

# Thermochemical Conversion of Polystyrene

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Joshua Ruland





# Thermochemical Conversion of Polystyrene

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Thesis report

by

Joshua Ruland

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*Thesis committee:*

Chair: Dr. Prof.dr.ir. W. de Jong  
Supervisors: Dr. Luis Cutz  
External examiner: Dr. Ana Somoza-Tornos  
Place: TU Delft Faculty of Mechanical Engineering (Department of Process & Energy)  
Project Duration: March, 2023 - May, 2024  
Student number: 4791630

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# Preface

This thesis represents not only my work at the keyboard, it is a milestone after two and half years at work for my MSc.Sustainable Energy Technology at TU Delft. As I reflect on the years of research and study, I am deeply grateful for the opportunities to grow as a researcher and contribute to the existing body of knowledge into a sustainable future.

The journey to this point has been one of intellectual challenge and persistent effort, driven by an abiding fascination to create a sustainable future and a deep belief in the importance of this work. The questions addressed within these pages have been a source of deep reflection and have shaped my perspective on Thermochemical recycling of plastics.

I extend my sincere thanks to my academic advisor, Dr. Luis Cutz, for their unwavering support and guidance throughout this process. Their expertise and insights have been invaluable, not just to this thesis, but to shaping my broader understanding of Thermochemical technologies and plastic recycling. I am also deeply appreciative of the members of my thesis committee, Dr. Prof.dr.ir Wiebren de Jong and Dr. Ana Somoza Tornos for their constructive critique and engagement with my work.

My gratitude also goes to my peers and colleagues at TU Delft, whose camaraderie and collaborative spirit have made my time here both productive and pleasant. I must acknowledge the staff at Process and Energy Department which have aided in this research.

Lastly, I want to express my love and appreciation to my family and friends for their unwavering support and encouragement throughout my academic pursuits.

This thesis is intended for industry and academia, with the hope that it contributes to creating a sustainable future. It is my desire that the findings presented here not only advance the field of thermochemical plastic recycling but also inspire further inquiry and exploration.

*Joshua Ruland*

*TU Delft*

*May 2024*

# Abstract

In Europe, 20.7 Mt of Polystyrene (PS) was produced in the year 2021, mostly consisting of packaging, insulation, and food utensils. Like many other kinds of plastics, they take hundreds of years to naturally degrade in the environment. To prevent the buildup of plastics in our environment, recycling technology will have to be employed. Current recycling technologies can be divided into three categories: organic, mechanical and chemical recycling. Organic recycling involves the use of biological organisms or enzymes to breakdown plastic into useful materials. Mechanical recycling technologies include processes such as dissolution and conventional mechanical recycling. Among chemical recycling, baseline technology includes pyrolysis that involves higher temperatures ( $>500^{\circ}\text{C}$ ) which produces char, gasses, and complex oils. Hydrothermal Liquefaction (HTL) of PS has shown promising results in tackling the problem plastic waste buildup in the environment. This process utilizes water as solvent and subjecting it to mild temperatures and pressures to produce less complex oils that contain building blocks such as monomeric compounds and high value chemicals (HVC). These compounds can then be used as platform chemicals or as source to manufacture new materials, as well as closing the loop on PS waste.

This thesis focuses on the use of catalysis to increase the selectivity for PS conversion through HTL to increase the yields of monomeric compounds and high-value chemicals (HVCs) at lower temperatures ( $<370^{\circ}\text{C}$ ) than current approaches. In this work, different catalysts were screened and the best performing catalyst was used to optimize the HTL process. The HTL process was optimized using a design-of-experience (DOE) approach for the following process conditions: temperature ( $330\text{-}350^{\circ}\text{C}$ ), catalyst loading (0-15%) and reaction time (30-60 minutes). The analytical techniques used to characterize the quality of oil as well as determine the amount of chemicals present are: Bomb Calorimetry, Ultimate analysis (CHN-analysis), Gas Chromatography-Mass Spectrometry with Flame Ionization Detection (GCMS-FID) and Two-Dimensional Gas Chromatography with Flame Ionization Detection (GCxGC-FID).

Results from a screening campaign indicated high yields of oil (90 wt%). Following this, a simple distillation was conducted to separate the lighter fraction from the heavier ones within 90 wt%. Ultimate analysis of the compounds showed high C,H, and N ratios similar to what was found in literature. Bomb calorimetry of the PS-Crude oil product showed of 40 MJ/kg, indicating that oil product is comparable to what is found in literature. GCMS-FID indicated that 17 wt% of styrene was produced from this process, along with 5.5 wt% of alpha-methyl styrene and other HVCs. The rest of the oil consists of heavy fractions (C-20) which could be go through another upgrading process.

After the screening campaign MgO was chosen as a catalyst to increase the yield of styrene. The yield of oil remain high with 80-90 wt% yield of oil in most cases. Aqueous phase and gas yields remain low ( $<5\text{ wt}\%$ ), while char can vary but also remains quite low ( $<10\text{ wt}\%$ ). Analysis of Bomb calorimetry showed similar results to screening with an average of 38 MJ/kg. CHNO also showed similar ratios of C,H, and N ratios. When looking at the GCMS-FID and GCxGC-FID, the amount of styrene remained at a maximum of 16-17 wt% with no significant increase. However, results of the research also showed that catalyst does have effect in increasing yield of styrene. Optimization for oil was conducted and optimum point for oil production is at  $340^{\circ}\text{C}$ , 34 minutes and 8% catalyst loading. The research will contribute to the growing body of research into processes for plastic waste valorization and offers more insight into catalytic hydrothermal liquefaction as well as experimental methodology to separate the oils into its components.

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# Nomenclature

## List of Abbreviations

CH <sub>4</sub>	Carbon Monoxide	HVC	High Value Chemicals
H <sub>2</sub>	Hydrogen	LDPE	Low Density Polyethylene
M <sub>w</sub>	Molecular weight	MgO	Magnesium Oxide
BaO	Barium Oxide	PAHs	Polycyclic Aromatic Hydrocarbons
Ch:KOH	Choline Chloride:Pottasium Hydroxide	PET	Polyethylene Terephthalate
CHNO	Carbon, Hydrogen, Nitrogen, Oxygen analysis (Ultimate analysis)	PP	Polypropylene
CO	Carbon Monoxide	PS	Polystyrene
DES	Deep Eutectic Solvent	PVC	Polyvinyl Chloride
DOE	Design of Experiments	TRL	Technology readiness level
EPS	Expanded Polystyrene	UN	United Nations
EU	European Union		
GCMS-FID	Gas Chromatography - Mass Spectrometry Flame Ionization Detector		
GCxGC-FID	Two-Dimensional Gas Chromatography with Flame Ionization Detection		
GPC	Gel Permeation Chromatography		
HIPS	High Impact Polystyrene		
HTL	Hydrothermal Liquefaction		

## List of Symbols

$\Delta G$	Gibbs Free Energy
$\Delta H$	Enthalpy
$\Delta S$	Entropy
g	grams
MJ	Mega Joules
mol	mole
wt%	Weight percentage

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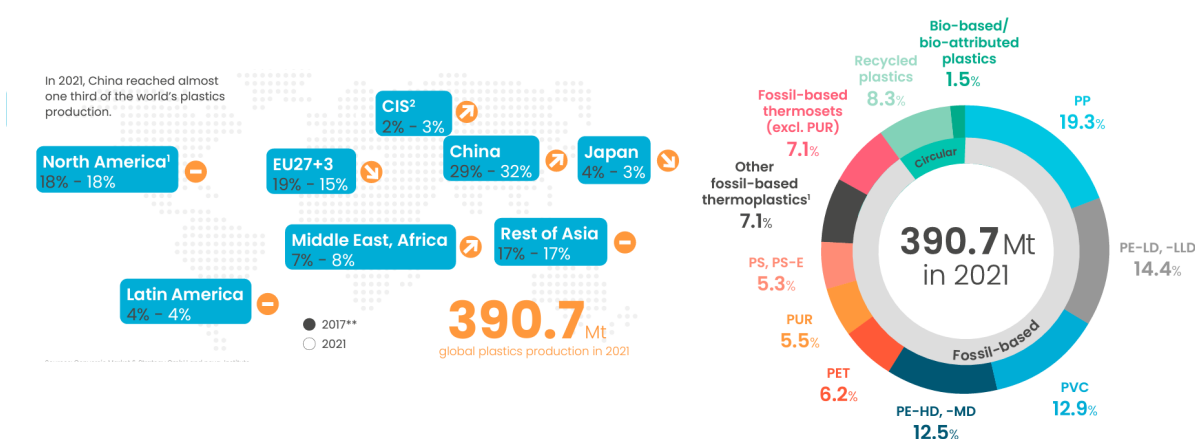
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# Introduction

Plastic pollution represents a critical global issue that has yet to be effectively addressed and is likely to worsen in the near future. In 2021 alone, 390.7 million metric tons of plastics were produced as stated by PlasticsEurope 2022. Alarming, the UN Environment Program (UN 2023) reports that every minute, an amount equivalent to one garbage truck full of plastic is dumped into the ocean. It is not surprising that our oceans contain more than 5 trillion plastic fragments of various shapes and sizes, with a total weight of 250,000 tons (Eriksen et al. 2014). The contamination of our oceans with plastic stands as one of the most urgent environmental challenges of our time, affecting and harming approximately 700 marine species.



**Figure 1.1:** Distribution of Plastic Types (PlasticsEurope 2022).

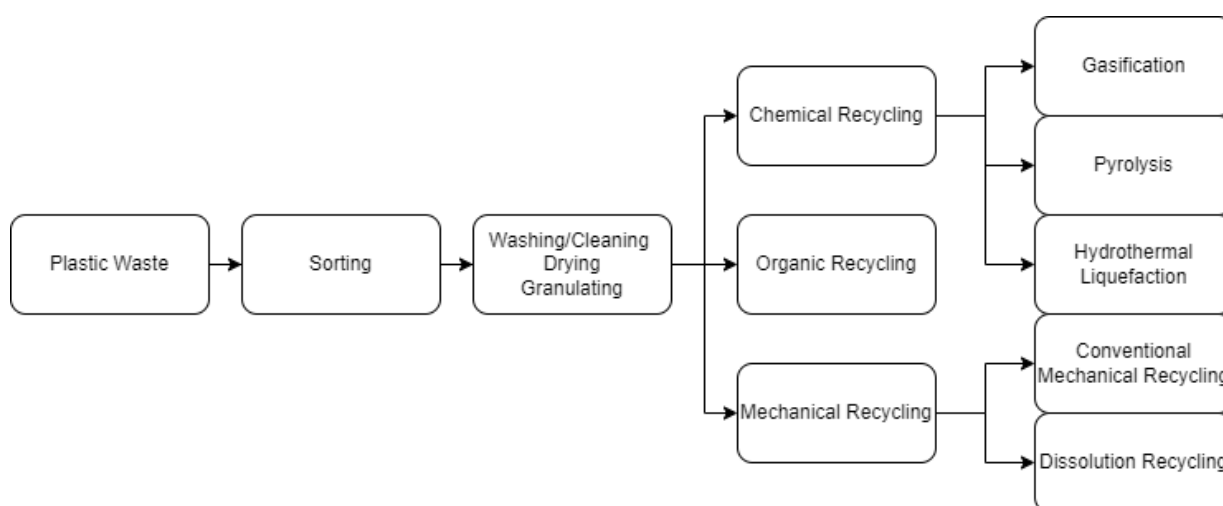
Figure 1.1 shows the amount of plastics produced in the year 2021. The total mass produced in that year was 390.7 Mt. The figure further divides the quantity of plastics produced into different kinds. As seen above, the majority of plastics produced are Polypropylene (PP) at 75.4 Mt, followed by Low-Density Polyethylene (LDPE) at 56.3 Mt and Polyvinyl-chloride (PVC) at 50.4 Mt. Polyethylene terephthalate (PET) is the most recycled plastic in Europe, with 58% of the plastic being recycled as stated in *PET: Why It's Not a Single-Use Plastic 2023*.

As seen in figure 1.1, approximately 5.5% of the plastic produced consists of PS or Expanded Polystyrene (EPS). Although PS is not the most used plastic compared to others it is still produced at 20,7 Mt per year (PlasticsEurope 2022). PS is also one of the plastics that could be expanded, they have amazing insulation capacity which will not be replaced anytime soon. The property of EPS is precisely why the recycling of the material is difficult, they have a large volume and low density which makes it difficult to transport and breakdown in reactors. The majority of plastics manufactured today are designed for single-use purposes, contributing to a cycle of production, consumption, and disposal that harms our environment by filling up landfills and polluting oceans. Rather than viewing plastics as mere waste, we have the potential to transform them into valuable resources for creating a wide range of products, including

HVCs and new PS. This concept is known as 'circular plastics,' which strives to create a closed-loop system for plastic utilization.

In 2021, nearly 25% of plastics end up in landfill as stated by the European Parliament (EU 2018). Figure 1.2 shows the different stages in the plastic recycling process. Plastics can be recycled by various methods, depending on the type of plastic and recycling facility (PlasticsEurope 2022). In Western Europe, the standard procedure for recycling begins with the collection of waste plastics. These materials often reach waste management facilities as a mixed assortment, necessitating an initial sorting process. Subsequently, the plastics are shredded and washed. A final sorting step follows to meticulously separate the different types of plastics. After this preparatory phase, the recycling process branches into three primary methods: mechanical recycling, chemical recycling, and energy recovery (PlasticsEurope 2022).

Organic recycling is also a recycling option, this is through the controlled microbiological treatment of plastics such as composting, biogasification, or through some microorganisms (fungi/bacteria) (PlasticsEurope 2022). The majority of plastics undergo mechanical recycling, with approximately 33% of plastics in Europe being recycled through this method (Ragaert 2023). The EU also aims to raise the recycling rate to 55% by 2030 (EU 2018). Mechanical recycling can then be subdivided into conventional mechanical recycling and solvent-based (dissolution) recycling. However, it is important to note that mechanical recycling also has its own drawbacks. The feasibility of mechanical recycling is restricted to plastics that are uncontaminated by other plastic types, dyes, or adhesives (Sedaghat 2018). Furthermore, as recycled plastics undergo multiple mechanical recycling cycles, the stress on the polymer chains gradually damages, resulting in a decline in their structural integrity. Consequently, mechanically recycled plastics have a much lower quality in comparison to their virgin plastic counterparts.



**Figure 1.2:** Recycling Process and Methods taken from Plastics Europe PlasticsEurope 2022

Due to the decrease in plastic quality, chemical recycling is needed. Chemical recycling is a process that allows the complete breakdown of plastics into its monomers. Thermochemical processes to recycle waste plastic can be divided into gasification, pyrolysis, and hydrothermal liquefaction (HTL). However, there are certain drawbacks associated with each of these processes. Gasification has the main drawback of having very high processing temperatures (700-1500 °C)(Kersten et al. 2014). At these high temperatures chemical components become broken down into syngas, carbon monoxide and hydrogen as well as other molecules. These molecules would then need to be upgraded to the desired products such as plastic monomers, fuels and/or HVCs (Segneri et al. 2022). Pyrolysis also occurs at high temperature (400-700°C) (Musivand et al. 2023) but not as high as gasification. However, its main drawback is that it produces a lot of char and gasses. HTL has the lowest operating temperature but the process operates at pressures ranging from 5-20 MPa. There has been research into HTL of different kinds of plastics such as PE, PP, and PET as seen in (Laredo et al. 2023). However, there has only been a handful of research on the breakdown of polystyrene (PS) via HTL. Some have tried using supercritical HTL (Kwak et al. 2006) and (Seshasayee et al. 2020); while others have attempted subcritical HTL (Passos et al. 2020). Few of the

drawbacks of PS breakdown via HTL includes its high energy and pressure conditions. HTL of PS currently requires a lot of energy which makes it expensive to operate (Bai et al. 2019). However, catalyst could be used to lower the reaction temperature and increase the monomer yield. The main goal of this thesis will be to research options into catalytic HTL of PS to improve oil yields and lower processing conditions. The hope is that lowering the cost of the process could incentivize companies to recycle these plastics more in the future.

## 1.1. Research Question

Considering all of the information above, the following research question has been formed:

### Research Question

What is the most efficient approach for the HTL of PS to produce HVCs using catalysis while optimizing different operational variables of the process?

This could then be split into 3 sub-questions:

### Research Question 1

Which type of catalyst could be used for HTL of PS?

### Research Question 2

Which high-value chemicals could be produced from HTL of PS?

### Research Question 3

Which operational parameters (Temperature, Catalyst loading, and Reaction time) could produce the highest amount of high-value chemicals from HTL of PS?

The first question is based on research from Marquez et al. 2023, which describes that basic catalysts efficiently degrade PS. This paper uses pyrolysis but in this work several basic catalysts will be screened using HTL to determine which one produces the largest amount of monomeric compounds.

The second question explores which types of high-value chemicals are produced. Typical compounds found in pyrolysis and/or HTL of PS oils are styrene, benzene, toluene, ethylbenzene and alpha-methylstyrene seen in (Kwak et al. 2006, Seshasayee et al. 2020).

In the third research question, the catalyst chosen from the first question is optimized for its catalyst loading, reaction time, and temperature. Currently, there has been research on HTL in sub- and supercritical water (Savage 1999, Bai et al. 2019, Musivand et al. 2023). However, this has not been done with the presence of a catalyst.

## 1.2. MSc Thesis Project Scope

### Research Objective

The objective of this research is to identify the optimal mix of heterogeneous basic/acidic catalysts for use in the hydrothermal liquefaction of PS. By fine-tuning the operational parameters, the study seeks to maximize the yield of high-value chemicals from this process. This study will consider a wide range of catalysts and parameters to identify a sustainable and economically viable process for transforming PS waste into valuable products. In order to successfully accomplish this research, two sets of catalytic HTL campaigns will be carried out. This research will be performed at the Process & Energy laboratory at TU Delft. The initial campaign will involve screening catalysts and comparing the performance of various zeolites, alkaline earth metals, and deep-eutectic solvents. The second campaign will focus on fine-tuning the various reaction parameters, including temperature, retention time and catalyst loading. This is conducted through a Design of Experiments (DOE) approach to maximize the yields of PS-Crude produced and monomeric compounds. A wide range of comprehensive characterization techniques will be employed such as Ultimate Analysis, Bomb Calorimetry, Gas Chromatography - Mass Spectrometry Flame Ionization Detector (GCMS-FID), and Two-Dimensional Gas Chromatography with Flame Ionization Detection (GCxGC-FID). This will provide a deeper understanding of the impact of the HTL process and if catalyst enhanced the selective cleavage of PS into monomeric compounds.

## 1.3. Structure of the Report

The purpose of this report is to add to the small amount of research available in PS recycling. While working on this thesis (2023/2024), there have been less than 10 research papers on PS recycling via HTL. The amount of research is important considering that there have been large number of publications co-liquefactions of different plastic types and plastic-biomass mixtures but these have mostly considered only PET and PE (Passos et al. 2020, Conti 2020), however, there have been only a number of publications of PS recycling.

The structure of the report is as follows. Beginning with the theoretical background of the research which includes the description of the feedstock and the possible catalyst that could be of used. Followed by an explanation of other competing technologies that are used to thermochemically convert plastics to chemicals or molecules. Then finally about hydrothermal liquefaction and how it works.

In the third chapter, the focus shifts to explaining the experimental method, covering the basic procedure for hydrothermal liquefaction, the collection method, the materials involved, and the chosen experimental parameters, along with the analysis methods utilized.

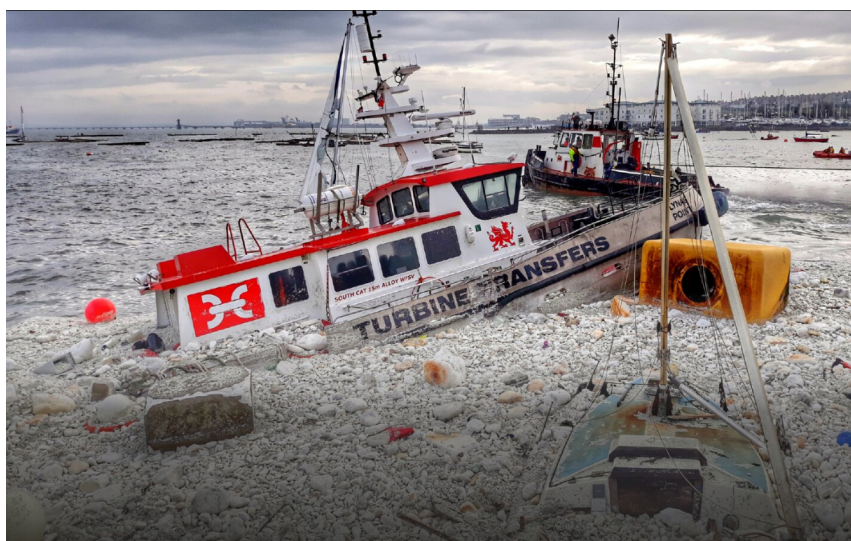
In the fourth chapter, the results of the experiments are shown. Beginning with the screening campaign of which catalysts were selected and why some were successful while others were failures. Of the experiment that did work, characterization of the product has been done, this is done through Bomb calorimetry, gas chromatography with flame-ionization detection (GC-FID) and Two-Dimensional Gas Chromatography with Flame Ionization Detection (GCxGC-FID). as well as Ultimate analysis (CHN-analysis).

The final chapter concludes the results of the research as well as recommendations on how future scientist could further their research into PS recycling via hydrothermal liquefaction.

