12-15-2021 9:45 AM

# Thermochemical Conversion of Plastic to Value Added Products

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A thesis submitted in partial fulfillment of the requirements for the Master of Engineering Science degree in Chemical and Biochemical Engineering

## Recommended Citation

Maslak, Anastasia L., "Thermochemical Conversion of Plastic to Value Added Products" (2021). *Electronic Thesis and Dissertation Repository*. 8299.
https://ir.lib.uwo.ca/etd/8299

# Abstract

In this study, the use of pyrolytic cracking for managing non-recyclable plastic waste by conversion into value-added liquid and gaseous products was investigated. A single-stage reactor and a novel, two-stage reactor set-up were used for experiments involving polyethylene and polypropylene. Parameters including feedstock composition, feed rate, temperature and residence time were studied. The two-stage approach was investigated to overcome existing transportation limitations involved in the typical plastic waste lifecycle. Bulky plastic collected in towns and cities must be transported to industrial facilities typically located elsewhere for reprocessing. Both HDPE and LDPE showed promising results for olefin recovery with ethylene gas yields of 26.6% and 34.1% of the original polymer, respectively. A maximum hydrogen yield over all the experiments of 46.2% which was obtained using LDPE. The economic feasibility of scaling up the processes was analyzed. It was found that the two-stage set up increased the gas yields of both hydrogen and ethylene and rendered the process to be economically viable with a payback period of 3 years.

# Keywords

Plastic recycling, pyrolysis, thermal decomposition, polyethylene, polypropylene, monomer recovery, ethylene, propylene, hydrogen

# Summary for Lay Audience

The persistence and dispersion of plastic waste has been proven to be a very visible and damaging environmental issue. Enhanced by the COVID-19 global pandemic, the world's plastic use and consumption is drastically increasing. New technologies need to be developed to address concerns of waste accumulation.

In this study, a thermochemical technology called pyrolysis was used to convert plastic waste into value added products. Pyrolysis involves the thermal decomposition of polymers in the absence of oxygen at elevated temperatures. The aim of this process is to deconstruct the polymer materials back into their "building block" monomer components, so that new plastic can be remade of the same quality as the virgin material. In this study, an analysis was performed on plastic feedstock demonstrating the ability to convert an overall percentage of 34.1% into the gaseous monomer form.

Other products from pyrolysis include oil and other gaseous components. The oil collected showed promise to be used as a fuel, and the other gas components can be recycled back to the process for use in powering the plant. An economic evaluation was done to demonstrate the economic feasibility of this system.

# Co-Authorship Statement

| |
|---|
| Chapter 3 |
| Authors: Anastasia Maslak, Sadegh Papari, Tahereh Sarchami, Stephanos Horvers, Franco Berruti |
| Anastasia Maslak performed all the pyrolysis experiments, data analysis and writing. Sadegh Papari and Tahereh Sarchami helped with the analytical work, data analysis and experimental work. Stephanos Horvers assisted with the pyrolysis experiments and data analysis of the single-stage pyrolysis work. Franco Berruti supervised the research work. |

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|---|
| Chapter 4 |
| Authors: Anastasia Maslak, Maddalena Laghezza, Franco Berruti |
| Maddalena Laghezza and Anastasia Maslak collaborated on the mass and energy balances used in Chapter 4. Maddalena Laghezza provided the methodology and calculations for the techno-economic evaluation. Franco Berruti supervised the work. |

# Acknowledgments

The completion of my thesis comes from the support and assistance of many people.

First, I would like to thank my supervisor Dr Franco Berruti for his guidance, instruction, and support. I am so appreciative of the opportunity to join your team. Your feedback and insights pushed me to elevate the quality of my work and dig deeper into my research.

Next, I would like to thank my post doc supervisor Dr Sadegh Papari for all his assistance running experiments, as well as providing guidance and mentorship. I would also like to thank Dr Tahereh Sarchami for her support in the analytical lab and willingness to constantly answer my many questions as well as Thomas Johnston for his help in the pilot plant.

Thank you to all my friends and colleagues at ICFAR. You made coming to work so enjoyable and provided me with the invaluable opportunities to pick your brains and collaborate on your work. I would especially like to highlight my sincere gratitude towards Maddalena Laghezza, Nicolas Sarmiento, Stephanos Horvers, Islam Elghamrawy, Shokooh Karami, Heejin Lee and Dharavi Balusani for all your help.

To my family and friends outside of the lab. Thank you for all the unwavering kindness, and instilled appreciation of achieving a work life balance. Thank you to my wonderful parents and sister, as well as my roommate Katie and dear friends Pranav, Sammi, Olivia, Paige, Rachelle, Tori and Ammi.

Thank you

# Dedication

*To my sister, Ollie*

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# 1 Introduction and Background

## 1.1 Research Motivation

Plastic waste pollution has become an issue that is heavily scrutinized by the international community. Most plastics used today are derived from fossil hydrocarbons. They are often not biodegradable [1] . In 2015, the global production of resins and fibers was estimated to be 380 Mt. [2] Industrial development has pushed the manufacturing and disposal of plastics [2]. Plastic products play an important role in society, as they provide advantages of being lightweight, and versatile over similar materials. However, their improper disposal can lead to the contamination of the environment [2]. Plastic pollution has become a concern for marine and freshwater ecosystems as well as soil ecosystems. Some researchers have suggested that plastic waste is so pervasive in the environment if could be used as a geological indicator for the proposed Anthropocene era [3]. Microplastics, defined as plastics smaller than 5 mm [4], have been investigated due to their potential impact on health. Microplastics can be released into the environment through two different sources, primary and secondary [5]. Primary microplastics are produced as smaller sizes and enter the environment as such. An example would be microbeads in personal care and cosmetic products [6]. Secondary microplastics are derived from plastic waste being dispersed into the environment and undergoing various forms of degradation to smaller sizes [7]. Studies suggest that when microplastics enter the body they can pass through the intestinal barrier and cause negative health effects or further serve as a vector for microorganisms and/or toxic chemicals [7]. Smaller microplastics have the potential to irritate cells and tissue as a foreign presence [4]. In 2018, China banned the importation of plastic waste from other countries. This ban pushed richer countries to export their plastic waste to developing countries. However, in 2019 the United Nations' Basel Convention was amended to include plastic waste. Now many countries, including Canada, must develop initiatives to handle their own plastic waste [8]. This has created an incentive for developments in improving and extending recycling technologies. In Canada 3 million tonnes of plastic waste reach their end of life annually, with only 9% of that being recycled [9] . In 2016, an estimated 29,000 tonnes found its way to pollute the natural environment [9]. This leaves a gap that should be bridged with innovative solutions.

There are several effective options that can be used to process and repurpose plastic waste. Mechanical recycling can be used to convert recycled material into new plastic products. However, this involves the degradation of the polymers, resulting in limitations with using mixed plastics, composite blends, and contaminated polymers. The low cost of virgin plastics reduces the economic feasibility of this process [10]. Chemical recycling, where the plastic's polymer chain is broken down into its monomer components, is seen as a favorable alternative because it allows for recycled plastic to be created with the same quality as the virgin material. Pyrolysis is a form of chemical recycling that employs thermal decomposition in an oxygen-free environment and will be examined under the scope of this thesis.

This study introduces an innovative two-stage approach for recycling plastic waste. The first stage will utilize thermal decomposition techniques to transform the solid plastic waste into a liquid oil that can be easily transported from waste collection sites located within municipalities to virgin plastic manufacturing locations, typically located away from major urban centres. This study represents an original contribution to the management of plastic waste through the utilization of a secondary furnace to further crack down pyrolysis oil/waxes into the monomer building blocks that can be utilized for repolymerization. In this thesis, continuous pyrolysis will be discussed to convert plastic waste to value-added oil and gas products. I will elaborate on the effects of reactors' temperature, residence times, feed rates, and feed compositions on the yields and quality of the products.

## 1.2 Literature Review

### 1.2.1 *Thermoplastics and Thermosetting Polymers*

One key characteristic that is used to classify polymers is the glass transition temperature. With an amorphous polymer, the temperature at which the structure shifts towards a viscous liquid or rubbery state is defined to be the Glass Transition Temperature, $T_g$ [11]. If at the $T_g$ the polymer softens and adopts a viscous liquid state the polymer can be classified as a thermoplastic. Thermoplastics have many desirable properties such as improved strength, toughness, and hardness. Whereas thermosetting polymers undergo an irreversible solidification process resulting in mechanical properties that are not temperature dependent. At higher temperatures these polymers will undergo chemical decomposition and structural degradation [12].

### 1.2.2 *7 Classes of Plastics- Uses and Opportunities for Recycling*

An identification system from the Society of the Plastics Industry is used to group plastics into 7 classes [13]. These groups are: 1) Polyethylene Terephthalate (PET) , 2) High Density Polyethylene (HDPE), 3) Polyvinyl Chloride (PVC), 4) Low Density Polyethylene (LDPE), 5) Polypropylene (PP), 6) Polystyrene (PS), and 7) Mixed-use plastics [14]. The first group, PET, is the typical component used to make drinking bottles [14] is easily recyclable and doesn’t lose its quality over repeated cycles [15] . High density polyethylene has applications in packaging such as shampoo and detergent bottles [14]. High density polyethylene is also easily recyclable, so long as there are no contaminants or other components mixed in the batch [16]. Polyvinyl chloride is used in the manufacturing of commercial cling wrap and cosmetic containers [14]. It is also used for the construction of pipes. The high chlorine content in PVC as well as other additives make it challenging to recycle and requires separation from other materials prior to its processing [16]. Low density polyethylene is a commonly used polymer used in applications such as squeeze bottles and garbage bags [14]. Low density polyethylene must be separated for its recycling. Additives, including coloring, can affect its value [16]. Polypropylene is found in yogurt containers, medicine bottles and straws. It is one of the least recycled post-consumer plastics due to the difficulty in removing contaminants [16]. Polystyrene, trademarked as Styrofoam in its expanded form, is used in take-out food containers. Due to its low density and bulkiness, it is challenging and expensive to transport [16]. Conventionally #7 mixed plastics are difficult to recycle using traditional methods due to impurities and contaminants. Polypropylene and PE are two of the largest percentage components of typical municipal solid waste (MSW) [17]. These plastics were investigated under the scope of this thesis to represent common post-consumer mixed plastics.

### 1.2.3 *Polyethylene and Polypropylene*

Polyethylene is the most widely used plastic polymer [18]. It has the simple base structure of repeated $CH_2$ units. Overall, it has many desirable characteristics that explain its widespread use; including low price, good chemical resistance, good processibility and the ability to utilize it for complex shapes, and visual appeal. It is used in a wide range of applications ranging from film packaging to piping. Polyethylene can further be classified based on its density. Low density polyethylene has a molecular chain with significant branching, making it difficult to compact into dense structures. This gives it the physical properties of being a tough but flexible substance. It is also extremely resistant to water [19]. Overall, its characteristics make it suitable for use in food and non-food packaging and as a film. High density polyethylene has a linear molecular chain formation, making it able to pack together more tightly [20]. This characteristic structure provides greater stiffness making it more suitable to use in applications such as containers and plumbing features [21]. The melting point of HDPE is known to be 130°C whereas the melting point of LDPE is 110°C [22].

Polypropylene is a saturated linear hydrocarbon. Its repeating units include a methyl $CH_3$ group [23]. It contributes to approximately 24.3% of MSW [19], and it is used in a variety of applications such as flowerpots, car bumpers and furniture [19]. It is also commonly used in “fast-turnover” food packaging items such as yogurt and ice cream containers [23].

### 1.2.4 *Possible Outcomes: Recycling*

There are two main end of life options for plastic waste: the pathway of disposal to landfill or recycling. There are four different types of recycling technologies: primary, mechanical (secondary), tertiary (chemical) and lastly, energy recovery (quaternary) [24].

Primary recycling is defined as the reuse of recovered plastic in products with utilization and performance qualities similar to those of the original material [25]. A simple example would be the reuse of take-out containers. Another common example would be the recycling of polyethylene terephthalate (PET) waste into a PET bottle. This type of reprocessing is typically limited to a few cycles due to deterioration of the plastics’ mechanical properties upon each cycle. It also requires that the type of plastic have very low impurities [26].

Secondary recycling is defined as the reuse of recovered plastics in products with performance qualities that are less than that of the original product [25]. This type of recycling is also referred to as mechanical recycling. An example would be recycling PET waste into a new fiber. Thermoplastics, or plastics that can be melted can be remoulded into different shapes for other purposes. This includes recycling HDPE products into buckets and bins [16]. Polyvinyl chloride is also a good candidate for this type of recycling as it has been shown that the profile of virgin PVC was similar to that of recycled PVC [27]. This type of recycling has the same drawbacks as primary recycling, it is limited to high purity plastic, and can only be reprocessed through a limited number of cycles before it loses its overall quality [26]. The feasibility of secondary recycling is also hindered by the addition of impurities and additives in the plastic feedstock. It is important to note that no country will be able to achieve recycling targets using only primary and secondary methods of recycling due to its inherent limitations [26].

Tertiary recycling, or chemical recycling, uses waste plastic as the feedstock in a process that generates chemicals and fuels [25]. This may include the total depolymerization of the polymer to its monomers, or partial degradation to secondary valuable materials [28].

Lastly, quaternary recycling is energy recovered from waste plastic by incineration [25]. This is an effective method for reducing the overall volume of plastic waste. However, there is strong societal opposition due to emissions associated with incineration [28]. Plastics typically contain small amounts of chlorine in their additives. When burned these create dioxins [29].

Generally, chemical recycling is viewed as the most favorable recycling option because it allows for recycled plastic to be created that is of the same quality as the virgin material. In this way, the environment is not further exploited and there is no need for the extraction of new materials to make more plastic. This follows the principles set forth towards achieving a circular economy, in which products and materials are designed to be kept in circulation, rather than ending up in a landfill.

### 1.2.5 *Market Place Perspective and Needs Analysis*

The global market for LDPE was USD 56.6 Billion and is projected to grow 3% through 2025 to reach USD 76.05 Billion [30]. This is mainly driven by food and non-food packaging. The largest market for PE is Asia Pacific [30]. The global HDPE market is also projected to grow at a rate of 4% from USD 70.7 Billion in 2020 to 89.5 billion by 2026 [30]. The market for recycled plastics is closely linked to the virgin product market. The COVID-19 pandemic has also created an aggressive surge in the demand for and use of single-use plastic products. From January to March of 2020 in Wuhan, medical waste increased from 40 t/d to a peak of 240 t/d, exceeding the incineration capacity [31] .

Disposable face masks were used for the protection of both health care workers and of the public. They are made of various polymers such as PP, PE, or polyester. Due to the COVID-19 pandemic, there was an unprecedented surge in their manufacturing and use worldwide [32]. As of February 2020, China raised is production of medical masks to 14.8 million per day [33]. This increase in demand and production volume presents opportunities for sustainable solutions in waste management.

### 1.2.6 *What is pyrolysis?*

Pyrolysis is a thermal degradation process that occurs under the absence of oxygen, using intense heat, for a short duration of time [19]. This method is implemented to depolymerize the polymeric chain compounds of biomasses and of plastics. The main advantage of this type of thermochemical conversion technique is that the products are essentially an energy source that can be efficiently/feasibly stored [8]. Pyrolysis reactions typically yield a solid, a liquid and a gas. There are many challenges that hinder the development of recycling technologies. One being the addition of additives and impurities to the plastic that make them difficult to recycle [8]. Pyrolysis is seen as a favourable solution because it can be used to block the transfer of additives and harmful substances into new products by thermal destruction or through selective segregation in one of the phases. Plastics also tend to degrade over time. This degradation can take place from exposure to sunlight, air, water, hot or cold thermal stress. Degradation can be categorized as chemical, mechanical and biological [34]. Bacterial degradation is effectively nonexistent, however, there exists success in the identification of microorganisms that could be used to degrade plastic material [35] . This type of physical degradation prevents the employment of mechanical recycling techniques, but pyrolysis can handle this type of contamination [8]. Pyrolysis is also a very flexible process since the parameters can be altered and adjusted to optimize the final products [19].

Typically, the thermal cracking of PE and PP is carried out at high temperatures (>700 °C) to produce a mixture of olefins (C1-C4) and aromatic compounds (benzene, toluene, and xylene). At lower temperatures (400-500 °C) a waxy product is produced consisting of largely paraffins, as well as char [28].

The mechanism for cracking polyolefins consists of four steps: initiation, depropagation, inter- or intra- molecular hydrogen transfer followed by b-scission and termination [28].

### 1.2.7 *Slow, intermediate, fast pyrolysis, and ultra-pyrolysis*

Slow pyrolysis occurs at temperatures between 350 and 500 °C, a 1 – 10 °C/min heating rate, and under a prolonged vapour residence time. This type of pyrolysis favours the production of char [36]. Fast pyrolysis takes place at higher temperatures between 500 and 700 °C and with heating rates above 1000 °C/min. The vapour residence time is typically a few seconds [36]. This type of pyrolysis favours the production of the oil product. Ultrapyrolysis employs even shorter residence times. Ultrapyrolysis has been shown to tune the process in order to maximize the yield of the desirable products while minimizing the secondary reactions that lead to low value products such as coke and methane [37].

### 1.2.8 *Temperature Influence*

Pyrolysis tends to take place in the range of 500 – 700 °C. Lower temperatures favour the production of wax, while higher temperatures favour oil and the gas fraction. Kumar et al. [38] , reported that at high temperatures the pyrolysis reaction rate will increase, and the reaction time will decrease. This is because at a high temperature, there is easier cleavage of the polymer chain bonds which decreases the reaction time [38].

### 1.2.9 *Oil Applications*

Plastic oil obtained from the pyrolysis of mixed plastic waste tends to have similar properties to that of diesel fuel. A study done by Singh et al. in 2011 shows that the pyrolysis plastic oil obtained from mixed plastic waste at 450 °C had a similar composition in terms of components to that of fuels such as diesel and gasoline. The pyrolysis plastic oil could be blended with diesel to effectively be used in diesel engines. Increased CO emissions were reported [39].

In 2016, Sharuddin et al., made a comparison between the characteristics of pyrolysis oil from different types of plastic and the commercial standard value (ASTM 1979). From the experimental results found in literature it could be seen that both PP and HDPE are comparable to the commercial diesel value while LDPE was comparable to the standard for commercial gasoline [19].

**Table 1 Plastic Waste Oil Versus Commercial Standard Values for Gasoline and Diesel; Adapted from Sharuddin et al. 2016**

| | Types of Plastic (Experimental Value) | | | Commercial standard value (ASTM 1979) | |
|---|---|---|---|---|---|
| Physical Properties | HDPE | LDPE | PP | Gasoline | Diesel |
| Calorific Value (MJ/kg) | 40.5 | 39.5 | 40.8 | 42.5 | 43 |
| API Gravity @ 60 F | 27.48 | 47.75 | 33.03 | 55 | 38 |
| Viscosity (mm^2/s) | 5.08 | 5.56 | 4.09 | 1.17 | 1.9-4.1 |

| | | | | | |
|---|---|---|---|---|---|
| Density @ 15°C (g/cm^3) | 0.89 | 0.78 | 0.86 | 0.780 | 0.807 |
| Ash (wt %) | 0.00 | 0.02 | 0.00 | - | 0.01 |
| Octane number MON (min) | 85.3 | n.a. | 87.6 | 81-85 | - |
| Octane number RON (min) | 95.3 | n.a. | 97.8 | 91-95 | - |
| Pour point (°C) | -5 | n.a. | -9 | - | 6 |
| Flash point (°C) | 48 | 41 | 30 | 42 | 52 |
| Aniline point (°C) | 45 | n.a. | 40 | 71 | 77.5 |
| Diesel Index | 31.05 | n.a. | 34.35 | - | 40 |

### 1.2.10 *Char and Applications*

Under slow pyrolysis conditions there is substantial char formation from plastic pyrolysis [19]. A 2013 study from Jamradloedluk and Lertsatitthanakorn [40] looked at the characterization and utilization of char derived from the fast pyrolysis of HDPE. This study extruded char to produce briquettes, which were suitable to use as fuel to boil water [40] . However, the char obtained from PE and PP pyrolysis is mainly made up of inorganic material, limiting its application as a fuel. There has been research to point to its use in road surfacing and as a building material additive. There has also been focus placed on its use as an adsorbent in removing heavy metals from water [19].

### 1.2.11 *Gas applications*

Pyrolysis gas has received less attention because it has typically been considered as an auxiliary fuel to power pyrolysis processes. However, pyrolysis gas from polyolefins (such as polyethylene) has a high olefin content [26]. Olefins such as ethylene and propene can be separated from the other components and used as a feedstock in the productions of polyolefins. In 2021, the global price of ethylene was estimated to be value at $1.01/kg [41]. Pyrolysis gas can also be used to generate electricity and power the pyrolysis process [19]. Other gaseous components that are typically recovered from pyrolysis gas are hydrogen and methane. Hydrogen is a valuable gas that when produced from fossil-based technologies can cost around $1.80/kg [42]. Methane prices are reliant on the price of natural gas and vary greatly with location. In the US in 2021 the price was averaged around $0.08/kg [43].

## 1.3 Previous Studies on Plastic Pyrolysis

Plastic pyrolysis has been extensively studied in the literature. A study by Achilias et al. [24] looked at implementing a fixed bed reactor system for the pyrolysis of LDPE, HDPE, and PP. This was done under the presence of an acid FCC catalyst. With a low temperature of 450 °C a high liquid yield was recorded for the model polymer system (46.6% LDPE, 38.5% HDPE and 67.3% PP). The liquid oil was mainly aliphatic in its composition, presenting potential to be recycled back into new plastics or refined fuels [24].

