Enhancing TGA-MS Techniques for Improved Gas Detection in Petcoke Gasification

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Sammendrag

Denne studien undersøker hvordan petroleumskoks brytes ned under varme ved hjelp av en teknikk kalt termogravimetrisk analyse-massespektrometri. Forskningen hjelper oss å forstå hvordan endringer i temperatur, luftkontroll og størrelsen og typen koksprøver påvirker denne nedbrytningsprosessen. De første eksperimentene viste at da temperaturen økte fra 25°C til 900°C, ble det mye vekt tap, spesielt mellom 500°C og 700°C. I løpet av denne fasen ble gasser som karbonmonoksid, karbondioksid og metan frigjort på grunn av nedbrytning av komplekse kjemikalier i koksen.

Videre ble det testet om å holde koksen ved spesifikke høye temperaturer over lengre tid, eller å varme den opp saktere, ville frigjøre mer gass. Disse endringene førte ikke til at mer gass ble produsert, noe som tyder på at de naturlige egenskapene til petroleumskoks kan begrense hvor mye den reagerer under disse forholdene. Disse funnene indikerer at bare endring av temperatur eller oppvarmingshastighet ikke er nok til å endre betydelig hvordan petroleumskoks brytes ned.

Fremtidig forskning bør prøve nye tilnærminger, som å bruke høyere temperaturer, øke oppvarmingshastigheten og endre atmosfæren rundt koksen. Studien antyder også at det bør legges mer vekt på hvordan prøver av petroleumskoks blir forberedt for bedre resultater. Denne forskningen viser at nedbrytning av petroleumskoks er kompleks og krever en rekke strategier for å fullt ut forstå og forbedre prosessen.

Abstract

This study examines how petroleum coke breaks down under heat using a technique called Thermogravimetric Analysis-Mass Spectrometry. The research helps us understand how changes in temperature, air control, and the size and type of coke samples impact this breakdown process. The first experiments showed that as the temperature increased from 25°C to 900°C, a lot of weight was lost, especially between 500°C and 700°C. During this phase, gases like carbon monoxide, carbon dioxide, and methane were released due to the breakdown of complex chemicals in the coke.

Further experiments tested whether keeping the coke at specific high temperatures for longer times or heating it more slowly would release more gas. These changes did not lead to more gas being produced, suggesting that the natural properties of petroleum coke might limit how much it reacts under these conditions. These findings indicate that just changing temperature or heating speed isn't enough to significantly change how petroleum coke breaks down.

Future research should try new approaches, such as using higher temperatures, increasing the heating rate, and changing the atmosphere around the coke. The study also suggests that more attention should be given to how petroleum coke samples are prepared for better results.

This research shows that breaking down petroleum coke is complex and requires a variety of strategies to fully understand and improve the process.

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Chapter 1

Introduction

1.1 Background

Petcoke, a carbon-rich byproduct derived from refining heavy crude oil, boasts a high heating value and substantial carbon content, making it a valuable resource across various industries. It's not only integral to traditional energy sectors but also increasingly relevant in the production of battery materials due to its high purity and cost-effectiveness. Despite its potential, the gasification of petcoke presents significant challenges, primarily due to its high fixed carbon content and low volatile matter, which impede its reactivity[6].

This study aims to explore how modifications to the Thermogravimetric Analysis-Mass Spectrometry (TGA-MS) technique, applied specifically to Vianode's petcoke, can enhance the accuracy and sensitivity of gas detection during petcoke gasification. Enhancing these aspects is vital for developing more sustainable and economically viable gasification technologies that can support the growing demand for battery-grade materials.

Utilizing Thermal Gravimetric Analysis (TGA) and Mass Spectrometry (MS), this research tracks the weight changes and gas evolution of petcoke as it undergoes thermal decomposition. TGA helps describe the thermal behavior of petcoke, showing how it reacts to heat, while MS provides detailed insights into the types of gases released during this breakdown. By integrating TGA and MS, the study provides a comprehensive method to assess the changes in petcoke under controlled conditions, aiming to improve the production processes of battery-grade carbon materials.

1.1.1 Mass Spectrometry (MS) in Gasification Studies

Mass Spectrometry (MS) is a detailed technique that is very useful in studying how materials like petcoke break down when heated, a process known as gasification. MS works by identifying and measuring gases as they form, giving insights into what gases are produced and in what amounts. This is done by turning the gases into ions, which are then sorted and measured according to their mass.

Using MS in these studies helps to figure out what specific gases are made during gasification and how they form. It can also spot small amounts of certain gases that are important for fully understanding the gasification process. The ability of MS to give information in real time allows researchers to see how the gas makeup changes from the start to the end of the process.

1.1.2 Development of TGA-MS Methodology

In this study, we introduce a new method by combining Thermal Gravimetric Analysis (TGA) and Mass Spectrometry (MS), which we call TGA-MS. This method uses the accuracy of TGA to measure weight changes and combines it with the capability of MS to analyze gas

composition in real time. Together, these techniques offer a deeper understanding of how petcoke breaks down and turns into gas.

By using both TGA and MS together, we aim to get a detailed view of the gases that form at different stages of the petcoke breaking down. This new method not only gives us more detailed information than what we would get from TGA alone but also helps us explore how certain gases are linked to specific chemical reactions.

To sum up, this study uses the new TGA-MS method to improve research on turning petcoke into gas. We address the issue of weak signals in mass spectrometry, which makes it hard to detect gases, and suggest improvements to make it more sensitive and accurate. By combining real-time gas analysis with precise measurements of weight changes, we hope to provide useful insights that will help develop better ways to turn materials into gas efficiently.

Experimental Setup

In exploring petcoke gasification, creating a strong experimental method is crucial. Our study uses the TGA-MS approach, which requires careful control of many different test conditions to make sure the data we get is accurate and reliable.

As we dive deeper into our research, it's important to clearly describe the main conditions and settings we use in our experiments.

Heating Profile

First, how we heat the samples is really important for figuring out how petcoke breaks down when it gets hot. We slowly increase the temperature to mimic real-life conditions that petcoke would usually face. This helps us see how it reacts and changes at different heat levels, giving us a better understanding of its behavior during heating.

Using Inert Gases

In our experiments, we use inert gases like argon instead of regular air. This is important because it stops outside chemicals from messing with the results. By doing this, we make sure any changes we see in the weight of the petcoke come from how it naturally reacts to heat, not from anything else.

Using this gas helps us keep our experiments clean and clear, making it easier for other researchers to repeat them and get the same results. This step is a big part of how we make our research on petcoke gasification better and more reliable.