## Theoretical Background

### 2.1. Environmental Effect of Plastics and Polystyrene

Plastics are detrimental to the environment and human health for several reasons. Firstly, the widespread use of plastics has led to a severe pollution crisis. Plastic waste, often improperly disposed of or not recycled, finds its way into oceans, rivers, and natural habitats, causing harm to marine life and wildlife (UN 2023). Animals mistakenly ingest or become entangled in plastic debris, leading to injuries, suffocation, and death. Moreover, plastic waste eventually breaks down into microplastics (tiny particles that can contaminate water source), which can infiltrate the food chain and potentially harm human health when ingested (Nanda et al. 2021).

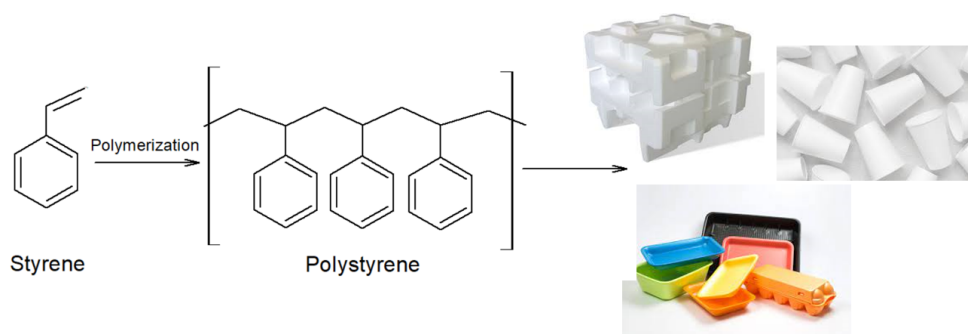


**Figure 2.1:** Styrofoam polluting oceans (Annkathrin et al. 2020.)

Secondly, the production and disposal of plastics contribute significantly to climate change and the depletion of finite resources (Ford et al. 2022). The manufacturing of plastics heavily relies on fossil fuels, leading to the release of greenhouse gases during extraction, production, and transportation. Furthermore, plastic incineration also releases harmful pollutants into the atmosphere (Verma et al. 2016). In the case of polystyrene burning, there has been concern that these could release carcinogenic toxins such as styrene and polycyclic aromatic hydrocarbons (PAHs) (Farrelly et al. 2017). The persistence of plastic waste in the environment, which takes hundreds of years to decompose, results in a wasteful consumption of resources. As a result, reducing plastic use and finding sustainable alternatives to dispose plastics are crucial steps to mitigate environmental damage and safeguarding the planet for future generations.

#### 2.1.1. Polystyrene

Polystyrene is a significant polymer with diverse applications ranging from disposable cups, forks, and plates to packaging foam and home insulation. Its name is derived from storax balsam, which was isolated



**Figure 2.2:** Styrene polymerization into styrofoam and products (Facts 2022, Britannica 2024, Cat 2019).

in 1839 by the German apothecary Eduard Simon from the American sweet gum tree. Notably, when Simon exposed styrol to air, light, or heat, it underwent a sudden transformation into a rubber-like substance. Presently, the production of styrene involves the alkylation of ethylene and benzene, both derived from fossil fuels (Britannica 2024). This process operates at high temperatures, reaching up to 600°C, making it energy-intensive and contributing to environmental concerns associated with greenhouse gas emissions. The production of styrene is not without any hazard, as in 2014 the International Agency for Research on Cander (IARC) has determined that styrene is a possible human carcinogen (Farrelly et al. 2017).

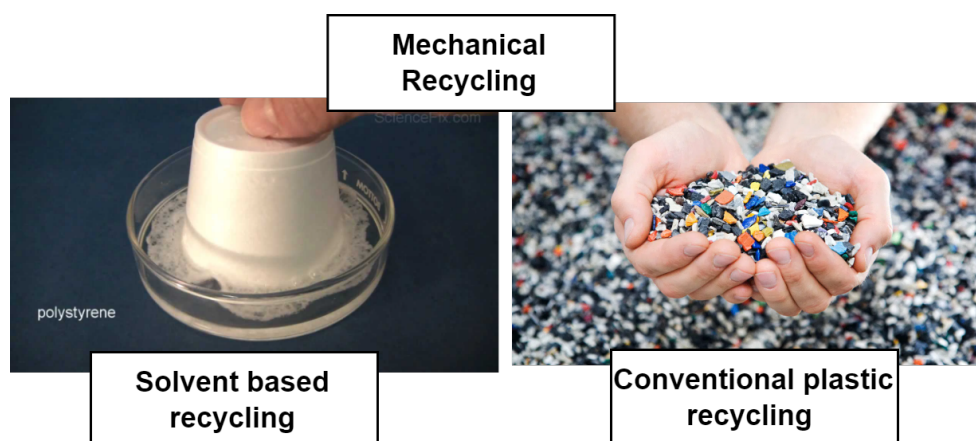
After the formation of styrene, it undergoes a self- polymerization reaction, leading to the creation of long chains. The double bonds in one styrene molecule continuously react with other styrene molecules, resulting in the formation of polystyrene as seen in Figure 2.2. This unique structure, which features single bonds between carbon molecules and benzene rings, imparts polystyrene with exceptional durability and waterproof properties. Its resilience is remarkable as it remains resistant even to the corrosive effects of acids or bases. However, this durability also poses a significant challenge when it comes to natural breakdown processes. Polystyrene has a melting point of approximately 240°C, and in the natural environment, it can take an astonishingly long time—ranging from 500 to 1 million years—to degrade fully. This prolonged persistence in the environment contributes significantly to the growing issue of plastic pollution (Britannica 2024). Given the issues related to polystyrene production, including the generation of carcinogenic monomers and significant greenhouse gas emissions, it is imperative to explore more sustainable methods for producing monomer and promote a circular economy.

Polymers and biomass are related in several ways, particularly in terms of their chemical compositions and the roles they play in various applications. Polymers are macromolecules composed of monomers. These monomers can be chemically linked together to form long chains or networks. Similarly, biomass refers to the organic matter derived from living or recently living organisms, such as plants and animals. This also consists of various macromolecules, including carbohydrates (e.g., cellulose, starch), proteins, and lipids, all of which are made up of repeating monomer units. This research hopes to use some of the information gathered from thermochemical biomass conversion and apply the concepts to PS conversion into raw chemicals for industry.

## 2.2. Recycling Technologies

### 2.2.1. Organic Recycling

Organic recycling, also known as the biological method of plastic recycling, is a new field of recycling that offers a more environmentally friendly alternative to incineration or mechanical recycling. Biorecycling methods typically utilize enzymes or microorganisms that break down plastics into their basic organic molecules. These enzymes also be fine tuned to crate new polymers of other valuable products (Emadian et al. 2017). Biorecycling methods of recycling have gained a lot of attention due to the mild conditions that they require. Research from Yang et al. 2016 has shown that some fungal species were able to produce enzymes that could break apart PET. However, the main drawback of this process is that it takes significantly longer to break these plastics down to their base molecules.



**Figure 2.3:** Mechanical Recycling (Sciencefix 2012, Supply 2024 ).

### 2.2.2. Mechanical Recycling

Mechanical recycling is a process of recycling plastics into secondary raw materials without significantly changing their chemical structure. Most kinds of thermoplastics we are familiar with such as polystyrene, polyethylene, and polycarbonates, can be recycled mechanically with little to no impact on their quality. Mechanical recycling can then be categorized further into two processes as seen in Figure 2.3, conventional mechanical recycling, and solvent-based recycling. In accordance with EU standardization, recycling technology is classified as mechanical recycling when it doesn't substantially alter the chemical composition of the material, which is why dissolution recycling is also a part of mechanical recycling (Plastics Europe PlasticsEurope 2022).

#### Conventional mechanical recycling

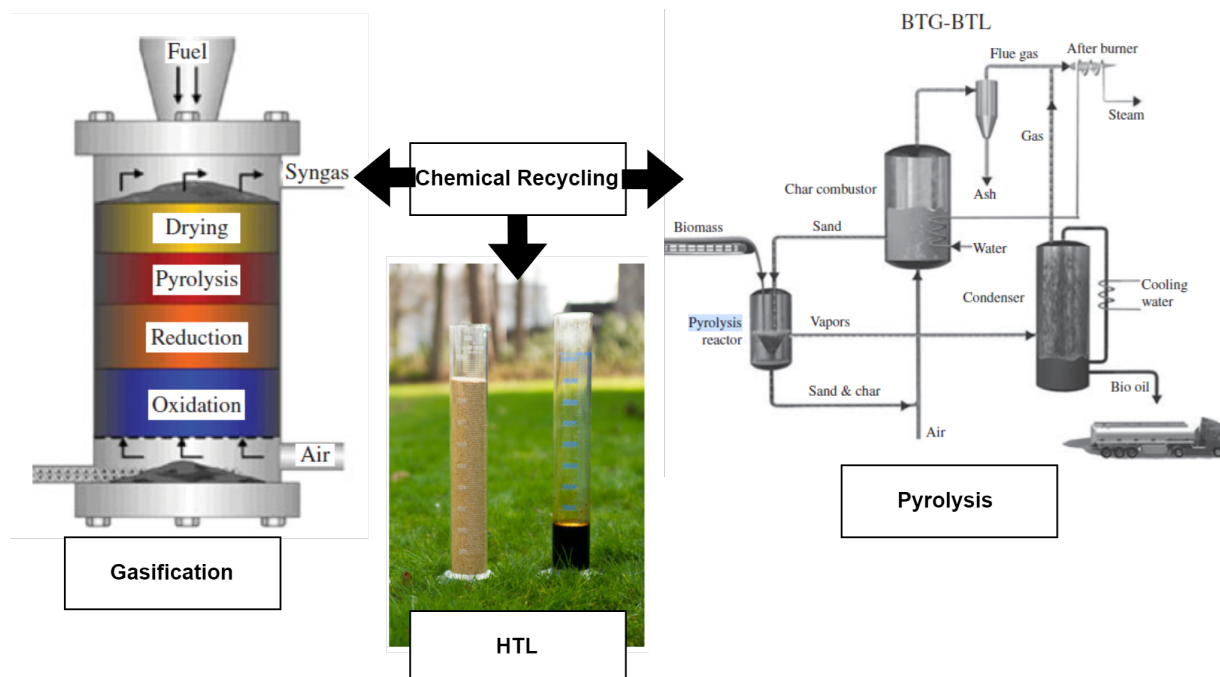
This is known as the conventional way to recycle, and typically is a process involving several steps. From sorting to washing, drying, grinding, re-granulating and compounding. All these steps occur in the same facility, an examples of this include a plastic recycling company TIVACO, located in Blandain, Belgium (Esser 2023). Currently, this is the most cost-effective form of recycling. However, it is only cost-effective depending on the feedstock destined for recycling. One of the main issues with plastic recycling is that plastics typically arrive at the facility with heavy contamination such as other plastics, adhesives, dyes, and metals (Ragaert 2023).

#### Dissolution Recycling/Solvent Based Recycling

This is a form of recycling, where a specific plastic is dissolved in an organic solvent. For example, expanded polystyrene foam (EPS) contains 95% air and the other 5% contains the actual polystyrene (Koerner et al. 2007). When polystyrene is introduced to acetone, the polarity of acetone causes hydrogen bonding with the molecules in polystyrene. This causes the polystyrene to lose its foam structure and the release of the air molecules. The process does not break down the structure of the polymers, only their macro structure. This is a more expensive way of recycling because it requires even more sorting of the plastics, and it could be difficult to determine which solvents could dissolve the specified kind of plastic (30 2020).

### 2.2.3. Chemical Recycling

Chemical recycling involves the decomposition of plastic into its elemental components, which entails disrupting the carbon bonds connecting the molecules and transforming them into raw materials (U.S. Government 2023). This form of recycling has the advantage of producing better quality materials than compared to materials produced from mechanical recycling. However, it is a much more energy-intensive process because it requires breaking down of these bonds. As quoted from Lase et al. 2023, chemical recycling in its most positive scenario will not be a competitive technology to mechanical recycling but a complementary one to help improve the rate of overall plastic recycling. Currently, there are 3 main types of thermo-chemical recycling processes this includes Pyrolysis, Gasification, and Hydrothermal Liquefaction as seen in Figure 2.4.



**Figure 2.4:** Chemical Recycling Technologies (Bellouard 2017, Kersten et al. 2014).

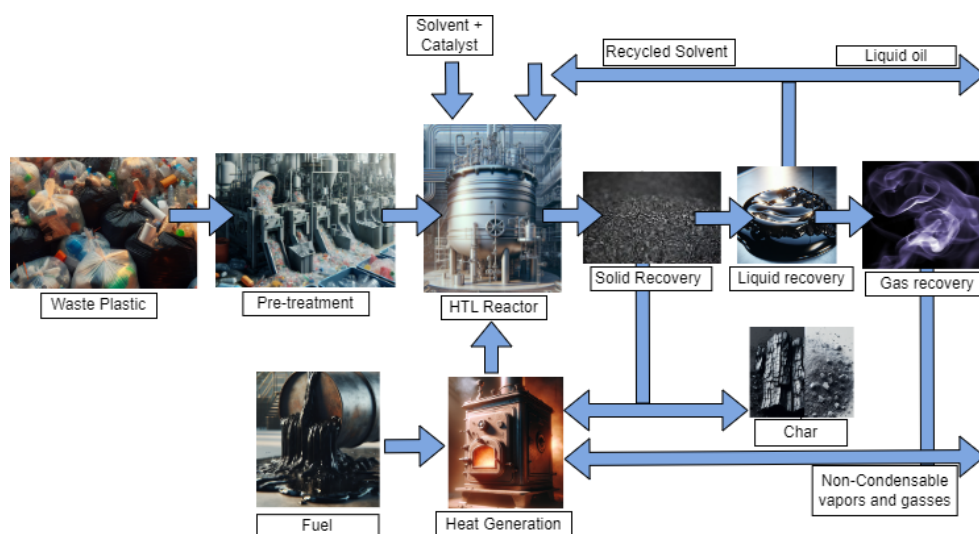
### Pyrolysis

Pyrolysis is a thermal decomposition process that occurs at high temperatures in the absence of oxygen. Organic materials, such as biomass or plastic, are heated to temperatures typically between 400-700°C and ambient pressures Musivand et al. 2023. This leads to their breakdown into smaller molecules. Unlike complete combustion, the lack of oxygen results in the production of heavy oils, solid char, and pyrolysis vapors. These vapors and liquids could then be upgraded to fuels for processes (Rahman et al. 2022). Moreover, in the context of plastics, pyrolysis serves as an effective method to break down plastic waste into valuable products, such as fuels or chemical feed stocks, making it a promising approach for recycling processes. There are already pyrolysis plants in Spain and Belgium treating mixed polyolefins and polystyrene with up to 65,000 tonne/year in capacity (Lase et al. 2023). A company named BioBTX, in the Netherlands is also looking into plastic recycling via pyrolysis. This is done to produce mostly aromatics such as Benzene, Toluene and Xylenes for the chemical industry. They have successfully achieved mini-scale pilot plants to produce these chemicals (BioBTX 2024). The primary drawbacks associated with pyrolysis include the demanding operational requirements and its potential to generate numerous volatile organic compounds (VOCs). Although there are precautions that can be taken to produce less dangerous gasses, there are still cases of these hazardous materials leaking into the environment (Paladino et al. 2021).

### Gasification

Gasification is a thermochemical conversion technology carried out at high temperatures while using an oxidizing agent to convert a liquid or solid fuel into a combustible gas product. This process occurs at relatively high temperatures of 700-1500°C. When air is used the gas product is typically H<sub>2</sub>, CO, CO<sub>2</sub> and CH<sub>4</sub> (Kersten et al. 2014). After this process, H<sub>2</sub> and CO could then be used in Fischer-tropsch process to produce higher molecular weight carbon chains. These longer chain carbons could then be used for a large number of products in the petrochemical industry and in refinery such as plastic monomers, methanol, ammonia and synthetic gasoline (Segneri et al. 2022). There are also plans for a gasification plant in Spain by AIMPLAS 2022 for treating non-recyclable mixed solid waste with a capacity of 400,000 tonne/year (Lase et al. 2023). Producing fuels from gasses via Fischer-tropsch can be an option to produce different kinds of fuels. However, this process is incredibly energy-intensive and gasses could escape into the environment and cause harm.

### 2.2.4. Hydrothermal Liquefaction and Solvolysis

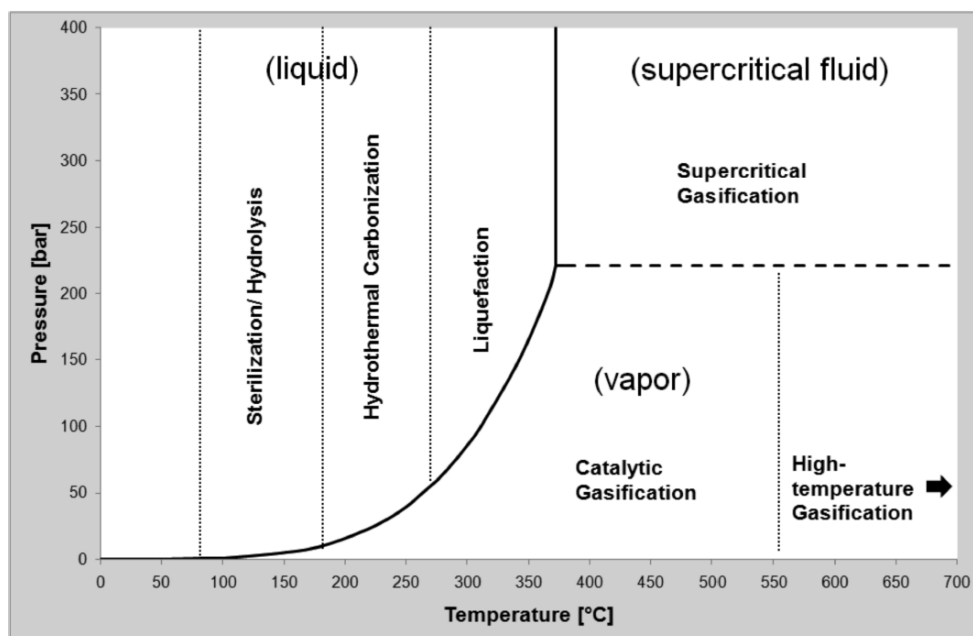


**Figure 2.5:** HTL Process diagram(Kersten et al. 2014).

Hydrothermal liquefaction has already been studied and operated at pilot scale for wet biomass. This is typically operated at pressures of 100-300 bar, in which case water is used as a solvent and reaction medium (Kersten et al. 2014). This process occurs at temperatures of 250-400°C to convert the feedstock into a liquid product. There are also instances where other solvents have been used for this reaction this is known as solvolysis. According to (Kersten et al. 2014), the process of hydrothermal liquefaction and solvolysis starts with the primary pyrolysis reaction. However, the main difference is that the reaction products are not being exposed to a vapor/gas phase such as in pyrolysis. The reaction instead occurs inside and outside of the particles, it is also not clear whether the solvent is part of the primary decomposition reaction. The other main reactions and transformations that occur during hydrothermal liquefaction of biomass include hydrolysis, dehydration, decarboxylation, hydrogenation, condensation and polymerization. This could be similar in the breakdown of plastics such as polystyrene.

Figure 2.5 depicts a description of HTL process for plastics inspired by (Kersten et al. 2014). The process begins with waste plastics entering the pre-treatment. This could mean several processes such as separation, drying, cleaning, washing, melting and/or pelletizing. Afterward, it is heated to the desired temperature for the reaction. It then enters the reactor with solvent and/or catalyst to aid in the process. After a certain time, the solids from the reaction are recovered. Some of these could be used to aid in heat generation while the rest such as char and ash is discarded or used for other processes. Afterwards there is a liquid recovery system where the oil product could be collected while the rest of the solvents are recycled back into the reactor. The final step is the gas recovery, HTL of PS has shown to produce small amounts of gas (<5 wt%) as seen in Passos et al. 2020. The gas phase typically contains some amount of CO or H<sub>2</sub> could be used to heat up the reactor further. The oil is the desired product of this reaction and it could be further purified.

### Sub- and Supercritical HTL



**Figure 2.6:** Application fields of hydrothermal processes - water properties from Kieseler et al. 2013, based on data from Wagner et al. 2002.

In solvolysis/hydrothermal liquefaction, the solvent becomes super heated and can reach the sub- and supercritical states which causes the cleaving of the polymer bonds. Supercritical point of water is reached at approximately  $>374\text{ }^{\circ}\text{C}$  and  $>23\text{ MPa}$  (Laredo et al. 2023), as seen in the figure 2.6, where all the three lines join. From this, we can also see approximately where the other reaction conditions occur, such as for gasification and hydrothermal carbonization. In the case of polystyrene recycling, there has been research into ethanolysis (using ethanol as solvent) (Ahmad et al. 2020). This has been shown, to reduce the reaction temperature when compared with water. However, this process showed more alkanes as products, which would be utilized as fuels. Similarly, solvolysis of PS has been done using n-hexane (Hwang, Choi, et al. 2001), acetone (Hwang, Kim, et al. 1999), and toluene (Saha et al. 2022).

