

# **Nitrogen Trifluoride and Furfural Supply Chains: Life Cycle Assessment and Techno-Economic Analysis**

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**Authorization to Submit Thesis**

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## Abstract

Nitrogen Trifluoride (NF<sub>3</sub>) is an inorganic compound widely used in the electronics industry for manufacturing various products, such as semiconductors, solar panels, and touch screens. However, NF<sub>3</sub> emissions that accumulate in the atmosphere have 17,200 times the global warming potentials of CO<sub>2</sub> over a 100-year time horizon. This study aims to provide economic and environmental impact assessments on the use of NF<sub>3</sub>. Additionally, a real case study for the Idaho semiconductor facility is used to assess the method and demonstrate the application of this study. The results show that slight reductions in abatement efficiency have dramatic impacts on mitigating greenhouse gas (GHG) emissions. The results also indicate that the cost of abatement is the primary driver of economic impact. It is also found that contaminants (e.g., SF<sub>6</sub> and CF<sub>4</sub>) within the cylinder potentially have more substantial GHG impacts than the actual NF<sub>3</sub>, owing in part to the relative ease with which NF<sub>3</sub> is destroyed through abatement. Furfural is an organic compound that is widely used in the chemical industry for manufacturing various products, such as pharmaceuticals, pesticides, and solvents. Furfural production from biomass feedstocks can be achieved through various conversion pathways (e.g., pyrolysis or hydrolysis). Sustainability assessments are conducted on a real case study in southern Idaho, to evaluate and verify the methodology and demonstrate the application of this study. The results show that the total cost for furfural production, using pyrolysis and hydrolysis, are approximately \$846 and \$980 per metric ton, and total emission is 267 and 1,095 kg CO<sub>2</sub> eq. per metric ton, respectively.

## **Acknowledgements**

I would like to thank the staff and faculty of the University of Idaho. I would especially like to thank Denise Engebrecht and Alice Allen for their assistance in navigating the graduation requirements of my program. My advisor, Dr. Amin Mirkouei, was instrumental in providing support and guidance for both researching and writing this thesis. I would also like to thank Dr. Amir Mohajeri for his assistance in writing. My involvement with both Drs. Mirkouei and Mohajeri was facilitated by my involvement with the Innovative Design and Manufacturing Laboratory (IDeaL) at University of Idaho. Finally, I should acknowledge Paula Smith, retired education coordinator at Micron Technology Inc., for her assistance in my educational endeavors.

### **Dedication**

I dedicate this work to my loving wife Courtney, and our young daughter Patricia. Thank you for being so understanding as I spent so much time working on this thesis, and my degree as a whole, to better both myself and our family.

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## **Statement of Contribution**

I, Matthew A. Thompson, claim primary responsibility and first author ownership of the work presented herein. The co-authors listed in the articles within this thesis provided some guidance during method development and analysis, as well as assistance editing prior to submission. The original draft was prepared by myself, Matthew A. Thompson, and initially edited by Dr. Amin Mirkouei, further review and editing was completed as a joint effort between Dr. Amin Mirkouei and Dr. Amir Mohajeri. As the primary author of each publication, I claim responsibility for the ideas and published data, that I produced to the best of my ability. Computer models for the techno-economic assessments presented in chapters 2 and 3 were developed by Drs. Mirkouei and Mohajeri.

## Chapter 1. Introduction

### 1.1. Research Challenges and Motivation

Anthropogenic climate change presents an existential threat to humanity, but is often a consequence of the advanced manufacturing and chemical processes that make modern life possible. To balance climate responsibility with the demands of modern society, industrial sustainability aims to reduce the environmental impact of these processes, while remaining economically viable.

Previous studies exist for both nitrogen trifluoride usage and furfural production, the two topics considered in the following chapters. In both cases, these studies tend to be focused on the technology itself, and less focused on the environmental and economic consequences of these technologies. Of the studies that did consider environmental or economic analysis, very few studies considered both of these objectives simultaneously.

#### 1.1.1. Chapter 2 Challenge

Nitrogen trifluoride ( $\text{NF}_3$ ) is the second most potent greenhouse gas known to man; only sulfur hexafluoride has a higher 100-year global warming potential.  $\text{NF}_3$  is ubiquitous within the electronics industry. The challenge for the industry is to minimize the impact of using  $\text{NF}_3$ , while still maintaining competitiveness in a particularly cut-throat industry. A real case study for the Idaho semiconductor facility is used to assess the method and demonstrate the application of this study.

#### 1.1.2. Chapter 3 Challenge

Furfural production from biomass has been an ongoing industrial process since the aftermath of the First World War. Today this is primarily conducted by hydrolysis, but pyrolysis technology has the potential to displace hydrothermal methods. Chapter 3 of this paper compares these two technologies from both an environmental and economic perspective. Chapter 3 presents a case study for producing furfural from sugar beet pulp (SBP), in southern Idaho.

#### 1.1.3. Motivation of thesis

Both chapters 2 and 3 are motivated by the desire to understand the environmental and economic impacts of chemicals used in the advanced manufacturing that make modern life possible. For a process to be sustainable, it must not only be economically viable, but also offer minimal environmental impacts. The dual-objective criteria proposed in this thesis can be applied to a myriad of industrial processes.

In the case of  $\text{NF}_3$ , the gas is heavily used in the electronics industry, primarily for removing oxides from wafer processing tools.  $\text{NF}_3$  is less hazardous than other cleaning gases, such as chlorine trifluoride, which may partially explain its high usage within the semiconductor industry. It is hard to imagine the modern world without cell phones, computers, and consumer electronics that are made possible by semiconductors. It is also no secret that cleanliness is a key characteristic of semiconductor fabrication. Chapter 2 proposes a decision-making framework to analyze the continued use of  $\text{NF}_3$ , suggesting the means by which the impacts can be reduced.

Furfural is a platform chemical that can serve as the basis for other chemical production. For instance, furfural can be used as the basis for gasoline and jet fuel production, making it of interest to the green energy industry. These are just two of the over 80 products that, directly or indirectly, that can come from furfural. Additionally, because furfural can be produced from agricultural residues, furfural synthesis offers an additional revenue stream for the agro-industrialists. The application of thermochemical processes to biorefining has the potential to displace the hydrothermal processes currently used for furfural production. Chapter 3 considers SBP as the source of biomass, which is of particular interest to the state of Idaho, which ranks second in sugar beets production in the U.S.

## **1.2. Research Objectives and tasks**

This thesis is based on life cycle assessment (LCA) and techno-economic assessment (TEA) to analyze industrial processes. OpenLCA version 1.8, an opensource software for performing lifecycle assessment, was used to assist in this analysis. Furthermore, MS Excel was used extensively to assist both the TEA and LCA.

Chapter 2 considered the path of  $\text{NF}_3$  through the supply chain, from production, transportation, use, and eventual destruction through abatement. After leaving the chemical plant where it is produced,  $\text{NF}_3$  travels to the semiconductor fab. It is piped through tools and eventually reaches the abatement process. Abatement, the process by which gases are broken down before entering the atmosphere, proved to be the key to understanding the impact  $\text{NF}_3$  would have on global climate change. As such, considerable time was spent learning about the mechanics of abatement.

Chapter 3 required an understanding of both pyrolysis and hydrolysis processes for modelling purposes. To assist in this, a literature review was conducted. Once this had been performed, the key challenges for both processes were identified. Specifically, hydrolysis requires large volumes of water to be heated well above boiling. Pyrolysis does not have the same water demands but occurs at a significantly higher temperature than hydrolysis. Ultimately, the energy demands of these two processes was the key to understanding both techno-economic and environmental impact aspects.

### 1.3. Research Scope

The techno-economic assessment (TEA) considers the economic viability of the proposed projects in terms of US dollars (USD). This includes both the variable costs (labor and utilities) and capital costs. Capital costs were amortized over time, to consider not only equipment costs, but also interest and depreciation. These economic models also considered maintenance, utilization rates, and annual productivity.

This research primarily considered environmental impacts from the perspective of anthropomorphic global climate change. Humanmade climate change, sometimes referred to as the greenhouse effect, is caused by the change in the Earth's albedo, or ability to reflect solar radiation. Greenhouse gases, such as carbon dioxide (CO<sub>2</sub>) or methane (CH<sub>4</sub>) make the Earth accept a greater amount of solar radiation. The knock-on effects of this, including melting of the polar ice caps and alterations to thermohaline circulation within the North Atlantic, and how these effects impact overall global temperature, are complex and beyond the scope of this thesis.

Coursework in Technology Management teaches that a good scope should state not only what is included, but also what is beyond the scope of work. The social aspects of sustainability, such as equality, diversity, and human safety, were not considered by either of the studies presented in this thesis. While these areas may be worthy of consideration in further work, they exist beyond the scope of this thesis.

### 1.4. Thesis Outline

This thesis is presented in manuscript format and consists of four chapters and one appendix.

Chapter 2 is a TEA and LCA of NF<sub>3</sub> in the semiconductor industry, considered through the context of a case study of semiconductor facility in Boise, ID. The paper identifies key areas of the process that impact environmental and economic impacts. Abatement efficiency and chemical contaminants were identified as two key areas for further analysis. This chapter is a conference paper published in the 2020 proceedings of the ASME IDETC/CIE: 25<sup>th</sup> Design for Manufacturing and the Life Cycle Conference, under the title "*Environmental and Economic Impacts of Nitrogen Trifluoride at an Idaho Semiconductor Facility.*"

Chapter 3 considers a proposed project in Southern Idaho to produce furfural from SBP. This chapter establishes that the production of furfural from SBP is viable, identifying hydrolysis and pyrolysis as two technologies for synthesizing furfural. TEA and LCA methodology are applied to determine which technology is preferable. Publicly available data from both the USDA and

Amalgamated Sugar (Idaho's sugar co-op) supports the notion that available SBP will support the proposed furfural project. Scientific literature also gives credence to the idea that SBP can be a good source of biomass for furfural production. This chapter has been submitted under the title "*Comparison of pyrolysis and hydrolysis processes for furfural production from sugar beet pulp: A case study in southern Idaho, USA,*" and is currently under review for publication in the Journal of Cleaner Production.

Chapter 4 draws general conclusions for this thesis and offers suggestions for future work, and considerations of what has been accomplished.

Appendix 1 provides the lingo code used for solving the model created in Chapter 3.

## Chapter 2. Environmental and Economic Impacts of Nitrogen Trifluoride at an Idaho Semiconductor Facility

This chapter was published in the 2020 proceedings of the ASME IDETC/CIE: 25<sup>th</sup> Design for Manufacturing and the Life Cycle Conference, under the title *Environmental and Economic Impacts of Nitrogen Trifluoride at an Idaho Semiconductor Facility*.

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### 2.1. Abstract

Nitrogen Trifluoride (NF<sub>3</sub>) is an inorganic compound widely used in the electronics industry for manufacturing various products, such as semiconductors, solar panels, and touch screens. However, NF<sub>3</sub> emissions that accumulate in the atmosphere have 17,200 times the global warming potentials of CO<sub>2</sub> over a 100-year time horizon. The abatement efficiency for NF<sub>3</sub> is high, although some amount of NO<sub>x</sub> is generated. This study aims to provide economic and environmental impact assessments on the use of NF<sub>3</sub>. Life cycle assessment method is applied for evaluating environmental aspects. Additionally, a real case study for the Idaho semiconductor facility is used to assess the method and demonstrate the application of this study. The results show that slight reductions in abatement efficiency have dramatic impacts on mitigating greenhouse gas (GHG) emissions. Even small unplanned releases of NF<sub>3</sub>, either through mechanical failure or human error, have significant environmental impacts, and every reasonable effort should be taken to avoid such incidents. The results also indicate that the cost of abatement is the primary driver of economic impact. It is found that the considerable distance from the chemical plant in Arizona to the point of use in Idaho contributed a minor portion of GHGs associated with the use of NF<sub>3</sub>. It is also found that contaminants (e.g., SF<sub>6</sub> and CF<sub>4</sub>) within the cylinder potentially have more substantial GHG impacts than the actual NF<sub>3</sub>, owing in part to the relative ease with which NF<sub>3</sub> is destroyed through abatement.

*Keywords:* Nitrogen trifluoride, greenhouse gas emissions, abatement, sustainability, semiconductors.

## NOMENCLATURE

### Parameters

$CC$	Capital cost
$TBS_i$	Total sale for the $i^{th}$ year
$TAX_i$	Total taxation for the $i^{th}$ year
$n$	Project lifetime (year)
$r$	Rate of interest (%)
$OC_i$	Operating cost for the $i^{th}$ year
$d$	Depreciation rate (%)
$RC$	Replacement cost
$x$	Interval input parameters
$P$	Pressure
$V$	Volume
$T$	Temperature
$m$	Mols present
$R$	Ideal gas constant

### Decision Variables

$TP$	Total profit
$PP$	Payback period
$NPV$	Net present value
$LCC$	Life cycle costing
$OC$	Operation cost
$SV$	Salvage value
$h$	Non-probabilistic reliability index
$y$	Continuous function of the inputs $x$
$\underline{y}$	Lower limit of the output $y$
$\bar{y}$	Upper limit of the output $y$

## 2.2. Introduction

*Motivation and Challenges.* Semiconductor manufacturing requires numerous chemicals for various purposes. One gas used in significant volumes in the electronics industry is nitrogen trifluoride (NF<sub>3</sub>) (Tsai, 2008). NF<sub>3</sub> is a potent greenhouse gas (GHG) emission, used by the semiconductor industry as an etchant and cleaner. The motivation of this study lies in understanding the environmental and economic impacts of using NF<sub>3</sub>. One of the challenges is the complexity of semiconductor processes. NF<sub>3</sub> is used in multiple processes, and any data about what percentage of total gas usage is proprietary. Additionally, unintentional releases may occur through a combination of mechanical failure or human error. Because of this, and the ambiguity associated with the abatement process, it is hard to quantify what percentage of the initial NF<sub>3</sub> reaches the atmosphere.

*Background.* NF<sub>3</sub> is an oxidizer and a toxic, compressed gas, that is both colorless and odorless. The LC<sub>50</sub> (lethal concentration of a toxin) of NF<sub>3</sub> is 6,700ppm over an hour, tested in rats (Praxair, 2016), meaning that despite being a toxic gas, NF<sub>3</sub> is markedly less hazardous than other fluorine bearing compounds used in the semiconductor industry, such as hydrogen fluoride (HF), fluorine (F<sub>2</sub>), or chlorine trifluoride (ClF<sub>3</sub>). For comparison, the LC<sub>50</sub> of ClF<sub>3</sub> is 229ppm over an hour, tested in rats (Matheson Tri-Gas Inc, 2008). The high usage of NF<sub>3</sub> may stem, in part, from the relative safety with which it can be handled. The toxic gas monitoring requirements associated with NF<sub>3</sub> are lower than with these other fluorinated compounds. This may also contribute to attempts to hide mistakes, whereas releases of more immediately hazardous materials would be harder to conceal (e.g., ClF<sub>3</sub> or F<sub>2</sub>). NF<sub>3</sub> is a hazardous gas, but rather than the toxicity associated with NF<sub>3</sub> is lower than with certain other gases used in the electronics industry.

The primary use of NF<sub>3</sub> and other perfluorocarbons is the cleaning of chambers (Hu et al., 2018), that is likely to encounter other gases (e.g., argon) and hazardous chemicals used in semiconductor manufacturing. Allgood (2003) proposed using C<sub>4</sub>F<sub>8</sub> as an alternative solution for the cleaning of chemical vapor deposition chambers due to lower economic and greenhouse impacts than NF<sub>3</sub> (Allgood, 2003).

After process use, NF<sub>3</sub> exits the system through abatement. The abatement process involves the use of heat to break down the constituent gases within the waste stream, then wet scrubbing the resultant emissions (Chen et al., 2019). The source of this heat can be electricity or the burning of natural gas. Wet scrubbing not only captures any remaining fluorides, but also cools gaseous emissions leaving the system. Operating a closed-loop system is one way to reduce water usage.

Much of this study is an attempt to quantify gaseous emissions leaving the system. Fluorides will leave the system through the fluoride waste stream, which is beyond the scope of this paper.

The term Global Warming Potential (GWP) is a measure of how much energy a given mass of a gas will absorb over a given amount of time, relative to the same mass of CO<sub>2</sub> (US Environmental Protection Agency, 2017). This is referred to as CO<sub>2</sub> equivalent (eq.) and is reported in kilograms. For example, 1kg of methane (CH<sub>4</sub>) will absorb 28-36 times as much energy as CO<sub>2</sub> over a 100-year time span, and therefore has a GWP<sub>100</sub> between 28 and 36kg CO<sub>2</sub> eq. CH<sub>4</sub> breaks down much faster than CO<sub>2</sub>, meaning the value for GWP<sub>500</sub> is significantly lower than the GWP<sub>100</sub>. CO<sub>2</sub> is the reference, meaning the GWP value for CO<sub>2</sub> is always one, regardless of the time period (Mirkouei, 2016; Mirkouei et al., 2016; Mirkouei and Kardel, 2017). It should be acknowledged that NF<sub>3</sub> breaks down in the atmosphere at a slower rate than CO<sub>2</sub>, and therefore the GWP<sub>500</sub> for NF<sub>3</sub> will be higher than the GWP<sub>100</sub>.

