presence of inhibitors such as furfural, 5-hydoxy-methyl-furfural (HMF), formic acid and levulinic acid from the pretreatment step [28].

Table 2.5: Eastern redcedar composition. Adapted from Ramachandriya et al.[21]

Components	Percentage (%)
Glucan	40.32
Xylan	8.45
Galactan	1.98
Arabinan	1.40
Mannan	6.00
Lignin	33.65

Ramachandriya et al. performed a study that investigated the effect of sulfuric acid and sodium bisulfite loading on glucan to glucose yield. 0, 1.25 and 2.5 % (w/dry weight of wood) sulfuric acid loadings and 0, 5, and 10% (w/dry weight of wood) sodium bisulfite loadings at 180°C were used[21]. Results showed that after the pretreated biomass underwent enzymatic hydrolysis for 96 hours, as sulfuric acid loading increased and sodium bisulfite loading was held constant, there was a slight increase in glucan to glucose yield and when sodium bisulfite loading was increased and sulfuric acid loading was held constant there was a larger increase in glucan to glucose yield when compared to the previous case[21]. This shows that sodium bisulfite loading has a larger impact on biomass digestibility than sulfuric acid loading. After a series of other experiments, an optimal point for pretreatment conditions was discovered, at a reactor temperature of 200°C, 3.75% sulfuric acid loading, and 20% sodium bisulfite loading[21].

The effects of high dry solid loadings on enzymatic hydrolysis was addressed in another study by Ramachandriya et al.[29] solid loadings tested ranged from 2% to 20%, at solid loadings of 16% and 20%, ones with metal balls and ones without metal balls were also tested. Results showed that glucan to glucose recoveries were comparable from 2% to 16% solid loadings, but at solid loading as high as 20%, glucan to glucose recoveries decrease. The author states that rheological challenges may be the cause of this decrease and an observation was made that the mixture resembles a paste at such a high solid loading[29]. Even with the decrease in glucan to glucose recovery, when enzymatic hydrolysate produced at 20% solid loading were fermented, there was no sign of inhibition of the yeast that was used.

2.6. References

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CHAPTER III

ASSESSING THE ENVIRONMENTAL SUSTAINABILITY OF THE PRODUCTION OF ETHANOL FROM SWEET SORGHUM

Abstract

Production of ethanol from biomass feedstocks has the potential to greatly reduce greenhouse gas emissions for fuel production. This work quantifies the potential environmental impact from the production of ethanol from sweet sorghum using several processing options. The Relative Mass Energy Economic (RMEE) system boundary selection method is used to provide a fair comparison between the processing options and corn ethanol. It defines the system boundary using mass, energy, and economic value of inputs to unit processes. Impact categories that are evaluated include: respiratory effects, terrestrial ecotoxicity, land occupation, greenhouse gas emissions, and non-renewable energy use. Water use for each process is also evaluated. The results show that a centralized process where sweet sorghum stem is transported to a processing facility to produce ethanol has significant negative environmental impacts when compared to corn ethanol and other processing options. Improvements in biomass yield and more efficient energy usage can help reduce the environmental impacts of the process.

Keywords: Lifecycle assessment, Biofuels, Sweet sorghum

3.1. Introduction

Surging energy demand, fossil fuel depletion, increased climate awareness, and energy security concerns have resulted in research on alternative sources of energy with biomass being one of those sources. Biomass feedstocks have the potential to replace conventional fuels and reduce greenhouse gas (GHG) emissions. Conventional biomass feedstocks include corn, wheat, sugarcane, sugar beets, and sweet sorghum[1]. Increased crop yields, improved fertilizer efficiency and innovation in biomass conversion processes are leading to improved profitability of biofuel production[2].

Annual ethanol production in the United States in 2012 was 12.7 billion gallons[3], most of which was produced from corn. Because corn is the most dominant biomass feedstock in the United States, there have been numerous life cycle assessments (LCAs) performed on corn ethanol production[4-8]. These studies have focused primarily on GHG emissions and fossil fuel use and have not focused on land usage, respiratory effects, and land and water pollution. Sweet sorghum is a high energy, drought resistant crop that can thrive in a variety of climates and soil conditions. When compared to corn, sweet sorghum could be a potentially more attractive biomass feedstock because of its low nutrient and water requirements. There are studies on the production of biofuels from sweet sorghum; Cai et al[9] investigated the life-cycle energy use and GHG emissions from the production of ethanol from grain sorghum, forage sorghum and sweet sorghum and Köppen et al[10] performed a screening assessment that analyzed the GHG emissions and energy use along the entire life cycle of the sweet sorghum ethanol process for different production and use scenarios. Agricultural production of biomass can be an environmentally intensive process; therefore, the environmental sustainability of biofuel production processes must be assessed. Land use can be intensive, there are emissions to air, water, and soil from the use of fertilizers and plant protection, and harvesting and processing can be energy intensive[11].

This work rigorously quantifies the environmental implications of producing ethanol from sweet sorghum by focusing on six impact categories. The process for producing ethanol from sweet sorghum includes a modified forage chopper that harvests and cuts the sweet sorghum stalk down to six to eight inch billets. The billets are sent to a screw press that extracts the juice, the juice is fermented, the cellulose is converted to ethanol, and the bagasse is used to provide heat for the distillation column. A distillation column and a molecular sieve are used to produce anhydrous ethanol, and waste water is sent to a waste water treatment facility. Three processing options are evaluated in this work: 1) a farm scale decentralized process where all steps except the dehydration is performed on the farm, 2) a semi-centralized process where the distillation and dehydration are performed at a biofuel refinery, and 3) a centralized process where the sorghum stem is transported to a facility where the juice extraction, fermentation, distillation and dehydration are performed. A cradle to gate LCA is utilized to quantify the environmental impacts of the processes.

3.2. Materials and Methods

3.2.1. Life cycle assessment

Life cycle assessment (LCA) is a methodology for evaluating the environmental impacts of processes. The framework also leads to technological innovation by focusing research efforts on the parts of the process that are energy and environmentally intensive. This technique identifies areas of environmental impact, and it provides quantitative data that facilitates compliance with environmental regulations. It can also assist in informing decision and policy makers in areas of environmental protection[12]. An LCA investigation requires a goal and scope definition, inventory analysis, impact assessment, and an interpretation of the results, as outlined by ISO 14040:2006[12] and ISO 14044:2006[13]. This work utilized SimaPro 7.3.3 to aid in the development of the LCAs.

3.2.2. Goal and scope

The goal of the LCA is to evaluate the environmental impact of the production of ethanol from sweet sorghum. The following three processing options were considered: 1) decentralized, 2) semi-centralized, and 3) centralized processing. The production of ethanol from sweet sorghum was also compared to the production of ethanol from corn. The functional unit that served as the basis of comparison was 1 MJ of anhydrous ethanol produced. The impact categories include: respiratory inorganics, terrestrial ecotoxicity, land occupation, GHG emissions and non-renewable energy use. Water use for the three processing options and corn ethanol process will also be evaluated. This analysis only seeks to quantify the environmental impacts of the processes; it is not focused on the economics or the logistics.

3.2.3. System Boundary

The Relative Mass Energy Economic (RMEE) is a system boundary selection method that uses mass, energy, and economic value to define the system boundary for LCAs. Defining rigorous system boundaries reduces subjectivity, increases repeatability, and minimizes unreliable results[14]. Because the selection of the system boundary affects the completeness of the LCA, the goal is to have a system boundary that includes all major environmental impacts. The general rule for excluding steps from an LCA study is that a step may be excluded only if doing so does not change the conclusions of the study[13, 14]. It is difficult to prove that the exclusion of a step from a LCA study would not change the conclusions of a study. However, by using the RMEE methodology, a system boundary can be selected that excludes unit processes from the study without having to examine the entire system[14] and in this comparative LCA, provides equivalent system boundaries.

The selection of the cut-off criteria (Z_{RMEE}) is crucial. Inputs that do not meet the cut-off are excluded from the system boundary and this contributes to uncertainty in the LCA results. Statistical tests showed that as Z_{RMEE} increases, the 95% confidence interval also increases, therefore it is not recommended to use a Z_{RMEE} greater than 0.25[13]. The tests also show that Z_{RMEE} values from 0.05 to 0.25 have more than 90% of total environmental impacts likely to be inside the system boundary[15]. A Z_{RMEE} value of 0.05 was chosen for this assessment to provide for a more detailed analysis. The process schematic and system boundary for the three processing options can be seen in Figure 3.**6**.

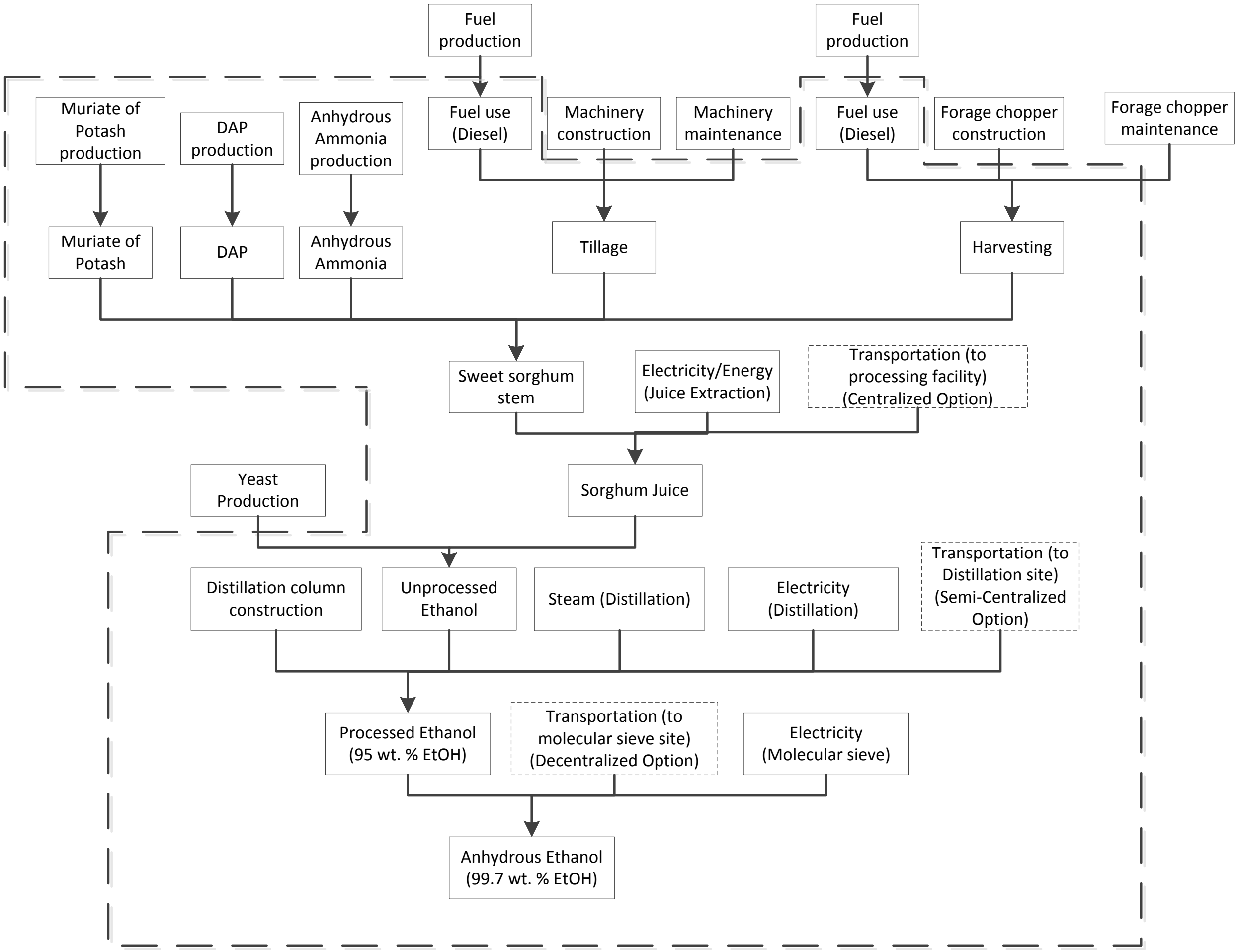

Figure 3.6: RMEE system boundary for the three processing options, boxes with dashed line borders are unit processes that are specific to certain processing options

3.2.4. Co-Products

The sweet sorghum and corn ethanol production processes produce co-products, including bagasse from sweet sorghum and dried distillers grains with solubles (DDGS) from corn. According to ISO 14040 and 14044, when considering the environmental impacts of co-products, three options are available: avoid allocation, expand the system boundary to include the use of co-products, or use allocation[12, 13]. System boundary expansion is used in this LCA to deal with the environmental impact from the co-products. The analysis was expanded to include the use of DDGS as cattle feed and the use of sweet sorghum bagasse as fuel only for the centralized processing option. In the decentralized and semi-centralized options, the bagasse will be fed to cattle since the juice extraction step occurs on the farm for both of those processes. The LCA will reflect an environmental credit for the cattle feed that is displaced by the DDGS and bagasse and also an environmental credit for extra electricity that is produced by burning of sweet sorghum bagasse.

3.2.5. Data collection

The data for sweet sorghum crop yields were gathered from a farming facility located on the campus of Oklahoma State University. These data include fertilizer usage and cultivation practices[16]. Data for the decentralized distillation was taken from the process simulation of a pilot plant. The pilot plant was scaled up to provide information for the semi-centralized and centralized distillation facilities. Fertilizer application of 107.6, 44.8, and 44.8 kg of nitrogen, phosphorus, and potassium[16] respectively were used for the analysis. Emissions from fertilizer use were collected from Nemecek[17]. Transportation costs per loaded mile and equipment costs were collected from Fryer[16] and fertilizer prices were collected from the USDA[18]. A National Renewable Energy Laboratory corn ethanol LCA[19] was modified and used as the basis for the comparative assessment. Energy use in the corn ethanol process is from a projected energy use study conducted by the Energy Resources Center at the University of Illinois at Chicago[20]. The ratios of avoided products to co-products for the corn ethanol process was obtained from a study on distillers grains displacement ratios for corn ethanol by the Argonne National Laboratory[21].

3.2.6. Assumptions

The production of the modified forage chopper is assumed to be similar to the production of a combine harvester, so the lifecycle inventory data for a combine harvester is used for the modified forage chopper. A biomass yield of 35 wet tons/acre is used as the basis for sorghum cultivation for all processing options. A fermentation efficiency of 90% is used and a juice expression ratio equal to 0.55 was used. The juice expression ratio is defined as the ratio of the mass of the sorghum juice to the mass of the sorghum stem. The environmental impacts from the construction of the processing facility considered the construction of the distillation columns and molecular sieve using data adapted from that of a corn ethanol production facility[22]. Sweet sorghum bagasse was assumed to be similar to sugarcane bagasse[23]. The avoided products for the corn ethanol process include corn grain, soybean meal and urea. An estimate of transportation distances from the farm to the processing facility is made using average transportation distance from farms in Iowa to corn ethanol processing plants[24]. The distance for the transportation of distilled ethanol to a molecular sieve site in the decentralized option is estimated to be 40km. The distance for the transportation of fermented ethanol in the semi-centralized option and the transportation of sorghum stalk in the centralized option is estimated to be 125km.

3.3. Results

This work utilized the IMPACT 2002+ life cycle impact assessment (LCIA) framework. IMPACT 2002+ is a combination of four methods: IMPACT 2002, Eco-indicator 99, CML (Institute of Environmental Sciences), and IPCC (International panel on climate change). It links life cycle inventory results with fourteen midpoint categories and four damage categories; the damage categories are: human health, ecosystem quality, climate change, and resources[25]. In this process, there are five impact categories of significance: respiratory inorganics, terrestrial ecotoxicity, land occupation, GHG emissions, and non-renewable energy. Since the IMPACT 2002+ impact assessment method does not include water use as an impact category, the BEES+ impact assessment method, developed by National Institute of Standards and Technology (NIST) is used to account for water use impacts. The results for each impact category for all evaluated processes can be seen in Table 3.**6**.

Table 3.6: Impact assessment results for the evaluated processes

Impact category	**Decentralized**	**Semi-Centralized**	**Centralized**	**Corn Ethanol**	**Unit**
Respiratory inorganics	1.3×10^{-5}	2.1×10^{-5}	1.1×10^{-4}	4.9×10^{-5}	kg particulate matter eq.
Terrestrial ecotoxicity	-15.1	-15.1	-19.7	0.6	kg TEG soil
Land occupation	2.9×10^{-2}	2.9×10^{-2}	1.2×10^{-1}	2.9×10^{-2}	m^2 arable
GHG emissions	3.7×10^{-2}	4.6×10^{-2}	9.7×10^{-2}	6.0×10^{-2}	kg CO_2 eq.
Non-renewable energy	0.7	0.8	1.3	0.9	MJ
Water intake	8.2	8.2	14.9	94.4	liters

3.3.1. Human Health

Figure 3.**7** shows a comparison between the three processing options and corn ethanol production for five impact categories. The impact category that falls under human health is respiratory inorganics and the reference substance is kg of particulate matter less than 2.5 microns. The centralized processing option stands out in this impact category. Figure 3.**8** shows a 123% increase in particulate matter released for the centralized option when compared to corn ethanol while the decentralized and semi-centralized options show a 74% and 57% reduction when compared to corn ethanol. The difference in this impact category when the processing options are evaluated is the effect of transportation. The centralized option transports sweet sorghum stalks to a processing facility while the decentralized option transports distilled ethanol to a molecular sieve site. Since the stalks are less dense than the ethanol, this increases the impacts from transportation, and 59% of the respiratory inorganics impacts for the centralized option comes from the transportation of sweet sorghum stem while transporting ethanol only accounts for 0.3% of the impacts for the decentralized option.

