UNIVERSITAT POLITÈCNICA DE VALÈNCIA

Escuela Técnica Superior de Ingeniería Industrial

WASTE-TO-X: UNDERSTANDING PLASTIC PYROLYSIS USING A WIRE MESH REACTOR

Trabajo Fin de Grado

Grado en Ingeniería de la Energía

AUTOR/A: Berenguer Casco, Marcos

Tutor/a: López Sánchez, José Javier

CURSO ACADÉMICO: 2024/2025

Bachelor's Thesis
experimental

Waste-to-X: Understanding Plastic Pyrolysis Using a Wire Mesh Reactor

Marcos Berenguer Casco

BA 467
2024/10

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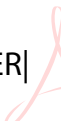|	
Title of Bachelor´s/ Master´s Thesis	Waste-to-X: Understanding Plastic Pyrolysis Using a Wire Mesh Reactor
Author:	Marcos Berenguer Casco
Enrolment number:	03795373
Supervisor:	Lukas Martetschläger
Assigned by:	Prof. Dr.-Ing. Hartmut Spliethoff Technical University of Munich Chair of Energy Systems Boltzmannstr. 15 DE-85748 Garching
Assigned:	15.04.2024
Handed in:	15.10.2024

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Acknowledgements

I would like to extend my deepest gratitude to my family and friends, who have been my cheerleaders, confidants, and companions. Thank you for your understanding, motivation, and the many moments of laughter and joy that helped me through the toughest days. I owe a special tribute to my two grandmothers, who, though no longer with us, continue to inspire me with their love.

To my tutor, Ieva Kiminaite, for her guidance, encouragement, and support throughout this journey, your expertise and patience have been invaluable in shaping this work. Finally, a big thank you to Clara Eckert, my workshop and lab partner, for your collaboration and the countless hours we spent together solving problems and sharing ideas.

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Abstract

Plastic waste poses as one of the most important problems related to environmental aspects and classical recycling methods have several limitations in treating large amounts of produced waste. The present study focuses on an alternative recycling method concerning one of the most used plastics, polystyrene. Pyrolysis was performed using a wire mesh reactor for converting polystyrene into chemicals and fuels of value, with emphasis on the improvement of yield. The influence of critical operating parameters, such as flash pyrolysis temperatures, holding times, and pressure levels, on the yield of volatiles was explored. A wire mesh reactor allowed high heating rates and effective decomposition of polystyrene. Additionally, the formed carbon black was analyzed for potential use.

The findings of our research show that in ideal conditions, both the yield and quality of tar significantly improve. It was noted that under specific conditions, temperature, pressure, and time all combined to enhance the conversion of polystyrene. Pyrolysis in a wire mesh reactor has great potential in the recycling of plastic waste into more value-added products and can indeed make environmental pollutants useful products. This work provides new insights into the disposal and valorization of waste polystyrene. Further research will be focused on process scalability studies, evaluating the efficacy of the process with several forms of plastic waste; hence, it offers a more applicable and sustainable waste management approach.

Key Words: Pyrolysis, Polystyrene, Wire Mesh Reactor, Carbon Black Analysis, Plastic Waste Recycling

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Abbreviations

Abbreviation	Meaning
AC	Alternating current
CO	Carbon monoxide
CO_2	Carbon dioxide
DTG	Derivative Thermogravimetric
HDPE	High density Polyethylene
ID	Intensity of the D band
IG	Intensity of the G band
K	Kelvin
PC	Polycarbonate
PET	Polyethylene terephthalate
PP	Polypropylene
PS	Polystyrene
PVC	Polyvinyl chloride
SFOR	Single First Order Model
SF	Shenfu coal
TGA	Thermogravimetric Analysis

Notation

Latin Symbols

Symbol	Unit	Explanation
c_v	%	Volatile matter concentration
E_a	J/mol	Activation energy
k_0	$1/s$	Pre-exponential factor of the SFOR
k	$1/s$	Reaction rate constant
m	kg, g	Mass
p	bar, MPa	Pressure
R	$J/(mol * K)$	Universal gases constant
T	$K, ^oC$	Temperature
t	s	Time
Y_v	%	Volatile yield

Greek Symbols

Symbol	Unit	Explanation
∞	-	Infinite
ρ	-	Model parameters of the SFOR to describe the temperature influence
θ	-	Model parameters of the SFOR to describe the influence of pressure
σ	-	Standard deviation

Indices

Symbol	Explanation
e.g.	For example,
empty	Empty mesh
exp	Exponential
filled	Mesh after being filled
final	Final
max	Maximum
min	Minimum
p	As a function of pressure
Rkt	After reactor
set	Self-selected reference value
T	As a function of temperature
$wt\%$	Volatile yield %

1 Introduction

1.1 Motivation

Plastic is a highly used material in modern life due to its versatility, durability, and low cost. However, its widespread use has led to significant environmental and health concerns, as the production and disposal of plastic are often not conducted in an environmentally sound or safe manner. One of the most pressing challenges is plastic pollution, which continues to escalate globally. The amount of plastic waste generated is growing rapidly, raising concerns about future waste management. In 2016 alone, global plastic production reached 335 million tons, with Europe contributing 60 million tons. This production rate is expected to double within the next 20 years (Drzyzga and Prieto 2019). Such growth highlights the urgent need for improved strategies in managing plastic waste, particularly through recycling and alternative disposal methods.

As can be seen in Table 1.1, the evolution of plastic production has increased significantly over the years.

Table 1.1: Global plastic production between 1950 and 2020 (Kabeyi and Olanrewaju 2023)

Year	Production (million tons)
2020	400
2015	322
2014	311
2013	299
2011	280
2009	250
2002	200
1989	100
1977	50
1950	1.5

Plastic is a non-biodegradable material (Asuquo 2018). Therefore, pollution is one of the greatest environmental challenges in modern times. Plastic waste ends up in the environment mainly through the process of landfilling and exportation to other countries, predominantly from high-income, developed countries (Belioka and Achilias 2024). This contributes to massive negative impacts on ecosystems affecting terrestrial, freshwater, and marine environments. The presence of microplastics further enhances these issues into general environmental and health concerns. Subsequently these plastics find their way into the fields mixed with other decomposing materials. As for plastics, they are non-biodegradable, so that they will remain on farmland, which consequently has a negative impact on the environment. (Prabhash Kumar 2018)

The conventional methods of plastic disposal, such as landfilling and burning, result in loss of resources and have disadvantages environmentally (Zink et al. 2018). Therefore, innovative approaches to effectively managing plastic waste are urgently needed. Conventional practices are landfilling and incineration, which entails losses of valuable resources and involve high environmental risks, such as soil contamination and air pollution. Mechanical recycling, though preferred in the sustainable options, faces significant bottlenecks in view of the low recyclability of many plastic types. (Kibria et al. 2023)

Pyrolysis is a promising approach for converting plastic waste into valuable chemical feedstocks and fuels. Unlike mechanical recycling, which is limited by the need for clean and sorted plastic, pyrolysis can process mixed and contaminated plastic waste, making it a more versatile solution. This method offers potential for more sustainable plastic waste management by breaking down polymers into simpler compounds that can be repurposed in various industrial applications. (Manam 2022).

As illustrated in Figure 1.1, taken from (Asuquo 2018), the primary purposes of recycling include reducing air and water pollution, lowering greenhouse gas emissions, and decreasing energy usage. Another important role of recycling is to save the use of fresh raw materials as well as to prevent the waste of valuables. These are some of the reasons why recycling should form part of a broad approach in managing solid waste to achieve sustainable development.
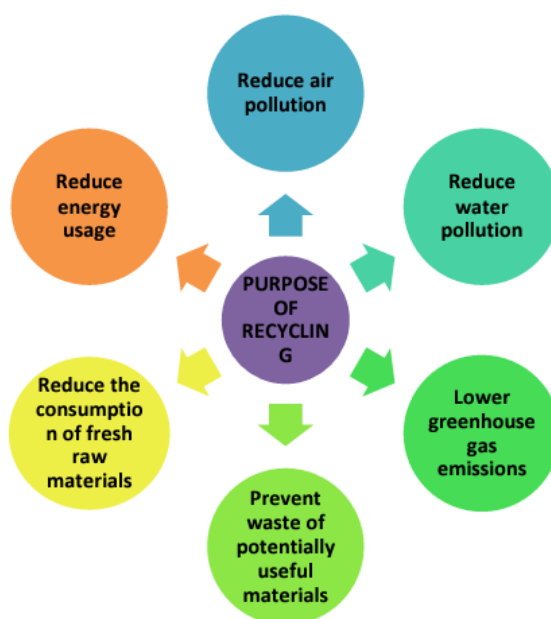
Figure 1.1: Purposes of recycling. (Asuquo 2018)

Of all the modern technologies for dealing with plastic waste, such as incineration, mechanical recycling, and chemical recycling, flash pyrolysis stands out as particularly promising. Flash pyrolysis is a thermochemical process during which organic materials are rapidly heated. (Hopewell Jefferson, Dvorak Robert and Kosior Edward 2009). Pyrolysis offers several advantages compared to the other methods. Pyrolysis accepts mixed and contaminated plastics; it can recover energy and produce reusable chemicals (Qureshi et al. 2020).

Flash pyrolysis distinguishes itself from other traditional pyrolysis methods due to its much higher heating rates (often exceeding 1000 ºC per second) and significantly shorter reaction times (typically less than 2 seconds). While conventional pyrolysis methods require longer residence times and slower heating rates, flash pyrolysis offers a more energy-efficient and cost-effective alternative for the rapid conversion of plastic waste into valuable products (Butler et al. 2011). These advantages make flash pyrolysis a particularly appealing technology in the context of large-scale plastic waste management.

As we can see in the following Figure 1.2, taken from (Eze et al. 2021), the different alternatives for plastic waste recycling nowadays. Most current practices involve mechanical recycling, incineration, and landfilling. Mechanical recycling often results in downcycling, where the recycled plastic exhibits inferior mechanical properties compared to the original material, such as reduced strength or durability. While mechanical recycling is effective for some types of plastics, it is limited by the degradation of material quality with each cycle. On the other hand, incineration, though capable of recovering energy through heat generation, also releases pollutants and greenhouse gases into the atmosphere. However, modern incineration systems have been developed to mitigate these emissions by incorporating advanced filtration technologies that reduce the release of harmful pollutants from the fumes. Landfilling, which is the least sustainable process, generates long-term environmental contamination. (Schade et al. 2024)
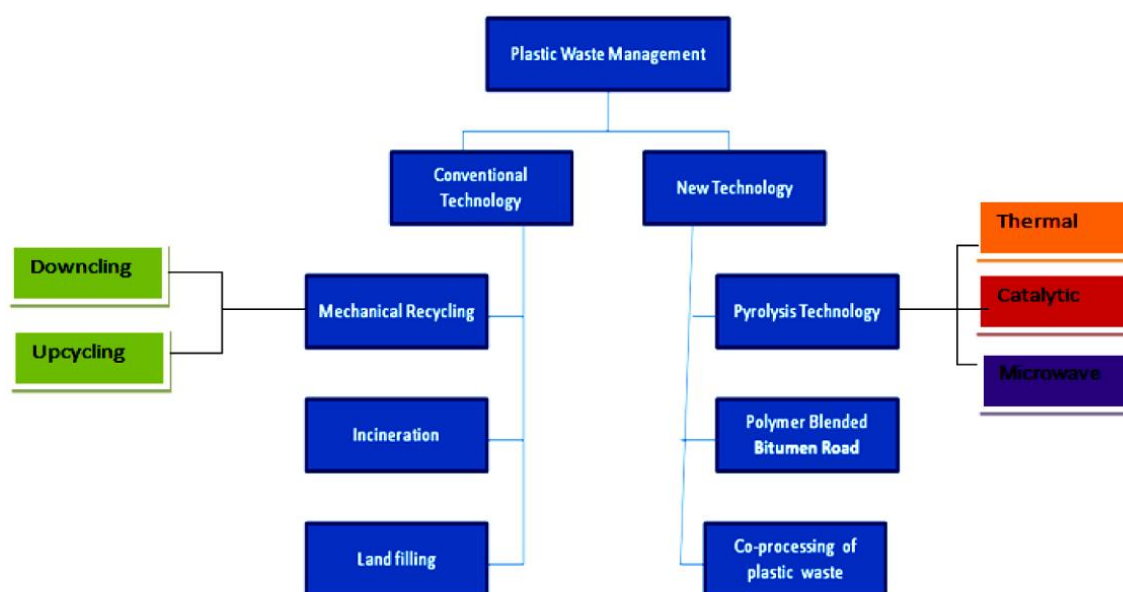
Figure 1.2: Conventional and new technology for plastics waste management (Eze et al. 2021)

The main advantage and one of the variants of flash pyrolysis that showed a high interest is its implementation in wire-mesh reactors on a small scale. Compared to traditional reactors, wire mesh reactors demonstrated higher heat and mass transfer rates (Westerhof, Roel & Brilman, Wim & Van Swaaij, Wim & Kersten, Sacha Industrial 2010).

Several crucial challenges in developing effective pyrolysis technologies include, among others, a detailed kinetic analysis that would help understand the reaction mechanisms and rates better (Lopez et al. 2018). Kinetic analysis is important in finding optimum operating conditions that would maximize yields of desirable products. It is also very critical to evaluate the process scalability for its environmental and economic viability to ensure that flash pyrolysis can be implemented as a feasible sustainable solution for the management of plastic waste. (Alvarado Flores et al. 2022)

Interest in studying the application of flash pyrolysis using wire mesh reactors for plastic recycling is motivated by the need to find a solution for the rising problem of plastic pollution and, at the same time, considering the possible value plastic waste could have as a renewable resource. Thus, by converting plastic wastes into valuable products using thermochemical processes like flash pyrolysis, we contribute to reducing environmental pollution, reducing dependency on fossil fuels, and promoting a circular economy (Slopiecka et al. 2012).

In addition to the environmental point of view, this offers high economic advantages. The products recovered in this process could include, i.e., oil, gas, and char, which in turn can be utilized as feedstocks or raw materials for a number of different products in the manufacture of fuels, chemicals, and other industrial materials. (Uçkun Kiran et al. 2014).

This study contributes to addressing the knowledge gaps related to the devolatilization kinetics of PS in flash pyrolysis. By investigating the influence of temperature and pressure on the release of volatiles, we have gained valuable insights into optimizing the conditions

for the efficient conversion of PS into useful products. These findings could inform the development of more effective methods for plastic waste treatment, particularly in processes that prioritize energy recovery and resource valorization. and knowledge gaps related to this area will contribute to the development of practical solutions that support the transition towards a more sustainable and circular economy (Brewer et al. 2011).

1.2 Task

This bachelor's thesis investigates the conversion of plastic waste into valuable products through flash pyrolysis using a wire mesh reactor. The study aims to address key knowledge gaps by exploring the effect of temperature, holding time, and pressure on the devolatilization of polystyrene during pyrolysis. By focusing on these variables, the research seeks to optimize the process for more efficient plastic waste treatment.

A key objective of the thesis is to estimate the kinetic parameters of PS flash pyrolysis using the Single First-Order Reaction model. This model helps describe the relationship between temperature and reaction rates, providing a deeper understanding of the pyrolysis process. The characterization of pyrolytic carbon deposits from PS is also an important focus, as it offers insights into the by-products formed during pyrolysis and their potential applications.

Furthermore, the study involves a comparative analysis of the results obtained from PS pyrolysis with those from a parallel study on polypropylene pyrolysis. This comparison helps identify differences in behavior between the two plastics under similar pyrolysis conditions, contributing to a broader understanding of plastic waste conversion.

The thesis also provides recommendations for improving the wire mesh reactor setup and optimizing process parameters to enhance efficiency and sustainability. The findings are discussed in the context of sustainable waste management, emphasizing the potential of flash pyrolysis as a solution to the growing problem of plastic waste.