NF<sub>3</sub> does not react with ozone or other atmospheric constituents, meaning it has a long lifespan once it reaches the atmosphere, calculated at 550 years by one source (Prather and Hsu, 2008). Additionally, NF<sub>3</sub> is a powerful GHG with a GWP<sub>100</sub> that is 17,200 times that of CO<sub>2</sub> (Weiss et al., 2008). Weiss et al. (2008) found that atmospheric NF<sub>3</sub> is increasing at a rate of 11% per year. Weiss et al. (2018) measured atmospheric concentrations to be  $4.5 \times 10^{-7}$  ppm with an annual increase of  $5.3 \times 10^{-8}$  ppm. NF<sub>3</sub> is known to have been used in rocket fuel since the early 1960s (Bronfin and Hazlett, 1966), making it impossible to know if NF<sub>3</sub> ever existed naturally in the atmosphere, or if atmospheric NF<sub>3</sub> is entirely a product of human industry. Weiss et al. (2018) determined that the background NF<sub>3</sub> in the atmosphere is naturally less than  $2.0 \times 10^{-8}$  ppm (Weiss et al., 2008). Although these concentrations appear small, it should be remembered that GWP<sub>100</sub> of NF<sub>3</sub> is higher than any known gas, with the exception of sulfur hexafluoride (SF<sub>6</sub>). The GWP<sub>100</sub> of SF<sub>6</sub> is 23,500 (Chen et al., 2019), but SF<sub>6</sub> is used by the electronics industry in smaller volumes than NF<sub>3</sub>. In 2008, NF<sub>3</sub> was conspicuously absent from the Kyoto Protocol, but it has since been added to subsequent agreements. Arnold et al. (2013) estimated that the atmospheric concentration of NF<sub>3</sub> is approximately  $8.6 \times 10^{-7}$  ppm (Arnold et al., 2013).

Prather and Hsu (2008) estimated the cost of NF<sub>3</sub> to be about \$20/kg (Prather and Hsu, 2008). Adjusted for inflation in 2019, the material cost of NF<sub>3</sub> is around \$24/kg (Bureau of Labor Statistics, 2019). This number only reflects the cost of the material from a supplier, and does not include the infrastructure to support its use. The actual cost of using NF<sub>3</sub> will include the cost of the material, plumbing, and other infrastructure for using the material, and the cost of operating the requisite abatement operation. The ability to safely purge NF<sub>3</sub> with nitrogen or another inert gas is also

required. The infrastructure for purging, ideally with bottled nitrogen from a dedicated source, must also be considered. A controller is required to monitor pressure transducers, actuate valves, and generate alarms when the system is outside of desired operating ranges. All mechanical connections will need to be enclosed within an exhausted gas cabinet. Finally, labor hours will be required to install and remove bottles.

**Table 2-1. An overview of earlier NF<sub>3</sub> studies, focusing on economic and environmental objectives**

Authors (Year)	Objectives		Abatement	NF <sub>3</sub>	LCA	Semiconductors
	Environmental	Economic				
Bronfin and Hazlett (1966)	✓	×	×	×	×	✓
Allgood (2003)	✓	×	×	×	×	✓
Yu et al. (2007)	✓	×	×	✓	✓	✓
Tsai (2008)	×	×	×	✓	✓	×
Weiss et al. (2008)	✓	×	✓	✓	✓	✓
Prather and Hsu (2008)	×	×	✓	×	×	✓
Yang et al. (2009)	×	×	✓	✓	✓	✓
Illuzzi and Thewissen (2010)	✓	✓	✓	✓	✓	✓
van der Meulen and Alesma (2011)	×	×	✓	✓	✓	✓
Arnold et al. (2013)	×	×	✓	✓	✓	✓
Ko et al. (2013)	×	×	×	✓	✓	×
Lee and Chen (2017)	✓	×	✓	✓	✓	✓
Hu et al. (2018)	✓	×	×	✓	✓	×
Guo et al. (2019)	✓	×	×	✓	✓	✓
Xu et al. (2019)	×	×	×	✓	✓	✓
Miyazaki et al. (2019)	✓	×	✓	✓	✓	✓
Chen et al. (2019)	✓	✓	×	✓	✓	✓
This study	✓	✓	✓	✓	✓	✓

Several studies investigated the economic and environmental impacts of NF<sub>3</sub> consumption (Table 2-1). The main focus of this study is on the following objectives:

**Environmental impact assessment:** The damage done to the atmosphere by NF<sub>3</sub> usage has been reported by Prather and Hsu and Weiss et al., using the life cycle assessment (LCA) method (Prather and Hsu, 2008; Weiss et al., 2008). Yu et al. (2007) applied the LCA method to compare and contrast C<sub>2</sub>F<sub>6</sub> (Yu Qian, Zhixian Huang, Zhiguo Yan, 2007). Meulen and Alesma (2010) applied the LCA method to assess the environmental impacts of NF<sub>3</sub> use in the production of photovoltaic solar panels (van der Meulen and Alsema, 2011).

**Economic and environmental assessment:** There is little existing research exclusively on the economic assessment of using NF<sub>3</sub>. Illuzzi and Thewissen (2010) suggested that the best way to reduce the cost of NF<sub>3</sub> consumption was to use less, although high costs would be incurred by engineering and qualifying new processes (Illuzzi and Thewissen, 2010). Yu et al. (2007) used LCA and life cycle costing to study the environmental and economic of NF<sub>3</sub> in comparison to C<sub>2</sub>F<sub>6</sub> (Yu

Qian, Zhixian Huang, Zhiguo Yan, 2007). They identified a trade-off between environmental and economic aspects but included little discussion of abatement.

Abatement process: Estimates varied slightly on the percentage of  $\text{NF}_3$  that reach the atmosphere. Prather and Hsu (2008) estimated that about 2% of  $\text{NF}_3$  survives abatement to reach the atmosphere, while Ko et al. (2013) found that 3% will reach the atmosphere. More recently, Lee and Chen (2017) reported zero percent emission, using a plasma-thermal abatement system. Yang et al. (2009) did similar research on an array of perfluorocarbons, using gas chromatography and reported near-total destruction of  $\text{NF}_3$ , although other perfluorocarbons, such as  $\text{SF}_6$  were less amenable to abatement (Yang et al., 2009). Guo et al. (2019) developed a stochastic dynamic model to study the uncertainties associated with abatement, dividing them into cost uncertainty and abatement uncertainty, to ascertain how these uncertainties impact decision making (Guo et al., 2019).

Table 2-1 presents only a few research studies (i.e., Illuzzi and Thewissen (2010) and Yu et al. (2007)) that considered both economic and environmental objectives in the semiconductor industry. Yu et al. (2007) considered the LCA methodology for evaluating environmental impacts of  $\text{NF}_3$ . They used the analytic hierarchy process model to derive a single criteria score by analyzing the environmental impact and life cycle costing of a product. To the best of our knowledge, there are several deficiencies in prior studies: (i) a multi-criteria method for assessing economic and environmental impacts and (ii) uncertainty incorporation to the models do not exist to enhance sustainability benefits across the  $\text{NF}_3$  life cycle. Therefore, the primary objective of this study is to develop a multi-criteria decision making framework to evaluate the environmental and economic impacts of using  $\text{NF}_3$ .

### 2.3. Materials and Methods

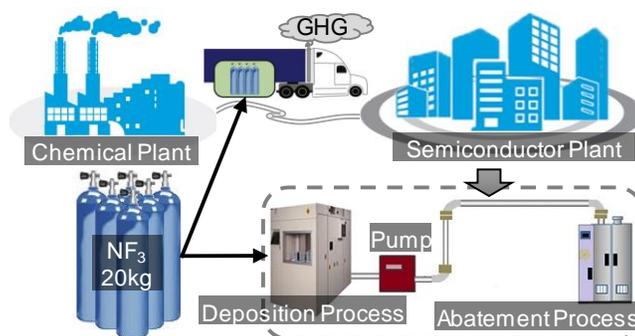
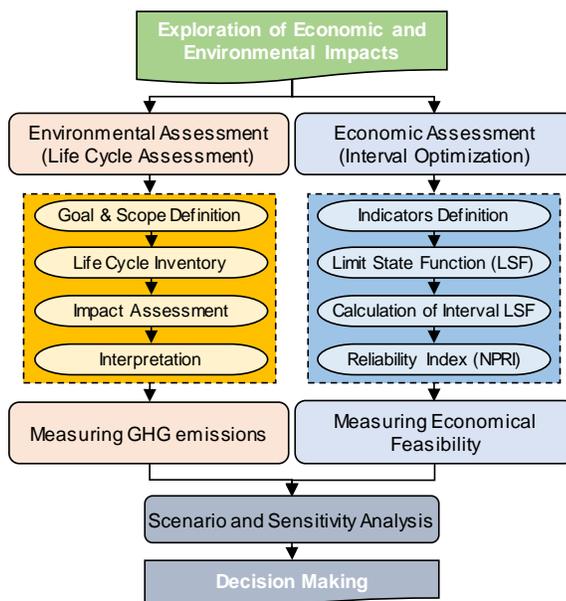


Figure 2-1 Schematic of  $\text{NF}_3$  supply chain.

There are two main stages across  $\text{NF}_3$  supply chains, which are upstream (suppliers from the chemical plant) and downstream (consumers in semiconductor company). Figure 2-1 demonstrates the key entities of  $\text{NF}_3$  supply chain. The multi-criteria decision making framework presented in this study, integrating environmental assessment, using LCA method and economic assessment, using interval optimization method (Figure 2-2).



**Figure 2-2 Multi-criteria decision making framework.**

### 2.3.1. Environmental Impact Assessment

Environmental impact analysis is used to evaluate the GWP, using LCA method. LCA conducted herein includes four phases: goal and scope definition, inventory analysis, impact assessment, and interpretation.  $\text{NF}_3$  life cycle includes production, consumption, any potential reuse/recycling, and eventual disposal. By applying LCA techniques to materials used in the semiconductor industry, it may be possible to gain insight and mitigate the environmental impacts of  $\text{NF}_3$  use.

*Goal and Scope.* The goal of this paper is to provide a “gate to grave” life cycle assessment of a single cylinder of electronics grade  $\text{NF}_3$  used at a semiconductor company in Boise, Idaho. The study will focus on GHG emissions. The functional unit is one cylinder (20kg) of  $\text{NF}_3$ . The pressure of the compressed gas cylinder, when full, is approximately 1,400psia, and the volume is 50L. The construction and maintenance of the cylinder to contain the gas will be outside the scope of this study. The study will start with the synthesis of  $\text{NF}_3$ , at the Versum Materials (formerly Air Products)

facility. The cylinder must then be transported to a facility in Boise for consumption purposes. Once installed in a gas delivery system,  $\text{NF}_3$  will be transported through piping to the point of use, before leaving the facility through the abatement system. A small portion of unused  $\text{NF}_3$  residual will be returned to the vendor when the cylinder returned for a refill, despite the fact the bottle has been marked as “empty.” The remainder of the  $\text{NF}_3$  will be converted to other materials.

**Table 2-2 Specifications of  $\text{NF}_3$  cylinder**

<b>Compound</b>	<b>Concentration (ppm)</b>	<b>GWP100 (kg <math>\text{CO}_2</math> eq.)</b>
$\text{CO}_2$	16	1
$\text{CO}$	25	-
$\text{N}_2$	126	-
$\text{N}_2\text{O}$	16	298
$\text{O}_2$ and Ar	110	-
$\text{SF}_6$	24	23,500
$\text{CF}_4$	564	6,630
HF	1	-
$\text{H}_2\text{O}$	<1	-

*Life Cycle Inventory.* A review of available literature relating to the synthesis and abatement of  $\text{NF}_3$  was conducted to collect data and information for the life cycle inventory. Specifications on the quality and tolerable contaminants in the compressed gas are publicly available. Using Charles’ law (Eq. 2-1) and the Ideal Gas Law (Eq. 2-2), where  $P, V, t, m,$  and  $R$  are pressure, volume, temperature, number of mols, and universal gas constant, respectively; it was possible to calculate the mass of contaminants within a single cylinder. Table 2-2 shows other contaminants found within the cylinder, using data from the manufacturer (Versum Materials, 2019). It was determined that a single cylinder contained 9g of  $\text{CF}_4$  and 0.6g of  $\text{SF}_6$ . Because the  $\text{GWP}_{100}$  for each of these substances is significant, this is the equivalent of 59.6kg and 14.1kg of  $\text{CO}_2$ , respectively. Some of these will be destroyed through abatement.

$$P_1V_1 = P_2V_2 \quad (2-1)$$

$$PV = mRt \quad (2-2)$$

Information about the source of electricity in Idaho is collected from Idaho Power, in which 46% of the electricity used is hydroelectric, 19% comes from other non-hydro renewables, and the rest comes from non-renewable energy sources (Idaho Power, 2019).

*Life Cycle Impact Assessment.* A product system was created to study the emissions from a single  $\text{NF}_3$  cylinder, and the  $\text{GWP}_{100}$  values were used to determine the equivalent mass of  $\text{CO}_2$ . Emissions were calculated for the transportation of  $\text{NF}_3$  from the chemical plant to the semiconductor company in Boise. Once on site,  $\text{NF}_3$  will go through a variety of tool cleanroom processes before being destroyed through abatement. Some amount of  $\text{NF}_3$  will enter the atmosphere, which will result in environmental impacts. Ultimately, this study investigates the relationship between the mass of gas, reaching atmosphere and environmental impact consequences.

*Interpretation.* The tabulated data was compared to  $\text{CO}_2$ , using  $\text{GWP}_{100}$  values to determine GHG emissions ( $\text{CO}_2$  eq.). A series of Pareto and sensitivity analysis were created to demonstrate the results, determine the major environmental and cost drivers, and compare different scenarios.

### 2.3.2. Economic Assessment

Economic analysis presented herein evaluates net present value (NPV), payback period (PP), and total profit (TP) for the defined  $\text{NF}_3$  life cycle. Besides, the interval parameters related to the economic assessment are obtained from the company balance sheet. In cases where data was not available, reasonable estimates were used. The mathematical formulations of TP, PP, and NPV for the proposed problem are calculated, using Eqs. (2-3)-(2-5) (Tang et al., 2018):

$$TP = -LCC + (TBS_i - TAX_i) \times n \quad (2-3)$$

$$PP = \frac{CC}{(TP/n)} \quad (2-4)$$

$$NPV = \sum_{i=1:n} \frac{(TBS_i - TAX_i)}{(1+r)^i} - LCC \quad (2-5)$$

The corresponding LCC is calculated, using Eq. (2-6):

$$LCC = CC + OC - SV \quad (2-6)$$

where:

$$OC = \sum_{i=1:n} \frac{OC_i}{(1+r)^i} \quad (2-7)$$

$$SV = \frac{RC \times (1-d)^{n-1}}{(1+r)^n} \quad (2-8)$$

Table 2-3 presents economic constraints to guarantee that  $\text{NF}_3$  supply is economically feasible. TP defined is expected to be larger than zero. PP is expected to be less than the allowable upper bound, where  $\text{PP}^u$  is the permitted upper limit. NPV must be larger than zero.

**Table 2-3 Economic constraints to find a feasible solution.**

Value	Constraint
Total Profit	$\text{TP} \geq 0$
Payback Period	$\text{PP} = \frac{\text{CC}}{(\text{TP}/n)} = \frac{n \times \text{CC}}{\text{TP}} \leq \text{PP}^u$ $\rightarrow \frac{n \times \text{CC}}{\text{TP}} \leq \text{PP}^u \rightarrow \text{TP} \geq \frac{n \times \text{CC}}{\text{PP}^u}$ $\text{NPV} = -\text{LCC} + \frac{\text{TP} + \text{LCC}}{n} \sum_{i=1:n} \frac{1}{(1+r)^i} \geq 0$
Net Present Value	$\rightarrow \text{TP} \geq \left( \frac{n}{\sum_{i=1:n} \frac{1}{(1+r)^i}} - 1 \right) \times \text{LCC}$

*Non-probabilistic reliability index (NPRI) for problems with interval parameters.* NPRI is employed to measure the reliable level of practical engineering problems subject to interval uncertainties. NPRI is further extended to measure the economically feasible degree in the economic assessment of  $\text{NF}_3$  supply. For a system with interval input parameters,  $x = (x_1, x_2, \dots, x_n)$ , the corresponding output  $y$  is defined by Eq. (2-9).  $y = g(x)$  is a limit state function (LSF) that separates the whole space into two regions, which are the safe and failure region. The NPRI can be calculated, using Eqs (2-10)-(2-12):

$$y = g(x) \quad (2-9)$$

$$h = y^c / y^r \quad (2-10)$$

$$y^c = (\bar{y} + \underline{y}) / 2 \quad (2-11)$$

$$y^r = (\bar{y} - \underline{y}) / 2 \quad (2-12)$$

*NPRI for  $\text{NF}_3$  supply.* TP, PP, and NPV constraints can be written into the LSF forms (Eqs. (2-13)-(2-15)). Interval parameters will lead to the variability of TP, PP, and NPV and then at least one of Eqs. (2-13)-(2-15) may not hold. Equations (2-13)-(2-15) should simultaneously hold to ensure that  $\text{NF}_3$  supply is economically feasible. Thus, Equation (2-16) can be employed to measure the economically feasible degree of  $\text{NF}_3$  supply with interval parameters.

$$y_1 = g_1(x) = TP \quad (2-13)$$

$$y_2 = g_2(x) = TP - \frac{n \times CC}{PPU} \quad (2-14)$$

$$y_3 = g_3(x) = TP - \left( \frac{n}{\sum_{i=1:n} \frac{1}{(1+r)^i}} - 1 \right) \times LCC \quad (2-15)$$

$$h_s = \min \{h_1, h_2, h_3\} \quad (2-16)$$

*NPRI behavior analysis.* The significance relevant to  $h_s$  is discussed in the following.