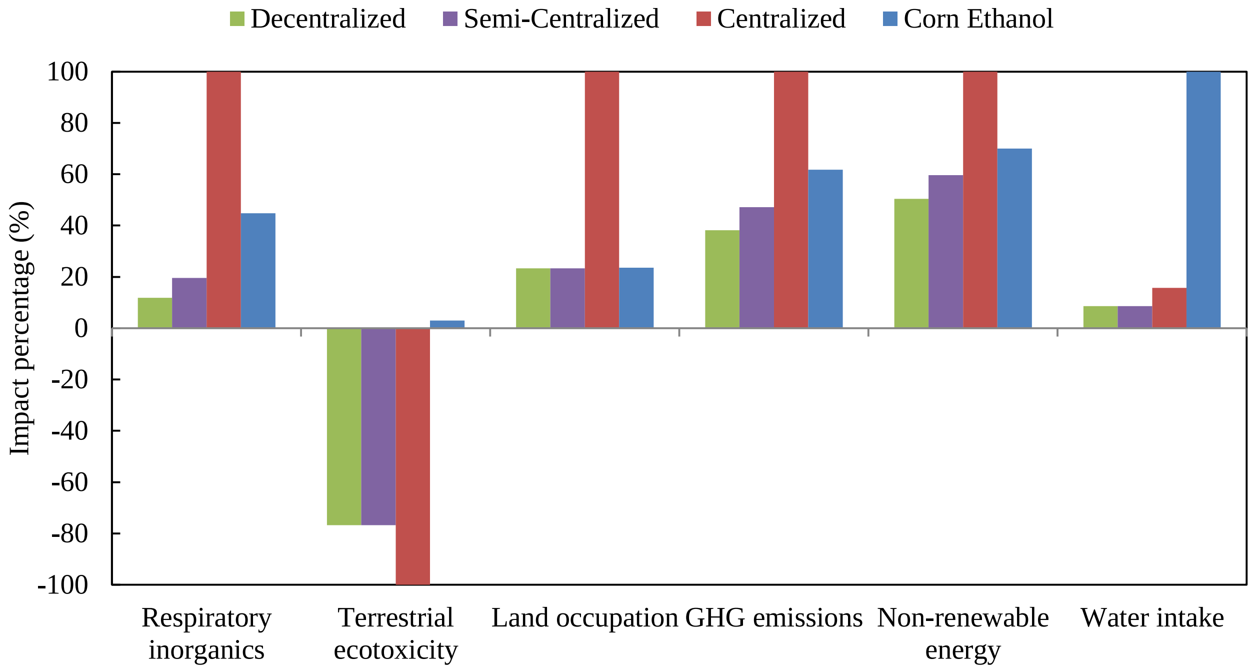

Figure 3.7: Comparison between the three processing options and corn ethanol production

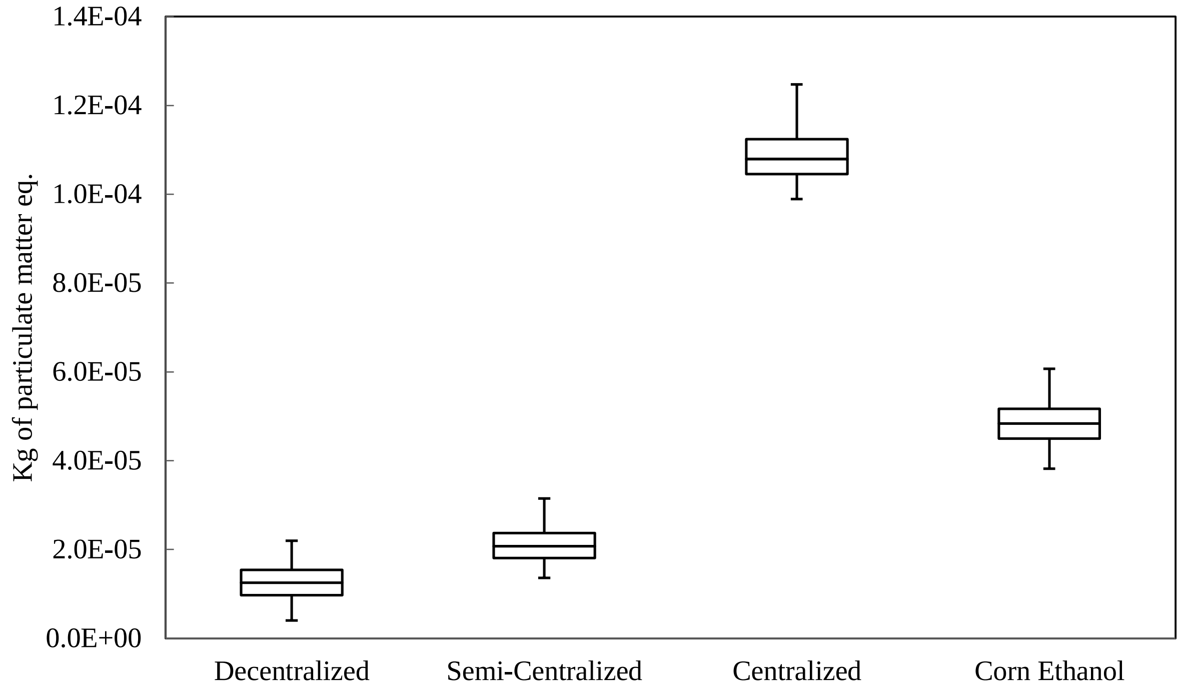

Figure 3.8: Impact assessment results for respiratory inorganics, per MJ of Ethanol. The top of the box is the 75th percentile, the middle is the median, and the bottom of the box is the 25th percentile. The top whisker is 97.5th percentile and the bottom whisker is 2.5th percentile.

3.3.2. Ecosystem Quality

There are two impact categories that were analyzed in the ecosystem quality damage category: terrestrial ecotoxicity and land occupation. Figure 3.**9** shows a comparison between the terrestrial ecotoxicity for the sweet sorghum processing options and corn ethanol. In terrestrial ecotoxicity, the impacts come from the cultivation of sweet sorghum; the negative sign for this impact category denotes a positive impact on terrestrial ecotoxicity. There is no positive impact in the cultivation of corn; this difference is due to the use of plant protection in the form of pesticides and insecticides. This study does not include plant protection use in sweet sorghum cultivation while there is for corn cultivation. The sweet sorghum plant removes Cadmium, Copper, Lead and Zinc and this improves the terrestrial ecotoxicity. The land occupation impacts include the area required to grow the crop and land required to build facilities and factories, although the latter accounts for around 0.1% of the land occupation impacts for all processes that are being evaluated. This is an impact category that is dependent on biomass yield, and in Figure 3.**10** though the three processing options utilize the same biomass yield, there is a difference in land use charge when compared to corn ethanol because of the different avoided products. In the centralized processing option there is a 358% increase in land use while the land use in the decentralized and semi-centralized options are similar to corn ethanol.

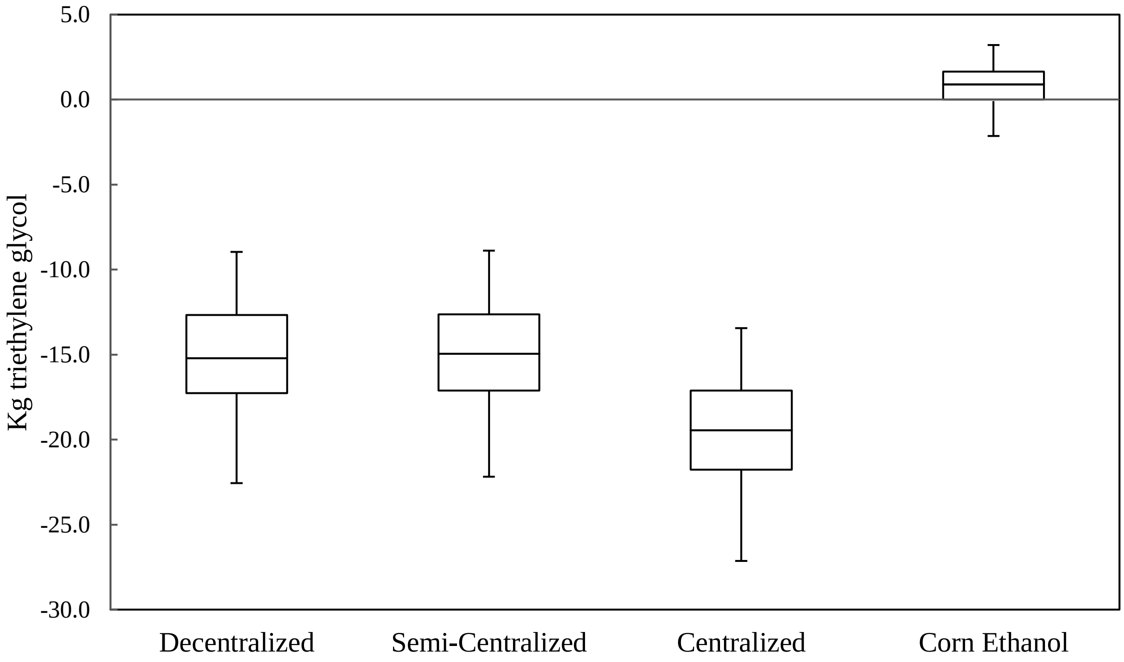

Figure 3.9: Impact assessment result for terrestrial ecotoxicity, per MJ of ethanol. The top of the box is the 75th percentile, the middle is the median, and the bottom of the box is the 25th percentile. The top whisker is 97.5th percentile and the bottom whisker is 2.5th percentile.

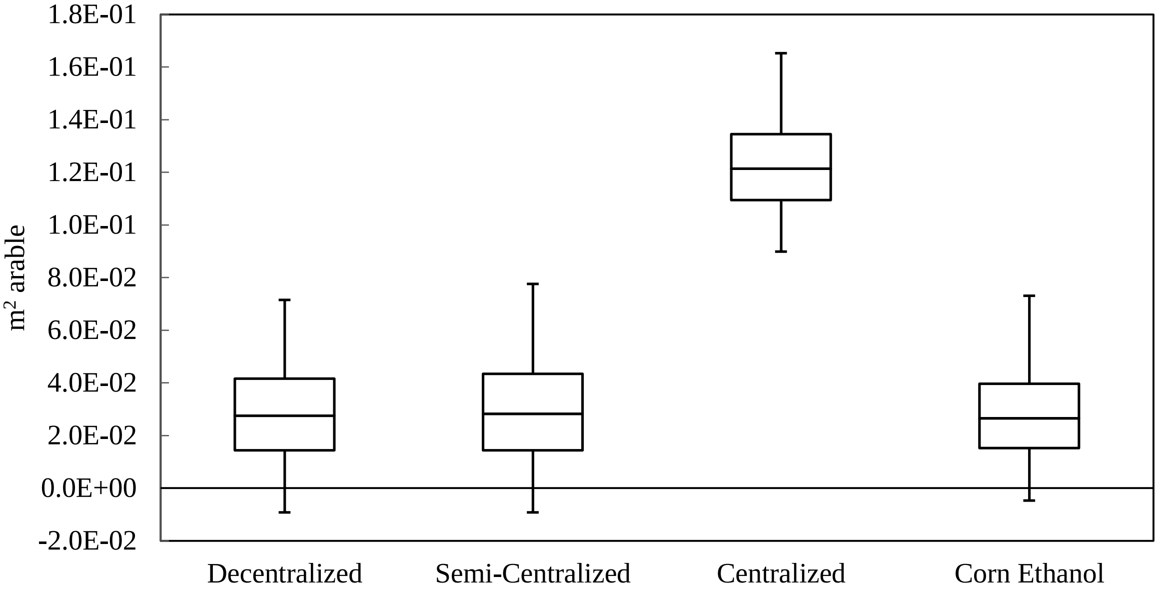

Figure 3.10: Impact assessment results for land occupation, per MJ of ethanol. The top of the box is the 75th percentile, the middle is the median, and the bottom of the box is the 25th percentile. The top whisker is 97.5th percentile and the bottom whisker is 2.5th percentile.

3.3.3. Climate Change

The only impact category that falls under climate change is GHG emissions and the unit is kg of equivalent carbon dioxide (CO_2) released to the atmosphere. This is an important metric that is a major focus of most life cycle assessments. In this process, some of the greenhouse gases that are released are CO_2, Methane (CH_4), and Nitrous oxide (N_2O). Figure 3.**11** shows the amount of equivalent CO_2 released to the air for every MJ of ethanol produced. The centralized option GHG emissions are significantly higher than the other processing options. When compared to corn ethanol there is a 62% increase in equivalent CO_2 released to the air for every MJ of ethanol produced in the centralized option, while for the decentralized and semi-centralized options there is an 39% and 25% decrease, respectively, when compared to corn ethanol. The difference is again due to the transportation; for the centralized option the transportation of sweet sorghum stem accounts for 69% of GHG emissions while distillation and reducing bagasse water content accounts for 20%. When the decentralized option is evaluated, 0.5% of GHG emissions come from transporting ethanol while 64% come from distillation and reducing the bagasse water content. Fertilizer production, waste water treatment and harvesting also contribute to this impact category.

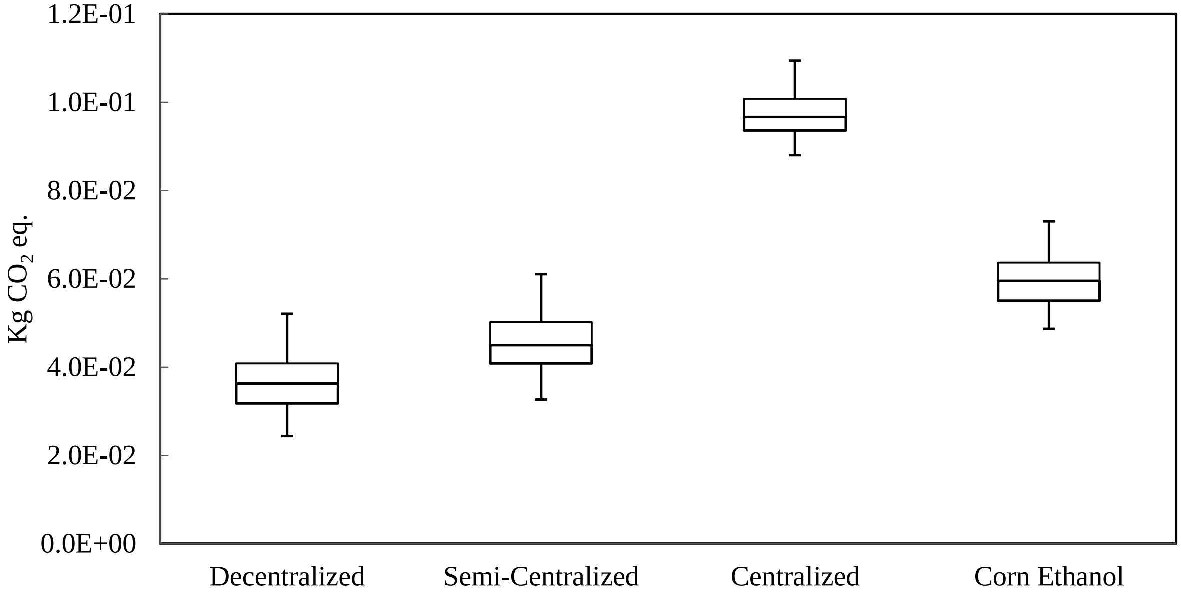

Figure 3.11: Impact assessment results for GHG emissions, per MJ of ethanol. The top of the box is the 75th percentile, the middle is the median, and the bottom of the box is the 25th percentile. The top whisker is 97.5th percentile and the bottom whisker is 2.5th percentile.

3.3.4. Resources

The resources damage category quantifies the amount of raw material required to produce the functional unit, and in this case non-renewable energy usage is the focus. This category would include any use of crude oil, natural gas, coal or uranium.

Figure 3.12 shows a comparison between the evaluated processes for every MJ of ethanol produced. Like in the GHG emissions impact category, the centralized option has a larger non-renewable energy use than the other processing options. When compared to corn ethanol, there is a 50% increase in non-renewable energy required to produce 1 MJ of ethanol for the centralized option; it requires 1.3MJ of non-renewable energy to produce 1 MJ of ethanol. The decentralized and semi-centralized options result in a 27% and 15% reduction, respectively, when compared to corn ethanol. The difference is again due to the transportation of the sweet sorghum stalks. For the centralized option, 71% of the impacts are from transportation of sweet sorghum stem while 18% come from distillation and bagasse water removal steps. When the decentralized option is evaluated, 0.6% of the non-renewable energy use comes from transportation of ethanol while 62% comes from the distillation and bagasse water removal process.