1.3 Outline of the Thesis

The thesis is organized into a series of chapters that systematically address the research problem of plastic waste conversion via flash pyrolysis. Each chapter builds on the previous one to guide the reader through the investigation of the devolatilization kinetics of polystyrene under various conditions. The chapters cover the background and significance of the study, a detailed review of relevant literature, the experimental design and methodology, the presentation and analysis of results, and a discussion of the findings in the context of sustainable waste management.

The theoretical background on the thermochemical conversion process with special attention to pyrolysis technology is presented in Chapter 2, overviewing the influence of pyrolysis parameters, namely temperature, holding time, and pressure on the pyrolysis products distribution. Chapter 3 presents the experimental setup employed to analyze plastic pyrolysis kinetics via flash heating conditions. Finally, Chapter 4 presents experimental results obtained on thermochemical processing using pyrolysis and solid product characterization.

2 Thermochemical Conversion

2.1 Basics of pyrolysis

Pyrolysis is a process during which materials are thermally decomposed in an inert atmosphere, unlike combustion, which requires oxygen (Mohan et al. 2006), typically at temperatures ranging from 300 to 1000 ºC (Sharma et al. 2014). During this thermochemical process organic materials decompose into lower molecular weight compounds like gases, liquids–oils or tars, and the potential formation solid char. The process of meeting the varying needs of the products and the difficulties posed by the various types of feedstock has been the subject of extensive research (Qureshi et al. 2020).

Pyrolysis technology is applied across various sectors in need of sustainable green technology, including waste management, renewable energy production, and sustainable agriculture. Pyrolysis offers a sustainable solution by converting various types of waste, including biomass, agricultural residues, and plastic waste, into valuable products. This process contributes to resource efficiency and environmental sustainability by enabling the recovery of energy and materials from a wide range of organic and synthetic waste streams (Nurazzi et al. 2020).

Several key parameters influence the formation of pyrolysis products, including temperature, residence time, heating rate, and pressure. Temperature plays a critical role, as higher temperatures accelerate the decomposition of the feedstock, impacting both the yield and the composition of the resulting products. Similarly, the residence time—how long the feedstock and its volatile products remain at the pyrolysis temperature—affects the distribution of gases, liquids, and solids produced. In addition, the heating rate and pressure also significantly influence the conversion process, as rapid heating and specific pressure conditions can lead to different product compositions and yields. (Zhao et al. 2018)

Figure 2.1 below, taken from (Maqsood et al. 2021), illustrates the typical process involved in the pyrolysis of plastic waste, detailing each step from the initial preparation of raw materials or feedstock to the final product recovery.
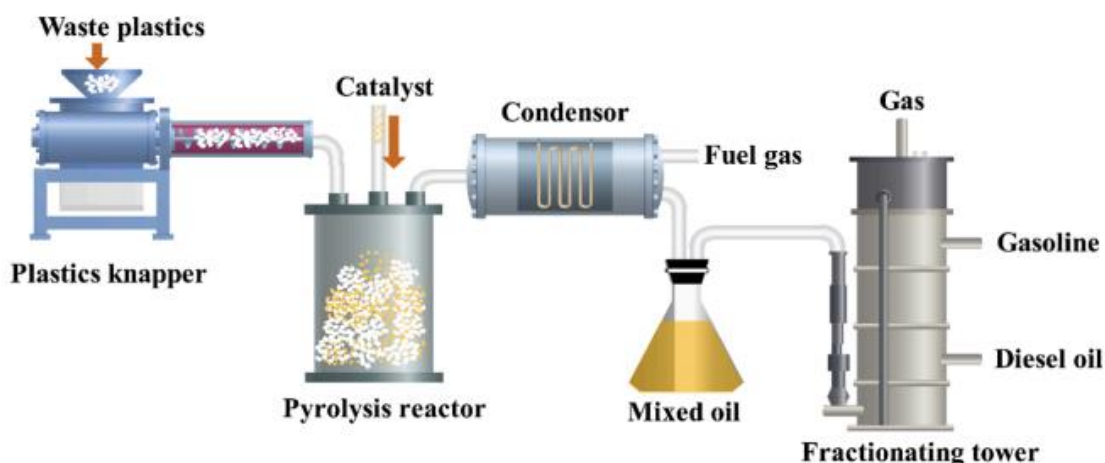
Figure 2.1: Flowchart of the plastic waste pyrolysis process (Maqsood et al. 2021)

Slow, fast, and flash pyrolysis are the three categories into which all current pyrolysis processes can be divided in terms of heating conditions (Al-Rumaihi et al. 2022). Flash pyrolysis is particularly effective for valorizing polystyrene, which accounts for 6% of total plastic consumption in the EU. The process has been extensively investigated for its ability to recover monomers, particularly styrene. The process of thermal degradation during PS pyrolysis occurs through a mechanism that involves the initiation of a radical, depolymerizing propagation, and radical coupling; the process evolves with an increase in temperature (Artetxe et al. 2015). Conditions of 470–505°C are considered the temperature range at which, according to the research of (Mo et al. 2014), the styrene yield is highest. Higher heating rates increase the amount of styrene produced while keeping the yields of gases within a certain range to prevent secondary reactions from taking place. Because of this, flash pyrolysis is a very effective method to recycle polystyrene and other waste plastics.

Common reactor setups for pyrolysis include fixed-bed reactors, fluidized-bed reactors, and rotary kiln reactors, each chosen based on operational needs and the characteristics of the feedstock. Fixed-bed reactors are relatively simple, suitable for batch processes, and are often used when precise control over temperature is required. However, they can have limited scalability and heat transfer, making them less ideal for large-scale operations (Motasemi and Afzal 2013). Fluidized-bed reactors are commonly selected for continuous pyrolysis processes, especially when high heat transfer efficiency and uniform temperature distribution are needed. This reactor type is widely used in industrial applications for processing biomass and waste plastics due to its ability to handle large volumes and varied feedstocks (Muhammad et al. 2015). Rotary kiln reactors, meanwhile, are chosen for continuous processes involving heterogeneous or bulky materials, as their rotating design ensures better mixing and heat distribution throughout the material (Andreas Hornung 2014). Each reactor type is selected based on simplicity, efficiency, and scalability, making them suitable for different pyrolysis goals and feedstock types.

In this study, a wire mesh reactor will be used, chosen for its ability to achieve rapid heating rates and precise control over temperature and residence time. This type of reactor

is particularly useful in flash pyrolysis, where short reaction times and efficient volatile release are important. This type of reactor configuration is especially beneficial for studies concerned with pyrolysis kinetics since it enables high heating rates and accurate control of pyrolysis parameters, hence giving extensive knowledge on the thermal decomposition of polystyrene.

From an environmental perspective, pyrolysis helps reduce greenhouse gas emissions and mitigates plastic pollution by converting waste into useful resources. Economically, it presents opportunities for generating revenue through the production of biofuels, chemicals, and renewable energy sources, thereby fostering economic growth and job creation in related industries (Lubongo et al. 2022).

In essence, pyrolysis represents a promising technology that addresses both environmental challenges and economic opportunities by converting organic materials into valuable products while promoting sustainability.

2.1.1 Chemical description of pyrolysis

The pyrolysis of plastics, including polystyrene, follows a free-radical chain reaction mechanism. This process starts with the initiation phase, where high temperatures cause the homolytic cleavage of bonds in the polymer chain, creating free radicals. In PS, the C-C bonds break to form styrene radicals (Devi et al. 2020). Following this, during the propagation phase, these radicals react with the polymer, causing further bond breaking and generating more styrene monomers, dimers, and oligomers (Manos et al. 2000). The termination phase occurs when radicals combine, forming stable molecules like gases or oils (Cuevas et al. 2024). This mechanism controls the overall breakdown of plastics into smaller molecules during pyrolysis.

These reactions are highly dependent on various factors, such as temperature, pressure, which can significantly influence the yield and composition of the final pyrolysis products (Cuevas et al. 2024).

Polystyrene primarily degrades into styrene monomers through random chain scission. The majority of PS pyrolysis yields styrene due to the stability of the styrene radical, with product yields reaching up to 70% under ideal conditions. Secondary reactions convert some styrene into toluene, benzene, and other light hydrocarbons. High temperatures or extended residence times may also lead to the formation of oligomers or tars, which reduce the overall monomer yield. (Marcilla et al. 2009)

2.1.2 Pyrolysis products

Wide range of products with different properties and applications can be produced during pyrolysis process. The main products groups of pyrolysis include gases, liquids, and solid residues. Each of these has distinct and unique characteristics and applications.

The main and most significant product of slow plastic waste pyrolysis is liquid oil, making it very valuable for further analysis (Lu et al. 2021). The liquid oil can have a yield, that depends on the feedstock composition, of up to 90 wt%. By-products include gases (ranging from 3 to 90.2 wt%), wax (0.4 to 92 wt%), char (0.5 to 78 wt%), and HCl (0.1 to 58 wt%) (Maqsood et al. 2021). The yields and properties of these pyrolysis products are significantly influenced by factors such as the type of plastic, the pyrolysis method employed (slow, fast, or flash pyrolysis), the type of reactor used, and the particle size of the feedstock (Maqsood et al. 2021).

As mentioned before, in addition to liquid products, pyrolysis of plastics produces a hydrocarbon-rich gas that is perfect for energy recovery because it has a heating value of 25–45 MJ/kg (Oasmaa et al.), depending on the plastic feed and conditions. At elevated temperatures, above 600 ºC, pyrolysis promotes the production of these hydrocarbon-rich gases rather than liquid products (Tokmurzin et al. 2022). In addition to hydrocarbon gas production, small amounts of other aromatic compounds, such as benzene, toluene, α-methyl styrene, diphenyl propane, styrene dimer, and styrene trimer, are also generated (Supriyanto et al. 2021).

The solid residue resulting from pyrolysis, known as char, is composed mostly of carbon atoms, along with certain inorganic minerals that have not been affected by the high temperatures of the process (Zhao et al., 2017). Char contains residual materials such as sand, glass, and metals. This solid fraction typically has a heating value ranging from 10 to 35 MJ/kg and a char content by weight of 20–50% (Shah et al. 2022). Additionally, the use of char as a soil amendment has gained popularity and, if it achieves significant expansion, could substantially aid in mitigating climate change (Lehmann & Joseph, 2009).

In conclusion, pyrolysis produces a range of valuable and diverse products such as liquid oil, gases, and char, with different properties and uses. The primary product, liquid oil, can yield up to 90% and is used in a variety of industrial applications. The gaseous product obtained has a high calorific value, ideal for energy recovery. Char, mainly made of carbon and inorganic minerals, finds several applications: as catalysts, soil amendments amongst others. Efficiency in pyrolysis, as well as the distribution of products, depends on the type of plastic, method of pyrolysis, and operational conditions. Optimization, therefore, is very important to achieve its full potential in sustainable plastic waste management.

2.1.3 Product use

Pyrolysis produces several valuable products, each with distinct applications based on its unique properties: gases, liquids, and solids. This products of plastic pyrolysis—solids, liquids, and gases—vary depending on the process temperature (F.J. Mastral et al. 2001).

The liquid oils produced from pyrolysis exhibit qualities comparable to those of conventional fuels, making them a viable renewable energy source (Aisien 2023). These liquid oils produced by pyrolysis of a plastic waste mixture provide a distillation profile similar to commercial gasoline. Moreover, these oils contain quantities of diesel fractions, and light hydrocarbons; therefore, they have a potential for fast pyrolysis with a heat to produce transportation fuels and chemicals. (Zhang et al. 2020)

A major plastic pyrolysis product, the solid residue known as char, is rich in carbon and inorganic minerals. Char's high surface area and adsorption capacity make it valuable for various applications. A common use of char is its conversion into activated carbon, which is crucial for air and water purification due to its ability to absorb contaminants (Zhao et al., 2017). Char also finds application as a soil amendment in agriculture, when applied to soil, it improves water retention and nutrient availability, and sequesters carbon, which is essential for climate change mitigation (Lehmann & Joseph, 2009). Finally, char can serve as a precursor to produce various chemicals, making it valuable across many industrial sectors (Rafique et al., 2020).

Generally, the characteristics and properties of the resultant char depend on the composition of the material being pyrolyzed, so its specific applications are heavily dependent on it. Considering its surface area and porosity, the main applications of char are as an adsorbent; nevertheless, the possible applications of char go beyond the traditional uses to include such emerging areas as char-based sensors and supercapacitors (Martín-Lara et al. 2021).

Another relevant pyrolysis product, pyrolytic carbon, is widely studied due to its diverse applications, from electrodes in electrochemical cells to biomedical implants (Dresselhaus et al. 2005). Understanding its structural properties is essential for optimizing its performance in these applications. As an outcome, in this study we characterized the carbon residues using Raman spectroscopy after the experiments. Raman spectroscopy is a powerful, non-destructive tool used to characterize carbon materials, providing valuable information about their molecular and structural properties (A. C. Ferrari and J. Robertson 2000).

Overall, the diverse applications of pyrolysis products demonstrate the significant potential of this technology in energy production, chemical synthesis, environmental management, and agriculture. By optimizing these applications, pyrolysis can become a valuable technology for sustainable resource management and reducing reliance on traditional fossil fuels.

2.2 Thermodynamics and kinetics of pyrolysis

This chapter presents the effects of pyrolysis on plastic waste, establishing a foundation for comparison with previous studies and informing preliminary predictions for the experiments conducted in this research. By examining how different parameters influence the yield and distribution of pyrolysis products, this analysis provides a baseline for optimizing process conditions and enhancing the conversion efficiency of plastic waste into valuable products. The general physical and chemical trends on the yield and composition of pyrolysis products will be outlined and explained below. These trends are primarily based on findings from previous research on the pyrolysis of different plastic fractions and solid fuels, along with fundamental physical and thermodynamic assumptions.

The thermogravimetric analysis (TGA) study aims to examine the thermal degradation behavior of the fuel sample under pyrolysis conditions by monitoring its weight loss as a function of temperature. This analysis provides insights into the decomposition pattern, while the derivative thermogravimetry (DTG) is used to measure the rate of weight loss. These techniques help characterize the thermal stability of the material and the key decomposition stages, but are not directly used for kinetic modeling in this study. (Royuela et al. 2024).

2.2.1 Influence of temperature

Temperature plays a critical role in pyrolysis kinetics and product distribution, as it directly influences the rate of decomposition and the yield of volatile products. Figure 2.2 (López et al. 2011) illustrates the derivative thermogravimetric (DTG) plot for the decomposition of five different plastic types: polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET), and polyvinyl chloride (PVC). The figure shows that each plastic type decomposes over distinct temperature ranges, reflecting their varying thermal stability.