- $h_s \geq 1$  then  $\underline{y}_1 \geq 0$ ,  $\underline{y}_2 \geq 0$  and  $\underline{y}_3 \geq 0$ , implying that  $NF_3$  supply with interval uncertainties is absolutely feasible.
- $0 < h_s < 1$  then  $\bar{y}_1 \geq 0$ ,  $\bar{y}_2 \geq 0$  and  $\bar{y}_3 \geq 0$ , while at least one of  $\underline{y}_1 < 0$ ,  $\underline{y}_2 < 0$  and  $\underline{y}_3 < 0$  implying that  $NF_3$  supply with interval uncertainties is partially feasible.
- $h_s < 0$  and at least one of  $\bar{y}_1 < 0$ ,  $\bar{y}_2 < 0$  and  $\bar{y}_3 < 0$ , implying that  $NF_3$  supply with interval uncertainties is completely infeasible.

#### 2.4. Case study and Results

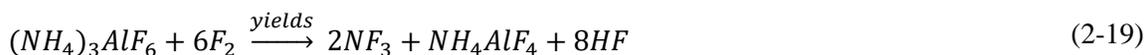
Idaho is home to the global headquarter of a major computer memory and data storage (e.g., flash drive memory) manufacturer that has strong research and development programs to assess new processes and equipment for promoting wafer fabrication. Development facilities are constantly installing and removing tools, as well as changing processes. Conversely, a production facility is optimized to maximize uptime and process as many wafers as possible. A production facility would generally be expected to use more chemicals and gases than a research laboratory. On the other hand, the constant changing of processes, tools, and materials creates more opportunity for human error. Small releases, caused either by mechanical failure or human error, can occur when installing a cylinder, breaking a gas line, or opening a production chamber. It is possible that a portion of these discharge events goes unreported by front line workers. In other cases, these releases may not even be detected.

This study analyzed NF<sub>3</sub> use to conduct the proposed economic and environmental assessments at the Boise semiconductor facility. Some necessary information is proprietary and unavailable, therefore, the following assumptions are made to complete the analysis:

- NF<sub>3</sub> is produced at a chemical facility in Tucson, Arizona.
- NF<sub>3</sub> is transported via truck to the point of use. This truck is assumed to carry 50 cylinders of NF<sub>3</sub>, with no other cargo. The truck travels the most direct route between Tucson, AZ, making no additional stops. The distance on this route is 1,037 miles.
- NF<sub>3</sub> is transported in cylinders containing 20kg of product. Larger bulk containers may exist in reality, but are ignored in this paper.
- Economic model was constructed from the corporate balance sheet and publicly available data, with reasonable estimates used when necessary.
- Equipment pricing estimates were based on data provided by Critical Systems Incorporated.

#### 2.4.1. *Environmental Assessment Results*

There are currently three accepted methods of synthesizing NF<sub>3</sub> on an industrial scale, which are (i) electrolysis of molten ammonium fluoride (NH<sub>4</sub>F) (Eq. 2-17), (ii) direct fluorination of NH<sub>4</sub>F (Eq. 2-18), and (iii) direct fluorination of ammonium hexafluoroaluminate (Eq. 2-19) (Miyazaki et al., 2019). NH<sub>4</sub>F is in a hydrofluoric solution to prevent an explosion. To increase the reaction rate, this is done at high temperature and pressure. Miyazaki et al. (2019) suggested a fourth method: chlorine trifluoride is used in a series of reactions with NH<sub>4</sub>F to generate NF<sub>3</sub> (Miyazaki et al., 2019). The method created by Miyazaki et al. (2019) may prove to be an effective means of generating the desired NF<sub>3</sub>, however, it is still under research and development.



All three of these methods have drawbacks, but Miyazaki et al. (2019) reported that the third method takes the longest and is the most expensive. The method used by Versum Materials (chemical manufacturing company) is not publicly declared, but it seems unlikely that a major chemical company would choose the most expensive method. Methods 1 and 2 are both endothermic, although data was not available for how much energy is required. This study will ignore the energy demands of

NF<sub>3</sub> synthesis. With Method 3 ruled out, the byproducts of NF<sub>3</sub> synthesis are either H<sub>2</sub> or HF. Although these are hazardous chemicals and have industrial applications, neither is considered waste.

Transportation of NF<sub>3</sub> could legally be conducted either by truck or aircraft, but it will be assumed in this paper that a truck carries NF<sub>3</sub> from the chemical plant to the point of use, along with 49 other cylinders. NF<sub>3</sub> is a hazardous material for Department of Transportation purposes, and the regulations surrounding transport are complex. The plant likely produces other chemicals and gases, that may or may not be compatible with NF<sub>3</sub>. Additionally, it is unlikely that modern “just in time” inventory practices would permit large volumes of NF<sub>3</sub> to be stored on site. A truck carrying 50 cylinders is not fully loaded, and more efficient arrangements are likely possible. Using rail transportation would reduce emissions from transport, but this may not be a viable option. Conversely, using cargo aircraft would significantly increase the carbon cost of transport.

Using GREET database (an open-source LCA platform), it was calculated that 1.4kg of CO<sub>2</sub> would be released by mile driven. Since NF<sub>3</sub> must be transported 1,037 miles, and the empty truck must return, this means the truck will release 2,903kg of CO<sub>2</sub>. This number can be divided by 50, reflecting the assumption that the truck contains 50 cylinders, for a CO<sub>2</sub> output from the transportation of 58kg. Additionally, 3.5g of NO<sub>x</sub> would be released per mile, or a total of 7.2kg, that can also be divided by the 50 cylinders on the truck, for a mass of 0.14kg of NO<sub>x</sub>. NO<sub>x</sub> has climate change properties but is primarily associated with breathing problems and acid rain.

The actual cleanroom processes have been treated as a ‘black box’ in this study. NF<sub>3</sub> has several uses, including as an etchant or a cleaning agent. Semiconductor processes are numerous, complex, and proprietary; thus, the exact use of the gas is ignored. This study also assumes that NF<sub>3</sub> processes within the fabrication tool are conservative, and gas is not destroyed except through abatement. The process will require energy inputs, as well as gases other than NF<sub>3</sub>, but those are beyond the scope of this paper.

There is some disagreement in the literature as to how much NF<sub>3</sub> can survive the abatement process and enter the atmosphere. Prather and Hsu (2008) stated that about 2% of NF<sub>3</sub> reaches the atmosphere, when small leaks and inefficiency of abatement are considered. Lee and Chen (2017) claimed that NF<sub>3</sub> could be destroyed with 100% efficiency, using a plasma torch, although NO<sub>2</sub> was created. Xu et al. (2019) used the assorted metal oxides to decompose NF<sub>3</sub> at temperatures above 300°C, with byproducts including NO<sub>2</sub> and NO (Xu et al., 2019). Lee and Chen (2017) reported better results in comparison to other studies (e.g., Prather and Hsu (2008) or Ko et al. (2013)) in terms of the current state of abatement technology.

Unlike  $\text{NF}_3$ , which has a 100% decomposition rate, the abatement of  $\text{SF}_6$  and  $\text{CF}_4$  is incomplete. Using the plasma torch method, Lee and Chen (2017) found that decomposition rates of both  $\text{SF}_6$  and  $\text{CF}_4$  vary by concentration. The decomposition rate for  $\text{SF}_6$  was 70-80%. Additionally, it was found that the decomposition rate for  $\text{SF}_6$  varied inversely with concentration. The decomposition rate of  $\text{CF}_4$  was found to be 30-40%, varying directly with concentration. Lee and Chen (2017) did not study concentrations less than 2,000ppm, but this data does offer insight into the abatement of these two contaminants. The study also found that destruction efficiency was inversely proportional to the flow rate, but the researchers did not study flow rates less than 100SLM (standard liters per minute). Lee and Chen (2017) flowed a significant volume of  $\text{N}_2$  gas through the abatement process. One potential drawback to research done by Lee and Chen is that they worked with ostensibly pure chemical species. In the real world, the waste stream might contain a myriad of gases from the cleanroom tool. Additionally, using Lee and Chen's (2017) abatement method,  $\text{NF}_3$  is completely destroyed, and therefore does not reach the atmosphere. The cylinder of  $\text{NF}_3$  accounts for the input of 9g of  $\text{CF}_4$  and 0.6g of  $\text{SF}_6$  contaminants, of which 5.4g and 0.1g reach the atmosphere, respectively. Using the  $\text{GWP}_{100}$ , 5.4g of  $\text{CF}_4$  has 35.8kg  $\text{CO}_2$  eq., and 0.12g of  $\text{SF}_6$  has 2.8kg  $\text{CO}_2$  eq.

#### 2.4.2. Economic Assessment Results

NPRI ( $h_s$ ) for  $\text{NF}_3$  supply is evaluated with the following assumptions:

- Project lifetime (n) is 10 years.
- Rate of interest (r) is 4%.
- Operation cost ( $OC_i$ ) for the  $i^{\text{th}}$  year is between \$6,900 and \$29,900.
- Total taxation ( $TAX_i$ ) and total sale ( $TBS_i$ ) for the  $i^{\text{th}}$  year are \$10,840 and \$936,000, respectively.
- Capital cost (CC) is commonly between \$69,500 and \$218,000.
- Depreciation rate (d) is between 21.3% and 45.8%.
- Represent replacement cost (RC) is between \$76,450 and \$239,800.

The uncertainty in the interval parameters resulted in the variation of TP, PP, and NPV of  $\text{NF}_3$  supply. The variation intervals for TP, NPV, and  $y_j = g_j(x)$  are shown in Table 2-4.

Substituting  $y_j$  and  $\bar{y}_j$  into Eqs. (2-10)-(2-12) leads to NPRI  $h_j$  ( $j = 1,2,3$ ) of Eqs. (2-13)-(2-15).

Thus, NPRI for  $\text{NF}_3$  supply can be calculated using Eq. (2-16). A value of 1.00 for  $h_s$  implies that the project will be absolutely feasible.

## 2.5. Discussion

The environmental analysis results indicate that the best way to reduce the environmental impacts of using  $\text{NF}_3$  is to maximize the efficiency of abatement process. Sensitivity analysis was conducted, wherein cylinders per truck were modified, to reveal the impact of transport on GHG emissions and profitability. In Case A, 75 cylinders were assumed per truck, Case B (base case study) assumed 50 cylinders per truck, and Case C assumed 25 cylinders per truck (Table 2-5). In all three cases, the project was shown to be economically viable (Table 2-6).

**Table 2-4 Variation intervals of uncertain variables.**

Uncertain Variables	Variation Intervals	NPRI Values
TP	$[6.94 \times 10^6, 7.29 \times 10^6]$	-
NPV	$[5.25 \times 10^6, 6.18 \times 10^6]$	-
$y_1 = g_1(\mathbf{x})$	$[6.94 \times 10^6, 7.29 \times 10^6]$	40.2
$y_2 = g_2(\mathbf{x})$	$[0.00 \times 10^0, 5.08 \times 10^6]$	1
$y_3 = g_3(\mathbf{x})$	$[6.83 \times 10^6, 7.26 \times 10^6]$	32.3

**Table 2-5 CO<sub>2</sub> eq. of emissions (kg) over 10 years**

Case	100% Abatement		97% Abatement	
	Low Use	High Use	Low Use	High Use
A (+50%)	$9.3 \times 10^3$	$4.0 \times 10^4$	$8.3 \times 10^5$	$3.6 \times 10^6$
B (basic)	$1.2 \times 10^4$	$5.0 \times 10^4$	$8.3 \times 10^5$	$3.6 \times 10^6$
C (-50%)	$1.9 \times 10^4$	$8.1 \times 10^4$	$8.3 \times 10^5$	$3.6 \times 10^6$

**Table 2-6 Profit (USD) over 10 years**

Case	Profit Low	Profit High	Economic Feasibility (NPRI)
A (+50%)	$6.95 \times 10^6$	$7.30 \times 10^6$	<input type="checkbox"/>
B (basic)	$6.94 \times 10^6$	$7.29 \times 10^6$	<input type="checkbox"/>
C (-50%)	$6.93 \times 10^6$	$7.29 \times 10^6$	<input type="checkbox"/>

It was found that the major cost driver was the capital cost of abatement equipment. Extending the useful service life of equipment, especially abatement equipment, reduces economic impact and maximizes profit. Transportation has only a small impact on the economy of using  $\text{NF}_3$ . The difference between Case A (high transportation efficiency) and Case C (low transportation efficiency) is negligible. Although unrealistic scenarios can be created where transportation is a significant factor, transportation is not found to be a primary driver of economic or environmental impact in realistic scenarios. Improvements in transportation are subject to diminishing returns, and offer a little meaningful reduction in environmental or economic impact.

Sensitivity analysis for GHG emissions reveals that a reduction in usage is correlated with a reduction in emissions, therefore this paper is consistent with the conclusion reached by Illuzzi and Thewissen (2010). The analysis also reveals that decreases in abatement efficiency will have a dramatic impact on GHG emissions. Transportation was found to be a small contributor to GHG emissions, although the portion of emissions attributable due to transportation becomes more significant as improved abatement removes  $\text{NF}_3$  emissions. A portion of GHG emissions is attributable to contaminants, such as  $\text{SF}_6$  and  $\text{CF}_4$ . Because these contaminants are less conducive to abatement than  $\text{NF}_3$ , one way to reduce total emissions will be to improve the purity of the gas. Such an improvement in purity may also have process benefits but would likely increase economic costs. The full impact of improving gas purity would be a potential area for further study. As the percentage of  $\text{NF}_3$  reaching atmosphere approaches 3%, all other sources of GHG become negligible in comparison.

## **2.6. Conclusion**

Process designs require simultaneous satisfaction and compromise of environmental and economic considerations due to the increasing public consciousness on sustainability issues. This study proposed a multi-criteria decision-making framework that accounts for both economic and environmental impacts of using  $\text{NF}_3$ , a critical material for semiconductor manufacturing. In this regard, this study conducted uncertainty examination in the economic analysis of the  $\text{NF}_3$  supply chain with interval parameters and NPRI that was employed to measure the economically feasible degree of  $\text{NF}_3$  supply. The results showed that the  $\text{NF}_3$  supply with interval uncertainties was feasible, and the best way to reduce the environmental impacts of using  $\text{NF}_3$  was to maximize the efficiency of the abatement process. Transportation is found to be a minor contributor to both GHG emissions and economic aspects in this study. Opportunities for future work include the application of LCA methodologies to the cleanroom processes, including energy demands of the tools, and any chemical occurring within the cleanroom process. Other environmental factors in semiconductor processing, such as other chemicals and gases, may also be studied.

## **2.7. Acknowledgement**

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## **Chapter 3. Comparison of pyrolysis and hydrolysis processes for furfural production from sugar beet pulp: A case study in southern Idaho, USA**

This chapter was submitted for publication in the Journal of Cleaner Production, under the title *Comparison of pyrolysis and hydrolysis processes for furfural production from sugar beet pulp: A case study in southern Idaho, USA*.

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### **3.1. Abstract**

Furfural is an organic compound that is widely used in the chemical industry for manufacturing various products, such as pharmaceuticals, pesticides, and solvents. Furfural production from biomass feedstocks can be achieved through various conversion pathways (e.g., pyrolysis or hydrolysis); however, it requires further investigation to reduce the total cost and meet the market needs. This study proposes a multi-objective decision making framework to compare techno-economic and environmental aspects of pyrolysis and hydrolysis technologies for furfural production from sugar beet pulp. Life cycle assessment method is applied for investigating the environmental impacts of converting organic materials to intermediate bioproducts (e.g., bio-oil) on-site, using a portable refinery unit. The techno-economic assessment employs an optimization model for minimizing the upstream and midstream costs (e.g., collection, transportation, and production). Sustainability assessments are conducted on a real case study in southern Idaho, USA, to evaluate and verify the methodology and demonstrate the application of this study. The results show that the total cost for furfural production, using pyrolysis and hydrolysis, are approximately \$846 and \$980 per metric ton, and total emission is 267 and 1,095 kg CO<sub>2</sub> eq. per metric ton, respectively. Therefore, the pyrolysis pathway results in lower emissions and costs due to the high water demand and low energy-density feedstock transportation associated with the hydrolysis pathway. It is concluded that on-site operations can reduce the total costs and emissions, and consequently stimulate furfural industry by addressing upstream and midstream sustainability challenges.

**Keywords:** Furfural; Portable Pyrolysis; Hydrolysis; Sugar Beet Pulp; Life Cycle Assessment; Techno-Economic Analysis.