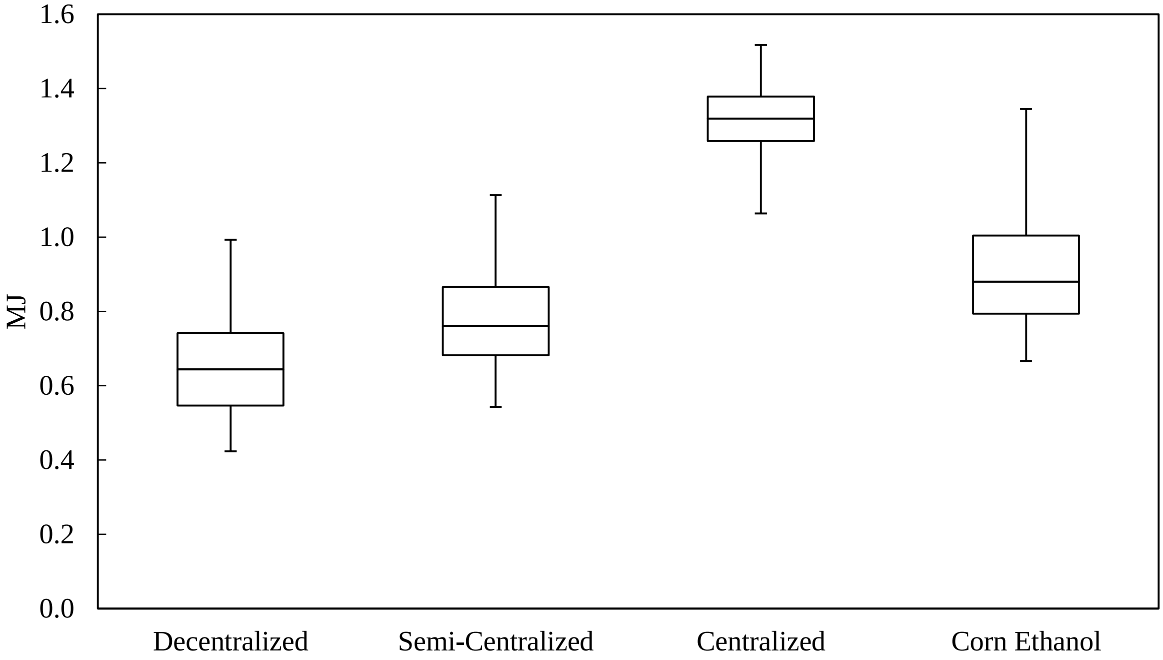

Figure 3.12: Impact assessment results for non-renewable energy, per MJ of ethanol. The top of the box is the 75th percentile, the middle is the median, and the bottom of the box is the 25th percentile. The top whisker is 97.5th percentile and the bottom whisker is 2.5th percentile.

3.3.5. Water use

Water usage is an important metric to be considered when evaluating biofuel production processes. This includes water used for irrigation and during fuel processing.

The corn ethanol and sweet sorghum ethanol processes have some differences. Since sweet sorghum is a hardy and drought resistant crop, this LCA does not include irrigation for the sweet sorghum crop but it is included for corn cultivation. In Figure 3.13, all three sweet sorghum processing options have a lower water use compared to corn ethanol. The decentralized, semi-centralized see a 91% reduction while the centralized processing options only results in an 84% reduction in water use during its entire life cycle when compared to corn ethanol.

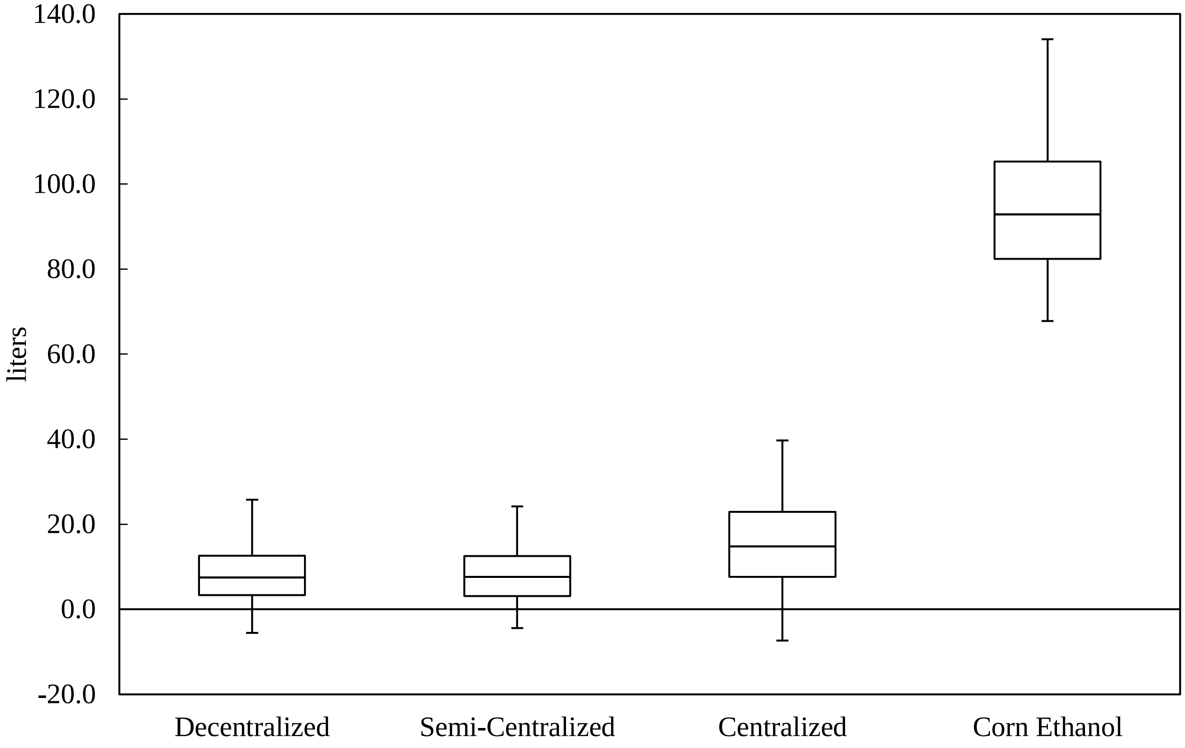

Figure 3.13: Impact assessment results for water intake, per MJ of ethanol. The top of the box is the 75th percentile, the middle is the median, and the bottom of the box is the 25th percentile. The top whisker is 97.5th percentile and the bottom whisker is 2.5th percentile.

3.3.6. Uncertainty Analysis

A Monte Carlo simulation was carried out in SimaPro 7.3.3 to test the uncertainty in the LCA impact category results. The uncertainty for each input is calculated using a pedigree matrix. The pedigree matrix has 6 factors: Reliability (U_1), Completeness (U_2), Temporal correlation (U_3), Geographical correlation (U_4), Further technological correlation (U_5), and sample size (U_6)[26]. These factors have a score and value associated with them and the user assigns the score and value according to which category the life cycle inventory data source is used. A basic uncertainty factor (U_b) is also added[26], which is based on expert judgment associated with certain inputs, outputs and emissions. These six factors from the pedigree matrix and the basic uncertainty factor are used to calculate an overall uncertainty factor that can be entered for each input, output, and emission. Since this LCA uses the ecoinvent database extensively, there are inputs to the process in simapro that are from different geographic regions, this uncertainty analysis helps account for differences due to geographic location.

3.3.7. Sensitivity analysis

A sensitivity analysis was performed on biomass yield and avoided products ratio for the decentralized option. Biomass yields of 25, 35, and 45 tons per acre were used. The sensitivity analysis on biomass yield in Figure 3.**14** and Table 3.**7** shows an improvement in all impact categories as biomass yield increases. When compared with corn ethanol, a 25 and 45 tons per acre biomass yield results in a 43% and 53% reduction in equivalent CO_2 released and a 51% and 59% reduction in non-renewable energy use. This is a result of a reduced quantity of inputs required per unit mass of sweet sorghum, less fertilizer use, harvester use, and emissions.

Table 3.7: Sensitivity analysis on biomass yield

Impact category	**25 tons/acre**	**35 tons/acre**	**45 tons/acre**	**Unit**
Respiratory	1.9×10^{-5}	1.3×10^{-5}	9.5×10^{-6}	kg

inorganics				particulate matter eq.
Terrestrial ecotoxicity	-14.9	-15.1	-15.2	kg TEG soil
Land occupation	7.7 x 10^{-2}	2.9 x 10^{-2}	1.7 x 10^{-3}	m^2 arable
GHG emissions	4.1 x 10^{-2}	3.7 x 10^{-2}	3.5 x 10^{-2}	kg CO_2 eq.
Non-renewable energy	7.1 x 10^{-1}	6.6 x 10^{-1}	6.4 x 10^{-1}	MJ
Water intake	12.9	8.2	5.5	liters

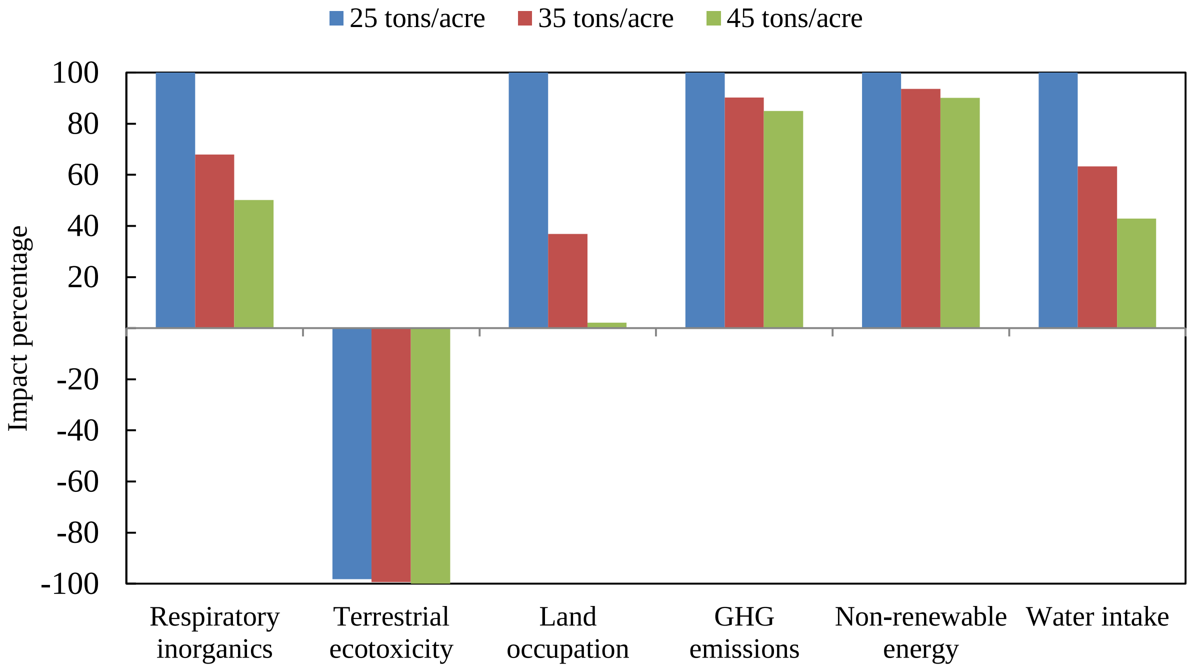

Figure 3.14: Sensitivity analysis on biomass yield

3.4. Conclusion

For the production of ethanol from sweet sorghum, the choice of processing options has a significant impact on the environmental outlook of the process. The decentralized and semi-centralized options are the most attractive from an environmental impact standpoint. Both processing options yield similar or lower environmental impacts in all impact categories when compared to corn ethanol production. In terrestrial ecotoxicity, the decentralized and semi-centralized options result in a positive environmental impact. The main difference between the processing options is the energy density of the material being transported and the transportation distance and the avoided products. Because the semi-centralized and centralized processes still depends on individual farmers to provide the biomass feedstock, the environmental impacts from the production of the biomass for all processing options are the same, the difference in results come from the increased transportation distances and accounting for the lower density of the sorghum stem that is being transported in the centralized option. When the decentralized option is evaluated, it can be seen that transportation plays a small role in the environmental impacts of the process. This can also be seen in the semi-centralized option, but in the centralized option it is the most important part. The non-renewable energy use results show that not only does the centralized option have a larger environmental impact; it also has a larger economic impact. For every MJ of ethanol produced, 1.3 MJ of non-renewable energy is required.

This analysis also shows that land usage has a large impact on the life cycle assessment. Production of ethanol from sweet sorghum results in a larger land use charge than the production of ethanol from corn in the centralized processing option. This difference is because the avoided products for the centralized sweet sorghum ethanol process is different than that of the decentralized and semi-centralized options. The corn ethanol process has DDGS as a co-product while the decentralized and semi-centralized options have bagasse. This displaces soybean meal, urea, and corn grain for use as animal feed. The displacement of soybean meal and corn grain results in a land use credit for the corn ethanol process, a larger land use credit than that from the centralized sweet sorghum process since electricity production is the only displaced product. This is important because land required for the cultivation of sweet sorghum requires tilling, harvesting and fertilizer inputs and this is arable land that will not be used to grow food for consumption.

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CHAPTER IV

LIFE CYCLE ASSESSMENT OF THE PRODUCTION OF ETHANOL FROM EASTERN REDCEDAR

Abstract

This study evaluates the environmental impacts of an ethanol production system using Eastern redcedar (*Juniperus virginiana* L.) trees as the biomass feedstock using life cycle assessment (LCA) methodology. A process simulation was developed using Aspen Plus® to model the acid bisulfite pretreatment, enzymatic hydrolysis, fermentation, and distillation steps. A cradle-to-gate LCA was conducted to evaluate the environmental impacts from the cutting down of the trees to the production of anhydrous ethanol. 1 MJ of equivalent energy and the relative mass, energy and economic (RMEE) system boundary selection method was used. The environmental impacts of a redcedar ethanol process were compared to production of corn ethanol. Inventory data for the system were collected and used to calculate a life cycle impact assessment (LCIA) using the IMPACT 2002+ and BEES+ framework in Simapro 8.0.0. Four impact categories were evaluated: land occupation, water use, greenhouse gas (GHG) emissions, and non-renewable energy use. Results indicate that acid bisulfite pretreatment contributed to 65% of GHG emissions, 81% of non-renewable energy use, and 77% of water use during the life cycle of the process.

Keywords: Redcedar, Lignocellulosic, Life cycle assessment, Simapro, IMPACT 2002+, BEES+,

4.1. Introduction

In recent years, there has been a great effort in investigating alternative feed stocks for fuel production in the United States. This has been done due to increased awareness of the environmental impacts of fossil fuels and as a way to achieve energy independence [1]. The Energy Independence and Security Act (EISA) of 2007 passed by the United States Congress mandates the production of 21 billion gallons of advanced biofuels by the year 2022, 16 billion of which must come from lignocellulosic feed stocks [2]. Right now, the most widely used feed stock for bio ethanol production in the United States is corn. The production of the feed stock is an important factor in the outcome of the environmental analysis. Cultivation of crops such as corn required land transformation that can release enough CO_2 to cancel out any benefits from the displacement of fossil fuels [3, 4]. There is also another issue that comes from the cultivation of biofuel feed stocks, a food vs fuel debate. Land that is being used to grow crops for fuel could be used to grow crops for food. Countries that depend on food imports can be affected by an increase in crop cultivation for biofuels [5]. Due to these challenges, research has been devoted to feed stocks that do not require crop cultivation or are waste products.

LCA is a methodology that is used for the evaluation of environmental impacts of a process. It is governed by ISO 14040:2006 and 14044:2006, and it has four steps: goal and scope definition, inventory analysis, impact assessment, and interpretation [6, 7]. It also allows for identifying areas of improvement in processes. LCA only deals with environmental impacts, it does not take into account economic, social, and political factors [8]. There have been LCAs performed on the lignocellulosic feedstocks corn stover[9, 10] and switchgrass[9] for the production of ethanol as fuel. Most LCAs on biofuel production are focused on energy use, land occupation impacts and GHG emissions whether it is a cradle-to-gate or a cradle-to-grave analysis[11]. It is important to perform LCAs on emerging renewable energy technologies to identify those that have the best impact environmental impacts and to identify steps in the process that must be further optimized to reduce environmental impacts. When looking into advanced biofuels as defined by EISA, a comparison to a competitor like corn ethanol is also beneficial. A study performed by Argonne National Laboratory (ANL) showed that when woody biomass is compared to corn as a feedstock for ethanol production, woody biomass results in a lower fossil energy use, total energy use, and GHG emissions[12].

Eastern redcedar (*Juniperus virginiana* L.), a softwood that is a member of the cypress family and is common to the central and eastern United States, is being investigated as a feed stock for the production of ethanol[13]. It is able to easily adapted to different soil and climate conditions [14] and its encroachment is a concern to ranchers and farmers [15]. Its large root system makes it difficult for aquifers to recharge properly and a single eastern redcedar tree can absorb up to thirty gallons of water per day [16]. It also is a fire hazard due to the presence of volatile terpenes. This is a large concern in areas of low humidity, high winds, drought, and high temperatures [17]. Due to its abundance and the need to contain its spread, eastern redcedar could be a great candidate for biofuel production. To evaluate its viability as a bioethanol feed stock, the environmental impacts of a redcedar ethanol process was performed using life cycle assessment (LCA), a methodology for evaluating the environmental impact of processes. A cradle-to-gate

LCA is performed to incorporate environmental impacts of ethanol production from mechanical clearing to the production of anhydrous ethanol.

The goal of this LCA was to evaluate the environmental impacts of the production of ethanol from eastern redcedar trees as the feed stock. The functional unit is 1 MJ of energy from anhydrous ethanol produced at a bio refinery and an LCA of corn ethanol production was conducted so that a comparison could be made. The impact categories that were evaluated using the IMPACT 2002+ impact assessment method included: greenhouse gas (GHG) emissions, non-renewable energy use, and land occupation. Another impact category was used to account for water use, BEES+, developed by the National Institute of Standards and Technology (NIST) since the IMPACT 2002+ method does not have a water use category. This assessment only investigated the environmental impacts of the process and did not seek to make any conclusions on the economics or the logistics of the process.