The use of derivative thermogravimetric analysis is important because it provides detailed insights into the rate of mass loss at different temperatures, allowing us to precisely identify the key decomposition stages of each plastic. This data is crucial for optimizing pyrolysis conditions, as it enables the identification of temperature ranges that maximize volatile release or target specific products (Demirbas 2004). By understanding how different plastics behave thermally, we can better predict product yields and improve the efficiency of the pyrolysis process, ensuring more controlled and effective waste conversion.
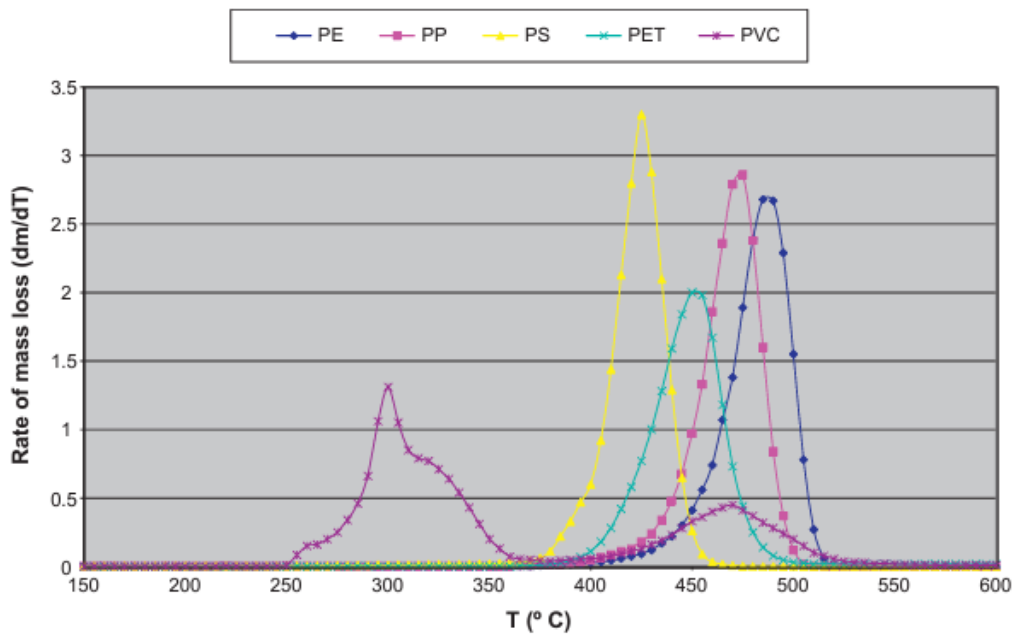
Figure 2.2: Derivative thermogravimetric (DTG) plot of the individual plastics (López et al. 2011)

The peaks in the graph represent the maximum rates of mass loss, which correspond to the most rapid phase of degradation for each plastic. The peak temperatures indicate when decomposition is at its highest, while the start and end temperatures show the range over which decomposition occurs.

The variations of the distinct thermal degradation behaviors highlight the importance of understanding the thermal stability of each plastic type. This information is critical for optimizing pyrolysis conditions, as adjusting the temperature can control the release of volatile products, ensuring efficient conversion of plastic waste into useful resources.

In the work of (Riesco-Avila et al. 2022), the effects of temperature and heating rate on the pyrolytic yield of a plastic waste mixture, primarily composed of PP, HDPE, and LDPE, were assessed. By evaluating temperatures between 380 and 460°C, the research aimed to identify optimal conditions for maximizing product yield in pyrolysis. Understanding these effects is essential for developing more efficient conversion processes, as the findings can inform adjustments in temperature and heating rate to enhance resource recovery from mixed plastic waste.
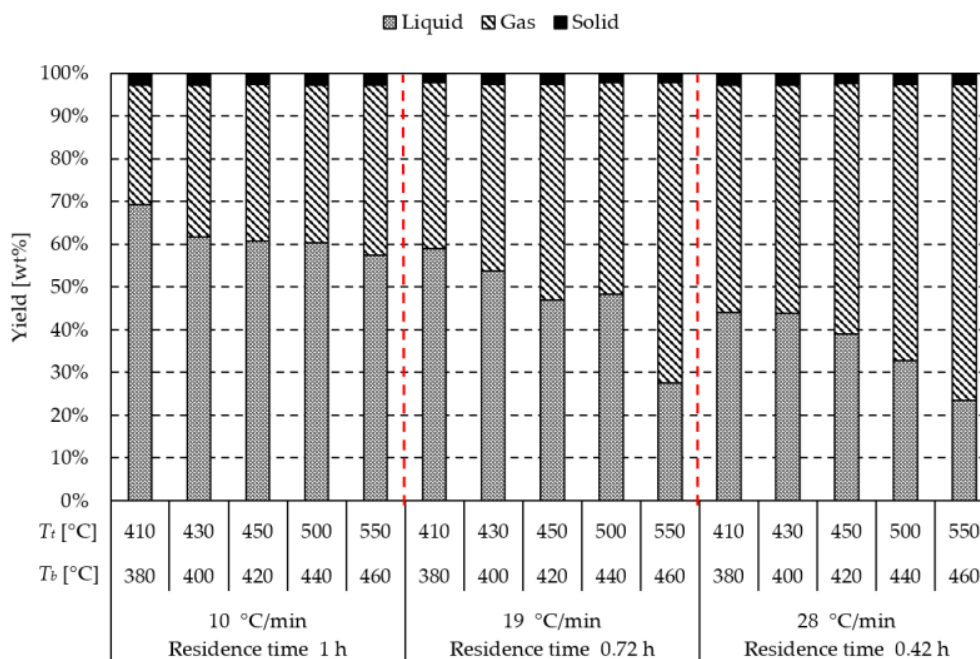
Figure 2.3: Pyrolytic-process yields (Riesco-Avila et al. 2022)

Figure 2.3 illustrates how temperature and heating rate influence the yield of the pyrolytic process. The data indicates that lower temperatures combined with longer residence times (low heating rates) favor maximum liquid production, as the slower heating allows for more complete conversion to condensable products. Conversely, higher temperatures and shorter residence times (high heating rates) increase the yield of gaseous products. However, this comes at the expense of overall pyrolytic yield, as elevated temperatures can lead to secondary reactions that reduce liquid and solid product formation. This understanding is essential for optimizing pyrolysis based on desired product outputs.

2.2.2 Influence of the holding time

Generally, longer holding times in pyrolysis result in an increased production of volatile compounds. This prolonged reaction allows for a more complete breakdown of the feedstock, which in this case is polystyrene plastic waste (Shaaban et al. 2014). In the study by Miandad et al., the effects of temperature and reaction time on the yield and quality of liquid oil produced from polystyrene pyrolysis were investigated. The findings showed that both factors play a crucial role in determining the efficiency and output quality of liquid oils derived from polystyrene.
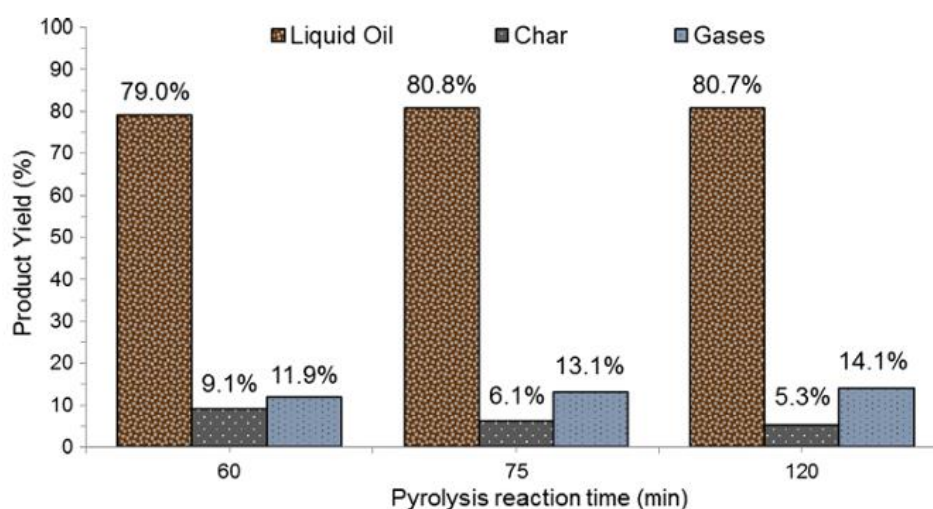
Figure 2.4: Effect of reaction time on polystyrene pyrolysis liquid oil, char and gas product yields at constant temperature (Miandad et al. 2016)

As can be seen in Figure 2.4, the study found that liquid oil yield was nearly the same at 75 and 120 minutes, while char production was slightly higher at 75 minutes. This suggests that extending the reaction time beyond 75 minutes does not significantly affect the yields, making 75 minutes the optimal reaction time. A shorter reaction time of 60 minutes leads to more char and less oil, showing it is not adequate for maximum conversion efficiency. These findings emphasize the importance of optimizing reaction time in the pyrolysis of polystyrene to achieve the best balance between liquid and char yields.

2.2.3 Influence of the heating rate

The heating rate and holding time are influenced by different factors, with the heating rate being primarily controlled by the desired rate of temperature increase, while holding time is more dependent on the reactor configuration. In the work of (Nisar et al. 2019), Figure 2.5 shows weight loss curves of polystyrene waste at different heating rates ranging from 5 to 20 ºC/min. The results show that higher heating rates lead to faster decomposition, which is critical for optimizing process conditions to control the rate and distribution of pyrolysis products efficiently.
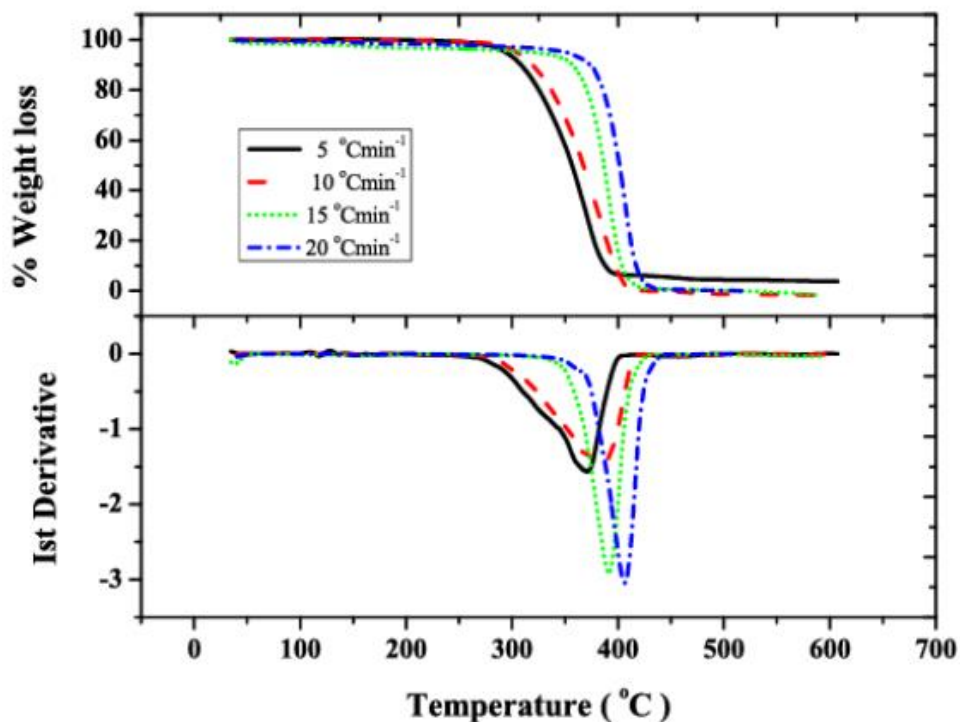
Figure 2.5: Thermograms of polystyrene waste in nitrogen atmosphere at different heating rates

The observed degradation is attributed to the degradation of polymer chains. The thermogravimetric analysis (TGA) curves indicate that an increase in the heating rate results in a shift of the decomposition towards higher temperature regions. At lower heating rates, thermal equilibrium is achieved more rapidly, leading to a stabilization of the degradation process. This behavior is due to the gradual distribution of heat throughout the material and the residence time of the sample at the temperature.

Understanding the influence of heating rate on the thermal decomposition of plastics is essential for optimizing pyrolysis processes. While polystyrene is the primary focus of this study, it is valuable to assess whether similar behaviors are observed in other plastics, such as polypropylene. By comparing the decomposition patterns of different types of plastics under varying heating rates, we can determine if these materials exhibit consistent thermal

responses. This analysis will help generalize findings across plastic types, contributing to more versatile and efficient pyrolysis applications.

We can find another similar study in the work of (Nisar et al. 2018), using a different plastic fraction, in this case, polypropylene. Figure 2.6 shows the weight-loss curves of polypropylene at different heating rates, ranging from 5 to 20 ºC per minute. The figure indicates that as the heating rate goes up, the maximum temperature values also increase.
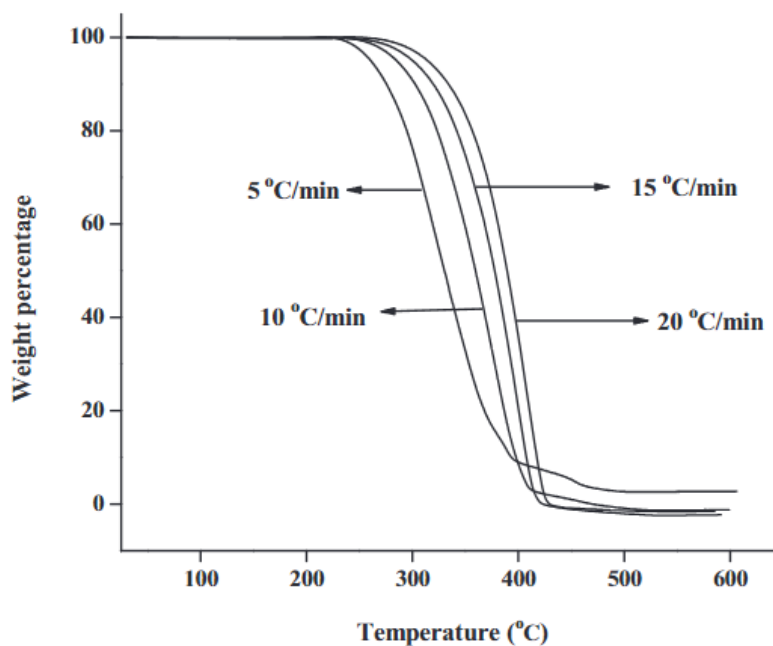
Figure 2.6: Thermograms of polypropylene in nitrogen atmosphere at different heating rates (Nisar et al. 2018)

2.2.4 Influence of pressure

In the study by Schubert et al., test runs with low-density polyethylene (LDPE) at pressures of 2, 5, and 10 bar produced varying amounts of liquid and gaseous products. The results indicated that higher pressures promote the formation of shorter hydrocarbon chains, as increased pressure enhances cracking reactions, resulting in more active bond breakage. Additionally, elevated pressures were found to reduce the amount of unconverted feed, suggesting that higher pressure conditions can improve the efficiency of the pyrolysis process by facilitating more complete decomposition of the LDPE material.
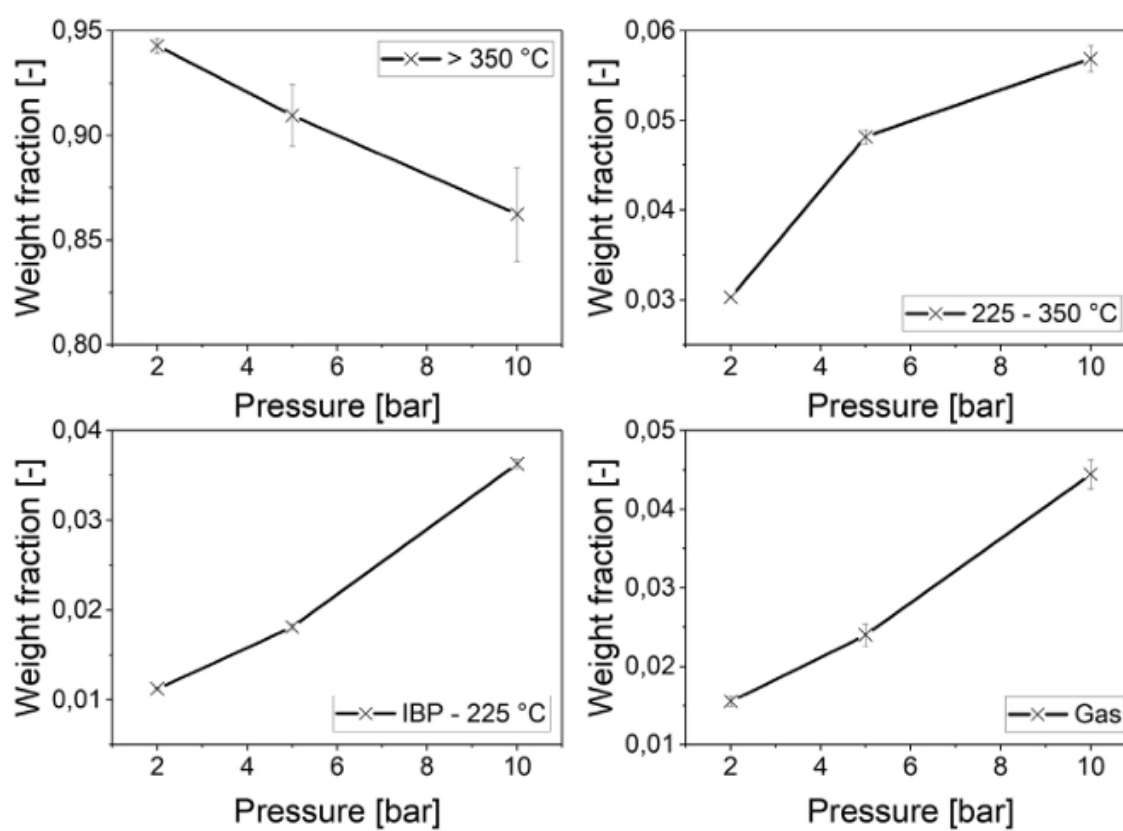
Figure 2.7: Relative product yields in dependence of the reactor pressure (Schubert et al. 2019)