Chapter 2

Theory

2.1 Petroleum coke

Petroleum coke, commonly known as petcoke, is a byproduct of the petroleum refining process and holds significant importance across diverse industries due to its versatility. Derived from the refining of petroleum, petcoke serves essential roles in manufacturing carbon anodes for the aluminum industry, graphite electrodes for steel making, and as a fuel source for solid fuel boilers that generate electricity. Furthermore, it contributes to the fuel composition for cement kilns.

Among the various grades of petroleum coke, "fuel-grade coke" stands out. While it exhibits high sulfur content and contains metals composition unsuitable for carbon anodes or graphite electrodes, fuel-grade coke remains a cost-effective alternative. It boasts a high heat content, typically exceeding 14,000 Btu/lb, and maintains a low ash content, generally below 1% by weight, distinguishing it from coals.

However, fuel-grade coke has its limitations. It is characterized by elevated sulfur concentrations, and many petroleum cokes contain higher levels of vanadium and nickel, making them less desirable for specific applications, particularly as a boiler fuel.

In conclusion, petroleum coke, especially in its fuel-grade variant, plays a pivotal role in various industries as a byproduct of petroleum refining. Its versatility, contributing to both fuel and material production, underscores its significance in the energy and manufacturing sectors, despite certain undesirable characteristics. [14]

2.2 Pyrolysis

Pyrolysis is a process where materials such as wood, coal, or plastic are heated in the absence of air. This lack of air is crucial because it prevents these materials from burning completely; instead, they break down into simpler substances. The products of pyrolysis include solids like charcoal, liquids such as oils, and gases like methane. Each of these products has various uses:

- Solids (Charcoal): Commonly used as fuel or in filtration systems.

- Liquids (Oils): These can serve as fuels or be used in the production of various chemicals.

- Gases: Can be burned to generate energy and include common fuels like methane.

Pyrolysis has numerous applications across different industries. For instance, it can transform agricultural waste such as corn stalks or sawdust into charcoal, oils, and gases, turning waste into valuable resources. It's also employed in recycling, where materials like used tires are broken down to create reusable products and reduce landfill waste.

Additionally, pyrolysis plays a significant role in energy production and environmental management. It helps simulate natural geological processes that form coal and oil, helping to explore new energy sources. Moreover, pyrolysis is being explored for its potential to minimize waste and generate energy sustainably, offering a method to convert waste materials into useful products in an eco-friendly manner. This makes pyrolysis a key technology in efforts to create cleaner energy solutions and promote recycling, thereby supporting environmental conservation efforts[5].

2.3 Gasification

Gasification is a way to transform materials like coal or biomass into a type of gas called synthesis gas, or syngas, which is mainly made up of hydrogen and carbon monoxide. This process happens by heating the material at high temperatures and pressures, which helps speed up a naturally slow process.

First, the material undergoes devolatilization, where it heats up and releases volatile substances. After this, the main part of gasification takes place, which involves complex reactions between the remaining solid part, known as char, and substances called gasifying agents, like steam and carbon dioxide. These reactions are intricate because they depend on many factors such as how the reactants are mixed, the size of the particles, the composition of the char, and changes in temperature and pressure.

The effectiveness of these reactions varies with the type of char used. For example, char from biomass is usually more reactive than char from fossil sources like coal. This is because the carbon structure in biomass char is more disordered, making it easier to break down.

In gasification, steam and carbon dioxide play a key role. They react with the char by breaking down its molecules, a process known as dissociative chemisorption. The inner surface area of the char is important because it provides many more sites for these reactions than the outer surface area.

The main reactions in gasification include burning the char with oxygen to create carbon dioxide, which happens very quickly and gives off heat. There is also a reaction with steam that produces carbon monoxide and hydrogen, and this absorbs heat. Another slower reaction with carbon dioxide also produces carbon monoxide and absorbs heat. There's also a reaction that involves hydrogen, but it's much slower and not usually important in gasification.

These reactions make gasification useful for different purposes, such as making chemicals, liquid fuels, and power. The heat released from burning part of the material helps drive the other reactions that need heat to work, making the process efficient despite its complexity[13].

2.4 ThermoGravimetric Analysis

Thermogravimetric analysis (TGA) is a highly regarded analytical method that is widely recognized for its capacity to unveil crucial details about the thermal behavior of diverse materials. At its essence, TGA revolves around the principle of "constant change in mass," a dynamic process that provides a glimpse into how materials respond to varying temperatures.

In a TGA experiment, a sample undergoes gradual heating while its weight is continuously

monitored. This ongoing weight measurement enables researchers to observe the material's mass evolution throughout different thermal processes. While specific behaviors may differ between materials, the fundamental characteristic of constant mass change remains integral to TGA's effectiveness.

Throughout TGA experiments, materials often exhibit consistent alterations in mass as temperature increases. These changes can manifest in distinct ways, each conveying important insights into the material's thermal properties:

Mass Loss: Elevated temperatures may lead to a gradual reduction in mass, indicating processes such as thermal degradation, decomposition, or vaporization. The extent and rate of mass loss provide valuable information about the material's stability and decomposition kinetics.

Mass Increase: Conversely, certain materials may experience a mass increase during specific temperature ranges, often associated with oxidation reactions. TGA allows for quantifying the extent and intensity of these reactions, elucidating the material's chemical reactivity and response to varying atmospheric conditions.

TGA generates a continuous record of these mass changes, which can be plotted against temperature or time. The resulting TGA curve serves as a visual representation of the material's thermal journey, offering comprehensive insights into its composition, stability, and reactivity [1].

2.5   Mass Spectrometry

Mass spectrometry is a powerful technique used to figure out the mass of molecules in a sample. It helps scientists identify unknown substances, measure amounts of specific chemicals, and understand the structure and properties of molecules.[2].

Ionization Source: Gateway to Gas-Phase Ions

The process starts by turning molecules into ions, which are electrically charged particles. This is done using a method called nanoelectrospray ionization, similar to how cars are painted in factories. This technique is great because it can create both positive and negative ions depending on what's needed for the experiment. It also works well with other equipment like chromatography columns, which help prepare samples for mass spectrometry. [2].

Mass Analyzer: Sorting by Mass-to-Charge Ratios

Once the molecules are ionized, they go through a device called a mass analyzer that sorts these ions based on their mass-to-charge ratios. There are different types of mass analyzers, and choosing the right one is important because it affects how well the ions are sorted. [2].

Ion Detection System: Decoding the Mass Spectrum

After sorting, the ions are detected and recorded. The results are shown on a mass spectrum, which is a chart displaying mass-to-charge ratios plotted against how many ions are at each ratio. Peaks on this chart show different ion types in the sample, and the height of each peak tells us how much of each type is present.

