

Plastic Wastes to Value-Added Products: Life Cycle Assessment and Techno-Economic Analysis

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Abstract

Municipal plastic wastes (MPW), formed by degradable and non-degradable components, have become an environmental hurdle. With a production of 380 million tons per year, the accumulated MPW would be around 12,000 million tons by 2050. Subsequently, MPW recycling has become a present obligation to future generations. Thermochemical technologies (e.g., pyrolysis) have shown great potential for MPW recycling into new materials or value-added products (e.g., hydrocarbon compounds). This study proposes a multi-criteria decision-making method to investigate the economic feasibility and environmental benefits of recycling MPW through a portable pyrolysis process unit near landfills. The proposed method consists of techno-economic analysis and life cycle assessment on a real case study in southeast Idaho, USA. The techno-economic analysis estimates the total cost of MPW to pyrolysis oil (p-oil). The life cycle assessment evaluates the environmental impacts of MPW-to-p-oil, including the global warming potential for a 100-year time horizon. The results indicate that the p-oil production cost per metric ton is \$228, while the total emission is 22.6 kg CO₂ per ton of MPW. It is evident that on-site operation can reduce MPW management and carbon footprint. It is concluded that MPW conversion to hydrocarbon products using the portable refinery unit near the collection sites can be a better practice in comparison to landfilling, as the main used method for solid waste disposal and one of the key sources of environmental pollution to the air, soil, and groundwater. Additionally, this study evaluates the potential of recycling polystyrene (PS) plastic wastes via a fixed bed (batch) slow pyrolysis reactor. The novelty lies in examining the reactor design, conversion parameters, and reaction kinetics to improve the process yield, activation energy, and chemical composition. Particularly, PS samples were pyrolyzed at 475-575 °C for 30 min under 69-103 kPa, and process yield, and product attributes were evaluated, using different methods to provide a better understanding of PS thermal degradation characteristics. The results show that PS decomposition started within 2 min from all temperatures, and the total decomposition point of 97% at 475 °C at approximately 5 min. Also, analytical results indicate that the average necessary activation energy is 191 kJ/mol. Pyrolysis oil from PS was characterized by gas chromatography-mass spectrometry, and the results show that styrene was produced 57-60% from all leading oil compounds (i.e., 2,4-diphenyl-1-butene, 2,4,6-triphenyl-1-hexene, and toluene), and 475 °C has the major average of conversion effectiveness of 91.3%. The results show that the reactor temperature remains the main conversion parameter to achieve the high process yield for oil production from PS. It is concluded that pyrolysis provides a sustainable pathway for PS waste recycling and conversion to value-added products. The proposed method and analytical results are compared with earlier studies to identify the directions for future studies.

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Dedication

I would like to dedicate this work to my loving wife Ashlee, our kids AnnMarie and Diego, and all my family for their sacrifices so that I can have a better life.

Thank you to all mis hermanas and hermanos who left all they knew in their native country to care for my parents' well-being. I am grateful that they have given me the opportunity and the freedom to pursue my dreams, and I hope that I have made them proud.

Thank you for being so understanding as I spent so much time working on this thesis and my degree to better myself and our family. And finally, I would like to dedicate my work to mis padres, hermanos, wife and kids. Esto es para ustedes, mis logros son tambien son sus logros por trabajar adurdamente dia a dia. All my accomplishments are also yours. Gracias!!

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Statement of Contribution

I, Galo Albor, 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 before submission. The original draft was prepared by me, Galo Albor, and edited by Dr. Amin Mirkouei, further review, and editing were completed as a joint effort between Dr. Amin Mirkouei and Dr. McDonald. As the primary author of each publication, I claim responsibility for the ideas and published data I produce to the best of my ability. Dr. Mirkouei and McDonald developed computer models for the techno-economic assessments and thermal analysis in Chapters 3 and 4.

Chapter 1. Introduction

1.1. Research Challenges and Motivation

Humanity is reaching the tipping point of climate change and fossil fuel dependency. Bioenergy is the fundamental step of innovation to reach equilibrium in environmental sustainability. Mixed feedstocks and waste recycling are valuable pathways to promote an environmental and economical solution to satisfy energy demands.

Recent performance has been on the conversion of different feedstock to biofuel production. The following chapters emphasize the processes, the environmental and economical, and conversion of mixed feedstocks to value-added products.

Chapter 2. Traditional bioenergy is derived from renewable resources (i.e., crops, invasive plants, and forestry residue). In addition, plastic waste is a potential energy source for fuel production via the thermochemical cracking (pyrolysis) process. However, Invasiveness and improper recycling management strategies for commercialization are significant hurdles to fully integrating mixed feedstocks to achieve cost-effective products. Nevertheless, mixed feedstocks have provided high efficiency in converting them into value-added products via thermochemical processes, which offers feasibility.

Chapter 3. Plastic consumption has increased exponentially since integration because it is a versatile product with low weight, strength, and durability. These characteristics make plastic essential for all industries, such as packaging, transportation, and consumer goods but promote significant environmental threats. The challenge is to reduce plastic waste and create a circular process that can convert current plastic waste into value-added products, such as oil and other end products. Therefore, a real case study was performed to investigate the market opportunity and sustainability benefits of plastic waste and to demonstrate the application of this study.

Chapter 4. Plastic waste value-added products from mixed plastic waste (MPW) feedstocks have the potential to mitigate improper recycling management and environmental degradation. Plastic waste accounts for 36 million tons out of 292 tons of total solid waste, which ends up in land fields for later incineration, which releases GHG and increases Global Warming Potential. Thermochemical cracking (i.e., pyrolysis) provides an excellent pathway to recycle and convert MPW into high-quality value-added products by decomposing large polymer molecules into small chains. Therefore, potentially reducing environmental degradation (or climate change). Chapter 4 of this paper analyses the potential of recycling polystyrene (PS) plastic via a slow pyrolysis process.

1.2. Motivation of Thesis

All chapters are motivated by the desire to understand different feedstock production's environmental and economic impacts to find innovative solutions to world issues. Innovations evolve in sustainability emphases to create economic, environmental, and social justice. Therefore, the material presented in this thesis can be applied to various processes in different activities.

Mixed feedstocks exploration provides researchers a key for an alternative energy source to reach the federal mandates and a pathway to generate bioenergy by producing value-added products due to its abundance and low cost. The applications of these products can include energy, environment, agriculture, and human health and safety. In addition, waste conversion into value-added products (e.g., fuel blend stocks and fertilizers) can significantly impact economic and environmental valorization. Chapter 3 combines LCA and TEA multi-criteria decision-making structure to explore sustainability benefits and commercialization feasibility of liquid hydrocarbon production.

Life cycle assessment (LCA) is a standard method for evaluating the environmental impact of plastic waste recycling and p-oil production process and distribution. The LCA application and software provide a competitive advantage to achieve more sustainable and efficient methods to make more sound decisions.

1.3. Research Objectives and Tasks

This thesis is based on a literature review to identify mixed feedstocks and technology for value-added products. OpenLCA 1.10.3 and European Reference Life Cycle Database assist with this work. In addition, MS Excel was utilized to help in both LCA and TEA.

Chapter 2 provides a detailed literature review; the narrative review presents the current bio-oil conversion technologies process, product values, barriers, and future research opportunities. Finally, a narrative review provides evidence of continuous technological innovation focusing on thermal conversion and upgrading bio-oil and implementation at the industry level.

Chapter 3 provides a standard LCA method, including the four phases procedure: Goal and Scope Definition, Life Cycle Inventory, Life Cycle Impact Assessment, and Interpretation requires an elevated understanding of LCA analysis. In addition, chapter 2 explores the sustainability benefits of MPW-based p-oil production that can promote carbon management systems and GHG emission mitigation efforts. Also, chapter 3 considers the supply chain, from pretreatment, conversion, and transportation to the final refinery for upgrading. Furthermore, chapter 3 required extensive

knowledge of thermochemical cracking (pyrolysis process) to conduct experiments and modeling purposes. Knowledge obtained by performing a literature review.

Chapter 4 required a working knowledge of pyrolysis for performing lab experiments, which was obtained by achieving a research assistant position with RSML, followed by completing Computer-aided design and Advanced Manufacturing Systems to design and accomplish the batch reactor development.

1.4. Research Scope

The literature review analysis completed in chapter 2 considers the literature review and narrative review by presenting the current bio-oil conversion technologies process, product values, barriers, and a future research opportunity. In contrast, a narrative review provides evidence of continuous technological innovation focusing on thermal conversion and upgrading bio-oil.

The life cycle assessment (LCA) investigated the environmental aspect of the plastic-to-oil life cycle by identifying and calculating the Greenhouse gas emissions, including CO₂, CH₄, and N₂O.

Coursework in Computer-aided design and Advanced Manufacturing Systems and Sustainability Food-Energy-Water teaches that a good scope should state what is included and what is beyond the scope of work. The social sustainability aspects were not considered by any of the chapters in this thesis. While this area is worthy of consideration in further work, it exists beyond the scope of this thesis.

1.5. Thesis Outline

This thesis is presented in manuscript format and consists of five chapters.

Chapter 2 studies a detailed Literature review, a comprehensive overview, and a classification of mixed feedstocks for analyzing a pathway to create value-added products. The work identifies critical areas that need further research and comparative analyses to assess the usefulness of identified approaches through narrative and narrative reviews. For example, a hybrid thermochemical process can be cost-effective for biofuel quality production.

Chapter 3 is a study of TEA and LCA of mixed plastic waste conversion to value-added products considered through the context of a case study in Eastern Idaho. This chapter establishes the production of p-oil from plastic waste is a cost-effective pyrolysis conversion process. TEA and LCA methodologies are applied to determine portable refinery is feasible. Scientific literature provides evidence that it is a practical and environmentally friendly approach for PW conversion to p-oil and

p-char production. This chapter is a conference paper published in the 2022 proceedings of the ASME IDETC/CIE: 27th Design for Manufacturing and the Life Cycle Conference under the title “*Mixed Plastic Waste Conversion to Value-Added Products: Sustainability Assessment and a case Study in Idaho.*”

Chapter 4 provides information on adequately performing pyrolysis conversion from PW to p-oil and p-char conversion. This chapter offers a detailed conversion process and byproduct analysis. In addition, TGA and characterization, and thermal analysis were performed to evaluate the quality of p-oil composition.

Chapter 5 draws general conclusions for this thesis and offers suggestions for future work and considerations of what has been accomplished.

Chapter 2. Literature Review of Renewable Products from Mixed Feedstocks and Plastic Wastes

2.1. Introduction

Motivation and Challenges. Humanity is reaching the tipping point of climate change and fossil fuel dependency. The world population is expected to reach 8 billion by 2023, estimated to be 7.6 billion. Bioenergy is vital for more conservative fossil fuel utilization (Kuloyo, 2012). The U.S. has grown an interest in new energy production directions (e.g., hydroelectric, geothermal, solar, wind, and biomass) in the persuasion to substitute fossil-based energy resources. Substitute biofuel can prevent energy and environmental crises, such as the late 1970 experience (i.e., crude oil shortage due to Arab embargo, increase in fuel demands, and environmental policies) (Hersh et al., 2019; US EPA, 1974). This interest allows the passage of the Energy Independence and Security Act (EISA) of 2007. The renewable energy sector accounted for approximately 11.5 quadrillion British thermal units (Btu), accounting for 11.4% of total U.S. energy consumption. Biomass is a vital source in the energy industry (Hansen et al., 2020; U.S. EIA, 2020a).

Liquid biofuel provides an alternative pathway to the dependency on conventional fuels, pharmaceuticals, and waste management. Utilizing mixed feedstocks (e.g., lignocellulosic biomass) and plastic wastes can satisfy global food supply availability, variability, and balance. The Environmental Protection Agency (EPA) has recognized that the U.S. generated approximately 292 million tons of biomass feedstocks in 2018, with about 94 million tons recycled (U.S. EPA, 2020). Innovation is needed to develop new and cost-effective strategies for managing non-recyclable waste. Current research focuses on mixed and plastic waste feedstocks biomass, providing new avenues to convert into value-added products, such as biochar, advanced biofuels, and green chemicals. The smart practice of recycling natural resources in a sustainable way can significantly impact climate change, rural economies, and energy sustainability. Natural resources can promote energy security and job creation and slow climate change as a national priority (Ciriminna et al., 2019). The private sector has explored mixed feedstocks utilization with a high yield on marginal lands, i.e., low profitability due to poor soil and undesirable characteristics (Barney, 2014; Quinn et al., 2015). Lewis and Porter et al. 2014 suggested that high moisture mixed feedstocks (e.g., cactus) can promote invasion risks and produce adverse biological impacts on natural ecosystems worldwide, which needs consideration before introducing new species (Lewis and Porter, 2014; Liao et al., 2013). Significant barriers exist to fully integrating mixed feedstocks (e.g., invasive species) to bioenergy, such as

meeting biomass market demand at a low cost and reducing invasiveness. Researchers have introduced new strategies for the biofuel crop approach, such as high-risk and low-risk. However, minimum laws and procedures can block the commercialization cultivation of invasive plants at the state and federal levels. Only four states (e.g., Oregon, Florida, Mississippi, and Maryland) have first regulated bioenergy crops (Quinn et al., 2015).

The bioeconomy industry requires extensive comprehension of mixed feedstock properties. The U.S. Department of Energy (DOE) classifies biomass as a sustainable renewable energy source derived from natural resources (e.g., agriculture, forest residues, energy crops, and algae). The U.S. can sustainably produce approximately 991 million dry tons per year of biomass derived from forest and agriculture residues (e.g., pine, wheat, corn stover, and barley). Biomass availability has increased in the last decade yielding approximately 20,000 acres; however, this type of biomass is currently not reported in the USDA Census of Agriculture (Langholtz et al., 2016). Achieving a sustainable bioeconomy has driven researchers to select herbaceous and woody biomass for their desirable agronomic traits (e.g., drought tolerance, salinity, and marginal lands). Such characteristics can enhance the competitive ability to limit irrigation, fertilizers, and pesticide use (Barney and Ditomaso, 2008; U.S. DOI, 2009). The EISA mandated decrees to produce 61 billion liters of biofuels. The current biomass production is not feasible to achieve this mandate, allowing the exploration of mixed feedstocks and promoting biofuel production (U.S. DOI, 2009). Mixed feedstocks provide researchers with a pathway to generate bioenergy by producing various value-added products due to material abundance and low cost (“Bioenergy,” 2020; Hersh et al., 2019). **Figure 2-1** illustrates application domains that can be produced with mixed feedstocks, including energy, environment, agriculture, and human health and safety. Cost-effective and environmentally friendly waste and biomass processes are needed. For example, plastic is universal in consumer goods. Over 9 billion tons of plastic waste have been created since market introduction, with approximately 80% ending in landfills (Geyer et al., 2017). Waste conversion into value-added products (e.g., fuel blendstocks and fertilizers) can significantly impact economic and environmental valorization.

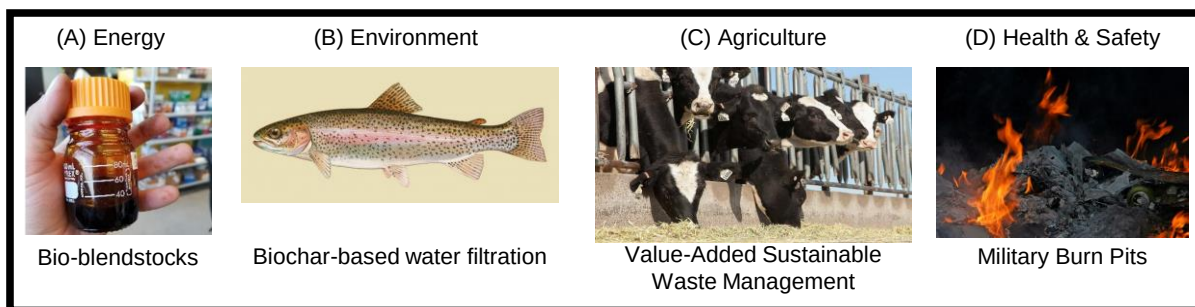


Figure 2-1. Application domains for converting mixed feedstocks to renewable products.