These findings align with previous observations that higher pressures influence pyrolysis product distribution by enhancing decomposition processes. This trend, shown in Figure 2.7, contradicts expectations based on Le Chatelier's principle (Andreas Lechleitner et al. 2006), but can be explained by several factors. Higher pressure may inhibit evaporation, reducing the vapor fraction and increasing residence time, while also improving heat transfer to the liquid phase. Additionally, it may directly enhance chain scission reactions, leading to more chain breaks under otherwise identical conditions. (Schubert et al. 2019)

2.2.5 Influence of the mixture composition

Apart from the impact of process parameters on the devolatilization kinetics of plastics, as discussed in the previous chapters, the chemical and structural composition of the fuel or feedstock is also a crucial factor in determining the volatile release (Zámostný et al. 2010). The study of Klaimy et al. (KLAIMY et al. 2021), aimed to evaluate how mixture composition affects pyrolysis oil yield and composition. A model mixture representing plastic waste was created, and virgin plastics (PP, PE, PS, and PET) were pyrolyzed at 550 and 600 ºC. The pyrolysis of these plastics produced hydrocarbons, primarily aromatic compounds like benzene, toluene, xylene, and styrene. The experimental results of the main components formed during pyrolysis are presented in Table 2.1.

Table 2.1: Major compounds formed from the pyrolysis of the PP/PE mixture

	Experimental % at 550 ºC	**Experimental % at 600ºC**
Benzene	7	14
Toluene	19	14
Xylene	39	35
Styrene	65	64

As mentioned, results show that pyrolysis primarily produces aromatic compounds, with up to 55% in the oil fraction for PP and 31% for PE at 550 ºC. However, when mixed polymers, like a 50/50 ratio of PE and PP, are pyrolyzed, the amount of aromatic compounds, particularly xylene, increases significantly (39%). The model mixture also reduced the quantity of waxy compounds and produced more aromatics than expected. The results indicate pyrolysis may be harnessed to transform combined plastic waste into high-value aromatics, especially with the help of optimal conditions. Nevertheless, it is well known that the product produced, and its quality are functions of key process parameters such as heating rate and temperature. By manipulation of these parameters the distribution between liquid, gaseous and solid products can be influenced by changing to modify the process for recovery of specific compounds.

Similar findings are reported in the work of Miandad et al., as shown in Figure 2.8, which illustrates the effect of different plastic types on pyrolysis product yields, especially regarding liquid oil production. Mixing various plastics significantly altered the yields, with polystyrene contributing most to the liquid oil yield. In contrast, polyethylene tended to produce wax unless mixed with PS, highlighting the influence of plastic type and combinations on product distribution and composition. These results emphasize the importance of feedstock selection in optimizing pyrolysis outcomes.
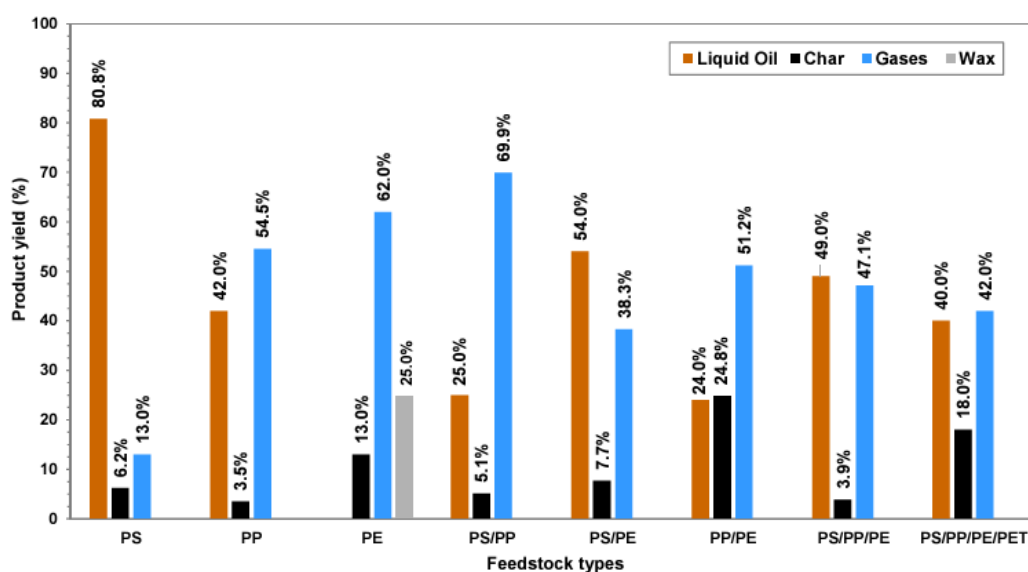
Figure 2.8: Effect of plastic waste types on pyrolysis yield (Miandad et al. 2017)

2.3 Single First Order Reaction Model

In kinetic studies on devolatilization, various mathematical models describing the rate of thermal decomposition are normally applied. The Malek method, while providing a quick overview of the reaction mechanism, has significant limitations. For instance, when experimental results fall somewhere between two theoretical models, the mechanism is unknown (Diaz Silvarrey and Phan 2016). Another approach, the heat conduction model, describes the transfer of thermal energy through a material due to a temperature gradient. This model is based on Fourier's Law of Heat Conduction, which states that the rate of heat flow through a material is proportional to the negative temperature gradient and thermal conductivity (S. J. Ojolo and S. O. Ismail 2012). In the present work, SFOR model has been adopted because of its simplicity and for being able to catch the overall kinetics of plastic pyrolysis. The SFOR model presents a simple structure to estimate the activation energy and reaction rate constants, thus being applied to analyze the devolatilization behavior of polystyrene in various conditions of pyrolysis.

The Single First Order Reaction (SFOR) model is used to analyze pyrolysis processes by simplifying them to a single first-order reaction. As seen in the work developed by Tremel (Tremel and Spliethoff 2013), this model assumes that pyrolysis can be described by a single kinetic reaction, which allows for predictions of the yield of volatile substances using a minimal set of parameters.

The SFOR model is particularly valuable because it enables the quantification of the effects of key thermodynamic parameters, such as temperature on pyrolysis yields. The model's simplicity makes it practical for modeling purposes, allowing for general predictions about the behavior of pyrolysis based on experimental data.

The detailed derivation of the equations shown in this chapter can be found in Appendix A, B and C.

2.3.1 Thermodynamic parameters describing pyrolysis

The model describes how pressure and temperature separately, and in combination, influence the yield of volatile components during pyrolysis.

Influence of temperature:

The model also describes the effect of temperature on the yield of volatile components. Temperature affects the rate of devolatilization, and this is modeled using a reference temperature T_{set} and a maximum temperature T_{max}, here the maximum volatile yield is achieved

The temperature dependence of the volatile yield is expressed by Equation 2.1:

(2.1)

$$\frac{dc_v}{dt} = -\theta c_v$$

The volatile concentration at time *t* is expressed with c_v. The rate constant that influences the rate of decline of the volatile concentration is expressed with θ.

The relationship between the volatile concentration and the yield is given by Equation 2.2:

(2.2)

$$c_{v,T} = c_{v,T_{set}} \cdot \frac{Y_v(T) - Y_{v,T_{set}}}{Y_{v,T_{max}} - Y_{v,T_{set}}}$$

The yield as a function of temperature is:

(2.3)

$$Y_v(T) = Y_{v,T_{set}} + \left(Y_{v,T_{max}} - Y_{v,T_{set}}\right) \cdot \left(1 - \exp\left(-\theta(T - T_{set})\right)\right)$$

This expression, Equation 2.3, shows that the volatile yield increases with temperature following an exponential trend, starting from the reference yield and approaching the maximum yield as temperature increases.

Influence of pressure:

The effect of pressure on volatile yield Yv at a reference pressure p_{set} is modeled by assuming an indirect proportionality between the rate of change of volatile yield and pressure. Equation 2.4 describes this relationship:

(2.4)

$$Y_v(p) = Y_{v,pset} - \left(ln\left(\frac{p}{p_{set}}\right)/\rho \right)$$

Where *p* is the operating pressure and *ρ* is a parameter representing the pressure influence, determined by least squares fitting using the setpoint pressure p_{set} = 1 bar and its respective volatile yield $Y_{v,pset}$.

The rate of devolatilization in the SFOR model, considering pressure, is given by Equation 2.5:

(2.5)

$$dY_v(t)/dt = A_v * exp\left(-E_{A,v}/(R*T)\right) * \left(Y_{v,final} - Y_v(t)\right)$$

Where A_v is the pre-exponential factor, related to the frequency of effective collisions leading to devolatilization and $exp\left(-E_{A,v}/(R*T)\right)$ is the Arrhenius term that shows how temperature (*T*) influences the reaction rate. Here $E_{a,v}$ is the activation energy and *R* is the ideal gases constant.

The final volatile yield dependent on pressure is further defined in Equation 2.6 as:

(2.6)

$$Y_{v,\text{final}}(p) = \Theta \cdot p \cdot Y_{v,p_{set}}$$

Where *θ* is a factor that accounts for the combined effects of temperature and pressure on the volatile yield.

Combined effects of pressure and temperature:

The combined influence of both pressure and temperature on volatile yield is represented by incorporating both factors into a single expression. The final volatile yield is expressed in Equation 2.7 as:

(2.7)

$$Y_{v,\text{final}}(p,T) = \Theta \cdot p \cdot Y_{v,p_{set},T_{set}}$$

The SFOR model reduces the complex pyrolysis process to a single first-order reaction, making it easier to predict volatile yields under different conditions. The model provides a strong framework for analyzing and optimizing pyrolysis processes in various operating environments because it considers only the temperature effect.

2.3.2 Kinetic parameters of pyrolysis

For a first-order reaction, the reaction rate is characterized by a temperature-dependent rate constant, which is defined using the Arrhenius equation:

(2.8)

$$k = k_0 \cdot exp\left(-\frac{E_a}{RT}\right)$$

Where k is the reaction rate constant, which depends on temperature, and k_0 is the pre-exponential factor or frequency factor

The focus is on maximizing the yield of volatile products, this maximum yield of volatiles (final yield after the reaction has completed) is represented with $Y_{v,\infty}$. The release of these volatile components can be considered a single reaction, assuming other reactions are negligible. The kinetic model used in this case is the SFOR model, which assumes that the release rate of volatiles follows first-order reaction kinetics:

(2.9)

$$\frac{dY_v(t)}{dt} = k_0 \exp\left(-\frac{E_a}{RT}\right)\left(Y_{v,\infty} - Y_v(t)\right)$$

The determination of Arrhenius parameters involves measuring the overall reaction rate constant, which is derived from experimental data under various temperatures and pressures. To determine the Arrhenius parameters, E_a and k_0, the least squares fitting method was used to reduce the error between the model's predictions and the experimental data. The parameters are iteratively optimized to achieve the best fit while minimizing the residual sum of squares. This method allowed us to accurately determine the kinetic parameters by identifying the values that best matched the observed data at various temperatures and pressures.

2.4 Polystyrene characterization

This chapter provides an overview of the polystyrene (PS) plastic studied in this thesis, detailing its thermal properties, chemical composition, and structural characteristics compared to other common pyrolysis feedstocks. Key properties such as heat resistance, molecular weight, and carbon content are examined, as they are essential for evaluating its

behavior under pyrolysis conditions. A thorough characterization of PS allows for a meaningful assessment of its conversion efficiency and product distribution, offering insights into its suitability relative to other plastics like polyethylene and polypropylene.

In recent years, there has been a growing interest in investigating the potential of polystyrene as a fuel source, particularly in waste-to-energy applications. This paper seeks to characterize the properties of polystyrene, with a focus on its pyrolysis behavior and potential use as an alternative fuel. These properties will also be compared to other plastics and traditional fuels.

2.4.1 Polystyrene

Polystyrene, a hard and inexpensive plastic, is one of the most significant and commonly used materials (Capricho et al. 2022). Polystyrene is a polymer widely used in various applications due to its heat resistance, lightweight nature, and good strength and durability. It is commonly found in products like packaging materials, household appliances, and computer housing. A variety of products, such as packaging, home appliances and computer housing, are among the applications. PS comes in two forms: expanded and solid, and they can be recycled in both. Expanded polystyrene (EPS) is lightweight and often used for insulation and packaging, while solid PS is denser and used in more durable applications. The recyclability of PS in both forms enhances its sustainability for industrial use. (Maafa 2021)

Analyzing the main properties of the PS sample, it is revealed as a carbon-rich feedstock with a high volatile content. These characteristics suggest that PS is highly suitable for thermochemical recycling through pyrolysis, leading to high yields of pyro-oil and styrene depending on the conditions. (Royuela et al. 2024)

Table 2.2 presents the proximate analysis values of three ASR samples from the literature, which were used in earlier studies to examine pyrolysis behavior.

Table 2.2: Proximate analysis of PS

Literature	(Prathiba et al. 2018)	(Ahmad et al. 2020)	(Basha y Sulaiman 2020)
Moisture (%)	0.01	0.00	-
Fixed carbon (%)	1.07	0.22	0.40
Volatile matter (%)	95.87	99.78	99.6
Ash (%)	3.05	0.00	0.00

All three sources confirm that polystyrene has a very high volatile matter content, ranging from 95.87% to 99.78%, and low fixed carbon content. However, there is significant variation in ash content; one source reports 3.05% due to possible contamination or additives, while another reports no detectable ash.

2.4.2 Comparison with other fuels

Using the literature to establish a foundation for comparison in the categorization of polystyrene as a pyrolysis fuel, average proximate values for coal (Craig J. Donahue and Elizabeth A. Rais) and biomass (Shen et al. 2010) are displayed below, as well as PS and other plastic fractions (N. Othman, N. E. A. Basri, M. N. M. Yunus, L. M. Sidek 2008).