Mass spectrometry involves ionizing molecules, sorting them by their mass-to-charge ratios, and using a mass spectrum to understand what's in the sample and in what amounts. The

choices made in each step, from how to ionize the molecules to how to detect them, are crucial for getting accurate results. [2].

2.6 Petroleum Coke Thermal Processes

Pyrolysis (Thermal Decomposition)

During pyrolysis, petcoke undergoes thermal decomposition, breaking down complex hydrocarbons into simpler products. This process involves the conversion of petcoke (C_nH_m) into solid carbon (xC), hydrogen gas (yH_2), and various volatile organic compounds (VOCs)[10].

Combustion Reactions

The presence of oxygen during heating induces combustion reactions. Carbon in petcoke reacts with oxygen, forming carbon dioxide (CO_2) and carbon monoxide (CO), shown by the reactions:

- $C + O_2 \rightarrow CO_2$

- $2C + O_2 \rightarrow 2CO$

These reactions contribute to the overall release of energy.

Boudouard Reaction (Carbon Gasification)

The Boudouard reaction is a critical gasification process, particularly noticeable by sharp peaks in the CO_2 profile. This reaction involves the reduction of carbon dioxide by carbon to produce carbon monoxide:

- $CO_2 + C \rightarrow 2CO$

Water-Gas Shift Reaction

Gas chromatographic analysis often shows significant production of hydrogen (H_2) and carbon monoxide (CO). The presence of calcium in petcoke ash may catalyze the water-gas shift reaction, where CO and water vapor (steam) convert into carbon dioxide and hydrogen:

- $CO + H_2O \rightarrow CO_2 + H_2$

Carbon Oxidation Reactions

At lower temperatures, carbon oxidation reactions become prominent, resulting in the exothermic oxidation of carbon, primarily producing carbon dioxide:

- $C + O_2 \rightarrow CO_2$

Smaller-sized particles enhance these carbon oxidation reactions due to their increased surface area.

Gasification Efficiency

Petcoke gasification achieves a high conversion efficiency of 99% with smaller-sized particles at elevated temperatures. This indicates an effective conversion of petcoke into gaseous products, highlighting its potential as a fuel source[10].

2.7 Literature Review

2.7.1 High Temperature Pyrolysis of Petroleum Coke

This study discusses the removal of sulfur from petcoke during high-temperature pyrolysis, using both thermogravimetric analysis-mass spectrometry (TGA-MS) and reactive molecular dynamics simulations based on earlier studies.

Petcoke samples with varying sulfur contents were heated to see how temperature affects sulfur removal. The experiments showed that high temperatures were more important than the size of the petcoke particles for effective sulfur removal. For example, six samples from Qingdao all showed about 80% sulfur removal when heated above 1673 K [21].

Gas Product Identification via TGA-MS: The TGA-MS method helped identify sulfur gases released during petcoke heating. The research identified several stages of weight loss, including water evaporation and the release of gases like hydrogen and sulfur gases such as sulfur dioxide (SO_2) and small amounts of carbon disulfide (CS_2).

ReaxFF MD Simulations: Alongside the experiments, simulations gave a detailed view of how sulfur compounds change during heating. These showed how sulfur compounds break apart and form new ones like COS, C_2S, CNS, CHOS, and HS, especially from compounds like thiophene.

Together, these methods provided deep insights into how sulfur is removed from petcoke at high temperatures, showing the detailed steps and transformations that sulfur compounds go through [21].

2.7.2 TGA-MS Analysis of High-Sulfur Petroleum Coke

The research conducted by Kocaefe and colleagues on green coke pyrolysis offers a comprehensive examination of both the gas and solid phases during pyrolysis under controlled industrial-like conditions[11]. This study significantly extends the understanding of green coke's behavior under thermal stress, specifically focusing on its structural changes and volatile release patterns.

Key Findings from Kocaefe's Research on Green Coke Pyrolysis:

Thermal Decomposition: Green coke undergoes significant transformations when subjected to high temperatures. Initial dehydration is followed by the release of volatile hydrocarbons at around 400°C. As the temperature approaches 450-600°C, non-condensable gases like hydrogen and methane begin to emerge prominently.

Structural Transformations: Alongside gas evolution, significant structural changes occur within the coke matrix. The realignment of crystallites during heating leads to denser coke structures, which is crucial for applications like anode fabrication in aluminum electrolysis, where structural integrity and density are vital.

Kinetics of Gas Evolution: The study employs a kinetic model that adapts to the varying conditions of pyrolysis, providing insights into the rates of gas release. This modeling helps in understanding how different conditions affect the release rates of hydrogen, methane, and other volatiles.

Effects of Pyrolysis Conditions: By manipulating the heating rates and the final pyrolysis temperature, the study delineates how these factors influence the yield and composition of gases released. Higher heating rates lead to quicker but less thorough volatile release, underscoring the importance of optimizing heating conditions based on the desired output.

Industrial Application and Optimization: The findings are particularly relevant for designing and controlling industrial kilns used in calcination processes. The ability to predict gas yields and structural outcomes based on specific heating profiles allows for more efficient and controlled processing of green coke into calcined coke[11].

2.7.3 Temperature-Resolved Evolution and Speciation of Sulfur during Pyrolysis of Petroleum Coke

Understanding the sulfur evolution during petroleum coke (PC) pyrolysis is crucial for improving thermal processes in various industrial applications. Recent studies [20] have shed light on how sulfur behaviors change under varying temperatures and how this affects gasification processes. This review integrates findings from the literature with results obtained from the study of high-sulfur petroleum coke pyrolysis, highlighting key transformations in sulfur speciation across different temperature ranges and heating rates.