Mixed Feedstocks. Previous work has explored different pathways for producing biofuels and green chemicals from invasive species (Bamey, 2014). Buddenhagen et al. (2009) studied terrestrial biofuel production using a biofuel crop invasive risk assessment system. Their results showed that climate is a significant factor for invasiveness, especially by extensive cultivation, and methods, such as risk assessment, should be developed for predicting invasion risks (Buddenhagen et al., 2009). Chimera et al. (2010) investigated the dangers of introducing energy crops to various regions and climates to test naturalization and invasive tendencies. Their review revealed that energy crops are likely to naturalize and become invasive compared to non-biofuel plants (Chimera et al., 2010). Barney et al. (2011) studied regionally appropriate high-yield biomass energy crops through a world climate sustainability assessment on mixed feedstocks. The result indicates that selecting the right crop can help achieve mixed feedstock sustainability in the U.S. ecoregions (Barney and DiTomaso, 2011). Gordon et al. (2011) studied bioenergy crops' potential invasiveness using the Australian Weed Risk Assessment system. Their results demonstrated that the Weed Risk Assessment system could identify an average of 90% and 70% of the invaders and non-invaders, respectively. This means invasive species cultivation can be maximized while avoiding invasiveness (Gordon et al., 2011). Lewis et al. (2014) studied mixed feedstocks as a gateway to satisfy biofuel needs by utilizing risk mitigation strategies. Their results indicated that the proper strategy selection could avoid invasion risk by assessing invasion risk and preventing the introduction and spread of invasive plants for biofuel cultivation that can effectively balance biofuel production and invasiveness risk (Lewis and Porter, 2014). Recently, Meerbeek et al. (2015) conducted a mixed feedstock study as a potential biomass production by identifying the most invasive and accessible species with anaerobic digestion processes. Their results illustrated a high average yield of 7.3 tons per hectare, while the risk of invasion is minimized during the process and moderate during harvest and transportation (Meerbeek et al., 2015).

Plastic Waste Mixed Feedstocks. Earlier studies have established pathways to confront human environmental impacts. For instance, Eriksson et al. (2009) studied the potential of plastic waste as a source of energy supply by doing a CO₂ assessment and incineration of landfill wastes. Their results showed that plastic is a highly effective mixed feedstock to generate electricity by incineration (Eriksson and Finnveden, 2009). Dorado et al. (2014) studied mixed feedstocks and plastic wastes as biomass for fuel production by catalytic fast pyrolysis process and micro-pyrolyzer for evaluation purposes. The results indicated an excellent total aromatic yield conversion from the mixture of aliphatic polymers and polyethylene terephthalate (Dorado et al., 2014). Recent studies have shown that multiple mixed feedstocks can harness energy to balance global waste and energy demand. Infiesta et al. (2019) studied municipal solid waste conversion to renewable energy using thermochemical processes. Their results indicated that the thermochemical process could convert municipal solid waste to renewable fuels (Infiesta et al., 2019). Chaudhary et al. (2020) analyzed municipal solid wastes as mixed feedstock for biofuels polygeneration by modeling gasification polygeneration (i.e., entrained flow, circulating fluidized bed, dual fluidized bed) via Aspen Plus. Their results showed that solid waste provided higher efficiency when only power and biofuels were the products using circulating and dual fluidized beds (Chaudhary et al., 2020).

Value-Added Products. Earlier studies have mitigated the high-demand energy crops and subsequent value-added products by integrating mixed feedstocks (invasive plants) because of widespread distribution, non-crop status, and high production (Young et al., 2011). Fu et al. (2011) used genetic modifications to study mixed feedstocks for biofuel production. Their result showed that genetic modification could lower the production cost for biomass fermentation and increase yield per hectare (Fu et al., 2011). Koçar et al. (2013) did a comprehensive review of mixed energy crops (invasive species) in marginal lands as potential biomass to produce biofuel. The analysis shows promising results incorporating energy crops as a gateway to increase biofuel production (Koçar and Civaş, 2013). Liao et al. (2013) studied the potential of invasive species as mixed feedstock for value-added products (e.g., biochar, biogas, and biofuels) via the pyrolysis process. Their results show that oil and char yield varies depending on the mixed feedstock and temperatures (Liao et al., 2013). El-Mostafa et al. (2014) analyzed *Opuntia ficus-indica*, an invasive species, for its adaptation to marginal lands and its nutritional and health benefits. Their results indicated that opuntia has fatty biochemical composition compounds, such as anti-inflammatory, antioxidant, antimicrobial, and neuroprotective properties (El-Mostafa et al., 2014). Recent studies revealed the promising pathway of mixed feedstocks into value-added products. Stafford et al. (2017) studied invasive plant control in developing value-added products using cost-sharing business modeling. They concluded that public-private partnerships could help achieve market equilibrium and social-economic sustainability

(Stafford and Blignaut, 2017). Recent studies have provided valuable insights into mixed feedstocks' biochemical properties for producing value-added products. Neiva et al. (2020) analyzed energy and pharmaceutical production from mixed feedstocks and invasive species extracts. Their results indicated that the extraction yield ranges from 0.5% to 37% of dry weight, varying with species and solvent use (Neiva et al., 2020). Máximo et al. (2020) analyzed invasive species attributes for pharmaceutical development by studying worldwide invasive species. Their result illustrates that mixed feedstock species showed an excellent indication of biological activities (e.g., antioxidants, antimicrobial, and antifungal) (Máximo et al., 2020). Further details are provided by (Meereboer et al., 2020; Vijay et al., 2020).

2.2. Narrative Review

A narrative literature review develops the research aim, which studies the main idea and defines previous studies chronological advancements. The narrative review analyzes the promising pathway of converting mixed feedstocks and plastic wastes into biofuels and value-added products. This study identifies the evolution of research in mixed feedstock species and plastic wastes to bioproducts and existing barriers to bioeconomic growth. The most current biomass is corn stover, wheat, rice, barley, sugarcane, and wood (Langholtz et al., 2016).

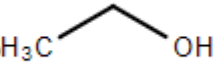
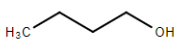
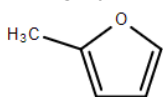
2.2.1. Biomass-derived Products

Fuel Blend-Stock. The bioeconomy is essential to the U.S. national energy independence of fossil fuels and penetration of non-food species to contribute to national renewable energy targets for the biomass of 588 to 936 million tons by 2040. In addition, biofuels are dynamic design variables that can be optimized with modern engines to revolutionize the transportation industry. DOE has studied more than 400 potential mixed feedstocks and has found that 14 chemical families are promising solutions for boosting spark and ignition engine efficiency. For example, researchers have identified that a bleeding furan mixture and cyclopentanone can increase engine efficiency by approximately 10% while achieving emission standards (Farrell et al., 2018; Wagner et al., 2019).

Currently, there are three generations of biofuels, as Table 1 illustrates their general composition and advantages. The first generation is derived from sugar, starch, oilseed crops, and animal fats. These crops and wastes produce ethanol, alcohol, butanol, and propanol through fermentation. The second generation of biofuels is made up of cellulose. Cellulose is a byproduct widespread of mixed waste biomass, such as corn stover, corncobs, straw, and wood byproducts. Finally, the third generation of biofuels is produced from algae on a non-commercialized scale. According to the USDA, Ethanol is the most utilized and made available biofuel, accounting for

approximately 94 percent of all production in 2011 and 2012 with about 13.8 billion gallons. In 2018, ethanol production was about 16.1 billion gallons, a 16 percent increase since 2011. Ethanol production is essential to local economies because it accounts for over 68,000 jobs, \$43 billion in the gross domestic product, and \$23 billion in household income, which reflects all the research projects among all national laboratories in the Department of Energy (Sarisky-Reed, 2020). **Table 2-1** summarizes biochemicals that can produce fuel additives or replacements.

Table 2-1. General composition and advantages of fuel compounds

Compounds	Generation	Advantages	Fuel Chemical Composition	Ref.
Ethanol	First-generation organic compound	Ethanol is a renewable, domestically produced transportation Ethanol accounts for 68,600 direct jobs Furthermore, Ethanol provides \$66 billion to the gross domestic product and household income	$\text{CH}_3\text{CH}_2\text{OH}$ 	(“Biofuels Basics,” 202AD; Davis et al., 2013)
Biodiesel	First-generation organic compound	Domestic renewable fuel Low levels of sulfur It contains approximately 10% built-in oxygen	H_3COOCH_3 	(Prusty et al., 2008; Satari et al., 2018)
Butanol	Second generation organic compound	Domestic renewable fuel Higher energy density, lower hygroscopicity, lower Reid vapor pressure Critical for meeting emission targets	$\text{C}_4\text{H}_9\text{OH}$ 	(Zhang, 2016)
2-methylfuran	Second generation organic compound	Derived from cellulosic biomass Bioethanol substitute	$\text{C}_5\text{H}_6\text{O}$ 	(Jeřak et al., 2016)
Alkane	Hydrocarbon-Third-generation organic compound	Derived from fatty acids Direct transportation fuel	$\text{C}_n\text{H}_{2n+2}$	(Radakovits et al., 2010)

2.2.2. Organic Personal Care Compounds

The demand for biobased cosmetics has increased, making it more cost-effective to produce and innovate biotechnology. In 2019, the personal care market reached approximately \$15 billion,

with 20% accounting for biobased derived resources (Sarisky-Reed, 2020). Biochemicals provide a pathway to decrease environmental hazards and eliminate toxic inputs in the human body. Organic materials are essential in personal care product production (e.g., perfumes, lotion, shampoo, and mascara) that every individual uses, such as acetone, an organic compound with the chemical formula of C_3H_6O , a chemical additive in polish remover. Malonic acid is a high-value specialty chemical in pharmaceuticals, flavors, fragrances, and other materials. The DOE has identified malonic acid as one of the “Top 30 Value-added chemicals”. Malonic acid derived from organic biomass can provide great potential to replace petroleum base valued products (U.S. DOE, 2015; Werpy and Petersen, 2004).

2.2.3. Nutritional Supplements

Humanity has utilized organic biomass as a food source, a local agricultural economy, and livestock since ancient civilizations (Hernández-Urbiola et al., 2011; Vazquez-mendoza et al., 2017). In the last decade, scientific evidence has shown that organic compounds derived from mixed feedstocks biomass provide essential properties of fatty composition (e.g., minerals, vitamins, polyphenols, antioxidants, polyunsaturated fatty acids, and anti-inflammatory) that can provide significant health benefits. Bioactive compounds like lignin can be converted into chemicals for food flavoring practices, tea production, jam, juice, and oil extraction (El-Mostafa et al., 2014; Sarisky-Reed, 2020). Phytochemicals have been classified as carotenoids, phenolics, and alkaloids. In addition, phytochemical bioactive plant compounds have been linked to reduced risk in major chronic illnesses due to their nitrogen, sulfur, and/or selenium content (García-Solís et al., 2009). The representation of a general chemical formula for phenols is shown below in **Figure 2-2**. In addition, polyphenols are studied due to their antioxidants properties and anticancer activity, among other preventions, such as inflammation, cardiovascular and neurodegenerative diseases (Aruwa Christianan Eleojo et al., 2018; El-Mostafa et al., 2014; Ventura-Aguilar et al., 2017).

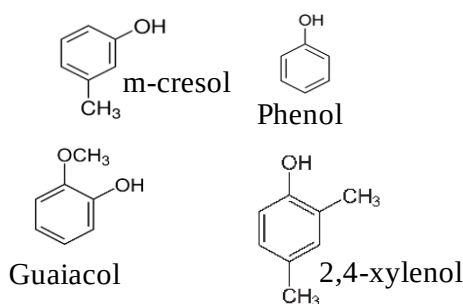


Figure 2-2. General structure of phenols

2.2.4. Cleaning Products Compounds

Surfactants and solvents are chemicals derived from biomass and bioactive in producing detergents and cleaners. Surfactants and solvents can be found on many detergents and other cleaning products in the \$13 billion industry. Cleaning products are essential in everyday activities for high gene due to their ability to remove a wide range of materials from diverse surfaces without discharging hazardous waste that can impact environmental and social costs (Sarisky-Reed, 2020; “Technology,” 2020). Fatty alcohols with more than 12 carbons are also utilized to produce household products. Fatty alcohols are linear alcohols, bioproducts from ethoxylation and sulfation, usually made from tallow, vegetable oils, or petroleum. However, these fatty alcohols can be produced from renewable mixed feedstocks from carbohydrates’ microbial fermentation. Figure 2-3 represents palmityl alcohol’s chemical structure ($C_{16}H_{34}O$) (Biddy et al., 2016).



Figure 2-3. Cetyl (or Palmityl) alcohol

2.2.5. Plastics and Other Material Compounds

With climate acceleration, companies are making a pathway to reduce hazardous waste by producing bioproducts like plastics. Biobased plastic can substitute traditional plastics due to its durability and biodegradability. Furfural is one example of making plastics. It is also essential to produce furfuryl, tetrahydrofurfuryl, and maleic anhydride alcohol, which contains anti-corrosion properties and crucial chemicals in plastic production from the automotive to the drinking industries. Lignocellulosic and hemicellulose biomass provides promising quantities of furfural. Furfural delivers a wide range of applications, from producing plastics to agrochemicals and pharmaceutical products. By producing biobased products, companies can increase the opportunity to achieve market equilibrium and establish a sustainable bioeconomy. It is estimated that over 50% of furfural is used to produce furfuryl alcohol yearly. Furthermore, furfuryl alcohol is essential for creating value-added products such as DVDs (Biddy et al., 2016; Sarisky-Reed, 2020).

2.3. Discussion

Many technologies and conversions have emerged (e.g., biological, chemical, and thermochemical) in the growing global concern about environmental degradation due to fossil-fuel reliance. However, they have not been able to achieve efficiency and profitability for the commercialization of transportation fuels and chemicals, but have not yet been reached. This failure can be attributed to market failure, where revenue is more critical than the sustainability of natural

resources. However, decreasing energy use or focusing on efficiency can significantly impact bottom-line profits providing more incentives for researchers to innovate and test emerging technologies to fulfill the national mandates for new renewable energy standards and goals or objectives. Studies have reported that various thermochemical processes provide the most cost-effective and economical method for substituting fuels for fossil fuels. Thermochemical conversions can be a conglomeration of multiple methods into one approach to produce value-added products. For example, developing a hybrid conversion can reduce the cost of transportation of oils by removing oxygen and reducing acidity, making it an efficient and cost-effective approach to producing value-added products (Marker, 2005; “Technology,” 2020).

Integrating multiple technologies and energy systems, such as thermal liquefaction (i.e., high pressure, low temperatures, higher time residents), can reduce bottleneck issues. HTL can potentially reduce the cost of upgrading and producing biomass-based transportation fuels and value-added products. Researchers have experimented with hybrid conversion processes in the last decade, such as Cheng et al. (2016), which show an increment of approximately 30 wt.% by integrating HDO with a catalyst. Implementing a hybrid conversion process can increase efficiency and lower all operations costs. Biofuels and biochemicals can be fossil-based substitutes; however, they need to reach the petroleum cost and performance competency (Cheng et al., 2016). The U.S. DOE has stated that jet fuel accounts for approximately 13%, while gasoline accounts for 53% of total transportation fuel.

On the other hand, biofuels only account for 5% of total transportation fuel (“Use of energy for transportation - U.S. Energy Information Administration (EIA),” 2020). Nevertheless, biofuel adoption can have a positive outlook in the future to come. EIA has projected that biofuels (e.g., ethanol, biodiesel, and biobutanol) will have a promising increase of up to 9% by 2040 as biofuels become more competitive with a total share of approximately 14% by 2050 (U.S. EIA, 2020b).

2.4. Technological Recommendations

Creating a circular economy that can provide a positive alternative to traditional eco-efficiency methodology is essential to overcome the plastic waste problem. Eco-efficiency focuses on maintaining value-added products and resources as long as possible by reducing waste generation. On the other hand, a circular economy provides suitable attention to HTL and supercritical treatment and pyrolysis as gateways for fuel and chemical sustainability and market equilibrium. In addition to alleviating the plastic dilemma, the world has accumulated over six billion tons of plastic, and it is expected to surpass twelve billion tons by 2050 (Chen et al., 2019).

2.4.1. Hydrothermal Liquefaction

Hydrothermal Liquefaction (HTL) technology is a technology that can provide an avenue for producing high-quality third-generation biomass-based fuels and chemicals derived from mixed feedstocks and plastic waste biomass. According to prior studies, the HTL process is achieved by temperatures ranging from 250-500°C through heated water and compressed simultaneously to critical points conditions. Various mixtures of mixed feedstocks have different critical points depending on their components and concentrations—(Caneghem et al., 2019; Chen et al., 2019; Gupta and Demirbas, 2010). HTL provides distinctive competitive advantages due to its physicochemical properties (i.e., dielectric constant, ion product, a liquefaction process, solubility of organics, and diffusivity and viscosity), which improves the bio-oil quality and yield (Gupta and Demirbas, 2010; Hansen et al., 2020; Ramirez et al., 2015). Saber et al. (2016) researched algae conversion and bio-oil upgrading to biofuels through the HTL process and catalytic hydrotreatment ranging from 360-400°C and a residence time of approximately 2 ½ hours (Saber et al., 2016). Liu et al. (2018) stated that the HTL and catalytic method provided promising results of a surprising 50% bio-oil yield while using an Rh/C catalyst and HHV of 30 M.J./kg (Liu et al., 2018). HTL provides a complex bio-crude oil that can be utilized for chemical upgrading. Madsen et al. (2017) studied bio-crude compounds' characteristics via the HTL process and 2D gas chromatography. The results indicated that 73 fatty acids were found in C₁₈ and C₂₀ compounds. The most abundant fatty acid was palmitic acid, monoglycerides, indanones, alkylated benzenediols, and chromen-2-ones, which generally are not identified (Madsen et al., 2017). Seehar et al. (2020) studied bio-crude production by influencing temperatures and catalysts via the HTL process. The results concluded that bio-crude yield at 350°C was 32.34 wt.% with the least solid residue (4.34 wt. %) on subcritical catalytic conditions. However, the maximum energy recovery was approximately 69% and 51.14 for subcritical and supercritical (Seehar et al., 2020).