Proximate analysis of coal measures the moisture, volatile matter, fixed carbon, and ash content in a coal sample. This analysis involves heating the coal to 900 ºC in a nitrogen atmosphere, then maintaining it at 900 ºC while switching the atmosphere to air, and measuring the mass loss during these steps. (Craig J. Donahue and Elizabeth A. Rais)

Table 2.3: Proximate analysis of coke and coal

	Coke	**Anthracite Coal**
Moisture (%)	0.1	0.2
Volatile matter (%)	0.5	2.7
Fixed carbon (%)	92.9	88.6
Ash (%)	6.6	8.5

In the proximate analysis of biomasses, on the other hand, volatile matter, fixed carbon, and ash contents are normalized to obtain moisture-free (dry) values, as this allows for more meaningful comparisons of sample characteristics. Therefore, the moisture content is excluded. (Özyuğuran and Yaman 2017)

As can be seen in Table 2.4, the proximate analysis provides key information on the composition of various biomass samples, including volatile matter, fixed carbon, and ash content. By examining these parameters, we can assess the behavior of different biomasses under thermal decomposition conditions, which is critical for optimizing pyrolysis processes.

Table 2.4: Proximate analysis of biomasses

	Saw dust	Tea waste	Bagasse
Volatile matter (%)	82.70	85.00	73.78
Fixed carbon (%)	15.00	13.60	14.95
Ash (%)	2.30	1.40	11.27

As shown in Table 2.5, the proximate analysis outlines the key compositional parameters of various plastic samples. In this section, the plastic samples are divided into 4 samples namely Polystyrene (PS), Polypropylene (PP), Polyethylene (PE), Polycarbonate (PC),

Table 2.5: Proximate analysis of plastics

	PS	PP	PE (LDPE)	PC
Residual content (%)	0.67	0.22	0.67	0.67
Volatile matter (%)	52.01	99.44	96.76	79.73
Fixed carbon (%)	47.99	0.00	1.68	20.10
Ash (%)	0.00	0.67	1.57	0.17

All pure plastics have low ash content and high volatile content. On the contrary, coal contains more fixed carbon but also a higher ash content and moderate volatile matter. While biomasses contain more internal moisture and less fixed carbon than coal, they are comparable in terms of volatile and ash contents.

3 Experimental implementation and setup

3.1 Structure of the system

The following Figure 3.1 shows the setup system used to carry out the flash pyrolysis of plastic in a wire mesh reactor. This setup enables controlled and efficient pyrolysis by providing precise temperature regulation and an inert atmosphere, essential for analyzing the thermal degradation of plastics. Every component of the setup is numbered for posterior clarification.
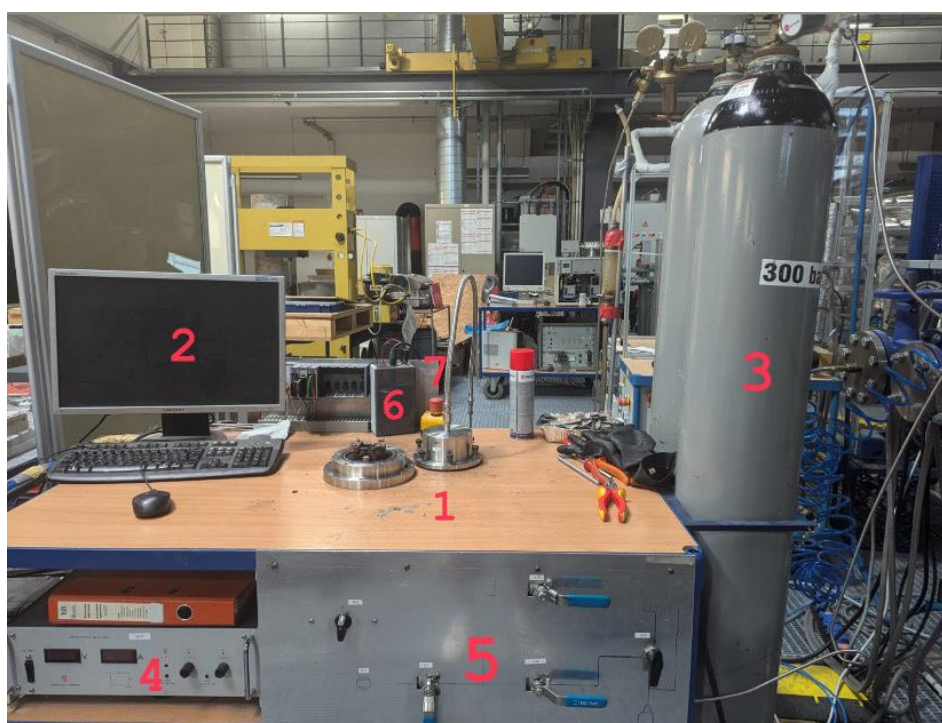
Figure 3.1: Experimental setup with the numbered components

The wire mesh reactor (1) is constructed to have a base plate that supports two high-current electrodes and a lid that can be tightly closed using six Allen screws before every experiment. The system will use, in this case, only N_2, which is fed directly from its respective gas cylinder (3).

The management of system control is facilitated by a computer (2) utilizing Labview software, which enables real-time observation and accurate modifications of process parameters. Feeding of the reactor operating energy is conducted by means of the power supply unit (4) that makes possible resistance heating of the wire mesh.

In the above setup, to monitor the temperature inside the reactor accurately, two fine wire type-K thermocouples are fixed on the wire mesh using crocodile clips (6). These thermocouples offer very precise temperature readings, which are essential to maintain controlled reaction conditions. The control valves (5) regulate the flow of gases, while the emergency stop switch (7) of the apparatus ensures safety as it allows prompt shutdown when necessary. More details about the flow of gas and the system structure can be found in the RI system flow diagram provided in Figure 3.2.
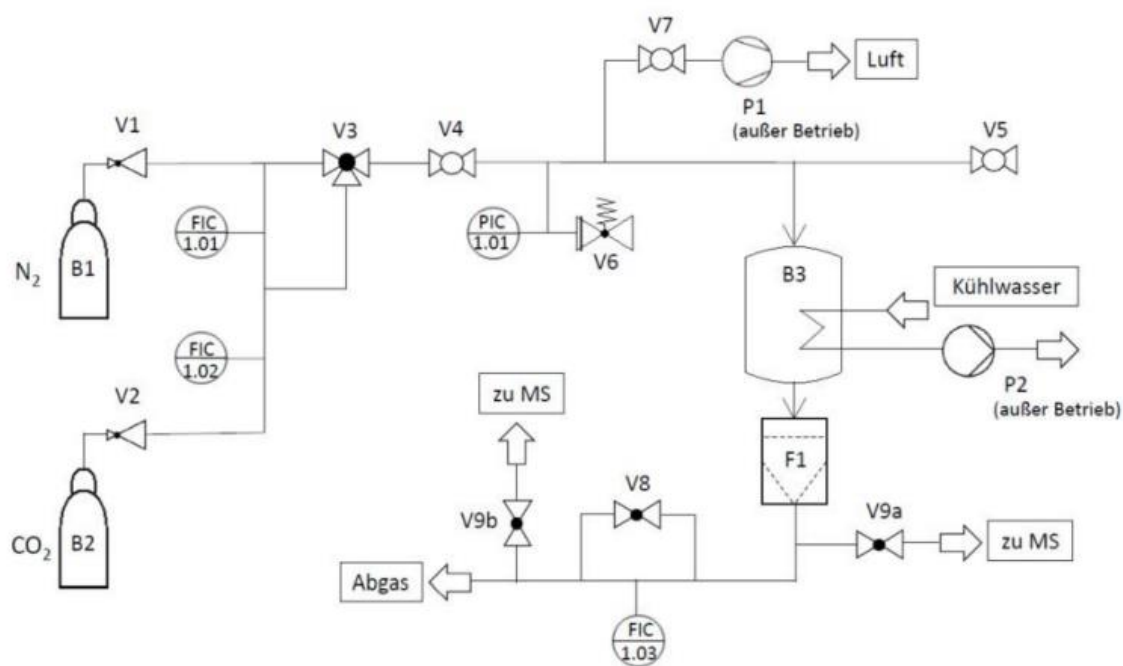

Figure 3.2: RI flow diagram of the test system

3.1.1 Wire mesh reactor

Figure 3.3 presents a detailed diagram of the wire mesh reactor used in this study. Each component of the reactor is labeled with a corresponding number, as indicated in the figure. The following provides a description of each numbered part.

Figure 3.3: Close view from above of a wire mesh reactor

The wire mesh reactor (1) is made up of a base plate with two high-current electrodes (5) and a cover (2) that can be fastened to the base plate using six Allen screws before starting the experiments. This configuration ensures that the setup remains stable during operation. The gas inlet (4) is centrally located beneath the reactor's electrodes to maintain an even flow profile throughout the mesh, which is essential for consistent results.

As the gas flows through the reactor, it exits via the lid, carrying with it any volatile pyrolysis by-products that are released. A sintered metal filter is integrated into the lid to capture and separate tar substances, preventing them from contaminating the gas stream.

Fuel samples are secured in place using stainless steel wire meshes, which are held between the high-current electrodes (5) with two wing nuts. This design utilizes the resistance heating properties of the wire mesh to achieve reaction temperatures as high as 1200 °C by applying the necessary voltages. Reaching these high temperatures is crucial for enabling different pyrolysis and combustion processes.

The temperature of the wire mesh is carefully measured using two fine wire thermocouples of type K, which are attached via crocodile clips (6) in the reactor. These thermocouples

provide accurate temperature readings, which are essential for maintaining controlled experimental conditions and ensuring reliable outcomes.

There are two types of thermocouples: type K and type S. Each type is appropriate for a particular temperature range. Type S is attached to the upper pair of crocodile clips and is suitable for usage in temperatures between 1200 and 1800 ºC. The type K thermocouple wires are fastened to the bottom clamps. Since only tests at temperatures up to 1200 ºC were conducted in this work, only thermocouples of type K were required.

The heating process in a wire mesh reactor is controlled by a power regulation unit that uses alternating current (AC) to supply power. The use of AC allows for precise control of heating rates and temperatures. This setup also permits thermocouples to be directly attached to the sample holder for accurate temperature monitoring. During experiments at atmospheric pressure, the reactor's products can be extracted from the heated zone and collected in a removable trap, which can then be weighed to directly measure tar yields. (Gibbins et al. 1989)

3.1.2 Control software Labview

The control software Labview, used for data analysis during lab work, is an environment that supports data acquisition and programming for digital and analog real-time controls. Labview is differentiated from all other data acquisition programs by having an extensive library of mathematical and statistical functions, in addition to its highly modular graphical programming language G. Graphic programming allows the code to be self-documented, flexible and reusable. Functions should be placed in a library and can then serve as routines to be called into any program. It can save a lot of development time and allow researchers to build/modify their own programs. Moreover, Labview runs on a powerful computer since it requires substantial processing and required amounts of memory and it is ideal for testing of new user interfaces, analysis algorithms or monitoring paradigms. (Kalkman)

Figure 3.4 displays the user interface of Labview control software used to control the experimental setup. The experimentation starts after feeding the test parameters into the system. Each of the elements in the software interface is clearly numbered for better clarity, with each section thereafter explained in detail. Such a step-by-step procedure allows for the entry and observation of the parameter with precision, hence allowing for consistent replicable experimental conditions for every test.
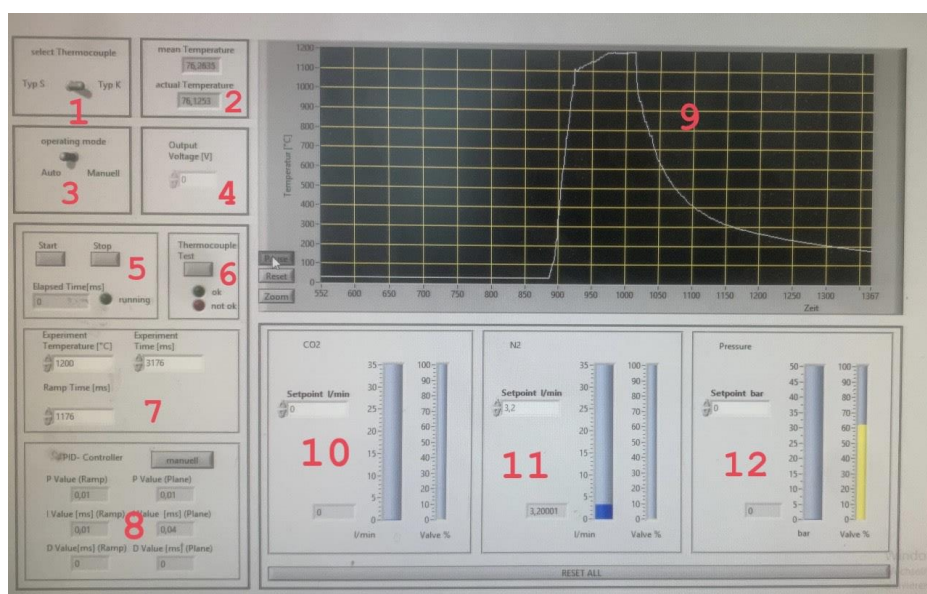
Figure 3.4: The user interface of the control software Labview

Switch 1 allows selection of the thermocouple type in use. Display 2 provides a real-time readout of the current temperature measurement. Switch 3 toggles between two operational modes: *Auto* and *Manual*. For both thermocouple testing and main experimental procedures, *Auto* mode is utilized. However, *Manual* mode can be selected to individually assess network functionality. In *Manual* mode, Window 4 enables direct voltage adjustment, whereas this function is disabled in *Auto* mode.

Buttons labeled 5 are used to start or stop the test while the system tracks the time. Button 6 is specifically for running the thermocouple test, which automatically checks the connection status of the wire networks.

In Window 7, you can set the test parameters such as heating time, test duration, and temperature. Window 8 displays the settings of the PID controller, which you can adjust either manually or automatically based on your test parameters. These settings help the system reach the target temperature quickly and accurately, minimizing overshoot and maintaining stability.

Window 9 provides a graph showing the temperature over time. Below that, Window 10 shows the flow rate of carbon dioxide, and Window 11 displays the flow rate of nitrogen. Window 12 indicates the pressure inside the reactor. You can set desired flow rates and pressure in their respective windows, and the current values will appear below in shaded areas.

3.2 Welding machine

Figure 3.5 shows the resistance welding press used in this process, with two main active operational modes: the *Solder* position (2), which allows continuous welds to be performed; and the *Weld* position (3) which creates individual welding points. The intensity of the weld can be precisely adjusted with a potentiometer (1) on the head of the machine.

To achieve the best weld strength of continuous weld seams in *Solder* mode, it is recommended to set the potentiometer between levels 3 and 4. In spot welding, on the other hand, a temperature a bit higher than this is desirable, which involves increasing the potentiometer by about 2 levels compared to *Solder* mode. Such adjustments are critical in ensuring the appropriate strength and durability of welds in wire mesh bags, thereby allowing for the distinct requirements inherent to each specific welding application.

Figure 3.5: Spot welding machine to produce wire mesh nets

3.3 Preparation and execution of the experiments

3.3.1 Net welding

Initially, stainless steel wire mesh made from material 1.4401, with a mesh size of 42 µm, is cut into rectangular pieces and folded accordingly. The mesh is then welded along its two longer edges using a spot-welding device, as illustrated in Figure 3.5. This process forms a pocket-like structure, which remains open on one end, allowing for the insertion of a sample. Following this, type K thermocouple wires are attached to the wire mesh: the nickel wire ("red") is spot welded to the top left corner, and the nickel-chromium wire ("blue") to the top right. Both wires are then secured with crosswise spot welds in the middle section.

3.3.2 Net testing

A temperature test is performed on the wire meshes produced in accordance with Chapter 3.2 to ensure that they continue to function properly at elevated temperatures. In order to accomplish this, the nets are first clamped empty into the wire mesh reactor using the two copper plates.