Pyrolysis Temperature and Heating Rate Effects Petroleum coke pyrolysis experiments conducted under different heating rates (10 K/min, 30 K/min, and 50 K/min) demonstrate significant variations in sulfur release patterns and weight loss profiles. The TG and DTG curves, as depicted in the figure 2.1, show how increasing the heating rate generally accelerates weight loss, particularly evident above 500°C, where major sulfur-containing gases are released. The high-temperature desulfurization phases are critical, especially above 900°C, where complex sulfur compounds like thiophenes begin to break down significantly.
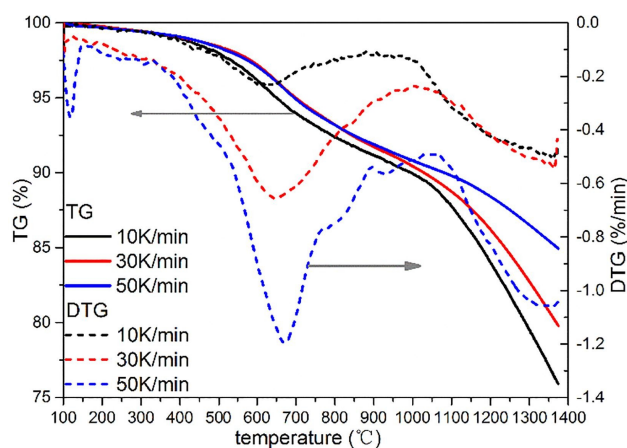
Figure 2.1: *"TG-DTG curves of petroleum coke under different heating rate"* [20]

Sulfur Species Evolution During pyrolysis, multiple sulfur-containing gases such as H_2S, SO_2, CH_3SH, COS, and CS_2 evolve, as indicated by mass spectrometry data as shown in figure 2.2. The release of these gases tends to increase with higher pyrolysis temperatures, displaying notable peaks at specific temperatures which are influenced by the heating rate. For instance, substantial releases of H2S occur below 750°C, mainly attributed to the transformation of mercaptans into gas-phase products, as seen in the detailed mass spectrometry analysis. The presence and transformation of thiophenes and sulfoxides are particularly notable, showing specific peaks and troughs in their evolution, which are directly tied to the temperature phases observed in the TG-DTG data.
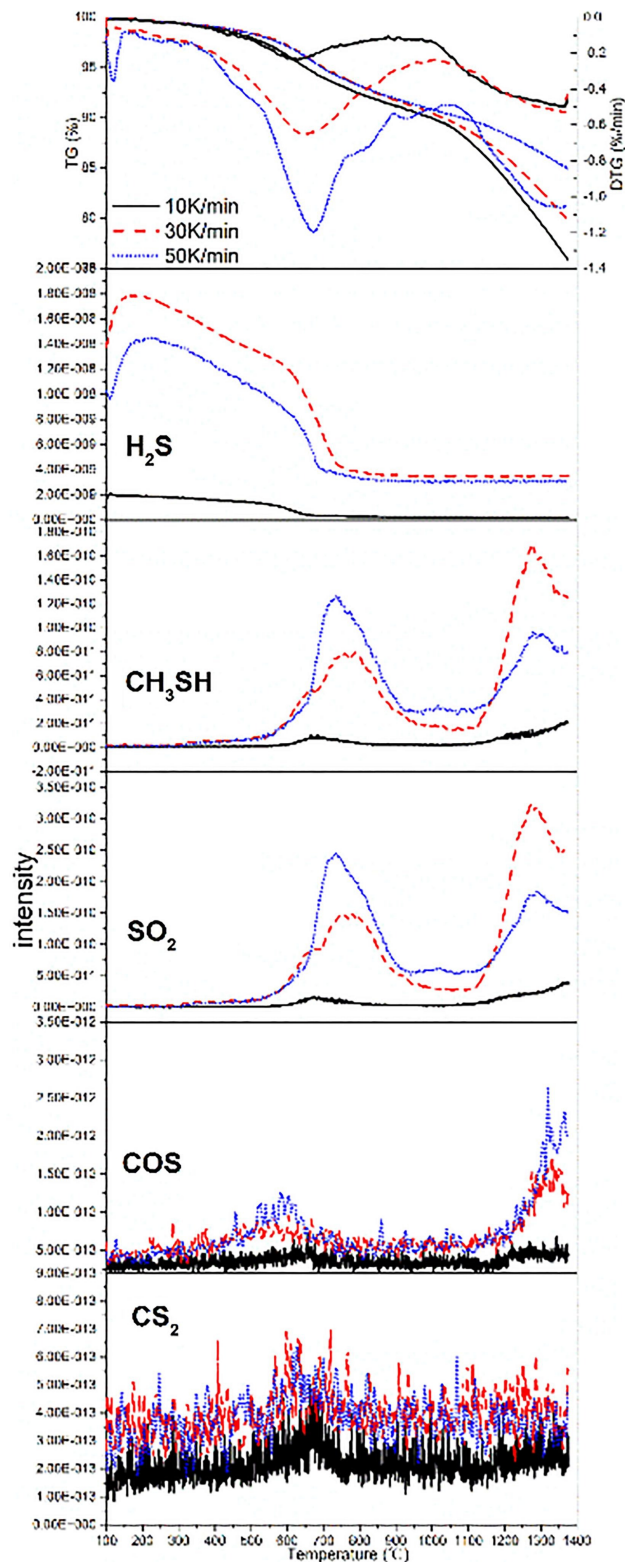
Figure 2.2: "*TG-MS analysis of sulfur-containing gas release characteristics with temperature variation*" [20].

Sulfur Transformation Mechanisms The transformation and release patterns of sulfur species during petroleum coke pyrolysis involve complex chemical reactions influenced by the thermal stability of the sulfur compounds present. For example, the transformation of thiophenes and sulfoxides into various sulfur gases is a critical aspect of the desulfurization process, especially evident in the rapid changes noted between 500°C and 900°C, and then again above 1100°C shown inf figure 2.3. These transformations are crucial for reducing sulfur

emissions in practical applications, such as in fuel combustion or gasification processes where environmental regulations require lower sulfur outputs.
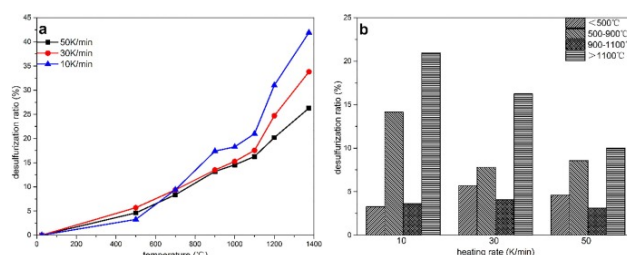
Figure 2.3: "*Desulfurization ratio variation with temperature increased (a); Cumulative desulfurization ratio in different temperature ranges (b)*"[20].

Implications for Industrial Applications The insights gained from these studies are essential for optimizing the pyrolysis processes of petroleum coke, particularly in customizing the pyrolysis conditions based on the sulfur content and desired sulfur removal efficiencies. The ability to tailor the heating rate and final pyrolysis temperature can help in managing the sulfur emission levels more effectively, ensuring compliance with environmental standards while maintaining high energy efficiency in industrial processes[20].

2.7.4 Predicting Pyrolysis of Petroleum Coke: A Comparative Analysis of Models and Experiments

This article [9] presents a comprehensive study on the pyrolysis behavior of petroleum coke, a byproduct of oil refining noted for its high carbon content and calorific value. The research is pivotal for its dual approach in employing both an independent parallel reaction (IPR) model and a backpropagation neural network (BPNN) to predict and analyze the kinetics of petroleum coke's pyrolysis, aiming to enhance the efficiency of its applications in energy production and material processing.