2.4.2. Pyrolysis Conversion or Treatment

Pyrolysis process is a thermal treatment technology in the absence of oxygen, producing liquid, solid, and gaseous as intermediate products. Pyrolysis provides a competitive advantage over other technologies due to its ability to produce pyrolysis oils and chemicals from mixed feedstocks and plastic waste biomass (Hansen et al., 2020; Sotoudehnia and McDonald, 2022). Earlier studies have confirmed that biodiesel can replace petroleum diesel by implementing high moisture and non-recyclable mixed feedstocks. Demiral et al. (2012) studied corncob bio-oil production via pyrolysis. Their result indicates a maximum oil yield of 26.44 wt.% under 500°C, which could be used as a renewable fuel or chemical feedstock (Demiral et al., 2012). Dhanalakshmi et al. (2020) analyzes

pyrolysis technology on woody and grass agricultural waste for bio-oil recovery. The result illustrated that pyrolysis is a promising alternative in biomass conversion to bio-oil as an intermediate product achieving a maximum yield of 47.10 wt.% under 500°C (Dhanalakshmi et al., 2021). Liang et al. (2015) study the production of potato peel wastes bio-oil and bio-char via pyrolysis. Their results show a successful conversion to bio-oil and bio-char. In addition, the result detected a significant amount of hydrocarbon compounds, such as alkanes which are very similar to aliphatic compounds in transportation fuels (Liang et al., 2015). Struhs et al. (2021) studied the thermochemical conversion of lignocellulosic biomass to bio-blendstocks production. The result shows that pyrolysis is an efficient conversion pathway for bio-oil recovery using fractionation strategies (Struhs et al., 2021). Sotoudehnia et al. (2022) explored the lignocellulosic and agriculture plastic waste to liquid fuels by catalytic pyrolysis under 500-600°C. The result revealed that the liquid hydrocarbon compounds produced are comparable to those found in gasoline (Sotoudehnia and McDonald, 2022).

Therefore, attention should be given to pyrolysis technology on current and future fuels and chemical conversion generation to improve the commercialization competency and techno-economic sustainability benefits across the renewable industry. **Figure 2-5** illustrates the pyrolysis reactor that can enable the conversion process of mixed feedstocks and plastic waste, improve liquid yield, and factors that can determine intermediate products (e.g., bio-oil) quality while minimizing inherent quality issues. The future focus will be on the thermal stability of liquid products and understanding physics and chemistry in producing thermal-stable liquid blendstocks to achieve a renewable, value-added product pathway (Sotoudehnia and McDonald, 2022).

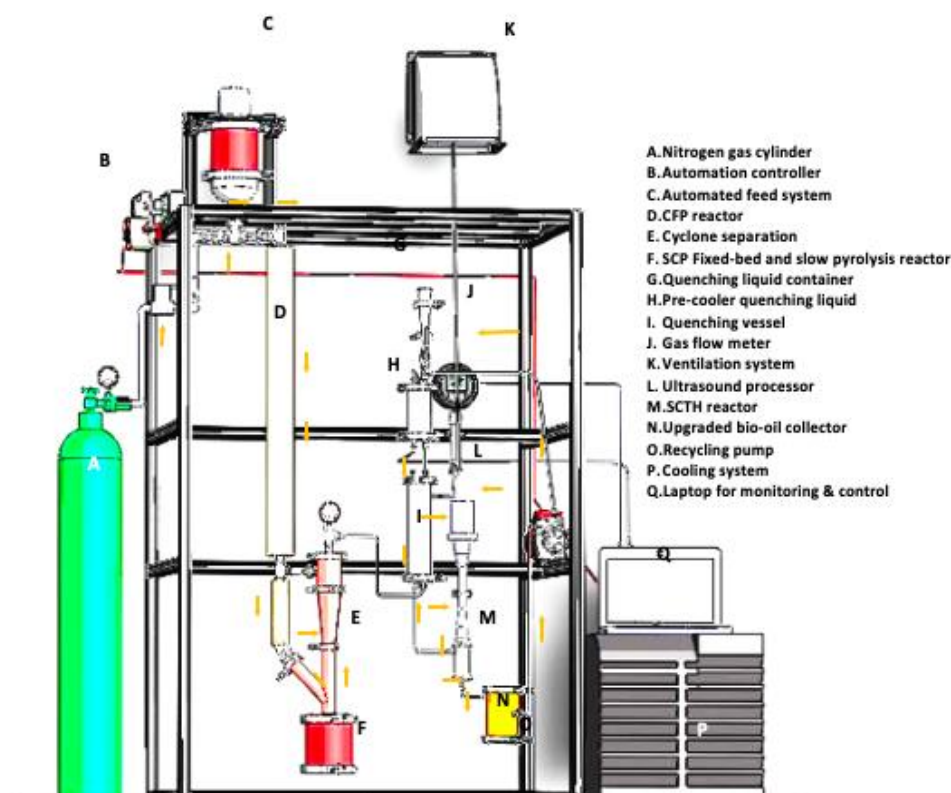


Figure 2-4. Schematic of the proposed pyrolysis reactor

2.5. Conclusions and Future Directions

Over the years, incredible technological innovations have emerged to tackle the bio-oil and chemical conversion efficiency and cost-effectiveness to achieve affordable products and market accessibility by using mixed biomass feedstocks without compromising the human food chain, natural resources, and environmental welfare. This work offers different technological conversions for sustainable and renewable production of fuels and green compounds, dependent on the end products (i.e., personal care, pharmaceutical, nutrition, and green plastics).

The presented narrative review provides a synopsis of the current bio-oil conversation technologies process, product values, barriers, and future work opportunities. Furthermore, the narrative review provides evidence that thermal conversion technologies have had significant momentum in the last decade despite the COVID-19 pandemic. Furthermore, it is evident from both reviews that there is a continuous need for more focused research on thermal (e.g., HTL and pyrolysis) conversion and upgrading bio-oil and chemicals and implementation at the industry level. The main concern on bio-oil production is high hydrogen and oxygenate content due to their negative impact on other attributes. In addition, the current conversion technologies are unable to provide

sustainability. Therefore, it is essential to continue developing mixed feedstocks to bio-oil conversion pathways, which provides opportunities to achieve national energy priorities (e.g., energy security, domestic resources, and rural economies) to achieve environmental goals. Therefore, significant development efforts and research are needed on biofuels and green chemical production to overcome the traditional conversion shortcomings for fuel and chemical production and achieve sustainable commercialization.

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Chapter 3. Mixed Plastic Waste Conversion to Value-added Products: Sustainability Assessment and A Case Study in Idaho

This chapter was published in the 2022 proceedings of the ASME IDETC/CIE: 27th Design for Manufacturing and the Life Cycle Conference, under the title “*Mixed Plastic Waste Conversion to Value-added Products: Sustainability Assessment and A Case Study in Idaho.*” **This paper received the best paper award at the ASME conference.**

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3.1. Abstract

Municipal plastic wastes (MPW), formed by degradable and non-degradable components, have become an environmental hurdle. With a production of 380 million tons per year, the accumulated MPW would be around 12,000 million tons by 2050. Subsequently, MPW recycling has become a present obligation to future generations. Thermochemical technologies (e.g., pyrolysis) have shown great potential for MPW recycling into new materials or value-added products (e.g., hydrocarbon compounds). This study proposes a multi-criteria decision-making method to investigate the economic feasibility and environmental benefits of recycling MPW through a portable pyrolysis process unit near landfills. The proposed method consists of techno-economic analysis and life cycle assessment on a real case study in southeast Idaho, USA. The techno-economic analysis estimates the total cost of MPW to pyrolysis oil (p-oil). The life cycle assessment evaluates the environmental impacts of MPW-to-p-oil, including the global warming potential for a 100-year time horizon. The results indicate that the p-oil production cost per metric ton is \$228, while the total emission is 22.6kg CO₂ per ton of MPW. It is evident that on-site operation can reduce MPW management and carbon footprint. It is concluded that MPW conversion to hydrocarbon products using the portable refinery unit near the collection sites can be a better practice in comparison to landfilling, as the main used method for solid waste disposal and one of the key sources of environmental pollution to the air, soil, and groundwater.

Keywords. municipal plastic wastes; portable refinery; pyrolysis oil; value-added products; life cycle assessment; techno economic analysis; sustainability.

3.2. Nomenclature

Parameters

AMPW	Amount of MPW (metric ton)
P_{yu}	Annual MPW pyrolysis utilization (metric ton/yr)
E_{c-cs}	Annual capital cost of p-char storage (\$/yr)
E_{c-gr}	Annual capital cost of grinding (\$/yr)
E_{c-py}	Annual capital cost of MPW pyrolysis (\$/yr)
E_{c-tr}	Annual capital cost of double-trailer truck (\$/yr)
C_{Su}	Annual p-char storage utilization (metric ton/yr)
E_{v-cs}	Annual variable cost of p-char storage (\$/yr)
E_{v-gr}	Annual variable cost of grinding (\$/yr)
E_{v-os}	Annual variable cost of p-oil storage (\$/yr)
E_{v-py}	Annual variable cost of MPW pyrolysis (\$/yr)
E_{v-tr}	Annual variable cost of double-trailer truck (\$/yr)
E_1	Pretreatment cost (\$/yr)
E_2	Conversion cost (\$/yr)
E_3	Storage cost (\$/yr)
E_4	Distribution cost (\$/yr)
D	Distance (miles)
G_{Ru}	Annual grinder utilization (metric ton/yr)
O_{Su}	Annual bio-oil storage utilization (metric ton/yr)
O_{p-oil}	P-oil production GWP (kg CO ₂ eq.)
O_{trans}	P-oil transportation GWP (kg CO ₂ eq.)
O_{up}	Environmental impacts of upstream GWP (kg CO ₂ eq.)
Q_{p-oil}	Quantity of produced p-oil (metric ton)
RCO_2	Emissions rate of CO ₂ (kg CO ₂ eq./kg CO ₂)
RCH_4	Emissions rate of RCH ₄ (kg CH ₄ eq./kg CO ₂)
RN_2O	Emissions rate of N ₂ O (kg N ₂ O eq./kg CO ₂)
TRu	Annual truck utilization (metric ton/yr)
β_{p-oil}	Oil production GHG emissions factor (kg CO ₂ eq./ton)
β_{p-oil,CO_2}	Oil production CO ₂ emission factor (kg CO ₂ /ton)
β_{p-oil,CH_4}	Oil production CH ₄ emission factor (kgCH ₄ /ton)
β_{p-oil,N_2O}	Oil production N ₂ O emission factor (kg N ₂ O/ton)

β_{trans}	Oil transport GHG emission factor (kgCO ₂ eq/ton-mile)
β_{trans,CH_4}	Oil transport CH ₄ emission factor (kg CH ₄ /ton-mile)
β_{trans,CO_2}	Oil transport CO ₂ emission factor (kg CO ₂ /ton-mile)
β_{trans,N_2O}	Oil transport N ₂ O emission factor (kg N ₂ O/ton-mile)
β_{up}	Upstream GHG emissions factor (kg CO ₂ eq./ton)
β_{up,CH_4}	Upstream process CH ₄ emission factor (kg CH ₄ /ton)
β_{up,CO_2}	Upstream process CO ₂ emission factor (kg CO ₂ /ton)
β_{up,N_2O}	Upstream process N ₂ O emission factor (kg N ₂ O/ton)

Decision Variables

$Char_{bct}$	P-char from conversion site (b) to storage site (c) during time period t (metric ton)
Oil_{bcdt}	P-oil mass from conversion site (b) to storage site (d) during time period t (metric ton)
Oil_{cet}	P-oil mass from storage site (c) to distribution center (e) during time t (metric ton)
P_{abt}	Plastic mass from collection center (a) to conversion (b) during time t (metric ton)

3.3. Introduction

The increase in fossil fuel dependency and petroleum-based products (e.g., transportation fuels and plastics) consumption requires special attention to avoid depleting the natural resources due to the rapidly growing population and high global demand for improving the quality of life. Plastic is a well-diverse and highly versatile consumer product due to its low weight, high strength, and durability. These characteristics make plastics essential for many industries, such as packaging, transportation, and consumer electronics. As a result, the demand for plastic-based products is growing, where 99% of plastic production is petroleum-based, accounting for approximately 9% of global oil and gas consumption (Nielsen et al., 2020). The increasing demand for plastic-based products results in direct or indirect waste generation, depending on their application range. Municipal plastic waste (MPW) is one of the main sources of environmental pollution and a global hazardous threat due to its toxic leachates into the soil and groundwater, as well as inherent gas emissions to the air (Idumah and Nwuzor, 2019). According to Environmental Protection Agency (EPA), MPW disposal is approximately 292 million tons of waste or 4.9 pounds per capita per day (EPA, 2017). Prior studies report that over 3.4 billion tons of non-degradable plastic wastes will be generated annually by 2050 (EPA, 2020a), and 32 million tons of plastic wastes enter the oceans per year (EPA, 2020b). Plastic waste pollution costs approximately \$2.5 trillion per year, including ocean

damage, greenhouse gas (GHG) emissions, and land pollutants (Soloviy, 2019). Recent studies indicate that MPW management is currently low, and it has been reported that only 9% of plastic waste has been recycled since its inception (EPA, 2017). The continuous disposal of plastic waste predicts severe environmental and health hazards, such as bacterial contamination, increased methane, and disease risk (EPA, 2020a). The existing plastic recycling operations are not cost-competitive due to the low quality of intermediate and final products, which reduces the sustainability benefits of a circular economy. MPW can be reused to generate new brand plastics and value-added liquid hydrocarbon products that stand as a better strategy solution to tackle the environmental problems and compensate for petroleum-based products. The US Department of Energy (DOE) has recently invested \$25 million in plastic wastes recycling to combat plastic pollution across food-energy-water systems and achieve a circular economy (DOE, 2021; Mirkouei, 2020).

3.3.1. Background

Improving the existing technologies (e.g., thermochemical, and biochemical processes) can provide opportunities to recycle petroleum-based wastes to recycle MPW, such as polyethylene terephthalate (PET), high-density polyethylene (HDPE), polyvinyl chloride (PVC), low-density polyethylene (LDPE), polypropylene (PP), and polystyrene (PS), and overcome the global environmental crisis due to the high demand and consumption over the past decade. Pyrolysis is one of the commercialized thermochemical processes that can convert MPW to pyrolysis oil (p-oil) and pyrolysis char (p-char) with high process yield and product quality (**Figure 3-1**).

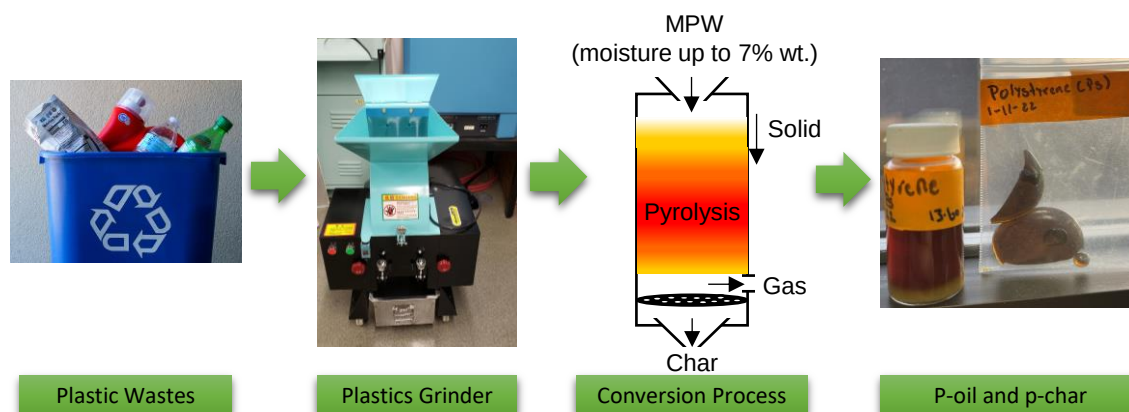


Figure 3-1. Plastic waste to value-added products

Pyrolysis can break down long-chain hydrocarbons into small polymer molecules (shorter-chain hydrocarbon) at high temperatures (400-600°C) (Mirkouei et al., 2016; Mirkouei and Kardel,

2017) P-oil from plastics pyrolysis can be upgraded to different liquid hydrocarbons with many applications due to various boiling points, including transportation fuels (e.g., kerosene and diesel) and motor oil (Bilal and Iqbal, 2019). Prior studies reported that catalytic pyrolysis has a high process yield (up to 75%) and could be a viable solution for plastic recycling and overcome sustainability challenges (Meys et al., 2020). Despite the advantages, catalytic pyrolysis has several disadvantages, such as high catalyst cost and low refinery lifetime. The American Chemistry Council (2011) reported that a commercial facility could process between 7,500 and 10,000 tons per year with a capital cost ranging from \$4 million to \$11.5 million (American Chemistry Council, 2011). Transparency market research (2021) reported that the plastic wastes recovery market is expected to reach \$100 million by 2027 (Press Release Newswire and Rohit, 2021).