4.2. Materials and Methods

4.2.1. Process description

The process for converting redcedar into ethanol that is being evaluated in this study is based on research that was done on the development of an effective pretreatment process[13] and demonstration of ethanol production using separate hydrolysis-fermentation process[18] and simultaneous saccharification and fermentation (SSF) process[19]. The process begins with mechanical clearing. The tree is delimbed and the logs are transported to a processing facility where the logs undergo a veneering and size reduction step developed by Forest Concepts, LLC[20]. The logs are passed through a veneer lathe that peels the surface of the wood, which is then sent through a rotary shear configurable muncher where the peeled redcedar is reduced to 2 mm particles[20]. Energy consumption for the size reduction was 150 MJ Mg^{-1} of dry wood [20]. The crumbled particles were sent to a pretreatment reactor and the pretreatment method used was an acid bisulfite process[19]. A mixture of redcedar particles, sulfuric acid, sodium bisulfite and water is placed in a reactor at 90°C with a reactor agitation speed of 150 rpm for 3 hours. The sulfuric acid loading is 3.75 g/100g of dry wood, the sodium bisulfite loading of 20g/100g of dry wood, and the liquid to solid ratio is 5 to 1. After 3 hours, the temperature is increased to 200°C and held for 10 min and the reactor is then cooled to 55°C. The next step involved an enzymatic hydrolysis step using Accelerase® 1500 (Dupont Biosciences, Palo Alto, CA, USA) with an enzyme loading of 0.5 mL/g of glucan[18]. After the enzymatic hydrolysis, the sugars were fermented, the solids fraction was separated and the lignin was used as fuel for the pretreatment reactor. The ethanol was distilled and anhydrous ethanol was produced using a molecular sieve. Figure 4.15 shows the process modeled in Aspen Plus process simulation software developed by AspenTech using simulation data from a National Renewable Energy Laboratory (NREL) report on the production of ethanol from corn stover [21].

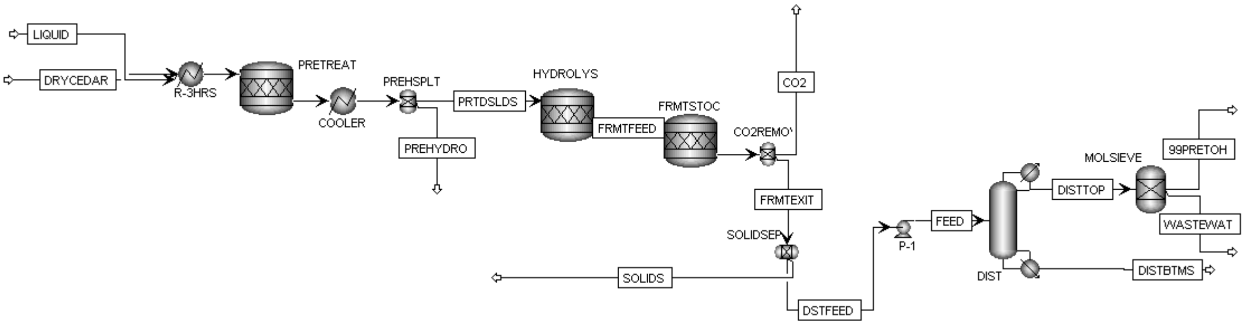

Figure 4.15: Aspen simulation process diagram for redcedar ethanol production

4.2.2. System boundary selection

The system boundaries for both processes were developed using the relative mass energy economic (RMEE) system boundary selection method. The system boundary for the redcedar ethanol process is shown in Figure 4.16. This system boundary selection method includes and excludes processes from the system boundary by considering the mass, energy and economic ratio of every input to the process to the final product. The aim of the system boundary selection is to include enough of the environmental impacts of the process to reach a conclusion. Using RMEE, a system boundary can be generated without having to examine the entire process [22]. To develop a system boundary using RMEE, a cut-off criteria (Z_{RMEE}) of 0.05 was chosen. Analysis of different Z_{RMEE} values showed that values from 0.05 to 0.25 included at least 90% of environmental impacts in the system boundary [23]. Note that in Figure 4.16, the cultivation of redcedar is not considered because it is a naturally occurring species.

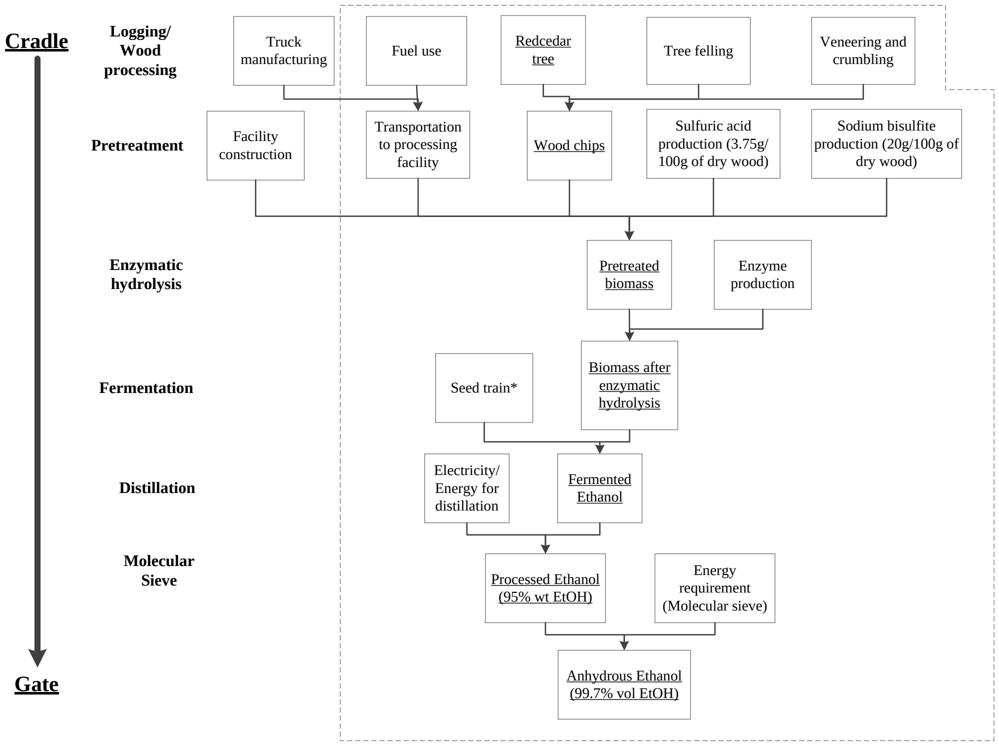

Figure 4.16: RMEE system boundary, *A seed train is a cascade to grow the metabolically less active cells from a glycerol stock (or agar slant) to a seed rector (a reactor that contains actively growing cells for inoculating the commercial production tanks).

4.2.3. Assumptions

The lifecycle assessment in this study used SimaPro 8.0.0 to aid in the development of this analysis. The following assumptions were made:

- Sulfite from paper pulping unit process was used as a substitute for sodium bisulfite in SimaPro.
- Sodium bisulfite was replaced with ammonium bisulfite in the Aspen Plus simulation.

- Energy requirement for the pretreatment reactor was calculated by accounting for total enthalpy change of redcedar biomass and water in the reactor, heating of sulfuric acid and sodium bisulfite was considered to be a minor contributor to the energy requirements.
- In the Aspen Plus simulation; glucan, mannan, and galactan were treated as cellulose while lignin was treated as vanillin.
- Redcedar specific heat was calculated using the Choi-Okos equation[24]
- Pretreatment energy was calculated using an energy balance shown in equation 1 where Q is the pretreatment energy, m is the mass of the reactor feed, and ΔH is the change in enthalpy.

$$Q = m \times (\Delta H_{total}) = m_{water} \times \Delta H_{H_2o} + m_{redcedar} \times \Delta H_{redcedar} \tag{1}$$

The corn ethanol LCA is based on an NREL study performed on a dry mill corn ethanol process, the co-product was dried distillers grains with solubles (DDGS)[25]. To account for the environmental impacts of the DDGS, a system expansion was performed to include the environmental credits to the corn ethanol process from the displacement of animal feed by the DDGS. The DDGS displaced corn grain, soybean meal and urea[25]. The redcedar process received environmental credits from lignin that was burned to fuel the pretreatment reactor using a lignin heat of combustion of 23 MJ/kg[26].

4.2.4. Uncertainty analysis

A Monte Carlo simulation was run in Simapro to determine the uncertainty in the results for both the redcedar and corn ethanol processes. Each input to every unit process had an uncertainty factor calculated based on different factors associated with the quality of the data. A pedigree matrix that accounted for reliability, completeness, age of data, geographic correlation, and technological correlation was used to generate an overall uncertainty factor for each input and output to the process[27].

4.3. Results

4.3.1. GHG emissions

The IMPACT 2002+ impact assessment method gives GHG emissions in units of equivalent CO_2 released. It uses CO_2 as the reference substance and other GHG impacts from other substances are normalized using a multiplier that reflects their global warming potential (GWP). In Figure 4.17, the average equivalent CO_2 released per MJ of ethanol for the redcedar ethanol and the corn ethanol process are 0.18 and 0.06 kg respectively. When compared to corn ethanol, the redcedar process results in a 200% increase in equivalent CO_2 released during the life cycle of the process.

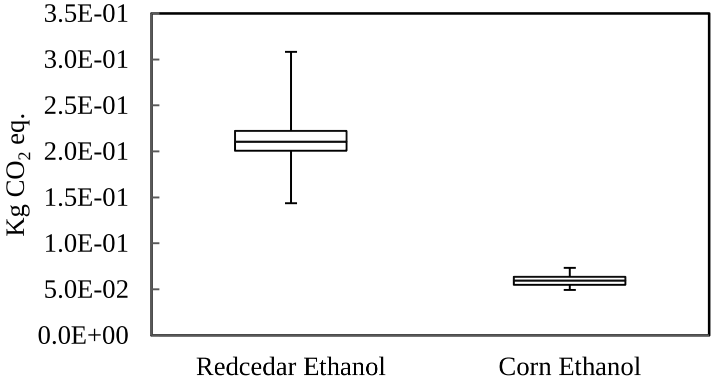

Figure 4.17: GHG emissions impact category comparison between redcedar ethanol and corn ethanol, per MJ of ethanol produced. The top of the box is the 75th percentile, the middle is the median, and the bottom of the box is the 25th percentile. The top whisker is 97.5th percentile and the bottom whisker is 2.5th percentile.

Figure 4.18 shows the breakdown of process impacts. The energy requirement for the pretreatment reactor and the production of sodium bisulfite account for 33% and 32% of equivalent CO_2 emissions, respectively, meaning that the pretreatment step accounts for 65% of total GHG emissions. The impacts that are considered under pretreatment energy are those that are a result of steam produced by burning natural gas to achieve the desired reactor temperature of 200°C. Treatment of waste water from the process accounts for 21%, the waste water treatment that was used for this process was the activated sludge process, which is used in the pulp and paper industry[28]. Electricity required to produce biomass particles and steam required for distillation both account for just 6% and 7% of total equivalent CO_2 released, respectively.

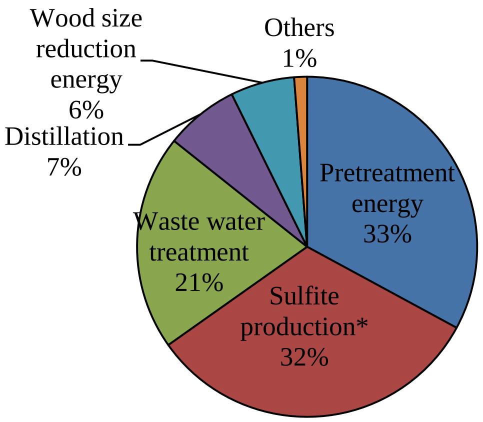

Figure 4.18: Process breakdown of GHG emission impacts. *Sulfite production was used to simulate sodium bisulfite production in SimaPro 8.0.0

4.3.2. Non-renewable energy use

The non-renewable energy use category accounts for the energy derived from a depletable resource, which includes: crude oil, natural gas, coal or uranium. The reference unit for this impact category is MJ of non-renewable energy. In Figure 4.19, when redcedar ethanol is compared to corn ethanol, there is a 189% increase in non-renewable energy use in the redcedar process. The non-renewable energy use for redcedar is 2.6 MJ of non-renewable energy per MJ of ethanol produced and for corn; it is 0.9 MJ of non-renewable energy per MJ of ethanol produced. The larger variability in the non-renewable energy use for the redcedar ethanol process is due to larger uncertainty in input and output data in the LCA. These include uncertainties in the process simulation and also in the estimate for the pretreatment reactor energy requirement; increased variability is also present in the other impacts categories.

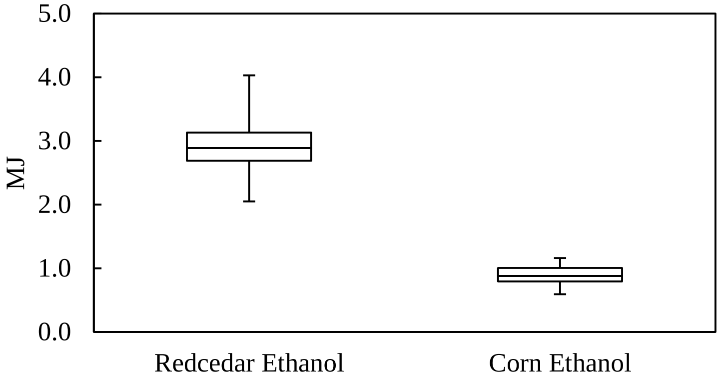

Figure 4.19: Non-renewable energy use impact category comparison between redcedar ethanol and corn ethanol, per MJ of ethanol produced. The top of the box is the 75th percentile, the middle is the median, and the bottom of the box is the 25th percentile. The top whisker is 97.5th percentile and the bottom whisker is 2.5th percentile.

The breakdown of non-renewable energy use for different aspects of the process in Figure 4.20 show that energy for the pretreatment reactor accounts for 39% of total non-renewable energy use and with the production of sodium bisulfite accounting for 42% of energy use, the total pretreatment contribution is 81%. Steam for distillation accounts for 8%, wood size reduction each account for 6% while waste water treatment and other parts of the process make up the remaining 4% and 1%.

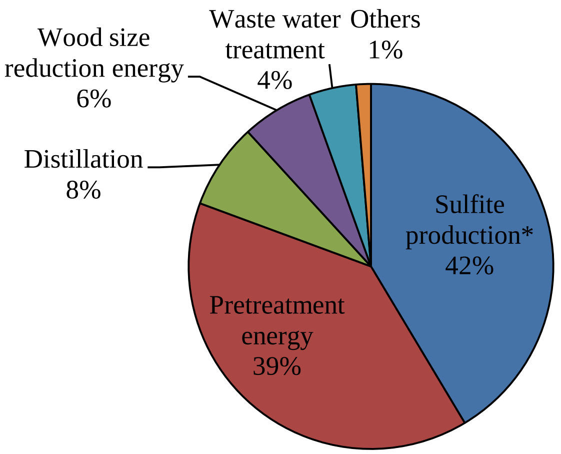

Figure 4.20: Process breakdown of non-renewable energy use impacts. *Sulfite production was used to simulate sodium bisulfite production in SimaPro 8.0.0

4.3.3. Land occupation

Land occupation impact accounts for land taken up for cultivation and for construction of facilities. The reference unit for this impact category is m^2 of arable land. In Figure 4.21, land occupation for the redcedar process is less than that of corn ethanol. When compared to corn ethanol there is a two order of magnitude difference and a 98% reduction in land requirement for each process. This analysis did not attribute a land credit from the mechanical clearing of redcedar. For each MJ of ethanol produced; the redcedar process requires 5.5×10^{-4} m^2 of arable land while the corn ethanol process requires 2.9×10^{-2} m^2 of arable land.

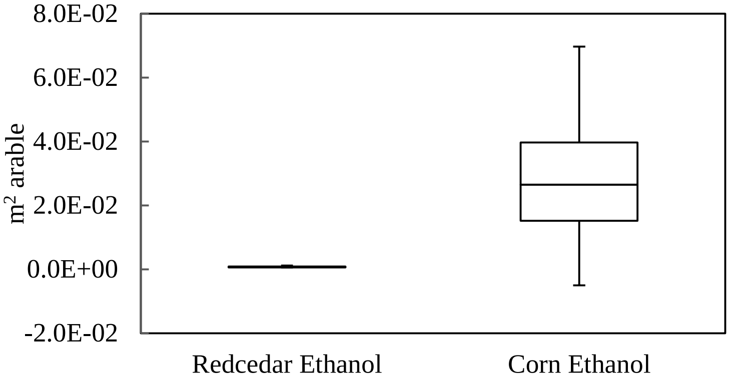

Figure 4.21: Land occupation impact category comparison between redcedar ethanol and corn ethanol, per MJ of ethanol produced. The top of the box is the 75th percentile, the middle is the median, and the bottom of the box is the 25th percentile. The top whisker is 97.5th percentile and the bottom whisker is 2.5th percentile.

4.3.4. Water use

This impact category accounts for water usage throughout the life cycle of a process. The reference unit is liters of water and in Figure 4.22 the water usage for both processes can be seen. Redcedar ethanol and corn ethanol consume 626 liters and 95 liters of water respectively during their life cycle. When compared to corn ethanol, redcedar ethanol sees a 559% increase in water use.