High density polyethylene has been shown to produce a high oil yield from pyrolysis [19]. Sing and Kumar  [38] demonstrated their highest liquid yield, 23.96 wt. %, at 450 °C. Between 500 °C and 550 °C a viscous liquid and wax product was obtained. At 550 °C this wax/oil yield was 79.08 wt. %. These experiments were carried out using batch conditions [38]. High density polyethylene pyrolytic oil tends to have a low sulfur content.

Low density polyethylene at lower pyrolysis temperatures, also produces high oil and wax yield. Achilias et al. [28] used waste products and model polymers in a 450 °C pyrolysis unit with an FCC catalyst to get oil/wax yields or 99.5 wt. % and 91.5 wt. % respectively. The reactor was a fixed bed laboratory-scale reactor [28]. At higher temperatures the gas yield has been shown to increase. Williams [44] demonstrated this with their LDPE pyrolysis experiments carried out over 500-700 °C at 50 °C intervals. As the temperature increased the wt.% of the gas yield also increased suggesting that increasing the temperature increases the amount of cracking of wax to oil and oil to gas. The gas composition also changed over this temperature range, with ethene and propene showing a significant increase in yield over the temperature range. At 700 °C a 26.86 wt. % of ethene was recorded [44]. A fluidized bed pyrolysis reactor was used for these experiments.

High density polyethylene and PP also exhibit similar trends during single stage pyrolysis over a range of temperatures.

### 1.3.1 *Previous Studies on Two-Stage Plastic Pyrolysis*

Several studies have been conducted to crack the intermediate oils and waxes at a high temperature and short residence times. A study by Zassa et al. [45] looked at employing a second cracking reactor for tertiary recycling in a batch process. An inert carried the oils and waxes produced from pyrolysis to the second reactor. During this stage olefins were produced. The cracking unit used for these experiments was a reactor consisting of a stainless-steel pipe of a 0.6m and 0.007m ID. This reactor was a 3-zone oven, each one being 0.2 m long. The reactor operated at 900 °C with a maximum residence time of 1.3 s. The cracking products were condensed in a 3 m long pipe quenched in a cold bath. The results from this experiment have a yield of up to 45 wt. % ethene monomers from the original polyethylene [45].

A 2021 study by Suarez-Toriello et al. [46] looked at employing a two-stage approach for the pyrolysis of waste plastics. This experiment was done on the bench scale using a batch approach. The system was first purged with nitrogen to remove any moisture and impurities. The first reactor had a heating rate of 10 °C/min from room temperature to 500 °C and then the temperature was held for 1 h. The volatile matter then went directly to the second stage reactor containing a H-ZSM-5 catalyst. Using LDPE this paper reported a 57.1% yield of liquid products , 6.4 % yield of solid products and a 36.5 % yield of gaseous products [46]. The monomer yield was not included in this study.

A 2020 study by Park et al. [26] used a novel two stage approach to the pyrolysis of polystyrene. This set up consisted of two reactors. The first being a heated auger and the second a fluidized bed reactor. In the auger the feed material was heated to approximately 300 °C with the intention of first increasing the bond length of the molecules. Then the temperature of the fluidized bed reactor was set between 500 and 800 °C. With this technique a styrene monomer yield of 26.3 wt % was observed [47]. This research group also fed LDPE to this reactor setup. With a $N_2$ fluidizing medium the highest ethene yield of 34.5 wt % with a 74.6 wt % gas yield was achieved when the auger reactor was set to 300 °C and the fluidized bed reactor to 730 °C [26].

Hajekova et al. [48] took a decoupled approach to the recycling of LDPE and PP by employing the co-pyrolysis of their oil/waxes with naphtha in a two-stage set-up. First a batch reactor set to 450 °C was used to co-pyrolyze LDPE and PP and promote the formation of oil/wax products. These products were then mixed with naphtha in a 10% mass solution and fed through a tubular flow reactor with temperatures ranging from 740-820 °C and residence times of 0.09 to 0.54 s. A steam to feedstock mass ratio of 0.5 was used.  This method of steam cracking showed to produce ethene yields in the range of 20-25 wt % with the naphtha mixture [48].

## 1.4 Research Objectives

When considering the research motivation and state-of-the-art information gathered from the literature, there exists gaps in investigating pyrolysis to recycle common mixed-use plastic waste, as well as studies utilizing a downstream furnace to employ secondary cracking following initial thermal decomposition. The main objectives of this study, aimed at addressing these existing gaps, are summarized as follows:

- Investigate pyrolysis as a solution for the tertiary recycling of plastic waste.
- Investigate two-stage pyrolysis as a means of converting plastic waste into value-added products while addressing transportation bottlenecks.
- Investigate the effect of reactor and furnace temperature, as well as residence time and feed rate on oil and gas, yield, and quality.
- Characterize the oil and gas for identification of potential uses.

This work will aim to improve upon existing knowledge of single-stage pyrolysis of plastic by cataloguing results from various temperature and feedstock conditions. A novel setup will be used to investigate the addition of a secondary furnace on downstream cracking as mentioned above.

# 2 Materials and Methods

The following section describes the materials and methods used. While this study aims to address existing gaps in literature with mixed-use and contaminated waste plastics, the fundamentals of the proposed process was first studied under well controlled conditions using pure polymers. Virgin plastics were used to understand the influence of other parameters on the process. Artificial mixes of these pure polymers were created to maintain well characterized conditions. Validation tests were later conducted using simulated plastic waste.

## 2.1 Feedstock Characterization/ Preparation

The virgin LDPE and HDPE pellets were obtained from NOVA Chemicals Ltd., (Calgary, Alberta) and used as a feedstock. Virgin PP pellets were obtained from the Fraunhofer Project Centre for Composites Research (London, Ontario). Waste pellets of PP were obtained through cutting, melting and reforming waste yogurt containers. The yogurt containers were rinsed and shredded using a paper cutter. The strips of plastic were then cut using scissors into 1 $cm^2$ squares. A silicon ice cube tray of dimensions 24x12x1 cm with 160 1 $cm^3$ grid was filled with 1 $cm^2$ squares and placed in the furnace at 130 °C above the PP melting temperature. The silicone tray was removed from the oven, cooled, and the plastic pellets were collected.

### 2.1.1 *Ultimate Analysis*

Ultimate analysis was used to determine the carbon, hydrogen, nitrogen, and oxygen content of the feedstock, using a Thermo Flash EA 1112 elemental analyzer (CHNSO). The system was calibrated using the first four samples, 0.5, 1, 2, and 2.5 mg of BBOT (2,5- Bis (5-tert-butyl-benzoxazol-2-yl) thiophene) (CE Elantech, NJ, US). Each of the tin capsules contained 1-2 mg of plastic feedstock and 8-10 mg of vanadium pentoxide to achieve complete conversion of sulphur. Samples were combusted at 900 C in a stream of helium with a known volume of oxygen. This technique produces $N_2$, $CO_2$, $H_2O$ and $SO_2$ which were then subjected to separation and quantification using gas chromatography, which comprises of a steel column 2 m long and 5 mm in diameter, and helium as a carrier gas (flow rate of 140 mL $min^{-1}$). The elements were detected using a Propack model thermal conductivity detector (TCD).

## 2.2 Experimental Setup

The pyrolysis experiments were carried out in a bench scale pyrolysis unit made of 316 stainless- steel. The reactor was opened and cleaned daily to collect any residue and prevent cross contamination.

### 2.2.1 *Single-Stage Reactor*

Plastic is placed in a feed hopper. A screw feeder is controlled by a motor that pushes the plastic into the reactor. The screw feeder section prior to the reactor is heated using electric heat tracing to improve the feeding of the plastic. Nitrogen is fed into the system through a port on the hopper and controlled by a flow meter. The reactor itself is 1.4 L and heated using an induction heating system. An extraction trench is located at the bottom of the reactor which can be closed off when not required. The reactor can be mixed using a paddle powered by an electric motor. The exhaust gases from the reactor enter a ½” line that is heated by electric heat tracing. For one stage pyrolysis there is a two-component condenser train. To ensure a proper mass balance, all parts of the condensation train (including the connecting lines) are weighed before and after performing each experiment. The first condenser is heated in an oil bath at approximately 50 °C and the second condenser is in an ice bath at 0 °C. The non-condensables leaving the condenser train then pass through a cotton filter before the gas sample collection port, where they are then vented to atmosphere.

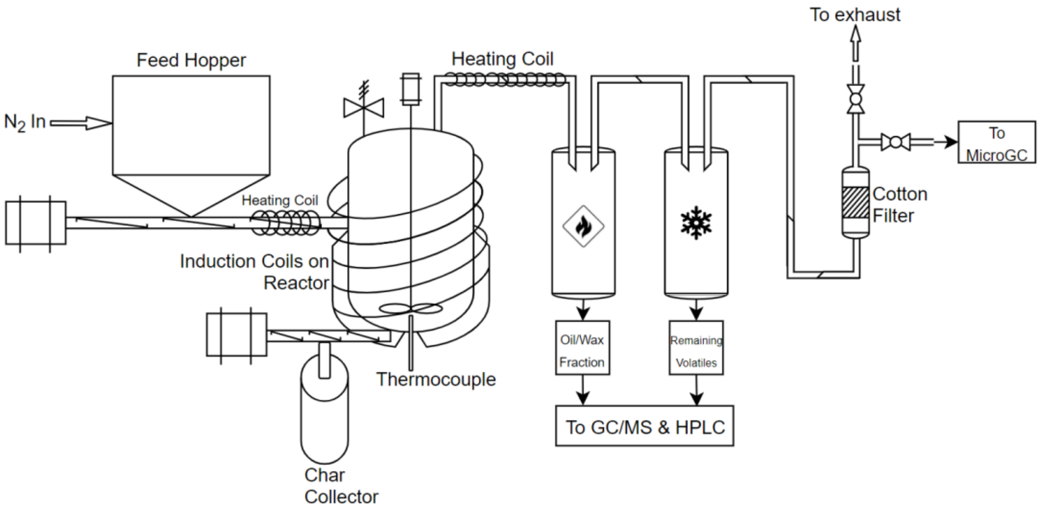

**Figure 1 Single Stage Reactor Set Up. Adapted from Horvers, 2021.** [49]

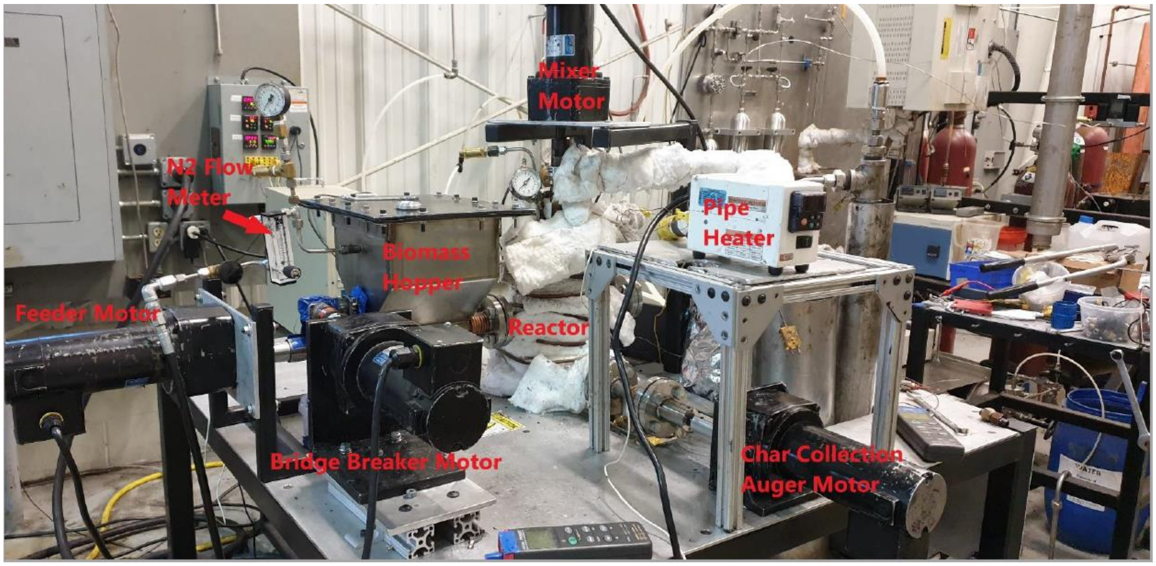

**Figure 2 Single Stage Reactor Components**

### 2.2.2 *Double-Stage Reactor and Furnace*

The double stage pyrolysis set up included a secondary furnace placed in sequential order after the heated exhaust line of the reactor (Figure 3). This furnace could be set up to 1200 °C. A piece of Inconel tubing was used inside the furnace due to its heat resistant properties. Glass beads of 1mm$^3$ size were used in the reactor to improve the heat transfer capabilities of the reactor. The glass beads were mixed using a reactor paddle. A thermocouple was placed on the top of the reactor bed to measure the bed temperature. Another thermocouple was used at the exit of the furnace to measure the real temperature of the gases upon leaving the furnace. The gases from the furnace then entered the condenser. The condenser had no tubing to prevent the build-up of wax that would plug the system and create pressure issues. The condenser was kept iced. The exhaust tubing was then vented to atmosphere with a detachable sampling port to collect gas sample bags.

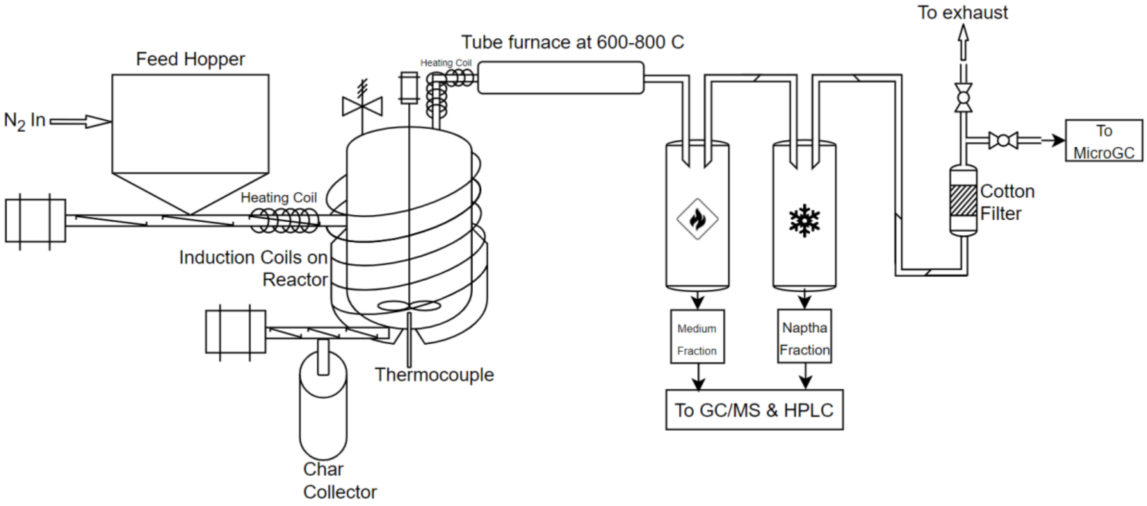

**Figure 3 Double Stage Reactor Set Up. Adapted from Horvers, 2021.** [49]

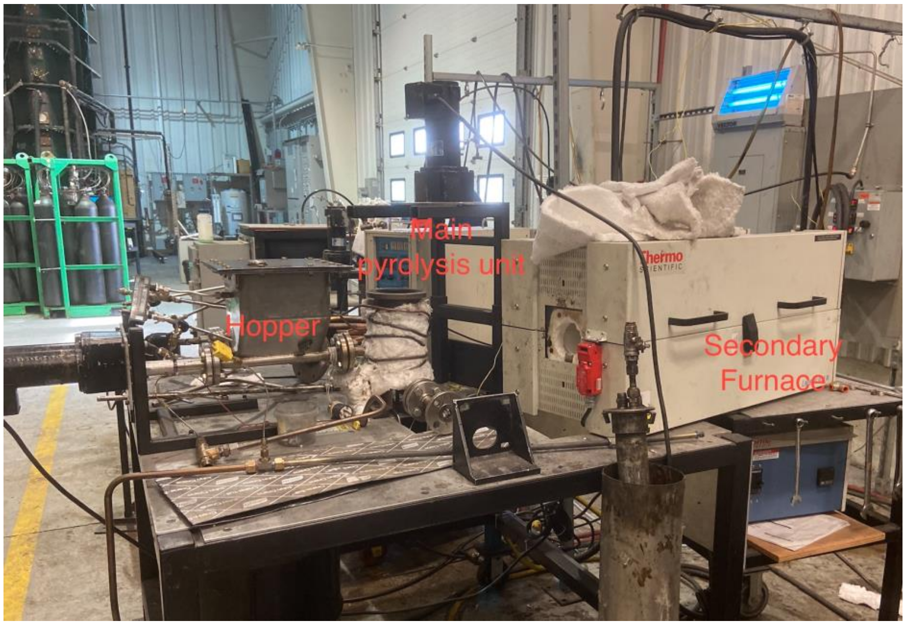

**Figure 4 Double Stage Reactor Components**

## 2.3 Experimental Methods

The major objective of the experiments was to be able to effectively characterize the oil and gas samples collected. There was negligible char collected, therefore it was not considered for analysis. To achieve the beforementioned objective, several analytical methods were used. The oil sample was investigated as a potential fuel, therefore GC-MS, HHV, and Karl Fischer Titrations were performed.

### 2.3.1 *GC-MS*

GC-MS was used to characterize the main components of the oil samples obtained. A 50 mg sample of each oil/liquid was dissolved in 2 ml of the solvent, 2-propanol. The solvent was used to extract the compounds from the samples. The samples were shaken for 30 minutes and filtered through a 0.2- micrometer filter three times to remove particulates. The samples were then placed in the fridge for preservation until being ran through the GC-MS system. The GC-MS system consists of a gas chromatograph coupled to a quadrupole mass spectrometer (GC-MS QP 2010, Shimadsu) using a capillary column (DB5MS, 30 m Å~ 0.25 mm i.d.; film thickness: 0.25 μm). Electron ionization (EI) was used with an ion source temperature of 200 °C and an interface temperature of 250 °C. In EI, the instrument was used in SCAN mode initially to confirm the identity of the compounds. The GC system was equipped with a split/splitless inlet. The injector temperature was 200 °C. An AOC-20S autosampler with a 10 μL syringe was used for injections of 1 μL at a rate of 10 μL s -1. The carrier gas was helium (UHP) at a constant flow of 1.5 mL min -1. The oven temperature program had an initial temperature of 40 °C held for 10 min, rising by 10 °C/min to 300 °C which, was held for 30 min, with a total run time of 75.0 min. This temperature program was selected to provide adequate separation of most of the compounds of interest.

### 2.3.2 *Higher Heating Value (HHV)*

To classify the potential of the oil samples to be used as fuel, the higher heating values were needed. To measure the higher heating values of the samples, a bomb calorimeter (C200, IKA, Germany) was used. A sample of each oil/wax collection between 0.3-0.4 mg was weighed and placed in the bomb. Two replicates were recorded for each sample. The calibration process was carried out in the sample vessel using pelletized benzoic acid (IKA C723, IKA, Germany).

### 2.3.3 *Karl Fischer Titration*

Moisture content is a defining characteristic of fuel. To determine the moisture content of the samples, the Karl Fischer Titrator (Mettler Toledo Model V20) was used. A small amount of each sample was taken into a hypodermic needle. The needle was then weighed, and a single drop was added to the Karl Fischer Titrator; the needle was then re-weighed and the difference, which indicates the quantity; was input into the device. After 90 seconds, the moisture content was determined and displayed.

### 2.3.4 *Micro-GC*

To analyze the gas products from the process, samples were taken during the reaction using Teflon bags (1L, Hedetech). The detachable samples bags were connected to the exhaust line of the process, 5 minutes into the reaction. A cotton filter was placed in between the line and the sample port to prevent any contaminants from damaging the equipment. A Varian mobile Micro-GC (CP-4900) equipped with M5. (Molecular Sieve., 10 m), PPU (PolarPlot U, 10m), and 5 CB (CP-Sil, 5 CM, 8 meter) column modules was used to analyze the concentration of H2, CH4, CO, CO2, C2H4, C2H6, C3H6, C3H8, and C4H10. Helium and Argon (99.999%) were used as carrier gases for the thermal conductivity detector (TCD) at a pressure of 80 psi. The carrier gases were passed through an external gas clean moisture and oxygen filter to eliminate any suspended moisture and traces of oxygen associated with the carrier gas. The gas components from each sample were detected over a period of 3 minutes and automatically integrated using the Galaxie software. Due to the high utilization frequency, the micro-GC was conditioned every week. The conditioning time was extended overnight to remove any water present inside the column from either gas samples or the carrier gas. The conditioning was carried out by maximizing the oven temperature. Conditioning the column was done to improve the efficiency. Each gas sample was analyzed a minimum of three times, and the average was calculated to determine the gas concentration. Results were analyzed by comparing peaks to a database of known compounds and their peaks.

# 3 Experimental Results and Discussion

## 3.1 Feedstock characterization

The results of the ultimate analysis of the pellets are shown in Table 2. Oxygen was calculated by the remaining difference. Blends of these pellets were also used.