#### State-of-Art of HTL of PS

There has been a small amount of research on the process of hydrothermal liquefaction of polystyrene. Although such studies are limited, they are available, as seen in Figure 2.1, the most popular research has been from Passos et al. 2020 and Seshasayee et al. 2020. Research by Seshasayee et al. 2020 has been particularly successful, producing greater than 90 % conversion. Most of this reaction occurs at pressures above 25 MPa and temperatures above  $350\text{ }^{\circ}\text{C}$ . With relatively high oil yields especially when the reaction is set at  $350\text{ }^{\circ}\text{C}$ . Another research into the breakdown of polystyrene has been done by Passos et al. 2020. However, the method used in this process achieved very little conversion compared to the one from Seshasayee et al. 2020. This could just be because of the short reaction time. This would mean that for a breakdown of PS to occur a temperature of  $350\text{ }^{\circ}\text{C}$  and reaction time of 30 minutes will have to occur. Other than that, the reaction in Seshasayee et al. 2020 at  $350\text{ }^{\circ}\text{C}$  achieved a theoretical higher heating value of 40-45 MJ/kg, which is comparable to fuels such as gasoline.

Based on the paper Rossi 2023 the Technology Readiness Level (TRL) of HTL has reached a scale of 8. There has been an increase in the number of commercial HTL plants and several companies have demonstrated the technology at scale. There are approximately 23,000 ton/annnum of production capacity for HTL biocrude production. Fast Pyrolysis Bio-Oil (FPBO), this value has a production which has exceeded 200,000 metric tons with a TRL of 9 for a few years (Rossi 2023). However, this is only for biomass recycling. The process of thermochemical recycling plastic is slightly different. Plastic recycling via HTL is currently still in its R&D stage, there are however companies such Licella (Licella 2024), which has

been able to perform advanced Cat-HTR. Similar to this thesis, Licella believes that compared to pyrolysis and gasification technologies, HTL can be more efficient by creating more oil with less energy.

<i>Polystyrene Type and References</i>	<i>Pressure (MPa)</i>	<i>Temperature (C)</i>	<i>Reaction Time (min)</i>	<i>Conversion (%)</i>	<i>Products (wt%)</i>		
					<i>Gas</i>	<i>Liquid</i>	<i>Solid</i>
<b>PS (Seshasayee et al. 2020)</b>	25	350	30	99	1	87	1
	25	350	60	98.5	1	82.5	1.5
	25	400	30	99.5	1	56.5	0.5
	25	400	60	99	0.5	52.5	1
	25	425	30	99.7	1	48.7	0.3
	25	425	60	100	2	46	0
	25	450	30	98	1	37	2
	25	450	60	93	1	30	7
<b>PS (Passos et al. 2020)</b>	-	350	20	21.1	2.6	4.3	72.2
	-	350	20	0	3.4	4.7	94

<i>Polystyrene Type and References</i>	<i>Pressure (MPa)</i>	<i>Temperature (C)</i>	<i>Time (min)</i>	<i>Conversion (%)</i>	<i>Specified Products (wt%)</i>		
					<i>Toluene</i>	<i>Ethyl benzene</i>	<i>Other</i>
<b>HIPS (Kwak et al. 2006)</b>		370	5	80			
	24-32	380	15	100	25	17	58
	24-32	390	3	100	23	13	64
<b>PS (Bai et al. 2019)</b>	30	490	10	77	14	51.3	11.7

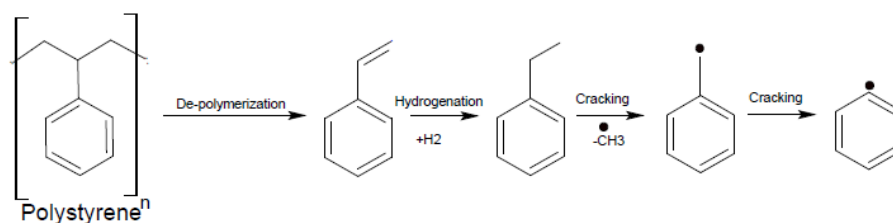
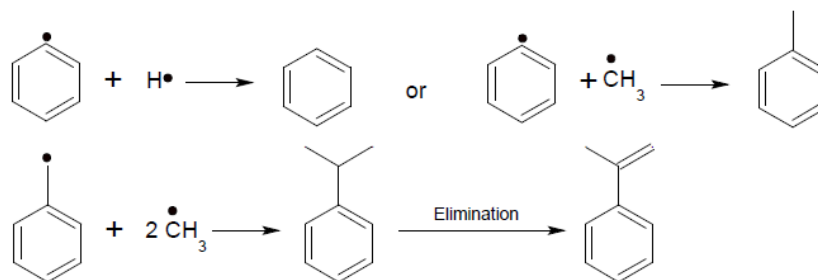
**Table 2.1:** Reaction conditions and product yields from HTL

Table 2.1 shows two more research works into hydrothermal liquefaction of polystyrene. An example of supercritical HTL process can be seen in Kwak et al. 2006 where HTL temperatures vary around 370°C for around 5-15 minutes providing crude oil yields higher than 80%. GCMS of the products were also done and it was found to contain relatively large amounts of toluene and ethyl benzene. In the paper Bai et al. 2019, it can be seen that the process has a high selectivity for ethyl benzene, however these reaction conditions are much harder to achieve than the previous ones.

Figure 2.7 shows the degradation mechanism of PS in subcritical water based on the diagram provided in Zhao et al. 2019. As described in this paper Zhao et al. 2019, polymer decomposition typically involves chain initiation, free radical reaction, and termination reactions. The reaction typically begins with a polystyrene C-C chain breaking apart into radicals in the presence of heat. As seen in Figure 2.7, these radicals can form different products such as styrene and/or ethyl benzene. The breakdown of polystyrene also promotes the release of methyl, benzyl, and phenyl radicals. These radicals will inevitably collide in random with each other forming variety of products such as toluene, cumene, benzene and other aromatic compounds.

## 2.3. Screening Campaign

In order to undertake research on such an innovative subject, it is important to initiate a screening campaign for breaking down polystyrene via HTL. This can be conducted by looking through existing literature. Fortunately there have been demonstration on research into catalyst that has been used for thermochemical conversion of biomass (Mamilla et al. 2019) and other plastics (Marquez et al. 2023).

**Hydrothermal cracking reaction:****Possible free radical reactions:**

**Figure 2.7:** Hydrothermal cracking reaction as described in Zhao et al. 2019.

### 2.3.1. Catalyst for Polystyrene

There has not been any research on catalytic hydrothermal liquefaction of polystyrene. However, upon closer examination of the structure of biomass products, particularly lignin and cellulose, one can see that they have a resemblance to plastic polymers. They are long repeating units mostly made out of carbon-to-carbon bonds. Of course, plastics are purely made of carbon bonds which are much more stable, making it especially difficult to break down. As previously discussed, polystyrene is notoriously challenging to degrade. However, there have been instances where successful breakdown has been achieved, such as in the previous section. Despite such advancements, it remains essential to find more sustainable and efficient methods for dealing with polystyrene waste to address the broader environmental concerns associated with its persistent presence in the environment.

A catalyst that could be explored is in the form of deep eutectic solvents (DES), which are solvents that have been used for pre-treatment and dissolution of biomass. The hypothesis is that these catalysts could work in breaking down plastics like how they break down biomass. Mamilla et al. 2019 has shown that some DES could be used to breakdown biomass into oil for lignin. This deep eutectic solvent is known as KOH:ChCl from Yahaya Alhassan 2016. However, this catalyst can only be reacted at a lower temperature of  $250^\circ\text{C}$ , which is significantly lower than the temperature needed to breakdown PS of  $350^\circ\text{C}$  as described in Kijeński et al. 2005.

The conditions needed for plastic breakdown usually require extreme conditions, so in order to reduce the reaction conditions and decrease the activation energy of the reaction a catalyst will have to be used. Marquez et al. 2023 describes the process of pyrolysis, wherein polystyrene is subjected to high heat and catalysis, resulting in its decomposition. This breakthrough reveals that under specific conditions, polystyrene can be broken down solely through the application of heat and catalytic reactions.

The HTL process undergoes a thermochemical transformation similar to that of pyrolysis; therefore, a catalyst used for pyrolysis may be applicable for HTL as well. Marquez et al. 2023 describes polystyrene breakdown via pyrolysis using heterogeneous acid catalysts. Figure 2.9 describes the various ways in which polystyrene is broken down thermochemical in the presence of  $\text{Brønsted}$  acid catalyst.

### 2.3.2. Acid vs Basic catalyst

As previously mentioned in Zhao et al. 2019, the thermochemical reaction of PS involves the initiation, propagation, and termination of polymer chains. In this process, the reaction commences with the formation of carbonation from  $\beta$ -scission—a mechanism that occurs during thermal cracking and leads to the generation

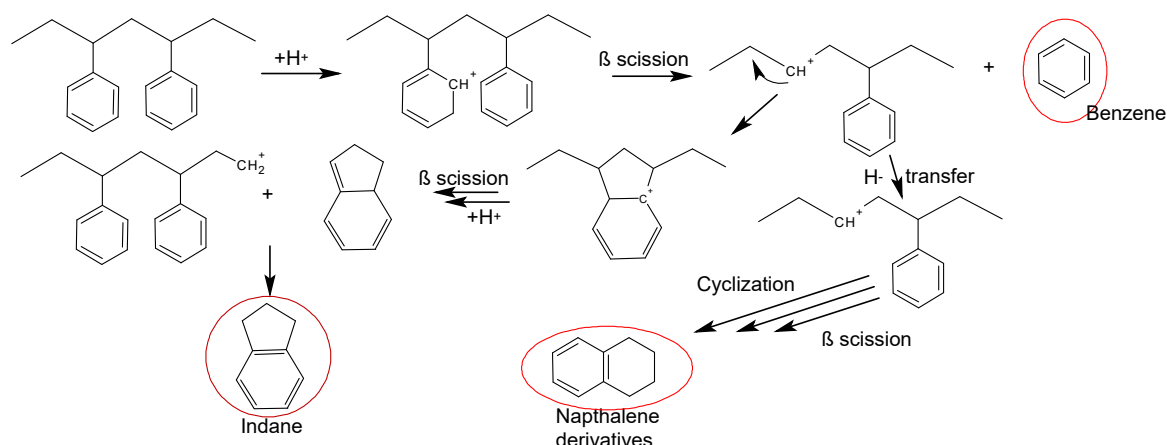
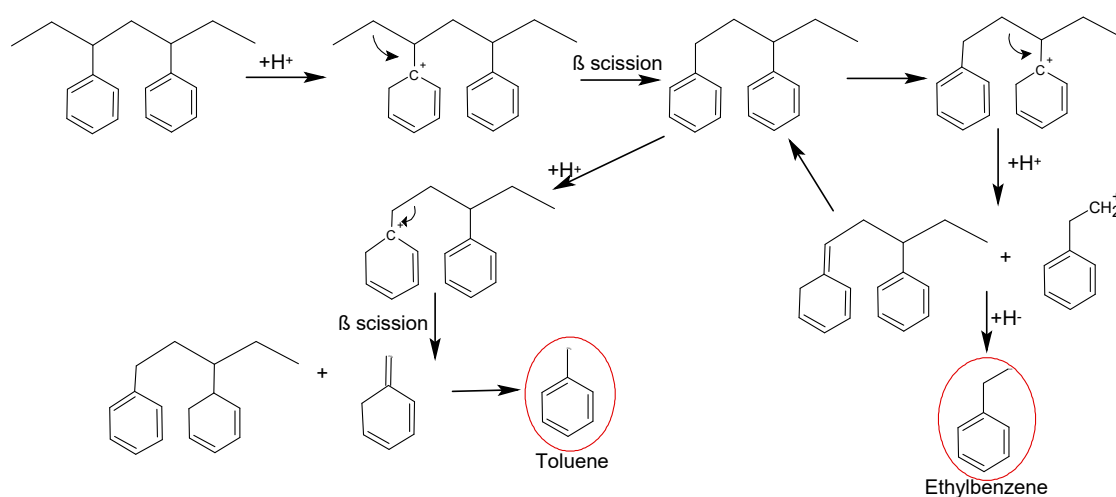
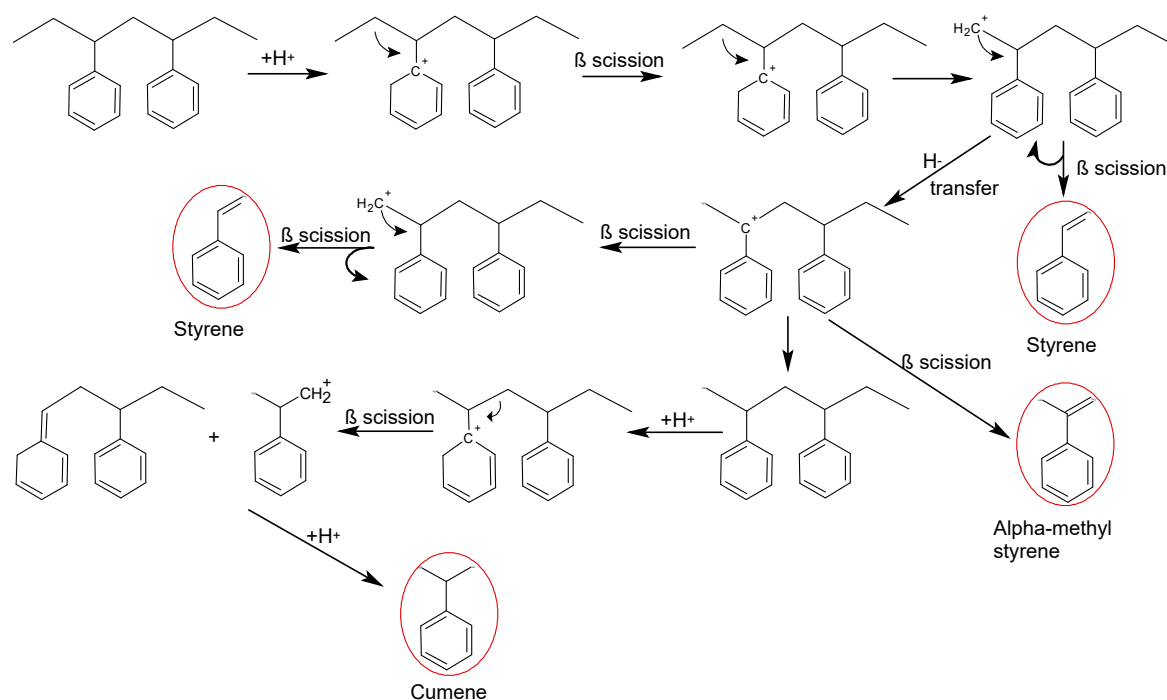
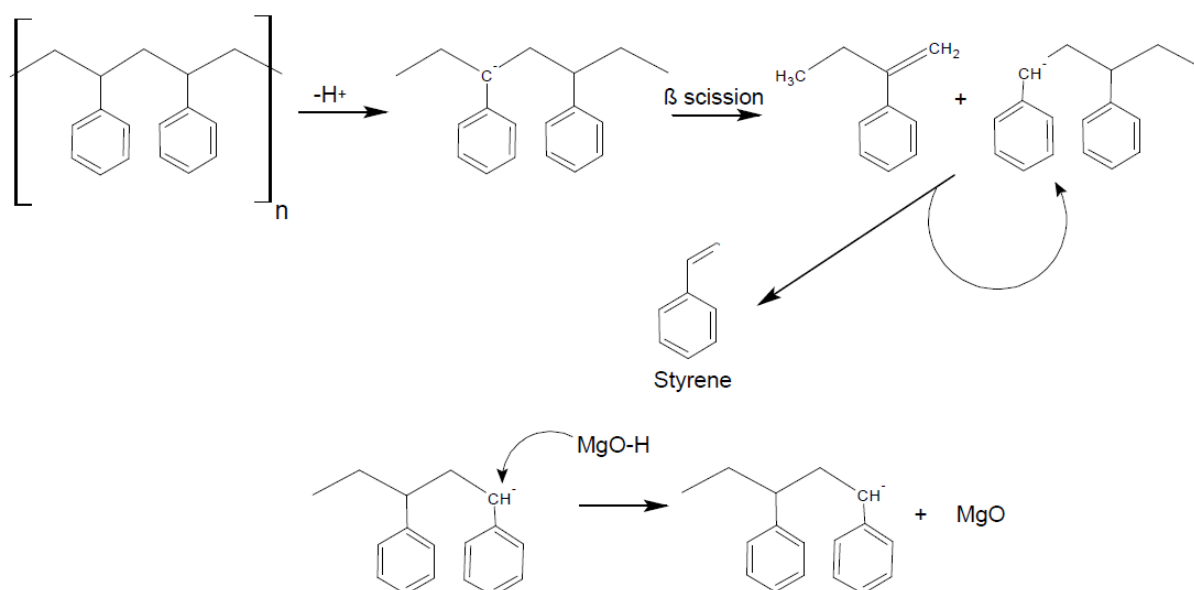
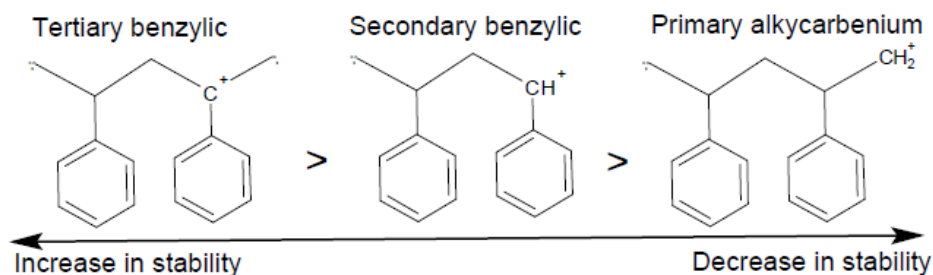
**Indane and Napthalene formation:****Toluene and Ethylbenzene formation:****Styrene, Alpha-methyl styrene and cumene formation:**

Figure 2.8: Thermochemical breakdown in the presence of Brønsted acid catalyst Marquez et al. 2023.

### Conversion of PS in the presence of a basic catalyst:



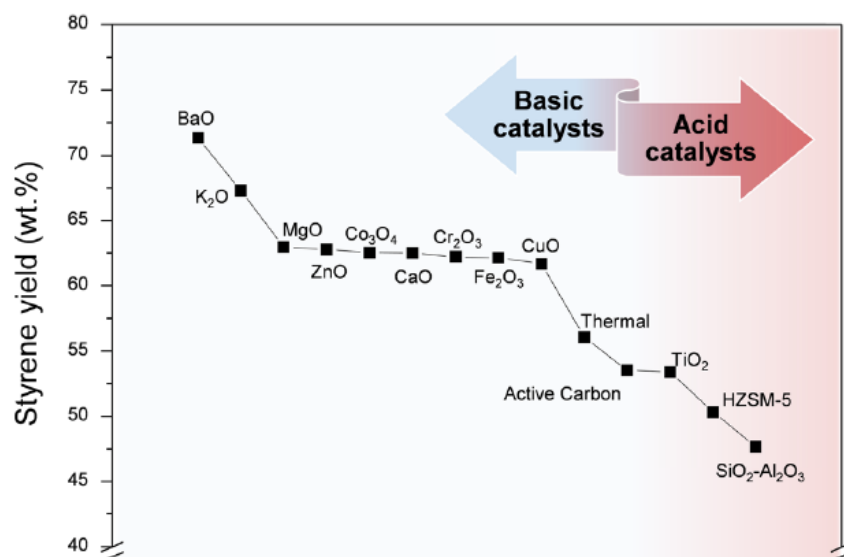
**Figure 2.9:** Thermochemical breakdown of PS in the presence of a heterogeneous basic catalyst during pyrolysis Marquez et al. 2023.



**Figure 2.10:** Stability of carbocations formed in the thermochemical breakdown of polystyrene Marquez et al. 2023.

of highly reactive, short-lived free radicals. These radicals produce different cations, either a primary alkylcarbenium secondary or tertiary benzylic carbocation as seen in Figure 2.10. Because of the possibility of breaking down PS via an acid catalyst, ZSM-5 was used to also test its viability in the screening campaign. ZSM-5 is a type of zeolite with a crystalline, microporous aluminosilicate material. It is known for its strong Brønsted acid properties. These acid sites are highly active in a variety of acid-catalyzed reactions, such as hydrocarbon cracking, isomerization, and the synthesis of fine chemicals (Roach et al. 2012).

To give an overview of how the different products of thermochemical breakdown of PS can be formed Figure 2.8 is shown. From the styrene formation part of the figure, styrene could be produced after other side reactions and rearrangement of carbonation occurs. However, some styrene will constantly re-polymerize with the main branch. This is where the catalyst could help stabilize this reaction, the basic catalyst helps stabilize the carbonation of polystyrene and prevent the re-polymerization of styrene as seen in Figure 2.9, Which would lead to an increase in styrene selectivity.



**Figure 2.11:** Graph of styrene yield using various catalyst with in pyrolysis process (Marquez et al. 2023).

Figure 2.11 shows the trend in various basic catalysts used for the thermochemical breakdown of polystyrene at 350°C. In this process, it could be seen that there is a 72% yield of styrene when BaO was used as a catalyst. Upon reviewing figure 2.9, KO seems like a viable candidate to test for screening. However, KO also cannot be bought directly from Sigma Alrich, it will have to be synthesized in the lab. Due to limited time during the thesis KO was not to be screened. The catalyst that was chosen for screening was BaO and MgO. The difference in using basic and acidic catalysts lies in their mechanisms of action and product selectivity, with basic catalysts favoring the production of styrene as the major product and showing potential for more environmentally friendly PS recycling compared to acid-catalyzed degradation Marquez et al. 2023.