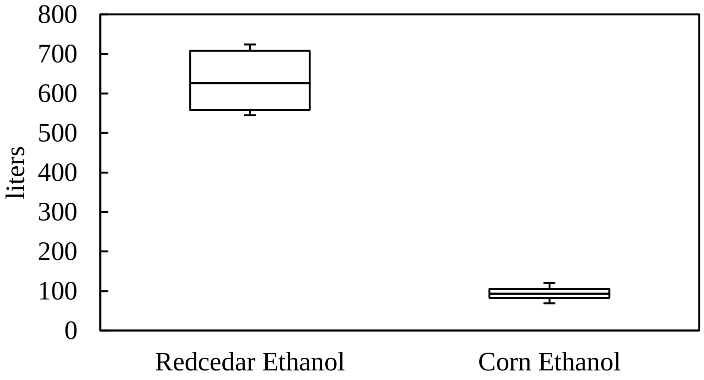

Figure 4.22: Water use impact category comparison between redcedar ethanol and corn ethanol, per MJ of ethanol produced. The top of the box is the 75th percentile, the middle

is the median, and the bottom of the box is the 25th percentile. The top whisker is 97.5th percentile and the bottom whisker is 2.5th percentile.

In Figure 4.23, a breakdown of process contribution to water usage show that the production of sodium bisulfite for the pretreatment step accounts for 75% of all water usage. Pretreatment energy accounts for only 2% and process water, which includes water required for the production of steam, pretreatment, enzymatic hydrolysis and fermentation accounts for 15%. The remaining contributions come from wood size reduction, which accounts for 6% and other parts of the process, which account for the remaining 2%.

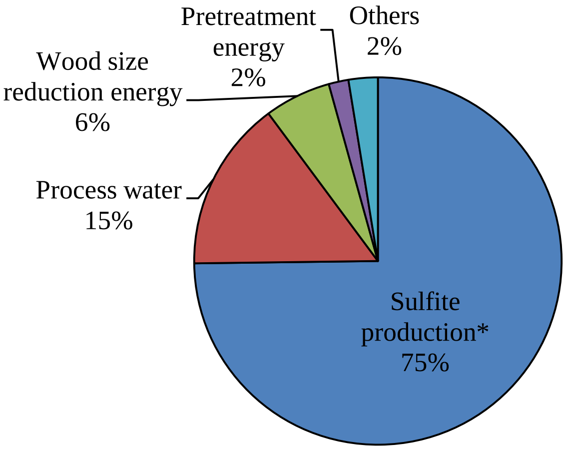

Figure 4.23: Process breakdown of water use impacts. *Sulfite production was used to simulate sodium bisulfite production in SimaPro 8.0.0

4.3.5. Sensitivity analysis

A sensitivity analysis was performed on the process to see the effects of sodium bisulfite loading on the impact categories, the results in Table 4.8 summarize the results that are in Figure 4.24 through 4.Figure 4.27. Sodium bisulfite loadings of 10, 15, and 20 g per 100 g of dry wood were evaluated while sulfuric acid loading was kept at 3.75 g per

100g of dry wood. Results have shown that increasing sodium bisulfite loading results in improved delignification and improves digestibility of pretreated biomass[13].

Table 4.8: Sensitivity analysis results for redcedar ethanol production for different sodium bisulfite loadings. 3.75g/100g sulfuric acid loading

Impact category	**10% $NaHSO_3$**	**15% $NaHSO_3$**	**20% $NaHSO_3$**
Land occupation (m^2 arable)	$6.2x10^{-4}$	$7.3x10^{-4}$	$7.8x10^{-4}$
GHG emissions (kg CO_2 eq)	0.2	0.2	0.2
Non-renewable energy use (MJ)	1.9	2.2	2.9
Water use (liters)	575	626	641

Results in Figure 4.24 show that as bisulfite loading increased, so did land occupation. When the configuration with the highest land occupation was compared to the corn ethanol process, there was an order of magnitude difference. The 20% $NaHSO_3$ loading required $7.8 \times 10^{-4} m^2$ while the corn ethanol process required $2.9 \times 10^{-2} m^2$ of arable land per MJ of ethanol produced.

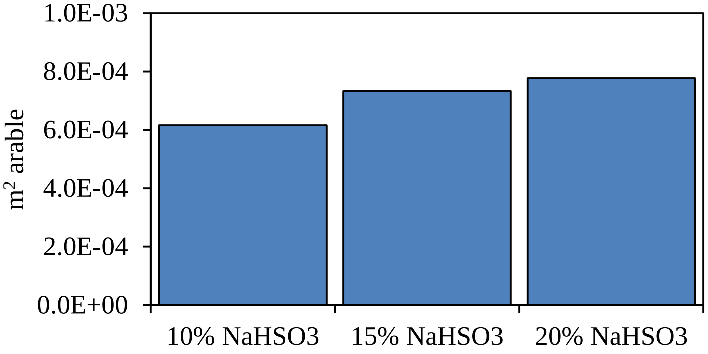

Figure 4.24: Land occupation impact assessment sensitivity analysis results for redcedar ethanol production for different sodium bisulfite loadings. 3.75g/100g sulfuric acid loading, per MJ of ethanol produced

In Figure 4.25, GHG emissions for the different configurations are shown. The same trend that was present in the land occupation impact category was also present in GHG emissions. When the bisulfite loading was increased GHG, emissions increased. The 10% bisulfite loading resulted in the lowest GHG emissions, this was due to the configuration having more available lignin. With a lignin loss of 2.41%[13], there was enough lignin to completely fuel the pretreatment reactor. Extra energy from lignin to make electricity or other energy products was not used to offset other non-renewable energy in your analysis, thus no credits were given for this. The 20% bisulfite loading suffers in this category due to a lignin loss of 54%[13]. The high delignification for that bisulfite loading and the increased digestibility of the pretreated biomass meant there was less lignin available for use as fuel when compared to the 10% and 15% bisulfite loading options.

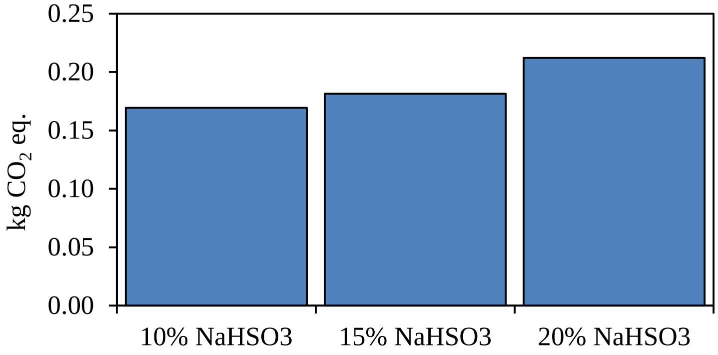

Figure 4.25: GHG emissions impact assessment sensitivity analysis results for redcedar ethanol production for different sodium bisulfite loadings. 3.75g/100g sulfuric acid loading, per MJ of ethanol produced

Non-renewable energy use data in Figure 4.26 showed that the worst performing option was 20% bisulfite loading and the best performing was 10% bisulfite loading. At 2.9 MJ of non-renewable energy required per MJ of ethanol produced, the 20% bisulfite loading was more energy intensive when compared to the other options. More lignin is left over in the configurations with lower bisulfite loading resulting in increased displace non-renewable energy use.

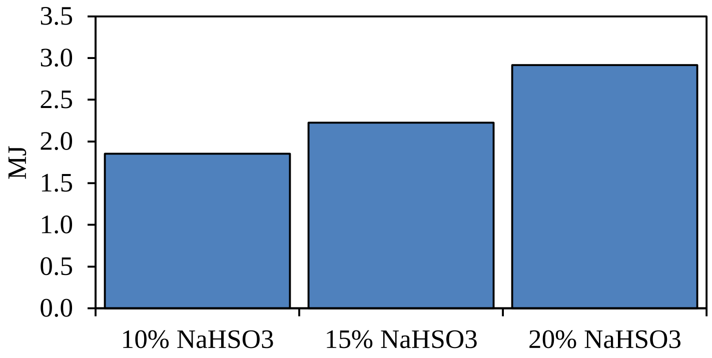

Figure 4.26: Non-renewable energy use impact assessment sensitivity analysis results for redcedar ethanol production for different sodium bisulfite loadings. 3.75g/100g sulfuric acid loading, per MJ of ethanol produced

In Figure 4.27, water use per MJ of ethanol produced for all configurations showed that once again, best performing configuration was the one with the lowest bisulfite loading. This analysis only accounted for water use in the conversion process and during raw material production, it does not account for water used by the redcedar tree. The impact assessment resulted in Figure 4.23 showed that 75% of water use impacts are from sodium bisulfite production, so decreased sodium bisulfite requirement resulted in lower water use.

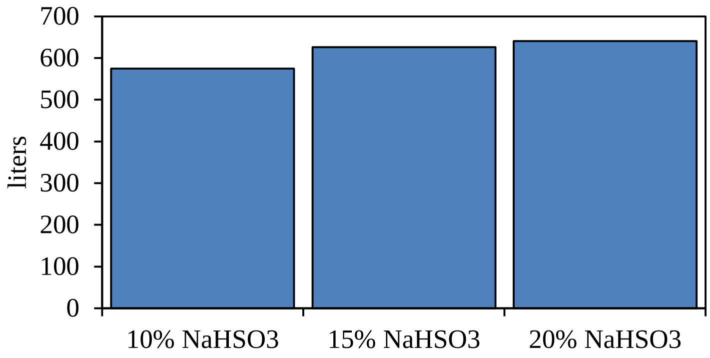

Figure 4.27: Water use impact assessment sensitivity analysis results for redcedar ethanol production for different sodium bisulfite loadings. 3.75g/100g sulfuric acid loading, per MJ of ethanol produced

4.4. Conclusions

The production of ethanol from redcedar, when compared to an already established corn ethanol, falls short in delivering lower environmental impacts. The comparison is of a relatively new and not fully optimized redcedar ethanol process to a corn ethanol process that been commercialized and is an established bioethanol process. This results in redcedar ethanol only having a better environmental outlook in one of the four impact categories that were investigated, that being land occupation. Since the redcedar in this analysis is not being cultivated, it has an advantage in this category; unlike corn, it does not require land to be dedicated to its cultivation. In water usage, corn ethanol performs better than redcedar ethanol; the largest contributor to water usage for redcedar ethanol is sodium bisulfite production. When non-renewable energy use and GHG emissions are also evaluated, the pretreatment step accounts for 81% and 65% of impact for those impact categories, this means that any improvement to the process will have to include the pretreatment process and this is an area in need of further optimization. It would be beneficial to explore other pretreatment processes that have a lower environmental footprint. A techno-economic study on the different sodium bisulfite loadings should be performed to see how the reduced glucose yield from the enzymatic hydrolysis steps affects the economics of a configuration with a lower sodium bisulfite loading.

4.5. References

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CHAPTER V

CONCLUSIONS AND FUTURE WORK

5.1. Conclusions

For the first study comparing the production of ethanol from sweet sorghum to the production of ethanol from corn, environmental impacts varied depending on the processing option that was evaluated. The decentralized processing option came out as the preferred option for respiratory inorganics, GHG emissions, non-renewable energy use, and water use when average values were compared. The difference between the decentralized option and the semi-centralized options for all categories was not statistically significant. The environmental impacts for the centralized option are higher for all impact categories that were evaluated except for terrestrial ecotoxicity and water use though the only categories where it was statistically higher were: respiratory inorganics, land occupation, and GHG emissions. The difference between the centralized processing option and the decentralized and semi-centralized option is due to the impacts from transportation. The density of sweet sorghum stem that requires transportation in the centralized processing option is lower than that of fermented ethanol and distilled ethanol. Results of the sweet sorghum processing options were compared to a study on carbon and energy balances performed by Elsayed et al. on the production of biofuels from various feedstocks. Equivalent GHG emissions for sugar beets was 0.04 kg of equivalent CO_2, while equivalent GHG emissions for the decentralized, semi-centralized, and centralized options were 0.037, 0.046, and 0.097 kg of equivalent CO_2 respectively.

The second study that compared the production of ethanol from eastern redcedar and the production of ethanol from corn showed that environmental impacts for the redcedar ethanol production process was higher for GHG emissions, non-renewable energy use, and water use. When a sensitivity analysis was performed, evaluating the impacts of sodium bisulfite loading and use of a biomass recycle, 10% sodium bisulfite loading, which was the lowest one evaluated resulted in similar GHG emissions to the 15% and 20% options which have higher glucan to glucose yields. This is a result of the lower lignin loss which means more lignin is available for use as fuel to produce steam, there is enough lignin available to produce enough energy to fuel the pretreatment reactor. The same is seen when non-renewable energy use is evaluated, the increase in available lignin provide a great benefit in this category and when the 10% option without a biomass recycle is compared to the 20% option with and without a biomass recycle, the 10% option results in lower non-renewable energy use. When the production of ethanol from lignocellulosic feedstocks is compared to gasoline production, most studies have found a reduction in GHG emissions and fossil energy use[1], this study does not. Different lignocellulosic feedstocks require different pretreatment[2], each carrying their own environmental impacts. For the redcedar ethanol process, which is in its infancy, there is a need for optimization so that the environmental impacts can be reduced. As Table 5.9 shows, an ethanol production process using redcedar as a feedstock results in a 150% increase in GHG emissions when compared to the production of gasoline from crude oil and in Table 5.10, a 58% increase in non-renewable energy use.

Table 5.9: GHG emissions comparison for different ethanol fuel sources to gasoline from crude oil. Gasoline GHG emissions from Elsayed et al.[3], per MJ of fuel produced

	GHG emissions (kg CO_2 eq./MJ)	GHG emissions change (%)
Gasoline	8.0×10^{-2}	-
Sweet sorghum (decentralized)	3.7×10^{-2}	-54
Sweet sorghum (semi centralized)	4.6×10^{-2}	-43
Sweet sorghum (centralized)	9.7×10^{-2}	+21
Redcedar ethanol	2.0×10^{-1}	+150
Corn ethanol	6.0×10^{-2}	-25

Table 5.10: Non-renewable energy use comparison for different ethanol fuel sources to gasoline from crude oil. Gasoline non-renewable energy use from Elsayed et al., per MJ of fuel produced

	Non-renewable energy use (MJ/MJ fuel)	Non-renewable energy use reduction (%)
Gasoline	1.2	
Sweet sorghum (decentralized)	0.7	-42
Sweet sorghum (semi centralized)	0.8	-33
Sweet sorghum (centralized)	1.3	+8
Redcedar	1.9	+58
Corn ethanol	0.9	-25

5.2. Future work

- A sensitivity analysis should be performed comparing system boundary expansion to different allocation methods (mass, economic value, energy content)
- A cradle to grave analysis should be performed for sweet sorghum ethanol production and redcedar ethanol production, comparisons should be made to different transportation options like: E10, E85, E100, gasoline, and compressed natural gas (CNG) vehicles
- Different co-products use should be explored and their environmental benefits evaluated
- Perform techno economic studies on different ethanol production processes and configurations

5.3. References

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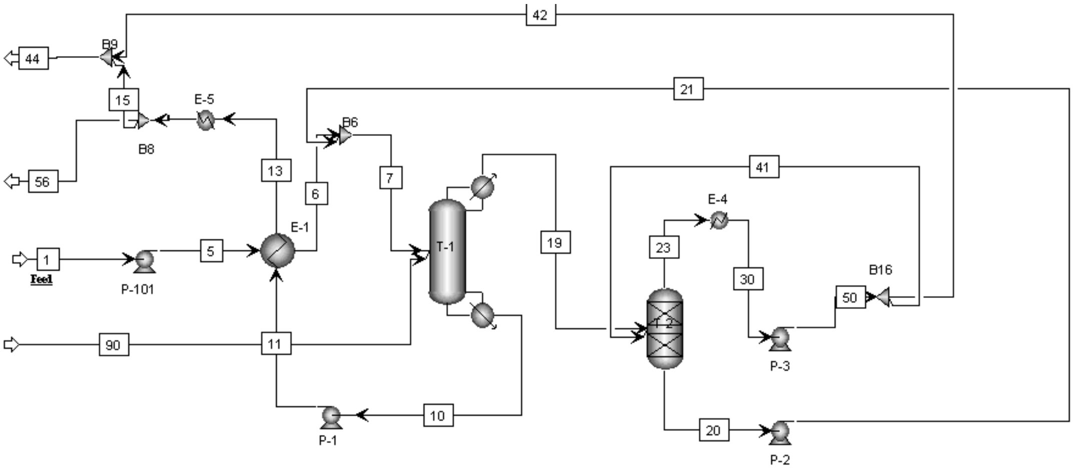
APPENDICES

Process simulation work

Production of ethanol from sweet sorghum



Property method: NRTL

Model summary

HeatX	
Name	**E-1**
Hot side property method	NRTL
Hot side Henry's component list ID	
Hot side electrolyte chemistry ID	
Hot side use true species approach for electrolytes	YES
Hot side free-water phase properties method	STEAM-TA
Hot side water solubility method	3
Cold side property method	NRTL
Cold side Henry's component list ID	
Cold side electrolyte chemistry ID	
Cold side use true species approach for electrolytes	YES
Cold side free-water phase properties method	STEAM-TA
Cold side water solubility method	3
Exchanger specification	
Units of exchanger specification	F
Exchanger area [sqft]	21.5
Constant UA [Btu/hr-R]	
Minimum temperature approach [F]	1.8