**Table 2 CHNS(O) Analysis Results for Feedstock**

| Sample | Hydrogen | Carbon | Nitrogen | Sulfur | Oxygen+ Ash |
|---|---|---|---|---|---|
| HDPE | 1.5 ± 0.2 | 83.6 ± 0.8 | 9.1 ± 0.0 | 0.4 ± 0.1 | 1.6 ± 1.1 |
| LDPE | 0.0 ± 0.0 | 83.5 ± 0.3 | 13.0 ± 0.0 | 0.4 ± 0.0 | 3.1 ± 0.3 |
| PP | 7.5 ±10.7 | 84.9±0.9 | 0.01±0.0 | 0±0 | 7.6±11.6 |
| Waste PP | 0 | 80.4 | 0 | 0 | 19.7 |

## 3.2 Single-Stage Pyrolysis Experimental Data

### 3.2.1 *Single- Stage Pyrolysis Yields*

Figure 5 displays the effects of temperature on product yields during the single stage pyrolysis of LDPE and HDPE pellets. Using LDPE pellets, the liquid yield decreased (65% to 17%) as the pyrolysis temperature increased from 550 °C to 700 °C. Negligible char was collected during any of the experiments. Therefore, this resulted in an inverse trend in the gas yield. These results are typical of polyethylene pyrolysis [28]. At a lower temperature, most of the liquid yield was a wax fraction. At higher temperatures (700 °C) the liquid yield was an oil. This is aligned with previous studies on LDPE pyrolysis [50]. With the HPDE feedstock, the liquid yield decreased (66% to 11%), as the pyrolysis temperature increased from 550 °C to 700 °C. The wt. percent of gases increased as the temperature increased. Again, at lower temperatures, most of the liquid yield was wax

(Figure 6) , and at the higher temperatures there was more of an oil product. Sogancioglu et al. (2017) reported similar trends using waste HDPE with a liquid yield of 87.62 wt % at 500 °C [51].

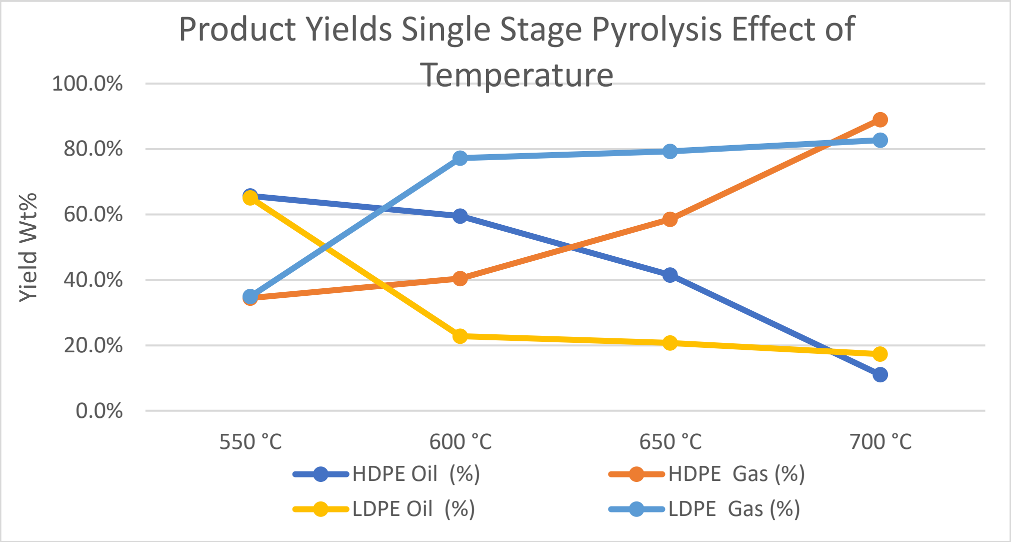

**Figure 5 The recorded wt. % yields of both oil and gas for HDPE and LDPE over the 550°C-700°C temperature range. As the temperature increases the oil yield decreases and the gas yield increases**

**Figure 6 Left: wax product collected from oil fraction at lower temperatures. Right: liquid oil collected from the oil fraction at the higher temperatures.**

Experiments using blends of HDPE and LDPE were also completed at 550 °C. This was done to artificially simulate mixed plastic waste. As observed in Figure 7, a comparison chart was made to explore the relationship between the yields of liquid for blends and pure products. Noticeably, higher oil yields were recorded using the blends. This synergistic effect is not well understood. It could be attributed to the interactions between the different molecular structures of the branched LDPE vs the linear HDPE.

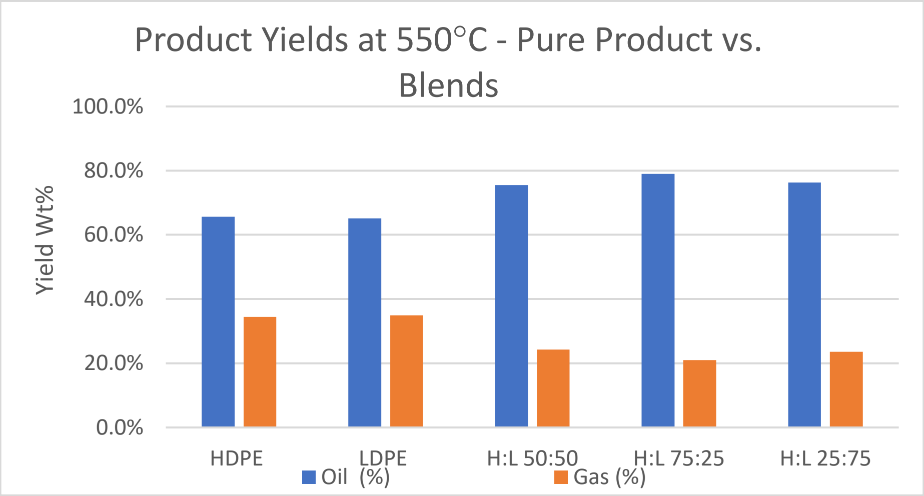

**Figure 7 The product yields of pure product vs. blends at 550°C. H:L is ratio of HDPE Plastic to LDPE Plastic in the feedstock. The oil yield increased when blends were used as compared to their individual counterparts.**

### 3.2.2 *Single-Stage Pyrolysis HHV*

The heating value of the products is a good indication of their potential application for direct use as a fuel. The HHV was highest (46.2 MJ/kg) for HDPE and (45.7 MJ/kg) for LDPE at 550 °C and slightly decreased with an increase in temperature. All samples were in the range expected for diesel-like products [52]. The HHV results for blends were higher than the HHV values of pure products. This is indicative of the synergistic effects of mixing plastic and could again be due to the different branching nature of the two plastics.

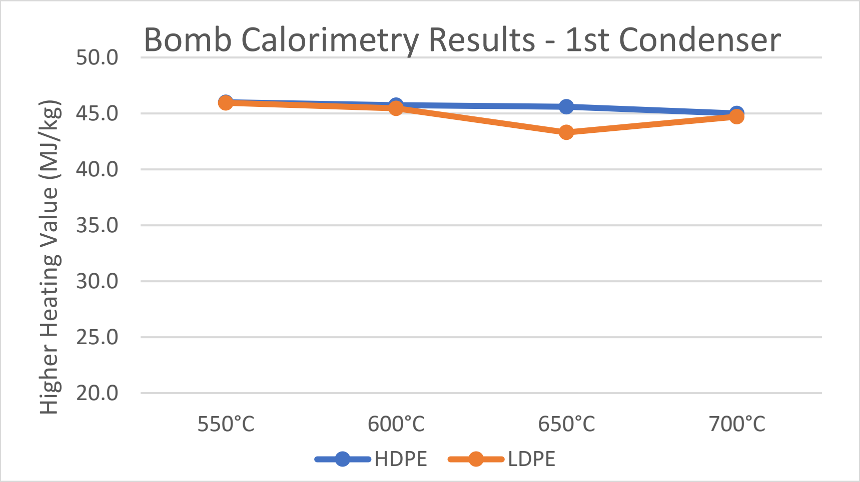

**Figure 8 The bomb calorimetry results from the oil samples collected during single stage pyrolysis from 1st condenser (hot oil bath). All HHVs are within 42-46 MJ/kg range.**

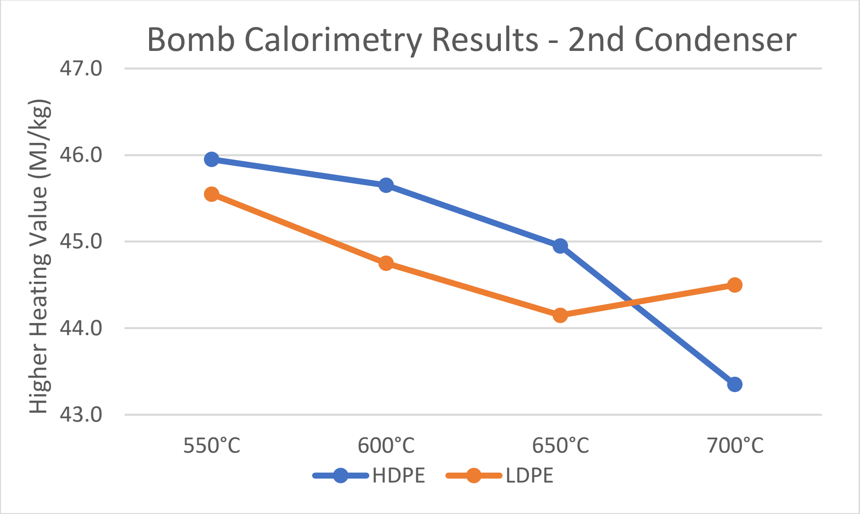

**Figure 9 The bomb calorimetry results from the oil samples collected during single stage pyrolysis from 2nd condenser (ice bath). All HHVs are within 43-46 MJ/kg range.**

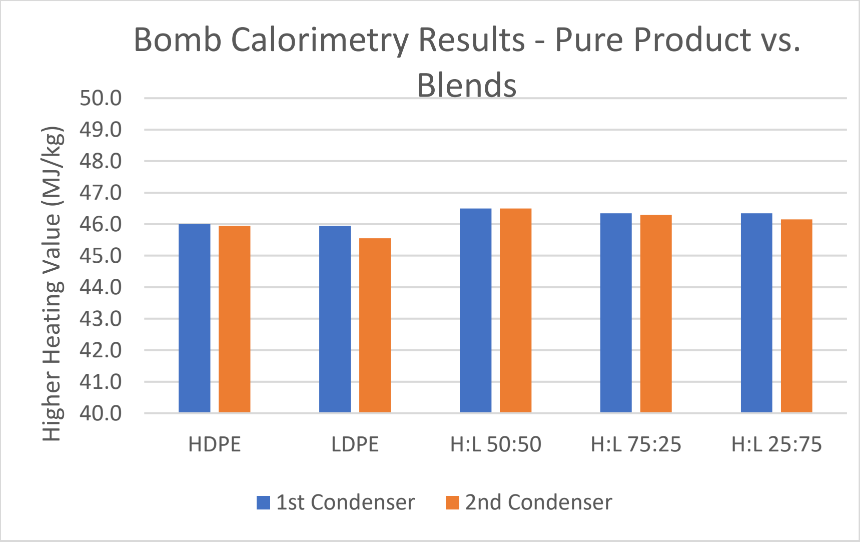

**Figure 10 The bomb calorimetry results from the oil samples collected during single stage pyrolysis, All HHVs are within 45-47 MJ/kg range. This chart depicts pure products vs blends. H:L is ratio of HDPE plastic to LDPE plastic in the feedstock.**

### 3.2.3 *Single-Stage Pyrolysis Karl Fisher Titration*

Overall, the wax and oil samples collected during single stage pyrolysis were determined to have a negligible water content of less than 1%. These results align with what has been previously reported in literature of a highly viscous oil/wax product [53] [54].

### 3.2.4 *Single- Stage Pyrolysis GC-MS*

Gas chromatography -mass spectrometry analysis was performed on all the oils collected between 550 °C and 700 °C. From HDPE pyrolysis (Figure 11), there was a larger amount of lighter C6-C11 compounds collected at higher temperatures (the second condenser at 650 °C, as well as 700 °C). This trend can be attributed to further cracking of the hydrocarbon chains at elevated temperatures. A 2019 study by Al- Salem using a fixed bed reactor noted the same trend, with a high amount of gasoline range hydrocarbons (C6 - C11) present in their pyrolysis oil samples. During their experiments, the gasoline profile increased with elevated temperatures [55]. A similar trend was displayed during LDPE pyrolysis. With LDPE there was a noticeable difference in the amount of C6-C11 compounds in the second condenser at the higher temperature compared to the first. At 650 °C this was 66.7 % C6-C11 in the second condenser, compared to 44.9 % in the first condenser. At 700 °C this was 69.0 % in the 2nd condenser as compared to 45.9 % in the 1st condenser. These results are consistent with data found in the literature [56] [55].

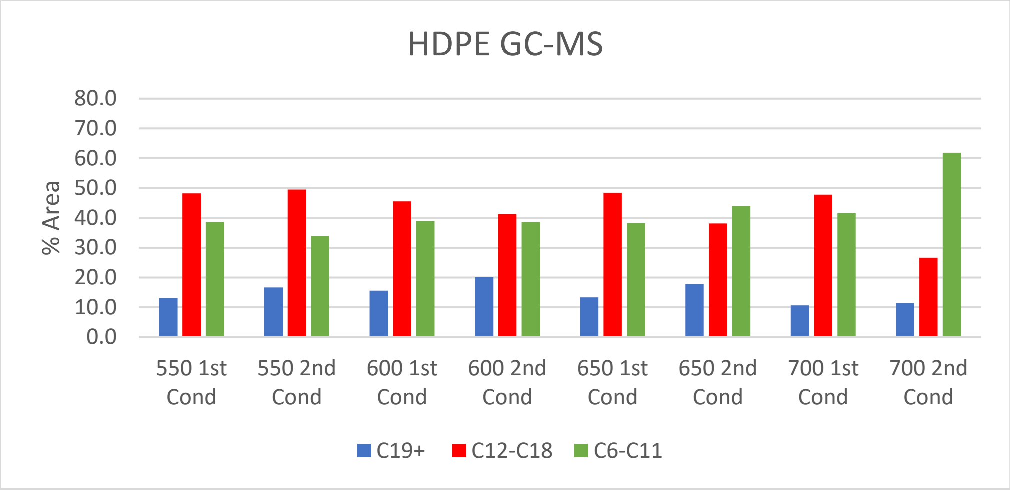

**Figure 11 The % area of hydrocarbons that were present in GC-MS analysis of oil samples collected from HDPE single stage pyrolysis. Shorter hydrocarbons are more abundant at higher temperatures.**

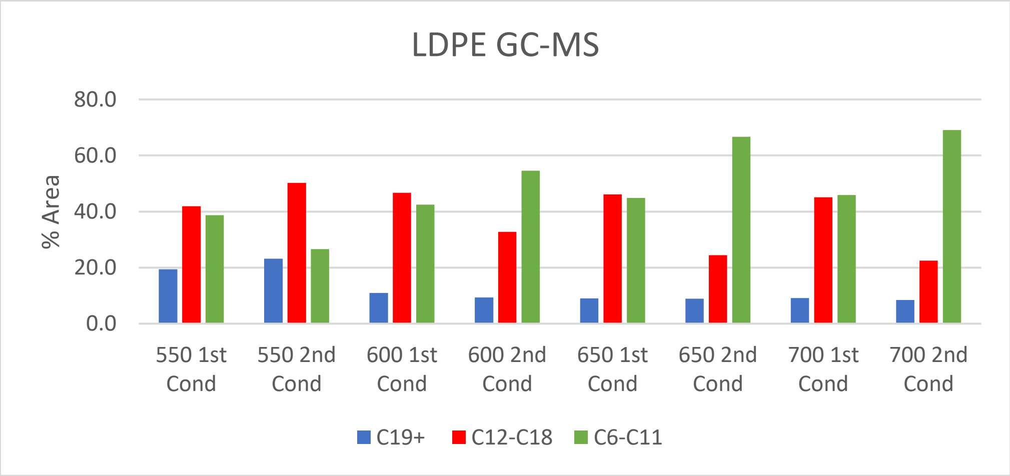

**Figure 12 The % area of hydrocarbons that were present in GC-MS analysis of oil samples collected from LDPE single stage pyrolysis. Shorter hydrocarbons are more abundant at higher temperatures (650°C-700°C).**

Gas chromatography -mass spectrometry analysis was also performed on the samples collected during the experimental runs using blends of both HDPE and LDPE (Figure 13). From these results there is no meaningful variation in the product composition of the different blend ratios. These experiments were all carried out at the same temperature conditions. This is to be expected as the results of the individual LDPE and HDPE experiments at 550 °C were very similar in product type percent areas. This indicates that temperature plays a larger factor in product composition than the plastic feedstocks used. Across all of the blends there was a dominant amount of C12-C18 hydrocarbons followed by C6-C11 hydrocarbons and smaller amounts of C19+.

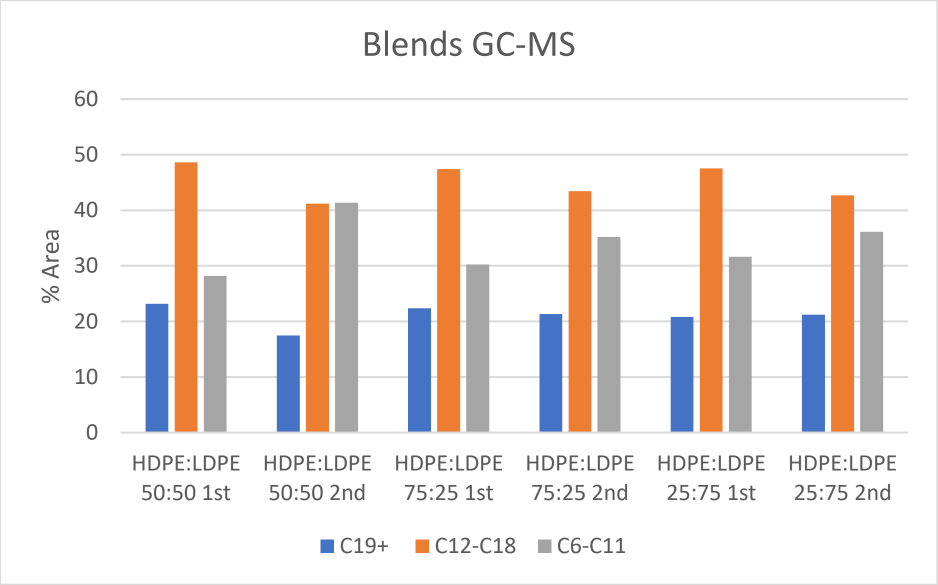

**Figure 13 The % area of hydrocarbons that were present in GC-MS analysis of oil samples collected from blends of HDPE and LDPE single stage pyrolysis.**

### 3.2.5 *Single-Stage Pyrolysis Gas Analysis*

Gas samples were collected at 550 °C and 700 °C for both HDPE and LDPE. The results of those samples are highlighted in Figure 14. At the lower temperature of 550 °C there was a larger amount of ethylene present in the sample, for HDPE this was 22.3 % while for LDPE this was 29.6 %. At the higher temperatures there were larger amounts of methane produced. The yield of methane for HDPE increased from 41.1% to 47.0 % while with LDPE went from 38.1% to 48.24 %. This is explained because at elevated temperatures there is further cracking of heavier molecular weight compounds to smaller molecules like methane. The presence of $CO_2$ at 700 °C is indicative of possible contamination or issues with the sampling process as there are negligible amounts of $0_2$ present in the feedstock (as depicted in Table 2 ). The results of the gas analysis and the observed trends are consistent with reported data in the literature [57] [38] .

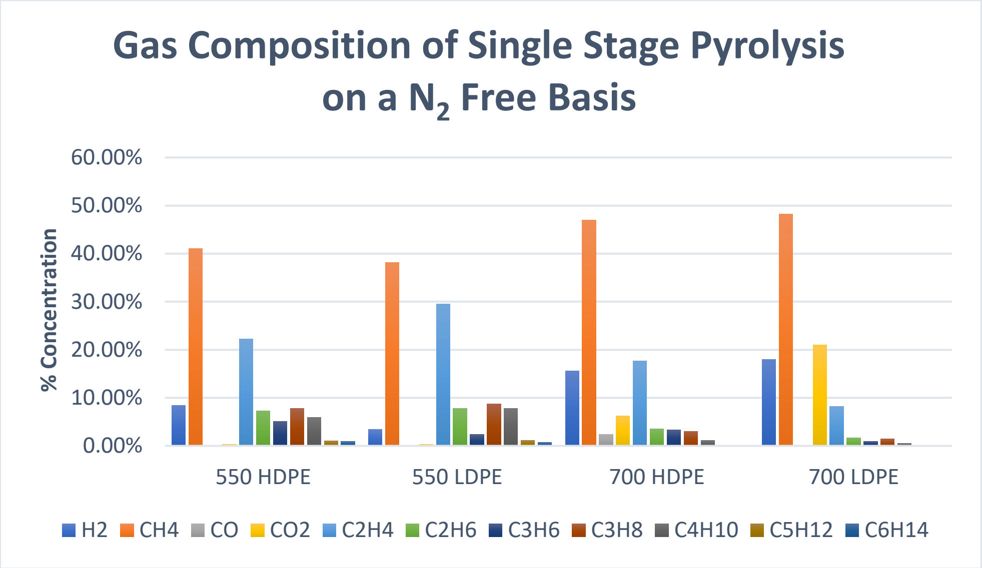

**Figure 14 The concentration of various gas components collected from 550°C and 700°C single stage pyrolysis for both HDPE and LDPE feedstock. There was a higher concentration of methane at the higher temperature.**

## 3.3 Two-Stage Pyrolysis Experimental Data

The next set of experimental data includes the addition of a secondary furnace downstream of the pyrolysis unit to further promote cracking of the polymer compounds. This setup is shown in Figure 3. The secondary furnace was utilized with the intention of overcoming bottleneck issues that currently exist within the plastic recycling process. The second furnace allows for the system to be decoupled. Bulky waste produced can undergo the first pyrolysis reaction to become a liquid, wherein it can easily be transported and then be further cracked into its monomer (or gaseous) components.