Plastic Waste Recycling Strategies. Various studies have conducted feasibility analyses for plastic waste recycling using different conversion technologies (e.g., pyrolysis and liquefaction) and provided the gateway to reduce the degradation of diverse ecosystems (Table 3-1) (Nanda and Berruti, 2021). The pyrolysis process showed a promising recovery approach from mixed landfill plastic wastes (Dorado et al., 2014). Recent studies reported that the main parameters for process yield are the conversion temperature (162-340°C), pressure (138-690 kPa), and operation time (0.5-2.5 h) for producing C₁₀-C₅₀ hydrocarbon products (Sikdar et al., 2020). Banu et al. (2020) reported up to 85% process yield for plastic conversion via pyrolysis with temperatures between 450°C and 650°C and pressure from 800 to 4295 kPa while maximizing output and reducing the production cost (Banu et al., 2020). A comprehensive overview for mitigating the plastic waste crisis and producing value-added products has been given by recent studies (Cabanes and Fullana, 2021).

Environmental Impact Assessment. Plastic wastes recycling provides numerous environmental benefits, such as mitigating global warming potential (GWP), ozone depletion, human toxicity, terrestrial acidification, and ecotoxicity (Oliveira and Magrini, 2017). Life cycle assessment (LCA) is a standard method for evaluating the environmental impacts of plastic waste recycling and engineered materials production, considering different system boundaries and functional units. Several studies have applied the LCA method, and their results show the environmental benefits of plastic waste recycling in different countries (Nabavi-Pelesaraei et al., 2017). Benavides et al. (2017) conducted an LCA study on plastic wastes conversion to value-added products. The study concluded that by transforming waste into products can reduce up to 14% of GHG emissions compared to original petroleum-based products by utilizing 58% less water and 96% lower consumption fossil fuels (Benavides et al., 2017). In addition, several studies reported that processing plastic waste is less harmful in comparison to open dumping and sanitary landfilling (Chhabra et al., 2021).

Techno-Economic Assessment (TEA). A recent study reported that current MPW-based oil on 2018 market value at \$37 million, and it expects to grow approximately 10% per year and reach \$100 million by 2027 (Energy Weekly News, 2021). In addition, other studies reported that plastic waste has a value of up to \$1,200 per metric ton (**Table 3-1**). However, there is little research exclusively on the economic assessment of non-recyclable plastic wastes, and most of the conducted studies have several assumptions (American Chemistry Council, 2011). Gracida-Alvarez et al. (2019) reported that plastic waste conversion to energy recovery is a promising application on an industrial scale (Gracida-Alvarez et al., 2019). Several studies also noted that the conversion of plastic wastes to various products and byproducts could minimize the total costs and maximize profitability (Gopinath et al., 2020; Riedewald et al., 2021).

Table 3-1. Comparable economic and environmental studies on mixed plastic waste conversion

Study	Environmental	Economic	Pyrolysis	Resource	Method
(Shelley and El-Halwagi, 1999)	×	✓	✓	Municipal Solid Waste	TEA & Experimental
(Eriksson and Finnveden, 2009)	✓	×	×	Municipal Solid Waste	LCA
(Kalargaris et al., 2017)	×	×	✓	Plastic waste	Experimental
(Benavides et al., 2017)	✓	×	✓	Plastic waste	LCA
(Fivga and Dimitriou, 2018)	×	✓	✓	Plastic	TEA & HYSY
(Gracida-Alvarez et al., 2019)	×	✓	✓	High-density Polyethylene	TEA
(Ghodrat et al., 2019)	×	✓	✓	Mixed Plastic	TEA
(Larrain et al., 2020)	×	✓	✓	Mixed Polyolefins	TEA
(Gopinath et al., 2020)	×	✓	✓	Landfill waste	TEA
(Buchner et al., 2020)	×	✓	×	Polyurethane rubber	TEA
(Meys et al., 2020)	✓	✓	✓	Polypropylene Plastic packaging waste	TEA & LCA
(Riedewald et al., 2021)	×	✓	✓	Municipal solid waste	TEA
(Chhabra et al., 2021)	✓	✓	✓	Municipal solid waste	TEA & LCA
This Study	✓	✓	✓	Mixed Plastics	TEA & LCA

3.3.2. Goal and Scope

This study proposes a multi-criteria decision making method, including LCA and TEA studies to (a) explore the sustainability benefits of liquid hydrocarbons production from MPW and (b) explore the commercial feasibility of liquid hydrocarbons production, using an actual case study in southeast Idaho, USA, for validating the proposed methods and models. Furthermore, the economic and environmental analyses aim to determine the viability of p-oil and p-char production under the possible use of portable refinery units for converting MPW to value-added products near the collection sites and reduce the environmental footprint of MPW management. The assessment covers the total supply chain cost for p-oil and p-char production and distribution. In addition, the LCA method evaluates the GWP₁₀₀ of plastic waste-based oil production processes and distribution networks. Finally, a case study in southeast Idaho investigates the sustainability benefits of the proposed conversion process in regions with a high density of plastic wastes. In addition, it demonstrates the applicability of the method in recycling petroleum-based wastes.

3.4. Materials and Methods

The pyrolysis process for MPW to value-added products is divided into collection/transportation, pretreatment, conversion, storage, and distribution. MPW are collected and transported to the portable refinery unit close to the collection center. The pretreatment process for size reduction uses a VeconPlan Vaz 1600-M-XL grinder. The pyrolysis refinery unit was used to perform MPW conversion experiments to determine the process yield and primary products (i.e., p-oil, p-char, and p-gas). The pyrolysis process involves the thermochemical decomposition of plastic wastes at a higher temperature (300–600°C) in the absence of oxygen. Aspen HYSYS process simulator was used to model the pyrolysis reactor with a capacity of approximately 50 metric tons per day while using a continuously stirred-tank reactor (CSTR) due to their ability to model kinetic reactions (**Figure 3-2**). The reactor was purged with nitrogen at a 10-20 L/min flow rate to control the reactor residence time and promote feedstock decomposition. MPW enters the reactor at room temperature, and the pyrolysis unit operates under 0-379 kPa pressure and 400-600°C temperature with a residence time of 20-60 min. The converted condensable vapor goes through a condenser unit to separate the primary pyrolysis byproducts. Finally, the obtained p-oil and p-char are transported to an upgrading facility or p-char distribution center, respectively. The moisture content of MPW is one of the critical parameters affecting process yield and products quality (Li et al., 2017). This study MPW using a portable pyrolysis conversion pathway. The developed methodology in this study includes LCA for evaluating environmental impacts and TEA modeling for assessing the total cost of p-oil production from MPW (**Figure 3-3**).

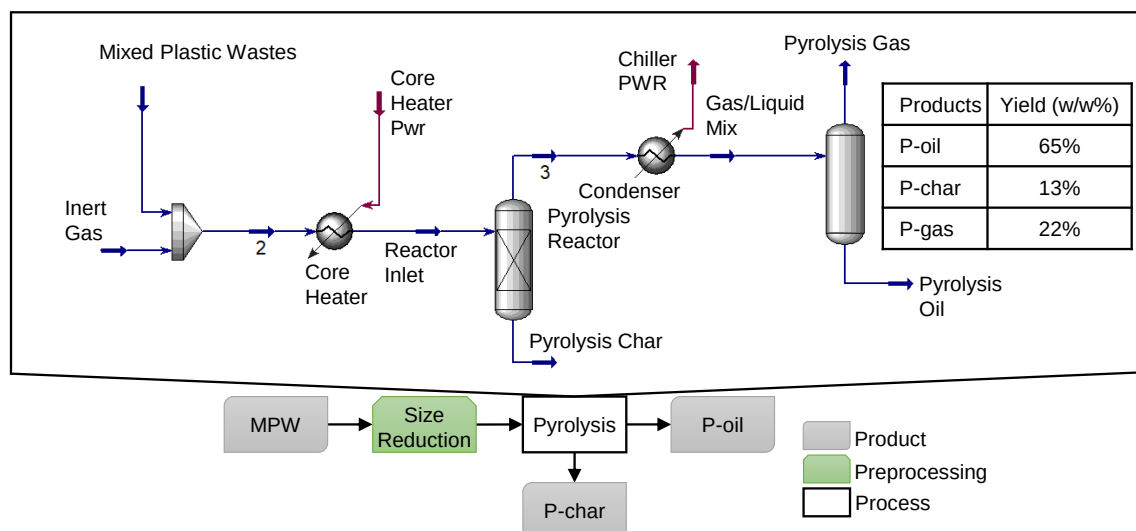


Figure 3-2. Schematic Aspen HYSYS simulation of p-oil and p-char production

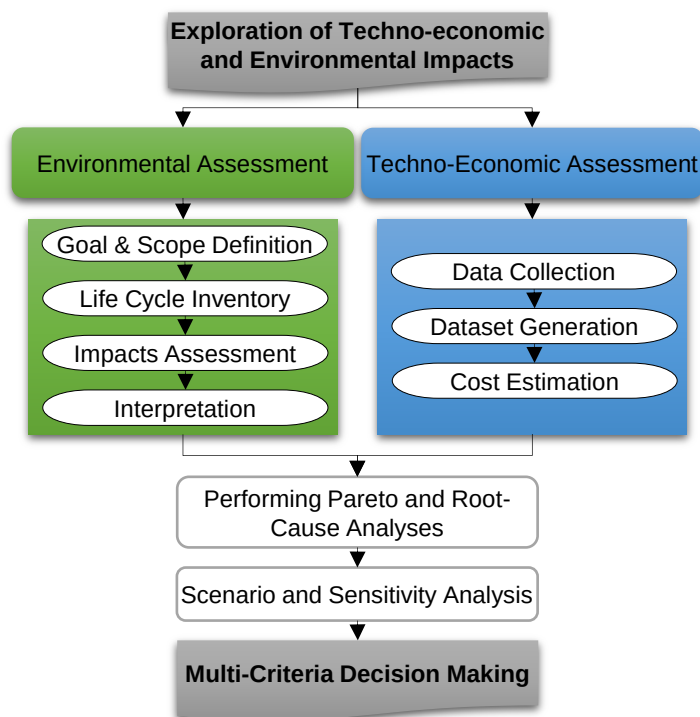


Figure 3-3. Multi-criteria decision-making framework for sustainability assessments

3.4.1. Environmental Impact Assessment

The LCA study includes four phases (i.e., goal and scope definition, life cycle inventory, life cycle impact assessment, and interpretation) for performing the environmental impact of converting MPW to value-added products utilizing OpenLCA databases and data from previous studies to assess.

Goal and Scope Definition. The goal is to measure the life cycle impacts of pyrolysis MPW to value-added products. Particularly, this study investigates GHG emissions, including CO₂, CH₄, and N₂O, and the emission factor is in kg CO₂ equivalent with the emissions being 1 kg CO₂ eq./kg CO₂, 28 kg CO₂ eq./kg CH₄ and 265 kg CO₂ eq./kg N₂O. Methods and data were obtained from the Intergovernmental Panel on Climate Change (IPCC) for a 100-year time horizon (Forster et al., 2007). The scope of this work involves various segments that can be classified into three sectors: (a) upstream, including MPW collection and on-site pretreatment, (b) midstream, including the conversion of MPW into products (e.g., p-oil, p-char, and p-gas), and (c) downstream, including distribution of p-oil for future upgrading and p-char for end-use. In addition, the LCA study has considered a grave-to-gate system, including recycling MPW and bringing them back to life as input materials for any applications (**Figure 3-4**). The utilized units in this study are a metric ton of MPW and a gallon of p-oil.

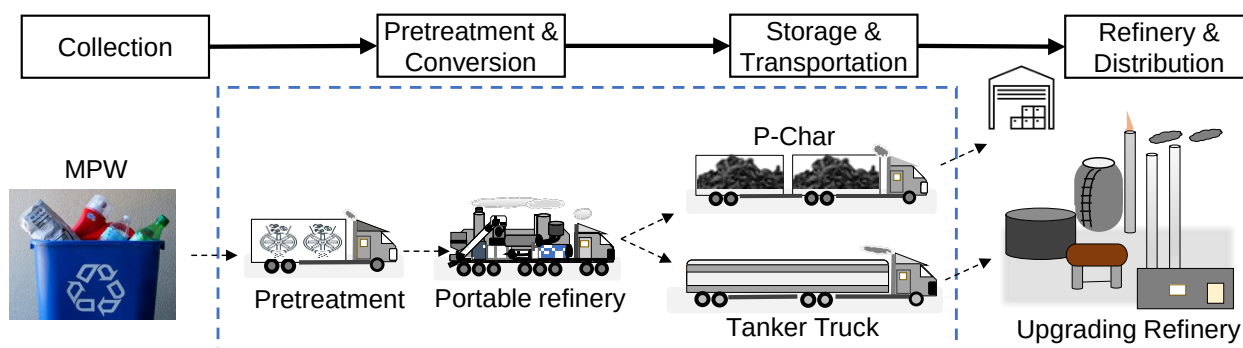


Figure 3-4. A grave-to-gate systems boundary (dotted line) for MPW to p-oil and p-char

Life Cycle Inventory Analysis. The MPW conversion and distribution processes were analyzed using quantitative data from the European Reference Life Cycle Database and OpenLCA databases for the input and output parameters (OpenLCA, 2019). The necessary equipment operated during the upstream collection of MPW included a dump lorry and skid-steer. Input into the centralized collection stage is petroleum based MPW, transportation fuels (e.g., diesel), and heavy equipment lubricants. Outputs comprise CO₂ emitted from MPW and equipment operations emissions. Therefore, the GHG emissions factor for the upstream consists of collecting and hauling and feeding MPW into the grinder for size reduction. Upstream pretreatment inputs are disposal MPW diesel, and the outputs are pretreated MPW and GHG emissions. GWP is impacted by plastic dust release and the quality of the feedstock. The midstream process starts by processing the pretreated MPW through a pyrolysis process, using nitrogen as an inert gas and heat elements source powered by electricity. Pyrolysis inputs are pretreated feedstocks, nitrogen for feeding, electricity for

thermochemical, and water for condensing/cooling purposes. The outputs conversion includes p-oil and p-char as value-added products and pyrolysis gas as emissions. The breakdown of MPW pyrolysis by the percentage of products weight are 65% p-oil, 13% p-gas, and 22% p-char, respectively (Chen et al., 2019). Non-biogenic GHG and ash are additional emissions from the conversion process and combustion of p-gas. During the downstream process, produced p-oils and p-chars will be transported by tanker trucks or double-trailer trucks (consuming diesel fuel) to upgrading refineries or distribution centers, respectively. The emissions produced by fuel consumption depend on the distance from the conversion refinery to the upgrading or distribution sites. The p-char produced can also be applied in the pretreatment or pyrolysis processes as the heat source for drying MPW or thermochemical conversion.

Life Cycle Impact Assessment (LCIA). LCIA was accomplished by utilizing the CML-IA baseline method, developed by Chalmers University of Technology (version 2.0.5), and production systems using OpenLCA (an open-source LCA software), aiming at p-oil production from MPW. The total GHG emissions are calculated using Equations (3-1) -(3-6) system boundaries method of the p-oil production and the inputs and outputs to perform LCA.

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

$$O_{up} = A_{MPW} \times \beta_{up} \quad (3-2)$$

$$\beta_{p-oil} = R_{CO2} \times \beta_{p-oil, CO2} + R_{CH4} \times \beta_{p-oil, CH4} + R_{N2O} \times \beta_{p-oil, N2O} \quad (3-3)$$

$$O_{p-oil} = Q_{p-oil} \times \beta_{p-oil} \quad (3-4)$$

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

$$O_{trans} = Q_{p-oil} \times \beta_{trans} \times D \quad (3-6)$$

Interpretation. The results from the conducted LCA study show the quantitative analysis of the environmental impacts involved in recycling 100 metric tons per day of MPW. This study uses the GWP₁₀₀ time horizon to analyze GHG emissions and human toxicity. Considering this information is crucial to understanding the environmental impacts of the defined system boundary (input and outputs parameters) and will be a key for enhancing sustainability benefits. The emissions produced by the value-added products (e.g., p-oil and p-char) are categorized as non-renewable since 99% of plastic production is petroleum-based. The major contributor to GWP₁₀₀ is CO₂ emitted from MPW management, reducing when MPW is reused to other products, such as HDPE, p-oil, or p-char. Additional major GHG contributors are pretreatment and transportation operations.