Hot side outlet pressure [psia]	50
Cold side outlet pressure [psia]	0
EO Model components	
Hot side EO Model components	
Cold side EO Model components	
Inlet hot stream temperature [F]	226.4
Inlet hot stream pressure [psia]	45
Inlet hot stream vapor fraction	0
Outlet hot stream temperature [F]	165.8
Outlet hot stream pressure [psia]	50
Outlet hot stream vapor fraction	0
Inlet cold stream temperature [F]	80.1
Inlet cold stream pressure [psia]	50
Inlet cold stream vapor fraction	0
Outlet cold stream temperature [F]	152.9
Outlet cold stream pressure [psia]	50
Outlet cold stream vapor fraction	0
Heat duty [Btu/hr]	148031.7
Calculated heat duty [Btu/hr]	148031.7
Required exchanger area [sqft]	21.4
Actual exchanger area [sqft]	21.5
Average U (Dirty) [Btu/hr-sqft-R]	100
Average U (Clean)	
UA [Btu/hr-R]	2142.9
LMTD (Corrected) [F]	69.1
LMTD correction factor	0.9
Thermal effectiveness	
Number of transfer units	
Number of shells in series	1
Number of shells in parallel	
Total feed stream CO2e flow [lb/hr]	0
Total product stream CO2e flow [lb/hr]	0
Net stream CO2e production [lb/hr]	0
Utility CO2e production [lb/hr]	0
Total CO2e production [lb/hr]	0
Utility usage	
Utility cost	
Hot utility ID	
Cold utility ID	

Pump

Name	**P-1**	**P-2**	**P-3**	**P-101**
Property method	NRTL	NRTL	NRTL	NRTL
Henry's component list ID				
Electrolyte chemistry ID				
Use true species approach for electrolytes	YES	YES	YES	YES
Free-water phase properties method	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA
Water solubility method	3	3	3	3
Model Type				
Specified discharge pressure [psia]	45	45	45	50
Specified pressure increase [psi]				
Specified pressure ratio				
Specified power required [hp]				
Pump efficiencies	1	1	1	1
Driver efficiencies				
Suction area [sqft]				
Hydraulic static head [ft-lbf/lb]				
Number of curves				
Operating shaft speed [rpm]				
Impeller diameter [ft]				
EO Model components				
Fluid power [hp]	7.4E-02	6.2E-03	1.7E-02	8.6E-02
Calculated brake power [hp]	7.4E-02	6.2E-03	1.7E-02	8.6E-02
Electricity [kW]	5.5E-02	4.6E-03	1.3E-02	6.4E-02
Volumetric flow rate [cuft/hr]	40.3	3.2	8.9	33.6
Calculated discharge pressure [psia]	45	45	45	50
Calculated pressure change [psi]	25.3	26.7	27.1	35.3
Calculated pressure ratio				
NPSH available [ft-lbf/lb]	0	0	33.1	33.1
NPSH required				
Head developed [ft-lbf/lb]	64.1	71.7	81.3	82.9
Pump efficiency used	1	1	1	1
Net work required [hp]	0.1	0.0	0.0	0.1
Specific speed, operating				
Suction sp. speed, operating				
Head coefficient				
Flow coefficient				
Total feed stream CO2e flow [lb/hr]	0	0	0	0
Total product stream CO2e flow [lb/hr]	0	0	0	0
Net stream CO2e production [lb/hr]	0	0	0	0
Utility CO2e production [lb/hr]	0	0	0	0
Total CO2e production [lb/hr]	0	0	0	0

Utility usage
Utility cost
Utility ID

RadFrac

Name	T-1	T-2
Property method	NRTL	NRTL
Henry's component list ID		
Electrolyte chemistry ID		
Use true species approach for electrolytes	YES	YES
Free-water phase properties method	STEAM-TA	STEAM-TA
Water solubility method	3	3
Number of stages	13	13
Condenser	NONE	NONE
Reboiler	NONE	NONE
Number of phases	2	2
Free-water	NO	NO
Top stage pressure [psia]	18.3	18
Specified reflux ratio		
Specified bottoms rate [lbmol/hr]		
Specified boilup rate [lbmol/hr]		
Specified distillate rate [lbmol/hr]		
EO Model components		
Calculated molar reflux ratio	11.9	0.8
Calculated bottoms rate [lbmol/hr]	125.9	7.9
Calculated boilup rate [lbmol/hr]	19.4	10.6
Calculated distillate rate [lbmol/hr]	10.4	10.3
Condenser / top stage temperature [F]	206.6	182.2
Condenser / top stage pressure [psia]	18.3	18
Condenser / top stage heat duty [Btu/hr]	0	0
Condenser / top stage subcooled duty		
Condenser / top stage reflux rate [lbmol/hr]	124.5	8.3
Condenser / top stage free water reflux ratio		
Reboiler pressure [psia]	19.7	18.3
Reboiler temperature [F]	226.3	194.7
Reboiler heat duty [Btu/hr]	0	0
Total feed stream CO2e flow [lb/hr]	0	0
Total product stream CO2e flow [lb/hr]	0	0
Net stream CO2e production [lb/hr]	0	0
Utility CO2e production [lb/hr]	0	0
Total CO2e production [lb/hr]	0	0

Condenser utility usage		
Condenser utility cost		
Condenser utility ID		
Reboiler utility usage		
Reboiler utility cost		
Reboiler utility ID		
Basis for specified distillate to feed ratio	MOLE	MOLE
Specified distillate to feed ratio		
Basis for specified bottoms to feed ratio	MOLE	MOLE
Specified bottoms to feed ratio		
Basis for specified boilup ratio	MOLE	MOLE
Specified boilup ratio		
Calculated molar boilup ratio		
Calculated mass boilup ratio	0.2	2.0

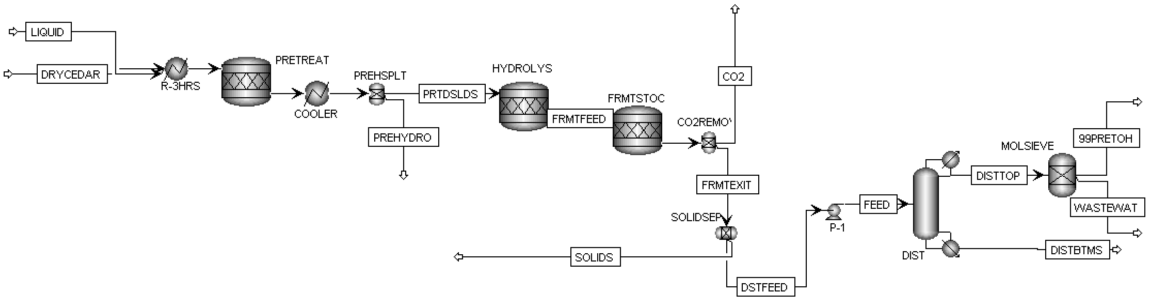
Mixer

Name	**B6**	**B9**
Property method	NRTL	NRTL
Henry's component list ID		
Electrolyte chemistry ID		
Use true species approach for electrolytes	YES	YES
Free-water phase properties method	STEAM-TA	STEAM-TA
Water solubility method	3	3
Specified pressure [psia]	0	0
Temperature estimate [F]	160	125
EO Model components		
Outlet temperature [F]	156.1	131.6
Calculated outlet pressure [psia]	45	45
Vapor fraction	0	0
First liquid /Total liquid	1	1
Total feed stream CO2e flow [lb/hr]	0	0
Total product stream CO2e flow [lb/hr]	0	0
Net stream CO2e production [lb/hr]	0	0

Name	**B8**	**B16**
Property method	NRTL	NRTL
Henry's component list ID		
Electrolyte chemistry ID		
Use true species approach for electrolytes	YES	YES
Free-water phase properties method	STEAM-	STEAM-TA

	TA	
Water solubility method	3	3
First outlet stream		
First specified split fraction		
First calculated split fraction	0.15	0.25
First actual volume flow [cuft/hr]		
First limit flow [lbmol/hr]		
First volume limit flow [cuft/hr]		
First cum limit flow [lbmol/hr]		
First cum volume limit flow [cuft/hr]		
First residual fraction		
Second outlet stream	0.85	0.75
Second specified split fraction	0.85	0.75
EO Model components		
Second calculated split fraction	0.85	0.75
Second actual volume flow [cuft/hr]		
Second limit flow [lbmol/hr]		
Second volume limit flow [cuft/hr]		
Second cum limit flow [lbmol/hr]		
Second cum volume limit flow [cuft/hr]		
Second residual fraction		
Total feed stream CO2e flow [lb/hr]	0	0
Total product stream CO2e flow [lb/hr]	0	0
Net stream CO2e production [lb/hr]	0	0

Production of ethanol from redcedar



Property method: NRTL

Model summary

Heater		
Name	**COOLER**	**R-3HRS**

Property method	NRTL	NRTL
Henry's component list ID	HC-1	HC-1
Electrolyte chemistry ID		
Use true species approach for electrolytes	YES	YES
Free-water phase properties method	STEAM-TA	STEAM-TA
Water solubility method	3	3
Specified pressure [atm]	5	1
Specified temperature [C]	55	90
Specified vapor fraction		
Specified heat duty [cal/sec]		
EO Model components		
Calculated pressure [bar]	5.06625	1.01325
Calculated temperature [C]	55	90
Calculated vapor fraction	0	0
Calculated heat duty [cal/sec]	-843115.181	90465.9823
Temperature change [C]		
Degrees of superheating [C]		
Degrees of subcooling [C]		
Pressure-drop correlation parameter		
Net duty [cal/sec]	-843115.181	90465.9823
First liquid / total liquid	1	1
Total feed stream CO2e flow [kg/hr]	0	0
Total product stream CO2e flow [kg/hr]	0	0
Net stream CO2e production [kg/hr]	0	0
Utility CO2e production [kg/hr]	0	0
Total CO2e production [kg/hr]	0	0
Utility usage		
Utility cost		
Utility ID		

	Sep			
Name	**CO2REMOV**	**MOLSIEVE**	**PREHSPLT**	**SOLIDSEP**
Property method	NRTL	NRTL	NRTL	NRTL
Henry's component list ID	HC-1	HC-1	HC-1	HC-1
Electrolyte chemistry ID				
Use true species approach for electrolytes	YES	YES	YES	YES
Free-water phase properties method	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA
Water solubility method	3	3	3	3
Inlet flash pressure [bar]	0	0	0	0

First outlet flash temperature				
First outlet flash pressure				
First outlet flash temperature change				
First outlet flash vapor fraction				
First outlet flash temperature estimate				
First outlet flash pressure estimate				
Second outlet flash temperature				
Second outlet flash pressure				
Second outlet flash temperature change				
Second outlet flash vapor fraction				
Second outlet flash temperature estimate				
Second outlet flash pressure estimate				
EO Model components				
Heat duty [cal/sec]	-5415.0871	-15.734724	8.8977E-10	1.1122E-10
Total feed stream CO2e flow [kg/hr]	131.845997	0	0	0
Total product stream CO2e flow [kg/hr]	131.845997	0	0	0
Net stream CO2e production [kg/hr]	0	0	0	0
Utility CO2e production [kg/hr]	0	0	0	0
Total CO2e production [kg/hr]	0	0	0	0
Utility usage				
Utility cost				
Utility ID				

Pump

Name	**P-1**
Property method	NRTL
Henry's component list ID	HC-1
Electrolyte chemistry ID	
Use true species approach for electrolytes	YES
Free-water phase properties method	STEAM-TA
Water solubility method	3
Model Type	
Specified discharge pressure [atm]	3
Specified pressure increase [bar]	
Specified pressure ratio	
Specified power required [kW]	
Pump efficiencies	
Driver efficiencies	
Suction area [sqm]	
Hydraulic static head [m-kgf/kg]	
Number of curves	

Operating shaft speed [rpm]	
Impeller diameter [meter]	
EO Model components	
Fluid power [kW]	0.02283569
Calculated brake power [kW]	0.07723695
Electricity [kW]	0.07723695
Volumetric flow rate [l/min]	6.76112308
Calculated discharge pressure [bar]	3.03975
Calculated pressure change [bar]	2.0265
Calculated pressure ratio	
NPSH available [m-kgf/kg]	6.28075158
NPSH required	
Head developed [m-kgf/kg]	21.5861142
Pump efficiency used	0.29565764
Net work required [kW]	0.07723695
Specific speed, operating	
Suction sp. speed, operating	
Head coefficient	
Flow coefficient	
Total feed stream CO2e flow [kg/hr]	0
Total product stream CO2e flow [kg/hr]	0
Net stream CO2e production [kg/hr]	0
Utility CO2e production [kg/hr]	0
Total CO2e production [kg/hr]	0
Utility usage	
Utility cost	
Utility ID	

DSTWU

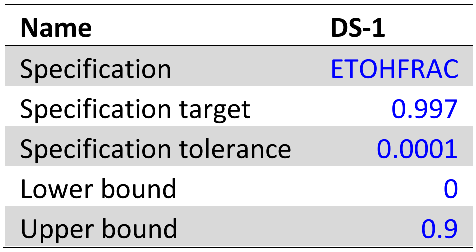
Name	**DIST**
Property method	NRTL
Henry's component list ID	HC-1
Electrolyte chemistry ID	
Use true species approach for electrolytes	YES
Free-water phase properties method	STEAM-TA
Water solubility method	3
Number of stages	
Reflux ratio	-2
Light key component recovery	0.85
Heavy key component recovery	0.05
Distillate vapor fraction	0

Minimum reflux ratio	1.32153229
Actual reflux ratio	2.64306457
Minimum number of stages	23.1993964
Number of actual stage	33.2322306
Feed stage	33.570987
Number of actual stage above feed	32.570987
Distillate temperature [C]	96.8364484
Distillate to feed fraction [C]	115.721837
Total feed stream CO2e flow [kg/hr]	0
Total product stream CO2e flow [kg/hr]	0
Net stream CO2e production [kg/hr]	0

RStoic

Name	**FRMTSTOC**	**HYDROLYS**	**PRETREAT**
Property method	NRTL	NRTL	NRTL
Henry's component list ID	HC-1	HC-1	HC-1
Electrolyte chemistry ID			
Use true species approach for electrolytes	YES	YES	YES
Free-water phase properties method	STEAM-TA	STEAM-TA	STEAM-TA
Water solubility method	3	3	3
Specified pressure [atm]	1	0.986923267	5
Specified temperature [C]		50	200
Specified vapor fraction			
Specified heat duty [cal/sec]	0		
EO Model components			
Outlet temperature [C]	62.7428673	50	200
Outlet pressure [bar]	1.01325	1	5.06625
Calculated heat duty [cal/sec]	0	-112836.269	779245.89
Net heat duty [cal/sec]	0	-112836.269	779245.89
Calculated vapor fraction	0.278422427	0	0.987188673
First liquid / total liquid	1	1	1
Total feed stream CO2e flow [kg/hr]	0	0	0
Total product stream CO2e flow [kg/hr]	131.845997	0	0
Net stream CO2e production [kg/hr]	131.845997	0	0
Utility CO2e production [kg/hr]	0	0	0
Total CO2e production [kg/hr]	131.845997	0	0
Utility usage			
Utility cost			
Utility ID			

Design Specs



Name	DS-1
Specification	ETOHFRAC
Specification target	0.997
Specification tolerance	0.0001
Lower bound	0
Upper bound	0.9

CASE STUDY: LIFE CYCLE ASSESSMENT STUDY OF PROCESS CONFIGURATION FOR MANUFACTURE OF POLYMER GRADE LACTIC ACID

Life Cycle Assessment Study of Process Configurations for Manufacture of Polymer Grade Lactic Acid

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Abstract

This work is based on the polymer grade lactic acid process developed in [1]**.** It is an extension of the work described in the previous paper. Based on economic studies carried out in Aspen Process Economic Analyser, two process configurations have been devised. The first configuration is the one described in the paper. The second configuration is similar to the first one except for a distillation column in the methanol recycle stream. This therefore becomes a classic case of a trade-off between purity and cost. The first configuration yields high methyl lactate purity as compared to the second configuration. However, the high purity comes at a higher cost. In this paper a Life Cycle Assessment (LCA) study has been performed on the two configurations to further investigate the pros and cons of the two process configurations. The LCA study has been carried out in SimaPro v8.0.0 and the Impact 2002+ LCA methodology has been adopted. 1 kg of pure lactic acid product is the functional unit on which the study is based. Although this paper utilizes the economic analysis results for the two configurations, its main focus is on the Life Cycle Assessment study.

Keywords: Lactic acid, Sustainability, Life cycle assessment, SimaPro, Impact 2002+

Introduction

Lactic acid is a weak organic acid with a hydroxyl group next to a carboxylic group. Traditionally, lactic acid with ~85% purity has been used extensively in the food industry. A comprehensive summary about the properties and applications of lactic acid has been provided in [1]. More recently however, highly pure lactic acid has been getting prominence for its use in the polymer industry as a precursor for poly lactic acid. [2] provides details about poly lactic acid manufacture methods, properties and uses. Poly lactic acid is getting more popularity by the day primarily because of its versatile applications. Additionally, poly lactic acid being biodegradable, not only provides substantial environmental benefits but also offers economical profits with environmental tax saving. Moreover, the raw material used for lactic acid production in the process comes from renewable sources like bagasse, corn or starch via fermentation. Hence, the scarce non-renewable fuel resources aren't depleted further and the carbon footprint does not increase significantly.

Process Description

The lactic acid process under consideration is the one described in [3] and further developed in [1]. As the process has already been described in detail in the aforementioned references, we will provide only a short description here. The process can be roughly divided into three stages.