### 3.3.1 *Two- Stage Pyrolysis Residence Times*

The residence times for each corresponding $N_2$ flow rate can be found in Table 3. A detailed sample calculation can be found in the appendix. Calculations were based off the GC-MS and Micro-GC results from single stage pyrolysis using HDPE.

**Table 3 Two-Stage Pyrolysis Residence Times**

| $N_2$ Flow Rate (LPM) | Residence Time (s) |
|---|---|
| 1 | 6.6 |
| 5 | 2.6 |
| 7.5 | 1.9 |
| 10 | 1.5 |
| 15 | 1.0 |
| 15 x1.5 Feed rate | 1.0 |
| 15 x2 Feed rate | 0.9 |
| 15 3/8” tube | 1.0 |

### 3.3.2 *Two-Stage Pyrolysis Yields*

Figure 15, Figure 16 and Figure 17 demonstrate the effect of using a secondary furnace on the oil yields collected. Overall, while using the secondary furnace the recorded oil yields were much smaller than when using the single reactor and condenser train as demonstrated in Figure 5. This is explained by the vapors being exposed to higher temperatures which enhances the cracking effect, increasing the gaseous product yield. Char was again considered negligible during the collection process, which is explained by the absence of any contaminants in the virgin feedstock. With HDPE and LDPE and varying the residence time there was little variation in the oil yield collected with the % ranging from 8 to 20.75 wt. % over the set of experiments. Following the previously mentioned phenomena of longer residence times resulting in further cracking, it should be expected that there would be larger oil yields at the longer residence times. Variations could be explained by issues in the oil collection process. Adjustments to the condenser were made by removing the central line to prevent clogging issues that were seen in some earlier experiments. When this feature was removed, it led to some wax formation in the exhaust line. This wax could not always be collected, and a slight yield loss was experienced at higher nitrogen flow rates (longer residence times). No yield was calculated for some experiments where errors occurred such as incomplete feeding, or condenser leak that would make the results incorrect. In Figure 15 and Figure 16 the experiments at the longer residence times were completed with a different set point for the secondary furnace (800 °C rather than 850 °C). This is depicted by different colours on the bar graphs. This was done because operating conditions were optimized as the experiments were continued. As seen in Figure 17 when other factors were changed there was again little variation or noticeable trends in the oil yield with results consistent around 10-15%. One outlier was the experiment conducted at the higher reactor temperature. This could present the fact that the reactor temperature has a larger influence on the amount of cracking and could be further investigated. The LDPE 500/850 run was repeated and a standard deviation of 5% was calculated between the oil sample yield collected. This is represented by the error bars in Figure 16 and Figure 17.

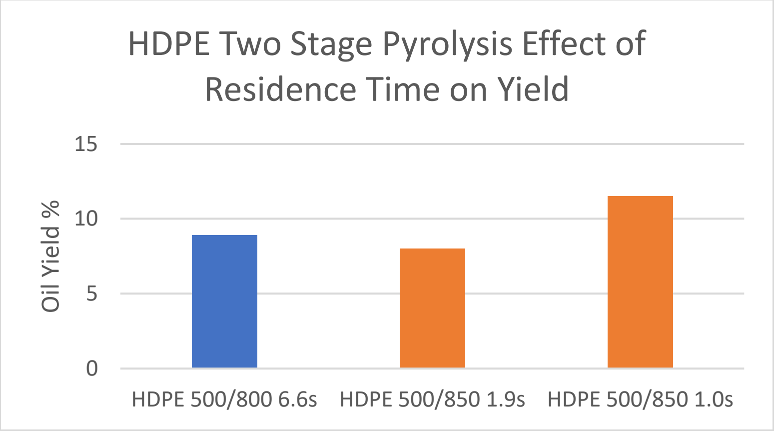

**Figure 15 The wt.% oil yield of samples collected during HDPE two-stage pyrolysis with adjustments to residence time. Blue indicates a set point of 800 °C for the secondary furnace versus orange indicates a set point of 850 °C.**

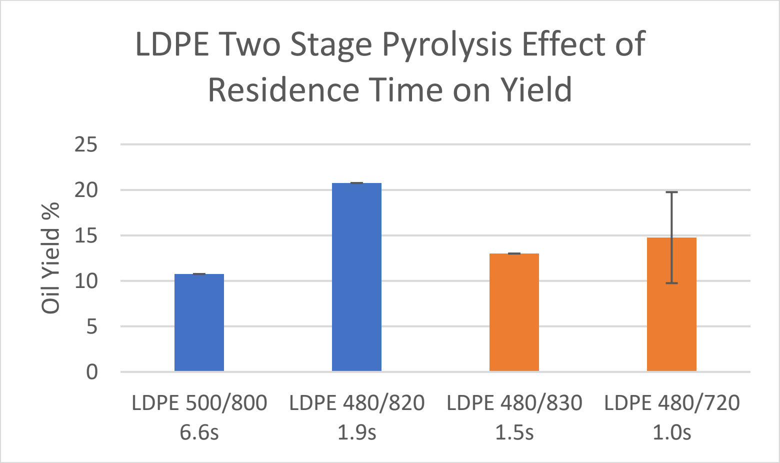

**Figure 16 The wt.% oil yield of samples collected during LDPE two-stage pyrolysis with adjustments to residence time. Blue indicates a set point of 800 °C for the secondary furnace versus orange indicates a set point of 850 °C.**

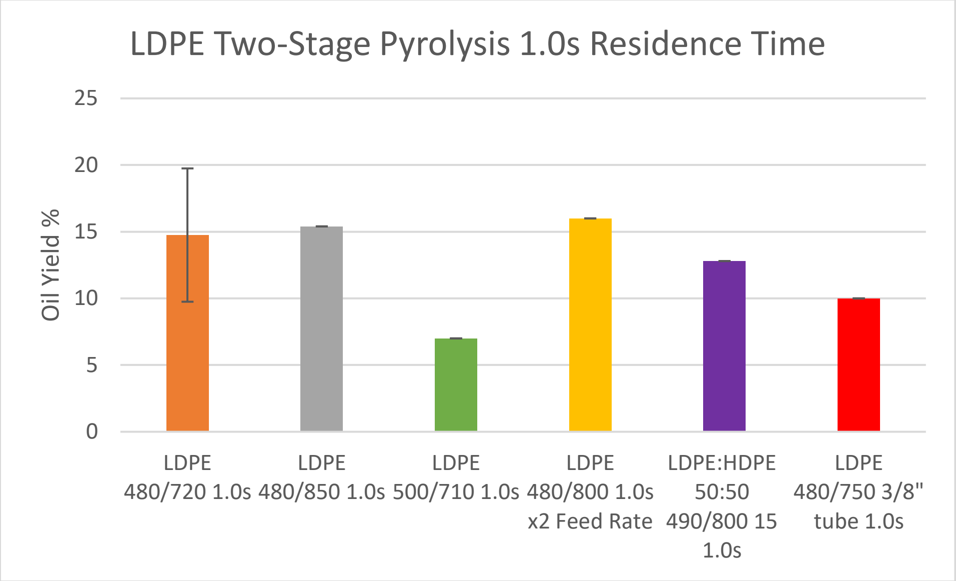

**Figure 17 The wt. % oil yield of samples from LDPE two-stage pyrolysis collected during the 1.0s residence time experiments. All the yields within 5-20 wt. %.**

The experiments using waste polypropylene resulted in a mostly char product that was difficult to collect and therefore accurate yields were not collected from these experiments.

### 3.3.3 *Two-Stage Pyrolysis HHV*

The calorimetry results from the two stage pyrolysis experiments can be seen in Figure 18. Except for the experiments conducted at the 2.6s residence times, all the oil samples collected had a HHV of over 44.0 MJ/kg. Adding the standard deviation to the average for the samples collected at the 2.6s residence time, they exceeded 40 MJ/kg. The typical HHV for diesel is in the range of 42 – 46 MJ/kg [52]. This demonstrates the potential application of the oil fraction as a fuel.

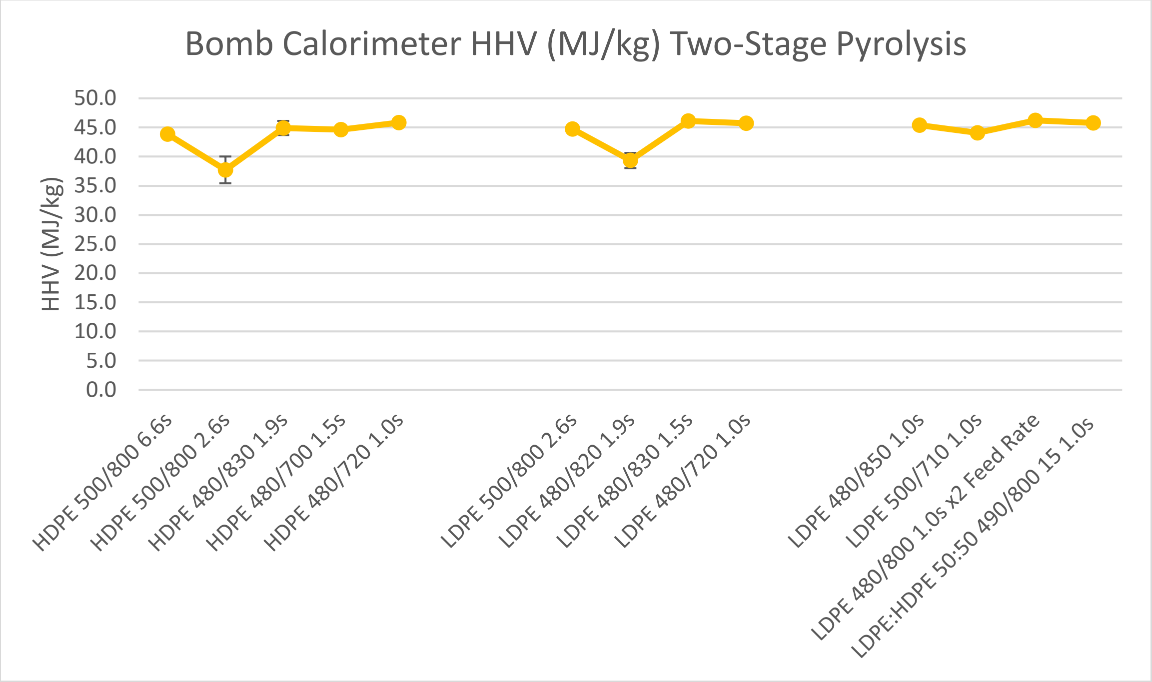

**Figure 18 The HHVs of samples from two-stage pyrolysis collected during the 1.0s. All the HHVs are over 37MJ/kg.**

### 3.3.4 *Two-Stage Pyrolysis GC-MS*

Gas chromatography -mass spectrometry analysis was performed on the oils produced from varying residence times between 6.6s and 1.0s for both HDPE and LDPE. When analyzing the results of the GC-MS, the top 15 compounds were selected from each sample. They were then grouped based off carbon number and bond nature. As the residence time decreases, the expectation would that there would be less overcracking of the carbon chain molecules and there would be larger percentage of longer carbon chain molecules present in the samples. From the literature it is known that increasing the residence time fosters the formation of aromatics and greater degradation [58]. This trend was observed using the HDPE feedstock (Figure 19 and Figure 20). At the longest residence time of 6.6s with the smallest nitrogen flow rate of 1 LPM, there was the highest percentage of C6-C12 compounds and their corresponding peaks. With a shorter residence time from using a higher nitrogen flow rate there was a higher concentration of

C12-C18 compounds. As evident in  Figure 19, this increased over time. When looking at the nature of the bonds there were more aromatic type compounds at the longer residence times of 6.6s to 2.6s versus at the shorter times of 1.9s to 1.0s where these bonds were predominantly olefinic. This is aligned with trends described in the literature [53].

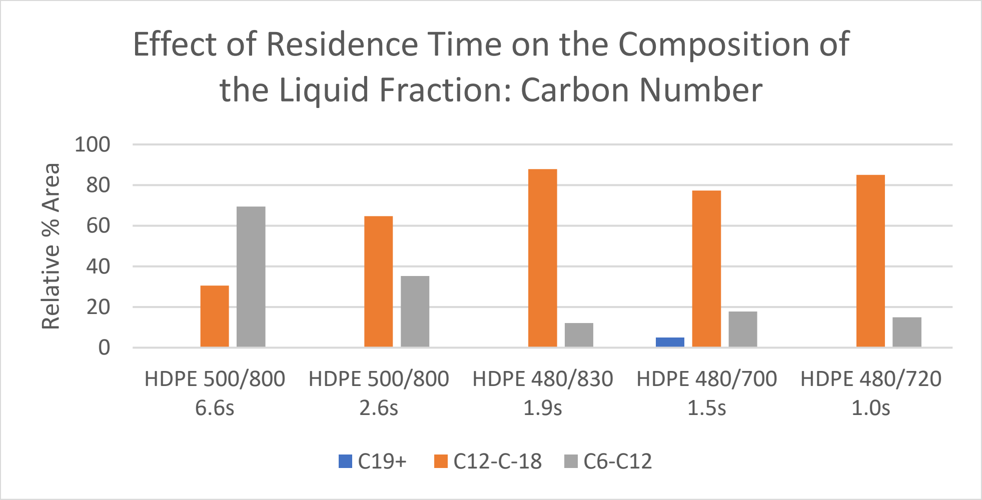

**Figure 19 The results of GC-MS analysis on the samples collected from HDPE two - stage pyrolysis. These results demonstrate the effect of residence time on the carbon number in the liquid fraction. The number of shorter C6-C11 compounds (grey) decreases as the residence time is also decreased.**

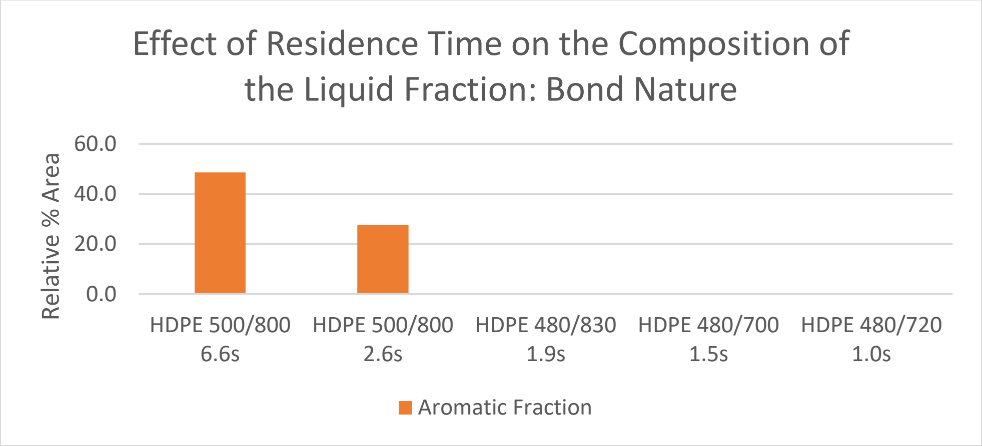

**Figure 20 The results of GC-MS analysis on the samples collected from HDPE two - stage pyrolysis. These results demonstrate the effect of residence time on the bond nature in the liquid fraction. There is a larger aromatic fraction at longer residence times.**

Similar trends were observed through adjusting the residence time using LDPE as the feedstock (Figure 21 and Figure 22). An insufficient sample was collected during the 6.6s run, there was still a noticeable pattern with the highest percentage of C6-C12 collected during the experiments using longest residence times, while at the shorter residence times there is less degradation and as such more longer chain hydrocarbons. There are only aromatic type bonds present in the longer residence times (Figure 22). These compounds are predominantly benzene and toluene, which is aligned with what has been previously reported in literature [53] [58].

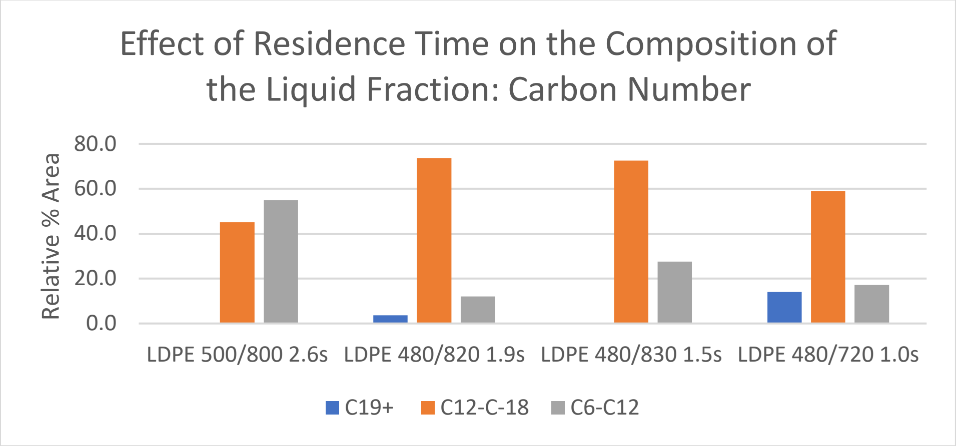

**Figure 21 The results of GC-MS analysis on the samples collected from LDPE two - stage pyrolysis. These results demonstrate the effect of residence time on the carbon number in the liquid fraction. The number of longer C12-C18 compounds (orange) and C19+ compounds (blue) increase as the residence time is decreased.**

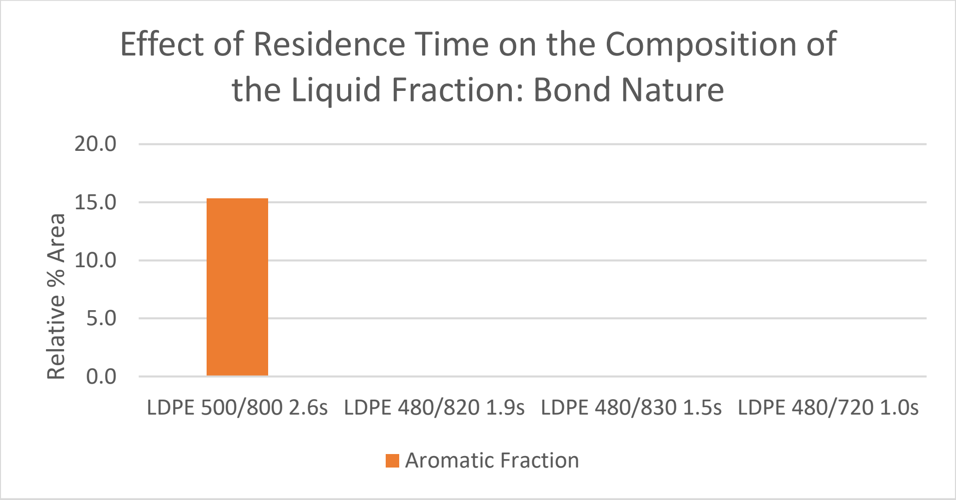

**Figure 22 The results of GC-MS analysis on the samples collected from LDPE two - stage pyrolysis. These results demonstrate the effect of residence time on the bond nature in the liquid fraction. An aromatic fraction is only present at the longest residence time.**

## 3.4 Gas Composition Analysis

### 3.4.1 *Gas Analysis Two-Stage HDPE Pyrolysis*

Micro-GC was used to analyze the composition of the gas samples taken downstream of the two-stage pyrolysis process. First, the results of varying the residence times using the HDPE feedstock were analyzed. During experiments that had the longest residence time, there was more overcracking and methane and hydrogen were the predominant products. As the residence time was shortened, the percent yields of the monomer ethylene increased. This trend can be observed in Figure 23 . At 6.6s there was the smallest amount of ethylene at 10 wt. %. As the residence time was shortened, larger ethylene yields were recorded with a 30 wt. % yield recorded at both the 1.5s and the 1.0s residence times. Considering a gas yield of 88.5% for the 1.0s run, this resulted in an overall monomer recovery of 26.6 % from the feedstock. An inverse trend was recorded with regards to methane and hydrogen (Figure 24). This is similar to reported trends in literature that methane and hydrogen yields will increase with a longer residence time [59].

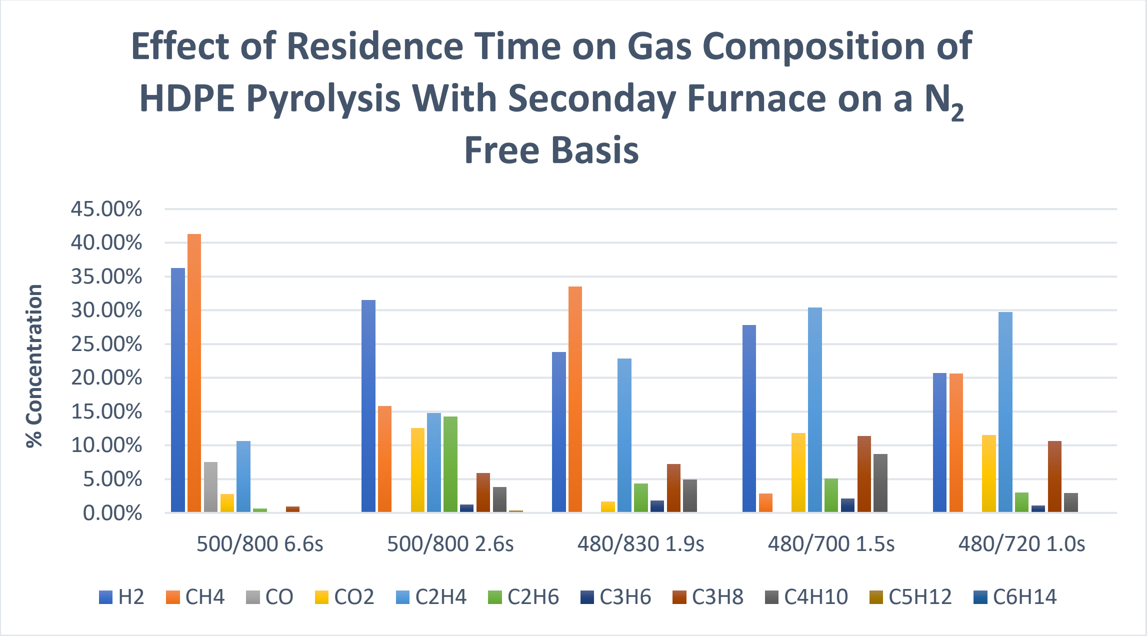

**Figure 23** The concentration of select gas compounds present in samples collected during HDPE pyrolysis using a secondary furnace. The amount of ethylene (light blue) increased as the residence times was shortened.