3.4.2. Techno-Economic Analysis

The formulated mathematical model (Eq. 3-7) calculates the total cost of p-oil production from MPW using mobile pyrolysis refinery units. The TEA model considers capital and operational costs of pretreatment (Eq. 3-8), conversion (Eq. 3-9), p-oil and p-char storage (Eq. 3-10), and distribution (Eq. 3-11) steps. This study does not consider the collection cost of MPW since most cities have programs for plastic waste management (US EPA, 2015). The primary objective is to estimate the expenses of converting MPW to p-oil over a 1-year time horizon. Details about the parameters, variables, and indices are provided in the Nomenclature section.

$$Total\ Cost = E_1 + E_2 + E_3 + E_4 \quad (3-7)$$

$$E_1 = \sum_a \sum_b \sum_t (E_{C-gr} + E_{V-gr}) \times \frac{P_{abt}}{GR_u} \quad (3-8)$$

$$E_2 = \sum_a \sum_b \sum_t (E_{C-py} + E_{V-py}) \times \frac{P_{abt}}{PY_u} \quad (3-9)$$

$$E_3 = \sum_b \sum_c \sum_t (E_{C-cs} + E_{V-cs}) \times \frac{Char_{bct}}{CS_u} + \sum_b \sum_d \sum_t (E_{C-os} + E_{V-os}) \times \frac{Oil_{bdt}}{OS_u} \quad (3-10)$$

$$E_4 = \sum_c \sum_e \sum_t (E_{C-tr} + E_{V-tr}) \times \frac{Oil_{cet}}{TR_u} \quad (3-11)$$

3.5. Case Study

Idaho is the fastest-growing state in the USA, with a total population increase of 2.9% in 2021 (Bureau, 2021). Idaho is attractive to people from across the country for its diverse amenities and lower cost of living. Some amenities include living in a less dense city providing reasonable commutes, diversity of outdoor activities, and prosperity. This study explored a case study in southeast Idaho counties, such as Madison, Bonneville, Bannock, and Bingham (**Figure 3-5**). Southeast Idaho process approximately 802 metric tons per day or 292,846 metric tons per year of plastic waste with an estimated population of 353,762, according to the US Census Bureau (**Table 3-2**) (Bureau, 2019). The total number of collection sites is 12, assuming the local authorities will distribute the plastic waste to the centralized recycling facility. This study utilizes various equipment for pretreatment (grinding), refinery (pyrolysis), and transportation (trucks).

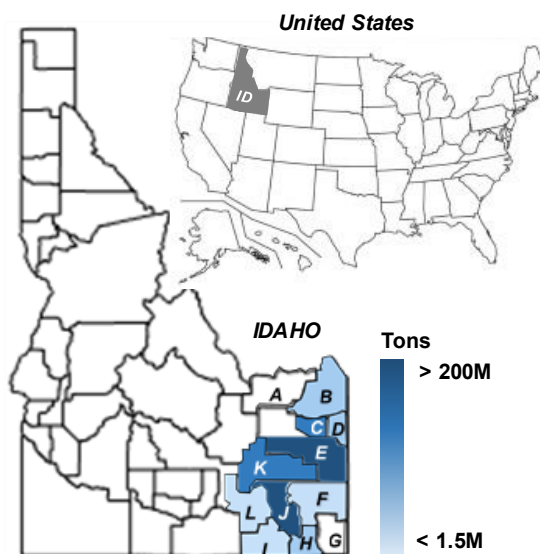


Figure 3-5. Southeast Idaho MPW collection area (Bureau, 2019)

Table 3-2. Southeast Idaho MPW collection area (Bureau, 2019)

Geographic Area	2019 Population	MPW per Day	MPW per Year
A. Clark	845	4,225	1,542,125
B. Fremont	13,099	65,495	23,905,675
C. Madison	39,907	199,535	72,830,275
D. Teton	12,142	60,710	22,159,150
E. Bonneville	119,062	595,310	217,288,150
F. Caribou	7,155	35,775	13,057,875
G. Bear Lake	845	4,225	1,542,125
H. Franklin	13,876	69,380	25,323,700
I. Oneida	4,531	22,655	8,269,075
J. Bannock	87,808	439,040	160,249,600
K. Bingham	46,811	234,055	85,430,075
L. Power	7,681	38,405	14,017,825
Total	353,762	1,768,810	645,615,650

Additionally, the following assumptions are made, using the available data and estimates reported in published studies:

- The refinery capacity for portable pyrolysis is 50 tons of MPW.
- The time horizon is one year.
- All dollar amounts used in this study are US dollars (USD).
- MPW collection cost is omitted due to existing programs by local authorities in regions with a high density of MPW (US EPA, 2015).
- The annual schedule refinery process is 328 days and 12 hours per day (Mirkouei, 2016).
- The average MPW available is 322,162 metric tons in the southeast Idaho region (Bureau, 2019).

- Loader and grinder utilization rates are 60,000 and 37,500 per year, respectively (Struhset al., 2020).
- MPW pretreatment rate is assumed 100%.
- Pyrolysis conversion process yields for p-oil, p-char, and p-gas are 65%, 13%, and 22%, respectively (Riedewald et al., 2021).
- The round-trip distance from the mobile refinery facility to the upgrading facility is 420 miles (676 km) (ArcGIS 2019).
- The refinery capacity for a single mobile pyrolysis unit is 50 metric tons of ground MPW.
- The time horizon is one year.
- All dollar amounts used in this study are US dollars (USD).
- MPW collection cost is omitted due to existing programs by local authorities in regions with a high density of MPW (US EPA, 2015).
- The annual schedule refinery process is 328 days and 12 hours per day (Mirkouei, 2016; Thompson et al., 2021).
- The average MPW available is 322,162 metric tons in the southeast Idaho region (Bureau, 2019).
- Loader and grinder utilization rates are 60,000 and 37,500 per year, respectively (Struhset al., 2020).
- MPW pretreatment rate is assumed 100%.
- Pyrolysis conversion process yields for p-oil, p-char, and p-gas are 65%, 13%, and 22%, respectively (Riedewald et al., 2021).
- The round-trip distance from the mobile refinery facility to the upgrading facility is 420 miles (676 km) (ArcGIS 2019).
- The round-trip distance from the mobile refinery facility to the p-char storage facility is assumed to be 100 miles (160 km) (ArcGIS 2019).

3.6. Results

The results indicated that the proposed approach could recycle 32,800 metric tons of MPW and produce 21,320 metric tons of p-oil (approximately 608,899 gallons of hydrocarbon fuel) over a one-year time horizon. The collection and sorting costs are omitted, assuming that the local authorities in regions with a high density of municipal solid wastes have a program to manage and recycle the wastes (US EPA, 2015). The total cost and unit p-oil cost, employing two portable refineries (Main Case Study) with 100 metric tons per day capacity, is estimated at \$4,860,637 per year and \$228 per metric ton (\$0.88 per gallon of p-oil), respectively. However, the pretreatment cost outweighs the cost of MPW disposal management, as well as negative environmental impacts. For example, if a metric ton of disposable MPW costs approximately \$33,000 per metric ton, the total benefit lost from the ecosystems for 32,800 metric tons would be roughly \$1,082,400,000 (Soloviy, 2019). **Table 3-3** presents the capital and operational costs of each process. Approximately 78% of the total cost is due to operating costs. The grinding and pyrolysis processes are the two major operational cost-drivers due to high energy consumption, particularly 43 gallons per hour in eight-hour shift grinding operations.

Table 3-3. Capital and operational costs, and annual utilization rate for each process

Step to step	Process	Capital cost (\$/yr)	Operational cost (\$/yr)	Utilization rate (metric ton/yr)
a to b	Grinding	214,800	751,900	1,137,500
a to b	Pyrolysis	485,298	1,256,503	16,400
b to c	P-char storage	80,798	167,034	4,264
b to d	P-oil storage	182,653	383,571	21,320
c to e	Transportation	87,588	285,846	50,000
Total	-	1,239,073	2,844,854	1,229,484

The conducted LCA study explores the proposed approach in this study as a solution to overcome the current MPW crisis that the world is enduring. The environmental impacts of recycling 100 metric tons of MPW per day results in approximately 2,262 kg of CO₂ eq. for producing a metric ton of p-oil and p-char. **Table 3-4** presents the results of the MPW pyrolysis process using the data from OpenLCA (v1.10.3) and prior published studies and defined assumptions for the proposed southeast Idaho case study.

Table 3-4. Total emissions for 100 metric ton of p-oil and p-char from MPW

Process	CO ₂	N ₂ O (10-5)	CH ₄ (10-4)	GWP
Collection/transportation	8.06	6.31	3.23	17.61
Grinding	922.42	722.05	370.05	2,014.52
Conversion	81.95	64.15	32.88	178.98
P-oil transportation	22.14	17.33	8.88	48.36
P-char transportation	1.05	0.82	0.42	2.29
Total	1,035.63	810.67	415.47	2,261.76

The results show that plastic recycling using pyrolysis is a sustainable approach in regions with a high density of MPW. The analysis expresses the effectiveness of reducing environmental impacts during the plastics-to-oil recycling process by eliminating MPW disposal to landfills. The majority of GWP emissions are saved from discharging into the environment and prevent health damage to ecosystems. The data from the LCA analysis was used for conducting Pareto analysis, which is essential to compare the results and gain a sound understanding of each step. Pareto analysis is utilized to analyze each process overall GHG emissions (kg CO₂ eq.) across pyrolysis pathways and compare the GWP environmental impacts of end-use of MPW in its life cycle (**Figure 3-6**).

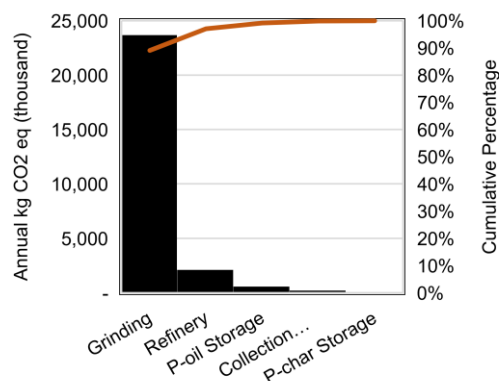


Figure 3-6. Pareto analysis of the impact of each process on the environment

The Pareto analysis, known as the 80/20 law, was used to identify 20% of causes (processes) that are responsible for 80% of problems (emissions). Even in cases where the data does not strictly follow the rule, the analysis can be informative. Inputs and outputs are unequally distributed, which causes some inputs to contribute more than others to the environment and economic outcomes. The pretreatment step contributes to most of the GHG emissions and GWP. Reducing the pretreatment emissions could be achieved by employing new technologies and renewable fuels, such as biodiesel.

3.7. Sensitivity Analysis and Discussion

MPW-based hydrocarbon products can complement conventional petroleum-based fuels for internal combustion engines (Kalargaris et al., 2017). Several parameters and variables can affect TEA and LCA results of p-oil production. Sensitivity analysis is conducted herein to explore the effects of significant parameters on economic and environmental performance. The results show that grinding, conversion, and transportation are three key factors. Key benchmarks assessed in the sensitivity analysis include the number of refinery units utilized and their total cost. Four 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 understand better the cause and effect of techno-economic and environmental variables throughout the MPW-based oil life cycle. Scrutinizing the supply chains (e.g., grinding and transportation) illustrates that the emissions from fuel combustion had significant impacts on total GHG emissions. In addition, p-gas from the MPW conversion process comprises propane, ethylene, ethane, methane, carbon dioxide, carbon monoxide, and butane. Additionally, root-cause analysis demonstrates the facets of economic, environmental, and safety challenges, as well as the potential causes throughout the plastics-to-oil life cycle.

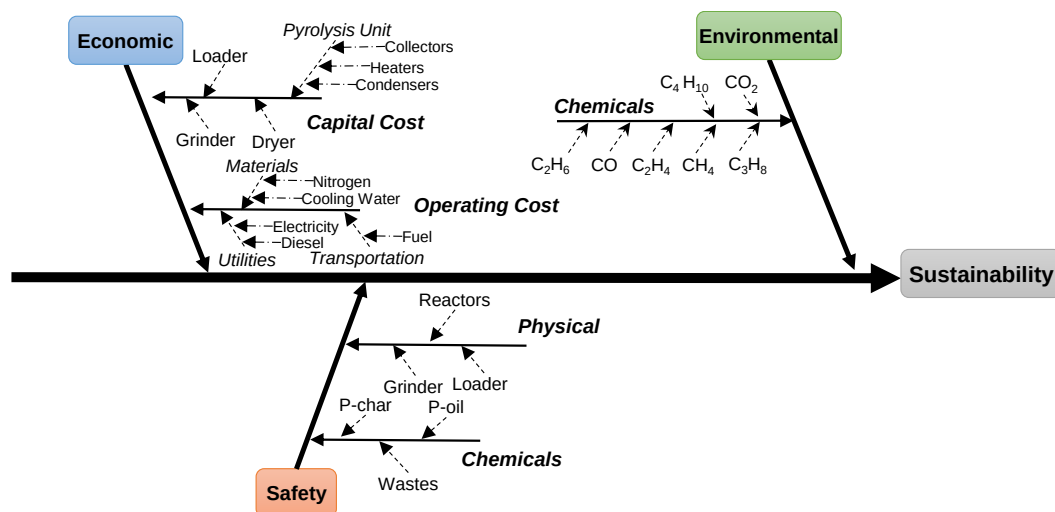


Figure 3-7. Fishbone diagram for sustainability root-cause analysis

Impact of Transportable Pyrolysis Refinery cost. Examining the effects of refinery cost is important to assess the viability of MPW-based oil production since the conversion process is one of the major cost-drivers. Therefore, two case studies have been evaluated: Case Study 1, the refinery cost is reduced by 50%, and Case Study 2, the refinery cost is increased by 50% compared to the Main Case Study. The results indicated that changes in refinery cost significantly affect the total cost (Table 3-5). The overall annual cost decreased in Case Study 1 by about \$2,090,073 (-43%) and Case Study 2, the annual cost increased by \$2,597,622 (+ 59%).

Table 3-5. Effects of portable refinery unit on the overall annual cost

Case Studies	Annual Overall Cost (\$)	Annual Refinery Cost (\$/yr)		
		Capital Cost	Operational Cost	Labor Cost
Main Case Study	4,346,249	673,234	1,256,503	432,410
Study 1(-50% cost)	2,777,404	336,617	628,251.5	216,205
Study 2(+50% cost)	6,943,871	1,009,851	1,884,755	648,615

Two refineries were utilized in all three case studies with a capacity of 100 metric tons per day for recycling MPW. As a result, the amount of recycled MPW remains constant, and GWP (kg CO₂ eq.) emissions stay the same in all case studies (**Figure 3-8**).

Impact of the Accessible Amount of MPW. The available amount of MPW is a primary commercialization barrier for p-oil production. Since the availability can vary depending on local policy conditions, this study investigated the effects on the commercial feasibility of p-oil. The total amount of MPW disposal is 322,162 metric tons per day and was calculated based on the population

in southeast Idaho for the main case study. The total amount of processed MPW is 32,800 metric tons per year. The total disposal amount of MPW obtainable is vital because it is the main parameter and changing the amount of available MPW affects the total annual cost. Therefore, it is essential to use multiple refineries to recycle annual MPW disposal. The implementation of refineries could affect the total yearly cost of the conversion and distribution supply chain and the total annual GWP emissions. The Main Case Study considers two refineries. In Case Study 3, the available amount of MPW decreased by 50%, and in Case Study 4, the available MPW increased by 50%. Table 3.6 provides the estimated cost and environmental impacts for each case study.

Table 3-6. Effects of available amount of MPW on associated costs and environmental impacts

Studies	Amount of MPW (metric ton)	P-oil Production (\$/gallon)	GWP (kg CO₂ eq./metric ton)
Main Case Study	32,800	0.88	2,261.76
Study 3(-50% MPW)	16,400	1.18	1,759.57
Study 4(+50% MPW)	49,200	0.83	3,161.08

In comparison with Main Case Study, the results show that p-oil production cost per metric ton (or \$/gallon) increased by approximately 34% (\$0.30) in Case Study 3, while p-oil production cost decreased by about 6% (\$0.05) in Case Study 4. Also, GWP100 decreased by approximately 502 CO₂ kg eq. per metric ton in Case Study 3 (22%), while GWP100 increased by around 899 CO₂ kg eq. per metric ton in Case Study 4 (28%). The effects of MPW availability on the different case studies are shown in **(Figure 3-9.)** The unit price for p-oil production from disposal MPW indicates a reasonable comparison to the prices reported in recently published studies with similar operation capacity **(Table 3-7)**. Recycling MPW has the potential to address national priorities (e.g., plastic wastes management and recycling) and sustainability challenges (e.g., environmental pollution from single-use plastics). Using MPW for p-oil and p-char production can increase investment in recycling processes, create jobs in the US, and reduce MPW discharge to the environment (Hersh et al., 2019; Hersh and Mirkouei, 2019).