Stage 1: The process starts with the reaction of calcium lactate, obtained as a fermentation product, and sulphuric acid to give calcium sulphate crystals and liquid lactic acid which are passed through a series of physical separators (centrifugal separator, falling film evaporator and filter) to yield 60% pure lactic acid (wt. % on dry basis).

Predominant Reaction: Calcium Lactate + Sulphuric Acid → Lactic Acid + Calcium Sulphate

Stage 2: The crude lactic acid obtained from stage 1 is then passed through a bubble column reactor where it reacts with the rising methanol vapours which are sparged through the bottom of the reactor. This esterification reaction yields methyl lactate and water. The bubble column reactor is actually a counter current reactive distillation column in which the aforementioned reaction takes place in the reaction section and the unreacted methanol vapours along with water vapours rise through to the distillation section where they are separated. Crude liquid methyl lactate trickles to the bottom of the bubble column and is collected for further processing. The crude methyl lactate is then treated through a separator column and a filter to yield 98.5 % (wt. % on dry basis) pure methyl lactate. Stage 2 is the pivotal phase of the process since the methyl lactate purity decides the final lactic acid purity.

Predominant Reaction: Lactic Acid + Methanol →Methyl Lactate + Water

Stage 3: The isolated methyl lactate is then hydrolysed through a hydrolysis reactor to yield highly pure polymer grade lactic acid (99 wt. % on dry basis). This is a de-esterification reaction which yields lactic acid and methanol. The methanol vapours formed are then recycled back to the bubble column inlet. The ingenuity of the process lies in the fact that pure lactic acid is used an auto catalyst resulting in no extra impurities due to the catalyst.

<u>Predominant Reaction: Methyl Lactate + Water → Lactic Acid + Methanol</u>

Since stage 2 and stage 3 are the two key phases of the overall process, a process simulation was carried out for these two stages only.

Process Configurations

A sustainable process was developed based on the aforesaid process as described in [1]. The process simulation was carried out in Aspen Plus v8.2. Figure 1 shows the Process Flow Diagram developed in Aspen Plus (Configuration 1). Several other process configurations were examined to find the best option which yields the maximum product purity with minimal cost. The cost analysis was performed using Aspen Process Economic Analyser (APEA).

While evaluating various process configurations, two configurations came forward as the best probable options. A more detailed analysis was therefore carried out on these two configurations to evaluate their advantages and shortcomings. Configurations 1 has been shown in Figure 1 and configuration 2 is depicted in Figure 2. It can be seen from the two figures that there is only a minor difference in the two configurations. Configuration 2 is devoid of the separator column which purifies the methanol before it is recycled back to the feed. The separator in configuration 1 separates the methanol from water and other impurities and therefore increases the purity of methyl lactate produced in the bubble column reactor. However, the separator comes at a price and therefore it is a case of trade-off between quality and economy as is the case with most industrial settings. Table 1 provides a brief economic analysis of the two configurations. Please note that the only difference between the two configurations is the separator column discussed and therefore all the changes in the cost are a direct result of including/excluding the separator column.

Table 1: Economic analysis results for the two configurations

Configuration	Total Project Capital Cost (USD)	Total Operating Cost (USD per year)	Total Raw Materials Cost (USD per year)	Total Utilities Cost (USD per year)	Total Product Sales (USD per year)	Payback Period (Years)
Configuration 1	5,753,800	1,918,520	246,500	41,659	4,743,180	**6.28**
Configuration 2	4,689,640	1,913,990	246,500	40,422	4,723,020	**4.59**

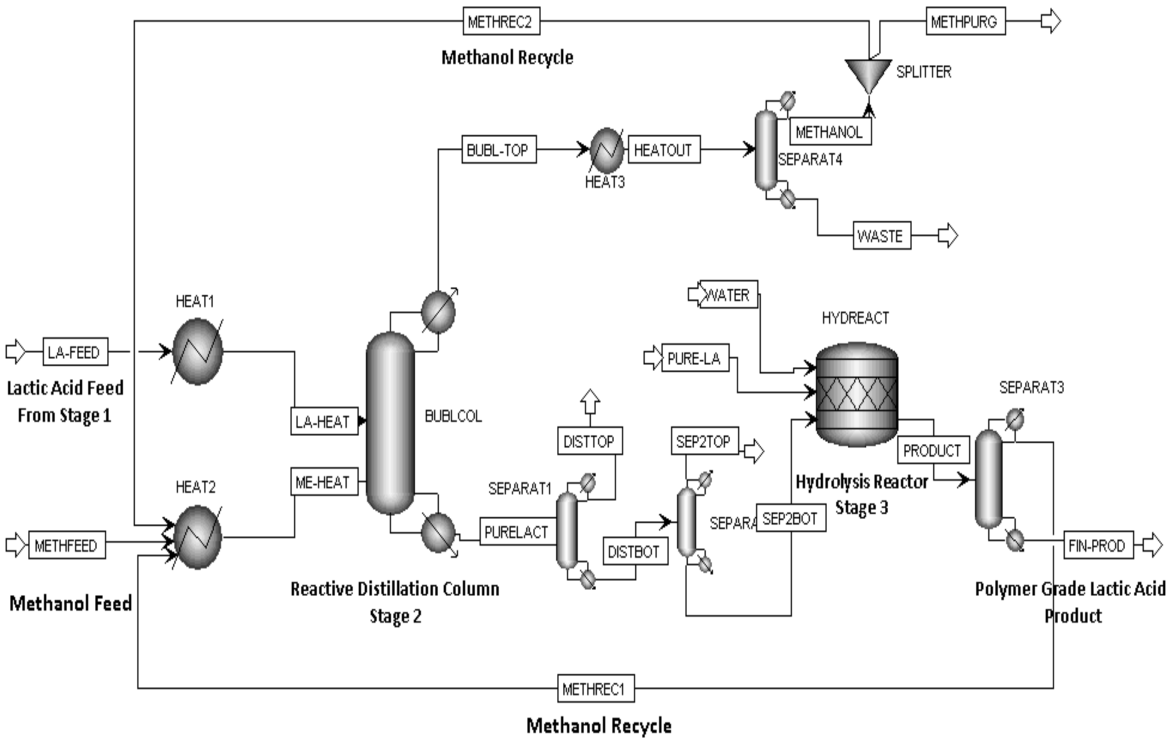

Figure 28: Configuration 1 which includes the separator column (Separat4) for methanol purification before recycle

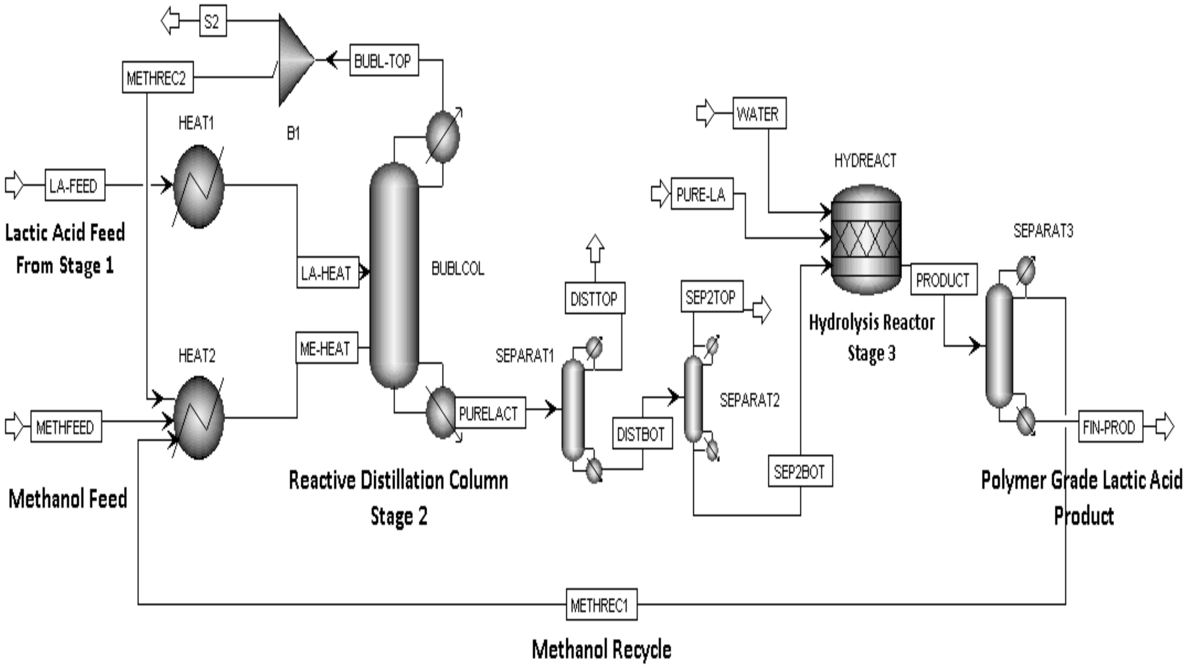

Figure 29: Configuration 2 which excludes the methanol separator column

Background about LCA

Life Cycle Assessment can be defined as a technique used to assess the environmental impacts of a process or a product which can be attributed to the life cycle of the product or process. [4] The impact categories generally used are ozone layer depletion, global warming, aquatic acidification, eutrophication, stress on human health and ecosystems, depletion of natural resources like land and water. [5] defines LCA as “a methodology or technique for identifying, measuring, and evaluating all the energy and material flows that result from making, using, and disposing of a target product or material”. LCA came to the fore in the 1970s when it transitioned from a mere energy analysis to a more inclusive environmental burden analysis. [6]. It developed further in the 1980s and 1990s with the inclusion of environmental costing, making it a more pragmatic option for overall environmental analysis. However, it wasn’t until the 21st century, when the social feature was incorporated, that it got a comprehensive outlook and industries started using it for decision making. Subsequently, environmental policies and standards have now started to become life-cycle based. In USA, the Environmental Protection Agency (EPA) started to promote LCA and various LCA networks have now been established. [6]

[5] discusses the following possible motivating factors for conducting a LCA on a product or process in an industrial setting:

1) The ecosystem is being adversely affected by human activities leading to polluting the environment and this damage could be controlled if the LCA reveals any specific source of pollution.
2) Earth's resources, especially non-renewable fuels and water have been declining at an alarming rate due to overuse and the same could be used more efficiently.
3) A process is being operating at less than optimal conditions leading to higher environmental costs coupled with a less flattering public image

Materials and Methods

As mentioned earlier this study focusses on a comparative study of two process configurations to produce polymer grade lactic acid. As both process configurations produce the same end product, we have concentrated our efforts on the gate to gate stage of the process. LCA results for the cradle to gate and the gate to grave stages for both the configurations will be identical and therefore wouldn't affect the decision making. Impact 2002+ is the LCA methodology that has been used for this study.

[7] describes the Impact 2002+ methodology as follows: "*The new IMPACT 2002+ life cycle impact assessment methodology proposes a feasible implementation of a combined midpoint/ damage approach, linking all types of life cycle inventory results (elementary flows and other interventions) via 14 midpoint categories to four damage categories.*"

There are four basic steps adopted in any LCA study:

1) Goal and Scope Definition
2) Inventory Analysis
3) Life Cycle Impact Assessment
4) Interpretation

Goal and scope definition

The goal of an LCA study states its intended purpose, the intended application, the reason for the study, the audience and how the results will be used. The scope includes the products under investigation, its function, allocation procedures, impact categories, impact assessment methodologies, assumptions, functional unit and system boundary[8, 9]. Since an LCA is in iterative process, as more data is collected, the goal and scope can be revised during the LCA process but setting a goal and scope at the beginning of the analysis is crucial. The functional unit for any LCA must be explicitly stated and should be related to the function of the final product. It is what all inputs and outputs are related to and when a comparative LCA is performed, both systems should have the same functional unit [10].

The selection of a system boundary is one of the most important aspects of an LCA; different system boundaries for the same process can result in different outcomes and conclusions. The system boundary includes unit processes that will be part of the analysis and as the LCA is conducted, the system boundary may need to be refined. As the system boundary is being developed, different parts of the life cycle need to be taken into consideration: raw material acquisition, transportation and distribution, usage and maintenance of products, waste disposal, reuse and recycling of products, manufacturing of equipment, and inputs and outputs into the main process [8].

The goal of this LCA is to quantify the environmental impacts in the global warming impact, non-renewable energy use, and respiratory inorganics impact categories of the production of polymer grade lactic acid at a 50,000kg/year capacity facility with a ten year lifespan. A comparison between two process configuration, an optimized and a non-optimized one is conducted. The analysis will be performed in SimaPro 8.0.0 using the Impact 2002+ impact assessment method. This LCA is a cradle-to-gate LCA; it takes into consideration all impacts from the production of raw material to the development of the final product. All unit processes present in the simulation are included in the system boundary and so are impacts from raw material production and transportation to the facility. Impacts from construction of the facility is not included in the analysis, it is assumed to be negligible when spread out over the lifespan of the process.

Inventory analysis

The inventory analysis step of an LCA involves collection of input and output data for the unit processes that are included within the system boundary. Just like the goal and scope definition, as the LCA is performed, more is known about the process or if there are changes to the system boundary, there might be new data requirements or changes to the goal and scope based to the collected data. Data required include: energy and raw material inputs, products, co-products, waste, emissions, and other environmental factors

[8].The data collection also includes relating each input and output to the functional unit and reference flow, validation, and allocation of impacts when co-products are present.

Life cycle impact assessment (LCIA)

This step involves taken data collected from the inventory analysis and quantifying the environmental impacts for the chosen impact categories. Doing this allows the LCA practitioner to understand the environmental impacts. Impact categories for Impact 2002+ include: carcinogens, non-carcinogens, respiratory inorganics, ionizing radiation, ozone layer depletion, respiratory organics, aquatic eco toxicity, terrestrial eco toxicity, terrestrial acidification/nitrification, land occupation, aquatic acidification, aquatic eutrophication, global warming, non-renewable energy use, and mineral extraction [7].

Interpretation

Using results from the inventory analysis, and impact assessment the LCA practitioner draws conclusions that are consistent with what is laid out in the goal and scope definition in the interpretation step. Also called improvement assessment, this step requires critical evaluation of the LCA **[11].** Conclusions and recommendations are made based on the findings. Just like the previous steps, this is in iterative process and ISO 14040 states that “The interpretation should reflect the fact that the LCIA results are based on a relative approach, that they indicate potential environmental effects, and that they do no predict actual impacts on category endpoints” **[8]**. A visual representation of how the four categories on a LCA related and some direct application of LCAs can be seen in Figure **30**.

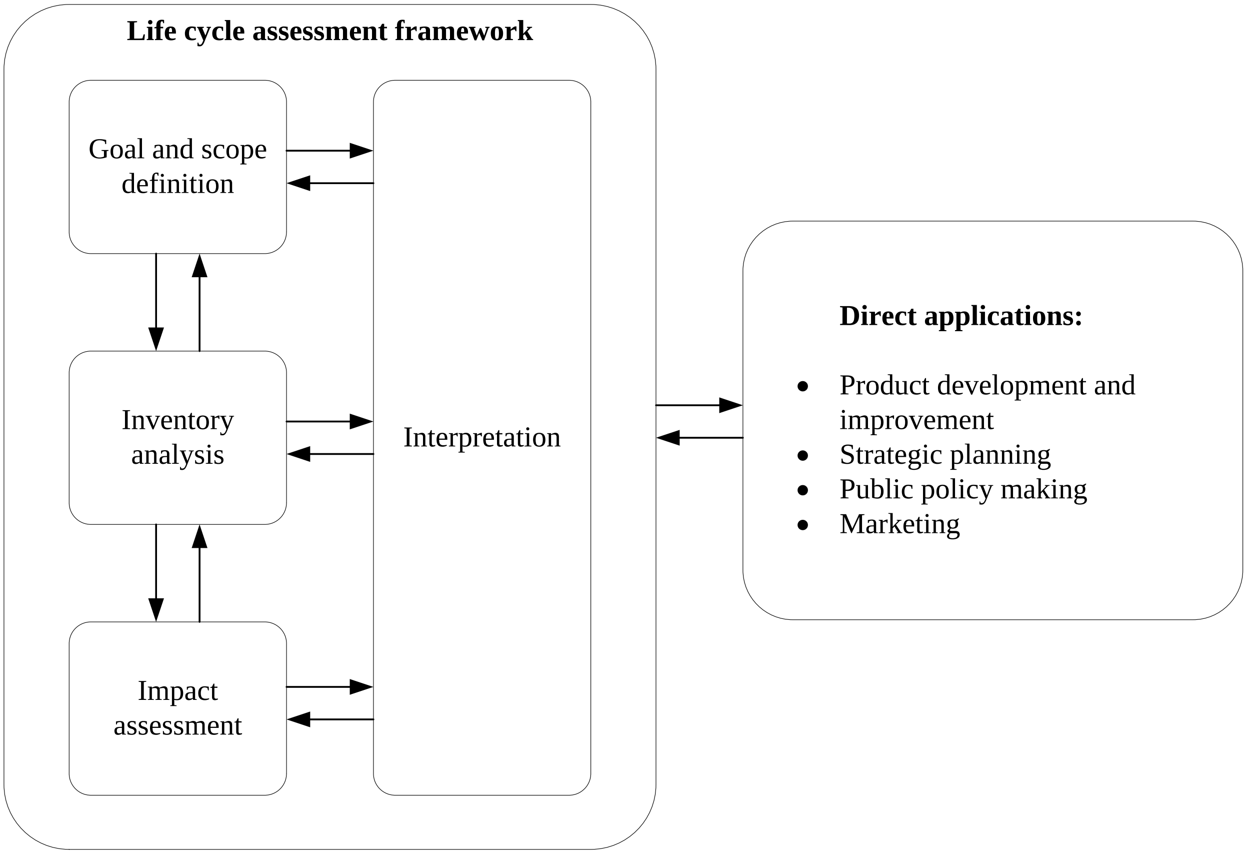

Figure 30: Life cycle assessment framework, adapted from ISO 14040

Results and Discussion

LCA results generated in SimaPro and are shown in Table 2, and it can be seen that Configuration 1 with Separator 4 has lower environmental impacts for each impact category than Configuration 2 without Separator 4. The results are presented in per kg of polymer grade lactic acid produced in the facility.