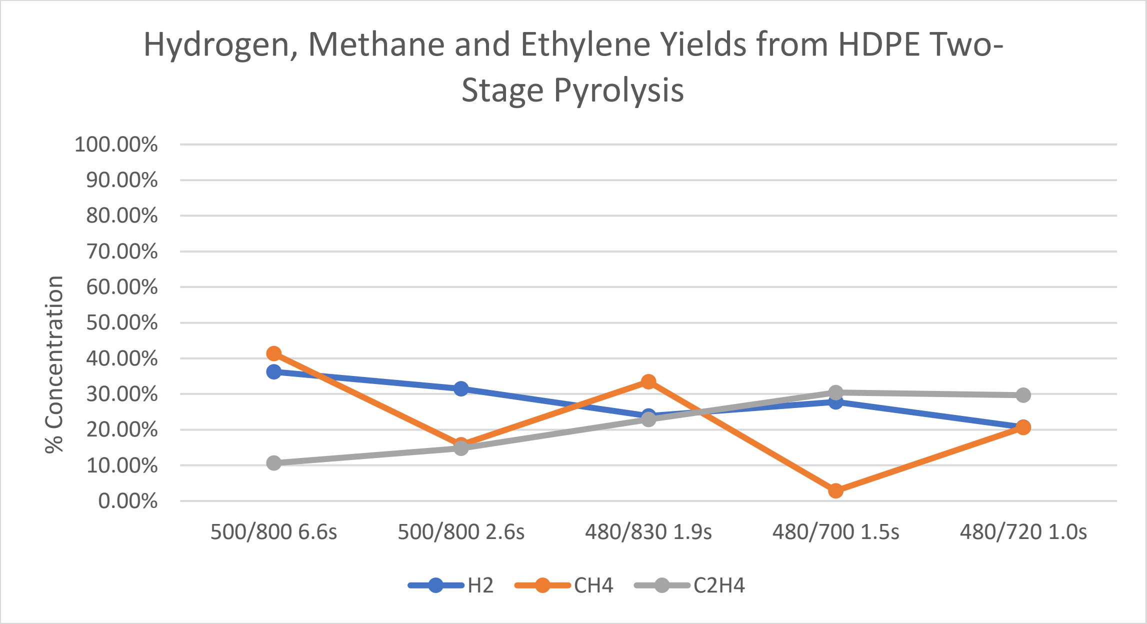

**Figure 24** This figure depicts the relationship between hydrogen, methane and ethylene yields as the residence time is adjusted during HDPE two-stage pyrolysis.

### 3.4.2 *Gas Analysis Two-Stage LDPE Pyrolysis*

The same trend was reported for the varying residence times with the LDPE feedstock (Figure 25 and Figure 26). Decreasing the residence time reduced the amount of over cracking of the hydrocarbon products, resulting in larger amounts of the monomer ethylene and smaller amounts of methane. As seen in Figure 26, the methane yield decreased as the residence time increased.

The results of the LDPE feedstock pyrolysis resulted in similar outcomes as compared to the HDPE feedstock pyrolysis. Increasing the residence time decreased the amount of overcracking which produced higher ethylene yields and heavier hydrocarbons. A 15 LPM $N_2$ flow rate, with a 1.0s residence time, produced the highest recorded ethylene yield 40 wt. %. Considering a gas yield of 85.25% for this run, this results in an overall monomer recovery of 34.1% from the feedstock.  When comparing this to other results in the literature this is significant. A study by Williams et al. from 1998 recorded 26.86 wt. % as their maximum monomer yield, a 1997 study by Lovett et al. recorded 37 wt. % as the maximum monomer yield and from Park K.B. in 2019 they recorded 34.50 % [44] [60] [26]. From the 1.0s residence time run, there was a hydrogen yield of 24 wt. %. Considering a gas yield of 85.25% this results in an overall yield of 54.56 % for the 1high value components.

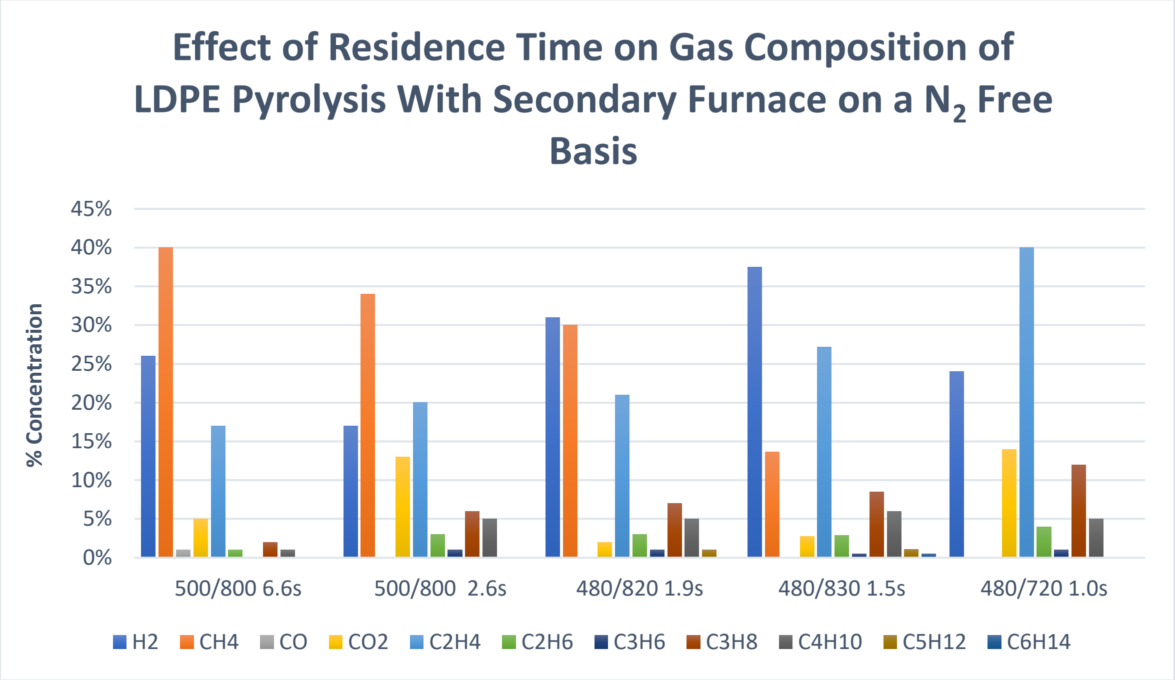

**Figure 25 The concentration of select gas compounds present in samples collected during LDPE pyrolysis using a secondary furnace. The amount of ethylene (light blue) increased as the residence times were shortened. The amount of methane (orange) decreased as the residence times were shortened.**

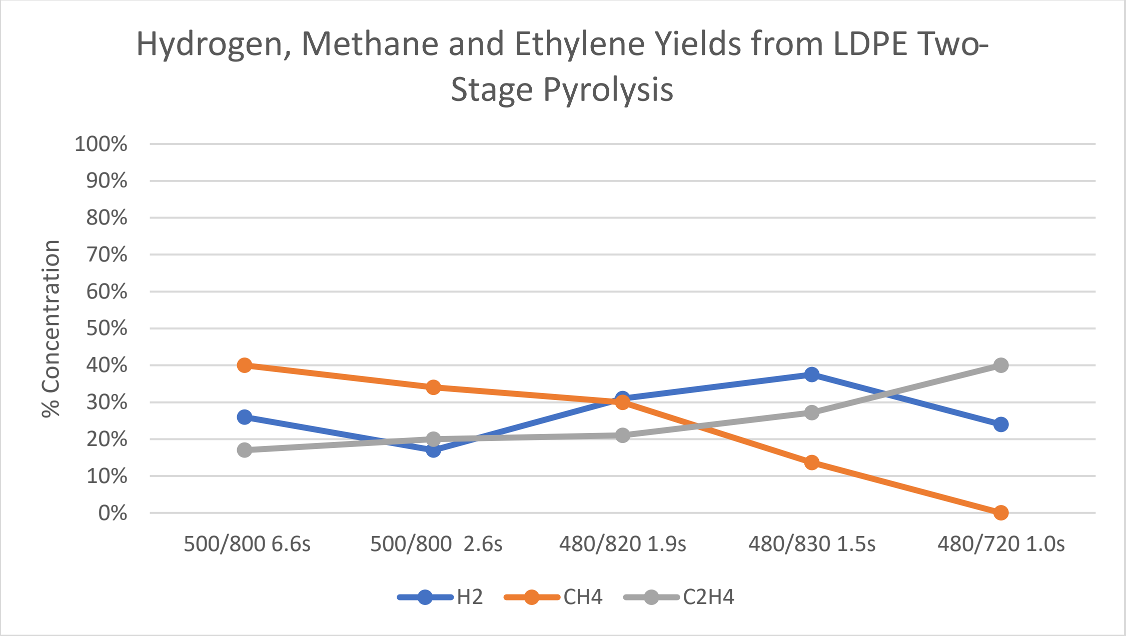

**Figure 26 This figure depicts the relationship between hydrogen, methane and ethylene yields as the residence time is adjusted during LDPE two-stage pyrolysis.**

### 3.4.3 *Gas Analysis Two-Stage LDPE Pyrolysis Temperature Adjustment*

Since the LDPE feedstock set to 500°C in the reactor and 850°C in the secondary furnace with a 1.0s residence time produced the highest weight percent monomer yield, these conditions were independently investigated. First, the impact of changing the temperature of both the reactor and the secondary furnace was analyzed while maintaining the same LDPE feedstock and residence time. Increasing the temperature of the furnace primarily resulted in larger amounts of methane in the feedstock. During this run there were also relatively larger amounts of carbon monoxide and carbon dioxide collected in the sample which was not expected. Possible reasons for this could be issues with the sampling process or contamination with air downstream of the pyrolysis unit. From the elemental analysis as seen in Table 2 , there are only very small amounts of $O_2$ in the feedstock, meaning that there should not be larger amounts of $CO_2$ or CO in the product. Then the same experiment was carried out keeping the set point of the furnace at 850°C, and the set point of the reactor was increased to 550°C. This produced more desirable results with high amounts of hydrogen and ethylene as well as slightly longer hydrocarbons such as propane. When considering the goal of optimizing the monomer yield, the best results were at the 500/850°C temperature conditions.

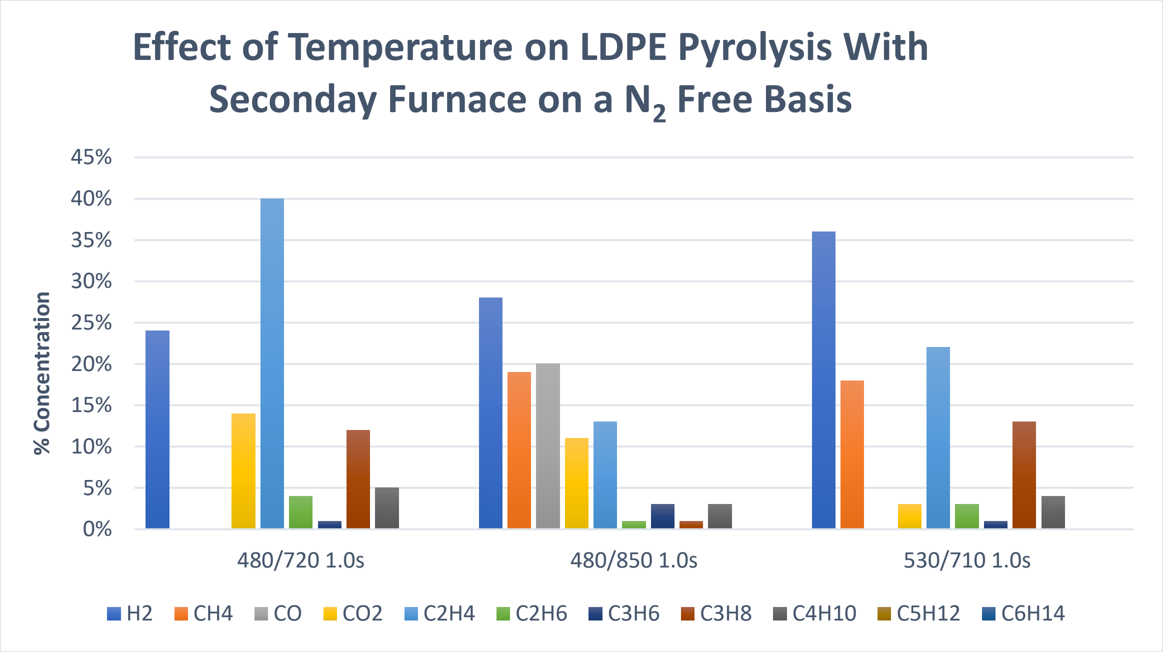

**Figure 27 The concentration of select gas compounds present in samples collected during LDPE pyrolysis using a secondary furnace. The temperatures in both the secondary furnace and the main reactor were adjusted to analyze the effect of temperature on gas composition. As the temperatures were increased more methane (orange) was produced.**

### 3.4.4 *Gas Analysis Two-Stage LDPE Pyrolysis Feed Rate Adjustment*

While maintaining the same temperature conditions, the impact of changing the feed rate was investigated. The temperature conditions were kept the same while the feed rate was increased using the motor on the screw feeder. A clear trend was realized during these experiments as seen in Figure 28. The phenomenon observed was that as the feed rate was increased, the amount of over-cracking also increased. This is evident with the larger amount of methane and hydrogen and smaller amount of ethylene at the faster feed rates.

This was confirmed by repeated experiments. While this may be counterintuitive as at the faster feed rate there is a shorter residence time (Table 3) and as presented earlier, shorter residence times should decrease the amount of over-cracking, these results can be explained by the reaction kinetics. Various reaction models for LDPE pyrolysis have been proposed in the literature. The most common model used for the thermal decomposition of polyethylene is a radical chain mechanism. The rate law obtained using this model is a function of the original polymer, ranging to the power of 0.5 and 1.5 [61] [62]. In a 2021 study by Dubdub et al., the Coats- Redfern model was used to demonstrate that an equi-mass waste plastic mixture including PS, PP and LDPE fit to a third-order reaction mechanism [63]. These proposed models demonstrate the dependence of the rate of the reaction on the amount of polymer added to the system. When the amount of feed is increased, the rate of the reaction will also increase. More conversion will lead to a greater product distribution of shorter chain molecules like methane. There is also gas-liquid interface, due to the presence of the melted feedstock entering the reactor and the gaseous degradation products that are leaving the reactor [64] that could impact the product distribution in the gas yield. A repeat experiment was conducted for the doubled feed rate and is depicted by error bars for the standard deviation between results in Figure 28. The standard deviation for each compound was below 5%, indicating good reproducibility of the results.

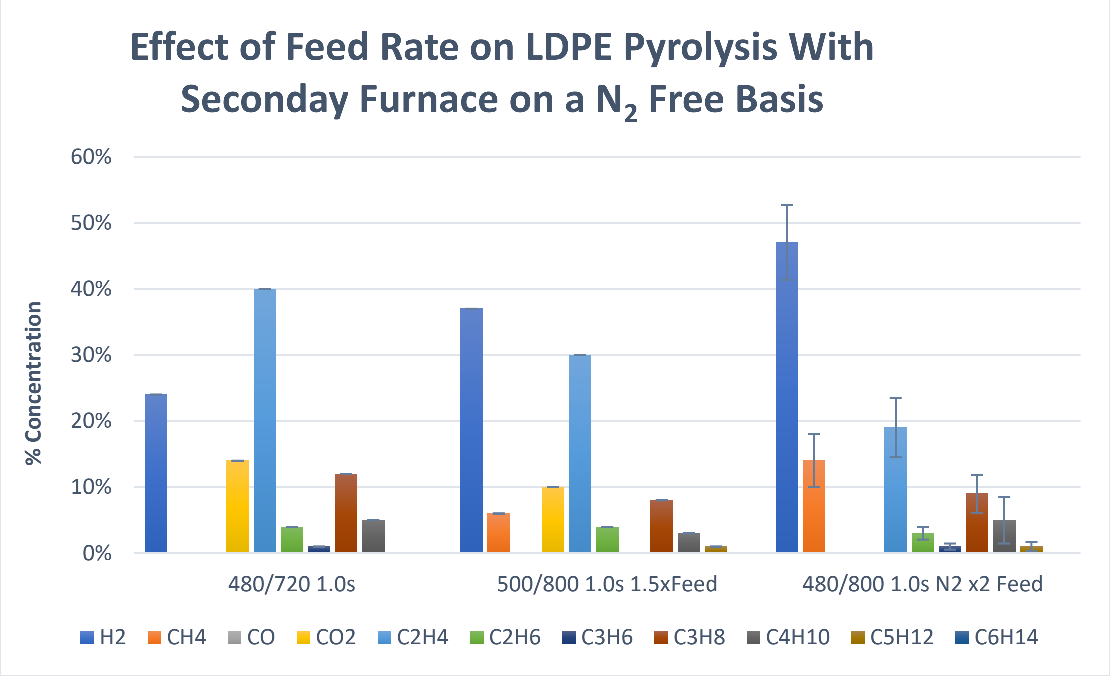

**Figure 28 The concentration of select gas compounds present in samples collected during LDPE pyrolysis using a secondary furnace. The feed rate of the plastic was adjusted to analyze its effect on gas composition. As the feed rate was increased more hydrogen (dark blue) was produced.**

### 3.4.5 *Gas Analysis Two-Stage Pyrolysis Feedstock Adjustment*

Feedstock compositions were tested at the same operating conditions of a 1.0s residence time, 500°C for the reactor with 850°C for the secondary furnace. Pure HDPE and LDPE were compared to a mixed feedstock containing 50% HDPE and 50% LDPE. When looking at the monomer yield pure LDPE had the highest amount of ethylene with a 40 wt. % yield, HDPE had a 30 wt. % yield and the mixed feedstock at a 39 wt. % yield. In this case, the blend had little effect on the product range distribution.

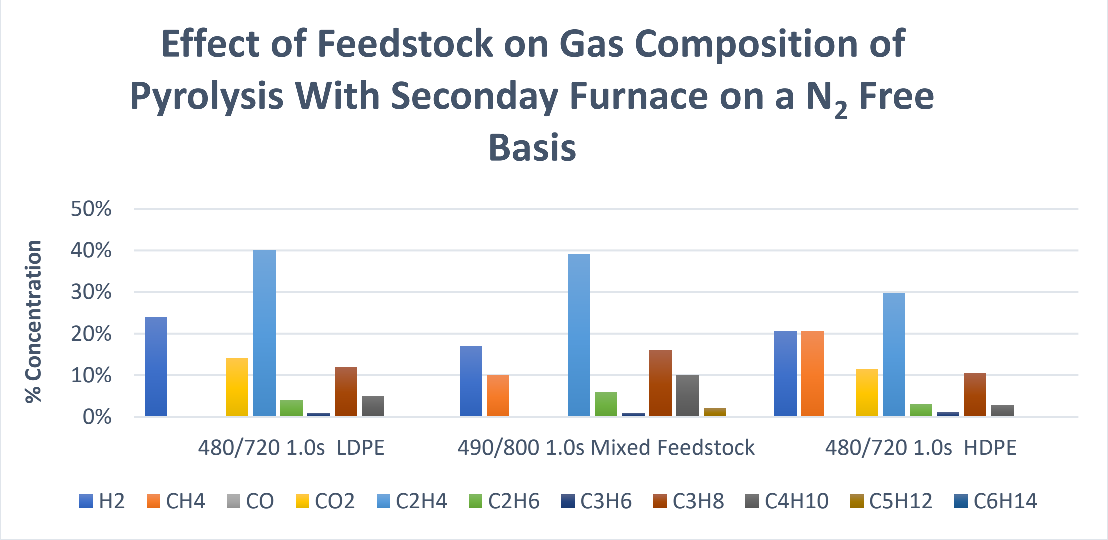

**Figure 29 The concentration of select gas compounds present in samples collected during pyrolysis using a secondary furnace. HDPE, LDPE and a 50:50 blend of both plastics were used as feedstock for these experiments, all of the other conditions were kept the same.**

### 3.4.6 *Gas Analysis Two-Stage LDPE Pyrolysis Tube Dimensions Adjustment*

Another way to adjust the residence time for the reactor was to alter the size of the tube in the furnace. For one experiment a smaller, 3/8” tube was used. This increased the contact area ratio between the gases in the furnace and the hot metal and decreased the residence time from 1.03 to 0.98 seconds. Compared with similar trends previously analyzed, when the residence time is decreased it is expected that there is less over-cracking and higher yields of longer chain hydrocarbons [58].