**Abbreviations:** GHG, greenhouse gas; GWP<sub>100</sub>, 100-year global warming potential; H<sub>2</sub>SO<sub>4</sub>, sulfuric acid; LCA, life cycle assessment; RMCGP, revised multi-choice goal programming; SBP, sugar beet pulp; TC, total cost; TEA, techno-economic assessment; TGHG, total GHG emissions

### 3.2. Introduction

*Motivation and Challenges.* Furfural has a myriad of industrial uses (e.g., solvents and precursor chemicals) in various sectors (e.g., healthcare and basic materials) (Chandel et al., 2018); however, the major challenge is the low production process yield, that subsequently increases the production cost (Nhien et al., 2016; Yemiş and Mazza, 2017). Mariscal et al. (2016) provided an in-depth overview of the state of the furfural industry, including discussions of the chemistry and multiple production techniques, reporting that the price of furfural can be approximately \$1,500 per ton. Furfural is a platform chemical, with a carbonyl function group and a furan ring, that can be used directly or indirectly to make over 80 chemicals and fuels (Rodríguez Montaña et al., 2020). In 2019, global furfural production was a \$551 million (USD) industry, and is projected to be worth over \$700 million by 2024 (Rodríguez Montaña et al., 2020). Furfural can be produced from 5-carbon sugars known as pentoses (Chandel et al., 2018). The wide range of products from furfural makes it a chemical of interest for not only the energy industry, but also agrochemical and pharmaceutical manufacturing. Furfural can be synthesized from petrochemical sources, but it can be friendly to the environment, using renewable resources, such as sugar beet pulp (SBP). The major cost-driver for furfural production from biomass feedstocks is midstream operations, including conversion and upgrading processes (Mariscal et al., 2016). Particularly, the conversion of lignocellulose to green chemical products is hampered by immature, underdeveloped technology (Chandel et al., 2018), which can render petrochemical technologies more cost-effective than biomass processing technologies. In addition to midstream operations, extra upstream required steps (e.g., harvesting, collection, and transportation low energy density feedstocks) can increase the total cost for green chemical production (Erickson et al., 2011).

*Background.* Furfural production from *xylose* (wood sugar) was pioneered by the Quaker Oat company in the 1920s. The process used by Quaker treated oat hulls with dilute sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) to increase the process yield of furfural production (Binder et al., 2010). In 2013, it was reported that about 98% of furfural produced from feedstocks were sourced from either corncobs or bagasse (Cai et al., 2013), owing to the relative abundance, low cost, and high pentosan content of these materials. Pentosan is a five-carbon polysaccharide found in lignocellulose, which is especially conducive to

furfural production. Wheat straw can be used to generate furfural (Liu et al., 2014), and there has been promising research on the use of water hyacinth (*Eichhornia crassipes*), which is rich in pentosan and has high water content (Poomsawat et al., 2019). Tomaszewska et al. (2018) identified SBP as an increasingly promising material for furfural production, citing improving market conditions. Table 3-1 provides a comprehensive classification of recent research studies on furfural production from various biomass feedstocks, considering at least one of the following factors conducted in this study:

- *Environmental assessment.* Earlier studies have conducted environmental impact assessments of furfural production from different feedstocks wood and oat hulls (Binder et al., 2010), corncob and bagasse (Nhien et al., 2016), and baru (*Dipteryx alata*) residue (Rambo et al., 2020). Binder et al. (2010) suggested furfural produced from *xylose* as an alternative to petrochemicals for reducing the environmental impacts. They also studied the use of Lewis acids to improve furfural yields. Nhien et al. (2016) studied furfural production from corncob and bagasse, using hydrolysis, and reported that environmental and economic objectives are not mutually exclusive, and the optimization of heat integration and process intensity can fulfill both aspects. Rambo et al. (2020) studied the sustainability of furfural production from baru residues, using pyrolysis technology, reporting that baru could be a good source for furfural production due to high process yield and low moisture content.
- *Techno-economic assessment (TEA).* Several studies have conducted cost analysis for furfural production from biomass feedstocks in Netherlands (Kühnel et al., 2011), South Korea (Nhien et al., 2016), India (Chandel et al., 2018), and Argentina (Casoni et al., 2018). Kühnel et al. (2011) reported that biochemical processing of SBP for furfural production could be economically viable. Silva et al. (2017) performed an economic analysis on furfural production from sugarcane bagasse, using a Rosenlew reactor, which had lower energy demands than conventional distillation processes. Casoni et al. (2018) conducted a techno-economic study for furfural production from sunflower seed hulls, and found that the price of levoglucosenone, a co-product of furfural during pyrolysis reactions, was the key variable in determining profitability. Chandel et al. (2018) studied lignocellulose biorefinery technologies, including furfural production from agricultural and forestry residues. They resulted that the furfural industry is in a nascent stage, requiring further technological advancements to be truly economically viable. (Gómez Millán et al., 2020) performed a TEA for furfural production using hydrolysis technology, and reported a 5 year return on investment.
- *Pyrolysis process.* Pyrolysis is a thermochemical process for converting biomass to intermediate products (i.e., pyrolysis oil, char, and gas) in the absence of oxygen under 400-600°C and 15-20

psi (Hersh and Mirkouei, 2019). One of the main parameters for cost reduction is conversion processes yield, and Mao et al. (2012) found that furfural yield dropped significantly as temperatures rose to above 190°C. Pyrolysis technology can be used in conjunction with H<sub>2</sub>SO<sub>4</sub> to fully utilize biomass feedstocks for furfural production. Santos et al. (2018) reported a 64% process yield for furfural production with pyrolysis technology. Cao et al. (2020) reported that pretreatment with 3% H<sub>2</sub>SO<sub>4</sub> solution (by weight) allows reducing the temperature of pyrolysis process (from 500°C to 300°C), and subsequently reduce the production cost.

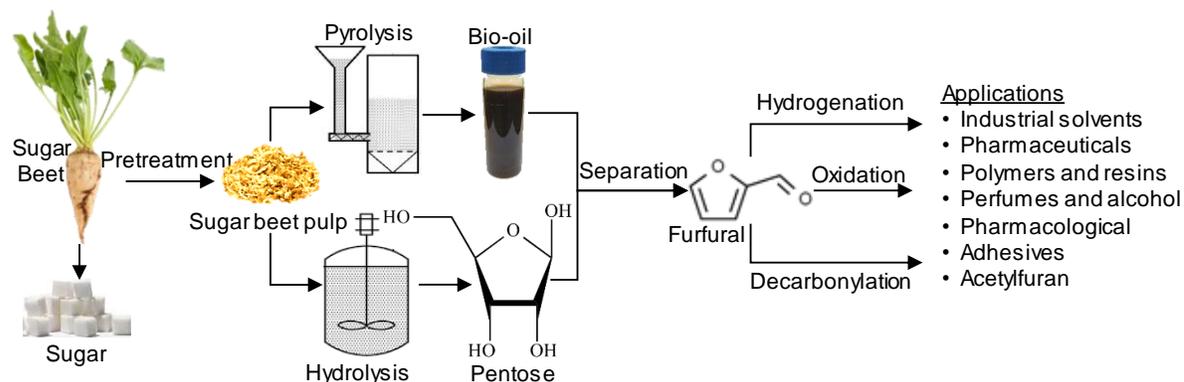
- *Hydrolysis process.* Hydrolysis is a chemical process where hot water or steam is used to extract furfural directly from biomass feedstocks (Cieciura-Włoch et al., 2019). Mao et al. (2012) found that furfural yields were increased by using ferric chloride (FeCl<sub>3</sub>) and acetic acid (CH<sub>3</sub>COOH) to aid in the hydrolysis of corn husks. Liu et al. (2014) reported that Lewis acids (e.g., FeCl<sub>3</sub> or AlCl<sub>3</sub>) could be effective catalysts for furfural production, however, recycling chemical hazard wastes (e.g., acids) remain the main environmental challenges. Nhien et al. (2016) conducted a design and optimization study, and resulted that optimizing the distillation process can reduce the energy consumption and cost of furfural production. Kamzon and Abderafi (2017) compared the hydrolysis yields of SBP with bagasse, and resulted that SBP can produce marginally greater yields of furfural and other desirable chemicals. Cieciura-Włoch et al. (2019) studied furfural production from SBP by employing hydrolysis process and applying dilute solutions of H<sub>2</sub>SO<sub>4</sub> or hydrochloric acid (HCl). They reported approximately 65% process yields, although lower temperatures were required for maximum yield when HCl pretreatment was used.

**Table 3-1 Recent economic and environmental studies on furfural production from biomass feedstocks**

Study	Objectives		Product	Technology		Resource
	Environmental	Economic	Furfural	Pyrolysis	Hydrolysis	
(Binder et al., 2010)	✓	×	✓	×	✓	Wood & oat hulls
(Kühnel et al., 2011)	×	✓	✓	×	✓	SBP
(Mao et al., 2012)	×	×	✓	×	✓	Corn cobs
(Liu et al., 2014)	×	×	✓	×	✓	Wheat straw
(Nhien et al., 2016)	✓	✓	✓	×	✓	Corn cob & bagasse
(Wang et al., 2016)	✓	×	✓	✓	×	Corn Stalk
(Mariscal et al., 2016)	×	×	✓	×	×	-
(Kamzon and Abderafi, 2017)	×	×	✓	×	✓	SBP & bagasse
(Silva et al., 2017)	×	✓	✓	×	×	Bagasse
(Chandel et al., 2018)	×	✓	✓	✓	×	Forest/agricultural residues
(Kim et al., 2019)	✓	×	✓	✓	×	Goat excreta
(Poomsawat et al., 2019)	×	×	✓	×	✓	Water hyacinth
(Cieciura-Włoch et al., 2019)	×	×	✓	×	✓	SBP
(Hossain et al., 2019)	×	✓	✓	✓	×	Corn Stover
(Cao et al., 2020)	×	×	✓	✓	×	Corn husks
(Rodríguez Montaña)	×	×	✓	×	×	-

et al., 2020)						
(Rambo et al., 2020)	✓	×	✓	×	✓	Baru
(Gómez Millán et al., 2020)	×	✓	✓	×	✓	Birch
(Zang et al., 2020)	×	✓	✓	×	✓	Switchgrass
This Study	✓	✓	✓	✓	✓	SBP

*Objectives.* The main contributions of this study are: (i) the proposed multi-objective decision making framework, including TEA and LCA studies to compare pyrolysis and hydrolysis pathways for furfural production from SBP (Figure 3-1), (ii) the integrated sustainability ideology and technological aspects to explore the commercial feasibility of furfural production, using mixed-mode (i.e., portable and fixed) conversion technologies, and (iii) the presented case study in southern Idaho, USA for demonstrating the application of the methodology and verifying the models. The decision making framework evaluates the use of portable pyrolysis refinery units to convert SBP to intermediate products (e.g., bio-oil and biochar) on-site and transfer high-energy density products to upgrading facilities that can alleviate transferring low-energy density SBP. LCA and TEA studies conducted herein evaluate global warming potential (GWP) and total cost of SBP-to-furfural production, including collection, grinding, drying, conversion, storage, and transportation. The multi-objective decision making framework investigates optimal solutions that can simultaneously minimize the total cost and environmental impacts. Ultimately, the case study examines the sustainability benefits of the conversion pathways in regions with high production volumes of SBP.

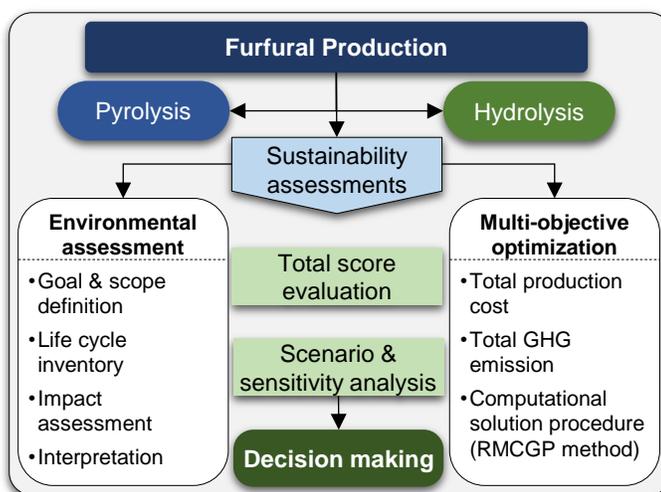


**Figure 3-1 Furfural production from sugar beet pulp, using pyrolysis and hydrolysis technologies (Danon et al., 2014; Mao et al., 2012)**

### 3.3. Materials and Methodology

This study compares the market opportunity and sustainability benefits of furfural production from SBP, employing either hydrolysis or pyrolysis conversion pathways. The developed methodology in this study includes LCA for environmental impacts analysis and mathematical optimization modeling for TEA to evaluate GHG emissions and total cost of furfural production (Fig.

3-2). For comparison purposes, both conversion pathways encompass four steps: collection/transportation, pretreatment, conversion, and separation. SBPs are collected and transported either to the portable pyrolysis refinery unit near the collection site or to hydrolysis refinery facility. Pretreatment operations include two steps for pyrolysis process: (i) size reduction, using a grinder and (ii) drying, using a rotary drier, along with pyrolysis char and gas that are byproducts of pyrolysis process. For hydrolysis, pretreatment includes only grinding operations. After pretreatment, the intermediate products of pyrolysis process are transported to either bio-oil upgrading facility for furfural production or biochar distribution center. Particularly, pretreatment and conversion operations are on-site for pyrolysis pathway, however, all operations (pretreatment, conversion, and separation) are in the separation facility for hydrolysis pathway.

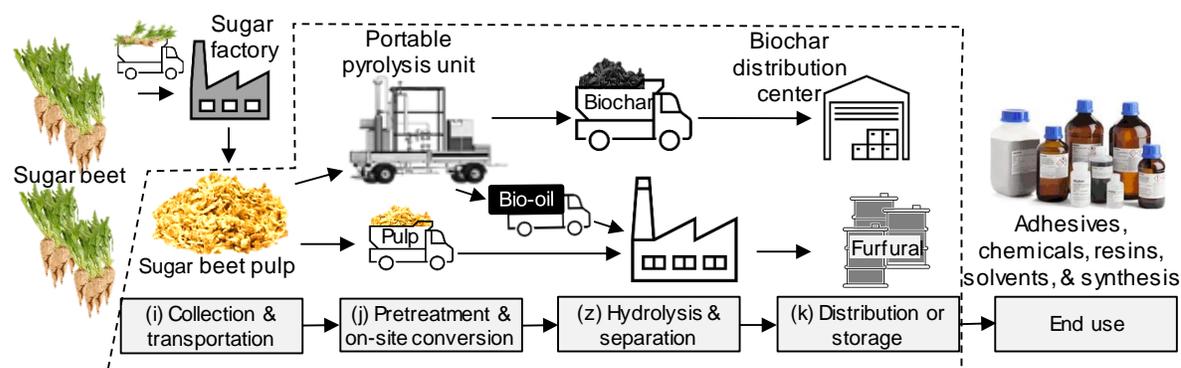


**Figure 3-2 Multi-objective decision making framework for sustainability assessments**

### 3.3.1. *Environmental impacts assessment*

This study investigates GHG emissions (i.e., CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O) and global warming potentials for a 100-year time horizon (GWP<sub>100</sub>), which considers the potential global warming impact relative to CO<sub>2</sub> over a specified interval (US Environmental Protection Agency, 2017). Particularly, different gases degrade at different rates, so the time allowed is a significant consideration. GWP of CO<sub>2</sub> for any time horizon is one, and GWP<sub>100</sub> of N<sub>2</sub>O is approximately 265, while GWP<sub>100</sub> of CH<sub>4</sub> is reported between 28 and 36 (IPCC, 2007). In other words, 1kg of N<sub>2</sub>O in the atmosphere has a 100-year impact on global warming as 265kg CO<sub>2</sub> eq./kg N<sub>2</sub>O; thus, GWP<sub>100</sub> of N<sub>2</sub>O is 265. LCA conducted herein includes four phases: goal and scope definition, life cycle inventory, life cycle impacts assessment, and interpretation, which are described below.

*Goal and scope definition.* Environmental impacts of furfural production from SBP via pyrolysis pathway need to be explored in comparison with hydrolysis pathway. The general scope of this study for both hydrolysis and pyrolysis pathways encompasses two main segments and several operations: (i) upstream segment, including SBP collection and transportation; and (ii) midstream segment, involving pretreatment, conversion (hydrolysis or pyrolysis), and separation, and storage. The above-described scope considers a gate-to-gate system boundary, and for both pathways, the functional unit is set as one metric ton of furfural (Fig. 3).



**Figure 3-3 A gate-to-gate system boundary (dotted line) for SBP to furfural life cycle assessment**

*Life cycle inventory.* To accurately evaluate the SBP-based furfural production, data was obtained from multiple studies and reports (EPA, 2014; Nugent and Oliver, 2009; OpenLCA, 2019). Equipment used for SBP collection includes a loader and single-trailer truck. For pyrolysis pathway, the upstream inputs are SBP, diesel-based energy, and lubricants required by the machinery, and the outputs are GHG emissions from collecting and hauling of SBP to portable pyrolysis units, located 10 km away from the sugar factory. The midstream operations start by loading SBP to an on-site grinder and then into a dryer for pretreatment purposes. Pretreatment inputs are raw SBP and diesel-based energy, and outputs are ground/dried SBP and GHG emissions from water vapor and fuel combustion. After pretreatment, dried SBP enters the portable pyrolysis unit, requiring  $N_2$  and heat. Electricity is produced by a diesel generator. Pyrolysis inputs are pretreated SBP, nitrogen, and diesel to produce electricity, while outputs consist of biochar, bio-oil, pyrolysis gas, as well as emissions from pyrolysis and diesel combustion. The produced biochar and pyrolysis gas is used for drying, and the rest is transferred to the distribution center, using diesel trailer trucks. The produced bio-oil is transported by diesel tanker trucks to a separation facility. Separation inputs are bio-oil, polyurethane, and electricity for furfural extraction and separation, and outputs are furfural and chemical wastes, as well as emissions. Hydrolysis pathway is modeled with a collection phase similar to pyrolysis, with SBP transported by diesel trailer trucks to hydrolysis conversion and separation facilities. SBP pretreatment requires only grinding and occurs in the same manner as modeled for pyrolysis. After

grinding, SBP enters the conversion stage, which requires water, heat, and sulfuric acid. Energy is generated by a diesel generator. After conversion, furfural is separated from the collected slurry before being stored.