High Methane Production
The study identifies a significant methane production during petroleum coke pyrolysis, mainly occurring in the second stage of the process, which begins at around 450°C and peaks near 600°C. This stage is crucial as it correlates with the maximum pyrolysis peak observed in the thermogravimetric (TGA) and differential thermogravimetric (DTG) curves. Methane generation is attributed to the cracking of aliphatic components within the petroleum coke, involving the breakdown of complex aryl-alkyl ether bonds and other macromolecular structures. Methane's presence is further confirmed in the mass spectrum, noted by dominant fragments with m/z values of 13, 14, 15, and 16, marking its substantial release and cessation by around 850°C.

A Comparative Analysis of Models and Experiments
The research also investigates the thermal decomposition of six different types of petroleum coke sourced from various regions in China, using nonisothermal TGA coupled with thermogravimetry-mass spectrometry (TG-MS). This extensive analysis, supported by kinetic modeling with the IPR model and predictive modeling using BPNN, reveals that petroleum coke pyrolysis primarily occurs in three stages, with significant volatile release and mass loss observed between 250 to 900°C. Both models demonstrated high accuracy in predicting these transformations, aligning closely with experimental data. Notably, the BPNN model excelled in forecasting thermal behaviors based on variables such as heating rate, temperature, and elemental composition, showcasing its potential to refine pyrolysis processes.

The juxtaposition of the IPR and BPNN models highlights the advantages of using ad-

vanced neural networks for managing complex datasets and generating precise predictions crucial for optimizing industrial processes such as calcination and gasification. This approach enhances product quality and energy efficiency in industries that utilize petroleum coke[9].

2.7.5 Desulphurization of Syrian Petroleum Coke through Thermal Treatment

Petroleum coke, a byproduct of the refining process, often contains sulfur compounds that need to be removed to enhance its utility and reduce environmental impact. Thermal treatment has emerged as an effective method for desulphurization, offering advantages over traditional chemical processes. In this literature review, we explore the stages and mechanisms involved in the desulphurization of petroleum coke through thermal treatment.

Initial Stage (300-1075 K): During the initial stage, characterized by temperatures ranging from 300 to 1075 K, desulphurization is minimal, typically less than 1% per 100 K temperature increase. This stage primarily involves the evaporation of moisture and volatile matter present in the coke. Water removal occurs around 400-500 K, leading to a slight increase in calorific value. At approximately 800 K, the evaporation of volatile matter results in the desorption of sulfur compounds, including H2S and RSH. The release of sulfur gases is primarily attributed to the desorption of chemisorbed sulfur in coke pores or on the coke surface.

Second Stage (1075-1175 K): Desulphurization increases sharply during the second stage, with an average rate of approximately 18%. Most of the sulfur removed in this stage originates from the decomposition of thermally-stable sulfur compounds bound in side chains.

Third Stage (1175-1450 K): In the third stage, desulphurization slows down to around 8%, with evidence suggesting that sulfur separation ceases around 1300 K. The formation of sulfur hydrocarbon complexes, as well as reactions with metal-hydrocarbon compounds present in the coke, contribute to the decrease in desulphurization efficiency.

Final Stage (Above 1450 K): At temperatures above 1450 K, desulphurization rates vary between 13% and 22%. Inhibition of desulphurization may occur at 1500 K due to the formation of thermally-stable metal sulfides. However, temperatures above 1600 K are expected to lead to a marked increase in desulphurization, as energy levels are sufficient for the decomposition of sulfur-hydrocarbon compounds.

This study shows effective desulphurization of petroleum coke can be achieved through thermal treatment up to temperatures of 1700 K, with increased residence times of up to 180 minutes. This method offers a viable approach to reducing sulfur content while minimizing adverse effects associated with higher temperature treatments [8].

2.7.6 Pyrolysis characteristics analyzed through TG–MS

This study [19] shows the recent progress in extracting natural gas from deep underground layers has sparked interest in how coal can continue to produce gas even at later stages, especially through a process called pyrolysis. This review looks at a study that used a method combining heat analysis and mass spectrometry (called TG–MS) to study how coal breaks down and releases gas in the Songliao Basin. The study shows that during the breakdown of coal, both hydrocarbons (like methane) and other gases are produced, and this has important implications for understanding how much gas can be generated later on.

Coal samples from the Yingcheng coal mine were heated in controlled conditions to simulate natural processes deep underground. The tests showed that methane gas starts to

form at about 300 °C, reaches a high point at 480 °C, and continues to be produced up to about 850 °C. This is much longer than other gases from coal. This shows that coal can produce a significant amount of gas later in its breakdown process—about 17% more than what we used to think, which is important for considering coal as a future natural gas source.

The study also developed a model to explain how and when gas is formed from coal in the Shahezi Formation, an area within the Xujiaweizi Fault Depression. Unlike most models that expect gas production to happen quickly and at once, this model shows a steady production of methane over time without sharp peaks.

Moreover, the study questions old beliefs about when coal stops producing gas, showing that methane can be released even at much higher temperatures. This suggests that coal can still be a valuable gas source at stages previously thought unproductive.

Overall, this research not only improves our understanding of how coal can produce gas but also helps to make better models for finding natural gas in coal-rich areas. By increasing the maximum temperature for these tests to 1000 °C, the study gives a clearer picture of how much gas coal can really produce, which is vital for evaluating old, mature coal deposits in terms of their gas production potential[19].

Chapter 3

Method

3.1 TGA-MS Methodology

3.1.1 Overview

This study uses Thermal Gravimetric Analysis combined with Mass Spectrometry (TGA-MS) to analyze the breakdown of petroleum coke (petcoke). This section outlines the steps we followed, focusing on how we prepared the samples, controlled the experiment's temperature, and analyzed the results.

3.1.2 Sample Preparation and Experiment Setup

We prepared the petroleum coke samples to be consistent and comparable. The samples were finely ground to make sure they heat evenly and then weighed, with each sample being about 34 mg. They were placed in high-temperature-resistant alumina crucibles to avoid any reactions with the container.

3.1.3 Temperature Program

We controlled the temperature carefully throughout the experiment. Starting at room temperature, we increased the heat gradually to 900°C at a rate of 10°C per minute for one experiment and changed it accordingly to the results. This slow increase helps us see how the petcoke breaks down and what gases it releases at different temperatures. We used argon gas to fill the space around the sample, preventing any unwanted reactions with oxygen.