## Materials and Methods

### 3.1. Catalyst screening

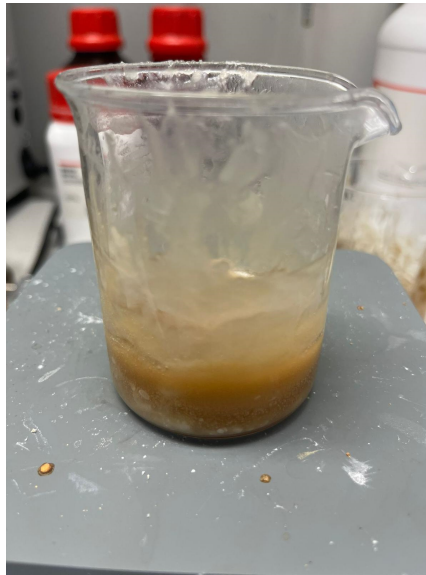
The catalysts screened were defined based on a thorough literature review that includes previous experimental research on pyrolysis and HTL of PS in Kwak et al. 2006, Savage 1999, Marquez et al. 2023. Catalysts are used in HTL to improve the rate of reaction and reduce operational conditions (e.g., temperature(°C) and pressure(bar)), this is because catalyst offer a lower energy pathway for the reaction to occur. From research in pyrolysis, it was found that alkaline earth metal oxide favors the production of the styrene monomer (Marquez et al. 2023). Based on Marquez et al. 2023 findings and the commercial availability of catalysts, magnesium (MgO) and barium oxide (BaO) were chosen. Since these papers are based on pyrolysis, acidic catalyst was also explored in this research. For a more acidic condition, ZSM-5 was chosen. The acid sites in ZSM-5 are highly active, which can help increase the amount of styrene in the product and keep it relatively stable (preventing it to react and form polymers) (Kijeński et al. 2005).

Another catalyst/solvent that was examined was a deep eutectic solvent (DES). This catalyst was chosen because Mamilla et al. 2019 shown that DES could be used as solvent for the breakdown of lignin. This catalyst was the only catalyst prepared at the chemical lab of the P&E. DES was prepared using choline chloride (ChCl) and potassium hydroxide (KOH) with a 1:2 ratio based on previous findings reported by (Mamilla et al. 2019, Yahaya Alhassan 2016). The mixing of these two compounds was carried out at 80°C for 1-2 h. A dark brown liquid/gel was formed and left to cool down as seen in Figure 3.1. However, this catalyst can only be reacted at a lower temperature (250 °C) than compared to the other catalyst. At temperatures above this, the KOH:ChCl will start to break apart their DES structure (Mamilla et al. 2019). This will cause the choline structure could deteriorate and releasing the chlorine.

### 3.2. Design of Experiments: Central Composite Design

Design of Experiments (DOE) is a systematic and structured approach to planning, conducting, and then analyzing experiments (ASQ.Org 2024). DOE helps find the best combination of factors or process variables to achieve a desired outcome. It is widely used in various fields, including science, engineering, manufacturing, and quality control, to efficiently gather information and make informed decisions. Followed by resource efficiency, DOE allows researchers to obtain meaningful results with a minimum number of experimental runs or tests, saving time and resources Zhu et al. 2018. Then finally for robustness testing, this helps determine how sensitive a system or process is to variations in factors, allowing for the identification of potential weaknesses or vulnerabilities.

The Central Composite Design (CCD) is a commonly employed method within Response Surface Methodology (RSM) which is a subset of DOE. This design incorporates a pattern that combines factors or fractional factors along with central points, and it also introduces an additional set of "star points" to allow for the assessment of curvature. In the context of this study, a 3-factor design was selected, involving temperature, residence time, and catalyst loading, with the aim of maximizing the yield of PS-Crude oil (Zhu et al. 2018). The CCD cube produced a model with 17 experimental points with random order and combinations of 3 factors, as shown in table 3.1. The equation produced from the correlations using Design Expert will be similar to 3.1.



**Figure 3.1:** DES of KOH:ChCl.

$$Y = a_0 + \sum_{i=1}^3 a_i X_i + \sum_{i=1}^3 a_{ii} X_i^2 + \sum_{i=1}^3 \sum_{i < j}^3 a_{ij} X_i X_j \quad (3.1)$$

Where:

Y: Predicted PS Crude oil yield

$X_1, X_2, X_3$ : Temperature, Residence time and Catalyst loading

$\alpha_0$  : Intercept

$\alpha_i, \alpha_j, \alpha_{i,j}$  : Coefficients of linear, quadratic terms

Factors	Levels		
	-1	0	1
Temperature (°C)	330	340	350
Residence time (min)	30	45	60
Catalyst loading (wt%)	0	7.5	15

**Table 3.1:** Levels of each factor for optimization

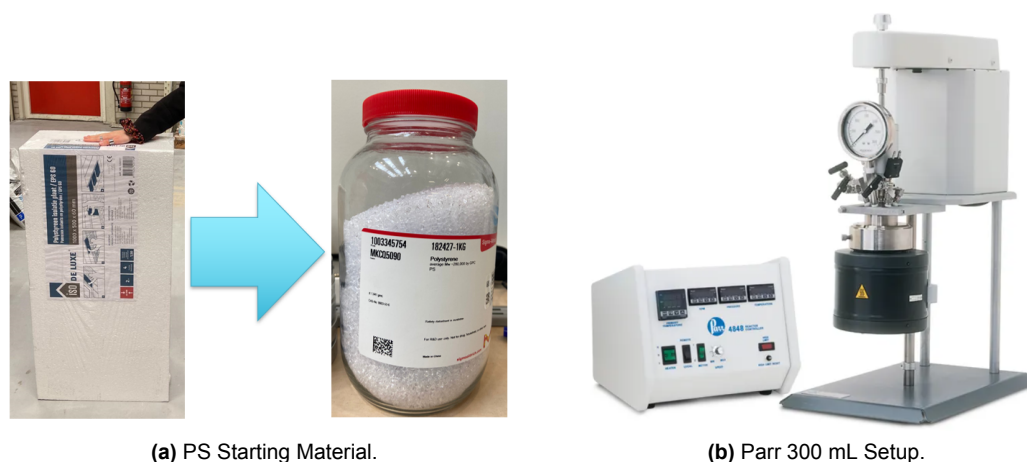
### 3.3. Hydrothermal Liquefaction Procedure

#### 3.3.1. PS samples

Figure 3.2, shows the feedstock material that was used for HTL. At first, the feedstock was intended to be commercially expanded polystyrene (EPS), that was used in construction. However, it was difficult to compress this material. There was also an attempt to first dissolve the EPS in acetone, however it was difficult to remove the acetone after dissolving the compounds. Due to its low density of EPS and small volume of the reactor (300mL), PS beads were acquired from Sigma-Aldrich with an average molecular weight ( $M_w$  of 280,000 g/mol. This will serve as the starting feedstock for PS.

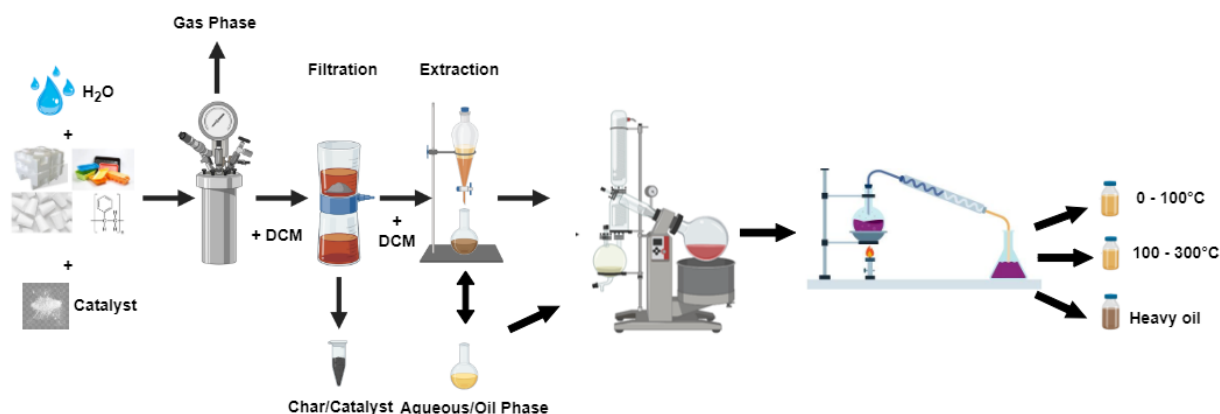
#### 3.3.2. Slurry preparation

Figure 3.3 shows the experimental procedure from slurry preparation to oil distillation. The first step in starting the experiment is to create a slurry with PS, water, and catalyst. The reactor used is a 300 mL



**Figure 3.2:** Starting material(a) and Parr Setup (b) (Company 2024)

autoclave reactor (Parr Instrument Company, Series 4560) with a stirrer as seen in Figure 3.2. In order to ensure safety in the operation of the reactor, the Maximum Allowable Water Loading (MAWL) was calculated. This is based on the instruction manual from Parr, which indicates that 80 % of the MAWL should be used as the total mass of the slurry for the maximum operational temperature that is defined in our design. Thus, each experimental run was performed with a total slurry mass of approximately 123.7 g. The PS/water ratio was set at 15 %wt. Milli-Q water was used as a solvent and is used as the remaining 85 %wt of total slurry. For the catalytic experiments, the loading of the catalyst varied between 0-15 %wt on a dry biomass basis. For the screening campaign the catalyst loading was kept at 5%wt.



**Figure 3.3:** Schematic HTL experimental procedure.

### 3.3.3. HTL experimental run

Most existing research on HTL takes place in super- and sub-critical phase of water. This is around 330-400 °C and pressures ranging from 15-22 MPa as seen in Kwak et al. 2006 and Savage 1999. We are however limited by the autoclave reactor, which can only reach a maximum of 350 °C.

For the screening campaign a temperature of 340 °C and residence time of 30 minutes was selected. Meanwhile, the CCD campaign occurs at temperatures varying from 330-350°C with a retention time of 15-60 minutes. To start the experiment, each run the autoclave was purged with nitrogen to create an inert environment. Then, the reactor controller was programmed with the operational temperature and 150 RPM stirring speed using the SpecView® software. Because the reactor is well sealed, the reaction pressure reaches climbs to around 100-160 bar, this depends based on the phase of water at these temperatures. The reactor was cooled when the reaction was finished. First, by using a hot water bath, then followed by

Compound	Boiling Points (°C)
Benzene	80.1
Toluene	110.6
Ethylbenzene	136
Styrene	145
Alpha-methylstyrene	166

**Table 3.2:** Boiling points of desired compounds at atmospheric pressure (approx.1 bar) Pubchem 2022.

an ice bath. The majority of experimental runs almost never yield significant amount of gaseous byproducts, so most of the gases were released into the fume hood and not collected. The slurry was then poured into a beaker, and extracted from the reaction by dissolving the mixture with Dichloromethane (DCM).

### 3.3.4. Collection phase

After completing the experimental run, two distinct phases could be observed: one was a liquid phase, and the other was solid. There were also some solid residue and oil stuck on the walls of the reactor and stirrer. These were then rinsed and dissolved in Dichloromethane (DCM). Most of the solids were dissolved by the DCM. Vacuum filtration was then done using a filter paper grade 3 and Büchner funnel attached to pump. The aqueous phase is first filtered followed by the oil/DCM phase. Some more DCM was used to so that the oil can go through the filter. This will result in catalyst and char remaining in the filter paper. This filter paper was then put on the crucible, and dried in the oven at 105°C for 24 hours. To recover the maximum amount of PS-Crude oil present in the aqueous phase (Aq.Phase), liquid-liquid extraction was conducted in a separatory funnel with the addition of DCM to aid in separation. Finally, DCM and water were removed from the oily and AP phases, respectively, using a rotary evaporator, resulting in the separation of oil crude and polar organic compounds, thus closing the total mass balance.

### 3.3.5. Simple distillation

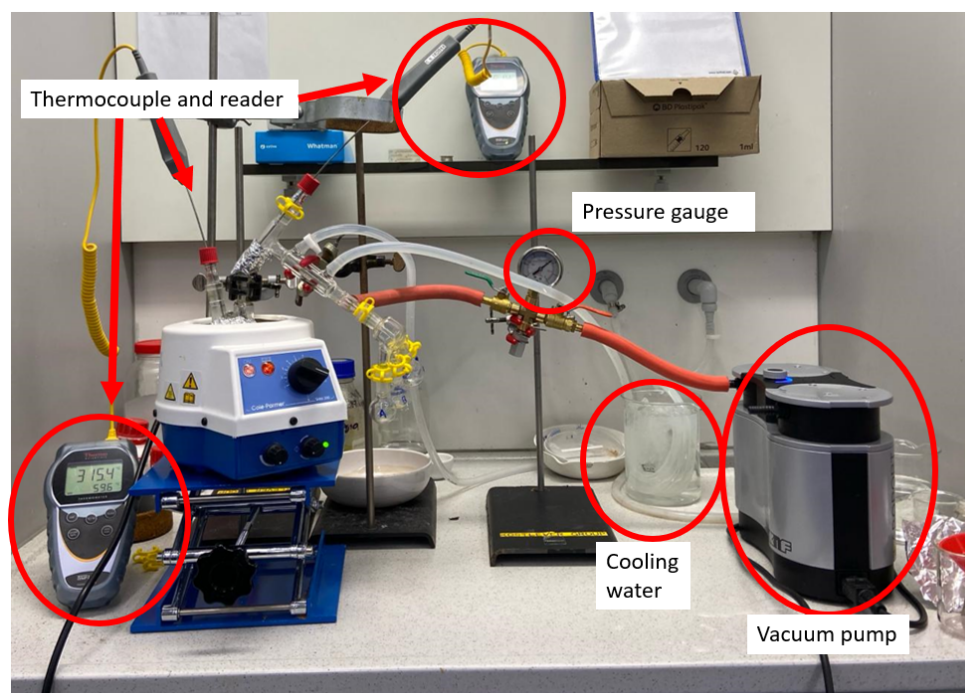
Separating the PS-crude oil into its fractions, was accomplished by simple distillation. The PS-crude oil is a complex mixture containing monomeric compounds, high value chemicals (HVCs) with lower boiling points as well as heavier fractions with higher boiling points. The boiling points of the desired products are seen in 3.2. Based on these desired boiling points, it was decided that the distillation should occur in steps of 0-100°C, 100-200°C and 200-300°C. Furthermore, the heavier fractions in the PS-crude oil makes it difficult to resolve in GCMS-FID and (GCxGC-FID). The PS-crude oils from the screening and CCD campaign were purified using a small-scale simple distillation column as shown in Figure 3.4. Simple distillation procedure was adapted from ASTM D86 method ASTM D86 2024.

## 3.4. Feedstock and product characterization

PS-Crude oil and aqueous phase were characterized in order to gain more in-depth information about the performance of the HTL experiments. The methods that were performed are described in the following sections.

### 3.4.1. HHV - Bomb Calorimetry

The oil produced from the experiments was loaded into the HHV-Bomb Calorimetry to find the oils Higher Heating Value (HHV). The HHV was measured using an adiabatic oxygen bomb calorimeter Model 1341 in accordance with ASTM standard D2015-00. The experiment starts with a small amount of cotton with a known calorific value immersed in 0.5 g of oil. The bomb was then loaded with 26 bar(g) of oxygen, and after ignition, the sample underwent combustion. The resulting HHV value was displayed on the screen bomb calorimeter controller and corrected by subtracting the HHV of the cotton from the value determined by the bomb calorimeter.



**Figure 3.4:** Shortpass distillation setup, equipped with vacuum.

### 3.4.2. Proximate and Ultimate Analysis

The ultimate analysis provides details regarding the composition of the primary elements in the sample, namely carbon, hydrogen, nitrogen, oxygen, and sulfur (CHNOS). This was done using the ASTM D5291 method by Intertek Belgium N.V. There was no need to screen for sulfur in polystyrene because it is a hydrocarbon based polymer; only CHNO was evaluated.

### 3.4.3. GCMS-FID and GCxGC-FID

Instrument	GC-MS/FID	GCxGC-FID
<b>Columns</b>	HP-5ms UI (30 m × 0.25 mm × 0.25 μm) to FID: Deactivated (1.43 m × 0.15 mm) to MS: Deactivated (0.53 m × 0.15 mm)	Rxi-17SilMS (30 m × 0.25mm × 0.25 μm) DB-1 HT (1 m × 0.25 mm × 0.10 μm) Deactivated (0.38 m × 0.25 mm)
<b>Injection</b>	Split/Splitless, 0.2 μl, 200:1, 280 °C	Split/Splitless, 0.1 μl, 200:1, 285 °C
<b>Carrier Gas</b>	UHP He, Split Flow of 240 mL/min 35 °C (hold 3 min)	UHP He, 1.5 mL/min 40 °C (hold 1.5 min)
<b>Oven Program</b>	35-325 °C, ramp rate 10 °C/min 325 °C	40-320 °C, ramp rate 4 °C/min 320 °C (hold 1 min)
<b>Offsets</b>	-	Secondary oven: 35 °C Modulator: 20 °C
<b>Modulation</b>	-	1,7 s, hot pulse 0.28 s
<b>FID</b>	200 MHz, 300 °C	300 °C, 200 HZ
<b>El Source</b>	70 eV, 230 °C	-
<b>MS Quad Detector</b>	2.7 scans/s, 30-300 m/z, 150 °C	-

**Table 3.3:** GC-MSFID and GCxGC-FID method and setting

The distillates of PS-Crude oil fractions from distillations were analyzed through as chromatography with flame-ionization detection (GC-FID), utilizing a Shimadzu GC-2010 gas chromatography system equipped

with both an autosampler and a flame ionization detector (FID). The fractions were also analyzed via the LECO QuadJet SD comprehensive two-dimensional gas chromatography (GCxGC) system (LECO Corporation, St. Joseph, MI, USA) configured with cryogenic LN<sub>2</sub> cooling, an L-PAL3 GC autosampler, a flame ionization detector (FID), and Chroma TOF(Time of Flight) SD data processing software.

The PS-Crude oil distillate fractions underwent analysis via one-dimensional GC-MS/FID. The equipment used included an Agilent 8890 GC system linked to an Agilent 5977B MS, both from Agilent Technologies based in Santa Clara, CA. Agilent's GC-MS MassHunter software facilitated data capture and interpretation, functioning at a 200 MHz collection rate and achieving a signal-to-noise ratio of 50. The qualitative composition of the samples was determined using the NIST 2020 mass spectral library, and FID signals provided the basis for quantitative calculations.

For comprehensive two-dimensional gas chromatography with flame ionization detection (GCxGC-FID), the analysis was performed on a LECO QuadJet SD system, which included an FID, an L-PAL3 autosampler for the GC, and LECO's ChromaTOF SD software for data analysis, all from LECO Corporation in St. Joseph, MI. The classification and quantification of the sample components followed the procedure detailed in (Vozka et al. 2019).

The concentration of each component within the samples was measured in weight percentage (wt%) and spanned a carbon number spectrum from C<sub>5</sub> to C<sub>32</sub>. The array of hydrocarbons analyzed covered n-paraffins, isoparaffins, various cycloparaffins (including mono-, di-, and tri-cycloparaffins), and aromatic compounds, which encompassed alkylbenzenes, cycloaromatics, alkylnaphthalenes, and biphenyls. Due to the GCxGC-FID method's inability to differentiate olefins from cycloparaffins, these were combined into a single category termed "olefins+cycloparaffins" for the purposes of this analysis.

## Results and Discussion

### 4.1. Catalysts Screening campaign

This section presents the outcomes obtained from employing the four catalysts during the HTL process. Multiple characterization techniques were conducted to evaluate the impact of each catalyst on both the yield and quality of the PS-Crude oil. This comparative analysis helped identify the best catalyst by revealing which ones performed the best overall. In total 4 catalyst were screened to breakdown PS in the HTL process: MgO, BaO, (Zeolite ZSM-5) and DES (KOH:ChCl).

#### 4.1.1. Product distribution of Screening campaign

Compared to the operational conditions described in previous research (Kwak et al. 2006), the initial experiment of the screening campaign was conducted at 300°C without any catalyst, to get a feel for the method and check the process's boundaries. Condition of 300°C has been shown to produce chlorine from PVC (Kwak et al. 2006). As seen in Figure 4.1, the polystyrene was partially broken down by the conditions in the reactor. However, with a very low PS-crude oil yield of 56%. The process also required a large amount of DCM to dissolve the oil (approximately 150mL). Here the char could also be observed as black solid on the filter paper. From this initial experiment, it was found that PS dissolves very well in DCM, to the point where it was difficult to evaporate DCM completely from PS.