*Life cycle impact assessment.* Impact analysis of competing product systems is performed using data from the case study in the Magic Valley region of southern Idaho. Pyrolysis and hydrolysis conversion pathways are converted to a product system, using OpenLCA (an open-source LCA software). Life cycle impacts assessment was conducted using the CML-IA baseline method, created by the University of Leiden (version 1.5.5) and Eqs. (3-1)-(3-16).

- *For pyrolysis pathway.* Total upstream (collection and transportation) emission factors and GWP are calculated, using Eqs. (3-1) and (3-2). Midstream (grinding, drying, and pyrolysis) emission factors and GWP for biochar and bio-oil production are calculated, using Eqs. (3-3) and (3-4). Biochar and bio-oil transportation emission factors and GWP are calculated, using Eqs. (3-5)-(3-8). Separation emission factors and GWP for furfural production are calculated, using Eqs. (3-9) and (3-10).

$$\Pi_{up} = R_{CO2} \times \Pi_{up,CO2} + R_{CH4} \times \Pi_{up,CH4} + R_{N2O} \times \Pi_{up,N2O} \quad (3-1)$$

$$GWP_{up} = M_{beet} \times \Pi_{up} \quad (3-2)$$

$$\Pi_{mid} = R_{CO2} \times \Pi_{mid,CO2} + R_{CH4} \times \Pi_{mid,CH4} + R_{N2O} \times \Pi_{mid,N2O} \quad (3-3)$$

$$GWP_{mid} = M_{beet} \times \Pi_{mid} \quad (3-4)$$

$$\Pi_{trans-char} = R_{CO2} \times \Pi_{trans-char,CO2} + R_{CH4} \times \Pi_{trans-char,CH4} + R_{N2O} \times \Pi_{trans-char,N2O} \quad (3-5)$$

$$GWP_{trans-char} = M_{char} \times \Pi_{trans-char} \times D \quad (3-6)$$

$$\Pi_{trans-oil} = R_{CO2} \times \Pi_{trans-oil,CO2} + R_{CH4} \times \Pi_{trans-oil,CH4} + R_{N2O} \times \Pi_{trans-oil,N2O} \quad (3-7)$$

$$GWP_{trans-oil} = M_{oil} \times \Pi_{trans-oil} \times D \quad (3-8)$$

$$\Pi_{sep} = R_{CO2} \times \Pi_{sep,CO2} + R_{CH4} \times \Pi_{sep,CH4} + R_{N2O} \times \Pi_{sep,N2O} \quad (3-9)$$

$$GWP_{sep} = M_{oil} \times \Pi_{sep} \quad (3-10)$$

- *For hydrolysis pathway.* Total upstream (collection and transportation) emission factors and GWP are calculated, using Eqs. (3-11) and (3-12). Midstream (grinding and hydrolysis) emission factors and GWP for pentose (C<sub>5</sub>H<sub>10</sub>O<sub>5</sub>) production are calculated, using Eqs. (3-13) and (3-14). Separation emission factors and GWP for furfural production are calculated, using Eqs. (3-15) and (3-16).

$$\Pi_{up} = R_{CO2} \times \Pi_{up,CO2} + R_{CH4} \times \Pi_{up,CH4} + R_{N2O} \times \Pi_{up,N2O} \quad (3-11)$$

$$GWP_{up} = M_{beet} \times \Pi_{up} \quad (3-12)$$

$$\Pi_{mid} = R_{CO2} \times \Pi_{mid,CO2} + R_{CH4} \times \Pi_{mid,CH4} + R_{N2O} \times \Pi_{mid,N2O} \quad (3-13)$$

$$GWP_{mid} = M_{beet} \times \Pi_{mid} \quad (3-14)$$

$$\Pi_{sep} = R_{CO2} \times \Pi_{sep,CO2} + R_{CH4} \times \Pi_{sep,CH4} + R_{N2O} \times \Pi_{sep,N2O} \quad (3-15)$$

$$GWP_{sep} = M_{pentose} \times \Pi_{sep} \quad (3-16)$$

*Interpretation.* GWP<sub>100</sub> (CO<sub>2</sub> eq. emissions) and water usage for pyrolysis and hydrolysis are the main environmental impacts that are studied herein. The provided information and results of the defined pathways help to identify the key factors for sustainable furfural production from various biomass feedstocks. Sensitivity and Pareto analyses were performed to compare the results through the lens of sustainability. GHG emissions from SBP-based products (e.g., bio-oil and biochar) are considered as part of the natural cycle (biogenic) that will be absorbed by new feedstocks. The largest contributor of GWP for both hydrolysis and pyrolysis product systems is the conversion process.

### 3.3.2. Techno-economic and multi-objective assessments

A multi-objective optimization model is formulated to explore the market opportunities for SBP-based furfural commercialization. The objective functions, Eqs. (3-17) and (3-18), aim to minimize the total cost (TC) and total GHG emissions (TGHG), respectively, for four main steps (i.e., collection/transportation, pretreatment, conversion, and separation) over a specific time horizon. Total cost includes operational and capital costs (e.g., materials, labors, and equipment) for each step. Notations of model parameters and variables are provided in the Nomenclature section.

- *Total cost for pyrolysis pathway.* The transportation activities involved in the pyrolysis process consist of delivering SBP from the collection sites ( $i$ ) to the portable refineries ( $j$ ), delivering biochar from the portable refineries to the distribution centers ( $k$ ), as well as delivering bio-oil from the portable refineries to bio-oil storage at a separation center ( $z$ ). Additionally, the costs account for establishing and operating the portable refineries, separation centers, as well as biochar and furfural storage facilities. The total cost for furfural production through pyrolysis pathway is calculated, using Eq. (3-17).

$$\text{Min } TC = C_1 + C_2 + C_3 + C_4 + C_5 \quad (3-17)$$

$$\text{Collection and transportation cost } (C_1) = \sum_i \sum_j \sum_t y_{beet_{ijt}} \times dis_{cr_{ij}} \times CCR \quad (3-17a)$$

$$\text{Pyrolysis cost } (C_2) = \sum_j x_{r_j} \times CFR + \sum_i \sum_j \sum_t y_{beet_{ijt}} \times CVR \quad (3-17b)$$

$$\begin{aligned} \text{Transportation cost } (C_3) \\ = \sum_j \sum_k \sum_t y_{char_{jkt}} \times dis_{rd_{jk}} \times CRD + \sum_j \sum_z \sum_t y_{oil_{jzt}} \times dis_{rs_{jz}} \times CRS \end{aligned} \quad (3-17c)$$

$$\text{Separation cost } (C_4) = \sum_z x_{s_z} \times CFS + \sum_j \sum_z \sum_t y_{oil_{jzt}} \times CVS \quad (3-17d)$$

$$\text{Storage cost } (C_5) = \sum_j \sum_k \sum_t y_{char_{jkt}} \times CS_{char} + \sum_z \sum_t y_{fur_{zt}} \times CS_{fur} \quad (3-17e)$$

- *Total GHG emission for pyrolysis pathway.* The total emissions for furfural production through pyrolysis pathway is calculated, using Eq. (3-18).

$$\text{Min TGHG} = GWP_{up} + GWP_{mid} + GWP_{trans\_char} + GWP_{trans\_oil} + GWP_{sep} \quad (3-18)$$

$$\text{Upstream emission } (GWP_{up}) = \sum_i \sum_j \sum_t y_{beet_{ijt}} \times \eta_{up} \quad (3-18a)$$

$$\text{Midstream emission } (GWP_{mid}) = \sum_i \sum_j \sum_t y_{beet_{ijt}} \times \eta_{mid} \quad (3-18b)$$

$$\text{Char transportation emission } (GWP_{trans\_char}) = \sum_j \sum_k \sum_t y_{char_{jkt}} \times dis_{rd_{jk}} \times \eta_{trans\_char} \quad (3-18c)$$

$$\text{Oil transportation emission } (GWP_{trans\_oil}) = \sum_j \sum_z \sum_t y_{oil_{jzt}} \times dis_{rs_{jz}} \times \eta_{trans\_oil} \quad (3-18d)$$

$$\text{Separation emission } (GWP_{sep}) = \sum_j \sum_z \sum_t y_{oil_{jzt}} \times \eta_{sep} \quad (3-18e)$$

**Model constraints.** The model encompasses capacity, flow conservation, structure, non-negativity, and binary constraints. Capacity constraints (Eqs. (3-19)-(3-21)) ensure that the portable refinery, distribution center, and separation center have sufficient capacity to convert the SBP to bio-oil, store biochar, and convert bio-oil to furfural. Equations (3-22) and (3-23) ensure that only specific amounts of SBP (determined by conversion yields,  $\alpha$  and  $\beta$ ), can be transformed into biochar and bio-oil, respectively. Equation (3-24) ensures that only a specific amount of bio-oil (determined by conversion yield,  $\gamma$ ), can be transformed into furfural. Equation (3-25) presents the annual available SBP to be processed. Equations (3-26) and (3-27) ensure that the flow of SBP from collection centers is possible to the portable refinery unit when the selected refinery is operating, and the flow of bio-oil from refineries is possible to the separation center when the selected separation center is operating. Equations (3-28) and (3-29) are the non-negative and binary constraints, respectively.

*Subject to:*

$$\sum_{i \in I} y_{beet_{ijt}} \leq Cap_{R_j} \quad \forall_j \in J, \forall_t \in T \quad (3-19)$$

$$\sum_{j \in J} y_{char_{jkt}} \leq Cap_{D_k} \quad \forall_k \in K, \forall_t \in T \quad (3-20)$$

$$\sum_{j \in J} y_{oil_{jzt}} \leq Cap_{S_z} \quad \forall_z \in Z, \forall_t \in T \quad (3-21)$$

$$\alpha \times \sum_{i \in I} y_{beet_{ijt}} - \sum_{k \in K} y_{char_{jkt}} = 0 \quad \forall_j \in J, \forall_t \in T \quad (3-22)$$

$$\beta \times \sum_{i \in I} y_{beet_{ijt}} - \sum_{z \in Z} y_{oil_{jzt}} = 0 \quad \forall_j \in J, \forall_t \in T \quad (3-23)$$

$$\gamma \times \sum_{j \in J} y_{oil_{jzt}} - y_{fur_{zt}} = 0 \quad \forall_z \in Z, \forall_t \in T \quad (3-24)$$

$$\sum_{i \in I} \sum_{j \in J} y_{beet_{ijt}} \geq \theta_t \quad \forall_t \in T \quad (3-25)$$

$$\sum_{i \in I} y_{beet_{ijt}} \leq M \times x_{rj} \quad \forall_j \in J, \forall_t \in T \quad (3-26)$$

$$\sum_{j \in J} y_{oil_{jzt}} \leq M \times x_{sz} \quad \forall_z \in Z, \forall_t \in T \quad (3-27)$$

$$y_{beet_{ijt}}, y_{oil_{jzt}}, y_{char_{jkt}}, y_{fur_{zt}} \geq 0 \quad \forall_i \in I, \forall_j \in J, \forall_k \in K, \forall_z \in Z, \forall_t \in T \quad (3-28)$$

$$x_{rj}, x_{sz} \in \{0, 1\} \quad \forall_j \in J, \forall_z \in Z \quad (3-29)$$

- *Total cost for hydrolysis pathway.* The collection and transportation activities involved in the hydrolysis process consist of delivering SBP from the collection sites ( $i$ ) to hydrolysis and separation centers ( $z$ ). The total cost for furfural production through hydrolysis pathway is calculated, using Eq. (3-30), including SBP collection/transportation, hydrolysis, separation, and furfural storage. It is assumed that the produced furfural will be held in storage adjacent to the separation center.

$$Min TC = C_1 + C_2 + C_3 + C_4 \quad (3-30)$$

$$Collection \text{ and } transportt \text{ ion } Cost (C_1) = \sum_i \sum_z \sum_t y_{beet_{izt}} \times dis_{ch_{iz}} \times CCH \quad (3-30)$$

$$Hydrolysis \text{ cost } (C_2) = \sum_z x_{h_z} \times CFH + \sum_i \sum_z \sum_t y_{beet_{izt}} \times CVH \quad (3-30b)$$

$$Separation \text{ cost } (C_3) = \sum_z \sum_t y_{pentose_{zt}} \times CVS \quad (3-30)$$

$$Storage \text{ cost } (C_4) = \sum_z \sum_t y_{fur_{zt}} \times CS_{fur} \quad (3-30d)$$

- *Total GHG emission for hydrolysis pathway.* The total emissions for furfural production through hydrolysis pathway is calculated, using Eq. (3-31).

$$Min TGHG = GWP_{up} + GWP_{mid} + GWP_{sep} \quad (31)$$

$$Upstream \text{ emission } (GWP_{up}) = \sum_i \sum_z \sum_t y_{beet_{izt}} \times \eta_{up} \quad (31-a)$$

$$Midstream \text{ emission } (GWP_{mid}) = \sum_i \sum_z \sum_t y_{beet_{izt}} \times \eta_{mid} \quad (31-b)$$

$$Separation \text{ emission } (GHG_{sep}) = \sum_z \sum_t y_{pentose_{zt}} \times \eta_{sep} \quad (31-c)$$

- *Model constraints.* Capacity constraint (Eq. (3-32)) ensures that the hydrolysis facility has sufficient capacity to store the SBP. Equations (3-33) ensures that only specific amounts of SBP (determined by percentage yield,  $\delta$ ), can be transformed to pentose. Equation (3-34) ensures that

only a specific amount of pentose (determined by percentage yield,  $\rho$ ), can be transformed into furfural. Annual available SBP to be processed is shown by Equation (3-35). Equation (3-36) ensures that the flow of SBP from collection sites is possible to the hydrolysis facility when the selected hydrolysis facility is operating. Equations (3-37) and (3-38) are the non-negative constraint and the binary constraint, respectively.

$$\text{Subject to:} \\ \sum_{i \in I} y_{beet_{izt}} \leq Cap_{H_z} \quad \forall_z \in Z, \forall_t \in T \quad (32)$$

$$\delta \cdot \sum_{i \in I} y_{beet_{izt}} - y_{pentose_{zt}} = 0 \quad \forall_z \in Z, \forall_t \in T \quad (3-33)$$

$$\rho \cdot y_{pentose_{zt}} - y_{fur_{zt}} = 0 \quad \forall_z \in Z, \forall_t \in T \quad (3-34)$$

$$\sum_{i \in I} \sum_{z \in Z} y_{beet_{izt}} \geq \theta_t \quad \forall_t \in T \quad (3-35)$$

$$\sum_{i \in I} y_{beet_{izt}} \leq M \times x_{h_z} \quad \forall_z \in Z, \forall_t \in T \quad (3-36)$$

$$y_{beet_{izt}}, y_{pentose_{zt}}, y_{fur_{zt}} \geq 0 \quad \forall_i \in I, \forall_z \in Z, \forall_t \in T \quad (3-37)$$

$$x_{h_z} \in \{0, 1\} \quad \forall_z \in Z \quad (3-38)$$

- The developed TC and TGHG models are combined to develop a multi-objective mixed-integer linear programming model for pyrolysis and hydrolysis pathways. Due to the complexity of the mixed models, a revised multi-choice goal programming (RMCGP) method is applied for finding the desired solutions for enhancing sustainability benefits, as presented in Eq. (3-40) along with the model constraints Eqs, (3-41)-(3-47) (Chang, 2008).

$$\text{Min } W_1(d_1^+ + d_1^-) + a_1(e_1^+ + e_1^-) + W_2(d_2^+ + d_2^-) + a_2(e_2^+ + e_2^-) \quad (3-40)$$

Subject to:

Pyrolysis process constraints (Eqs. (3-19)-(3-29)) or hydrolysis process constraints (Eqs. (3-32)-(3-38))

And

$$TC - d_1^+ + d_1^- = y_1 \quad (3-41)$$

$$y_1 - e_1^+ + e_1^- = g_{1.min} \quad (3-42)$$

$$g_{1.min} \leq y_1 \leq g_{1.max} \quad (3-43)$$

$$TGHG - d_2^+ + d_2^- = y_2 \quad (3-44)$$

$$y_2 - e_2^+ + e_2^- = g_{2.min} \quad (3-45)$$

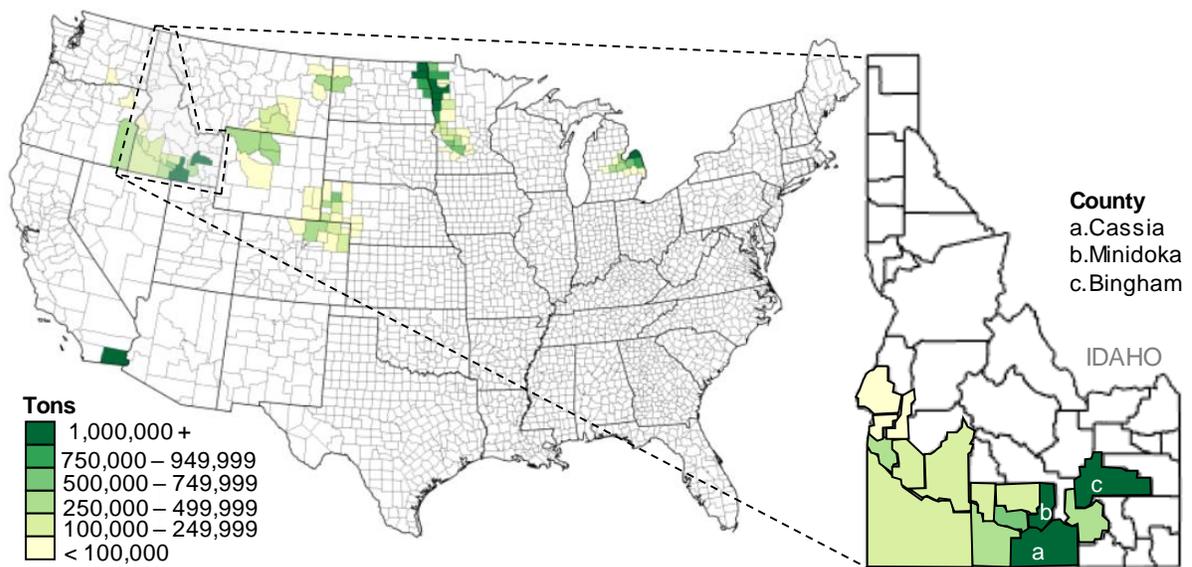
$$g_{2.min} \leq y_2 \leq g_{2.max} \quad (3-46)$$

$$d_1^+, d_1^-, d_2^+, d_2^-, e_1^+, e_1^-, e_2^+, e_2^- \geq 0 \quad (3-47)$$

where  $d_1^+$  and  $d_1^-$  are positive and negative deviation variables for  $TC$ ;  $d_2^+$  and  $d_2^-$  are positive and negative deviation variables for  $TGHG$ ;  $e_1^+$  and  $e_1^-$  are positive and negative deviations from  $|y_1 - g_{1.min}|$ ;  $e_2^+$  and  $e_2^-$  are positive and negative deviations from  $|y_2 - g_{2.min}|$ ; Equations (3-40) emphasize on finding a solution near the aspiration level for each objective and penalize the deviation away from the aspiration level. The details of RMCGP method and computational solution procedure (LINGO codes) can be found in Supplementary Materials.