As seen in Figure 30 there was more Pentane ($C_5H_{12}$) and Hexane ($C_6H_{14}$) produced with the 3/8” tube as compared to the larger tube which corresponds with this expected trend. However, there was also more methane produced which was not expected. Increasing the amount of contact that the gases have with the hot metal tubing could also increase the amount of heat transfer and thus molecular cracking. This phenomenon would explain the increased methane yield.

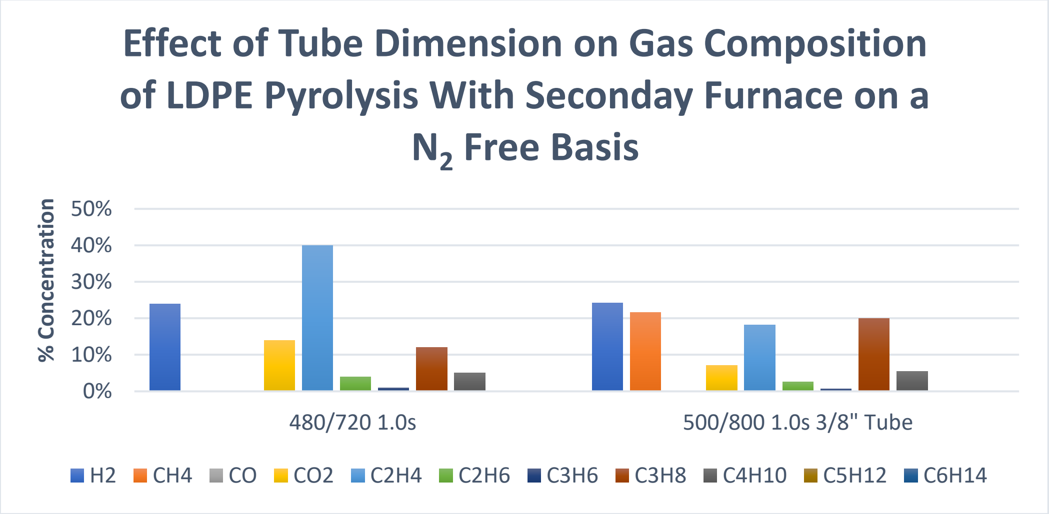

**Figure 30 The concentration of select gas compounds present in samples collected during LDPE pyrolysis using a secondary furnace. The gas composition from pyrolysis experiments using 3/8" tube were compared to a run using the same conditions. There is a larger amount of longer hydrocarbon molecules produced with the smaller tube as compared to the baseline conditions.**

### 3.4.7 *Gas Analysis Two-Stage Polypropylene Pyrolysis*

Waste PP was used as the feedstock for two experiments with different $N_2$ flow rates and gas residence times Figure 31. A lot of over-cracking occurred during both experiments with high amounts of methane present for both residence times (42% at 1 LPM and 41 % at 15 LPM) and low yields of the propylene. This could be explained by fillers and other contaminants such as coloring found in the waste samples. Results from the literature have also indicated that the addition of impurities in PP have led to higher gas yields indicating cracking being favored [65]. At the shorter residence time there were noticeably higher amounts of heavier hydrocarbons such as butane, propane, and propylene than at the longer residence time; 9%, 2%, 3% versus 3%, 1%, 1% respectively. This is similar to what has been reported in literature [28] [65].

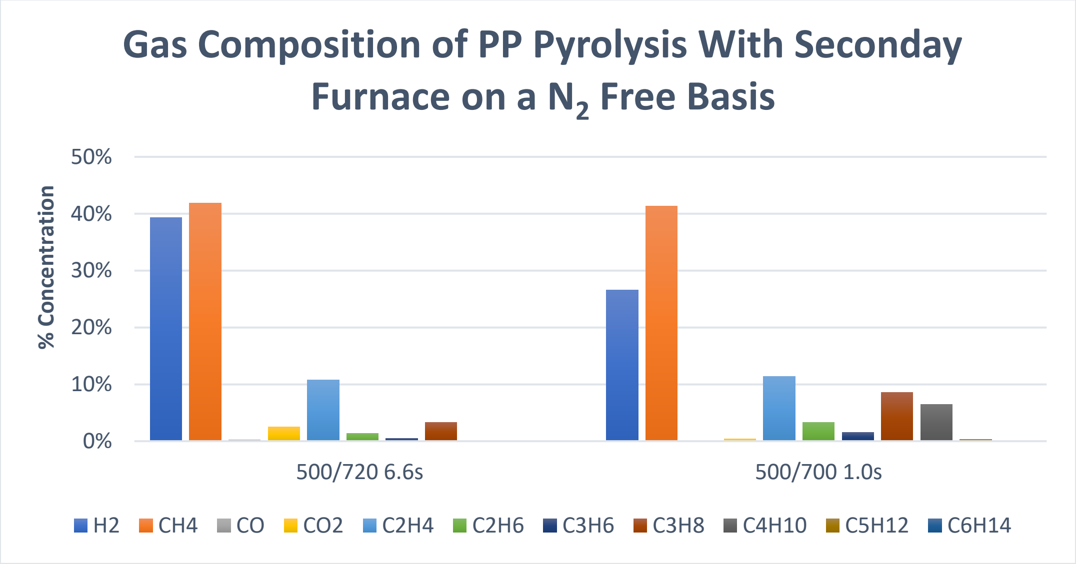

**Figure 31 The concentration of select gas compounds present in samples collected during Waste PP pyrolysis using a secondary furnace. Large amounts of methane (orange) were present during both experiments.**

### 3.4.8 *Gas Analysis Mixed Plastic Pyrolysis*

An exploratory run was completed at the 500/850°C temperature conditions using mixed plastics to mimic typical municipal plastic waste blends as described in the literature [17]. This blend was selected to be 41% LDPE, 34% HDPE and 25% PP of the virgin pellets based off typical waste compositions. A 1.0s residence time was used. The results from this run can be found in Figure 32. Overall, the yield of ethylene was lower than other experiments conducted at similar conditions. This could be attributed to the effect of PP on the sample. From the literature this compound is typically reduced to its monomer propylene [66]. In this sample there were more of the longer hydrocarbons present. More experiments would need to be conducted to make definitive conclusions.

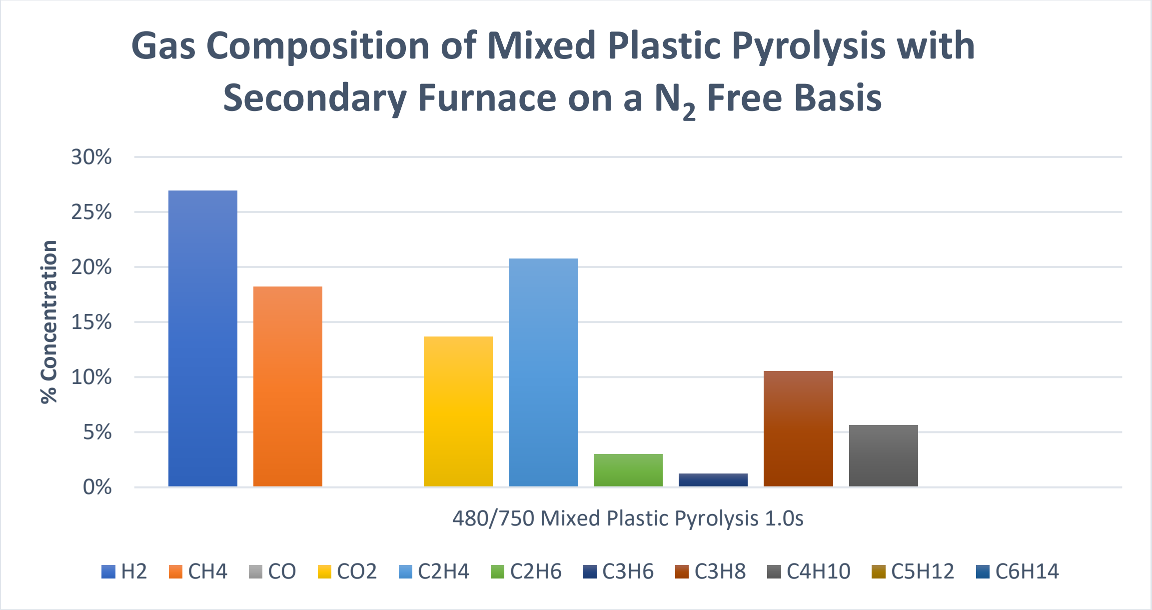

**Figure 32 The concentration of select gas compounds present in the sample collected using mixed plastic as the feedstock for pyrolysis using a secondary furnace.**

# 4 Techno-Economic Analysis

The following chapter provides a discussion of the economic sustainability and profitability of a two-stage waste plastic pyrolysis plant. The analysis is based on the results obtained from experiments performed using virgin polyethylene.

## 4.1 Mass and Energy Balance

The low heating value on a dry basis was calculated for both LDPE and HDPE using Equations 1 and 2:

$$HHV_{dry}\left(\frac{MJ}{kg}\right) = 0.3491 * C + 1.1783 * H + 0.1005 * S - 0.1034 * O - 0.015 * N - 0.0211 * A \tag{1}$$

$$LHV_{dry}\left(\frac{MJ}{kg}\right) = HHV_{dry} - 2.442 * 8.8936 * \frac{H}{100} \tag{2}$$

where C is the carbon content, H is hydrogen content, S is sulfur content, O is oxygen content, N is nitrogen content and A is the Ash content. The calculated value for HDPE was 8.45 kW and for LDPE it was 8.26 kW.

An energy balance was preformed using the first law of thermodynamics (Equation 3).

$$E_{in} = E_{out} + E_{loss} \tag{3}$$

Where $E_{in}$ in the energy input, $E_{out}$ is the energy output and $E_{loss}$ is the energy loss.

Based on the system Equation 3 was rewritten as

$$E_{in} = Q_{pw} + Q_s \qquad \textbf{4}$$

$$E_{out} = Q_{gas} + Q_{liquid} + Q_{char} \qquad \textbf{5}$$

$Q_{pw}$ is the energy content of the plastics and $Q_s$ is the energy required by the reactor to run at the set conditions. The potential recovered energy is the maximum energy recovered from the pyrolysis products and is the sum of the energy content from each product fraction (gas, solid, and liquid). Since the char production is negligible, the energy in the products can be written as in Equation 6:

$$E_{out} = Q_{gas} + Q_{liquid} \qquad \textbf{6}$$

The energy content calculation is based on the higher heating values of the compounds:

$$Q_{pw} = HHV_{pw} \qquad \textbf{7}$$

$$Q_i = X_i \times HHV_i \qquad \textbf{8}$$

Where $X_i$ is the mass yield of the products per kg of virgin plastic input and $HHV_i$ is the corresponding heating value.

The total energy recovery ratio (ERR) is defined in Equation 9:

$$E_{RRtotal(\%)} = \frac{Q_{Recovery}}{Q_{pw}} \times 100\% \qquad \textbf{9}$$

Where $Q_{pw}$ is the maximum energy potential of the plastic waste, it is a measure of the available heat of combustion obtained by plastic combustion.

Finally, the theoretical energy efficiency of the pyrolysis process can be calculated using Equation 10.

$$\eta(\%) = \frac{Q_{Recovery}}{Q_{pw} + Q_s} \times 100\% \qquad \textbf{10}$$

### 4.1.1 *Single-Stage Pyrolysis Mass and Energy Balance*

The mass and energy balance for the single stage LDPE and HDPE plant set up can be seen in Figure 33. Oil yields of 65.7% for HDPE and 65.5% for LDPE with a feeding rate of 0.72 kg/h accounted for oil being produced at a rate of 0.47 kg/hr. For the mass balance, only the yields of hydrogen, methane and ethylene were considered in the non-condensable fraction. Their concentrations were normalized. The LHV of the oil fraction was measured in kW to demonstrate the energy potential of the recovered portion.

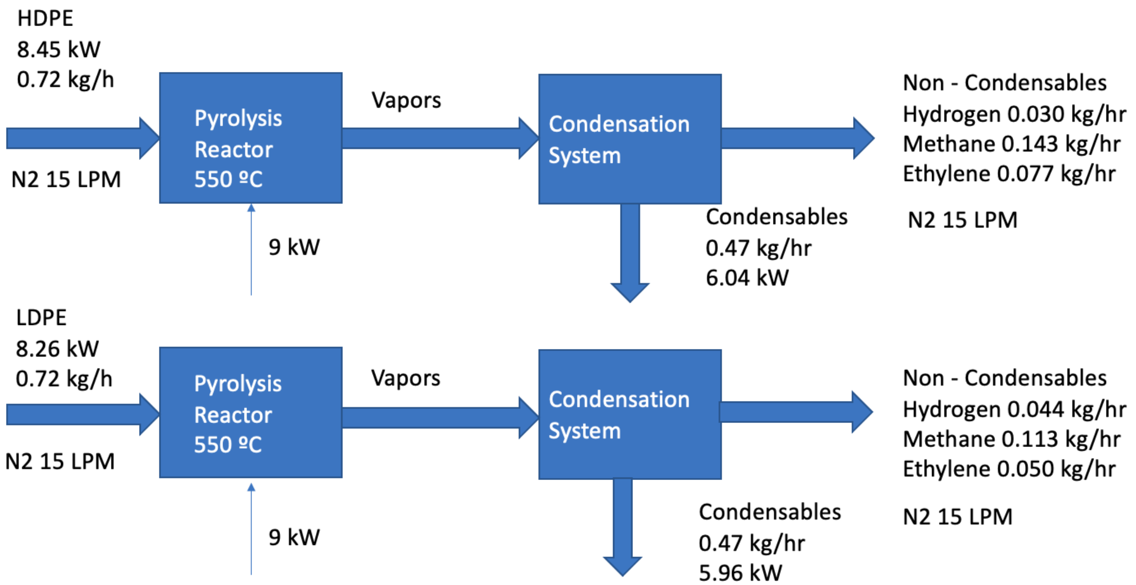

**Figure 33 A mass and energy balance conducted on the single stage pyrolysis plant.**

**Table 4 Energy Values Single-Stage Pyrolysis**

| | $Q_{pw}$ (MJ/kg) | $Q_s$ (MJ/kg) | $E_{in}$ (kW) | $Q_{liquid}$ (MJ/kg) | $Q_{gas}$ (MJ/kg) | $Q_{recovery}$ (MJ/kg) | $E_{out}$ (kW) | $E_{loss}$ (kW) | ERR (%) | η (%) |
|---|---|---|---|---|---|---|---|---|---|---|

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| HDPE | 45.20 | 50.90 | 19.2 | 30.2 | 20.7 | 50.8 | 10.17 | 9.1 | 112.5 | 54.6 |
| LDPE | 44.15 | 50.90 | 19.0 | 29.8 | 23.9 | 53.7 | 10.74 | 8.3 | 121.6 | 58.2 |

### 4.1.2 *Two-Stage Pyrolysis Mass and Energy Balance*

The mass and energy balance for the double stage LDPE and HDPE plant set up can be seen in Figure 34. Oil yields of 11.5% for HDPE and 14.75% for LDPE with a feeding rate of 0.72 kg/h accounted for oil fractions of 0.083 kg/h and 0.106 kg/h respectively. For the mass balance only the yields of hydrogen, methane and ethylene were considered in the non- condensable fraction. Their concentrations were normalized. The LHV of the oil fraction was measured in kW to demonstrate the energy potential of the recovered portion.

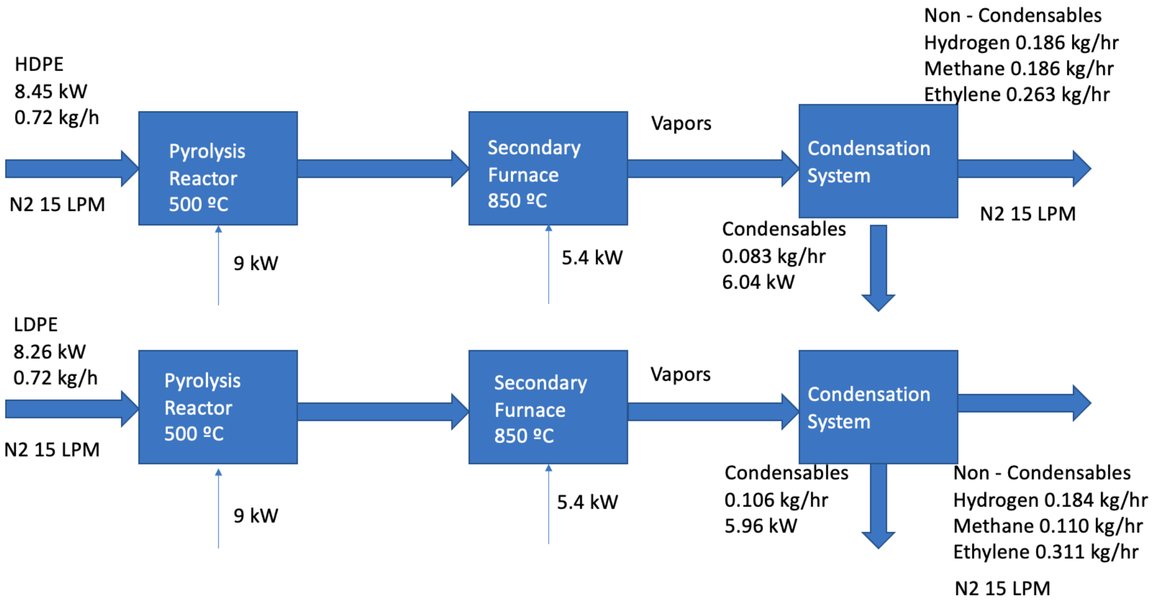

**Figure 34 A mass and energy balance conducted on a two-stage pyrolysis plant.**

Overall, the efficiency of the system is lowered when considering the two-stage pyrolysis plant because more energy must be put into the system with the secondary furnace. The calculated energy values of the system can be found in Table 5.

**Table 5 Energy Values for Two-Stage Pyrolysis Plant**

| | $Q_{pw}$ (MJ/kg) | $Q_s$ (MJ/kg) | $E_{in}$ (kW) | $Q_{liquid}$ (MJ/kg) | $Q_{gas}$ (MJ/kg) | $Q_{recovery}$ (MJ/kg) | $E_{out}$ (kW) | $E_{loss}$ (kW) | ERR (%) | $\eta$ (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| HDPE | 45.20 | 79.00 | 24.5 | 5.3 | 57.4 | 62.6 | 12.35 | 12.1 | 138.6 | 51.7 |
| LDPE | 44.15 | 79.00 | 24.3 | 6.7 | 55.0 | 61.7 | 12.18 | 12.1 | 139.8 | 51.3 |

For each of the given scenarios the following calculations and assumptions were used. The total capital investment consists of the fixed and working capital. The fixed capital includes direct costs and indirect costs. These costs were estimated based on percentages of the equipment costs according to approximations used by Peters et al 1991 [67]. The price of plastic pyrolysis oil was estimated based on the price of crude oil, at $0.377/kg [68]. The gas price was calculated using the normalized hydrogen, methane, and ethylene values. These values were approximated to be $2/kg for hydrogen, $1.01/kg for ethylene and $0.077/kg for methane [69] [41] [43].

Manufacturing costs consist of direct production costs, fixed charges, as well as plant overhead costs. General expenses include administrative costs, as well as distribution and marketing expenses. The raw material costs were assumed to be $0 since it will be a waste stream.

The labor costs were based on the following assumptions:

1) 8-hour shifts
2) 3 shifts per day
3) The average salary is $44,018 USD/year

Other manufacturing costs and expenses were estimated again based off percentages from Peters et al., 1991 [67]:

1) Maintenance and repair: 7% of equipment costs
2) Operating supplies: 15% of maintenance and repair
3) Laboratory charge: 15% of operating labour
4) Taxes: 13%
5) Plant overhead: 50% of total operating labour and maintenance
6) Administrative: 20% of operating labor
7) Distribution and selling: 5% of total product costs
8) Research and development: 3% of sales

Depreciation has been evaluated based on a 20-year period. The final value of the equipment was assumed to be $2000. The annual net cash income is the sum of the annual operating income after tax plus the depreciation.

The NPV and Payback time were used to assess the profitability of the plant. A discount factor of 5% was used.

$$A_{PV} = \frac{A_{CF}}{(1+d)^n} \quad \textbf{11}$$

$A_{CF}$ is the annual cash flow, d is the discount factor, and n is the reference year of the considered cased flow.

$$NPV = \sum_{i-1}^{N} A_{PV} - C_{TC} \quad \textbf{12}$$

Where, $A_{PV}$ represents the annual present value, N is the plant lifetime in years and $C_{TC}$ is the total capital investment.

## 4.2 Economic Analysis

### 4.2.1 *Applied Economic Scenarios*

The experimental parameters and yields obtained in Chapter 3 were applied to the following scenarios to develop an understanding of how these conditions may impact the profitability of a plastic pyrolysis plant. The base scenario was evaluated as the pilot scale plant with a feed rate of 0.72 kg/hr and with 4.5 workers per shift to run the plant. The plant was powered by electricity. Scenario 1 was the unaltered scale up of the base scenario. Under this scenario, a feed rate of 2500 kg/hr was used. It was approximated that included vacation and changeovers; 9 workers would be needed per shift to run the plant. Scenario 2 worked under the assumption that the plant was built in Quebec, where electricity costs are typically lower due to an abundance of hydroelectric plants. An energy price of $0.043 kW/h was used [70]. Scenario 3 altered the heating source for the plant, using natural gas rather than electricity. Scenario 4 considered using the methane produced by the process as a heat source for the plant. Part of the methane produced then acts as a recycled stream back to the process. These calculations were simplified to neglect the separation and additional gas treatments required. The methane required (as determined in scenario 3) was subtracted from the methane produced based on the experimental yields achieved. The remaining methane was considered available for sale while the rest was recycled through the process.