The reactor's crocodile clips are attached to the two thermocouples. The next step is to verify that the thermocouple wires are connected correctly using a thermocouple test. As can be seen in Figure 3.6, the diagram displays the correct welding of the thermocouple wires. In such a scenario, the temperature curve is monitored, and the voltage is manually adjusted to 5 volts. A logarithmic curve that approaches a temperature of 930 ⁰C must be established for the network to meet the requirements. Deviations in temperature within the tolerance range are within 930 ⁰C ±5%.
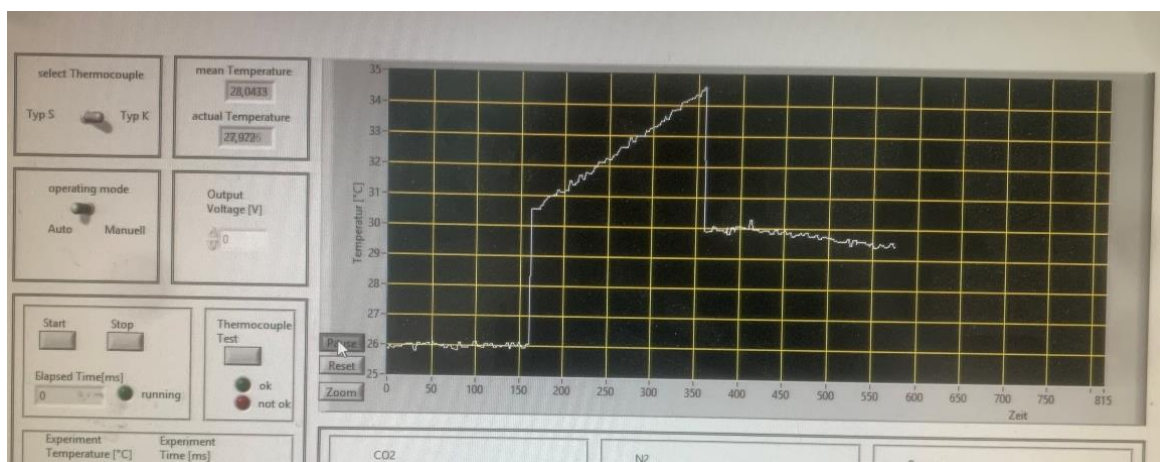

Figure 3.6: Correct display of the thermocouple test

3.3.3 Sample preparation

Nets that meet the necessary specifications—such as mesh size, thermal stability, and chemical resistance—are then filled with approximately 30 mg (±10 mg) of finely milled polystyrene plastic. Ensuring that the nets conform to these requirements is essential for maintaining consistent heat distribution and preventing material loss during the pyrolysis process. This controlled amount of PS allows for uniform heating within the wire mesh reactor, facilitating accurate measurement of pyrolysis yields and reliable data for further analysis.

Precision scales are used to weigh the net with the sample before and after it has been filled. The two ends are folded to keep fuel from leaking out and to guarantee that the sample is positioned in the center of the net, as shown in Figure 3.7.

Figure 3.7: Net filled up with polystyrene sample

3.3.4 Test execution

To accomplish the objectives of this study, specific parameters were selected and systematically varied during the flash pyrolysis tests. In each set of tests, only one parameter (temperature, pressure or holding time) is adjusted to observe its effect on the volatile yield. To ensure reliable results, each test is repeated three times.

Table 3.1 details the different test parameters, including temperature, pressure, heating rate, and residence time. These parameters were chosen to investigate their influence on

the pyrolysis of polystyrene and to optimize conditions for maximizing volatile yield. The controlled manipulation of these variables provides a comprehensive understanding of their impact on product distribution and process efficiency.

Table 3.1: Testing parameters

|	Temperature influence	Pressure influence	Holding time influence
Temperature (ºC)	500; 600; 800; 1000	500; 600; 800; 1000	800; 1000; 1200
Pressure (bar)	1; 15; 20; 25	1; 15; 20; 25	1
Holding time (s)	10	10	0,5; 2; 5; 10

The pressure must be adjusted manually using the V-5 valve (see RI flow diagram in Section 3.1). It is necessary to choose the flow rate based on the predetermined pressure. Table 3.2 outlines the relationship between gas volume flow rates and the corresponding operating pressures required for the desired test conditions. These values were calculated to ensure consistent pressure control throughout the pyrolysis process, which is essential for achieving accurate and reproducible results. By adjusting the gas volume flow to match the specified pressures, the setup maintains stable operating conditions, allowing for precise assessment of pressure effects on product yield and distribution.

Table 3.2: Gas volume flow to be set for the desired operating pressures

Operating pressure (bar)	1	5	10	20	40
Gas volume flow (L/min)	3.2	16	32	64	128

The pyrolysis test is started as soon as the pressure and flow rate are adjusted to the appropriate levels. In order to quickly identify deviations from the predetermined temperature, heating rate, and holding time parameters, the temperature curve is tracked using the control panel's display.

It is required to ensure a well-defined and stable temperature curve on the wire mesh over time. Figure 3.8 illustrates an almost ideal temperature curve of a successful test. The temperature quickly rises at a rate of 1000 K per second to the desired level, stays there for the set hold time, and then gradually decreases. After the reaction, the sample is weighed.
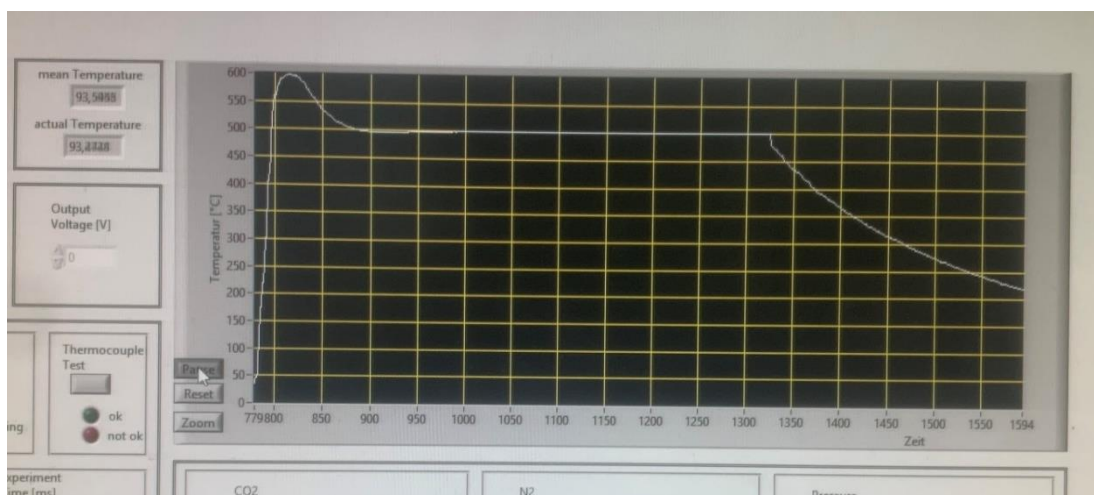
Figure 3.8: Ideal temperature curve of the test

3.4 Calculation of the volatile yield

To calculate the volatile yield, equation 3.1 is used.

(3.1)

$$Y_V = \frac{\left(m_{filled} - m_{filled,Rkt}\right)}{\left(m_{filled} - m_{empty}\right)}$$

Where, m_{filled} is the mass of the filled sample, $m_{filled,Rkt}$ is the mass of the sample after the reaction, and m_{empty} is the mass of the empty mesh.

The numerator, accordingly, gives the mass of the volatiles generated by the reaction, the denominator gives the total mass of the sample that can deliver volatiles. Therefore, it provides information on the fraction or yield of the volatile components that are released during reaction, carrying information on the extent of devolatilization or related processes.

3.5 Raman spectroscopy

This study used Raman spectroscopy to investigate the structural disorder of pyrolytic carbon after the pyrolysis experiments. The intensity ratio of the D band (around 1350 cm⁻¹) to the G band (around 1580 cm⁻¹) (ID/IG) was used to quantify the degree of disorder or defects in the carbon samples. Higher ID/IG ratios generally indicate more disordered carbon, whereas lower ratios indicate more graphitic or ordered carbon (A. C. Ferrari and J. Robertson 2000).

Raman spectroscopy was performed using an inVia™ Raman microscope equipped with a 785 μm near-infrared laser. The laser wavelength of 785 nm was chosen to reduce fluorescence, which can interfere with the detection of Raman scattering signals, and to boost the Raman signal from carbon-containing materials. Each measurement involved an exposure time of 120 seconds to achieve sufficient Raman signal intensity. Three repetitions (accumulations) were carried out for each measurement point.

An objective lens with 5x magnification was used, which provided a large enough field of view to locate and focus on specific spots on the samples. To avoid potential thermal damage to the samples, the laser power was reduced to 5% of its maximum output, ensuring that the Raman spectra obtained was unaffected by laser-induced heating or structural changes.

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4 Discussion of the results

4.1 Influence of pyrolysis process parameters

The following sections present, describe, and discuss the results obtained from flash pyrolysis of polystyrene samples, focusing on the effects of temperature, pressure, and holding time. Each test was repeated three times to ensure accuracy, with the results displaying a maximum standard deviation of 8%, indicating high reproducibility. This approach ensures that the findings are reliable, allowing for a thorough assessment of how these parameters influence the decomposition and product yield of polystyrene under controlled conditions.

4.1.1 Influence of temperature

This chapter describes the experimental conditions and procedures to study the effects of temperature and pressure on the devolatilization kinetics of polystyrene. In each experiment, the temperature was kept constant for a period of 10 seconds in order to capture the PS rapid devolatilization behavior. Tests were performed at atmospheric pressure of 1, 15, 20, and 25 bar. The resulting graph plots the temperature dependence of the volatile yield from PS at these pressures and provides an indication of how high temperature and pressure conditions may influence the rate and extent of volatile release.
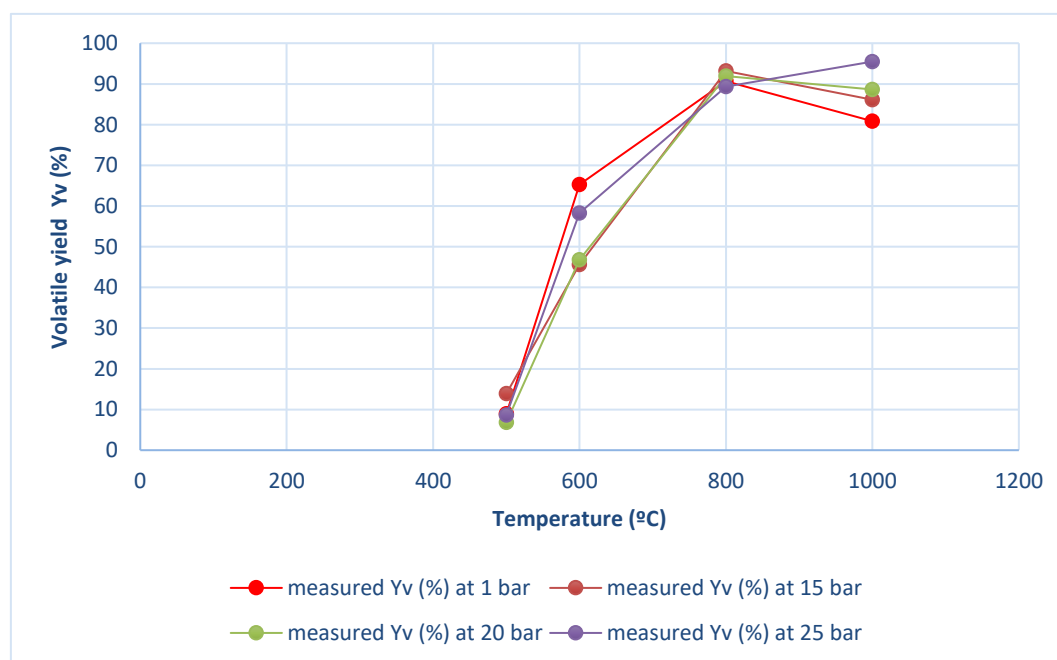
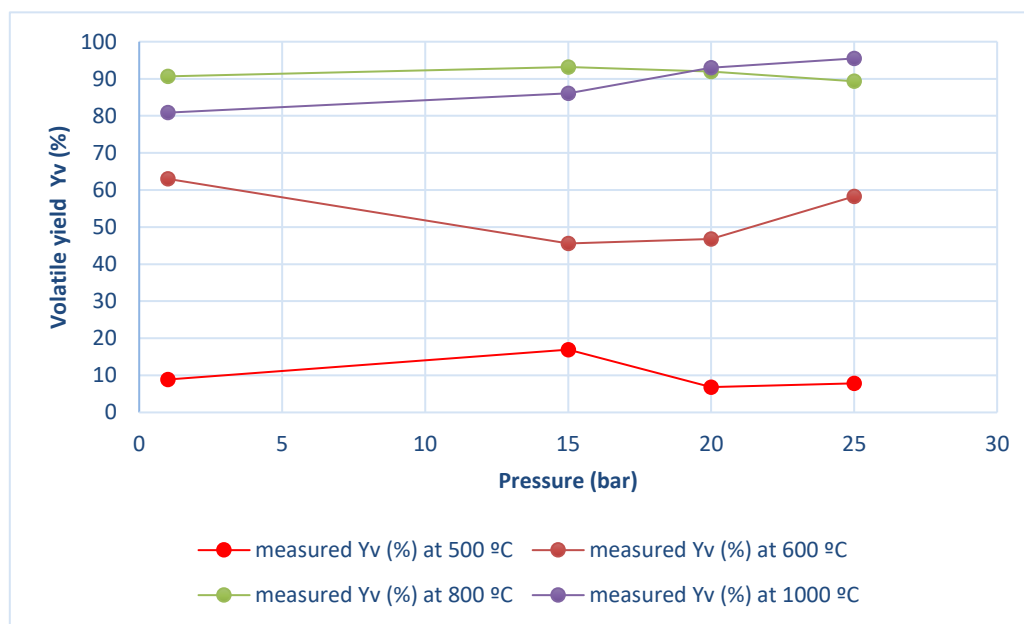**Figure 4.1:** Influence of temperature on volatile yield

Figure 4.1 illustrates, for polystyrene, the effect of temperature on the volatile yield at various pressures, 1, 15, 20, and 25 bar. In all instances, within the range 1–25 bar, an observable trend of yield increasing with temperature was observed to show an exponential rise when the temperature reached at or above 800 ºC. At 1 bar, from about 10% at 500 ºC, the yield increases to almost 90% at 1000 ºC, and it clearly follows that higher temperatures increase devolatilization significantly.

At elevated pressures, the yields are slightly higher for each temperature point, suggesting that increased pressure facilitates volatile release. Such is the case that the yield at 500 ºC and 15 bar is 15% higher in comparison with atmospheric pressure, and up to 95% at 1000 ºC. At 20 and 25 bar, the same trends at atmospheric and 15 bar pressures are repeated; yields close to 100% at 1000 ºC show that complete devolatilization occurred under such conditions.

These results align with previous research on the significant effects of temperature on the volatiles release during pyrolysis. High temperatures accelerate the degradation rate of chemical bonds in polystyrene, while high pressure favors this process, probably due to improved heat transfer and reduced losses of gases, thus promoting further reactions. Therefore, temperature is the driving force in pyrolysis and volatile release, while pressure acts as a secondary factor under certain conditions but does not substantially alter the overall trend. It would mean that temperature optimization is the important factor to be optimized in order to achieve maximum yields of volatiles, while increasing pressure gives incremental improvement.

4.1.2 Influence of pressure

While the previous section examined how temperature influences volatile release at various pressures, this section focuses on assessing how different pressures affect volatile release at specific temperatures. By conducting tests at atmospheric pressure (1 bar) and elevated pressures (15, 20, and 25 bar) for a consistent temperature range. The following figure shows how pressure affects the amount of volatile compounds released during the flash pyrolysis of polystyrene waste at different temperatures. For each set of parameters, the test was repeated three times in order to assure correct results.