### 3.4. Case Study

Recent studies from the U.S. Department of Agriculture (USDA) reported that the state of Idaho is second in sugar beet production (after the state of Minnesota), producing approximately 6.5 million tons of sugar beets annually, with over 170,000 acres cultivated (USDA, 2020). Cassia, Minidoka, and Bingham counties in southern Idaho produce over 58% of the state's production (Fig. 3-4). A real case study was conducted for furfural production from SBP in southern Idaho to compare the different production pathways, verify the models, and demonstrate the application of the proposed methodology.

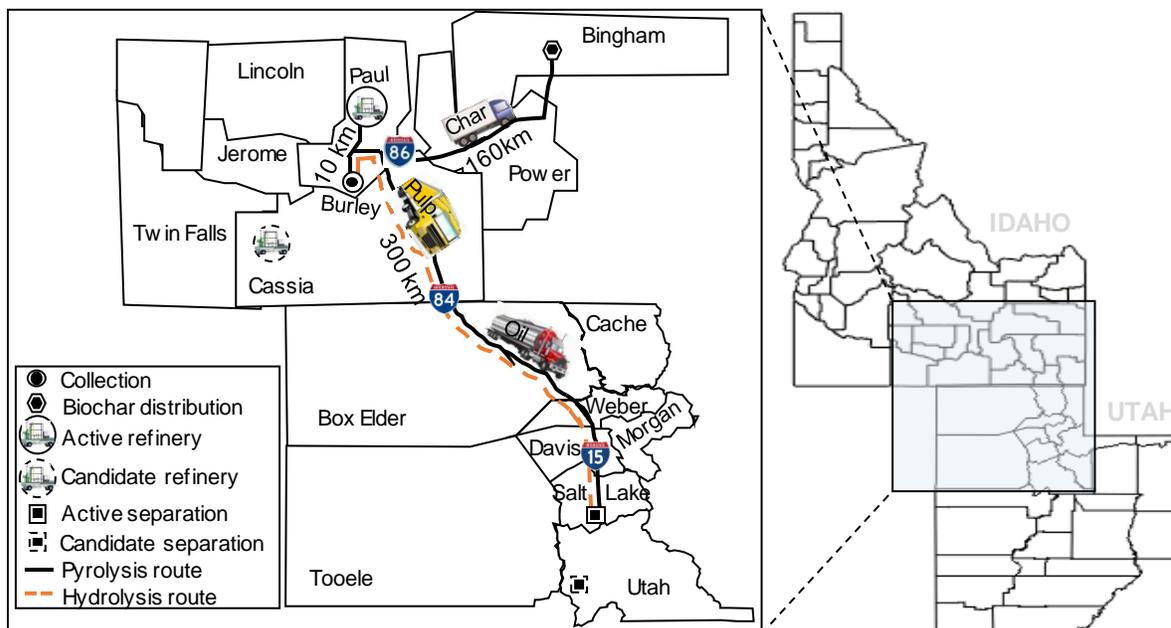


**Figure 3-4 Sugar beets production by state and county in the United States (left) and three main Idaho counties (a, b, and c) with over 1 million tons of sugar beets, considered in our case study (USDA, 2018)**

The following assumptions are made, using data from prior studies and USDA reports (Fig. 3-5):

- The time horizon in this study is one year.
- The type of equipment and tools (e.g., portable refinery, grinder, dryer, and loader) are known and assumed to have an effective lifetime of 10 years.
- All dollar amounts used in this paper are U.S. dollars (USD).
- Diesel is considered for SBP, bio-oil, and biochar transportation.
- On-site grinding is considered for SBP size reduction, using a grinder and diesel for both pyrolysis and hydrolysis pathways.
- Loader, grinder, dryer utilization rates for collection, sized reduction, and drying are 60,000, 37,500, and 40,000 tons per year, respectively (Struhs et al., 2020).
- SBP has 70-90 wt% moisture content (Hueze et al., 2019).
- Pyrolysis process requires drying, however, hydrolysis process doesn't require drying.
- Energy demand for drying is assumed approximately 9kWh per 100kg of wet SBP (Kudra and Mujumdar, 2009).
- Pyrolysis conversion process requires 0.93kg of N<sub>2</sub>, and the yields for biochar, bio-oil, and syngas are assumed 30%, 55%, and 15%, respectively (Struhs et al. 2020).
- This study assumes that GWP<sub>100</sub> value for CH<sub>4</sub> is 28, and the GWP<sub>100</sub> of N<sub>2</sub>O is 265 (IPCC, 2007).
- Pyrolysis refinery unit is assumed to have 50 dry tons capacity per day, and works 328 days for 12 hours per day (Mirkouei et al., 2017; Struhs et al., 2020).
- During hydrolysis process, 1kg of SBP is treated with 5kg of water and 0.005kg H<sub>2</sub>SO<sub>4</sub> at a temperature of 180°C (Cieciura-Włoch et al., 2019).
- Hydrolysis process is assumed to have 20g furfural yield per 1kg of wet SBP that enters into the hydrolyzer (Cieciura-Włoch et al., 2019).
- Pyrolysis pathway is assumed to have 77g furfural yield per 1kg of dried SBP that enters into the pyrolyzer (Hersh and Mirkouei, 2019).
- After processing at the portable refinery site in Paul, Idaho, bio-oil is transported by tanker trucks to the separation sites in Salt Lake City, Utah. The on-way distance is assumed 300km (ArcGIS 2019).
- Biochar is transported to Bingham distribution center, Idaho, and the one-way distance is assumed 160km (ArcGIS 2019).
- Pretreated SBP transported to the hydrolysis site in Salt Lake City, Utah, and the one-way distance is assumed 300km (ArcGIS 2019).

- Separation of furfural from water occurs through polyurethane membrane technology (Ghosh et al., 2007).
- Approximately 6 million metric tons of SBP are available annually in southern Idaho (Table 3-2).
- This study does not consider GHG emissions from chemical wastes.
- This study does not consider sustainability benefits of biochar in economic and environmental performance of furfural production.



**Figure 3-5 Shortest paths between collection, portable refinery, separation, and distribution sites**

**Table 3-2 List of sugar beet processing facilities in southern Idaho (Amalgamated Sugar, 2020)**

Address	Sugar Beet Processed Daily US tons (metric tons)
50 S 500 W, Paul, ID, 83347	17,000 (15,419)
138 W Karcher Rd, Nampa, ID, 83687	12,000 (10,884)
2320 Orchard Dr. E, Twin Falls, ID 83301	6,800 (6,168)

### 3.5. Results, Sensitivity Analysis, and Discussion

Several studies investigated various feedstocks, including SBP (Cieciura-Wloch et al., 2019), water hyacinth (Poomsawat et al., 2019), and corncobs (Nhien et al., 2016) for furfural production. Production parameters have also been studied, including temperature (Mao et al., 2012), and the use of CO<sub>2</sub> (Kim et al., 2019) or acid (Binder et al., 2010) to improve yield.

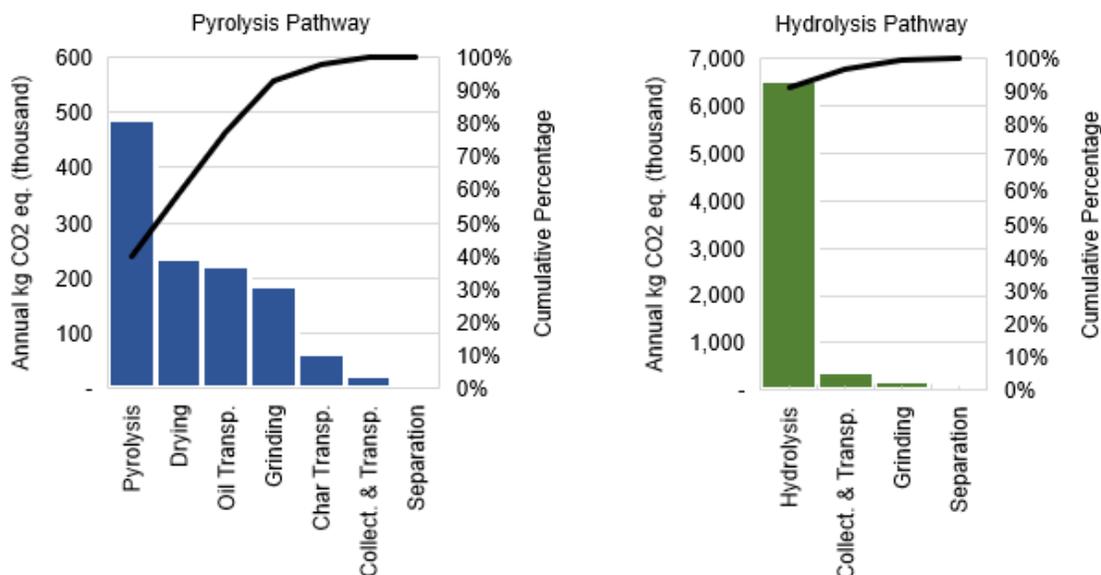
### 3.5.1. Environmental assessment results

Pyrolysis and hydrolysis pathways result in 267 and 1,095 kg of CO<sub>2</sub> eq., respectively, for producing a ton furfural. Additionally, hydrolysis process requires approximately 21,000 kg of water, whereas pyrolysis does not require extra water. This study does not consider the agricultural requirements for sugar beet production. Table 3-3 presents and compares the results of both pyrolysis and hydrolysis pathways, using the data from OpenLCA 1.8 and prior published studies, as well as defined assumptions from the proposed Idaho case study.

**Table 3-3 Total emissions for one metric ton furfural production from SBP**

Pathway Process	Pyrolysis (kg)				Hydrolysis (kg)			
	CO <sub>2</sub>	N <sub>2</sub> O (10 <sup>-5</sup> )	CH <sub>4</sub> (10 <sup>-4</sup> )	GWP	CO <sub>2</sub>	N <sub>2</sub> O (10 <sup>-5</sup> )	CH <sub>4</sub> (10 <sup>-4</sup> )	GWP
Collection	5.0	3.9	2.0	5.0	61.4	48.7	251.6	62.2
Grinding	40.8	32.0	16.4	41.0	28.6	22.4	117.2	29.0
Drying	51.4	40.3	20.6	51.6	—	—	—	—
Conversion	106.0	82.9	42.5	106.0	985.3	772.0	403.9	998.6
Oil transportation	48.2	37.8	19.4	48.4	—	—	—	—
Char transportation	14.0	1.1	5.6	14.1	—	—	—	—
Separation	0.7	0.5	0.3	0.7	5.2	4.1	21.5	5.31
Total	266	210	107	267	1,080	847	794	1,095

Pareto analysis is utilized for analyzing the overall GHG emission (kg CO<sub>2</sub> eq.) of each process within pyrolysis and hydrolysis pathways, and comparing the environmental impacts across SBP-to-furfural life cycle system (Fig. 3-6). Pareto analysis follows the 80/20 principle in that 20% of causes (processes) are responsible for 80% of problems (emissions). Even in cases where the data doesn't strictly follow the rule, the analysis can be informative.



**Figure 3-6 Pareto analysis of the impacts of each SBP-based furfural production process on the environment**

### 3.5.2. *Techno-economic and multi-objective assessment results*

To solve the developed mixed integer programming models, LINGO 9 software package is used, a well-developed software for solving linear and non-linear goal programming models (Paydar and Saidi-Mehrabad, 2015). The optimal solutions for the multi-objective model are obtained after solving eight cost and emission sub-problems for pyrolysis and hydrolysis pathways. In the main case study over a one-year time horizon, the pyrolysis pathway can convert 32,800 tons of SBP to 9,840, 18,040, and 4,592 tons of biochar, bio-oil, and furfural, respectively. The total annual cost and unit furfural cost, using two portable refinery units are estimated at \$3,885,554 per year and \$846 per metric ton, respectively. Table 3-4 presents the capital and operational costs of each point and process. Operational costs cover approximately 60% of the total cost. Particularly, the major operational cost drivers are drying (\$797,160/yr) and grinding (\$590,231/yr), as well as bio-oil/biochar transportation. Additionally, the major capital cost drivers are production (conversion and separation) processes. It is possible to reduce the drying cost if SBP is allowed to dry naturally in the field before mechanical drying or if pyrolysis products (e.g., gas and biochar) are used to produce drying heat (Struhs et al., 2020). On the other hand, the hydrolysis pathway over a one-year time horizon can convert 32,800 tons of SBP to 16,400 and 6,560 tons of pentose and furfural, respectively. The total annual cost and unit furfural cost for the main case with one hydrolysis refinery unit are estimated at \$6,426,828 per year and \$980 per metric ton, respectively. The results

show that approximately 90% of the total cost is due to operational cost, particularly, hydrolysis conversion process (Table 3-4).

**Table 3-4 Capital and operational costs, and annual utilization rate for each conversion pathway**

Point to Point <sup>0</sup>	Process	Pyrolysis			Hydrolysis		
		Capital Cost (\$/yr)	Variable Cost (\$/yr)	Utilization rate (metric ton/yr)	Capital Cost (\$/yr)	Variable Cost (\$/yr)	Utilization rate (metric ton/yr)
i to j	Collection/transportation <sup>1</sup>	72,828	39,618	60,000	72,828	442,529	60,000
i to j	Grinding <sup>2</sup>	184,363	590,231	37,500	184,363	590,231	37,500
i to j	Drying <sup>3</sup>	84,698	797,160	40,000	-	-	-
i to j	Conversion process <sup>4,5</sup>	204,606	44,638	16,400	34,826	2,391,750	16,400
j to z	Bio-oil transportation <sup>1</sup>	77,582	415,986	18,040	-	-	-
j to z	Separation <sup>7</sup>	574,484	142,011	18,040	100,933	272,661	164,000
j to k	Char storage <sup>1</sup>	80,798	167,034	9,840	-	-	-
j to k	Biochar transportation <sup>1</sup>	77,582	232,851	10,419	-	-	-
j to z	Furfural storage <sup>1</sup>	92,357	77,949	4,592	129,293	77,949	6,560

<sup>0</sup> Points as shown in Fig. 3; Refs: <sup>1</sup>(Mirkouei et al., 2017b); <sup>2</sup>(Zamora-Cristales et al., 2015); <sup>3</sup>(Kudra and Mujumdar, 2009); <sup>4</sup>(Hersh and Mirkouei, 2019); <sup>5</sup>(Struhs et al., 2020); <sup>6</sup>(Cieciura-Włoch et al., 2019); <sup>7</sup>(Ghosh et al., 2007).

The appropriate values for the weights ( $w_i, a_i$ ) are usually determined by decision makers (e.g., managers and researchers). In order to obtain  $g_{i.max}$  and  $g_{i.min}$ , the following sub-problems with specific objectives have been solved herein:

- $g_{1.min}$  can be obtained by solving Min TC (\$)
- $g_{1.max}$  can be obtained by solving Max TC (\$)
- $g_{2.min}$  can be obtained by solving Min TGHG (kg CO<sub>2</sub> eq.)
- $g_{2.max}$  can be obtained by solving Max TGHG (kg CO<sub>2</sub> eq.)