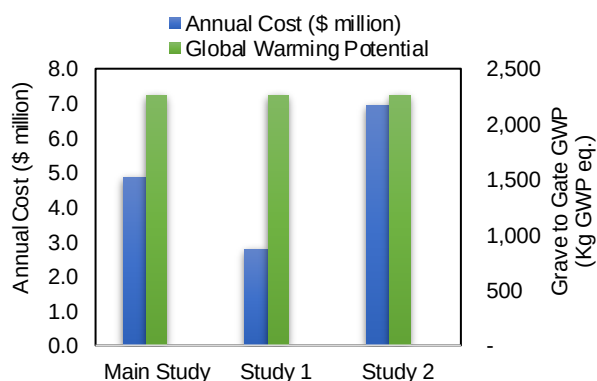


Figure 3-8. Effects of portable refinery unit on economic and environmental aspects

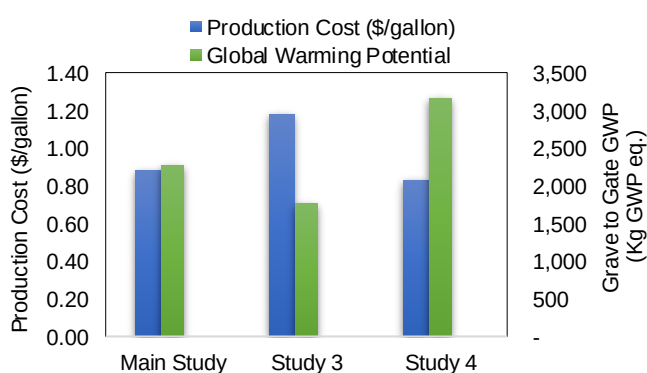


Figure 3-9. Effects of the available amount of MPW on economic and environmental aspects

In this study, the resulting unit price for p-oil production from disposal MPW indicates a reasonable comparison to the prices reported in recently published studies with similar operation capacity (**Table 3-7**). Recycling MPW has the potential to address national priorities (e.g., plastic wastes management and recycling) and sustainability challenges (e.g., environmental pollution from single-use plastics). Using MPW for p-oil and p-char production can increase investment in recycling processes, create jobs in the US, and reduce MPW discharge to the environment (Hersh et al., 2019; Hersh and Mirkouei, 2019).

Table 3-7. Estimated p-oil production cost comparison in recent studies

Technology	Capacity (metric ton/day)	p-oil production (\$/gal)	Ref.
Pyrolysis	100	0.16	(Fivga and Dimitriou, 2018)
Pyrolysis	500	0.09	(Gracida-Alvarez et al., 2019)
Pyrolysis	40	0.65	(Ghodrat et al., 2019)
Pyrolysis	110	1.03	(Riedewald et al., 2021)
Pyrolysis	100	0.60	(Almohamadi et al., 2021)
This study	100	0.88	-

While technological advance is evolving, it is essential to produce secondary products. Byproducts from MPW pyrolysis (e.g., p-char) can be applied for producing alternative, environmental-friendly products, such as asphalt, concrete, and building bricks. For example, MPW-based asphalt for road construction has shown superior performance compared to conventional tar roads. In addition, p-char from MPW could be integrated into concrete and building bricks, providing different plastic properties, which benefits the construction structures (Gopinath et al., 2020). The creation of byproducts helps facilitate the monetization of environmental benefits and avoids ecological costs, such as soil and air degradation. Earlier studies reported that pyrolysis could potentially reduce 50% to 73% less GHG emissions in comparison to other conventional methods, such as landfill disposal (Bora et al., 2020; Chhabra et al., 2021). **Table 3-8** compared the cost and emission of landfill disposal and pyrolysis pathways for plastic recycling.

Table 3-8. GHG emissions and costs comparison from landfill disposal for 1 ton of MPW

Method	Total Cost (\$/yr)	GHG emissions (kg CO ₂ eq./ton)	Ref.
Landfill disposal	36,150,000	4,290	(Bora et al., 2020; Lee et al., 2017)
This study	4,083,927	2,262	-

3.8. Conclusion

This study investigates the economic feasibility and sustainability benefits of producing MPW-based liquid hydrocarbon compounds (p-oil), using a portable refinery unit. A multi-criteria decision making was utilized to evaluate the proposed pathway, including LCA and TEA studies. The novelty of this study lies in exploring the sustainability benefits of MPW to value-added products (e.g., p-oil and p-char) and investigating the commercial feasibility of the proposed approach, using an actual case study in southeast Idaho, USA. In addition, the LCA study investigates the feasible use of portable refineries to convert MPW to value-added products near the collection sites and explores the environmental footprint of MPW management. The TEA study investigates the total cost of p-oil production, including grinding, conversion, storage, and transportation. The environmental assessment evaluates GWP (GHG emissions, CO₂ kg eq.) for a 100-year time horizon and grave-to-gate system boundary, including recycling MPW and bringing them back to life as input materials for any applications. The functional unit is a metric ton of MPW and a gallon of p-oil. The case study in southeast Idaho demonstrates the sustainability benefits of the proposed methods in regions with a high density of plastic wastes. Furthermore, it demonstrates the applicability of the method in recycling petroleum-based wastes. The total cost of p-oil production is approximately \$228 per metric

ton (\$0.88 per gallon of p-oil), and the total emission is about 2,262 kg CO₂ per 100 metric tons of MPW processed. It is concluded that recycling operations near the collection sites can reduce the unit price and carbon footprint of MPW management, address upstream and midstream sustainability challenges, and stimulate the plastic pyrolysis industry. Potential paths for future research and development include: (a) the exploration of social and biodiversity benefits associated with land, water, and habitat enhancement, (b) exploration of a mixed-mode conversion process and mixed-pathway transportation, and multiple-year operation to assess the broader sustainability benefits, and (c) exploration of upstream, midstream, and downstream segments to identify commercialization and policy barriers.

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Chapter 4. Fixed Bed (Batch) Slow Pyrolysis Process for Polystyrene Waste Recycling

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4.1. Abstract

This study evaluates the potential of recycling polystyrene (PS) plastic wastes via a fixed bed (batch) slow pyrolysis reactor. The novelty lies in examining the reactor design, conversion parameters, and reaction kinetics to improve the process yield, activation energy, and chemical composition. PS samples were pyrolyzed at 475–575°C for 30 min under 70–103 kPa. Process yields and product attributes were evaluated using different methods to understand PS thermal degradation characteristics better. The results show that PS decomposition started within 2 min from all temperatures, and the total decomposition point of 97% at 475°C at approximately 5 min. Additionally, analytical results indicate that the average necessary activation energy is 191 kJ/mol. Pyrolysis oil from PS was characterized by gas chromatography–mass spectrometry. The results show that styrene was produced 57–60% from all leading oil compounds (i.e., 2,4-diphenyl-1-butene, 2,4,6-triphenyl-1-hexene, and toluene), and 475°C has the major average of conversion effectiveness of 91.3%. The results show that the reactor temperature remains the main conversion parameter to achieve the high process yield for oil production from PS. It is concluded that pyrolysis provides a sustainable pathway for PS waste recycling and conversion to value-added products, such as resins and polymers. The proposed method and analytical results are compared with earlier studies to identify directions for future studies.

Keywords. Plastic Waste; Polystyrene; Slow Pyrolysis; Thermochemical Conversion; Pyrolysis Oil.

Abbreviations. EPA, Environmental Protection Agency; HDPE, High-density Polyethylene; LDPE, Low-density Polyethylene; MMT, Million Metric Tonnes; PE, Polyethylene; PET, Polyethylene Terephthalate; PP, Polypropylene; PS, Polystyrene; PVC, Polyvinyl Chloride; TPA, terephthalic acid.

4.2. Introduction

Motivation and Challenges. Plastic materials from petroleum-based resources play an essential role in many aspects of daily life due to their unique properties, such as low weight, high strength, and extreme durability. The top plastic applications are in electronic devices, medical equipment, cars, care products, and packaging. However, plastics are synthetic and composed of large molecules that make them difficult to recycle. Proper recycling methods can address the existing challenges, especially negative environmental impacts, such as marine and land pollution, resource depletion, and soil contamination. The United States (U.S.) Environmental Protection Agency (EPA) reported in 2018 that approximately 265 million metric tonnes (MMT) of municipal solid wastes were generated in the U.S., accounting for 32.4 MMT of plastics. Only 2.80 MMT of high-density polyethylene (HDPE) and polyethylene terephthalate (PET) were recycled, 5.1 MMT were utilized for energy recovery, and 24.5 MMT ended up in landfills (U.S. Environmental Protection Agency, 2020). EPA estimated an average of eight MMT of plastic waste worldwide is in oceans and freshwaters due to inadequate recycling infrastructure (U.S. Environmental Protection Agency, 2020). Recycling and converting various plastic wastes to value-added products can reduce environmental pollution and create a recycled plastic market for producing petroleum-derived products (e.g., gasoline, diesel, fuel oil, and lubricants). Due to global recycling efforts, approximately 25 million barrels of oil are expected to be replaced with recycled plastics by 2025. During the last decade, the total plastic recycling investment has been up to \$100 billion annually (DOE, 2022; Payne and Jones, 2021). Incineration, burning at high temperatures, is a standard plastic waste recycling processes at landfills for energy (heat or power) recovery (EPA, 2020). Sikdar et al. (2020) reported that low-density polyethylene (LDPE), HDPE, polypropylene (PP), and polystyrene (PS) are the most utilized and efficient sources for the recycled plastics market due to their kinematic viscosity, which is comparable to petroleum-based lubricants (Sikdar et al., 2020).

Background. Due to their versatility, the increasing demand for synthetic plastics also raises plastic pollution concerns. Millions of tons of plastic waste end up in oceans, rivers, and terrestrial ecosystems due to poor recycling management, causing degradation to all ecosystems. Prior studies have reported that plastic wastes will continue to grow from approximately 236 to 417 MMT from 2016 to 2030 at the current disposal rates. The main plastic recycling methods are mechanical, chemical, biological, and composting. Chemical recycling is an advanced form of recycling technology that can reduce the amount of plastic disposal in ecosystems and provides two significant advantages: selectivity and low energy requirement (Vollmer et al., 2020). Chemical recycling can also produce high-quality raw materials for new products, decreasing the demand for fossil fuels and

other nonrenewable resources. Chemical deconstruction can be classified as selective and non-selective methods (**Figure 4-1**). The selective process includes catalytic depolymerization and solvent-based reactive depolymerization. The non-selective process includes thermal depolymerization (DOE, 2021; Solis and Silveira, 2020; Tzinis, 2015).

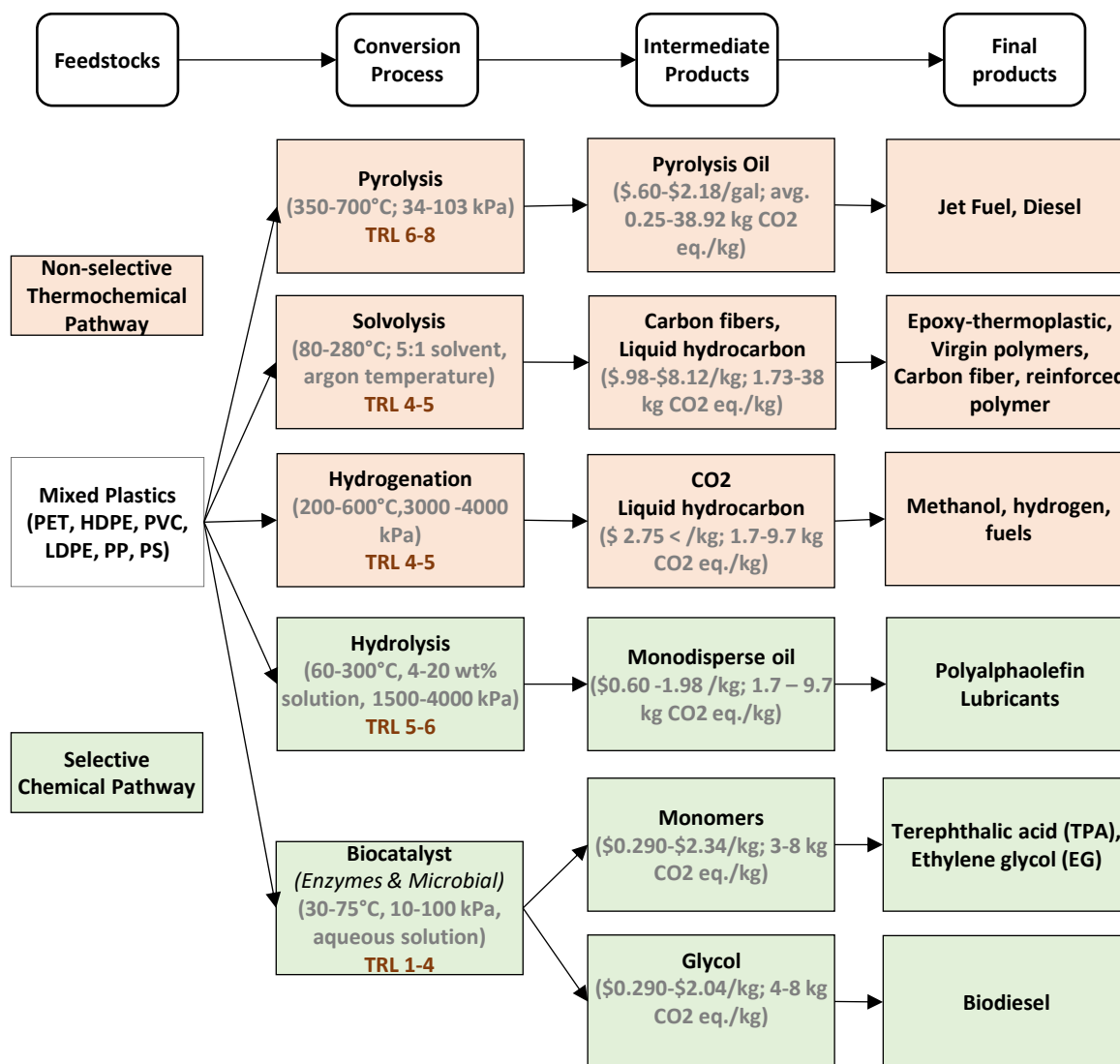


Figure 4-1. Fuel conversion pathways from plastic wastes

Selective Chemical Pathways: chemical depolymerization is a process that depolymerizes plastic into intermediates that can be purified as virgin-like or other chemicals as raw materials, not limited to hydrogenolysis, hydrolysis, and microbial-enzymatic processes. Hackler et al. (2021) studied the production of HDPE plastic waste polyolefin lubricant by hydrogenolysis catalytic conversion. The results showed that hydrogenolysis could be economically feasible with a total production cost ranging between \$0.48-\$1.20/kg and environmentally friendly, producing 0.6-1.98

CO₂eq/kg of total emissions (Hackler et al., 2021). Other studies have conducted research on hydrolysis and biocatalyst depolymerization for producing other intermediates (e.g., terephthalic acid and ethylene glycol). The results have shown potential environmental benefits over incineration or landfill disposal by 3.7-5.6 CO₂eq/kg (Ugduler et al., 2020). Singh et al. (2021) studied PET depolymerization by biocatalysts to produce monomers as intermediate products and terephthalic acid (TPA) as the final product. The results show potential for TPA production with a cost of \$1.93/kg and 3.7 kg CO₂eq/kg of total emissions, making enzyme-catalyst a promising technology (Singh et al., 2021). Billen et al. (2020) studied the biodegradation of polyethylene (PE) via macro-organisms to produce glycol as an intermediate and biodiesel as the final product. The results show a high cost of \$289.5 per ton and 4-8 ton CO₂eq/t, mainly due to the larvae making this process achievable but not equitable (Billen et al., 2020). Eukert et al. (2022) studied the enzymatic hydrolysis of PET to produce TPA and ethylene. The results show a cost of \$2.04/kg and 1.88 kg CO₂eq/kg total emissions (Eukert et al., 2022). Roux et al. (2021) studied the economic viability of upcycling PET into 5-furandicarboxylic acid as an intermediate product and producing polyethylene furanoate (PEF) and polytrimethylene terephthalate (PTT) as final products. Their techno-economic analysis results show that the production is approximately \$2.34/kg with a minimum selling price of \$3.13/kg, making it a feasible process (Roux and Varrone, 2021).