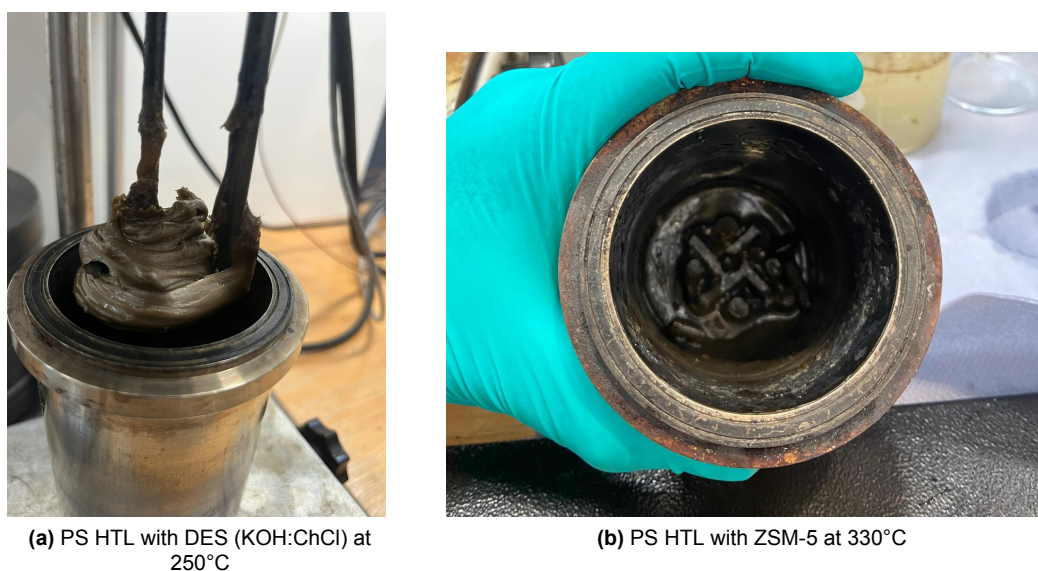


**Figure 4.1:** HTL of PS at 300°C, 45 minutes.

The second catalyst evaluated was the KOH:ChCl a DES. Due to the properties of this solvent, the operational conditions were set at 250°C for 30 minutes. The KOH:ChCl DES was unable to depolymerize PS because the temperature did not reach the adequate activation energy. The DES was only able to melt PS and clump them near the stirrer as seen in Figure 4.2. The paper Marquez et al. 2023 mentioned all polymerizations have a critical temperature ( $T_C$ ), in most cases this referred to as the ceiling temperature, at which the equilibrium and the Gibbs free energy is ( $\Delta G_p$ ) is 0. The  $T_C$  for PS is at 310°C, 277°C in gaseous conditions and 397°C when melted. In the conditions of 300°C it was possible to break some of

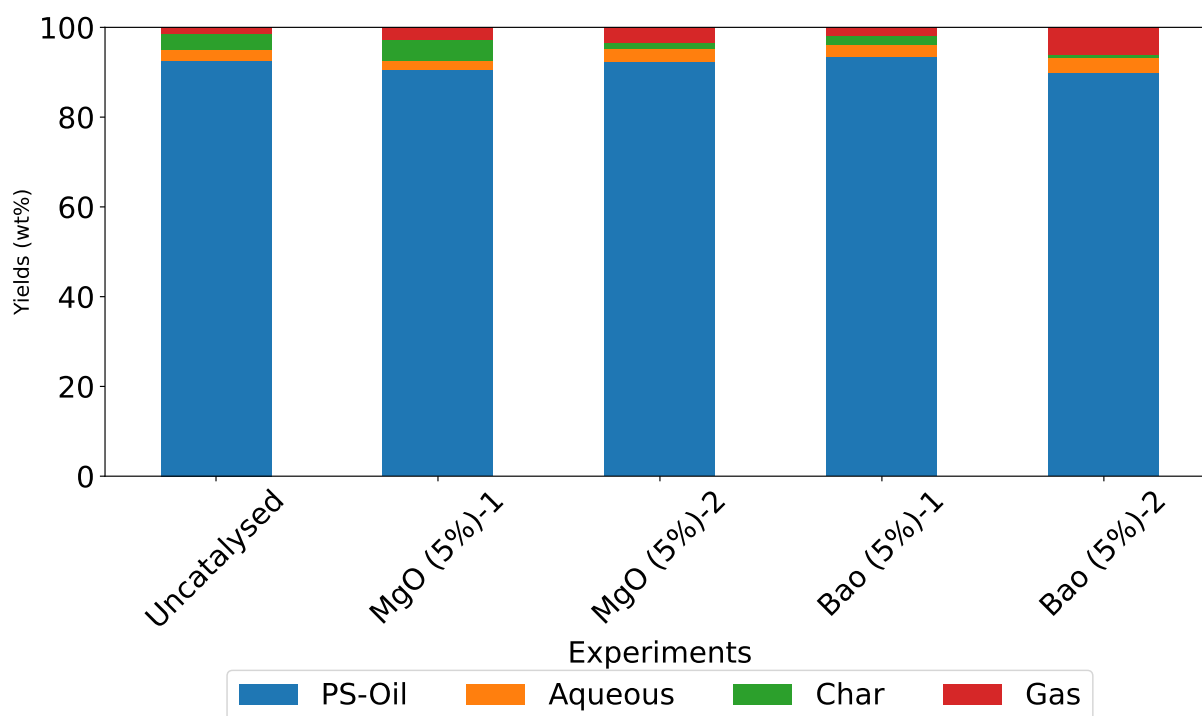
PS apart due to the residence time.

The zeolite ZSM-5 was the third catalyst to undergo HTL testing at 340°C and 30 minutes. However, the ZSM-5 was not effective in depolymerizing PS. The small PS pellets melted together and caused the stirrer of the reactor to become stuck. Some oil with an orange color was produced but not enough for analysis and so this sample was also discarded. Acidic catalyst seems to go through a different mechanism than the one described in Marquez et al. 2023, instead of depolymerizing the compounds, it could be that the catalyst actually re-polymerizes styrene back into polystyrene. The rest of the HTL tests including non-catalytic, MgO and BaO produced a significant amount of PS-crude oil after 30 minutes of residence time and at 340°C. Figure 4.3 shows the product distribution for the non-catalytic, MgO and BaO experiments.



**Figure 4.2:** Catalytic HTL of PS for DES and ZSM-5.

Figure 4.3 shows the product distributions of an uncatalysed HTL of PS as well as 2 runs each on with the catalyst MgO and BaO. MgO (5%)-1 represents the first run using this catalyst, while MgO(5%)-2 represents the second run of HTL. As can be seen from Figure 4.3, the best performing sample was the uncatalysed (93 wt%), followed by BaO (94 wt%) and MgO (91 wt%). The average oil yields for all the products are significantly high (>90 wt%) compared to previous HTL research using no catalyst. For example, Musivand et al. 2023 reports PS-crude oil yields between 34-83 %wt for experimental conditions ranging between 330-360 °C and residence times between 3-4h. Furthermore, Seshasayee et al. 2020, indicate that HTL at 350-450 °C and residence times between 30-60 min provide average PS-crude oil yields between 31-86 %wt. Seshasayee et al. 2020 achieved the highest PS-crude oil yield (86 %wt) at subcritical temperatures (350°C) and 60 min. In this sense, our results reduced the operational conditions by 10°C and 30 min to obtain in average higher yields than Seshasayee et al. 2020. Furthermore, our results support the hypothesis that high temperatures and prolonged residence times are not strictly required to initiate cracking processes in the PS backbone.



**Figure 4.3:** Product distribution for HTL of PS Uncatalysed, MgO(5%) and BaO(5%) at 340°C and 30 min.

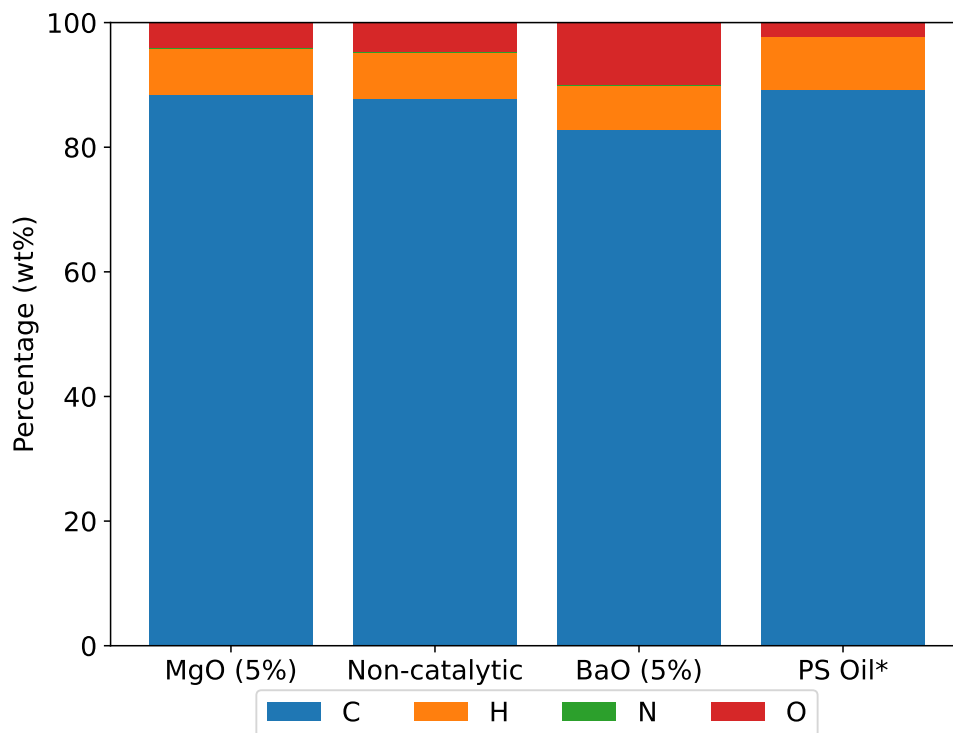
#### 4.1.2. Screening campaign PS-Crude oil characterization

Figure 4.4 shows the CHNO analysis of the different PS-Crude. The ultimate analysis is critical to understanding the chemical structure and properties of the PS-crude oil. For example, the carbon-to-hydrogen ratio might reflect the degree of saturation or unsaturation in the hydrocarbon chains, influencing the oil's reactivity and stability. Furthermore, it reveals the efficacy of the HTL process and any potential adverse effects or contaminants due to the process itself or presence of catalyst.

##### Ultimate (CHNO) analysis

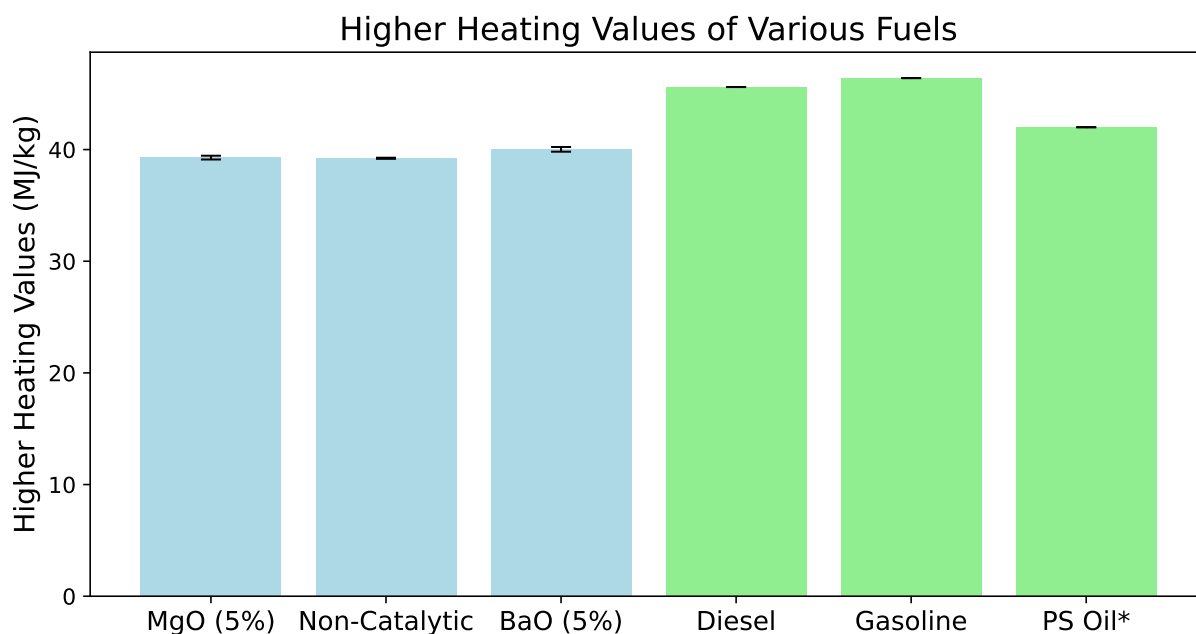
Since PS is a polymer composed of only hydrocarbons (consisting of carbon and hydrogen), it is expected that these will be the only components in the oil. The highest C content (88.4 wt%) was found in the MgO crude oil. This was then followed by the non-catalytic experiment with 87.8 wt%. The BaO crude oil was the one with the lowest amount of C content and with the highest (82.8 wt%) O content, twice the amount of oxygen compared to the other 2 samples. This could be due to BaO oxidized nature, the PS Crude oil becomes more oxygenated when compared to MgO and non-catalytic oils.

The PS-crude oils produced from the HTL process is comparable to the "PS oil" produced in Musivand et al. 2023 from HTL at 360°C and 3 hour retention time. The PS-oil reported by Musivand et al. 2023 contains C:89.3 wt%, H: 8.4 wt% and O: 2.3 wt%. Our PS-Crude oils have, on average, double the oxygen content of the ones produced from Musivand et al. 2023. This is attributed to the long residence times that allow for re-condensation reactions. Furthermore, our PS-crude oils are also comparable to the PS-oils reported by Seshasayee et al. 2020, which contain a C content in the range of 87.8-92.9 wt%, H content between 5.8-11.4 wt% and O content between 0.5-4.6 wt%. Nonetheless, this "PS oil" was produced at significantly higher temperatures, 350-450°C. This provides evidence that the PS-Crude oil produced by a low-temperature HTL is comparable in their elemental composition to other more energy-intensive HTL PS-Crude oils.



**Figure 4.4:** Ultimate analysis of PS Crude oil vs PS oil\* found in Musivand et al. 2023

**Bomb-calorimetry (High Heating Value (HHV))**



**Figure 4.5:** Average HHV results of non-catalytic, MgO and Bao PS-crude oils compared with Diesel, Gasoline and HIPS Musivand et al. 2023

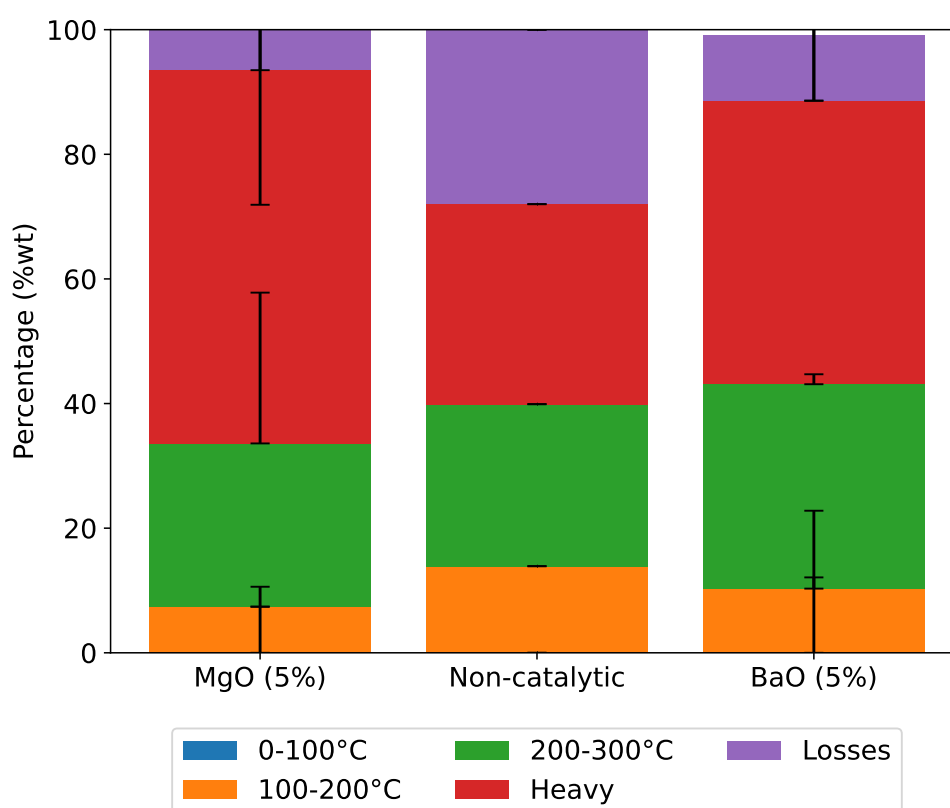
Figure 4.5 present the average HHV of PS-Crude produced from each experiment, non-catalytic, MgO and BaO. As can be seen from Figure 4.5, the HHVs of the PS-crude oils have high HHV values of 39-40 MJ/kg. This is still lower than then HHV of 42 MJ/kg that was produced Musivand et al. 2023, which could

be due to the higher oxygen content as seen in the Ultimate analysis 4.4. However, this HTL process was at 360°C and had a residence time of 3 h. The figure also shows that the PS oil produced slightly less energy than contained in fuels such as Diesel (45.60 MJ/kg) and Gasoline (46.40 MJ/kg) *values of various fuels - World Nuclear Association n.d.*

### Distillation of PS-crude oil

To quantify the amount of styrene and HVCs and determine the complexity of the PS-crude oils, a simple distillation of the PS-crude oils was carried out. The goal of this research is producing PS-crude oils with high quantities of styrene (boiling point = 145°C), ethylbenzene (boiling point = 136 °C), benzene (boiling point = 80 °C) and toluene (boiling point = 110 °C).

As can be seen from Figure 4.6, there is still a large amount of heavy oils with boiling points higher than 300°C for all samples. The non-catalytic experiment has the highest amount of heavy oil compared to MgO and BaO. In this sense, both catalysts show a positive effect in producing a larger amount of compounds (>40 wt%) in the 100-300°C boiling point ranges. It is important to note that there was still a large amount of losses from light compounds, this are most likely lost in the glassware. To improve this, it was decided to use a short pass distillation to prevent the loss of heat and volume in the glassware.



**Figure 4.6:** Distillate fraction produced from simple distillation.

### GCMS-FID and GCxGC-FID of Screening campaign

The distillate samples were then sent for GC-FID and GCxGC-FID analysis. These analytical techniques were employed to provide extensive and detailed characterization of the HTL PS-crude oils. The results of the GCMS-FID analysis as seen in figure 4.7 showed that the fractions between 100-300°C contained large amounts styrene and ethylbenzene. The sample which contained the largest amount of styrene was found in the sample which was MgO-catalyzed. BaO-catalyzed reaction seems to produce the lowest quantity of styrene which was not expected when compared from the data found in Marquez et al. 2023. The resulting pyrolysis oil produced in here Marquez et al. 2023 also showed that basic catalyst such as BaO produced approx. 72% styrene yield while MgO produced 63% yield.

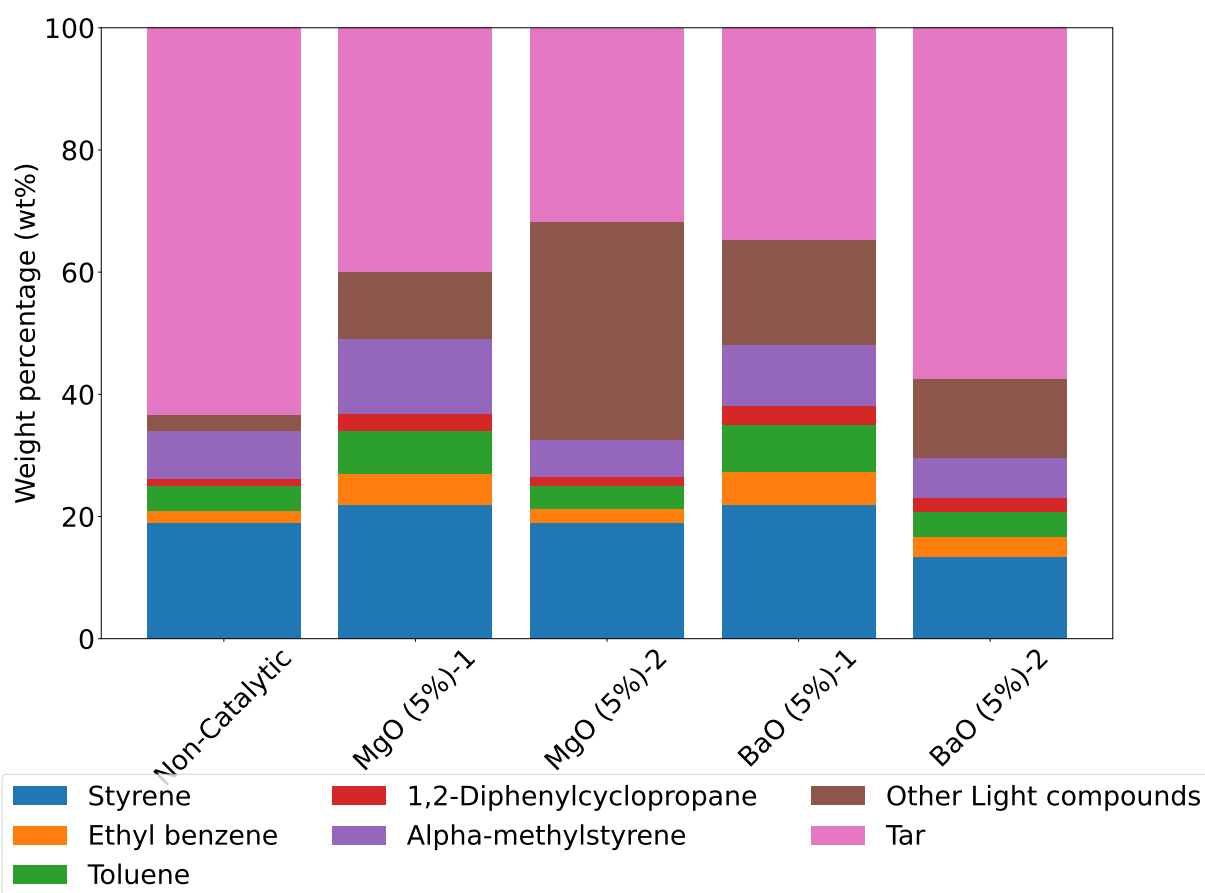
However, this is not the case in HTL, where we produced a maximum of 22wt% styrene in MgO(5%)-1, and BaO(5%)-1 in oil. And when we calculate for overall styrene yield, the maximum amount of styrene produced was 21wt%. BaO(5%)-1, produced the largest amount of styrene, however BaO(5%)-2 produced the least amount with an average of 12.08wt%. MgO(5%)-2 produced on average 17.5wt% of styrene.