### 4.2.2 *LDPE Single-Stage Pyrolysis Economic Analysis*

Table 6 provides a summary of the results from the calculations of the LDPE single-stage pyrolysis economic analysis. Figure 35 displays the payback period for each applied scenario.

**Table 6 LDPE Single-Stage Pyrolysis Economic Analysis**

| | | | | | |
|---|---|---|---|---|---|
| Gas Production [kg/y] | 1382 | 5016902 | 5016902 | 5016902 | 5016902 |
| Hydrogen (%) | 5% | 5% | 5% | 5% | 5% |

| | | | | | |
|---|---|---|---|---|---|
| Hydrogen Sale Price [USD/kg] | 2 | 2 | 2 | 2 | 2 |
| Methane (%) | 54% | 54% | 54% | 54% | 37% |
| Methane Sale Price [USD/kg] | 0.077 | 0.077 | 0.077 | 0.077 | 0.077 |
| Ethylene (%) | 41% | 41% | 41% | 41% | 41% |
| Ethylene Sale Price [USD/kg] | 1.01 | 1.01 | 1.01 | 1.01 | 1.01 |
| Gas Sale Price [USD/kg] | 0.55 | 0.56 | 0.56 | 0.56 | 0.54 |
| Oil Production [kg/h] | 0.5 | 1629.1 | 1629.1 | 1629.1 | 1629.1 |
| Oil Production [kg/y] | 2707 | 9383328 | 9383328 | 9383328 | 9383328 |
| Oil Sale Price [USD/kg] | 0.43 | 0.38 | 0.38 | 0.38 | 0.38 |
| Annual Income (sales) [USD/y] | 1,921.0 | 6,325,307.0 | 6,325,307.0 | 6,325,307.0 | 6,259,636.0 |
| Raw Material [USD/y] | 0 | 0 | 0 | 0 | 0 |
| Workers | 4.5 | 9 | 9 | 9 | 9 |
| Salary [USD/y] | 44,018 | 44,018 | 44,018 | 44,018 | 44,018 |
| Operating Labor [USD/y] | 198,081 | 396,162 | 396,162 | 396,162 | 396,162 |
| Utilities [USD/y] | 49,796 | 993,686 | 459,446 | 106,011 | 55 |
| Maintenance and Repair [USD/y] | 2,254 | 300,136 | 300,136 | 300,136 | 300,136 |
| Operating Supplies [USD/y] | 338 | 45,020 | 45,020 | 45,020 | 45,020 |

| | | | | | |
|---|---|---|---|---|---|
| Laboratory Charges [USD/y] | 29,712 | 59,424 | 59,424 | 59,424 | 59,424 |
| Taxes | 250 | 822,290 | 822,290 | 822,290 | 813,753 |
| Plant Overhead | 100,168 | 348,149 | 348,149 | 348,149 | 348,149 |
| Annual Manufacturing Cost [USD/y] | 424,621 | 3,008,895 | 2,474,655 | 2,121,220 | 2,006,727 |
| Administrative [USD/y] | 39,616 | 79,232 | 79,232 | 79,232 | 79,232 |
| Distribution and Selling [USD/y] | 2,548 | 18,053 | 14,848 | 12,727 | 12,040 |
| Research and Development [USD/y] | 58 | 189,759 | 189,759 | 189,759 | 187,789 |
| Annual General Expenses [USD/y] | 42,222 | 287,045 | 283,840 | 281,719 | 279,062 |
| Annual Total Product Cost [USD/y] | 466,843 | 3,295,940 | 2,758,495 | 2,402,939 | 2,285,789 |
| Annual Operating Income [USD/y] | -464,921 | 3,029,367 | 3,566,812 | 3,922,368 | 3,973,847 |
| Annual Depreciation [USD/y] | 1,510 | 198,383 | 198,383 | 198,383 | 198,383 |
| Income before Tax [USD/y] | -466,431 | 2,830,984 | 3,368,429 | 3,723,985 | 3,775,464 |
| Income after Tax [USD/y] | -466,681 | 2,008,694 | 2,546,139 | 2,901,695 | 2,961,711 |
| Annual Net Cash Income [USD/y] | -465,171 | 2,207,077 | 2,744,522 | 3,100,078 | 3,160,094 |

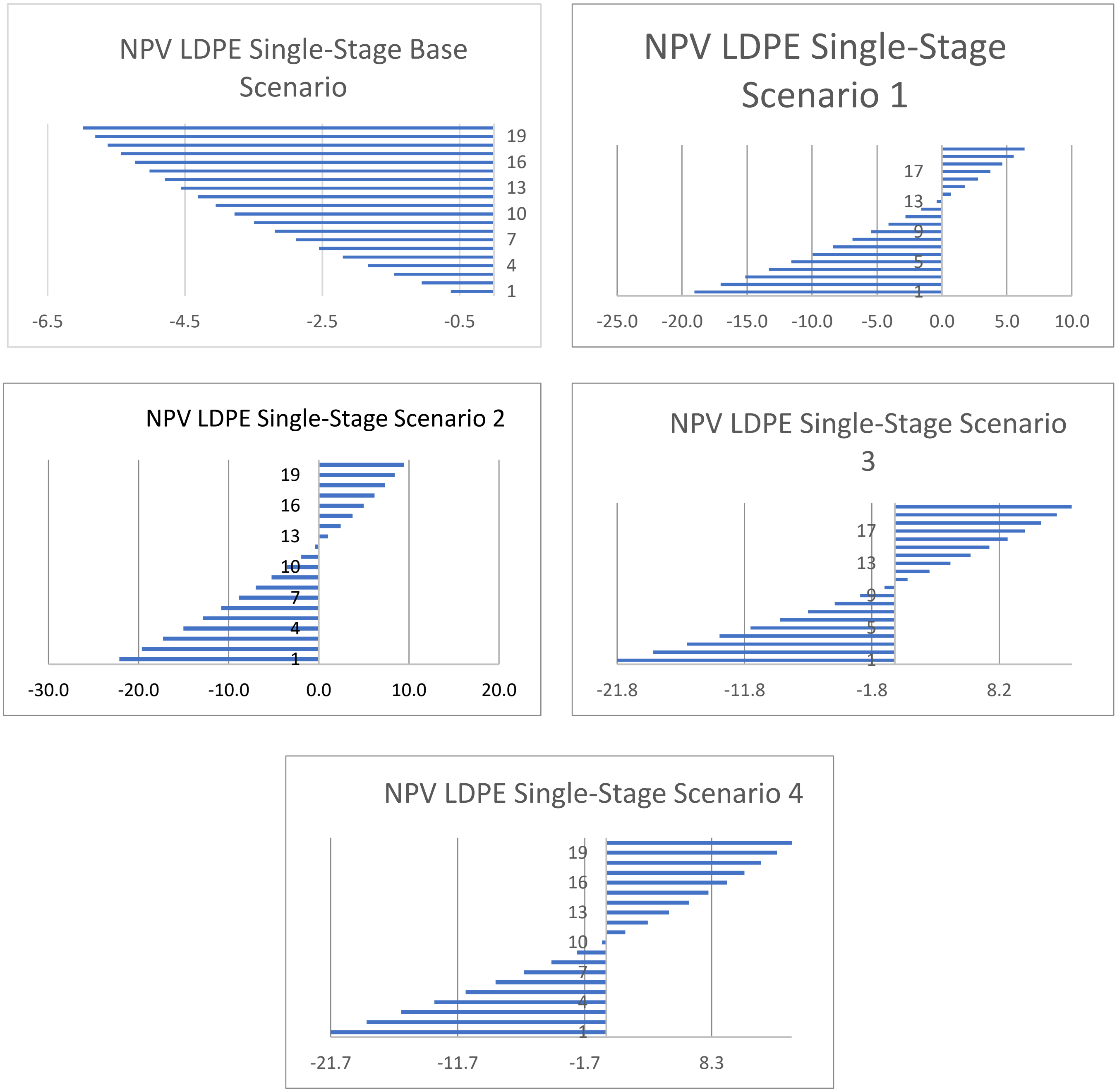

**Figure 35 The NPV of 4 "scale-up" scenarios as applied to a LDPE single-stage plant. The payback period is depicted on the y-axis. For each subsequent scenario the payback period is lowered and the NPV increases.**

With the single-stage reactor set-up, the pilot plant is not economically feasible. The NPV is always negative, even after 20-year lifespan. When the process is scaled up, it is profitable after the fourteenth year of operation. Again, this is not indicative of a financially feasible process. This value is improved in all the subsequent scenarios. In all scenarios there is a very large payback period of over ten years.

### 4.2.3 *HDPE Single-Stage Pyrolysis Economic Analysis*

Table 7 provides a summary of the results from the calculations of the LDPE single-stage pyrolysis economic analysis. Figure 37 Figure 37 displays the payback period for each applied scenario.

**Table 7 HDPE Single-Stage Pyrolysis Economic Analysis**

| | Base Scenario | Scenario 1 | Scenario 2 | Scenario 3 | Scenario 4 |
|---|---|---|---|---|---|
| Gas Production [kg/y] | 1382 | 4999104 | 4999104 | 4999104 | 4999104 |
| Hydrogen (%) | 12% | 12% | 12% | 12% | 12% |
| Hydrogen Sale Price [USD/kg] | 2 | 2 | 2 | 2 | 2 |
| Methane (%) | 57% | 57% | 57% | 57% | 37% |
| Methane Sale Price [USD/kg] | 0.077 | 0.077 | 0.077 | 0.077 | 0.077 |
| Ethylene (%) | 31% | 31% | 31% | 31% | 31% |
| Ethylene Sale Price [USD/kg] | 1.01 | 1.01 | 1.01 | 1.01 | 1.01 |
| Gas Sale Price [USD/kg] | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 |
| Oil Production [kg/h] | 0.5 | 1632.1 | 1632.1 | 1632.1 | 1632.1 |

| | | | | | |
|---|---|---|---|---|---|
| Oil Production [kg/y] | 2707 | 9401068.8 | 9401068.8 | 9401068.8 | 9401068.8 |
| Oil Sale Price [USD/kg] | 0.377 | 0.377 | 0.377 | 0.377 | 0.377 |
| Annual Income (sales) [USD/y] | 1,834 | 6,528,618 | 6,528,618 | 6,528,618 | 6,451,632 |
| Raw Material [USD/y] | 0 | 0 | 0 | 0 | 0 |
| Workers | 5 | 9 | 9 | 9 | 9 |
| Salary [USD/y] | 44,018 | 44,018 | 44,018 | 44,018 | 44,018 |
| Operating Labor [USD/y] | 198,081 | 396,162 | 396,162 | 396,162 | 396,162 |
| Utilities [USD/y] | 49,796 | 993,686 | 459,446 | 106,011 | 55 |
| Maintenance and Repair [USD/y] | 2,254 | 300,136 | 300,136 | 300,136 | 300,136 |
| Operating Supplies [USD/y] | 338 | 45,020 | 45,020 | 45,020 | 45,020 |
| Laboratory Charges [USD/y] | 29,712 | 59,424 | 59,424 | 59,424 | 59,424 |
| Taxes | 238 | 848,720 | 848,720 | 848,720 | 838,712 |
| Plant Overhead | 100,168 | 348,149 | 348,149 | 348,149 | 348,149 |
| Annual Manufacturing Cost [USD/y] | 424,610 | 3,035,326 | 2,501,086 | 2,147,650 | 2,031,686 |
| Administrative [USD/y] | 39,616 | 79,232 | 79,232 | 79,232 | 79,232 |
| Distribution and Selling [USD/y] | 2,548 | 18,212 | 15,007 | 12,886 | 12,190 |

| | | | | | |
|---|---|---|---|---|---|
| Research and Development [USD/y] | 55 | 195,859 | 195,859 | 195,859 | 193,549 |
| Annual General Expenses [USD/y] | 42,219 | 293,303 | 290,097 | 287,977 | 284,971 |
| Annual Total Product Cost [USD/y] | 466,829 | 3,328,629 | 2,791,183 | 2,435,627 | 2,316,658 |
| Annual Operating Income [USD/y] | -464,995 | 3,199,989 | 3,737,435 | 4,092,991 | 4,134,974 |
| Annual Depreciation [USD/y] | 1,510 | 198,383 | 198,383 | 198,383 | 198,383 |
| Income before Tax [USD/y] | -466,505 | 3,001,606 | 3,539,052 | 3,894,608 | 3,936,591 |
| Income after Tax [USD/y] | -466,743 | 2,152,886 | 2,690,331 | 3,045,888 | 3,097,879 |
| Annual Net Cash Income [USD/y] | -465,233 | 2,351,269 | 2,888,714 | 3,244,271 | 3,296,262 |

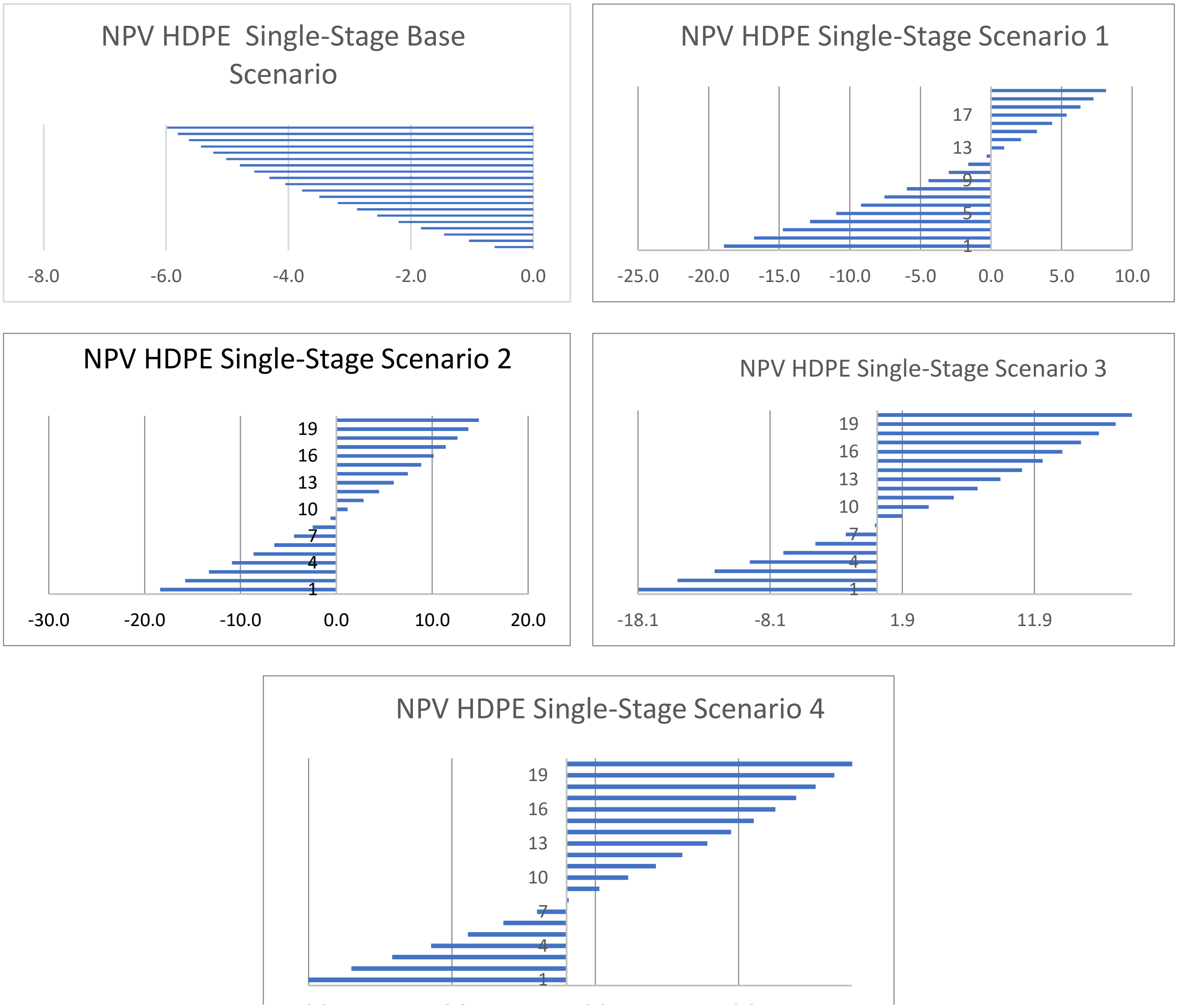

**Figure 37 The NPV of 4 "scale-up" scenarios as applied to a HDPE single-stage plant. The payback period is depicted on the y-axis. For each subsequent scenario the payback period is lowered and the NPV increases.**

With the single-stage reactor set-up, the pilot scale is not economically feasible. The NPV is always negative, even after 20-year lifespan. When the process is scaled up, it is profitable after the fourteenth year of operation. Again, this is not indicative of a financially feasible process. This value is improved in all the subsequent scenarios. However, in each scenario there is a very large payback period of over ten years. When compared to the LDPE single-stage analysis, the value of hydrogen makes a difference in the profitability of the plant. When the hydrogen yield is increased, the overall profits also increase.

### 4.2.4 *LDPE Two- Stage Pyrolysis Economic Analysis*

Table 8 provides a summary of the results from the calculations of the LDPE two-stage pyrolysis economic analysis. Figure 38 displays the payback period for each applied scenario.

**Table 8 LDPE Two-Stage Pyrolysis Economic Analysis**

| Gas Production [kg/y] | 3535 | 12276000 | 12276000 | 12276000 | 12276000 |
|---|---|---|---|---|---|
| Hydrogen (%) | 30% | 30% | 30% | 30% | 30% |
| Hydrogen Sale Price [USD/kg] | 2 | 2 | 2 | 2 | 2 |
| Methane (%) | 18% | 18% | 18% | 18% | 8% |
| Methane Sale Price [USD/kg] | 0.077 | 0.077 | 0.077 | 0.077 | 0.077 |
| Ethylene (%) | 51% | 51% | 51% | 51% | 51% |
| Ethylene Sale Price [USD/kg] | 1.01 | 1.01 | 1.01 | 1.01 | 1.01 |
| Gas Sale Price [USD/kg] | 1.13 | 1.13 | 1.13 | 1.13 | 1.12 |
| Oil Production [kg/h] | 0.106 | 368.75 | 369 | 368.75 | 368.75 |

| | | | | | |
|---|---|---|---|---|---|
| Oil Production [kg/y] | 611.7 | 2124000 | 2124000 | 2124000 | 2124000 |
| Oil Sale Price [USD/kg] | 0.377 | 0.377 | 0.377 | 0.377 | 0.377 |
| Annual Income (sales) [USD/y] | 4,222 | 14,659,861 | 14,659,861 | 14,659,861 | 14,565,336 |
| Raw Material [USD/y] | 0 | 0 | 0 | 0 | 0 |
| Workers | 5 | 9 | 9 | 9 | 9 |
| Salary [USD/y] | 44,018 | 44,018 | 44,018 | 44,018 | 44,018 |
| Operating Labor [USD/y] | 198,081 | 396,162 | 396,162 | 396,162 | 396,162 |
| Utilities [USD/y] | 50,021 | 1,224,029 | 565,949 | 130,585 | 68 |
| Maintenance and Repair [USD/y] | 2,611 | 347,673 | 347,673 | 347,673 | 347,673 |
| Operating Supplies [USD/y] | 392 | 52,151 | 52,151 | 52,151 | 52,151 |
| Laboratory Charges [USD/y] | 29,712 | 59,424 | 59,424 | 59,424 | 59,424 |
| Taxes | 549 | 1,905,782 | 1,905,782 | 1,905,782 | 1,893,494 |
| Plant Overhead | 100,346 | 371,918 | 371,918 | 371,918 | 371,918 |
| Annual Manufacturing Cost [USD/y] | 425,734 | 4,401,166 | 3,743,086 | 3,307,722 | 3,164,917 |
| Administrative [USD/y] | 39,616 | 79,232 | 79,232 | 79,232 | 79,232 |
| Distribution and Selling [USD/y] | 2,554 | 26,407 | 22,459 | 19,846 | 18,990 |

| | | | | | |
|---|---|---|---|---|---|
| Research and Development [USD/y] | 127 | 439,796 | 439,796 | 439,796 | 436,960 |
| Annual General Expenses [USD/y] | 42,297 | 545,435 | 541,487 | 538,875 | 535,182 |
| Annual Total Product Cost [USD/y] | 468,031 | 4,946,601 | 4,284,573 | 3,846,597 | 3,700,099 |
| Annual Operating Income [USD/y] | -463,809 | 9,713,260 | 10,375,288 | 10,813,264 | 10,865,237 |
| Annual Depreciation [USD/y] | 1,765 | 232,338 | 232,338 | 232,338 | 232,338 |
| Income before Tax [USD/y] | -465,574 | 9,480,922 | 10,142,950 | 10,580,926 | 10,632,899 |
| Income after Tax [USD/y] | -466,123 | 7,575,140 | 8,237,168 | 8,675,144 | 8,739,405 |
| Annual Net Cash Income [USD/y] | -464,358 | 7,807,478 | 8,469,506 | 8,907,483 | 8,971,743 |