Non-Selective Thermochemical Pathways: thermochemical depolymerization includes but is not limited to pyrolysis, solvolysis, hydrogenation, and gasification. Pyrolysis is a process in the absence of oxygen at high temperatures, promoting the decomposition of large polymer molecules to convert them into a mixture of small intermediate chemical compounds. The mechanical pretreatment processes before pyrolysis involve sorting, metal separation, and shredding. After the pyrolysis conversion process, the hydrocarbon vapors are condensed to produce pyrolysis oil. The non-condensable gases (syngas) and pyrolysis char (biochar) can be either utilized for reheating the pyrolysis process or sold for other purposes, such as energy recovery or chemical production. Previous studies have identified recycling plants with a capacity of up to 5000 metric tonnes per year with a proposed oil yield of an average of 67% while only producing 38.9-250.4 kg CO₂eq of emissions. Total production cost was also reported to range from \$0.75-\$9.49/gallon of liquid oil, achieving the breakeven point within 4-6.2 years. In addition, biochar can be recovered as a byproduct utilized on different products (e.g., asphalt, concrete, insulation, and energy source cement). Recycling plastics via the pyrolysis process can mitigate approximately 100 kg CO₂eq/ton compared to emissions generated by landfill disposal (Almohamadi et al., 2021; Chhabra et al., 2021; Neha et al., 2022; Pacheco-López et al., 2021). The solvolysis process involves utilizing solvents to cleave the rigid chemical structure of polymers for recycling fibers. The primary agents are water and

alcohols for the depolymerization reaction. The solvent concentration is an essential parameter in solvolysis. La Rosa et al. (2021) conducted a life cycle assessment of carbon fiber to reinforce thermoset composite via solvolysis. Their results indicated that solvolysis plastic recycling produces 0.58 kg CO₂eq/kg, making it affordable and environmentally friendly (La Rosa et al., 2021). Other researchers exploring solvolysis closed loop have reported total emissions ranging from 1.7-16.2 kg CO₂eq/metric while a total cost ranging from \$.98-1.4/kg of carbon-reinforce fiber recycled (Chaudhari et al., 2021; Kawajiri and Kobayashi, 2022; Khalil, 2018). Hydrogenation is the cracking of hydrocarbon bonds by a catalyst and the addition of hydrogen to produce alkene and alkyne compounds. This process uses a platinum metal catalyst on a strontium titanate nano cuboid. Zhao et al. (2021) studied a consequential life cycle assessment of HDPE via hydrogenation for producing gasoline and diesel. Their results show total emission of 331.4 kg CO₂eq/ton and a total production cost of \$220.3 per ton (Zhao and You, 2021).

Pyrolysis is categorized into two primary categories: fast and slow pyrolysis, which depends on operating conditions. The feedstock undergoes thermochemical decomposition between 300-500°C for slow pyrolysis and 400-650°C for fast pyrolysis, with a residence time of seconds for fast and anywhere from 10-90 minutes for slow (Lu et al., 2020). The products derived from plastic pyrolysis are oil, char, and gas. (Honus et al., 2018). Plastic waste pyrolysis supports oil production with general yields of 37-75%, while 10-20% of the byproducts are composed of gaseous hydrocarbons and 15-25% char solids (Nanda and Berruti, 2021; Wang et al., 2021). The slow pyrolysis process is an attractive technology for increasing the product yield of high-quality oil. As reported, a competitive advantage over other techniques includes long residence time, heat transfer control, and more effective control of inlet and outlet flow rates for better-quality products (Das and Tiwari, 2018). Regarding the pyrolysis products, char production is mainly favored at low temperatures between 300-450°C, oil at intermediate temperatures ranging from 450-800°C, while gas is dominant at high temperatures of about 800°C. The yield of oil, char, and gas varies depending on the plastic type, particle size, temperature, heating rates, use of solvents, and pressure during the conversion. Plastic waste pyrolysis has proven challenging to commercialize as a recovery method due to waste collection and sorting and the lack of a clear pathway to analyze the value-added products from recycled plastics. A supply chain process for collection is essential to implement circular economy practices that can achieve economic feasibility for upscaling the recycling process. Recent studies have researched pyrolyzing various plastic wastes (e.g., PET, HDPE, PVC, LPDE, PP, and PS), which assessed the effects of different feedstocks at temperatures ranging between 300-500°C. The various plastics contain different hydrogen/carbon (H/C) ratios, which is significant for oil conversion and economic feasibility (Nanda and Berruti, 2021; Wang et al., 2021). This study

focuses on oil and char production from PS wastes via the slow pyrolysis process. The oil produced from polystyrene consists mainly of styrene monomers, which can be used as raw materials to produce polystyrene for different industrial products (Mortezaeikia et al., 2021; Pan et al., 2020).

This study explores a fixed bed (batch) slow pyrolysis conversion process for converting plastic wastes to value-added products. The primary objectives and novelty of this study are to examine and improve the reactor design (e.g., height and capacity), conversion parameters (e.g., carrier gas pressure, reactor temperature, and residence time), and reaction kinetics (e.g., activation energy, heating rate, and chemical composition). The focus is determining the process yields, and PS-derived oil composition at different temperatures. The pyrolysis reactor operates at temperatures between 450-575°C for 30 min under 69-103 kPa. The PS samples were pyrolyzed at heating rates of 5, 10, 15, 20, 25, 35, and 50°C/min under nitrogen (30 mL/min) in temperatures ranging from 30 to 900°C, using thermogravimetric analysis (TGA). TGA and differential scanning calorimetry (DSC) was also used to analyze thermal degradation characteristics.

4.3. Materials and Methods

4.3.1. Pretreatment Processes

The pyrolysis experiments were performed with PS as the feedstock obtained from disposable household and food plastic wastes, including beverage cups, food containers, and Styrofoam packing. A V-180 plastic grinder machine was used to produce different PS particle sizes (2-6 mm). After grinding, PS samples were dried in an oven at 90-100°C for 12-24 h for size reduction. **Table 4-1** presents the physical properties of the used PS samples in this study.

Table 4-1. Polystyrene characteristics

Plastic Type	Particle Size (mm)	Density (g/cm³)	Calorific Value (kJ/g)
PS	2-6	1.05	41.0 ± 1.0

4.3.2. Pyrolysis Conversion Process

The slow pyrolysis of PS was conducted with 60-80 grams of PS samples in a stainless-steel batch reactor with temperatures between 475-575°C and pressures between 69-103 kPa with a residence time of 30 min (**Figure 4-2**). As the PS thermally degrades, pyrolysis products formed are condensable vapors, non-condensable products, and char. The batch reactor conditions are set with a programmable logic controller. Heating tape and a plate heater were used to supply heat to the batch reactor.

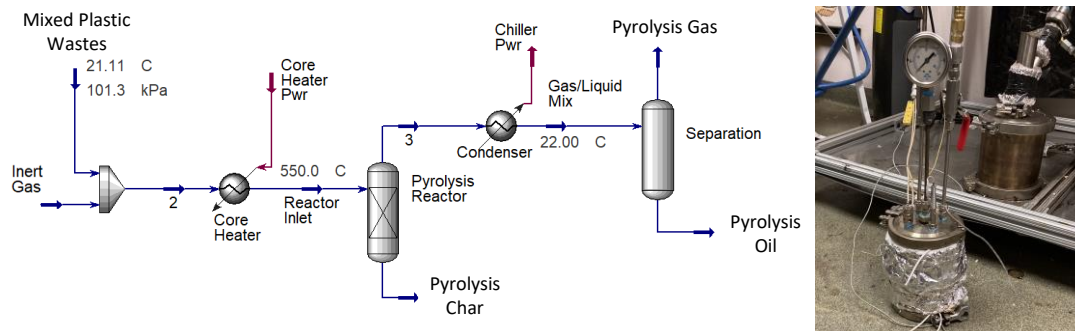


Figure 4-2. Fixed bed (batch) slow pyrolysis reactor for oil and char production from PS

Table 4-2 presents the main parameters of the proposed batch slow pyrolysis reactor. The pyrolysis gases exit the reactor to a condenser column at 5°C, are rapidly cooled, and the vapors condensed in an oil trap succeeding the condenser. The oil produced was collected and stored in a refrigerator at 5°C to prevent further chemical structure changes. The produced char was collected in the bottom of the reactor, weighed, and stored at room temperature. The mass difference estimated the yield of non-condensable gases byproduct. The experiment conditions were structured to analyze the temperature effects in the batch pyrolysis reactor. Experiments 1-3 were conducted to study the temperature of PS depolymerization at 475°C. In experiments 4-6, the reactor temperature was increased to 525°C. Finally, the batch reactor temperature was raised to 575°C in experiments 7-9.

Table 4-2. Slow pyrolysis reactor configurations

Parameters	Values
Reactor temperature (°C)	400-575
Reactor height (mm)	152
Reactor diameter (mm)	63.5
Condenser height (mm)	305
Condenser diameter (mm)	63.5
Reactor capacity (gram)	150

Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC)

TGA was performed on PS (5-6 mg), using a PerkinElmer TGA-7 instrument from 30 to 900°C at heating rates (β) of 5, 10, 15, 20, 25, 35, and 50°C/min under nitrogen (30 mL/min) to determine activation energy (E_a) and thermal degradation behavior. Isothermal TGA was also used to determine the mass yield of char during pyrolysis at a given temperature. The temperature was ramped from 30°C at 200°C/min to 475, 525, and 575°C and then held for 30 min. The TGA data

were analyzed using Pyris v11 software. Additionally, DSC was performed on the PS samples and char samples (8-9 mg) using a Perkin Elmer DSC-7 instrument from 25 to 250°C at a ramp rate of 10°C /min under N₂ (20 mL/min) to determine glass transition temperature (T_g).

4.3.3. Pyrolysis Oil and Char Analysis

The oil samples, 2 mg in CH₂Cl₂ (1 mL), containing 1,2,4-trichlorobenzene (800 µg/mL) as an internal standard, were analyzed by gas chromatography-mass spectrometry (GC-MS) using Trace 1300-ISQ ThermoScientific. Separation was achieved on ZB-5 capillary column (30 m × 0.25 mm Ø, 0.25 µm coating, Phenomenex, Torrance, CA, USA), using a temperature program of 40°C (1 min) to 280°C (10 min) at 5°C/min. The identity of the peaks was determined using authentic standards and matching spectra with the NIST 2017 library. Fourier-transform infrared (FTIR) spectra of PS and char samples were obtained using a Thermo-Nicolet iS5 spectrometer equipped with a ZnSe attenuated total reflection (iD5 ATR) accessory. FTIR spectra were baseline corrected using the Omnic v9.3 software (Thermo-Nicolet).

4.4. Results and Discussion

4.4.1. Thermal Analysis

TGA analyzed the thermal degradation and kinetic performance of PS. DSC and TGA are standard techniques that help measure thermal transition for identifying T_g and thermal degradation (T_d) for calculating activation energy under different conditions. The T_g of PS was 103.2°C. **Figure 4-3** presents the TGA results of PS, indicating that the kinetics degradation encompasses a single stage with no water content at the beginning of the degradation process. The cleaving of polymer structure chains can explain the observed degradation. The equilibrium is achieved fast with an increase in temperature. Previous studies reported that the pyrolysis of PS occurs in three stages (i.e., initiation, transfer, and termination) of the radical chain process (Kiran et al., 2000; Lu et al., 2021), which is crucial for designing and optimizing the pyrolysis conditions and vessels. Experiments were developed at three different temperatures (475, 500, and 575°C) to examine the effect of temperature on mass loss with respect to time.

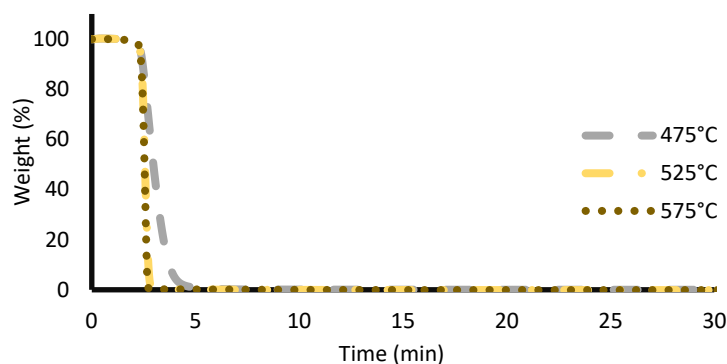


Figure 4-3. Isothermal TGA at 50 °C increments

Additionally, the isothermal TGA indicates that the decomposition of PS plastic waste started within 2 min from all temperatures and the total decomposition point of 97% at 475°C at approximately 5 min (**Figure 4-3**). By increasing the temperature from 475°C to 575°C, the reaction reached maximum rates and showed a 50%-time reduction for weight loss, while the complete decomposition was reached within 3 min. The TGA experiments indicate that PS waste degradation was achieved at a maximum point of 3 min and a temperature of 525°C at the specified heating rates. Previous studies determined iso-conversional methods are dependable for calculating the activation energy with the assumption of a first-order reaction model because maintaining a constant extent of conversion results in a reaction rate that is only a function of temperature (Mortezaeikia et al., 2021; Nisar et al., 2019).

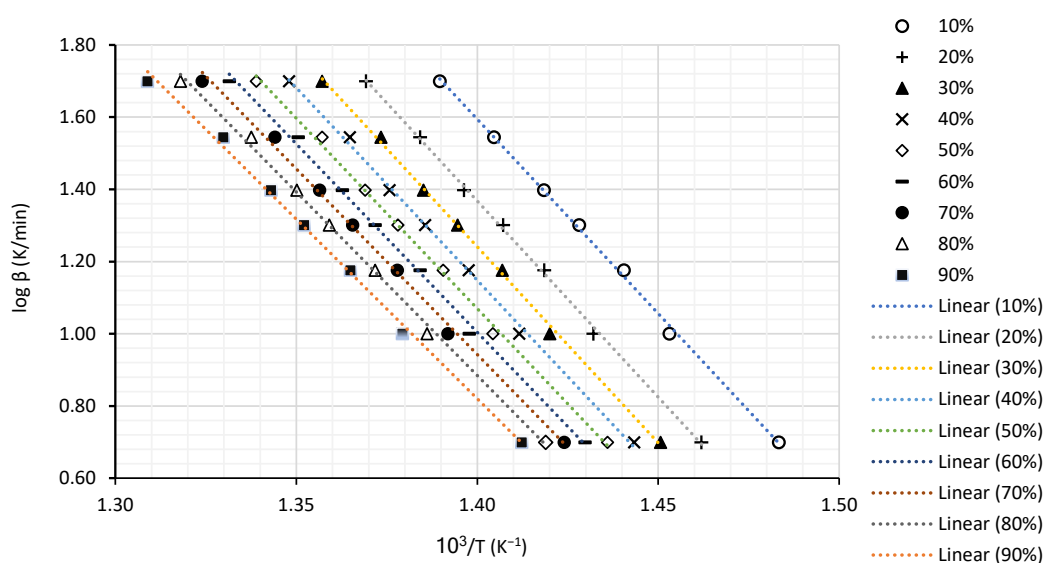


Figure 4-4. Apparent activation energy determination of PS

This study used the Ozawa Flynn Wall (OFW) equation to analyze PS waste thermal degradation kinetic parameters. **Figure 4-4** presents the iso-conversional effective activation energy dependencies of $\log\beta$ (K/T), which shows a linear regression of the OFW method in the conversion (α) range of 10-90%. The result indicates that iso-conversional lines have comparable kinetic parameters (Janković and Manić, 2021; Nisar et al., 2019). The analysis of E_a values shows that the degradation stage is constant at an average of 191 kJ/mol in $10\% \leq \alpha \leq 90\%$, with an almost linear relationship from $30\% \leq \alpha \leq 90\%$, and is led by a single reaction step (**Table 4-3**). The E_a analysis was compared with prior studies. For example, Nisar et al. (2019) reported activation energy ranging from 83.0 to 164 kJ/mol at heating rates of 5, 10, 15, and 20°C/min (Nisar et al., 2019). While utilizing TGA of PS waste and virgin PS, previous studies observed an activation energy of 137 and 172 kJ/mol (Chao-Hsiung Wu et al., 1993; Encinar and González, 2008). Aguado et al. (2003) reported 207-223 kJ/mol values at temperatures between 340-390°C (Aguado, 2003). The Activation energy of PS polymers can be heavily influenced by properties, such as molecular weight, density, and heating value. The result of this study is comparable with the findings reported by previous PS thermochemical decomposition reports.

Table 4-3. Activation energy of PS at different conversion factors

Conversion Factors (α)	Slope	E_a (J/mol)
10%	10.76	196
20%	10.87	198
30%	10.86	198
40%	10.67	194
50%	10.54	192
60%	10.43	190
70%	10.28	187
80%	10.16	185
90%	9.95	181
Average	-	191

4.4.2. Product Yield

This study focuses on developing a slow pyrolysis setup to maximize the oil conversion yield from PS. The grinder and oven were utilized as pretreatment for size reduction. The experiments were conducted at different temperatures (i.e., 475, 525, and 575°C) to explore the temperature effects on the yield (**Table 4-4**) and quality (thermal stability) of the desired oil produced.