Figure 4.2: Influence of pressure on volatile yield

Figure 4.2 shows the effect of pressure on volatile yield during PS pyrolysis at temperatures ranging from 500 to 1000 ºC. At 500 ºC, volatile yield remains below 20% at all pressures, which indicates that there is not enough thermal energy to break down the PS. Therefore, pressure will not have much effect. As temperature increases to approximately 600 ºC, the volatile yield increases to about 60–70 % at lower pressures; it decreases with increased pressure probably due to gases retained or recombined into non-volatile forms.

From these observations, at 800 ºC and for all pressures, the yield is above 90%. This shows that heat is more dominating than pressure in decomposition. The volatile yield remains high (over 80%) at the highest temperature of 1000 ºC, following a trend to increase slightly with rising pressure, which may suggest that at these elevated temperatures, while thermal energy drives the process, higher pressures may enhance efficiency in the release of volatiles.

These observations are in good accordance with the previous studies, where it was established that the volatile yield in pyrolysis is driven mainly by temperature, whereas pressure effects depend on available thermal energy. Indeed, high pressure has been reported to promote complete volatilization at high temperatures due to enhancements in the heat transfer and a reduction in gas escape, which will result in a maximization of the conversion efficiency of PS.

In the mathematical model, the sensitivity of the volatile yield to pressure is parametrized by ρ (see Section 2.3.1). In the equation, ρ is a sensitivity factor which adjusts the pressure effect on volatile production, and it denotes that as pressure is raised, volatile production decreases. A qualitative explanation is given by the increased partial pressure of volatile vapors which makes it energetically more difficult for devolatilization to occur. By utilizing least squares fitting with experimental data, ρ can be accurately determined. This is particularly useful in a system where pressure is one of the controllable variables which enable

optimization for maximum volatile yield. The following Table 4.1 contains the calculated ρ values for the model at 600 ºC.

Table 4.1: Least squares fitting results

p_{set}	1
$Y_{v,pset}$	62.9958
ρ	0.240175
Sum of errors	127.0094

The optimal value of ρ is approximately 0.2402, obtained by minimizing the sum of squared errors between the calculated yields and the measured data. The total sum of squared errors is 127.0094, indicating the cumulative difference between the model predictions and experimental data across different pressures. Figure 4.3 illustrates the relationship between pressure and volatile yield at 600 ºC, showing both the modeled and measured data points. The graph verifies that the model correctly captures the trend of declining volatile yield with pressure at 600 ºC.
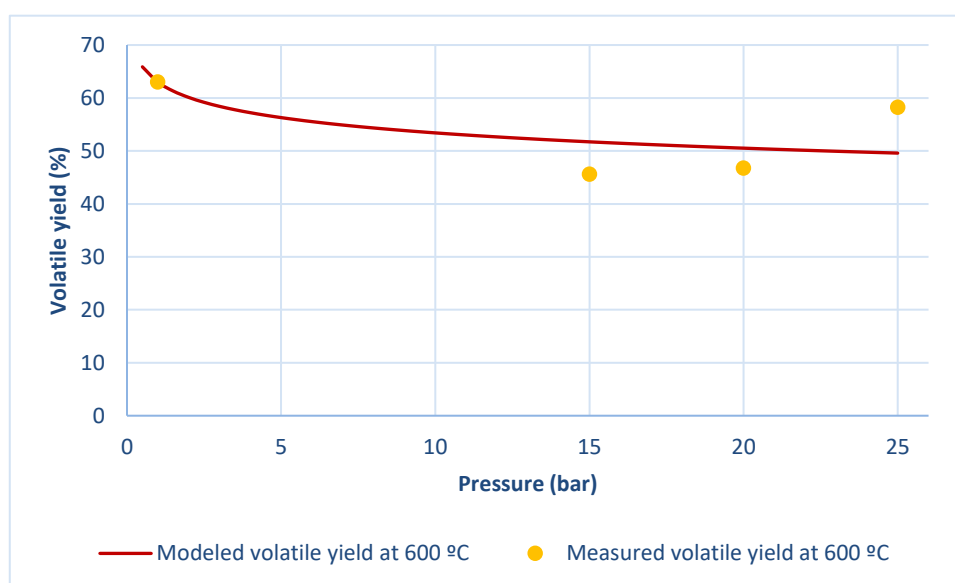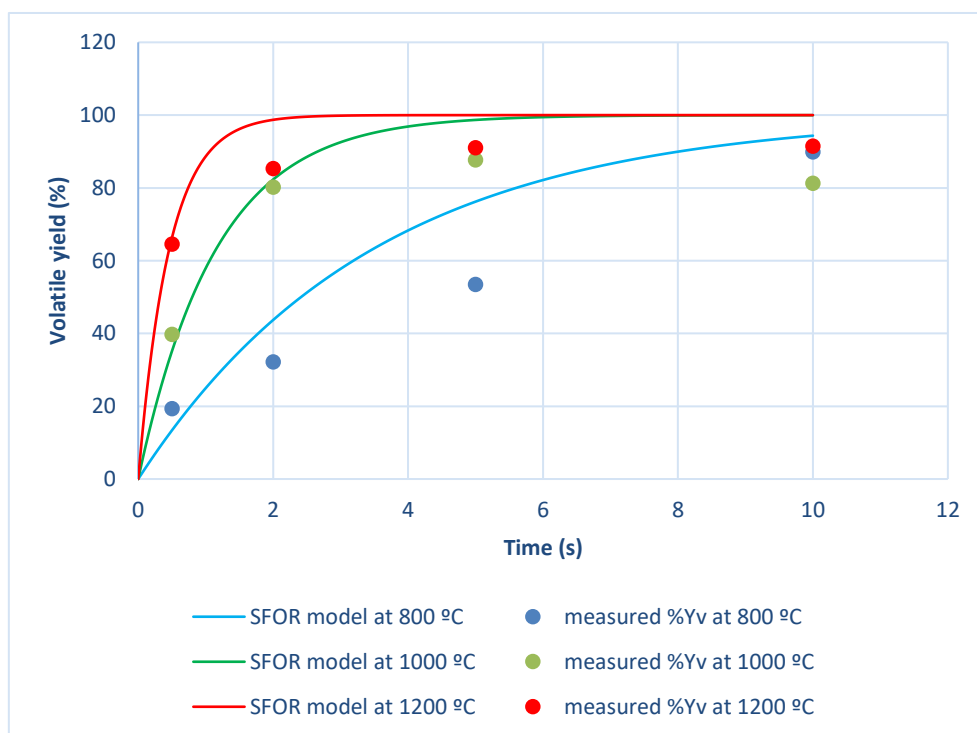

Figure 4.3: Model vs Experimental data of pressure influence on volatile yield

4.1.3 Influence of holding time

To fully comprehend the impact of temperature and holding time on volatile release during pyrolysis, we must investigate how the SFOR model (Single First Order Reaction) compares theoretical predictions to experimental data. This model compares theoretical predictions of volatile yields to experimental data to minimize the difference between calculated and observed values. Optimization techniques such as the least squares method are used to modify the kinetic parameters E_a and k_o in order to minimize the sum of squared errors. As mentioned, the model's accuracy is then validated by plotting experimental data against the results of the theoretical model.

To understand the influence of temperature and holding time during pyrolysis, the release of volatiles from the polystyrene fraction were investigated by holding the material at 800, 1000 and 1200 ºC for 10 seconds at varying pressures. The objective was to assess how different temperatures influence the rate and extent of volatile release.

The volatile yield obtained from pyrolysis at 800, 1000, and 1200 ºC over time is shown in Figure 4.4.

Figure 4.4: Volatile yield during polystyrene pyrolysis: Model vs. Experimental data

The chart demonstrates that as the temperature increases from 800 to 1200 ºC, the rate of volatile release also increases. This is observed by the rapid rise in volatile yield over a shorter period at higher temperatures.

In the case of 800 ºC, after 10 seconds, the yield of volatiles is about 80%. From the SFOR model, it is observed that there is a gradual increase in yield, showing quite a good fitting with the experimental data. That reflects that at 800 ºC, the reaction kinetics are comparatively slower. Therefore, volatiles were released with the increase in residence time. In this regard, the model successfully captured the kinetics, proving to be slower.

Within the first 2 seconds at 1000 ºC, the yield of volatiles is approximately 90% and will be considered to reach approximately 100% when time approaches 10 seconds. Much quicker compared with 800 ºC. The SFOR model also covers this faster release with good tracking of experimental data points. It means that at 1000 ºC, the thermal energy available is higher than the activation energy barrier of the pyrolysis reaction to cause faster degradation of PS into volatile components.

The yield of volatiles during the first second is almost 100% at 1200 ºC. This fast increase evidences that under this higher temperature, the reaction of pyrolysis has already become practically instantaneous. Model predictions of SFOR also show good accordance with experimental data, therefore, the goal of maximum yield will be fast. This behavior may indicate that at 1200 ºC due to high thermal energy, the reaction kinetics is highly accelerated, and volatiles are released quickly.

4.2 Raman spectroscopy

In this study, Raman spectroscopy was used to investigate the structural properties of pyrolytic carbon samples under various experimental conditions. The intensity of the D and G bands at 1350 cm^{-1} and 1580 cm^{-1}, respectively, was analyzed to determine the degree of disorder or defects in the carbon material.

The Raman spectra for each selected region was carefully collected, and the ID/IG ratios were calculated to determine the degree of disorder in the carbon network. The following section contains the detailed results of these analyses, including graphical representations of the Raman spectra and calculated ID/IG ratios for various experimental setups.

Figure 4.5 shows the Raman spectrum for the sample labeled PS 800 ºC 1 bar 10 s (Feed, Temperature, Pressure, Holding time), which prominently displays both the D and G bands.
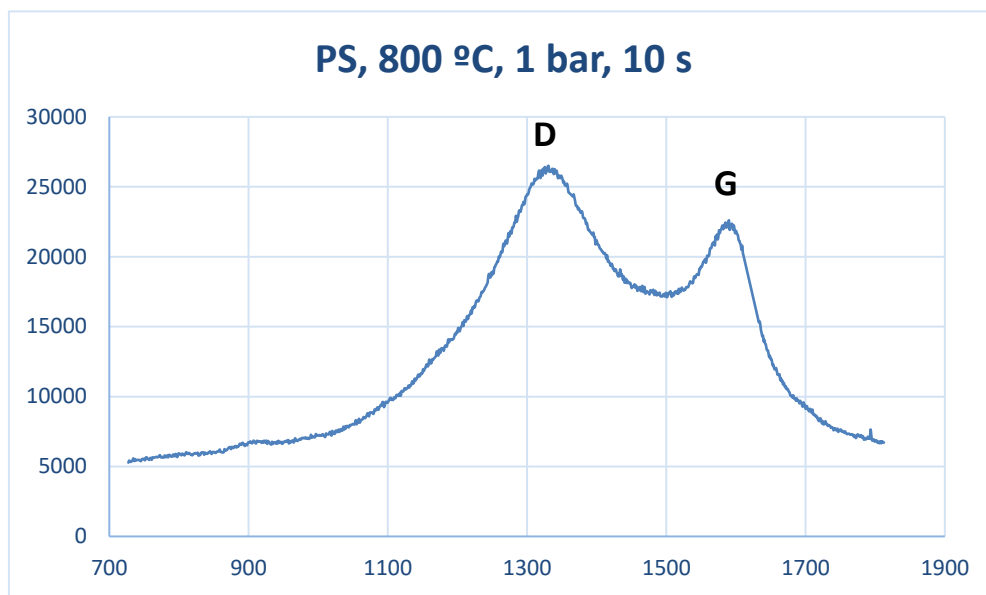
Figure 4.5: Raman spectrum of sample showing both D and G bands

In contrast, Figure 4.6 shows that the Raman spectrum for 1000 ⁰C, 25 bar, 10 seconds conditions, has a clear D band at 1350 cm⁻¹ but no distinct G band at 1580 cm⁻¹. This indicates that the sample has a higher level of structural disorder or defects.
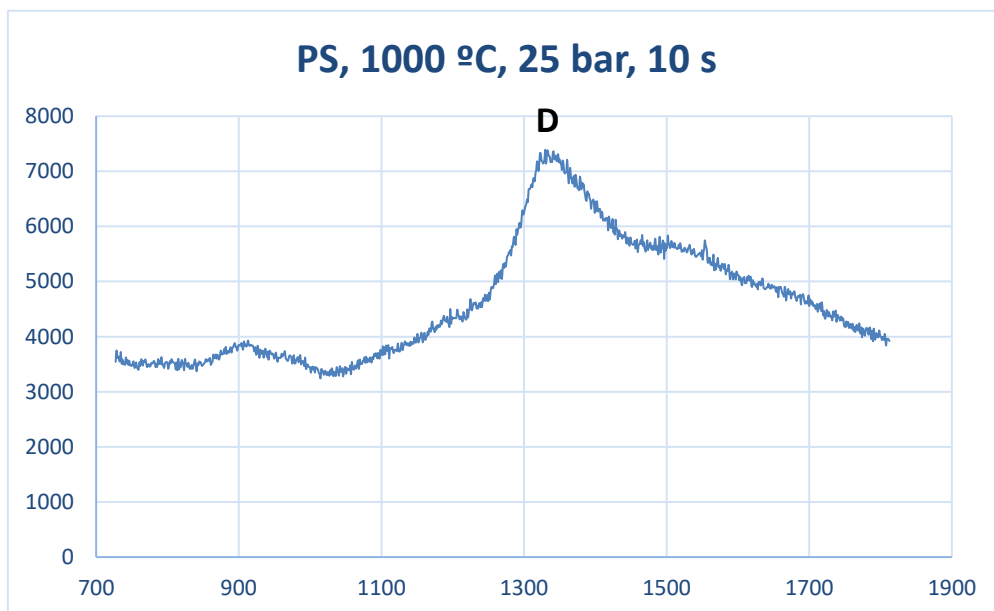
Figure 4.6: Raman spectrum of sample showing a D band and absence of a G band

Table 4.2 summarizes the Raman spectroscopy results, including experimental conditions (temperature, pressure, reaction time, and sample number) and calculated values for ID (D band intensity at 1300 cm⁻¹), IG (G band intensity at 1600 cm⁻¹), and ID/IG ratios.