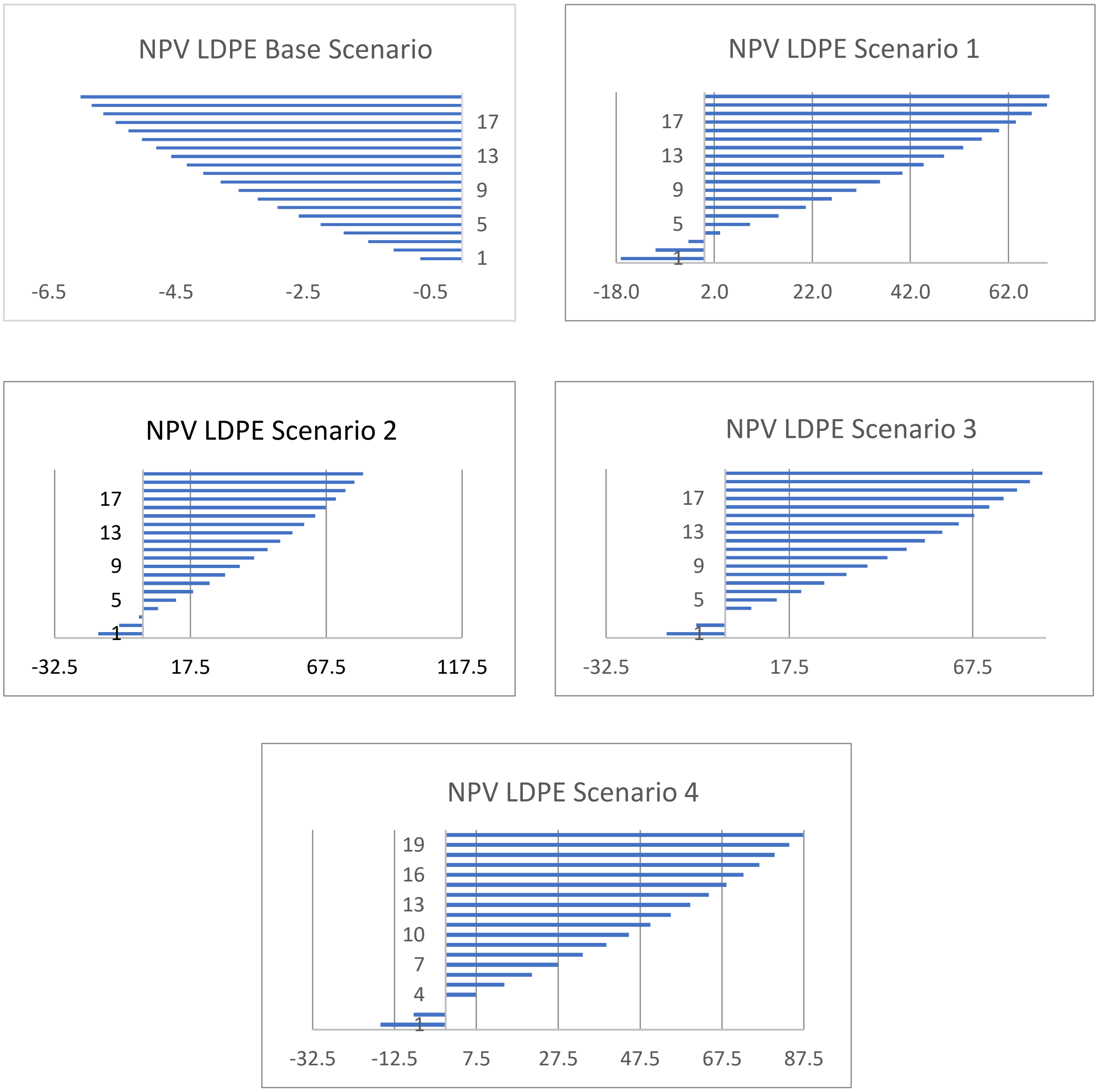

**Figure 38 The NPV of 4 "scale-up" scenarios as applied to a LDPE two-stage plant. The payback period is depicted on the y-axis. For each subsequent scenario the payback period is lowered and the NPV increases.**

When observing just the base scenario, the process is not economically feasible. The NPV is always negative, even after 20-year lifespan. When the process it scaled up, it is profitable after the fourth year of operation. This value is improved in all the subsequent scenarios. As can be seen in Table 8, by applying Quebec energy prices, there is a decrease in nearly $700,000 USD/year. This is indicative of the importance of considering the location and energy costs when building an electric plant. When natural gas is used to heat the plant, nearly $1,000,000 is gained as compared to Scenario 1. Finally, in Scenario 4, recycling the produced methane to heat the plant demonstrates how this again can decrease required costs to improve the feasibility, with a positive NPV of nearly 3 years. When compared to the single-stage process, increasing the ethylene and hydrogen as well as overall gas yields has a remarkable impact on the profitability and payback period of the plant.

### 4.2.5 *HDPE Two-Stage Pyrolysis Economic Analysis*

Table 9 provides a summary of the results from the calculations of the HDPE two-stage pyrolysis economic analysis. Figure 40 displays the payback period for each applied scenario.

**Table 9 HDPE Two-Stage Pyrolysis Economic Analysis**

| | | | | | |
|---|---|---|---|---|---|
| Gas Production [kg/y] | 3670 | 12744000 | 12744000 | 12744000 | 12744000 |
| Hydrogen (%) | 29% | 29% | 29% | 29% | 29% |
| Hydrogen Sale Price [USD/kg] | 2 | 2 | 2 | 2 | 2 |
| Methane (%) | 29% | 29% | 29% | 29% | 19% |
| Methane Sale Price [USD/kg] | 0.077 | 0.077 | 0.077 | 0.077 | 0.077 |
| Ethylene (%) | 41% | 41% | 41% | 41% | 41% |
| Ethylene Sale Price [USD/kg] | 1.01 | 1.01 | 1.01 | 1.01 | 1.01 |

| | | | | | |
|---|---|---|---|---|---|
| Gas Sale Price [USD/kg] | 1.02 | 1.02 | 1.02 | 1.02 | 1.01 |
| Oil Production [kg/h] | 0.083 | 287.5 | 287.5 | 287.5 | 287.5 |
| Oil Production [kg/y] | 476.9 | 1656000 | 1656000 | 1656000 | 1656000 |
| Oil Sale Price [USD/kg] | 0.377 | 0.377 | 0.377 | 0.377 | 0.377 |
| Annual Income (sales) [USD/y] | 3,933 | 13,656,377 | 13,577,696 | 13,577,696 | 13,479,567 |
| Raw Material [USD/y] | 0 | 0 | 0 | 0 | 0 |
| Workers | 5 | 9 | 9 | 9 | 9 |
| Salary [USD/y] | 44,018 | 44,018 | 44,018 | 44,018 | 44,018 |
| Operating Labor [USD/y] | 198,081 | 396,162 | 396,162 | 396,162 | 396,162 |
| Utilities [USD/y] | 50,021 | 1,224,029 | 565,949 | 130,585 | 68 |
| Maintenance and Repair [USD/y] | 2,611 | 347,673 | 347,673 | 347,673 | 347,673 |
| Operating Supplies [USD/y] | 392 | 52,151 | 52,151 | 52,151 | 52,151 |
| Laboratory Charges [USD/y] | 29,712 | 59,424 | 59,424 | 59,424 | 59,424 |
| Taxes | 511 | 1,775,329 | 1,765,100 | 1,765,100 | 1,752,344 |
| Plant Overhead | 100,346 | 371,918 | 371,918 | 371,918 | 371,918 |
| Annual Manufacturing Cost [USD/y] | 425,697 | 4,270,713 | 3,602,405 | 3,167,040 | 3,023,767 |

| | | | | | |
|---|---|---|---|---|---|
| Administrative [USD/y] | 39,616 | 79,232 | 79,232 | 79,232 | 79,232 |
| Distribution and Selling [USD/y] | 2,554 | 25,624 | 21,614 | 19,002 | 18,143 |
| Research and Development [USD/y] | 118 | 409,691 | 407,331 | 407,331 | 404,387 |
| Annual General Expenses [USD/y] | 42,288 | 514,548 | 508,178 | 505,566 | 501,762 |
| Annual Total Product Cost [USD/y] | 467,985 | 4,785,261 | 4,110,582 | 3,672,606 | 3,525,529 |
| Annual Operating Income [USD/y] | -464,052 | 8,871,116 | 9,467,114 | 9,905,090 | 9,954,038 |
| Annual Depreciation [USD/y] | 1,765 | 232,338 | 232,338 | 232,338 | 232,338 |
| Income before Tax [USD/y] | -465,817 | 8,638,778 | 9,234,776 | 9,672,752 | 9,721,700 |
| Income after Tax [USD/y] | -466,328 | 6,863,449 | 7,469,675 | 7,907,651 | 7,969,356 |
| Annual Net Cash Income [USD/y] | -464,563 | 7,095,787 | 7,702,013 | 8,139,989 | 8,201,694 |

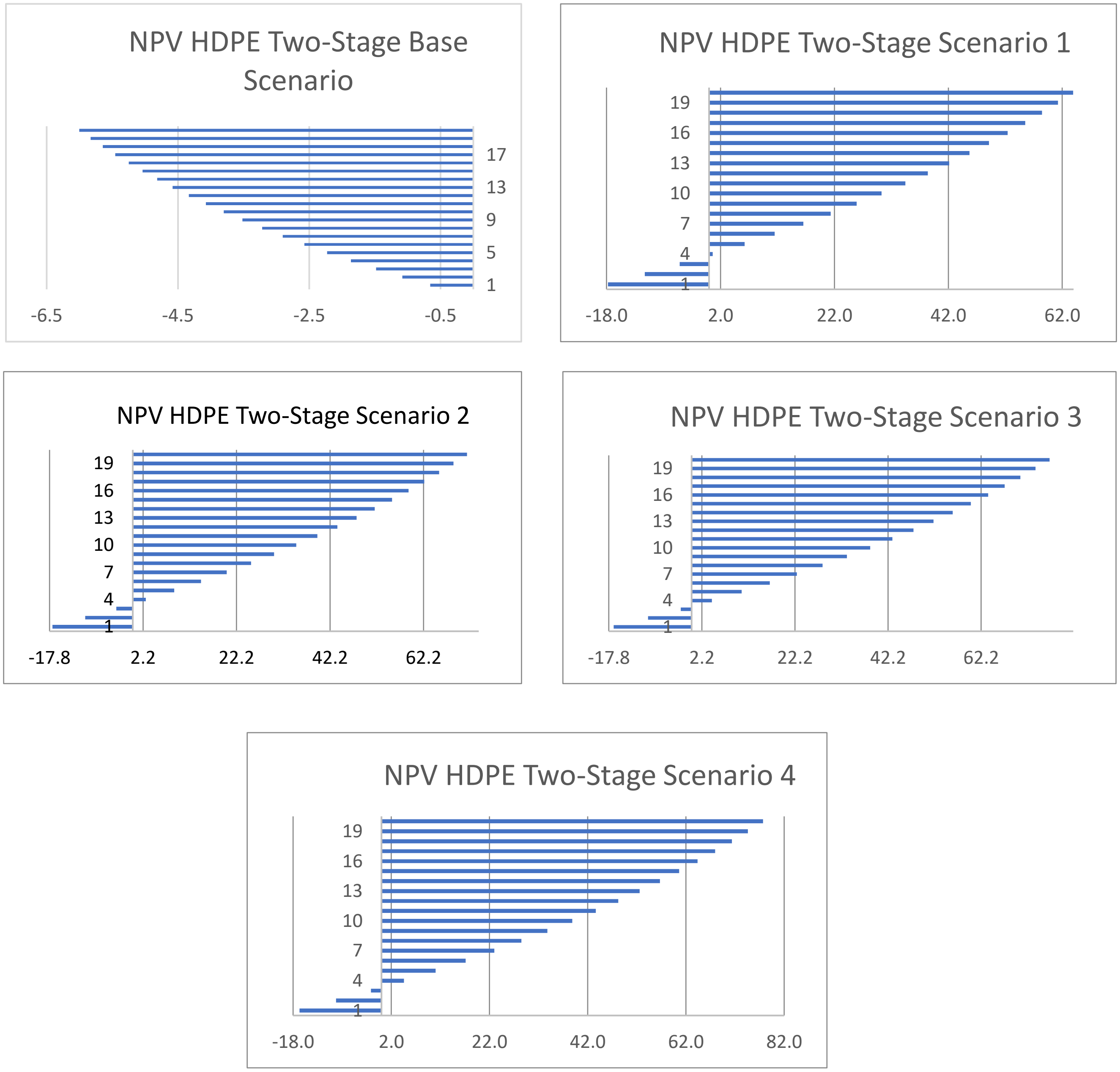

**Figure 40 The NPV of 4 “scale-up” scenarios as applied to a HDPE two-stage plant. The payback period is depicted on the y-axis. For each subsequent scenario the payback period is lowered and the NPV increases.**

The base scenario is not economically feasible. It always costs more money to operate the plant than can be made from profits.  When the process it scaled up, it becomes profitable after the fourth year of operation. This value is improved in all the subsequent scenarios. As can be seen in Table 9, by applying Quebec energy prices, there is a decrease in nearly $700,000 USD/year. When comparing the LDPE plant to the HDPE plant, the main difference is the amount of methane produced. Methane is the least profitable of the 3 gases considered for this analysis. In the LDPE plant more ethylene and hydrogen are comparatively produced. Both of these gases are of higher value than methane. Overall, this makes the LDPE plant more profitable than the HDPE plant.

# 5 Conclusions and Recommendations

With the world's plastic use and consumption drastically increasing, new technologies need to be developed to address concerns of waste accumulation. Chemical recycling provides a favorable avenue to minimize the need for new plastic resins. In this thesis, the chemical recycling of plastic was investigated using both a continuous single-stage and two-stage pyrolysis reactor. Liquid and gaseous products were collected and analyzed using GC-MS, Micro-GC, Karl Fischer Titration and Gas Chromatography.

Single stage pyrolysis was explored as a solution for the tertiary recycling of plastic waste. Lower temperatures led to higher liquid yields while higher temperatures led to more over-cracking and higher gas yields.

A secondary furnace was used to enhance downstream cracking of the vapors produced from the pyrolysis unit. These experiments were completed with the intention of identifying trends and opportunities using this set-up. The same trends in yields were observed during the two-stage experiments. Overall, the secondary furnace increased the amount of gas produced as compared to the single stage unit.

Operating parameters such as reactor and furnace temperature, residence time, and feed rate were altered to gain an understanding of their impact on operating outputs. With the reactor and secondary furnace set point conditions of 500 °C and 850 °C, maximum monomer recovery for HDPE and LDPE were achieved using the shortest residence time of 1.0 seconds. There was a 26.6 wt. % monomer recovery of the original feedstock using HDPE and 34.1 wt. % using LDPE. These temperature conditions were kept constant while the feed rate of the plastic was increased. Doubling the feed rate resulted in an increased hydrogen yield of 46.2 wt. % of the original polymer.

The liquid products collected during these experiments were analyzed and the results demonstrated their potential to be used as a diesel-like fuel. During two-stage pyrolysis, the conditions were altered to maximize the yields of ethylene and hydrogen produced. Using knowledge gained from the techno-economic evaluation, these are the two most valuable components that contribute to the financial success of any future reactor, so maximizing their yields will increase profitability. With the techno-economic evaluation it could be seen that the process became considerably more profitable when it was scaled up and the two-stage set up was used. None of the base scenarios themselves were economically feasible. However, looking at a two-stage HDPE and LDPE pyrolysis plant set up some of the most promising scenarios demonstrated payback periods of under 4 years. This is largely because of the increased profitability of the ethylene and hydrogen as a product compared to methane. This once again depicts the need to optimize reactor conditions in favor of the production of ethylene and hydrogen.

Overall, this research demonstrates the feasibility and potential of using a novel, two-stage pyrolysis reactor and furnace set up to enhance the chemical recycling of plastic waste.

### 5.1.1 *Recommendations*

To improve the accuracy and confirm the validity of these results, repeats of some of the experiments should be performed. As previously mentioned, to increase the profitability of any future scaled-up operations the yields of ethylene and hydrogen should be optimized. To do this there could be further investigation towards optimizing the reactor parameters including, temperature and pressure, to maximize these yields. A current limitation exists in the tubing material that is required to reach a higher temperature in the furnace. Other materials, such as quartz, could be selected for the furnace tubing as an alternative to reach higher temperatures in the secondary furnace.

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Appendices

## Appendix A: Sample Calculation Residence Time

Assumptions

Mass in: HDPE & N2

Mass out: Oil, Gas, N2

Volume of Reactor – Total Volume minus space of glass beads

HPDE MW (of repeat unit) 28.05g/gmol

N2 MW 28 g/gmol

HDPE feed at 12g/min

$$\frac{12\ g}{min}\ HDPE \times \frac{gmol}{28\ g} = 0.429\ \frac{gmol}{min}$$

N2 feed

$$0.5\ LPM\ N2 \times \frac{gmol}{22.4\ L} = 0.022\ \frac{gmol}{min}$$

$$v_2 = \frac{v_1 T_2}{T_1}$$

$$v_2 = \frac{\left(0.0013\left(\frac{gmol}{\mathrm{min}}\right)\right)773K}{298\ K}$$

$$v_2 = 0.0035\ \frac{gmol}{\mathrm{min}}$$

Oil Yield 0.115

Gas Yield 0.885

Non Condensables Volumetric Flow Rate

$$Volumetric\ Flow\ Rate\ \left(\frac{m^3}{s}\right) = Feed\ Rate\ \frac{gmol}{min} * Gas\ Yield\ * \%\ Comp * MW\ \frac{g}{gmol} * \left(\frac{1\ kg}{1000\ g}\right) * \left(\frac{1}{Gas\ Density\ \frac{kg}{m^3} @\ STP}\right) * \left(\frac{1\ min}{60\ s}\right)$$

H2

$$Volumetric\ Flow\ Rate\ \left(\frac{m^3}{s}\right) = 0.0427\ \frac{gmol}{min} * 0.885\ * 0.21 * 2\ \frac{g}{gmol} * \left(\frac{1\ kg}{1000\ g}\right) * \left(\frac{1}{0.0296\ \frac{kg}{m^3} @\ STP}\right) * \left(\frac{1\ min}{60\ s}\right)$$

$$Volumetric\ Flow\ Rate\ \left(\frac{m^3}{s}\right) = 0.000089$$

**Non-condensables**

| | Gas Density (@ 550 C) kg/m^3 | % Comp | MW (g/gmol) | Volumetric Flow Rate m^3/s |
|---|---|---|---|---|
| H2 | 0.0296 | 0.21 | 2 | 8.95361E-05 |
| CH4 | 0.234 | 0.21 | 16 | 9.06074E-05 |
| CO2 | 0.651 | 0.11 | 44 | 4.69142E-05 |
| C2H4 | 0.751 | 0.3 | 28 | 7.05797E-05 |
| C2H6 | 0.444 | 0.03 | 30 | 1.27909E-05 |
| C3H6 | 0.647 | 0.01 | 42 | 4.09624E-06 |
| C3H8 | 0.647 | 0.11 | 44 | 4.72043E-05 |
| C4H10 | 1.487 | 0.03 | 58 | 7.38378E-06 |

Condensables Volumetric Flow Rate

$$Volumetric\ Flow\ Rate\ \left(\frac{m^3}{s}\right) = Feed\ Rate\ \frac{gmol}{min} * Oil\ Yield\ * \%\ Comp\ * Critical\ Volume\ \frac{m^3}{gmol} * \left(\frac{1\ min}{60\ s}\right)$$

C21H44

$$Volumetric\ Flow\ Rate\ \left(\frac{m^3}{s}\right) = 0.427\ \frac{gmol}{min} * 0.115\ * 0.131 * 0.00121\frac{m^3}{gmol} * \left(\frac{1\ min}{60\ s}\right)$$

$$Volumetric\ Flow\ Rate\ \left(\frac{m^3}{s}\right) = 1.299E - 7$$

**Condensables**

| | Critical Volume m^3/gmol | % Comp | MW (g/gmol) | Volumetric Flow Rate m^3/s |
|---|---|---|---|---|
| C21H44 | 0.00121 | 0.131 | 296 | 1.29973E-07 |
| C17H34 | 0.00097 | 0.0746 | 238 | 5.93343E-08 |
| C15H30 | 0.00086 | 0.0809 | 210 | 5.70482E-08 |
| C13H26 | 0.00074 | 0.2187 | 182 | 1.32701E-07 |
| C12H24 | 0.00069 | 0.108 | 168 | 6.11037E-08 |
| C11H22 | 0.00063 | 0.128 | 154 | 6.61219E-08 |
| C9H18 | 0.00053 | 0.107 | 126 | 4.65002E-08 |
| C8H16 | 0.00047 | 0.083 | 112 | 3.19868E-08 |
| C7H14 | 0.00041 | 0.068 | 98 | 2.28606E-08 |

Volume of the pipe

Length

$$3\,ft \times \frac{0.3048\,m}{1\,ft} = 0.914\,m$$

Cross-sectional area

$$A = \pi r^2$$

$$A = \pi(0.0127m)^2$$

$$A = 5.06\ x\ 10^{-4} m^2$$

Volume

$$V = 5.06\ x\ 10^{-4} m^2 \times 0.914m$$

$$V = 6.44\ x\ 10^{-6} m^3$$

Volume of Reactor

V=0.0035 m^3

Total Volumetric Flow Rate

$$\dot{v} = sum\ of\ non - cond. + sum\ of\ cond. + N2\ V_2$$

$$\dot{v} = 0.0038\ \frac{m^3}{s}$$

Residence Time

$$\tau = \frac{V}{\dot{v}}$$

$$\tau = 1.034\ s.$$

# Curriculum Vitae

| | |
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