HTL of PS also produced other HVCs such as ethylbenzene, which is a compound that could be used as chemicals for industries but it can also be dehydrogenated to produce more styrene. However, this only produced a maximum of 5.5 wt% of the oil in BaO(5%)-1. For alphamethyl-styrene the maximum amount produced was 12.2 wt% of oil in MgO(5%)-1.

It is also important to note that there is also a large number of light organic compounds present, these are compounds below 300°C. This results from the some species that are only present in 1-2 wt% in the oil, these seem to be similar to 1,2-Diphenylcyclopropane. These compounds are alkane chains with 3 or more benzene rings. There were also some losses that occurred during distillation, which were also classified as other light compounds since they were released from PS-Crude oil but were not captured.

Another important observation is the large amount of heavy compounds or tar present, these are the compounds leftover after distillation. This is a heavy black oil substance which is similar to wax, perhaps further analysis such as Gel Permeation Chromatography (GPC) would be needed to determine its molecular weight. Since MgO catalyzed HTL has produced a more consistent amount of HVCs than the BaO catalyzed HTL, it was decided that the catalytic HTL will be continued with MgO as the catalyst.

Because there were some amount of DCM present, this effected the data of CHNO analysis. Since the analysis was done for C, H and N. It was assumed that O would make up the rest of the oil, however DCM was also present in GCMS-TOF data in small amounts. A correction will have to be done to correct this data because some chlorine from the DCM is present.



**Figure 4.7:** Breakdown of PS-Crude oil based on GCxGC-FID and GCMS-FID data.

## 4.2. DOE-Optimization campaign

Based on what was learnt from the screening campaign, some improvements into the experimental procedures were made. Firstly, it was found that there were a large amount of losses of light compounds when the distillation was conducted. To reduce the losses in these compounds from the oils, it was decided that a smaller distillation column was needed. A short pass distillation was used which was much more appropriate to separate oils into fractions below 300°C. Styrene and other light oil components were also found in the 200-300°C fraction. So it was decided to distill all of the compounds slowly and collect them together. GCMS-TOF results also confirmed that there were some amounts of DCM which persisted in the oil, and that made it difficult to close the mass balance for all the reading. After the distillates were analyzed, it was decided to find an average percentage of DCM present and subtract it from the yield of the PS crude oil.

### 4.2.1. Product distribution of DOE campaign

Run	Temp (°C)	Residence Time (min)	Catalyst Loading (wt%)	Oil (wt%)	Aq (wt%)	Char (wt%)	Gas (wt%)
1	340	45	7.5	96.11	2.86	0.59	0.59
2	340	45	7.5	89.27	2.32	6.14	0.27
3	330	60	7.5	62.69	3.40	30.40	3.51
4	350	45	0	97.11	1.29	1.24	0.36
5	340	60	0	81.96	1.19	1.35	15.50
6	330	45	0	96.81	1.67	1.29	0.00
7	340	45	7.5	91.32	1.72	3.87	1.09
8	340	45	7.5	97.46	2.48	0.04	0.00
9	340	30	15	42.77	1.13	52.91	1.19
10	340	30	0	92.94	1.72	7.38	0.00
11	330	30	7.5	17.86	0.92	76.88	4.35
12	350	60	7.5	91.21	1.35	7.54	0.00
13	330	45	15	27.09	5.17	38.85	26.89
14	350	30	7.5	91.82	5.28	0.47	0.43
15	340	45	7.5	95.83	1.67	1.29	1.15
16	340	60	15	81.41	1.73	3.87	12.99
17	350	45	15	79.41	4.80	5.55	8.25

**Table 4.1:** Experimental matrix and results of the DOE using a CCD approach.

Table 4.1 presents the detailed DOE matrix used to obtain the surface response model for the CCD. 17 experiments were conducted to show the influence of temperature (°C), residence time (min) and catalyst(%) loading on the HTL process. This number of experiments was strategically calculated to include an adequate number of factorial runs, axial runs, and center runs as mentioned in 3.

Figure 4.9 shows the product distribution of the reactions which yielded PS-Crude oil, aqueous, char and gas products. The table 4.1 shows the experimental results of the DOE. As seen here, majority of the product contained large amounts of PS-Crude oil. The run which produced the most amount of oil is from Run 8, with 97.46 wt% yield. This is surprising compared the oil yield produced by PS HTL in Kwak et al. 2006 at 80 wt%. Run 8 had conditions of 340°C, 45 minutes and 7.5% catalyst, this surprising since large yields of oil is typically observed in temperatures above 370°C (Kwak et al. 2006). According to Bai et al. 2019, the most amount of liquefaction occurs at temperature of 490°C for a yield of 77 wt%. Bai et al. 2019 also mentioned that increasing the reaction pressure and prolonging the reaction time also promote plastic liquefaction reaction. This was also true when looking at HTL runs but there is a point where this

stops being the case. The results of the experimental runs also showed it is in line with Zhao et al. 2019, which reports yields of 81.4-97.6 wt%.

Run 11 in particular produced the lowest yield of oil because this occurred at the lowest temperature 330°C and reaction time of 30 minutes as well as 7.5% catalyst loading (seen in Figure 4.8). The large char yield is also due to the how the char product was classified. After some of HTL runs, a yellow/orange plastic product can be seen, this is typically when the reaction does not reach adequate conditions for PS to breakdown completely. Run number 6, which also occurred at 330°C and for a slightly longer time of 45 minutes but without any catalyst has a relatively high oil yield. It could also be an indication that the increasing catalyst loading into the reactor causes an inhibition in the reaction and reduces the amount of product produced at low temperatures. To try and find the optimum conditions for the experiment, it would be wise to look at the CCD results.

Upon examining the catalyst post-HTL runs, as seen in Figure 4.8, it appeared largely unchanged from its original state at the beginning of the experiments. This could indicate that the catalyst could again be used for more experiments, however closer examination is needed. MgO was used as a catalyst but most likely it has reacted with water to form  $Mg(OH)_2$ . Most likely this was the case since the mass balance for water did not close, indicating some mass of oxygen and hydrogen have been transferred to form  $Mg(OH)_2$ . Other MgO catalyst that was collected also contained some unreacted PS which harden on the surface of the catalyst. A process will need to be developed to remove this unreacted PS from this catalyst.

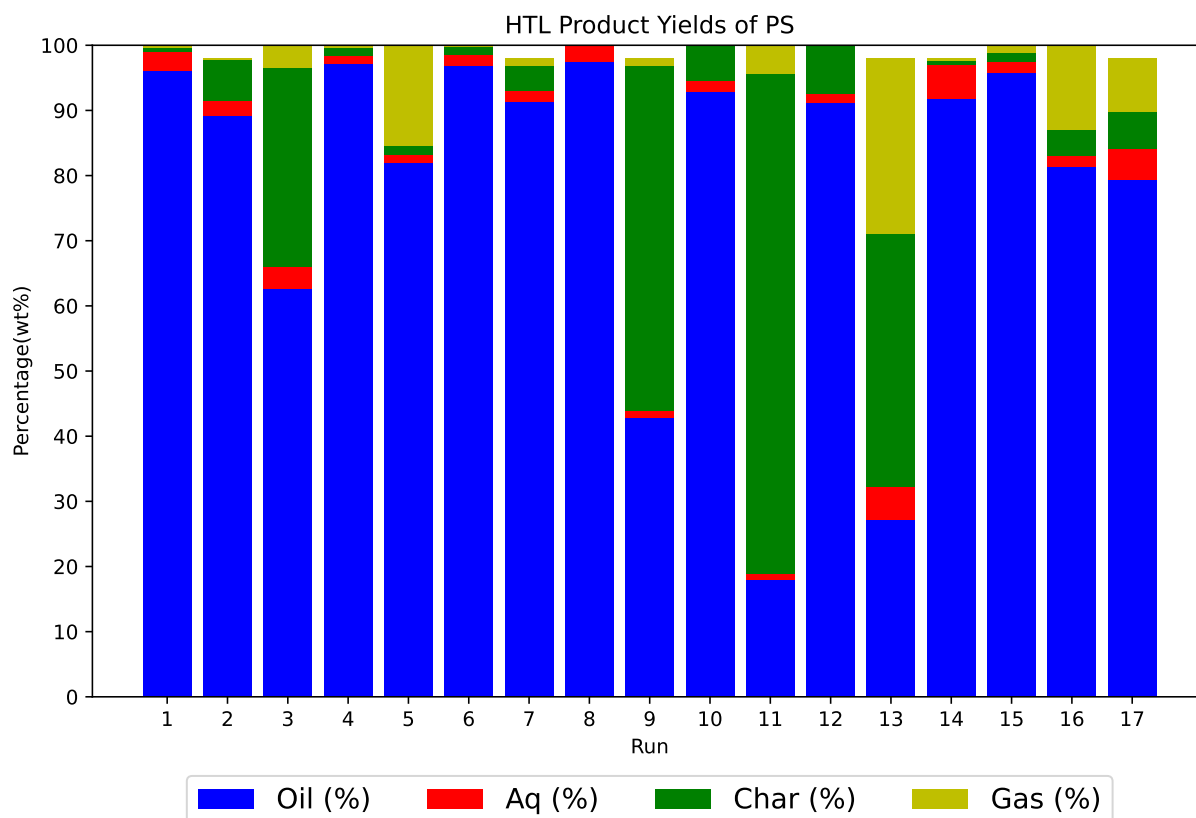


(a) Char and catalyst (Run 11, 330°C, 7.5 wt%, 30 min).



(b) Collected char and post-HTL runs.

**Figure 4.8:** Char and catalyst after HTL runs.



**Figure 4.9:** Product distribution of slurry into Aq.phase, Oil, Char and Gas.

#### 4.2.2. DOE oil characterization

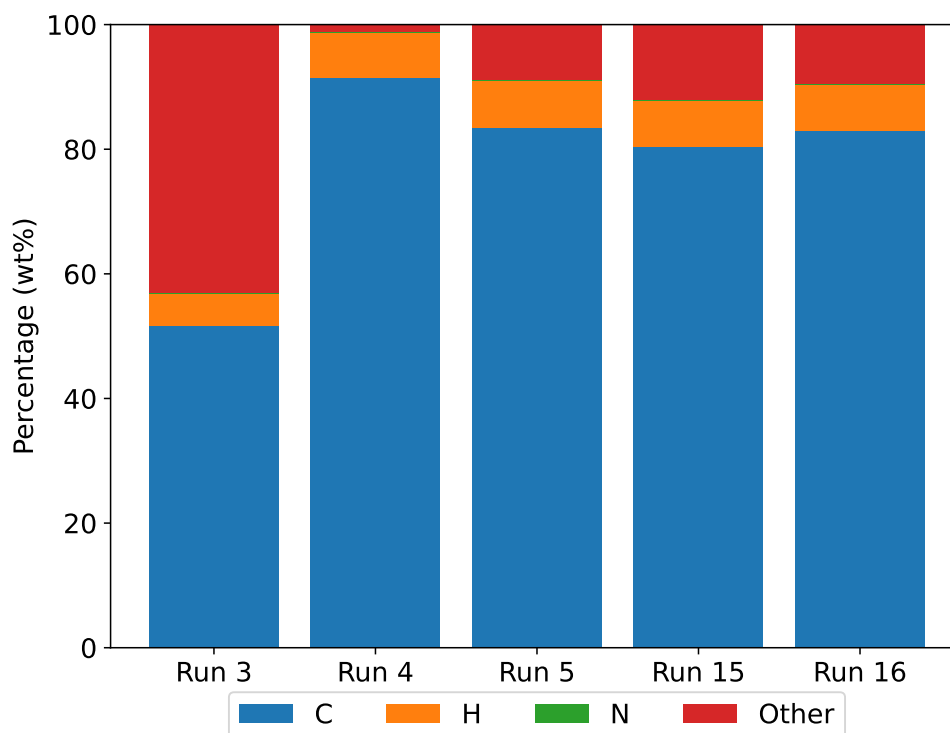
The oils produced in the 17 experiments were overall quite thick indicating that there is large amount of unbroken PS chains still present with the HVCs. This also made it difficult to conduct analysis of GCMS-FID and GCxGC-FID, because there too many compounds to classify. To improve the analysis of the PS-Crude oil product distillation was conducted similarly to screening campaign. However, due to time constraint it was not feasible to conduct distillation and analysis on all the PS-Crude oils. 5 random points were chosen to be distilled and analyzed, these samples are Run 3,4,5,15 and 16. Ultimate analysis, bomb calorimetry, GCMS-FID and GCxGC-FID were conducted to analyze the oils.

##### Ultimate (CHNO) analysis

Figure 4.10 shows the CHNO analysis of the different runs of PS-Crudeoil. Most samples contain less than 0.1 wt% Nitrogen. It can be clearly seen that there is a large amount of another element present in Run 3. This sample has 51.7 wt% of carbon, 5.1 wt% hydrogen and 43.1 wt% of another element. Some of this other element could be attributed to oxygen, however as we found out in the screening campaign, there were small amount oxygenated compounds seen in GCMS-FID analysis. The other element could be due to the presence of chlorine from DCM that was used as the extraction solvent. Analysis of the other experimental runs indicate similar amounts to the PS-Crude oil found in screening campaign and PS oil of Musivand et al. 2023. Run 4 contains the highest C content of 91.4 wt%, with H content 7.3 wt% and 1.2 wt% of other. Run 5, 15 and 16 have similar elemental content, with Run 5 having the highest C content of 83.5 wt%, H of 7.5 wt%, and other 8.9 wt%.

##### Bomb-calorimetry (Higher Heating Value (HHV))

The HHV experimental results are shown in Figure 4.11 taken from the bomb calorimetry. The results are similar to the results of the screening campaign averaging approximately 38 MJ/kg. The highest HHV being from Run 5 with 38.01 MJ/kg. This result is still lower compared HHV of the PS-Crude oil produced in Musivand et al. 2023. The lowest HHV found was 29.81 MJ/kg, which was from Run 3 of the experiments, this could be due the presence of DCM in the sample.



**Figure 4.10:** Ultimate analysis of some PS-Crude Oil.

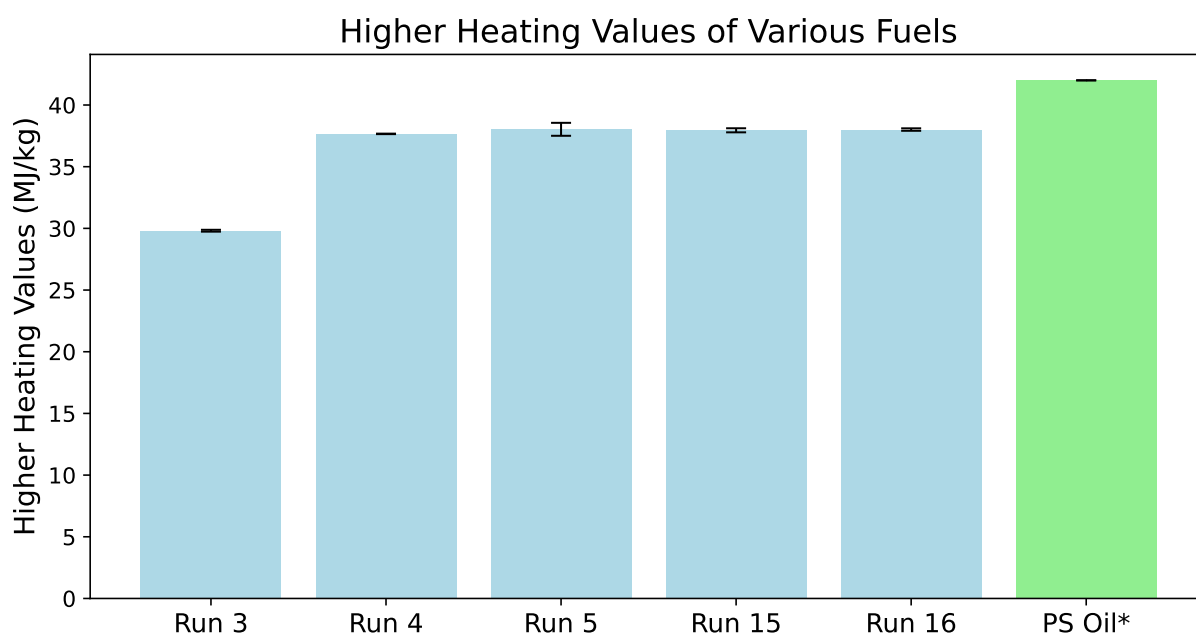
#### GC-FID and GCxGC-FID of DOE

After the PS-Crude oil was collected, a distillation process similar to that of the screening campaign was conducted. During the screening campaign, the temperature of the PS-Crude oil did not reach 300°C. For this phase, vacuum distillation was utilized to ensure that the boiling points of the distilled compounds could reach 300°C. From these distillations, a GCMS-FID analysis was conducted on the distillates. Figure 4.12 shows the distribution of compounds produced from the GCMS-FID analysis. Due to time constraint it was only possible to conduct distillation for a few oil samples. This was taken from Run 3,4,5, 15 and 16.

Here it could be seen that the largest percentage of styrene from PS-Crude oil produced was approx. 20 wt% in Run 3 and 16. While the lowest amount of styrene was produced in 4 wt%. However, this is when only looking at the yield from oil product. To have an idea of how much styrene was produced from the HTL of PS, one has to look at the product distribution. This value is multiplied with the yield of PS-Crude oil from table 4.1. Run 16 has the most amount of styrene with 17 wt%, since Run 3 had smaller yield of oil (63 wt%), the amount of styrene produced became 13 wt%. This higher than styrene yield (5.14 wt%) found in Zhao et al. 2019. Zhao et al. 2019 conducted the experiments of HTL of HIPS at 350°C. Run 16 was conducted at 340°C for 60 minutes and with 15% MgO, this has a lower reaction temperature compared to Zhao et al. 2019 of 350°C.

Other than styrene, there are also other chemicals which were found from the HTL of PS. These are alpha-methylstyrene, toluene and ethylbenzene. The second most abundant HVC found was alphas-methyl styrene, the largest amount of this compound found was in Run 4 (9 wt%) of oil. The lowest amount of alpha-methylstyrene found was in Run 3 (1 wt%). Zhao et al. 2019 reported a value of 2.1 wt%, much lower than what was found here.

The most amount of toluene found was approx. 5 wt%, this was found in Run 4 and 15. This is much lower than the amount of toluene produced in Kwak et al. 2006 (25 wt%) and Bai et al. 2019 (14 wt%). The maximum amount of ethylbenzene produced was 4 wt% in Run 4, while no ethylbenzene was found in experiment 3. Kwak et al. 2006 reached a temperature of 380°C and pressure of 24-32 MPa, Bai et al. 2019 had a reaction temperature of 490°C and pressure of 30 MPa. The experimental runs in this thesis only reached 350°C and a maximum pressure of 16 MPa. This showed that the catalyst had some effect of reducing conditions needed to breakdown PS via HTL.



**Figure 4.11:** HHV of selected PS-Crude oil from CCD.

Since the thermochemical breakdown process of PS is complicated and can go through several mechanisms as seen in the Theoretical background (2). There are also many other chemical products present such as trimers and dimers of PS breakdown, these are molecular chains of the PS that did not break completely. Examples of these include Cyclohexane, 1,3,5-triphenyl-, Benzene, (1-methylethyl)-, and Benzene, 1,1'-(1,3-propanediyl)bis-. Benzene, 1,1'-(1,3-propanediyl)bis- is present in large amounts in Run 4 (11 wt%). Perhaps, further treatment could be done to convert these into HVCs.

Run 3 also found to contain the largest amount of DCM with approx. 25 wt%. However, the other runs found to contain approximately 3-4 wt% of DCM in the PS-Crude oils. After looking more closely at these results, some compounds that were not there before, such as N-Benzyl-1H-benzimidazole. This is most likely an inaccuracy in determination of GCMS-FID or its classification. N-Benzyl-1H-benzimidazole has a molecular mass of approximately 208.56 g/mol ChemSpider n.d. Because GCMS-FID classifies the compounds based on molecular mass, other side products formed from the thermochemical breakdown of PS with a similar molecular weight was most likely categorized. According to 4.12 there were large amounts of this nitrogenated compound (N-Benzyl-1H-benzimidazole), however it is already known that there is only less than 0.1 wt% of nitrogen present in the oils as seen in 4.10. To check whether this analysis was correct a GCxGC-FID was also done.

To correct the data, the samples were also sent for GCxGC-FID, the results are classified differently in terms of their carbon numbers (C5 to C32). The results are shown in the Figure 4.13. Based on this data, it was confirmed that there was a classification error. The oils are complex, which made it hard to classify into specific compounds.