3.1.4 Analytical Technique

The TGA measures how much the sample's weight changes as it heats up, while the MS identifies the gases that come off the sample during heating. We routed the gases through a heated tube straight to the mass spectrometer, ensuring they stay in gas form for accurate analysis.

3.1.5 Data Acquisition and Analysis

The TGA-MS system automatically tracked the weight of the petcoke and identified the gases released at different temperatures. We set the mass spectrometer to look for specific gases that we expected to see as the petcoke broke down, helping us understand what happens during the heating process.

This practical approach helps us get a clear picture of how petcoke decomposes and evolves under controlled conditions, providing valuable data for improving gasification processes.

3.2 Experimental

Firstly, you'll have to follow a start-up procedure for the MS machine developed by the manufactures.

For example we choose the start temperature, normally the start temperature is the room temperature which makes it a easier temperature to reach in both the startup and when it is chilling down to after finished analysis. All this goes under the dynamic option, next is the max temperature and heating rate. The max temperature for the machine in use is 1600 degrees Celsius, but due to a malfunction in the sensor and the crucibles that exceeds when the heat reach 1000 degrees and above, there will be a glass formation. For time being and the first analysis the max heat is set to 900 degrees to be certain the glass formation is not a threat. For the heating rate there been a set a limit to 20 degrees / min so that the machine does not get too heavy a load. In the start the 10 and 15 degrees/min where used, just to get to see if there were main difference in those two.

The next is to determine which inert gas/atmosphere which will be used to flow to through the system, both the type of gas and which flow. If a to high flow were to be used, the samples in this instance which is pulverized petroleum coke could be blown away which would interfere and make the weight not reliable. Argon with 25-50 ml/min, argon being an inert gas and 25-50 ml/min not too big a flow. The window that displays the Dynamic method is shown in figure 3.1.
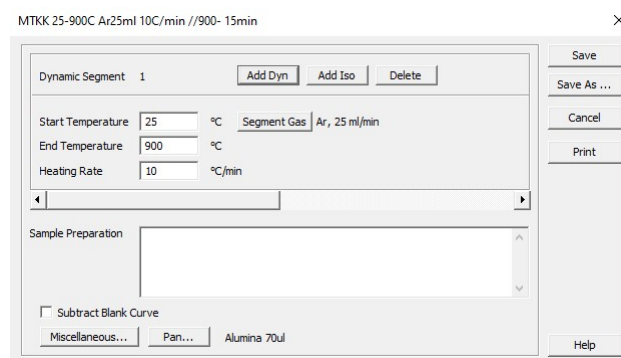
Figure 3.1: Software Dynamic Method

Lastly for the "method" we can add a isothermal mode, there is three different parameters to choose from holding temperature, holding time and which inert gas/atmosphere to use see figure 3.2. Here for the holding temperature it is for to see if there is any reaction in that set temperature over time, for example the first test analysis there was a holding time of 30 minutes at the temperature of 900 degrees with the same option as chosen beforehand in the inert gas/atmosphere.
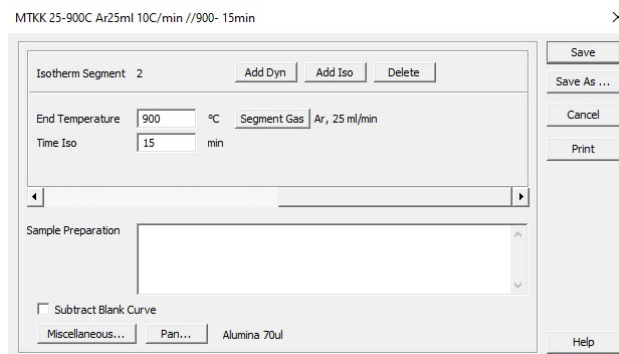
Figure 3.2: Software Isothermal Method

Crucible and Sample:

The crucible that is being used is made out of Alumina and always before they have to be used in the analysis they are weighed in. This to ensure that it is only the sample is getting analysed, the crucible is place onto the the censor by an automatic robot. On the sensor to get accurate weight there is being used an reference crucible to compare, both the blank crucible and reference crucible is the moved into a chamber that excluded from the surroundings, also this is to make accurate weighing.

After the blank crucible is done and ready to get samples to be put in, for every step including the crucibles disposable gloves has to be used to ensure any other materials get to intervene with the samples or crucibles. The Crucible is filled 2/3 of the way, more than that could make the samples getting blown out of the crucible by the gas/atmosphere that is being used. Less could make so that the result wont be affected as much.

Before the TGA setup is nearly complete the sample also has to be weighed in in put into chambers and positions like in figure 3.3.
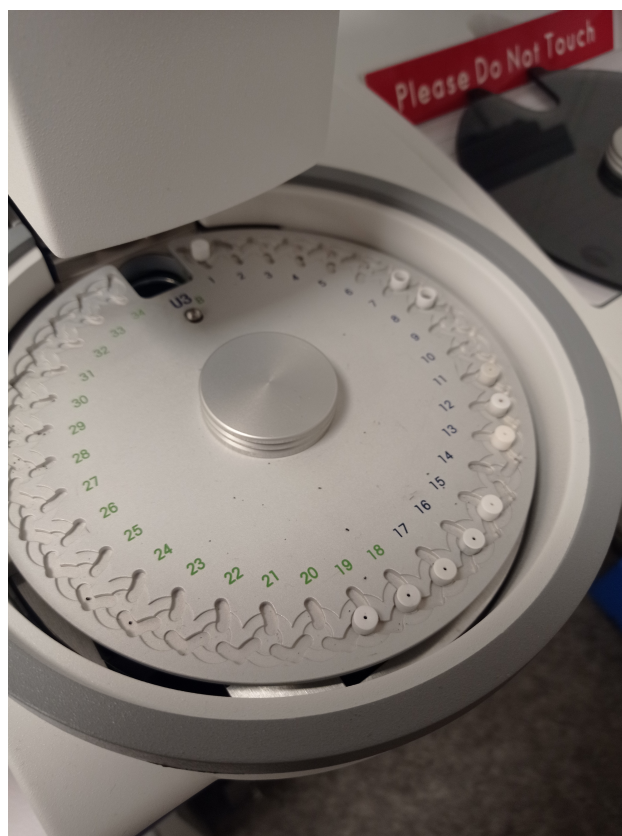
Figure 3.3: Crucible placed in and put in positions.

From the chamber where the TGA is done there is attached a tube that catches all of the gases that occurs during devolatilization and combustion, and is lead into the MS machine.