The results of the multi-objective model for both pyrolysis and hydrolysis pathways when ( $w_i, a_i = 1$ ) show that TC and TGHG are fully satisfied because the total deviation values are zero and the results of pyrolysis pathway are lower than hydrolysis pathway. In other words, TC and TGHG of pyrolysis and hydrolysis pathways have reached 100% aspiration levels, which is the percentage of goal achievement (Table 3-5). The results for both pathways when ( $w_i = 1, a_i = 2$ ) show that TC and TGHG are not fully satisfied because the total deviation values are not zero. TC and TGHG for pyrolysis pathway have reached 99.9% and 94.6% aspiration levels, respectively; however, TC and TGHG for hydrolysis pathway reached 99.4% and 100% aspiration levels, respectively.

**Table 3-5 Multi-objective optimization model results for each pathway when ( $w_i, a_i = 1$ ) or ( $w_i = 1, a_i = 2$ )**

Objective	Pyrolysis	Goal achievement (%)		Hydrolysis	Goal achievement (%)
<b>(<math>w_i, a_i = 1</math>)</b>					

TC (\$)	3,885,554	100	6,426,828	100
TGHG (kg CO <sub>2</sub> eq.)	1,294,288	100	10,433,680	100
Total deviation	0		0	
<b>(<math>w_i = 1, a_i = 2</math>)</b>				
TC (\$)	3,881,968	99.9	6,393,228	99.4
TGHG (kg CO <sub>2</sub> eq.)	1,225,152	94.6	10,433,680	100
Total deviation	72,722		33,600	

### 3.5.3. Sensitivity Analysis and Discussion

Several parameters and variables can affect TEA and LCA results of furfural production. Sensitivity analysis is conducted herein to explore the effect of major parameters on economic and environmental performance. The results show that conversion, drying (only in pyrolysis pathway), and transportation are three major parameters. Key parameters assessed in the sensitivity analysis include the conversion rates and the number of refinery units. Three scenarios are analyzed and compared with the main case study that provides further insights for enhancing sustainability benefits. Figure 3-7 presents a fishbone diagram to better understand the cause and effect of techno-economic and environmental variables throughout the SBP-to-furfural life cycle.

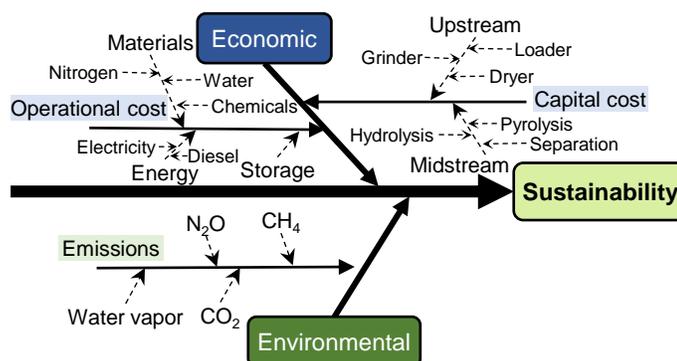


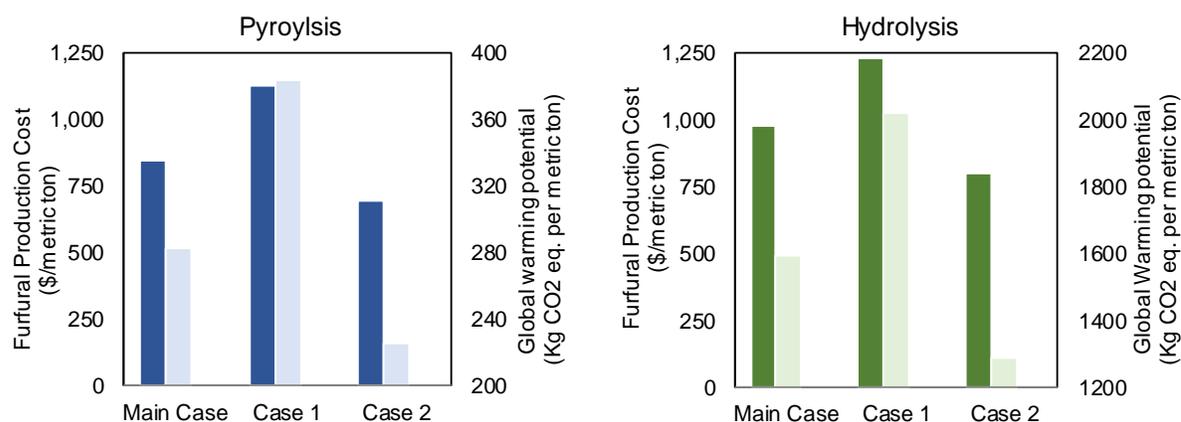
Figure 3-7 Fishbone diagram for sustainability root cause analysis

*Effect of conversion rates.* Since the conversion rates through pyrolysis and hydrolysis pathways can vary depending on various factors (e.g., biomass type/size and process configuration), we investigated the effect of this variable on the commercial feasibility and environmental impacts of furfural production. Two case studies are considered (Table 3-7): (i) Case 1, the conversion rate is 5% less than in the main case study and (ii) Case 2, the conversion rate is 5% more than in the main case study. Furfural production costs and GWP (kg CO<sub>2</sub> eq.) per metric ton have changed monotonically with the conversion rates (Fig. 8). In Case 1 for pyrolysis pathway, compared to the main case study, GWP could increase by 101 kg CO<sub>2</sub> eq. per metric ton of furfural (~36%), while Case 2 could decrease GWP by 57 kg CO<sub>2</sub> eq. per metric ton of furfural (~20%). The change in conversion rates for pyrolysis pathway would also mirror this trend and reduce furfural production cost due to the

change in the amount of produced biochar, bio-oil, and pyrolysis gas, and used for various purposes (e.g., SBP drying). Case 1 for pyrolysis pathway, compared to the main case study, would increase the furfural production cost by around 33%, and Case 2 would decrease the cost by around 18%. On the other hand, Case 1 for hydrolysis pathway, compared to the main case study, could increase GWP by 27%, while Case 2 could decrease GWP by 19%. Besides, furfural production cost per metric ton in Case 1 and Case 2 compared to the main case study could increase by around 25% and decrease by about 18%, respectively.

**Table 3-7 Effect of conversion rates on economic and environmental aspects of furfural production**

Cases	Conversion rates (%)	Furfural production cost (\$/metric ton)	GWP (kg CO <sub>2</sub> eq. per metric ton)
<b>Pyrolysis</b>			
Main Case	( $\alpha = 30\%$ , $\beta = 55\%$ , $\gamma = 25\%$ )	846	282
Case 1 (-5%)	( $\alpha = 25\%$ , $\beta = 50\%$ , $\gamma = 20\%$ )	1,125	383
Case 2 (+5%)	( $\alpha = 35\%$ , $\beta = 60\%$ , $\gamma = 30\%$ )	692	225
<b>Hydrolysis</b>			
Main Case	( $\delta = 50\%$ , $\rho = 40\%$ )	980	1,590
Case 1 (-5%)	( $\delta = 45\%$ , $\rho = 35\%$ )	1,228	2,019
Case 2 (+5%)	( $\delta = 55\%$ , $\rho = 45\%$ )	802	1,285



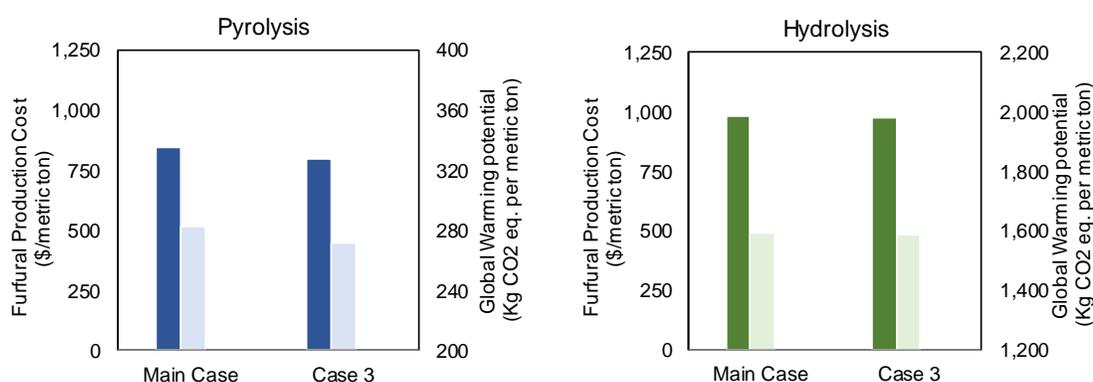
**Figure 3-8 Effect of conversion rates on sustainability performance of each pathway**

*Effect of number of refinery units.* The total amount of processed SBP (around 100 tons per day or 32,800 metric tons per year) in the main case study is based on the amount available in three selected sugar facilities in southern Idaho region (Table 3-2). The high SBP amount available requires the use of multiple refinery units for both pyrolysis and hydrolysis pathways. Therefore, we considered Case 3 in which the number of refineries is increased to four and two for pyrolysis and hydrolysis, respectively. In Case 3, compared to the main case study, furfural production cost per metric ton could decrease by around 6% and 1% for pyrolysis and hydrolysis, respectively (Table 3-8). Also, utilizing four and two refineries for pyrolysis and hydrolysis could decrease GWP by 11 and 5 kg CO<sub>2</sub> eq. per metric ton of furfural (around 4% and 0.3%) for pyrolysis and hydrolysis,

respectively (Fig. 3-9). Optimally, Case 3 with higher refinery units can produce the largest amount of furfural and address sustainability challenges by reducing the unit price of furfural production and environmental impacts.

**Table 3-8 Effect of number of refinery units on economic and environmental aspects of furfural production**

Cases	Refinery units	Furfural production cost (\$/metric ton)	GWP (kg CO <sub>2</sub> eq. per metric ton)
<b>Pyrolysis</b>			
Main Case	2	846	282
Case 3	4	798	271
<b>Hydrolysis</b>			
Main Case	1	980	1,590
Case 3	2	972	1,585



**Figure 3-9 Effect of portable refineries on sustainability performance of pyrolysis and hydrolysis pathways**

The results of this study indicate a reasonable comparison to recently published studies with similar feedstocks, operations, and process capacity, and discrepancies can be explained by differences in their applied methodology (Table 3-9).

**Table 3-9 Furfural production cost comparison with recently published studies**

Study	Technology	Capacity (ton/year)	Cost (\$/ton)	GHG (kg CO <sub>2</sub> eq.)	Biomass type	Year
<b>Pyrolysis</b>						
(Hossain et al., 2019)	Pyrolysis	7,938	1,700	-	Corn Stover	2019
This Study	Pyrolysis	4,592	846	267	SBP	2020
<b>Hydrolysis</b>						
(Wang et al., 2016)	Hydrolysis	360	-	1857	Corn Stalk	2016
(Gómez Millán et al., 2020)	Hydrolysis	5,000	1,900	-	Birch	2020
(Zang et al., 2020)	Hydrolysis	-	1,000	-	Switchgrass	2020
This Study	Hydrolysis	6,560	980	1095	SBP	2020

The economic and environmental benefits of biochar consumption for SBP drying and end use purposes (e.g., soil-plant health improvement in the agriculture sector and water treatment in aquaculture sector) were not considered in this study. However, it can help to enhance sustainability benefits across pyrolysis pathway, and subsequently reduce the TC and TGHG of furfural production. According to Santos et al. (2018), furfural produced from sugar residues can be an intermediary chemical for jet fuel production. Recently, furfural market price experienced significant market fluctuation due to various reasons, such as its extensive application and high market demand (Zang et al., 2020). Future research should extend LCA system boundary to include the soil benefits of co-products, e.g., biochar. Additional research could also include further process optimization, including reaction temperature, pressure, and residence time, as well as biomass type and size.

### **3.6. Conclusion**

Furfural production from renewable resources (e.g., SBP) has shown great potential to address sustainability challenges and the growing global market demand, which is currently around \$551 million. However, existing conversion technologies as the major cost and environmental contributors are at a nascent stage to meet the market needs. A multi-objective decision making framework is proposed in this study to assess techno-economic and environmental impacts of furfural production from SBP, using fixed hydrolysis and portable pyrolysis refineries. The proposed methodology herein can address three main deficiencies of prior studies, which are: (a) consideration of both techno-economic and environmental sustainability aspects, (b) comparison of hydrolysis and pyrolysis technologies, and (c) development of a multi-objective decision support system, computational solution, and evaluation procedure to facilitate identifying the sustainable pathway. This study couples the proposed multi-objective decision making framework with potential mixed-mode technologies (i.e., portable and fixed) for SBP-based furfural production. The motivation behind the proposed framework lies in overcoming the existing limitations and deficiencies for furfural production from renewable resources. As such, the resulting methodology integrates technological aspects with sustainability ideology to support broader commercial viability and overcome associated environmental hurdles. The results show that pyrolysis conversion pathway is simultaneously a cheaper process with lower environmental impacts than hydrolysis pathway for furfural production. The primary contributing factor of economic and environmental impacts for hydrolysis pathway is the energy consumption for heating a large volume of water. Hydrolysis process is associated with significantly higher variable (operational) cost in comparison to pyrolysis process. Potential paths for further research and development include (i) exploration of social and biodiversity benefits associated with land, water, and habitat enhancement, (ii) exploration of mixed-

mode technology, mixed-pathway transportation, and multiple-year operation to assess the broader sustainability benefits, and (iii) exploration of upstream, midstream, and downstream segments to identify techno-economic and policy barriers.

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### 3.8. Nomenclature

#### *Indices*

i	Set of collection sites
j	Set of conversion sites
k	Set of biochar distribution sites
z	Set of separation sites
t	Set of time

#### *Parameters*

$a_1$	Weight for deviation variables of aspiration level for $TC$
$a_2$	Weight for deviation variables of aspiration level for $TGHG$
$Cap_{D_k}$	Annual capacity of a biochar distribution unit (metric ton/yr)
$Cap_{H_j}$	Annual capacity of hydrolysis process (metric ton/yr)
$Cap_{R_j}$	Annual capacity of pyrolysis refinery (metric ton/yr)
$Cap_{S_z}$	Annual capacity of separation process (metric ton/yr)
$CCH$	Unit cost of SBP transportation from collection site to hydrolysis facility (\$/km)

$CCR$	Unit cost of SBP transportation from collection site to pyrolysis refinery (\$/km)
$CFH$	Fixed cost for operating hydrolysis process (\$)
$CFR$	Fixed cost for operating pyrolysis refinery (\$)
$CFS$	Fixed cost for operating separation process (\$)
$CRD$	Unit cost of biochar transportation from pyrolysis refinery to distribution center (\$/km)
$CRS$	Unit cost of bio-oil transportation from pyrolysis refinery to separation facility (\$/km)
$CS_{char}$	Unit cost of biochar storage (\$/ton)
$CS_{fur}$	Unit cost of furfural storage (\$/ton)
$CVH$	Variable cost of hydrolysis process (\$/ton)
$CVR$	Variable cost of pyrolysis refinery (\$/ton)
$CVS$	Variable cost of separation process (\$/ton)
$D$	Distance (km)
$dis_{ch_{ij}}$	Distance between collection center $i$ and hydrolysis facility $j$ (km)
$dis_{cr_{ij}}$	Distance between collection center $i$ and pyrolysis refinery $j$ (km)
$dis_{rd_{jk}}$	Distance between pyrolysis refinery $j$ and distribution center $k$ (km)
$dis_{rs_{jz}}$	Distance between pyrolysis refinery $j$ and separation facility $z$ (km)
$g_{1.min}$	Minimum of total cost
$g_{1.max}$	Maximum of total cost
$g_{2.min}$	Minimum of total GHG emission
$g_{2.max}$	Maximum of total GHG emission
$GWP_{sep}$	Separation process GWP (kg CO <sub>2</sub> eq.)
$GWP_{mid}$	Midstream processes GWP (kg CO <sub>2</sub> eq.)
$GWP_{up}$	Upstream processes GWP (kg CO <sub>2</sub> eq.)