To give a clear picture of the different compounds present, the compounds are classified differently. After correction of the yields of compounds based on the yields. It was found that Run 16 produced the largest amount of styrene at 16 wt%, only a small difference compared to the GCMS-FID data. Other molecules found in the samples also showed similar results to the GCMS-FID data. Since the instrument and software try to look for compounds, one group of compounds that were looked for were ortho-xylene (o-xylene), para-xylene (p-xylene), and meta-xylene (m-xylene). These are also HVCs that could be used in industry, however based on the Theoretical background (2) there were no mechanism that could lead to produce these products.

In Figure 4.12, the 'tar fraction' represents the residual product remaining after the distillation process. This fraction predominantly consists of high molecular mass compounds. It appears that the presence of a catalyst influences the tar content in the PS-Crude oil. This is evident when examining Run 5 and Run 16,

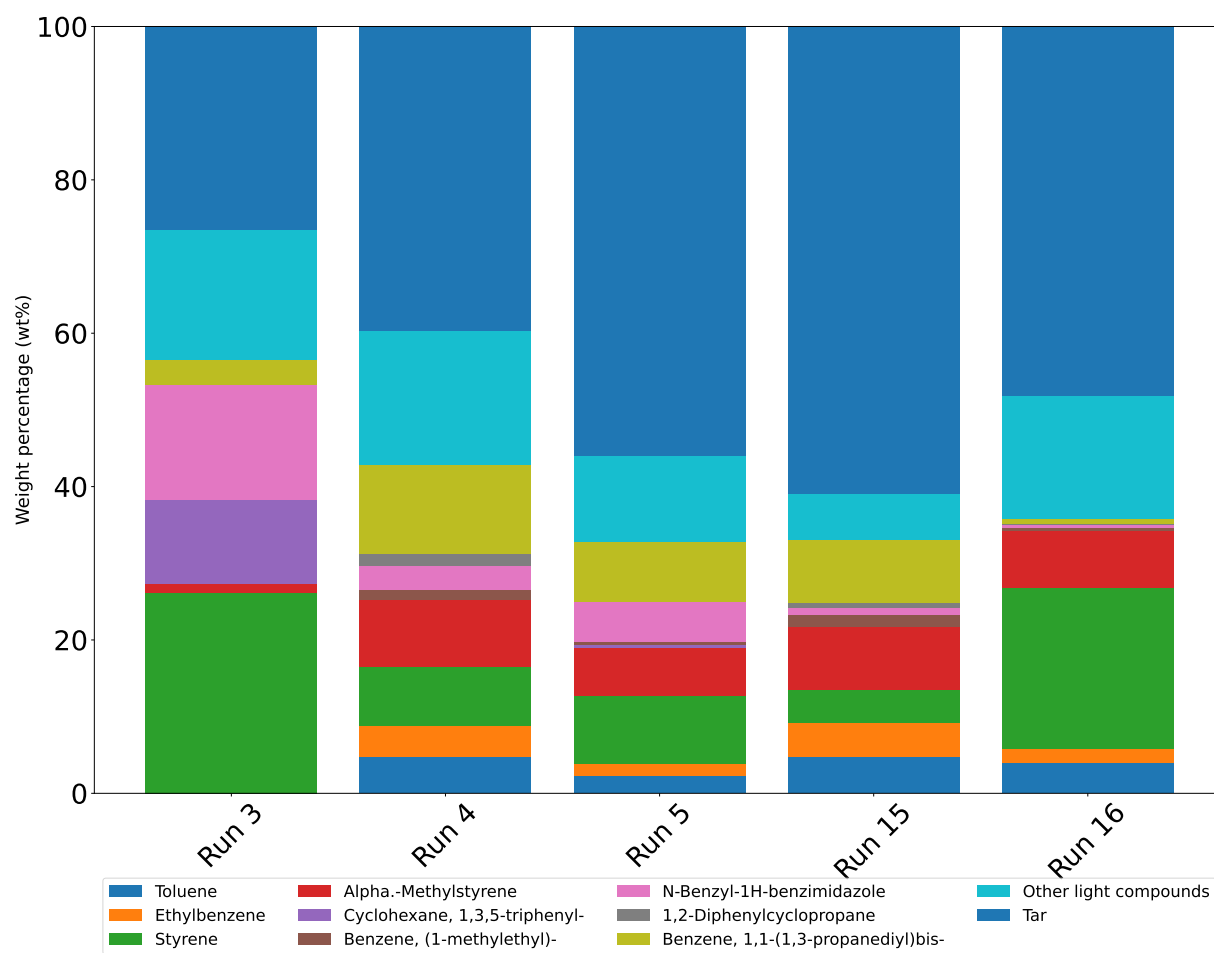


Figure 4.12: GC-FID results of DOE.

both conducted at the same operational conditions of 340°C and a 60-minute residence time. Notably, Run 5 was performed without any catalyst, whereas Run 16 included a 15% catalyst. Run 5 has a styrene yield of 6 wt%, while Run 16 has 17%. Then Run 5 has 45 wt% tar, while Run 16 has 39 wt% of tar. This suggests that catalyst usage plays a role in altering the tar yield and increasing the yield of styrene.

As mentioned before, PS-Crude oils from the runs produce a thick oil. After distillation of these oils, approx. 50 wt% of the oils are able to be boiled off and collected as distillate, there remains to be a large amount of tar or heavy oil that is leftover. This leftover product could also be classified for Gel Permeation Chromatography (GPC), so that the degree of depolymerization could be analyzed. The starting PS feedstock that was used had an average molecular weight of 280,000 g/mol, this value will most likely have decreased. Further upgrading of the heavy fraction of PS-Crude oil could also be done. One option is to repeat the HTL process on the heavy fractions of oil to see if it could promote an increase in HVCs. Another option would be to conduct another form of cracking of the heavy fraction.

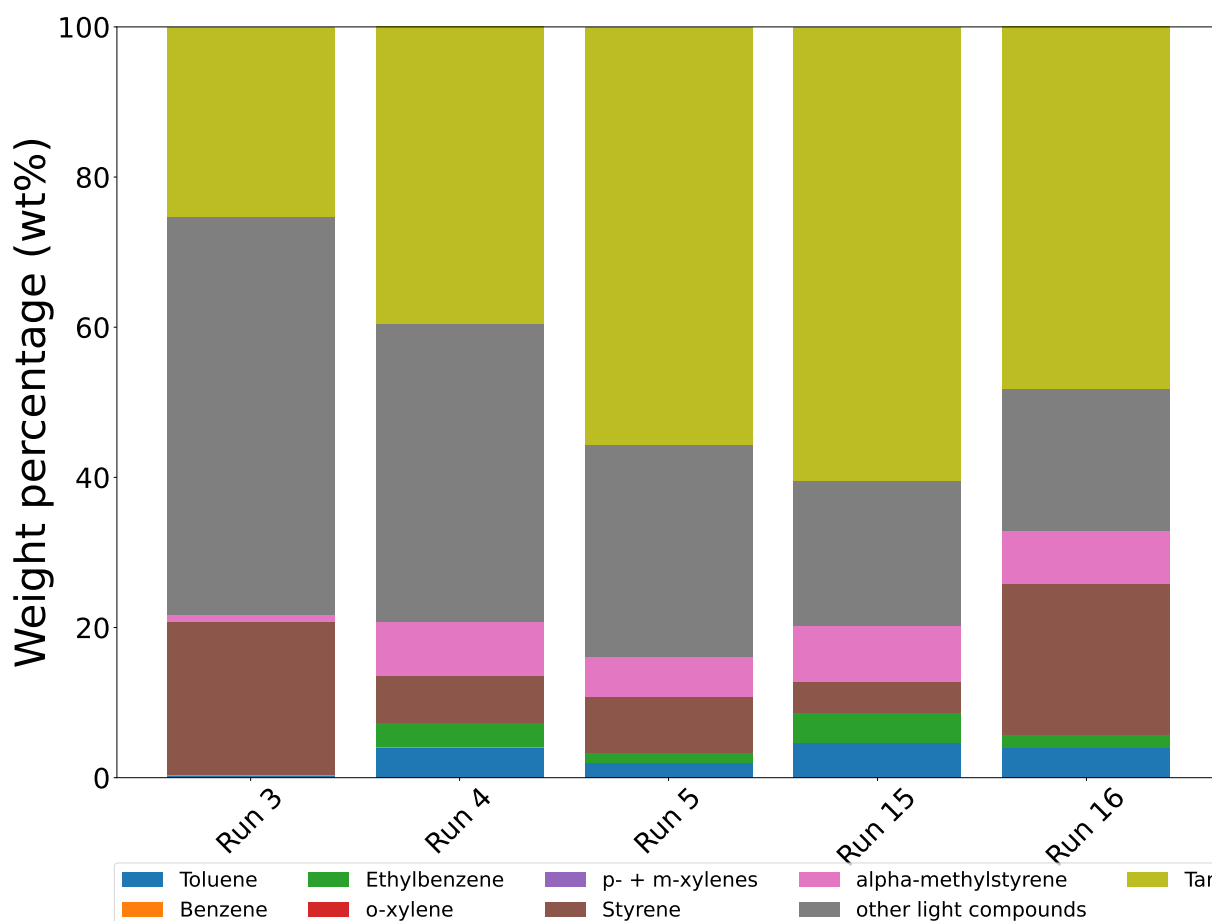


Figure 4.13: GCxGC-FID results of DOE.

#### 4.2.3. Optimization using CCD

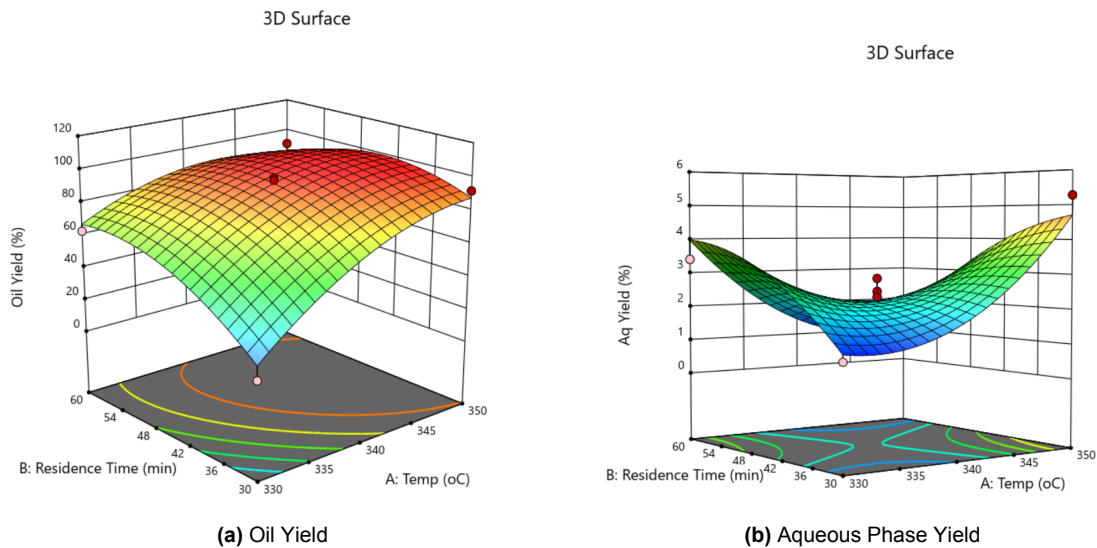
From the 17 experimental runs, a model was produced using Central Composite Design response model, which was used to accurately predict the HTL products. The model takes into account parameters of temperature, reaction time and catalyst loading. The response will provide a model for products of oil, char, aqueous and gas phases.

From the model, it seems that oil yield increases as temperature of reaction increases however, the PS-Crude oil yield does reduce slightly at 350°C. The optimum condition for PS-Crude oil yield (approx. 90 wt%) in this case is at around 340°C and 30 minutes. However, reactions occurring above 340°C will cause the oil to start breaking down into the gas and aqueous phase. This can be seen in the Aqueous phase yield of Figure 4.14. This is similar to biomass, where some of the products start to breakdown into the aqueous phase at higher temperatures and longer residence time (Conti 2020). In the case of PS, the aqueous phase yields remain quite low compared to biomass with a maximum of 4 wt% yield at 350°C.

In Figure 4.15, it can be seen that gas yields of the product will increase with an increasing residence time, which is in line with the hypothesis that long residence time will cause the oils to further breakdown into gasses. As seen in Figure 4.9, there is relatively small amounts of gas being produced with maximum only reaching 5 wt%, at reaction time of 60 minutes. The amount of char also increases with decrease in temperature. This point is reached at 330°C and 30 minutes with (approx. 20wt% yield). All un-reacted product as seen in 4.8 is also classified as char since it is all the solid yellowish residue leftover from the reaction. When most of the PS is broken down, it contains only small amount of black char.

#### Model equation and optimization parameters

From the 17 HTL experiments that were conducted a response model for the product yields were produced. Based on these responses, a model that best fit the quadratic equations were made using the help of



**Figure 4.14:** Oil and Aqueous Yield produced using Design Expert.

Design-Expert by Stat-Ease Inc. The main focus of this case is to maximize the PS Crude Oil, however the yields of Aq.phase, Char and Gas are also shown.

Parameter	PS-Crude oil	Aq. Phase	Char	Gas
<b>Maximum point</b>	<b>341°C-34 minutes-8% cat</b>			
Predicted yield (%)	80.71	2.13	18.14	1.7
Measured yield (%)	93.48	3.23	2.37	4.53
Relative error (%)	13.66	34.06	665.40	62.47
Absolute error (%)	-12.77	-1.10	+15.77	-2.83

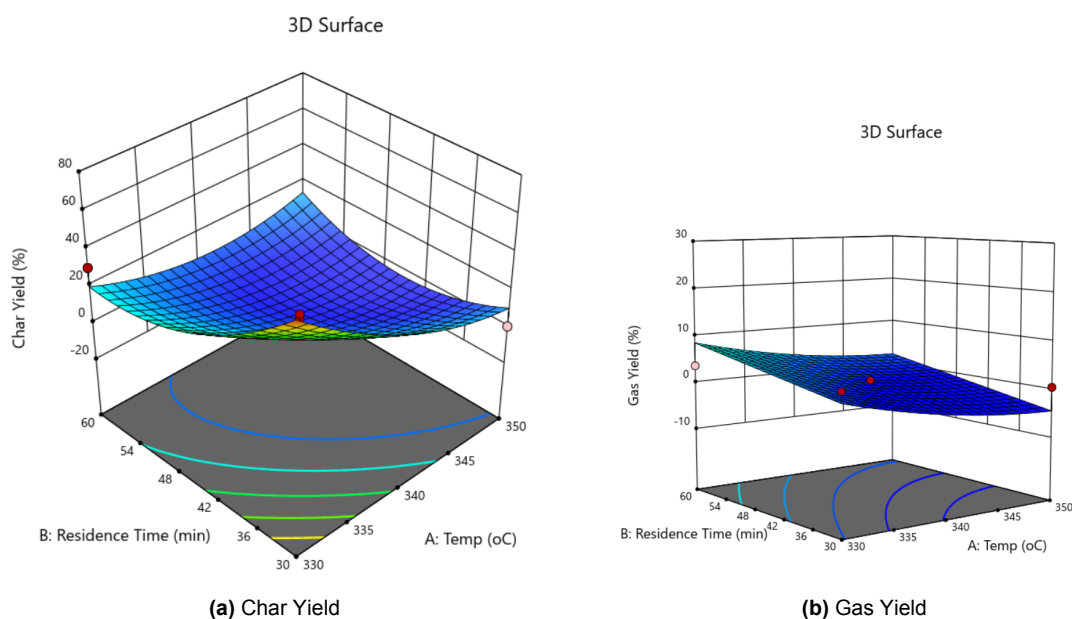
**Table 4.2:** Predicted yields for CCD's maximum PS-Crude oil point with relative and absolute errors are included.

$$\begin{aligned}
 \text{PS-Crude Oil (\%)} = & -17437.08 + 98.46A + 31.21B - 64.88C \\
 & - 0.076AB + 0.17AC + 0.11BC - 0.14A^2 \\
 & - 0.063B^2 - 0.089C^2
 \end{aligned} \tag{4.1}$$

$$\begin{aligned}
 \text{Aq.phase Yield (\%)} = & 1166.407.38A + 3.85B + 0.28C \\
 & - 0.11AB + 0.0025BC + 0.012A^2 \\
 & - 0.0028B^2 - 0.0024C^2
 \end{aligned} \tag{4.2}$$

$$\begin{aligned}
 \text{Char Yield (\%)} = & 14374.66 - 78.93A - 36.63B + 43.90C \\
 & + 0.089AB - 0.11AC - 0.096BC + 0.11A^2 \\
 & + 0.069B^2 - 0.028C^2
 \end{aligned} \tag{4.3}$$

$$\begin{aligned}
 \text{Gas Yield (\%)} = & 1629.45 - 9.76A + 0.047B + 20.65C \\
 & + 0.00068AB - 0.063AC - 0.0082BC + 0.015A^2 \\
 & - 5.6 * 10^{-6} B^2 + 0.12C^2
 \end{aligned} \tag{4.4}$$



**Figure 4.15:** Char and Gas Yield produced using Design Expert.

Where:

A: Temperature (°C)

B: Residence time (minutes)

C: Catalyst loading (%)

From the model, correlations were made using Design-Expert by Stat-Ease Inc. These produced the equations 4.1, 4.2, 4.3 and 4.4. The correlation analysis for the yields of PS-Crude oil, Aq phase, Char, and Gas revealed that the P-values for the "lack of fit" of the model were less than 0.05, signifying that the model is statistically significant. However, a discrepancy was observed between the Predicted  $R^2$  and the Adjusted  $R^2$  values for PS-Crude oil, with the Predicted  $R^2$  being 0.1987 and the Adjusted  $R^2$  being substantially higher at 0.8757. A difference greater than 0.2 between these two values may suggest the presence of a large block effect or a potential issue with the model or underlying data, underscoring the necessity for validation runs. For the Aq phase, Char, and Gas yields, the Predicted  $R^2$  values were negative, indicating that using the overall mean as a predictor might be more effective than the current model in these cases.

The Adequacy Precision metric reflects the signal-to-noise ratio of the model. In our case, the product yields demonstrated an Adequacy Precision ratio greater than 4, which is desirable. This suggests that the signals are distinguishable from the noise, indicating a model with sufficient discriminatory capability. In light of the findings, two validation experiments were conducted to assess the accuracy of the predictive model. The results indicated that the model's predictions were not as reliable as previously assumed. This discrepancy may be attributed to the suitability of the model fitting; employing higher-order equations could potentially enhance model accuracy.

Another factor affecting accuracy is the inherent nature of the batch reactor used in the process. The transient state—specifically, the time required for the reactor to reach the target reaction temperature—can vary with room temperature fluctuations. Past issues with the reactor failing to achieve the proper reaction temperature due to leaks further complicate the accuracy of the model.

Table 4.2 shows the predicted yields of PS-Crude oil, Aq.Phase, Char and Gas that was calculated using the equation produced from Stat-Ease software. All the supporting data to produce the equation of PS-Crude oil are present in the 6.

The figure also shows the measured yields after recreating 2 validation points. These two results are then compared to measure the absolute and relative error between the measured and predicted yields. There is a large error between the measured yield of char and its predicted yield.

# 5

## Conclusion

The projected expansion of polystyrene production suggests its continued growth for the foreseeable future. Accompanying the global rise in plastic manufacturing is the persistent challenge of environmental pollution. It is imperative to address the disposal of these plastics in ways that prevent further ecological harm. While mechanical recycling remains a crucial component of our recycling efforts, its efficacy diminishes with each cycle of the material. In such cases, chemical recycling becomes an important part of the puzzle. Techniques such as catalytic hydrothermal liquefaction (HTL) offer promising solutions by breaking down polystyrene into its constituent monomers and other valuable chemicals, thus supporting sustainable recycling practices and contributing to a circular economy.

### 5.0.1. Catalyst screening

The initial HTL of PS at 300°C suggests that it was possible to breakdown PS in the 300mL reactor, though with a small yield of 56 wt%. The catalyst screening was successful for the alkaline basic catalyst chosen. However, the same could not be said about ZSM-5 and deep eutectic solvents. ZSM-5 did not produce much oil because acidic catalyst seems to re-polymerize the polystyrene. Deep eutectic solvent cannot be used for depolymerization of polystyrene because the critical temperature ( $T_C$ ) did not reach adequate activation energy to breakdown polystyrene (310°C). The catalyst that successfully breakdown the PS via HTL was BaO and MgO, which are heterogeneous basic catalyst. The HTL process showed similar product distributions with high PS-Crude oil yields of (>90 wt%). The ultimate analysis of PS-Crude oil also showed similar ratios of C,H,N and O comparable to what was found in literature. One BaO catalyzed PS-Crude oil result showed a higher percentage of oxygen. The highest HHV found was from BaO catalyzed at 40.02 MJ/kg, this was similar to what was found in literature but still lower by 2 MJ/kg.

A distillation MgO and BaO catalyzed as well as uncatalyzed PS-Crude oils were conducted. Distillation of the oils were conducted however, there were significant losses in lighter fractions. Nonetheless, a GCMS-FID analysis was done on the distillates. The most amount of styrene produced in this case (21 wt%) was from a MgO catalyzed HTL, lower than what was found in literature. However, the other MgO catalyzed run produced significantly lower styrene yield, which reduced the yield of styrene to 17wt% overall. There was also a large amount of alpha-methylstyrene (12.2wt%) produced as well from MgO catalyzed HTL. Due to the high overall yields of oil and HVCs that were produced from MgO catalyzed HTL, MgO was chosen as the catalyst for the Design of Experiments.