Analysis of Mass Spectrometry Signals
In this study, the focus of using mass spectrometry was to identify and quantify the gases produced during the thermal decomposition of petcoke. We looked at the mass-to-charge ratios (m/z values) of the gases to distinguish different compounds based on their molecular weights.
Key Gases Monitored We tracked specific gases that are typically released during the gasification of petcoke. These include hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), sulfur dioxide (SO_2), methane (CH_4), and other hydrocarbons. The table (table 3.1) below lists the m/z values used to identify these gases:

Gas	Molecular Formula	m/z Values
Hydrogen	H_2	2
Carbon Monoxide	CO	28
Carbon Dioxide	CO_2	44
Sulfur Dioxide	SO_2	64
Methane	CH_4	16
Water	H_2O	18
Benzene	C_6H_6	78
Toluene	C_7H_8	91

Table 3.1: Common gases from petcoke decomposition and their m/z values.

Data Analysis For each detected gas, we measured the area under the curve for its peak using the software connected to the mass spectrometer. We then matched these measurements with temperature data from the TGA to understand how the petcoke breaks down at different temperatures. This approach helps us better understand which chemical bonds in the petcoke are breaking and at what temperatures, which is crucial for improving the gasification process and managing byproducts.

3.2.1 Heating Rate and Gas Flow rate

A pyrolysis experiment was conducted using a TGA-MS combined setup, with two distinct heating rates of 10°C/min and 15°C/min. The experiment aimed to analyze petcoke samples by subjecting them to varying temperature profiles, starting from 25°C and reaching a final temperature of 900°C. Argon gas served as the carrier medium, with flow rates of 25 mL/min and 50 mL/min facilitating the transportation of pyrolysis products to the MS machine.

The experimental setup utilized a closed tube pyrolysis system. The temperature programming for the pyrolysis involved heating the tube gradually from room temperature to 900°C, followed by maintaining this temperature for 30 minutes. Approximately 35 mg of milled petcoke powder that has been passed thru a 1mm sieve, was utilized for each TGA-MS pyrolysis experiment with different type of petcoke each experiment.

Four distinct experimental runs were conducted, each incorporating specific parameters: two runs involved a heating rate of 10°C/min, utilizing both 25 mL/min and 50 mL/min flow rates of argon, while the remaining two runs employed a heating rate of 15°C/min under the same flow rate conditions. Additionally, an isothermal step at 900°C for 30 minutes was included as part of the experimental protocol.

These parameters where used due some rules for the sensor and based on results done

by Jindi Huang [9]. In the article he mentions that in stage 2 (250°C to 900°C) there is a more significant mass loss and a much higher release of molecules volatiles. In Jindi Huang experiments[9] he uses a flow rate of 45mL/min and had a heating rate of 5, 10, 15 and 20°C/min which also had an influence on my choice of parameters in the first run.In table 3.2 the parameters is summarized.

In the MS analysis, it is necessary to predefine which volatiles to detect. According to research by Min Wang [19], coal pyrolysis not only releases basic compounds such as water, carbon monoxide, and methane but also aromatic molecules like benzene and toluene. These aromatic compounds arise from the breakdown of larger coal molecules. Another significant volatile to monitor is sulfur dioxide[15].

Table 3.2: Summary of TGA-MS Experimental Conditions

Parameter	Test 1	Test 2	Test 3	Test 4
Start Temp (°C)	25	25	25	25
End Temp (°C)	900	900	900	900
Heating Rate (°C/min)	10	15	10	15
Holding Time (min)	30	30	30	30
Holding Temp (°C)	900	900	900	900
Atmosphere	Argon	Argon	Argon	Argon
Sample Quantity (mg)	12	35	31	36
Flow Rate (mL/min)	25	25	50	50

3.2.2 Gas Generation

In the first TGA-MS experiment, the main goal was to closely examine the stages where there was an increase in gas generation and where these gases reached their highest concentrations. This involved identifying specific temperature ranges during the thermal decomposition process where gas production was most intense. By pinpointing these zones, the aim was to better understand the mechanics of decomposition and possibly optimize the process to either maximize or minimize the production of certain gases, depending on the desired outcomes. The experiment's design was tailored to capture detailed data around these critical temperature points, thus providing a clearer view of the reactions taking place.

Hydrogen

In light of the outcomes from the initial TGA-MS analysis, the methodological approach for the second run was adjusted to optimize conditions that could potentially increase hydrogen production during the thermal degradation of petcoke. The preliminary data showed a significant generation of hydrogen within the 600 to 900°C range, as discussed in section 4.1.2. This indicated that this interval was a key zone for petcoke pyrolysis and gas evolution.

For the subsequent experiments, the thermal profile was precisely tuned to the temperature range that showed peak hydrogen generation. An isothermal hold at 600°C allowed for a detailed examination of reactions initiating hydrogen release, while a subsequent isothermal hold at 800°C provided insights into the sustained generation or possible cessation of hydrogen at higher temperatures.

The choice of specific temperatures for isothermal holds was influenced by the observed chemical reaction rates. At 600°C, significant polycondensation reactions appear to trigger an initial increase in hydrogen production. As the temperature reaches 800°C, these reactions

become more vigorous, causing a peak in hydrogen release, which then stabilizes or levels off.

Given the subtle differences in results irrespective of a heating rate of 10°C/min or 15°C/min, and an argon flow rate of 25 ml/min or 50 ml/min, these parameters remained constant to isolate the effects of the targeted temperature holds. This decision was rooted in the initial findings that suggested minimal influence from these variables within the selected range.

The method further included continuous monitoring of gas evolution using mass spectrometry, with a particular focus on capturing the nuances of hydrogen's release profile across the critical temperature thresholds. This improved understanding of hydrogen's generation dynamics was invaluable for enhancing coal pyrolysis models and potentially informing industrial processes aiming to maximize hydrogen yield.

The insights gleaned from the first TGA-MS run provided a strong foundation for these methodological refinements, with the goal to delineate the thermal degradation pathways more clearly and to understand the influence of temperature controls on hydrogen production.

Carbon Monoxide and Carbon Dioxide

After observing how carbon monoxide (CO) and carbon dioxide (CO2) (see section 4.1.2) were produced in the initial TGA-MS experiment, especially between 400 to 500°C see figure 4.5, the next test was planned to focus more on these temperatures.

In the follow-up, fixed temperatures of 400 and 500°C were used to better understand when CO and CO2 production peaked. The hypothesis was that maintaining the sample at these temperatures might lead to more consistent and higher gas production, providing a clearer picture of the reaction kinetics.

The heating rate and the gas flow rate from the first test were not altered. This was done to ensure any differences observed could be directly attributed to the temperature changes. Gas production was continuously monitored with the mass spectrometer to collect real-time data, which helped observe how the gases changed over time and at steady temperatures.