Table 4-4. PS pyrolysis products' yield in various temperatures

Experiments	Temperature (°C)	Oil Yield (%)	Char Yield (%)
1	475	45.7	34.1
2	475	47.5	27.8
3	475	69.2	8.5
4	525	53.9	14.4
5	525	64.8	1.9
6	525	57.3	8.3
7	575	54.0	0.7
8	575	62.2	10.6
9	575	54.7	0.0

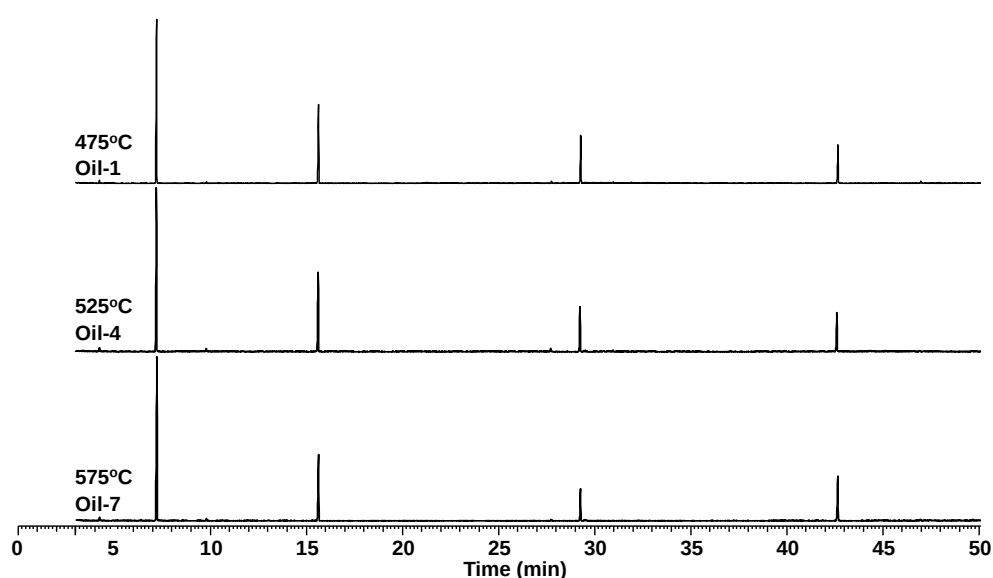
Exploring different temperatures at 30 minutes residence time allows for identifying the optimum temperature for slow pyrolysis of PS plastic waste while minimizing time and maximizing the oil yield. Miandad et al. (2016) determined that the decomposition started at 400°C while reaching the optimal decomposition point of 91% at 450°C, and while increasing the temperature to 650°C resulted in 4-5% of weight loss, using TGA. Furthermore, when using a batch reactor at a residence time of 75 min, oil yield increased from 76% to 80.8% when increasing temperature from 400-450°C while char decreased from 16% to 6.1% (Miandad et al., 2016b). Prior studies utilizing batch reactors reported that maximizing oil yields from 69% to 91% at temperatures of 400-475°C. Therefore, a controlled environmental condition (e.g., temperature and residence time) is a significant factor to consider while using small-scale reactors, maximizing oil yields, and minimizing char waste.

4.4.3. Product Characterization Results

The GC-MS analysis of PS condensed volatile products produced at 475-575°C and were analyzed by GC-MS equipment (Trace 1300-ISQ, ThermoScientific) under various retention times, and trace mass in different types of aromatic hydrocarbon compounds were present in the analysis (**Figure 4-5 and Table 4-5**). Furthermore, the degradation of PS tends to favor depolymerization reaction due to the high stability of benzylic radical intermediate, which leads to a high yield of aromatic compounds, such as styrene, toluene, and α -methyl styrene. The polyaromatic formation reactions of the radicals also lead to a noticeable concentration of polyaromatic hydrocarbons (i.e., 1,3-diphenyl-propane, 2,4-diphenyl – 1-butene, and 2,4,6-triphenyl- hexene). Therefore, it can be concluded that the results of this GC-MS study align with previous studies (Park et al., 2020). Jaafar et al. (2022) reported that volatile products obtained from PS feedstock via pyrolysis were composed primarily of styrene, α -methylstyrene, and toluene (Jaafar et al., 2022). Aguado et al. (2003) informed that ethyl benzene and toluene concentration increases at higher temperatures, while styrene compounds should decrease (Aguado, 2003).

Table 4-5. PS pyrolysis oil composition

Compound	M+ (m/z)	RT (min)	475 °C (mg/mg oil)	525 °C (mg/mg oil)	575 °C (mg/mg oil)
toluene	92	4.23	0.008 ± 0.003	0.012 ± 0.001	0.011 ± 0.004
ethyl benzene	106	6.39	0	0.001 ± 0.002	0.003 ± 0.001
styrene	104	7.2	0.570 ± 0.016	0.565 ± 0.029	0.600 ± 0.021
a-methyl styrene	118	9.8	0.002 ± 0.003	0.010 ± 0.000	0.007 ± 0.001
1,3-diphenyl-propane	196	27.76	0.008 ± 0.001	0.009 ± 0.003	0.003 ± 0.002
2,4-diphenyl-1-butene	208	29.28	0.178 ± 0.009	0.147 ± 0.026	0.101 ± 0.010
2,4,6-triphenyl-1-hexene	312	42.66	0.145 ± 0.010	0.139 ± 0.009	0.158 ± 0.012
Total			0.913 ± 0.012	0.883 ± 0.006	0.883 ± 0.022

**Figure 4-5. GC-MS chromatograms of PS pyrolysis oil-1, oil-4, and oi-5**

The pyrolysis chars were analyzed by DSC and FTIR spectroscopy. DSC was used on PS and char samples to investigate the transition temperature. The char samples 1, 2, 3, 4, 5, 6, and 8 were hard and glassy lumps in nature with T_g of 60, 65, 76, 60, 84, 82, and 87°C, respectively. The chars have a lower T_g (between 16 and 43°C lower) than PS, suggesting that the molar mass decreased. Solid char sample 7 was a powder and did not show a T_g . FTIR spectral analysis of PS pyrolysis char samples 1, 2, 3, 4, 5, and 6 were very similar to PS (**Figure 4-6 and 4-7**). DSC study shows that char sample characteristics are very similar to PS. Char samples 7 and 8 had bands associated with PS and char (Reeves, 2012).

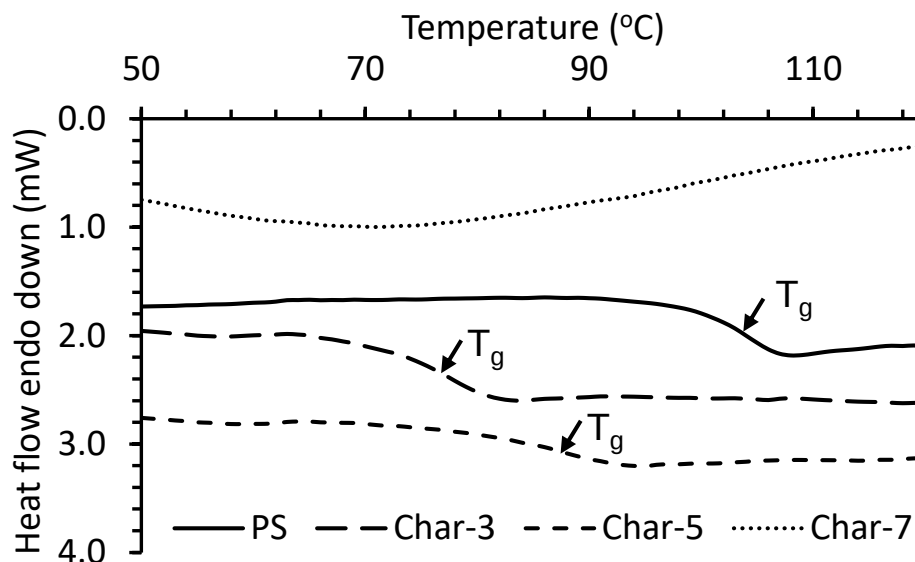


Figure 4-6. DSC thermograms of PS and char-3, char-5, and char-7

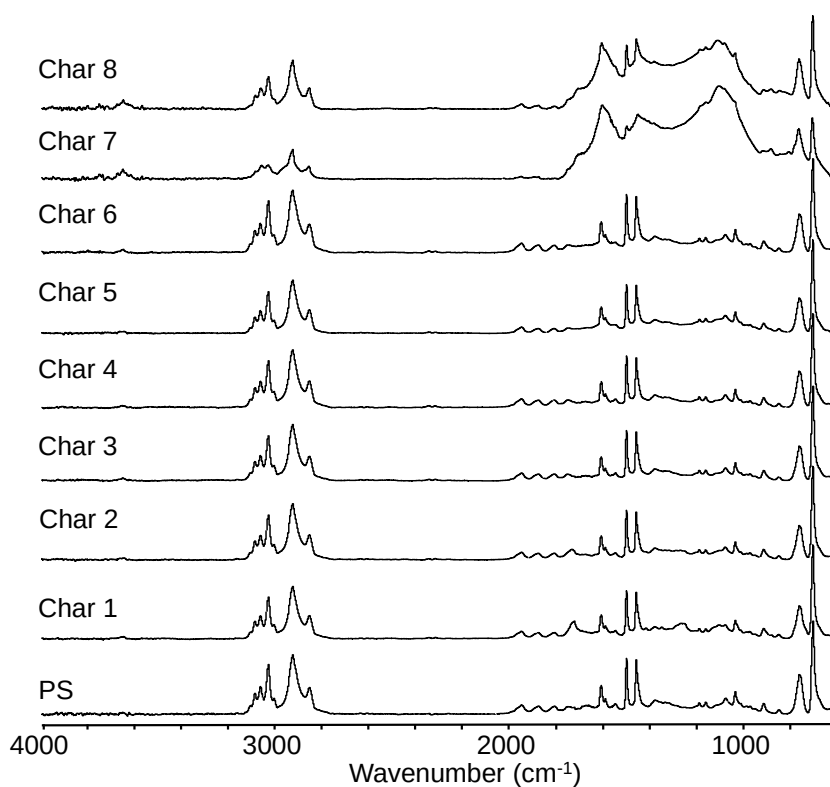


Figure 4-7. FTIR spectra of PS and char samples

Plastic is a highly versatile consumer product due to its low weight, high strength, and durability advantages, making it an essential part of many industries, such as packaging, transportation, and agriculture. However, plastic-based products have rigid chemical structures,

causing environmental degradation due to the lack of sustainable waste disposal methods. Pyrolysis is a thermochemical technology that operates in the absence of oxygen, degrading complex rigid molecule polymers into a short chain by heat and pressure application under inert conditions. The slow pyrolysis advantage is the duration leading to superior heat transfer and heat control flow rates of inlet and outlet with higher liquid yield making it a practical and sustainable waste management route for PS chemical recycling (Das and Tiwari, 2018). This study explored slow pyrolysis with 30 min of residence time to better understand the production of value-added products due to limited articles on the effects of reactor design and pyrolysis duration. In addition, the key parameters for producing high-quality intermediate products are feedstock type, conversion temperature, and residence time (Table 4-6). The intermediate products can be upgraded to value-added products, such as energy sources, fuel lubricants, and fuel additives (Figure 1). Currently, the technological readiness level (TRL) of plastic pyrolysis is between 6-8 (pre-commercial demonstration in expected conditions), which needs further studies, especially on reactor design for mixed plastics and scalability to reach TRL 9 (commercial operation in relevant environments). Future studies should conduct sustainability assessments (Mirkouei, 2016; Mirkouei and Kardel, 2017; Thompson et al., 2021) and root-cause analysis (Hansen et al., 2019, 2019; Mirkouei, 2020; Mirkouei et al., 2017) to identify key variables that affect total costs and environmental impacts (Nembhard et al., 2019).

Table 4-6. Recent studies on plastic waste recycling via pyrolysis process

Study	Research Focus	Feedstock Type	Temperature (°C)	Residence Time (min)	Process Yield (%)		
					Oil	Char	Gas
(Abbas-Abadi et al., 2014)	Process yield	PS	450-600	20	100.0	0.0	0.0
(Abnisa and Wan Daud, 2014)	Oil quality	PP	500	60	84.9	10.5	4.6
(Seifali Abbas-Abadi et al., 2015)	Process yield	LDPE	420-510	-	87.0	8.4	4.4
(Xue et al., 2015)	Pyrolysis oil and gases	HDPE, red oak	525-675	54-68	57.6	14.0	36.7
(Miandad et al., 2016a)	Process yield	PS	400-500	60-120	78.5	8.9	12.6
(Kunwar et al., 2016)	Pyrolysis gases	PS	500	-	71.0	27.0	2.0
(Miandad et al., 2017)	Process yield	PS, PE, PP, and PET	450	75	40.0	18.0	42.0
(Fivga and Dimitriou, 2018)	Techno-economic assessment	PE, PS, PP	530	-	87.2	8.7	4.1

Table 4-6 (continued)

(Thahir et al., 2019)	Process yield	PP	500-650	-	88.0	7.0	5.0
(Dwivedi et al., 2019)	Literature review	Various	300-900	20-150	84.0	3.0	13.0
(Mangesh et al., 2020)	Process yield	HDPE, LDPE, PP	300-900	30	67.5	17.3	15.3
(Hussain et al., 2020)	Pyrolysis oil and gases	PE	200-800	15-75	83.7	5.0	11.3
(Premalatha et al., 2021)	Process yield	PP	400-460	70	84.3	5.9	9.7
This Study	Process yield and characteristics	PS	475-575	30	69.2	8.5	22.3

4.5. Conclusion

This study successfully converted waste polystyrene to oil and char products. PS pyrolysis conversion demonstrated a one-step process, using Ozawa Flynn Wall and isothermal methods. The PS char (solid) product contained partially reacted PS, and further pyrolysis is required for complete conversion. The PS slow pyrolysis oil contained predominantly styrene with the presence of dimers and trimers. Styrene can produce PS or in vinyl-ester resins but needs to be refined and distilled to obtain a pure fraction. The results show that the conversion temperature remains the main parameter to achieve a high yield and quality for oil production from PS. It is concluded that pyrolysis can provide a sustainable pathway for PS waste recycling and conversion to value-added products, such as various chemical compounds. Future studies will (a) examine the use of the PS pyrolysis oil for use in polymers and (b) optimize the pyrolysis process for oil yield and styrene content.

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Chapter 5. Conclusion

5.1. Summary

In chapter 2, the literature review was performed to identify different biofuel technologies and processes through prior studies. The review provides evidence that thermochemical is the most efficient technology for mixed feedstock energy recovery conversion and implementation at the industry level.

In chapter 3 proposed the idea of converting municipal plastic waste (MPW) to p-oil via portable thermochemical conversion. Life cycle assessment (LCA) and techno-economic assessment (TEA) methods are applied to show the feasibility and sustainability benefits of producing MPW-based liquid hydrocarbon compounds using a portable refinery unit in a Southeast Idaho case study. The multi-criteria analysis showed that the thermochemical process offers both economic and environmental sustainability for implementation.

Chapter 4 evaluates the potential of polystyrene (PS) recycling via fixed bed slow pyrolysis reactor. A reactor was developed to carry out experiments to study the conversion parameters and reaction kinetics. The analysis showed that the conversion temperature remains the main parameter to achieve a high yield and quality for PS oil production.

5.2. Conclusion

In chapter 2, it was determined that more search was needed in technology diversification to provide future research with a solid foundation on which to design innovation in the future. For example, decades of research have been conducted on multiple conversion processes for energy recovery, all of which aided the implementation of co-conversion technologies. However, it was further determined that few technologies have focused on industrial implementation.

In chapter 3, it was determined that recycling operation near the collection sites is the most significant factor in reducing the unit price and carbon footprint. Also, it was concluded that despite the lower capital cost, p-oil produced by portable refinery means a cost-effective pathway. It was further determined that pyrolysis could reduce lower greenhouse emissions compared to landfill disposal.

In chapter 4, it was determined that the pyrolysis process could successfully convert PS waste to oil and char products. The PS slow pyrolysis oil contained predominantly styrene with the presence of dimers and trimers that can be repurposed to produce pure PS or vinyl-ester resins. It is concluded

that pyrolysis can provide a sustainable pathway for PS waste recycling and conversion to value-added products, such as various chemical compounds.

5.3. 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 sustainability's environmental and economic aspects.
- Evaluated the sustainability of MPW recycling from both an economic and environmental perspective.
- Proposed a real case study to produce pyrolysis oil from MPW in southeast Idaho.
- Provided results of fixed bed slow pyrolysis conversion process.

5.4. Opportunities for Future Research

Chapter 2 of this paper lays out different methods, approaches, and tools utilized by previous studies, most of which are from the past decade. Comparisons have been made of the most popular thermochemical processes. Future research has the opportunity to utilize the information that has been accumulated in this document and build upon it.

Chapter 3 considers the portable pyrolysis technology for pyrolysis oil production from MPW. First, the process was laid out on paper using data from multiple researchers researching pyrolysis oil from municipal plastic waste. The subsequent research step would take work from the theoretical methodology and applied to the current industrial recycling process for the MPW conversion to pyrolysis oil and char. As a result, sufficient waste is available to accomplish the process sustainability.

Chapter 4 lays out the steps to complete PS waste recycling possible. The process laid out in this study uses process knowledge, collaborators, researchers, and design from previous studies to produce pyrolysis oil and char. The next realistic research step would be to examine the use of the PS pyrolysis oil for use in polymers and optimize the pyrolysis process for oil yield and styrene content. Sufficient parameters for process optimization include temperature, residence time, and pretreatment of PS waste. Styrene, the main ps-oil compound byproduct, can be refurbished to produce pure PS plastic or vinyl-ester resins. This study did not consider other chemicals byproducts that can be regarded as hazardous chemicals.

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