### 5.0.2. Optimization campaign

After choosing MgO as the catalyst for HTL. An experimental matrix of all of the results were made with the help of Design Expert. This resulted in 17 experiments of HTL as well 2 validation. Similar to the screening campaign most products produce high yields of 80-90 wt%. Aqueous phase and gas yields produce are small being less than 5 wt% in most cases. Char yields can vary but also remain relatively low as well <5 wt%. Reaction temperature of 330°C with 30 minutes also produce char as well which was mostly unreacted and melted PS. 15 % catalyst loading also showed large amount of unreacted PS, indicating that too much catalyst inhibits breakdown of PS.

Due to time constraints, not all of the PS-Crude oils were distilled and analyzed. 5 random points of the experimental was chosen, these experimental runs 3,4,5,15, 16. Ultimate analysis of the PS-Crude oils showed that Run 3 contained large amount of another compound, after the GCMS-FID was conducted

it showed a large percentage of DCM present. Run 5, 15, and 16 showed similar C,H,N,O ratios. Run 4 showed very small amounts of oxygen. The results of HHV showed similar results for Run 4, 5, 15 and 16. The highest HHV was found in Run 5 with 38.01 MJ/kg, this result is still lower than what was found in the literature. The lowest HHV found in Run 3 showed the lowest HHV with 29.81 MJ/kg, also indicating that there is a large amount of DCM present.

Initially there were issues with collections of distillate during the screening campaign, however by employing the use of a shortpass distillation column more distillates were able to be collected. GCMS-FID and GCxGC-FID was then conducted on the distillates, the results showed the highest yield of styrene found in Run 16. When comparing the outcomes of Run 5 and Run 16 — both conducted under identical conditions yet differing in catalyst loading — it was observed that Run 16, which contains a catalyst, yielded a higher amount of styrene 17 wt%. Other chemicals such as alpha methylstyrene and ethylbenzene are also found but in smaller quantities.

The model was produced using the central composite design method based on the experimental yields of oil, aqueous, gas and char phase. This produced the graphs in Figure 4.14 and 4.15, the graphs showed that the optimum temperature to produce large amounts of oil was found to be around 341°C, at approximately 34 minutes and a catalyst loading of approximately 8%. However, high oil yields do not always translate into high yields of styrene.

The model developed through Design-Expert software has shown statistical significance in predicting product yields, as evidenced by the low P-values for "lack of fit." However, inconsistencies between Predicted and Adjusted  $R^2$  values for PS-Crude oil and negative Predicted  $R^2$  values for the Aq phase, Char, and Gas yields suggest that the model may require refinement.

Despite a strong signal-to-noise ratio indicated by Adequate Precision metrics, validation experiments have revealed differences between predicted and actual yields, which does raise questions about the model's reliability. Factors such as the batch reactor's performance and environmental variables may also influence these outcomes. The data from the Stat-Ease software and subsequent validation tests, detailed in Table 4.2 and Appendix 6, underscore the need for further investigation to improve the model's predictive accuracy, particularly for the Char yield where a significant prediction error was noted.

### 5.0.3. Overview of HTL process

HTL is an option to breakdown PS, there are however other approaches to increase the yield of styrene. The results of the research showed that PS can be broken down through HTL. The yield of PS-Crude oil produced from this process was high at 90 wt%. It showed that a basic catalyst can be employed to improve the yield of styrene. 17 wt% of styrene was produced in the best case with the optimum conditions being 340°C, 34 minutes and 8% catalyst loading. This process however also produces a large amount of thick heavy oil which could not be distilled. Further processing of these oils could be needed, one could conduct another HTL experiment on the heavy oils to see if more styrene monomer could be produced.

### 5.0.4. Recommendation for future approaches

After conducting the HTL experiments some recommendations could be made to improve the process and make it simpler in the case that future researches would like to attempt HTL of PS.

One main issue that persisted during the research was the difficulty in evaporating DCM, which in turn made difficult to measure the actual yield of oil produced. The only way it would be possible is to run all the oils through GCMS-FID or GCxGC-FID and then determine the different products by weight percentage.

Catalyst used remained unchanged even after being used for HTL. There are occasions where PS is not completely broken down, these contain some PS stuck to the catalyst. More research could be done on the catalyst and its viability to be used reused.

The lab work for conducting HTL this size can be tedious, because the larger size requires more time to heat up the reactor to the adequate temperature. After attending the Chemrec conference in Malaga, it was found that most researches decided to conduct these experiments in small scale micro reactors. Conducting experiments in micro reactors could help decrease the time it takes for HTL to take place. The research currently is limited to temperature below 350°C, however most research is thermochemical breakdown of PS involves temperatures above this. A smaller reactor can allow to reach higher temperatures faster and so more experiments can be done at a shorter time.

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Another main issue that came to mind after attending the Chemrec conference was the fact that PS that was used in these experiments are relatively clean compared to the ones found from waste. Waste PS could contain many other compounds ranging from food waste, coloring, other plastics and bromine. This ofcourse would cause many other side products to be produced from HTL process. In the future real plastic waste should be used as feedstock. For now this is only the beginning in the research into catalytic HTL of PS.

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6

## Appendix

## ANOVA for Quadratic model

### Response 1: Oil Yield

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	9784.55	9	1087.17	13.52	0.0012	significant
A-Temp	3007.00	1	3007.00	37.41	0.0005	
B-Residence Time	645.84	1	645.84	8.03	0.0252	
C-Catalyst Loading	2385.33	1	2385.33	29.67	0.0010	
AB	516.20	1	516.20	6.42	0.0390	
AC	676.52	1	676.52	8.42	0.0230	
BC	615.54	1	615.54	7.66	0.0278	
A <sup>2</sup>	811.64	1	811.64	10.10	0.0155	
B <sup>2</sup>	851.28	1	851.28	10.59	0.0140	
C <sup>2</sup>	105.64	1	105.64	1.31	0.2893	
<b>Residual</b>	562.72	7	80.39			
Lack of Fit	513.39	3	171.13	13.88	0.0140	significant
Pure Error	49.33	4	12.33			
<b>Cor Total</b>	10347.27	16				

Factor coding is **Coded**.

Sum of squares is **Type III - Partial**

The **Model F-value** of 13.52 implies the model is significant. There is only a 0.12% chance that an F-value this large could occur due to noise.

**P-values** less than 0.0500 indicate model terms are significant. In this case A, B, C, AB, AC, BC, A<sup>2</sup>, B<sup>2</sup> are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

The **Lack of Fit F-value** of 13.88 implies the Lack of Fit is significant. There is only a 1.40% chance that a Lack of Fit F-value this large could occur due to noise. Significant lack of fit is bad -- we want the model to fit.

### Fit Statistics

Std. Dev.	8.97	<b>R<sup>2</sup></b>	0.9456
Mean	78.42	<b>Adjusted R<sup>2</sup></b>	0.8757
C.V. %	11.43	<b>Predicted R<sup>2</sup></b>	0.1987
		<b>Adeq Precision</b>	10.6608

The **Predicted R<sup>2</sup>** of 0.1987 is not as close to the **Adjusted R<sup>2</sup>** of 0.8757 as one might normally expect; i.e. the difference is more than 0.2. This may indicate a large block effect or a possible problem with your model and/or data. Things to consider are model reduction, response transformation, outliers, etc. All empirical models should be tested by doing confirmation runs.

**Adeq Precision** measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 10.661 indicates an adequate signal. This model can be used to navigate the design space.

### Final Equation in Terms of Actual Factors

<b>Oil Yield</b>	=
-17437.08350	
+98.45745	Temp
+31.20893	Residence Time
-64.88460	Catalyst Loading
-0.075733	Temp * Residence Time
+0.173400	Temp * Catalyst Loading
+0.110267	Residence Time * Catalyst Loading
-0.138840	Temp <sup>2</sup>
-0.063196	Residence Time <sup>2</sup>
-0.089049	Catalyst Loading <sup>2</sup>

The equation in terms of actual factors can be used to make predictions about the response for given levels of each factor. Here, the levels should be specified in the original units for each factor. This equation should not be used to determine the relative impact of each factor because the coefficients are scaled to accommodate the units of each factor and the intercept is not at the center of the design space.

## ANOVA for Quadratic model

### Response 2: Aq Yield

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	24.26	9	2.70	2.16	0.1609	not significant
A-Temp	0.3042	1	0.3042	0.2439	0.6365	
B-Residence Time	0.2380	1	0.2380	0.1909	0.6753	
C-Catalyst Loading	6.06	1	6.06	4.86	0.0634	
AB	10.27	1	10.27	8.24	0.0240	
AC	0.0000	1	0.0000	0.0000	0.9966	
BC	0.3192	1	0.3192	0.2560	0.6284	
A <sup>2</sup>	5.65	1	5.65	4.53	0.0707	
B <sup>2</sup>	1.68	1	1.68	1.35	0.2841	
C <sup>2</sup>	0.0782	1	0.0782	0.0627	0.8095	
<b>Residual</b>	<b>8.73</b>	<b>7</b>	<b>1.25</b>			
Lack of Fit	7.69	3	2.56	9.87	0.0255	significant
Pure Error	1.04	4	0.2598			
<b>Cor Total</b>	<b>32.99</b>	<b>16</b>				

Factor coding is **Coded**.

Sum of squares is **Type III - Partial**

The **Model F-value** of 2.16 implies the model is not significant relative to the noise. There is a 16.09% chance that an F-value this large could occur due to noise.

**P-values** less than 0.0500 indicate model terms are significant. In this case AB is a significant model term. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

The **Lack of Fit F-value** of 9.87 implies the Lack of Fit is significant. There is only a 2.55% chance that a Lack of Fit F-value this large could occur due to noise. Significant lack of fit is bad -- we want the model to fit.

### Fit Statistics

Std. Dev.	1.12	<b>R<sup>2</sup></b>	0.7354
Mean	2.39	<b>Adjusted R<sup>2</sup></b>	0.3953
C.V. %	46.64	<b>Predicted R<sup>2</sup></b>	-2.7784
		<b>Adeq Precision</b>	5.3593

A negative **Predicted R<sup>2</sup>** implies that the overall mean may be a better predictor of your response than the current model. In some cases, a higher order model may also predict better.

**Adeq Precision** measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 5.359 indicates an adequate signal. This model can be used to navigate the design space.

## Final Equation in Terms of Actual Factors

<b>Aq Yield</b>	=
+1166.40250	
-7.37950	Temp
+3.85450	Residence Time
+0.028000	Catalyst Loading
-0.010683	Temp * Residence Time
+0.000033	Temp * Catalyst Loading
+0.002511	Residence Time * Catalyst Loading
+0.011587	Temp <sup>2</sup>
-0.002806	Residence Time <sup>2</sup>
-0.002422	Catalyst Loading <sup>2</sup>

The equation in terms of actual factors can be used to make predictions about the response for given levels of each factor. Here, the levels should be specified in the original units for each factor. This equation should not be used to determine the relative impact of each factor because the coefficients are scaled to accommodate the units of each factor and the intercept is not at the center of the design space.

## ANOVA for Quadratic model

### Response 3: Char Yield

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	7377.04	9	819.67	9.49	0.0036	significant
A-Temp	2198.51	1	2198.51	25.44	0.0015	
B-Residence Time	1115.81	1	1115.81	12.91	0.0088	
C-Catalyst Loading	1010.70	1	1010.70	11.70	0.0111	
AB	716.90	1	716.90	8.30	0.0236	
AC	276.39	1	276.39	3.20	0.1168	
BC	462.47	1	462.47	5.35	0.0539	
A <sup>2</sup>	499.86	1	499.86	5.79	0.0471	
B <sup>2</sup>	1016.90	1	1016.90	11.77	0.0110	
C <sup>2</sup>	10.11	1	10.11	0.1170	0.7424	
<b>Residual</b>	<b>604.83</b>	<b>7</b>	<b>86.40</b>			
Lack of Fit	578.61	3	192.87	29.42	0.0035	significant
Pure Error	26.23	4	6.56			
<b>Cor Total</b>	<b>7981.87</b>	<b>16</b>				

Factor coding is **Coded**.

Sum of squares is **Type III - Partial**

The **Model F-value** of 9.49 implies the model is significant. There is only a 0.36% chance that an F-value this large could occur due to noise.

**P-values** less than 0.0500 indicate model terms are significant. In this case A, B, C, AB, A<sup>2</sup>, B<sup>2</sup> are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

The **Lack of Fit F-value** of 29.42 implies the Lack of Fit is significant. There is only a 0.35% chance that a Lack of Fit F-value this large could occur due to noise. Significant lack of fit is bad -- we want the model to fit.

### Fit Statistics

Std. Dev.	9.30	<b>R<sup>2</sup></b>	0.9242
Mean	14.10	<b>Adjusted R<sup>2</sup></b>	0.8268
C.V. %	65.94	<b>Predicted R<sup>2</sup></b>	-0.1650
		<b>Adeq Precision</b>	10.9927

A negative **Predicted R<sup>2</sup>** implies that the overall mean may be a better predictor of your response than the current model. In some cases, a higher order model may also predict better.

**Adeq Precision** measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 10.993 indicates an adequate signal. This model can be used to navigate the design space.

## Final Equation in Terms of Actual Factors

<b>Char Yield</b>	=
+14374.65800	
-78.93385	Temp
-36.63180	Residence Time
+43.89613	Catalyst Loading
+0.089250	Temp * Residence Time
-0.110833	Temp * Catalyst Loading
-0.095578	Residence Time * Catalyst Loading
+0.108958	Temp <sup>2</sup>
+0.069070	Residence Time <sup>2</sup>
-0.027542	Catalyst Loading <sup>2</sup>

The equation in terms of actual factors can be used to make predictions about the response for given levels of each factor. Here, the levels should be specified in the original units for each factor. This equation should not be used to determine the relative impact of each factor because the coefficients are scaled to accommodate the units of each factor and the intercept is not at the center of the design space.

## ANOVA for Quadratic model

### Response 4: Gas Yield

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	610.49	9	67.83	1.69	0.2503	not significant
A-Temp	82.63	1	82.63	2.06	0.1943	
B-Residence Time	84.70	1	84.70	2.11	0.1894	
C-Catalyst Loading	139.95	1	139.95	3.49	0.1039	
AB	0.0420	1	0.0420	0.0010	0.9751	
AC	90.25	1	90.25	2.25	0.1772	
BC	3.42	1	3.42	0.0854	0.7786	
A <sup>2</sup>	8.90	1	8.90	0.2219	0.6519	
B <sup>2</sup>	6.579E-06	1	6.579E-06	1.641E-07	0.9997	
C <sup>2</sup>	194.77	1	194.77	4.86	0.0634	
<b>Residual</b>	280.66	7	40.09			
Lack of Fit	279.65	3	93.22	369.32	< 0.0001	significant
Pure Error	1.01	4	0.2524			
<b>Cor Total</b>	891.15	16				

Factor coding is **Coded**.

Sum of squares is **Type III - Partial**

The **Model F-value** of 1.69 implies the model is not significant relative to the noise. There is a 25.03% chance that an F-value this large could occur due to noise.

**P-values** less than 0.0500 indicate model terms are significant. In this case there are no significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

The **Lack of Fit F-value** of 369.32 implies the Lack of Fit is significant. There is only a 0.01% chance that a Lack of Fit F-value this large could occur due to noise. Significant lack of fit is bad -- we want the model to fit.

### Fit Statistics

Std. Dev.	6.33	<b>R<sup>2</sup></b>	0.6851
Mean	4.50	<b>Adjusted R<sup>2</sup></b>	0.2801
C.V. %	140.58	<b>Predicted R<sup>2</sup></b>	-4.0227
		<b>Adeq Precision</b>	5.2547

A negative **Predicted R<sup>2</sup>** implies that the overall mean may be a better predictor of your response than the current model. In some cases, a higher order model may also predict better.

**Adeq Precision** measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 5.255 indicates an adequate signal. This model can be used to navigate the design space.

## Final Equation in Terms of Actual Factors

<b>Gas Yield</b>	=
+1629.44875	
-9.76263	Temp
+0.046750	Residence Time
+20.64733	Catalyst Loading
+0.000683	Temp * Residence Time
-0.063333	Temp * Catalyst Loading
-0.008222	Residence Time * Catalyst Loading
+0.014538	Temp <sup>2</sup>
-5.55556E-06	Residence Time <sup>2</sup>
+0.120911	Catalyst Loading <sup>2</sup>

The equation in terms of actual factors can be used to make predictions about the response for given levels of each factor. Here, the levels should be specified in the original units for each factor. This equation should not be used to determine the relative impact of each factor because the coefficients are scaled to accommodate the units of each factor and the intercept is not at the center of the design space.

Experiments	PS-Crude Oil (%)	Aq.Phase (%)	Char (%)	Gas (%)
Uncatalysed	92.70	2.26	3.62	1.41
MgO 5%	90.61	1.89	4.64	2.87
MgO 5%	92.40	2.80	1.30	3.49
Bao 5%	93.44	2.69	2.05	1.82
Bao 5%	89.94	3.29	0.70	6.07

**Appendix tab1. Product distribution of slurry of screening campaign**

Sample Name	Styrene	Ethyl benzene	Toluene	1,2-Diphenyl cyclopropane	Alpha-methylstyrene	Other Light compounds	Tar
Non-Catalytic	18.94	1.98	4.05	1.28	7.79	2.56	63.41
MgO (5%)-1	21.90	5.17	6.92	2.85	12.22	10.93	40.01
MgO (5%)-2	18.93	2.23	3.92	1.36	6.12	35.77	31.67
BaO (5%)-1	21.88	5.44	7.69	3.20	9.88	17.25	34.93
BaO (5%)-2	13.43	3.30	3.99	2.28	6.64	13.01	57.65

**Appendix tab2. GC-FID analysis data of screening campaign**

Sample Name	Av from each run (MJ/kg)
MgO (5%)	39.28
Non-catalytic	39.22
BaO (5%)	40.02
Diesel	45.60
Gasoline	46.40
PS oil	41.90

**Appendix tab3. HHV data of PS-Crude oil of screening campaign**

Sample name	C	H	N	O
MgO (5%)	88.4	7.4	0.1	4.1
Uncat (5%)	87.8	7.4	0.1	4.7
BaO (5%)	82.8	7.1	0.1	10

**Appendix tab4. Ultimate (CHN) analysis results of screening campaign**

Experiments	Leftover	0-100°C	100-200°C	200-300°C	Heavy oil
Non-catalytic	59.9	0.0	7.4	26.2	6.4
MgO 5%-1	37.4	0.0	12.2	38.0	12.3
MgO 5%-2	26.8	0.0	15.6	13.9	43.7
Bao 5%-1	34.1	1.8	9.6	41.9	12.6
Bao 5%-2	56.9	0.0	11.1	23.7	8.5

**Appendix tab5. Distillation of oils in screening campaign**

Run number	Benzene	Toluene	Ethylbenzene	o-xylene	p- + m-xylenes	styrene	alpha-methylstyrene	other compounds (>300°C)	Tar
Run 3	0.01	0.33	0.10	0.00	0.00	20.30	0.96	53.08	25.22
Run 4	0.04	4.03	3.31	0.00	0.00	6.26	7.12	39.66	39.57
Run 5	0.02	2.01	1.33	0.00	0.00	7.44	5.26	28.34	55.60
Run 15	0.04	4.61	4.05	0.00	0.00	4.03	7.55	19.27	60.46
Run 16	0.07	3.95	1.71	0.00	0.00	20.11	7.05	18.88	48.24

**Appendix tab6. GCxGC-FID of DOE**

Sample name	Carbon	Hydrogen	Nitrogen	Other
Run 3	51.7	5.1	0.1	43.1
Run 4	91.4	7.3	0.1	1.2
Run 5	83.5	7.5	0.1	8.9
Run 15	80.4	7.4	0.1	12.1
Run 16	82.9	7.5	0.1	9.5

**Appendix tab7. Ultimate (CHN) analysis of DOE**

Run	HHV average
Run 3	29.81
Run 4	37.66
Run 5	38.03
Run 15	37.95
Run 16	38.01

**Appendix tab8. HHV data of DOE**

Run number	Toluene	Ethylbenzene	Styrene	Alpha.-Methylstyrene	Cyclohexane, 1,3,5-triphenyl-
Run 3	0.00	0.00	26.10	1.29	10.96
Run 4	4.80	4.03	7.64	8.74	0.00
Run 5	2.30	1.58	8.80	6.30	0.46
Run 15	4.82	4.33	4.37	8.23	0.00
Run 16	4.02	1.79	21.04	7.45	0.00

Run number	Benzene, (1-methylethyl)-	N-Benzyl-1H-benzimidazole	1,2-Diphenylcyclopropane	Benzene, 1,1-(1,3-propanediyl)bis-	Other light compounds	Tar
Run 3	0.00	14.93	0.00	3.22	17.00	26.51
Run 4	1.29	3.11	1.64	11.56	17.48	39.70
Run 5	0.40	5.10	0.00	7.83	11.23	55.99
Run 15	1.54	0.93	0.64	8.23	5.94	60.96
Run 16	0.32	0.48	0.00	0.64	16.02	48.24

**Appendix tab9. GCMS-FID of DOE**