$GWP_{\text{trans-char}}$	Biochar transportation GWP (kg CO <sub>2</sub> eq.)
$GWP_{\text{trans-oil}}$	Bio-oil transportation GWP (kg CO <sub>2</sub> eq.)
$M$	A large number
$M_{\text{beet}}$	Mass of beet pulp (metric ton)
$M_{\text{char}}$	Mass of produced biochar (metric ton)
$M_{\text{oil}}$	Mass of produced bio-oil (metric ton)
$M_{\text{pentose}}$	Mass of produced pentose (metric ton)
$R_{\text{CH}_4}$	Emissions rate of CH <sub>4</sub> (kg CO <sub>2</sub> eq./kg CH <sub>4</sub> )
$R_{\text{CO}_2}$	Emissions rate of CO <sub>2</sub> (kg CO <sub>2</sub> eq./kg CO <sub>2</sub> )
$R_{\text{N}_2\text{O}}$	Emissions rate of N <sub>2</sub> O (kg CO <sub>2</sub> eq./kg N <sub>2</sub> O)
$W_1$	Weight for deviation variables of $TC$
$W_2$	Weight for deviation variables of $TGHG$
$\eta_{\text{sep}}$	GHG emissions factor for separation processes (kg CO <sub>2</sub> eq. per ton)
$\eta_{\text{sep,CH}_4}$	CH <sub>4</sub> emission factor of separation processes (kg CH <sub>4</sub> per ton)
$\eta_{\text{sep,CO}_2}$	CO <sub>2</sub> emission factor of separation processes (kg CO <sub>2</sub> per ton)
$\eta_{\text{sep,N}_2\text{O}}$	N <sub>2</sub> O emission factor of separation processes (kg N <sub>2</sub> O per ton)
$\eta_{\text{mid}}$	GHG emissions factor for midstream processes (kg CO <sub>2</sub> eq. per ton)
$\eta_{\text{mid,CH}_4}$	CH <sub>4</sub> emission factor of midstream processes (kg CH <sub>4</sub> per ton)
$\eta_{\text{mid,CO}_2}$	CO <sub>2</sub> emission factor of midstream processes (kg CO <sub>2</sub> per ton)
$\eta_{\text{mid,N}_2\text{O}}$	N <sub>2</sub> O emission factor of midstream processes (kg N <sub>2</sub> O per ton)
$\eta_{\text{up}}$	GHG emissions factor for upstream processes (kg CO <sub>2</sub> eq. per ton)
$\eta_{\text{up,CH}_4}$	CH <sub>4</sub> emission factor of upstream processes (kg CH <sub>4</sub> per ton)
$\eta_{\text{up,CO}_2}$	CO <sub>2</sub> emission factor of upstream processes (kg CO <sub>2</sub> per ton)

$\eta_{up,N_2O}$	$N_2O$ emission factor of upstream processes (kg $N_2O$ per ton)
$\eta_{trans-char}$	GHG emissions factor for biochar transportation (kg $CO_2$ eq. per ton)
$\eta_{trans-char,CH_4}$	$CH_4$ emission factor of biochar transportation (kg $CH_4$ per ton)
$\eta_{trans-char,CO_2}$	$CO_2$ emission factor of biochar transportation (kg $CO_2$ per ton)
$\eta_{trans-char,N_2O}$	$N_2O$ emission factor of biochar transportation (kg $N_2O$ per ton)
$\eta_{trans-oil}$	GHG emissions factor for bio-oil transportation (kg $CO_2$ eq. per ton-mile)
$\eta_{trans-oil,CH_4}$	$CH_4$ emission factor of bio-oil transportation (kg $CH_4$ per ton-mile)
$\eta_{trans-oil,CO_2}$	$CO_2$ emission factor of bio-oil transportation (kg $CO_2$ per ton-mile)
$\eta_{trans-oil,N_2O}$	$N_2O$ emission factor of bio-oil transportation (kg $N_2O$ per ton-mile)
$\alpha$	Conversion rate of SBP-to-biochar (%)
$\beta$	Conversion rate of SBP-to-bio-oil (%)
$\gamma$	Conversion rate of bio-oil-to-furfural (%)
$\delta$	Conversion rate of SBP-to-pentose (%)
$\rho$	Conversion rate of pentose-to-furfural (%)
$\theta_t$	Annual available SBP (metric ton/yr)

#### *Decision Variables*

$d_1^+$	Positive deviation variable of $TC$
$d_1^-$	Negative deviation variable of $TC$
$d_2^+$	Positive deviation variable of $TGHG$
$d_2^-$	Negative deviation variable of $TGHG$
$e_1^+$	Positive deviation variable of aspiration level for $TC$
$e_1^-$	Negative deviation variable of aspiration level for $TC$

$e_2^+$	Positive deviation variable of aspiration level for <i>TGHG</i>
$e_2^-$	Negative deviation variable of aspiration level for <i>TGHG</i>
$x_{h_z}$	Binary variable when hydrolysis facility <i>z</i>
$x_{r_j}$	Binary variable when pyrolysis refinery <i>j</i>
$x_{s_z}$	Binary variable when pyrolysis refinery <i>j</i>
$y_1$	Aspiration level variable of <i>TC</i>
$y_2$	Aspiration level variable of <i>TGHG</i>
$y_{beet_{ijt}}$	Continuous variable for SBP mass transported from collection site <i>i</i> to pyrolysis refinery <i>j</i> during time period <i>t</i> (metric ton)
$y_{char_{jkt}}$	Integer variable for biochar mass transported from pyrolysis refinery <i>j</i> to distribution center <i>k</i> during time period <i>t</i> (metric ton)
$y_{fur_{zt}}$	Integer variable for furfural produced in separation center <i>z</i> during time period <i>t</i> (metric ton)
$y_{oil_{jzt}}$	Integer variable for bio-oil transported from pyrolysis refinery <i>j</i> to separation center <i>z</i> during time period <i>t</i> (metric ton)
$y_{pentose_{jt}}$	Integer variable for pentose produced in separation center <i>j</i> during time period <i>t</i> (metric ton)

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## Chapter 4. Conclusion

### 4.1. Summary

In chapter 2, the environmental and economic impact of using Nitrogen Trifluoride ( $\text{NF}_3$ ) was considered. A case study in Boise, Idaho, was presented to aid in the analysis. Several ideas to reduce greenhouse emissions were discussed, but the analysis showed that abatement efficiency proved to be the most important determinant of environmental impact.

Chapter 3 proposed a project to convert sugar beet pulp (SBP) to furfural, though either hydrolysis or pyrolysis technology. Life cycle assessment (LCA) and techno-economic assessment (TEA) methods are applied to comparing these two technologies in the context of a hypothetical case study in southern Idaho. The multi-criteria analysis showed that pyrolysis offers both economic and environmental advantages over hydrolysis.

### 4.2. Conclusions

In chapter 2, it was determined that the single most important factor for reducing environmental impact is abatement efficiency, with a significant impact from even small amounts of  $\text{NF}_3$  surviving the abatement step. Contaminants, such as sulfur hexafluoride ( $\text{SF}_6$ ), can have a disproportionately large greenhouse impact, owing to the lower abatement efficiency for these gases relative to  $\text{NF}_3$ . It was further determined that transportation had only a small environmental or economic impact.

In chapter 3, it was determined that despite lower capital costs, furfural produced by hydrolysis means is economically more expensive than that produced via the pyrolysis pathway. It was further determined that pyrolysis is responsible for significantly lower greenhouse emissions than hydrolysis. The energy requirements of heating the large volumes explain both the economic and environmental costs of hydrolysis.

### 4.3. Contributions

The work in this thesis provides the following contributions:

- Established a multi-criteria decision-making framework using LCA and TEA methodologies to consider both the environmental and economic aspects of sustainability.
- Evaluated the sustainability of  $\text{NF}_3$  from both an economic and environmental perspective. Ideas to improve are offered.
- Proposed a project to produce furfural from SBP in southern Idaho.

- Provided a comparison of hydrolysis and pyrolysis technologies for furfural.

#### **4.4. Opportunities for Future Research**

Chapter 2 of this paper lays out several steps the semiconductor industry can take to reduce the economic and environmental impacts of using  $\text{NF}_3$ . One of the solutions proposed was to reduce usage, but the research herein did not examine real-world changes to complex processes that would be required to reduce  $\text{NF}_3$  consumption. Other gases or chemicals were not considered, and might also prove interesting for further research.

Chapter 3 considers pyrolysis and hydrolysis technologies for furfural production from SBP. These processes were laid out on paper, using data from multiple researchers who have researched furfural production from biomass. The next logical research step would be to convert these theoretical processes into actual processes. A plethora of parameters are available for process optimization, including temperature, residence time, pretreatment pH, and choice of biomass. Levoglucosenone, a valuable co-product of furfural, is worthy of further study. This study also did not consider the chemical byproducts of either pyrolysis or hydrolysis, which may include hazardous waste.

## A.1. Appendix 1

### A.1.1. LINGO codes for solving the proposed multi-objective optimization model in Ch. 3:

!proposed RMCGP model for pyrolysis;

model:

sets:

collection/1..1/;;

refinery/1..2/;;

distribution/1..1/;;

separation/1..2/;;

period/1..1/;;

jlink(refinery):x\_r,Cap\_R;

klink(distribution):Cap\_D;

zlink(separation):x\_s,Cap\_S;

tlink(period):Teta;

ijlink(collection,refinery):dis\_cr;

ijtlink(collection,refinery,period):y\_beet;

jklink(refinery,distribution):dis\_rd;

jktlink(refinery,distribution,period):y\_char;

jzlink(refinery,separation):dis\_rs;

ztlink(separation,period):Fur;

jztlink(refinery,separation,period):y\_oil;

endsets

$\text{min} = w1 * (d1\_plus + d1\_negative) + a1 * (e1\_plus + e1\_negative) + w2 * (d2\_plus + d2\_negative) + a2 * (e2\_plus + e2\_negative);$

$\text{TC} = @\text{sum}(\text{collection}(i): @\text{sum}(\text{refinery}(j): @\text{sum}(\text{period}(t): y\_beet(i,j,t) * \text{dis\_cr}(i,j) * \text{CCR}))) + @\text{sum}(\text{refinery}(j): @\text{sum}(\text{distribution}(k): @\text{sum}(\text{period}(t): y\_char(j,k,t) * \text{dis\_rd}(j,k) * \text{CRD}))) + @\text{sum}(\text{refinery}(j): @\text{sum}(\text{separation}(z): @\text{sum}(\text{period}(t): y\_oil(j,z,t) * \text{dis\_rs}(j,z) * \text{CRS}))) + @\text{sum}(\text{refinery}(j): x\_r(j) * \text{CFR}) + @\text{sum}(\text{collection}(i): @\text{sum}(\text{refinery}(j): @\text{sum}(\text{period}(t): y\_beet(i,j,t) * \text{CVR}))) + @\text{sum}(\text{separation}(z): x\_s(z) * \text{CFS}) + @\text{sum}(\text{refinery}(j): @\text{sum}(\text{separation}(z): @\text{sum}(\text{period}(t): y\_oil(j,z,t) * \text{CVS}))) + @\text{sum}(\text{refinery}(j): @\text{sum}(\text{distribution}(k): @\text{sum}(\text{period}(t): y\_char(j,k,t) * \text{CS\_char}))) + @\text{sum}(\text{separation}(z): @\text{sum}(\text{period}(t): \text{Fur}(z,t) * \text{CS\_fur}));$

$\text{TC} - d1\_plus + d1\_negative = y1;$

$Y1 - e1\_plus + e1\_negative = g1\_min;$

$y1 \leq g1\_max;$

$y1 \geq g1\_min;$

$\text{TGWP} = @\text{sum}(\text{collection}(i): @\text{sum}(\text{refinery}(j): @\text{sum}(\text{period}(t): y\_beet(i,j,t) * \text{Eta\_Collection}))) + @\text{sum}(\text{refinery}(j): @\text{sum}(\text{distribution}(k): @\text{sum}(\text{period}(t): y\_char(j,k,t) * \text{dis\_rd}(j,k) * \text{Eta\_TransChar}))) + @\text{sum}(\text{refinery}(j): @\text{sum}(\text{separation}(z): @\text{sum}(\text{period}(t): y\_oil(j,z,t) * \text{dis\_rs}(j,z) * \text{Eta\_TransOil}))) + @\text{sum}(\text{collection}(i): @\text{sum}(\text{refinery}(j): @\text{sum}(\text{period}(t): y\_beet(i,j,t) * \text{Eta\_Conversion}))) + @\text{sum}(\text{refinery}(j): @\text{sum}(\text{separation}(z): @\text{sum}(\text{period}(t): y\_oil(j,z,t) * \text{Eta\_Separation})));$

$\text{TGWP} - d2\_plus + d2\_negative = y2;$

$y2 - e2\_plus + e2\_negative = g2\_min;$

$y_2 \leq g_2_{\max};$

$y_2 \geq g_2_{\min};$

!Capacity Constraint;

$\text{@for(refinery(j): @for(period(t): @sum(collection(i): y_{beet}(i,j,t)) \leq Cap\_R(j))};$

$\text{@for(distribution(k): @for(period(t): @sum(refinery(j): y_{char}(j,k,t)) \leq Cap\_D(k))};$

$\text{@for(separation(z): @for(period(t): @sum(refinery(j): y_{oil}(j,z,t)) \leq Cap\_S(z))};$

!Flow Conservation;

$\text{@for(refinery(j): @for(period(t): (Alpha * @sum(collection(i): y_{beet}(i,j,t)) -$

$\text{@sum(distribution(k): y_{char}(j,k,t)) = 0));$

$\text{@for(refinery(j): @for(period(t): (Beta * @sum(collection(i): y_{beet}(i,j,t)) -$

$\text{@sum(separation(z): y_{oil}(j,z,t)) = 0));$

$\text{@for(separation(z): @for(period(t): (Gamma * @sum(refinery(j): y_{oil}(j,z,t)) - Fur(z,t) = 0));$

$\text{@for(period(t): @sum(collection(i): @sum(refinery(j): y_{beet}(i,j,t))) = Teta(t));$

!linking Constraints;

$\text{@for(refinery(j): @for(period(t): @sum(collection(i): y_{beet}(i,j,t)) \geq x\_r(j))};$

$\text{@for(refinery(j): @for(period(t): @sum(collection(i): y_{beet}(i,j,t)) \leq x\_r(j) * M));$

$\text{@for(separation(z): @for(period(t): @sum(refinery(j): y_{oil}(j,z,t)) \geq x\_s(z))};$

$\text{@for(separation(z): @for(period(t): @sum(refinery(j): y_{oil}(j,z,t)) \leq x\_s(z) * M));$

!non-negativity & binary Constraints;

`@for(refinery(j):@bin(x_r(j)));`

`@for(separation(z):@bin(x_s(z)));`

`@for(collection(i):@for(refinery(j):@for(period(t):y_beet(i,j,t)>=0)));`

`@for(refinery(j):@for(separation(z):@for(period(t):y_oil(j,z,t)>=0)));`

`@for(refinery(j):@for(distribution(k):@for(period(t):y_char(j,k,t)>=0)));`

`@for(separation(z):@for(period(t):Fur(z,t)>=0));`

`d1_plus>=0;`

`d1_negative>=0;`

`d2_plus>=0;`

`d2_negative>=0;`

`e1_plus>=0;`

`e1_negative>=0;`

`e2_plus>=0;`

`e2_negative>=0;`

`TC>=0;`

`TGWP>=0;`

`Y1>=0;`

`Y2>=0;`

`end`

!proposed RMCGP model for hydrolysis;

model:

sets:

collection/1..1/;;

hydrolysis/1..2/;;

period/1..1/;;

jlink(hydrolysis):x\_h,Cap\_H;

tlink(period):Teta;

ijlink(collection,hydrolysis):dis\_ch;

ijmlink(collection,hydrolysis,period):y\_beet;

jtlink(hydrolysis,period):Fur,y\_pentose;

endsets

$\min = w1*(d1\_plus+d1\_negative)+a1*(e1\_plus+e1\_negative)+w2*(d2\_plus+d2\_negative)+a2*(e2\_plus+e2\_negative);$

$TC = @sum(collection(i):@sum(hydrolysis(j):@sum(period(t):y\_beet(i,j,t)*dis\_ch(i,j)*CCH)))+@sum(hydrolysis(j):x\_h(j)*CFH)+@sum(collection(i):@sum(hydrolysis(j):@sum(period(t):y\_beet(i,j,t)*CVH)))+@sum(hydrolysis(j):@sum(period(t):y\_pentose(j,t)*CVS))+@sum(hydrolysis(j):@sum(period(t):Fur(j,t)*CS\_fur));$

$TC-d1\_plus+d1\_negative=y1;$

$y1 - e1\_plus + e1\_negative = g1\_min;$

$y1 \leq g1\_max;$

$y1 \geq g1\_min;$

$TGWP = @sum(collection(i): @sum(hydrolysis(j): @sum(period(t): y\_beet(i,j,t) * dis\_ch(i,j) * Eta\_Collection))) + @sum(collection(i): @sum(hydrolysis(j): @sum(period(t): y\_beet(i,j,t) * Eta\_Conversion))) + @sum(hydrolysis(j): @sum(period(t): y\_pentose(j,t) * Eta\_Separation));$

$TGWP - d2\_plus + d2\_negative = y2;$

$y2 - e2\_plus + e2\_negative = g2\_min;$

$y2 \leq g2\_max;$

$y2 \geq g2\_min;$

!Capacity Constraint;

$@for(hydrolysis(j): @for(period(t): @sum(collection(i): y\_beet(i,j,t)) \leq Cap\_H(j));$

!Flow Conservation;

$@for(hydrolysis(j): @for(period(t): (Beta * @sum(collection(i): y\_beet(i,j,t)) - y\_pentose(j,t) = 0));$

$@for(hydrolysis(j): @for(period(t): (Gamma * y\_pentose(j,t) - Fur(j,t) = 0));$

$@for(period(t): @sum(collection(i): @sum(hydrolysis(j): y\_beet(i,j,t))) = Tetra(t));$

!linking Constraints;

$@for(hydrolysis(j): @for(period(t): @sum(collection(i): y\_beet(i,j,t)) \geq x\_h(j));$

$@for(hydrolysis(j): @for(period(t): @sum(collection(i): y\_beet(i,j,t)) \leq x\_h(j) * M);$

!non-negativity & binary Constraints;

@for(hydrolysis(j):@bin(x\_h(j)));

@for(collection(i):@for(hydrolysis(j):@for(period(t):y\_beet(i,j,t)>=0)));

@for(hydrolysis(j):@for(period(t):y\_pentose(j,t)>=0));

@for(hydrolysis(j):@for(period(t):Fur(j,t)>=0));

d1\_plus>=0;

d1\_negative>=0;

d2\_plus>=0;

d2\_negative>=0;

e1\_plus>=0;

e1\_negative>=0;

e2\_plus>=0;

e2\_negative>=0;

TC>=0;

TGWP>=0;

y1>=0;

y2>=0

end