**Table 4.2:** Summary of Raman spectroscopy results under various experimental conditions

T (ºC)	Pressure (bar)	RT (s)	Sample	ID (1300)	IG (1600)	ID/IG
1200	1	5	1	26396.18	24044.39	1.09781
1200	1	5	2	38771.96	35725.48	1.085275
1200	1	10	1	25252.26	22375.27	1.128579
1200	1	10	2	17541.54		
1000	1	5	1	11822.61	9533.436	1.24012
1000	1	5	2	20742.7	17621.57	1.17712
1000	1	10	1	24311.98	21496.65	1.130966
1000	1	10	2	10201.52	8341.577	1.222973
1000	25	10	1	12348.86	9414.191	1.311728
1000	25	10	2	7390.359		
800	1	5	1	29663.94	25556.67	1.160712
800	1	5	2	24982.86	21066.42	1.185909
800	1	5	3	26486.52	22607.54	1.171579
800	1	10	1	26486.52	22607.54	1.171579
800	1	10	2	9396.58	7228.64	1.29991
800	25	10	1	41751.45	37545.01	1.112037
800	25	10	2	27864.25	24632.99	1.131176

The ID/IG ratio, which measures the degree of disorder or defect in carbon material, varies with temperature, pressure, and reaction time. Higher temperatures (e.g., 1200°C) typically result in lower ID/IG ratios, indicating less structural disorder. However, there are some exceptions depending on other factors such as pressure and reaction time. In addition, some samples (e.g., 1200 ºC, 10s, sample 2, and 1000 ºC, 25 bar, 10s, sample 2) have missing IG values, which is due to the absence of a clear G band. Figure 4.7 shows the ID/IG ratio trend calculated at 1 bar varying with temperature.
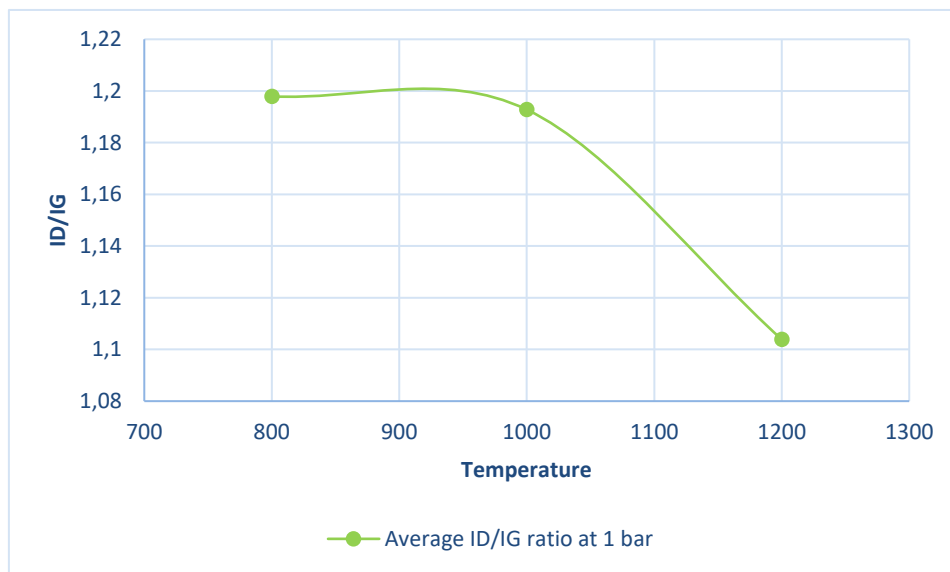
Figure 4.7: Calculated ID/IG ratio depending on temperature

Figure 4.8 shows the mesh structure used for Raman spectroscopy analysis, highlighting its detailed microstructure. The image captures the interwoven fibers of the mesh, which have been analyzed to observe the distribution and characteristics of carbon deposition during the pyrolysis process. The scale bar (200 µm) provides a reference for the mesh's dimensions, allowing for precise evaluation of areas where carbon residues accumulate, potentially influencing the structural integrity and thermal properties of the sample. This detailed observation aids in understanding the material's behavior under pyrolysis conditions.
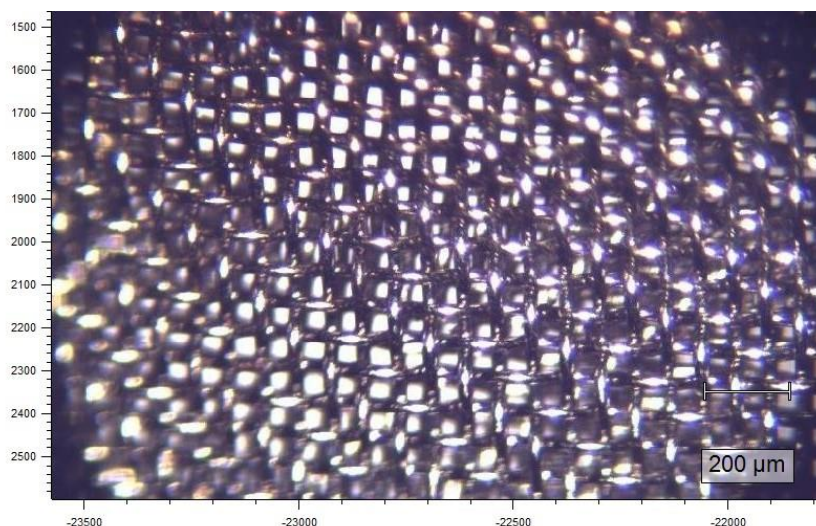
Figure 4.8: Mesh seen with Raman spectroscopy

Raman measurements were conducted on targeted areas of the samples, focusing on regions with visible carbon accumulation, such as darker areas commonly observed in polystyrene pyrolysis residues, as shown in Figures 4.9, 4.10, and 4.11. These areas were selected based on their appearance under a microscope, where regions with accumulated carbon filaments or material adhered to the mesh filaments were observed. This selection aims to identify variations in structural properties within different regions of the sample, providing insights into the carbon deposition patterns during pyrolysis.
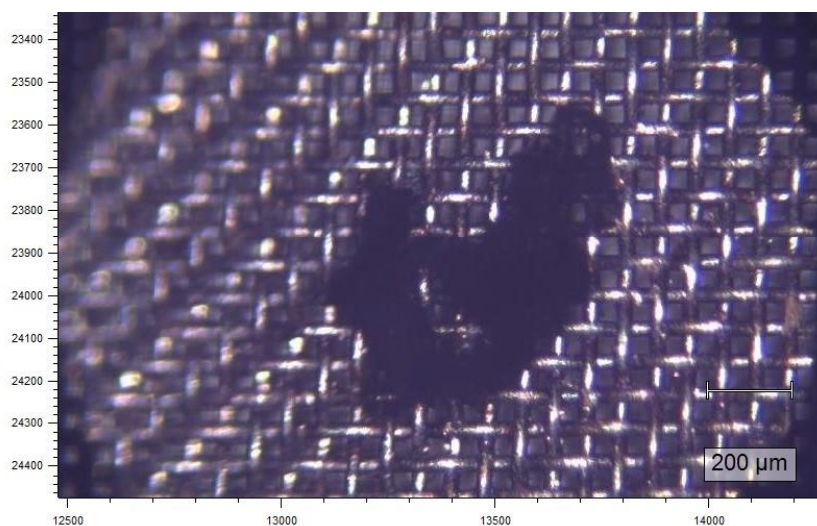
Figure 4.9: Mesh with carbon accumulation spot
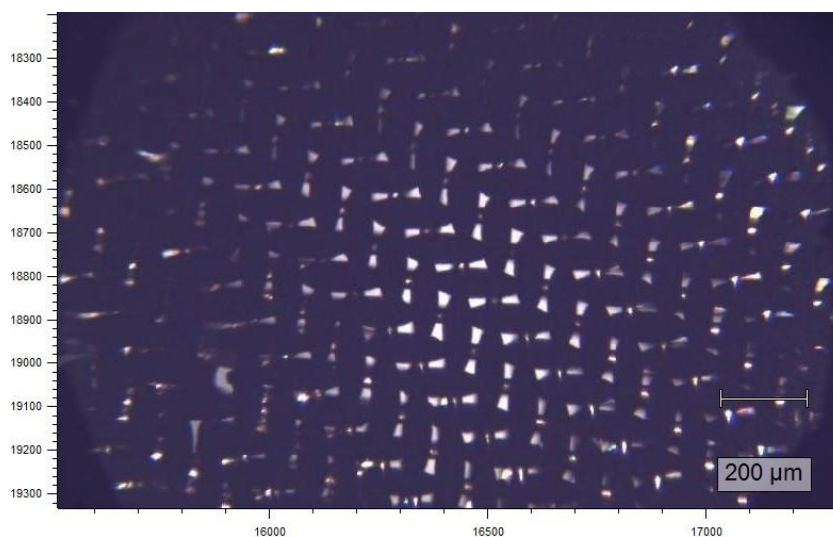
Figure 4.10: Mesh with carbon stuck on every filament
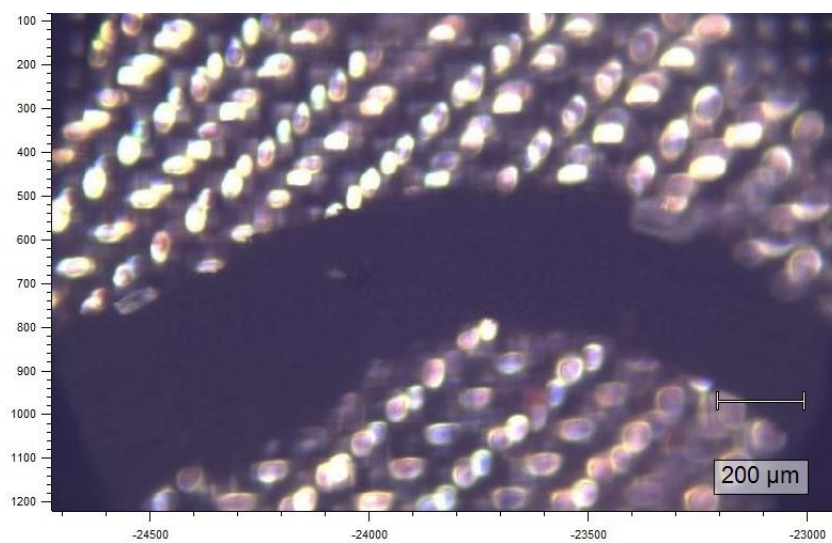
Figure 4.11: Mesh with accumulated carbon filament

5 Summary and Outlook

5.1 Summary

The main objective of this research was to find out whether plastic wastes, such as polystyrene, could be transformed into useful products via flash pyrolysis. Consequently, we want to establish how variation in temperature, holding time, and pressures would alter the quantity and quality of the pyrolysis products and their yields. To perform this, we used a wire mesh reactor that provides fast heating and has high efficiency of thermal decomposition of the material. Various experimental sets were elaborated to investigate the parameters that might affect the outcome of pyrolysis. These experiments have been controlled and monitored by software with the possibility of precisely modifying the reaction parameters.

These experimental results clearly indicated that temperature is the foremost factor that decides the devolatilization kinetics of PS. Its effect on the yield of volatiles was studied for four different temperatures: 500, 600, 800, and 1000 ºC. A progressive increase in volatile yield with temperature was obtained, indicating that higher temperatures substantially affect the release of volatiles.

The pressure effect was, on the other hand, tested at atmospheric pressure of 1 bar and at the higher pressures of 15, 20, and 25 bar. These results indicated that even though increased pressure could promote the initial release of volatiles at lower temperatures, such as 500 and 600 ºC, its effect was lower at higher temperatures, which may indicate that lower temperatures are controlled by heat and that pressure has little effect.

The influence of holding time and temperature on volatile release was simulated using the SFOR model, a single first order reaction which compares theoretical predictions against experimental data. In all cases, increasing temperature from 800 to 1200 ºC increased the volatile release rate. During heating at 800 ºC, only about 80% volatiles were released in only 10 seconds, while further increases with time took place more gradually, evidencing slower reaction kinetics at this temperature. At 1000 ºC, in the first 2 seconds, it reached approximately 90% and reached nearly 100% after 10 seconds, proving faster decomposition rates due to higher thermal energy. At 1200 ºC, within a single second, the volatile yield was almost 100%, showing that at this temperature the pyrolysis reaction is just about instantaneous.

Finally, Raman spectroscopy was also performed to investigate properties of pyrolytic carbon samples obtained in different conditions. The intensity ratios between the D and G bands were used for the quantification of disorder degree or defects in the carbon network. Generally, at high temperatures, the ID/IG ratio is lower, showing a less disordered structure. However, there are quite a few exceptions depending on the pressure and time of reaction.

Overall, the results strongly suggest that the temperature is, in fact, the major controlling factor for the devolatilization kinetics of polystyrene during flash pyrolysis, while higher temperatures result in significantly increased yields of volatiles. The pressure effect can be

characterized as secondary, with its effect diminishing with the increase in temperature. Holding time and temperature interaction significantly influences kinetics and the degree of decomposition. These insights are important to optimize the pyrolysis conditions for efficiently recycling polystyrene waste and developing sustainable strategies for waste management.

5.2 Outlook

The results obtained in this work form a foundation for future research on the pyrolysis of polystyrene and other wastes. Further studies may be done to understand the behavior of polystyrene during pyrolysis, investigating different parameters and various reactor designs that can facilitate gas release and, consequently, make the pyrolysis process more efficient.

Future research could concentrate on scaling up the wire mesh reactor technology for industrial applications, investigating its economic and recycling viability at a larger scale. Applications of kinetic models, like the SFOR model, in predicting plastic types of behaviors under different conditions would be improved with these studies.

Moreover, investigation into the mix of polystyrene with other varieties of plastic waste could be carried out under variant pyrolysis conditions to investigate the interaction of effects that would enhance the overall yield and quality of the products obtained. Expanding this research will support the development of more efficient and scalable recycling technologies contributing to sustainable waste management and circular economy goals.

Finally, one of the big goals for future research will be to increase the success rate of tests. Refining testing methodologies and enhancing reliability will be important in ensuring consistent, actionable results as the technology is furthered to larger-scale applications.

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Appendix

A) Derivation of the temperature dependence for the SFOR model

Initially, the temperature dependence of the volatile yield is considered. We start from Equation A.1:

(A.1)

$$\frac{dc_v}{dT} = -\theta \cdot c_v$$

This equation is then integrated on both sides and leads to:

(A.2)

$$ln(c_v/(Tmin = c_v, T)) = -\theta(T - T_{(min)})$$

Simplifying further gives:

(A.3)

$$c_v = c_{v,Tmin} \cdot \exp[-\theta(T - Tmin)]$$

Using the definition of the conversion X, we obtain:

(A.4)

$$X(T) = \frac{Y_v(T) - Y_{v,Tmin}}{Y_{v,max} - Y_{v,Tmin}} = \frac{c_{v,Tmin} - c_v}{c_{v,Tmin}} = 1 - \exp[-\theta(T - T_{min})]$$

Finally, we arrive at the following transformation:

(A.5)

$$Y_v(T) = Y_{v,Tset} + (Y_{v,max} - Y_{v,Tset})[1 - \exp(-\theta(T - T_{set}))]$$

B) Derivation of the pressure dependency for the SFOR model

To derive the pressure dependence, the Clausius-Clapeyron equation is used as a starting point:

$$\frac{d \ln p}{dT} = \frac{\Delta H_v}{RT^2}$$

First, by integrating this equation, the following expression is obtained:

$$\ln\left(\frac{p}{p_0}\right) = A - \frac{B}{T}$$

This expression is also known as the Antoine equation. The numerical constants A and B are determined through experimental investigations of the vapor pressure.

Since the vapor pressure depends on temperature proportionally, and the yield of volatiles is linearly correlated with temperature, the temperature T can formally be written as:

$$\frac{1}{T} = A - B \cdot Y_v(p)$$

Rearranging $Y_v(p)$ gives:

$$Y_v(p) = \frac{A}{B} - \frac{1}{B} \ln\left(\frac{p}{p_0}\right)$$

A point p_{set} is defined where:

$$\frac{A}{B} = Y_v(p_{\text{set}})$$

Now, the deviation of the yield can be expressed as:

$$Y_v(p) = Y_v(p_{\text{set}}) - \frac{\ln\left(\frac{p}{p_{\text{set}}}\right)}{\rho}$$

Where ρ is the pressure dependence parameter.

C) Derivation of the influence of the holding time of the SFOR model

We start with the fundamental equation of the SFOR model:

(C.1)

$$\frac{dY_v(t)}{dt} = k\left(Y_{v,\infty} - Y_v(t)\right)$$

By separating the variables and integrating both sides, we obtain:

(C.2)

$$\int_0^t \frac{dY_v(t)}{Y_{v,\infty} - Y_v(t)} = k\int_0^t dt$$

This results in:

(C.3)

$$\ln\left(\frac{Y_{v,\infty}}{Y_{v,\infty} - Y_v(t)}\right) = k \cdot t$$

Rearranging the equation to solve $Y_v(T)$ we get:

(C.4)

$$Y_v(t) = Y_{v,\infty} - Y_{v,\infty} \cdot \exp(-k \cdot t)$$