Table 2: Life cycle impact assessment results, per kg of polymer grade lactic acid produced

Impact category	**Configuration 1**	**Configuration 2**	**Unit**
Respiratory inorganics	4.2×10^{-2}	6.6×10^{-2}	kg of particulate matter

Global warming	116.3	181.8	kg CO_2 equivalent
Non-renewable energy	2132.6	3318.1	MJ

Respiratory Inorganics

This impact category deals with human health impacts from inorganic particulate matter release into the air. The reference unit is particulate matter than is 2.5 microns or less, this can include dust, sulphur and nitrogen oxides

Table 3: Unit process contribution to respiratory inorganics impact category, per kg of polymer grade lactic acid produced, units of kg of particulate matter

Unit process	Configuration 1	Configuration 2
Methanol	$2.5x10^{-4}$	$2.5x10^{-4}$
Process water	$2.1x10^{-7}$	$2.1x10^{-7}$
Lactic acid	$9.1x10^{-6}$	$9.1x10^{-6}$
Heater 1	$2.2x10^{-4}$	$2.2x10^{-4}$
Heater 2	$2.3x10^{-3}$	$2.3x10^{-3}$
Heater 3	$2.8x10^{-4}$	_
Bubble column	$2.3x10^{-2}$	$5.3x10^{-2}$
Separator 1	$1.2x10^{-3}$	$4.9x10^{-3}$
Separator 3	$5.2x10^{-3}$	$5.1x10^{-3}$
Separator 4	$1.0x10^{-2}$	_
Waste water treatment	$6.7x10^{-5}$	$3.0x10^{-5}$

Table 33 breaks down each unit process contribution to the impacts for the respiratory inorganics category. When both configurations are compared the Bubble Column Reactor, Separator 1 both see an increase in impacts in Configuration 2 where Separator 4 and Heater 3 are removed. Waste water treatment is the only unit process that sees a decrease in Configuration 2. Figure 284 shows the relative contribution of each unit process in both the Configuration 1 and Configuration 2. In both configurations, the Bubble Column Reactor accounts for a majority of impacts. In the Configuration 1 it accounts for 53% and in Configuration 2 it accounts for 81% of the impacts.

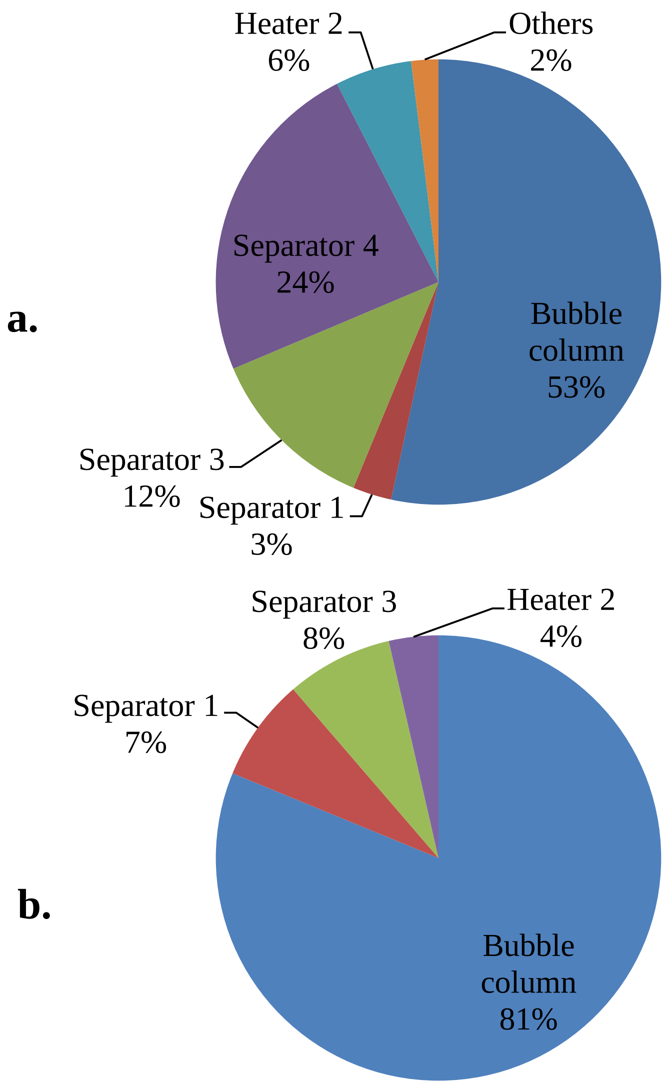

Figure 31: Breakdown of impact for respiratory inorganics impact category, a. non-optimized, b. optimized

Global Warming

The global warming impact category in the Impact 2002+ impact assessment method takes into account the potential global warming impacts of greenhouse gases (GHG) like methane (CH_4), carbon dioxide (CO_2), nitrous oxide (N_2O), hydrofluorocarbons and perfluorocarbons. The reference unit for this impact category is kg of CO_2 emitted during the life cycle of the process. Other greenhouse gases that are emitted have their global warming potential (GWP) used to convert their impacts to an equivalent CO_2 basis.

Table 4: Unit process contribution to global warming impact category, per kg of polymer grade lactic acid produced, units of kg of equivalent CO_2

Unit process	Configuration 1	Configuration 2
Methanol	0.9	0.9
Process water	$2.6x10^{-4}$	$2.6x10^{-4}$
Lactic acid	$1.0x10^{-2}$	$1.0x10^{-2}$
Heater 1	0.6	0.6
Heater 2	6.5	6.5
Heater 3	0.8	_
Bubble column	62.0	146.4
Separator 1	3.3	13.5
Separator 3	14.4	13.9
Separator 4	27.7	_
Waste water treatment	0.2	0.1

The unit process contribution for the global warming impact category in Table 4 shows a similar trend that is seen in the respiratory inorganics unit process contribution in Table 33 where Configuration 2 results in an increase in impacts from the Bubble Column Reactor and Separator 1. There is a decrease in equivalent CO_2 for Separator 3 and the waste water treatment. Figure **32**5 shows each unit process contribution as a percentage of impacts, once again, the Bubble Column take up the majority of impact for this category for both Configuration 1 and Configuration 2.

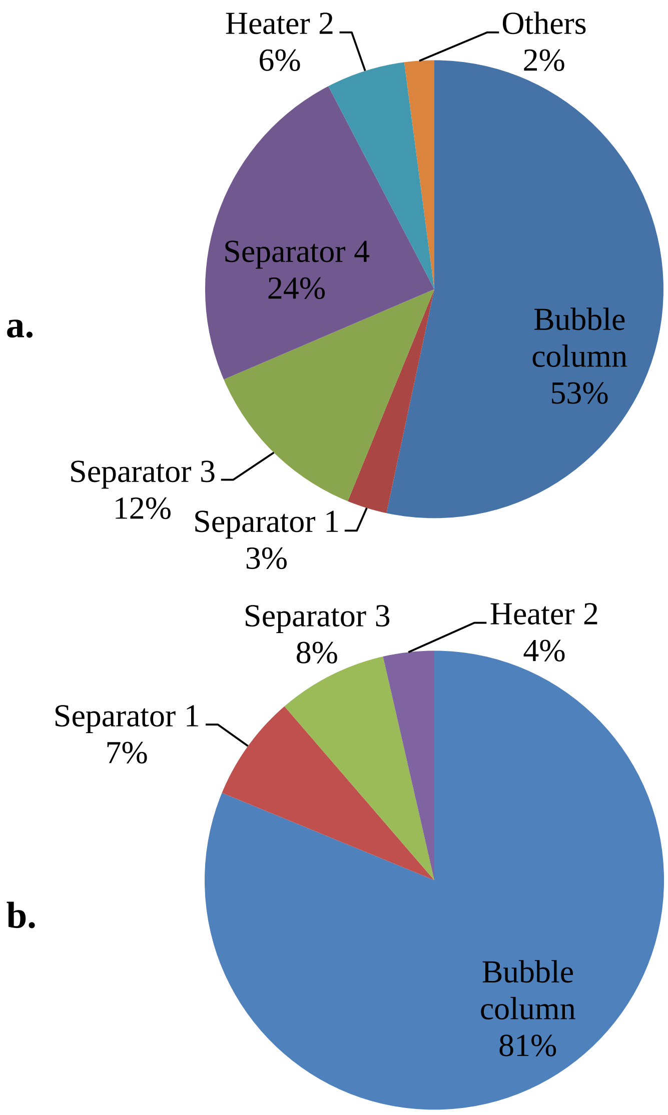

Figure 32: Breakdown of impact for global warming impact category, a. non-optimized, b. optimized

Non-renewable Energy Use

The non-renewable energy use category accounts for energy use from sources that can be depleted. These include crude oil, natural gas, coal, and uranium usage from the raw material acquisition stage to the final production of the polymer grade lactic acid. The reference unit for this impact category is MJ of energy from crude oil. Table 5 shows unit process contribution for this category and it exhibits trends that have already been observed in Table 3 and Table . Increase in contribution from the Bubble Column Reactor and Separator 1, and a decrease in contribution from Separator 2 and waste water treatment. In Figure **33**6 the percentage contributions are shown and the Bubble Column Reactor again is the largest contributor for both the Configuration 1 and Configuration 2 with an 80% contribution in Configuration 1 and a 53% contribution in Configuration 2.

Table 5: Unit process contribution to non-renewable energy use impact category, per kg of polymer grade lactic acid produced, units of MJ

Unit process	Configuration 1	Configuration 2
Methanol	49.2	49.2
Process water	$5.8x10^{-3}$	$5.8x10^{-3}$
Lactic acid	0.2	0.2
Heater 1	10.9	10.9
Heater 2	116.9	116.9
Heater 3	13.9	_
Bubble column	1121.3	2645.5
Separator 1	59.2	243.3
Separator 3	260.3	251.8
Separator 4	500.0	_
Waste water treatment	0.6	0.3

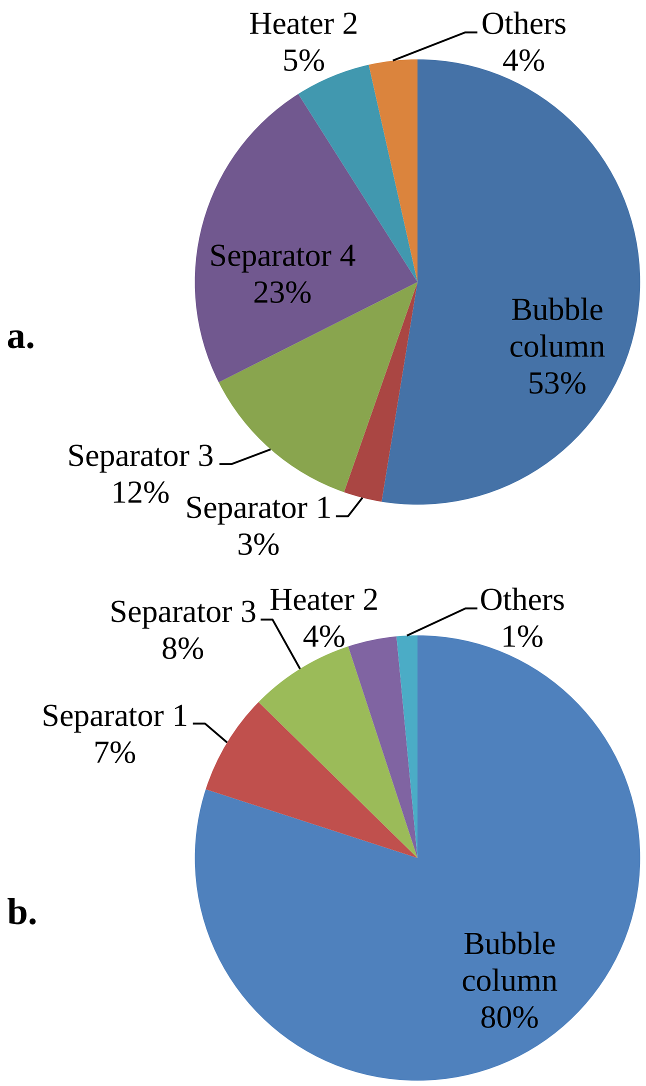

Figure 33: Breakdown of impact for non-renewable energy use impact category, a. non-optimized, b. optimized

Conclusion

The LCIA results have been able to highlight the stages of the process that have the largest contributions to the environmental impacts and the unit processes can be singled out for improvement. The bubble column is the largest contributor in each impact category that is investigated in this LCA. For Configuration 2, when the separator column in the recycle is removed, the bubble column unit process contribution for all three impact categories more than doubles. Another conclusion that can be drawn from the LCA is that the economic optimization of the process produces a configuration that is better from an economic standpoint but worse from an environmental standpoint.

Figure 7 gives a comparative summary of the two configurations for their environmental impact contribution towards each of the three categories. It can be noticed that Configuration 2 has ~40% higher impact in every category than Configuration 1. This result is attributable to the fact that since the methanol recycled back to the Bubble Column Reactor is of lesser purity, it leads to a higher steam requirement for the column. This increased steam requirement is the direct cause of the increased environmental impact. It can be noted that the steam requirement for the Bubble Column Reactor in Configuration 2 (3848.61 kg/day) is much higher than the combined steam requirement of the Bubble Column Reactor and Separator in Configuration 1 (2358.62 kg/day). Therefore, although Configuration 2 has higher profitability, it also has higher environmental impacts owing to higher fuel requirement.

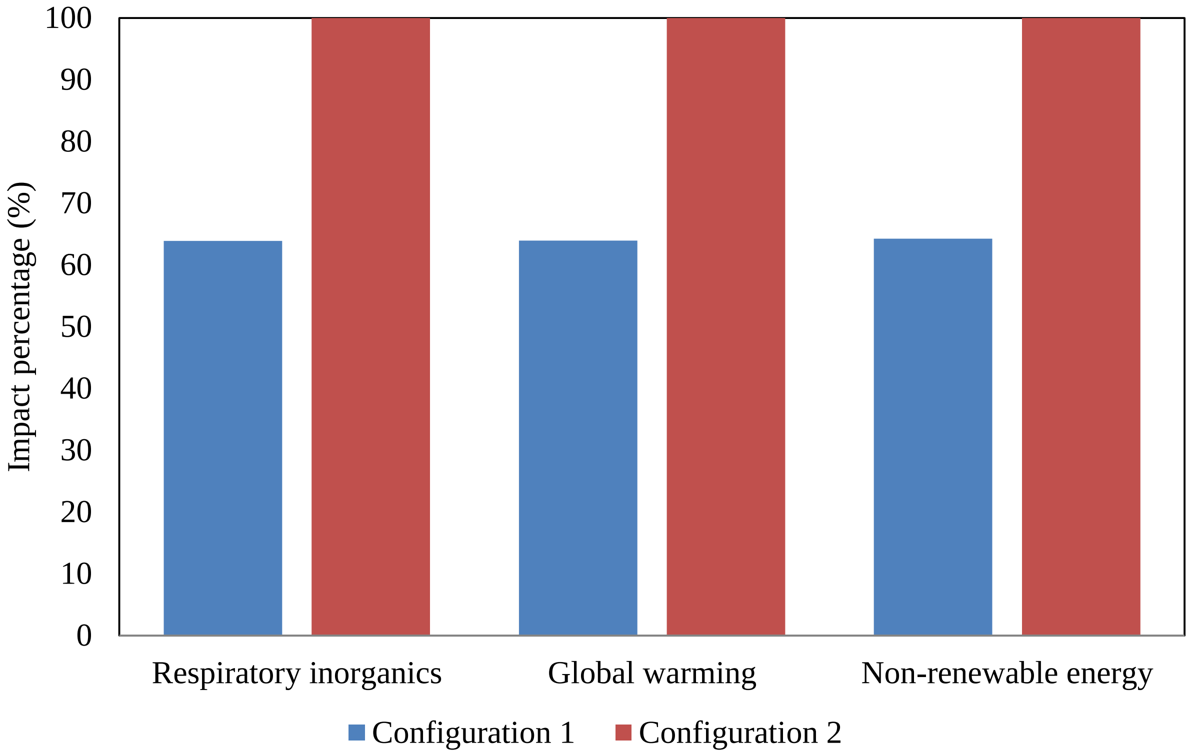

Figure 7: Comparison of Configuration 1 and Configuration 2 for each Impact Category

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Competing Interests

The authors declare no competing financial interest.

Author's Contributions

IO and SSB performed Life Cycle Assessment studies for the process presented in the paper. IO and SSB drafted the manuscript in collaboration with CPA. CPA provided consultation regarding the LCA analysis. KAH provided consultation regarding the LCA results. KAH reviewed the manuscript. All authors read and approved the final manuscript.

Acknowledgement

Associated Content

None

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