This methodical approach was based on insights from the first test. By keeping some conditions the same and only changing the temperature, it was possible to determine how these changes affected gas production. This approach helped clarify the gas production patterns and will aid in enhancing models that predict gas production from coal pyrolysis.

Methane

In the recent TGA-MS analysis, the methods were adjusted to better understand when methane production was highest. The focus was on detailed checks at specific temperatures—around 450°C where methane starts to increase, and near 630°C where it reaches its peak.

- **Close Temperature Monitoring:** The experiment controlled and closely monitored temperatures at critical points, specifically 450°C and 630°C. These temperatures were crucial because they marked the start and the highest point of methane production.

- **Improved Data Collection:** Data collection was enhanced by slowing the heating rate as the sample approached these critical temperatures. This allowed for collecting more data points and improved clarity in observing how gas production changed.

- **Broader Analysis Range:** The range of temperature analysis was slightly expanded beyond 450°C and 630°C. This helped in understanding both what happens before and after methane reaches its peak, providing insights into how methane is generated and the effects of other reactions that might occur.

These adjustments in the methodology helped gain a clearer and fuller understanding of how methane is generated from petroleum coke, from the start of its production, through the peak, and as it begins to decrease.

Weight Loss

The recent TGA-MS run for petroleum coke included an isothermal hold at 600°C to look into the reactions that cause significant weight loss. This method was aimed at understanding the thermal behavior and stability of petroleum coke components at this important temperature range, just after the most active stage with the largest weight drop (see figure 4.3).
During the isothermal hold at 600°C, the temperature was kept constant to allow for extended observation of the chemical reactions. This period helped in examining slower pyrolytic reactions that are not easily noticeable during continuous temperature rise. This is crucial because up to 500°C, petroleum coke rapidly breaks down, and keeping the temperature steady allowed for the observation of slower secondary reactions that also play a role in the ongoing breakdown and gas release from the material. Table 3.3 summarizes the second experiments parameters.

Table 3.3: Summary of TGA-MS Experimental Conditions second experiment

Parameter	Test 5	Test 6	Test 7	Test 8
Start Temp (°C)	25	25	25	25
End Temp (°C)	900	900	900	900
Heating Rate (°C/min)	10	10	10	10
Holding Time (min)	30	30	30	30
Holding Temp (°C)	600 and 800	400 and 500	450 and 650	600
Atmosphere	Argon	Argon	Argon	Argon
Sample Quantity (mg)	36	48	44	44
Flow Rate (mL/min)	25	25	25	25

3.3 Gas Generation at Lower Heating Rate

The recent TGA-MS experiment was designed to examine key temperature zones where gas generation increases, similar to the previous experiment (see section 3.2.2), but with a lower heating rate. This approach was guided by research [7] indicating that slower heating rates more closely mirror natural processes found in geological formations. For this experiment all the parameters is displayed in table 3.4.

3.3.1 Hydrogen

Building on the earlier TGA-MS results 4.2.1, the recent tests were designed to refine the understanding of conditions that maximize hydrogen production during coal's thermal decomposition. Significant hydrogen release was previously recorded between 600 to 800°C. The latest tests focused on this temperature range, employing a controlled heating rate of

5°C per minute, based on studies [7] that suggest slower heating rates more accurately reflect natural processes.

The experiments included prolonged periods at 600°C and 800°C to closely examine hydrogen release at these temperatures. These points were chosen because they matched significant increases in hydrogen noted in earlier tests. The slower heating rate allowed for clearer tracking of chemical reactions, providing deeper insights into hydrogen production during coal decomposition.

3.3.2 Carbon Monoxide and Carbon Dioxide

The recent experiments also explored the formation of carbon monoxide and carbon dioxide, particularly in the 400 to 500°C range where significant activity had been observed 4.2.2. A steady heating rate of 5°C per minute was used to better isolate and understand the behaviors of these gases at different temperatures.

3.3.3 Methane

For methane, the focus was on temperatures of 450°C and 630°C, where significant methane production was noted. Keeping the heating rate at 5°C per minute as the sample heated to these temperatures allowed for more detailed data collection and a clearer understanding of methane's behavior under these specific conditions.

3.3.4 Weight Loss

To investigate weight loss in petroleum coke, the tests maintained a temperature of 600°C, just after the most rapid breakdown phase noted in previous tests. The heating rate of 5°C per minute helped focus on slower reactions that might not be as apparent at higher temperatures. This approach helped reveal more about the secondary reactions that influence the stability and breakdown of the material.

Table 3.4: Summary of TGA-MS Experimental Conditions third experiment

Parameter	Test 9	Test 10	Test 11	Test 12
Start Temp (°C)	25	25	25	25
End Temp (°C)	900	900	900	900
Heating Rate (°C/min)	5	5	5	5
Holding Time (min)	30	30	30	30
Holding Temp (°C)	600 and 800	400 and 500	450 and 650	600
Atmosphere	Argon	Argon	Argon	Argon
Sample Quantity (mg)	55	37	37	43
Flow Rate (mL/min)	50	50	50	50

Chapter 4

Results and Discussion

4.1 Heat Rate and Gas Flow Rate

4.1.1 Weight Loss

The TGA and differential thermogravimetric analysis (DTG) curves illustrates four samples of same type of petroleum coke (Sample 1) where three of them were weighted in at around 35 mg and one were at 12 mg, with heating rates of 10 and 15 ° C / min under an atmosphere of argon with a flow rate of 25 and 50 ml / min. The pyrolysis process of the petroleum coke reveal a weight loss of approximately 8% when the temperature reaches 900°C and were kept at 900°C for 30 min as shown in figure 4.1.

This pyrolysis process is divided into three stages. In the first stage, occurring from room temperature to 200°C, physical and chemical changes like drying, liquefaction, diffusion and flow may occur. The second stage, between 200-500 °C, involves the breakdown of large molecules, leading to the production of water, hydrocarbons, and carbon monoxide. The final stage, typically occurring at temperature higher than 500°C, this stage involves processes such as polycondensation and aromatization. Here, complex chemical reactions lead to the generations of hydrogen, methane, carbon dioxide, and carbon monoxide. This stage typically exhibits the fastest weight loss, with the maximum weight loss recorded at 626 - 631°C. This stage represents a critical phase were significant chemical transformations occur, resulting in the liberation of volatile components[19].

These reactions contribute to the formation of more stable molecular structures and the release of gaseous by-products. Each stage of the pyrolysis process represents distinct thermal and chemical transformations, contributing to the overall evolution of the petcoke composition and properties. These stages are characterized by varying rates of weight loss and the generation of different volatile and gaseous products, reflecting the complex nature of composition under pyrolytic conditions.
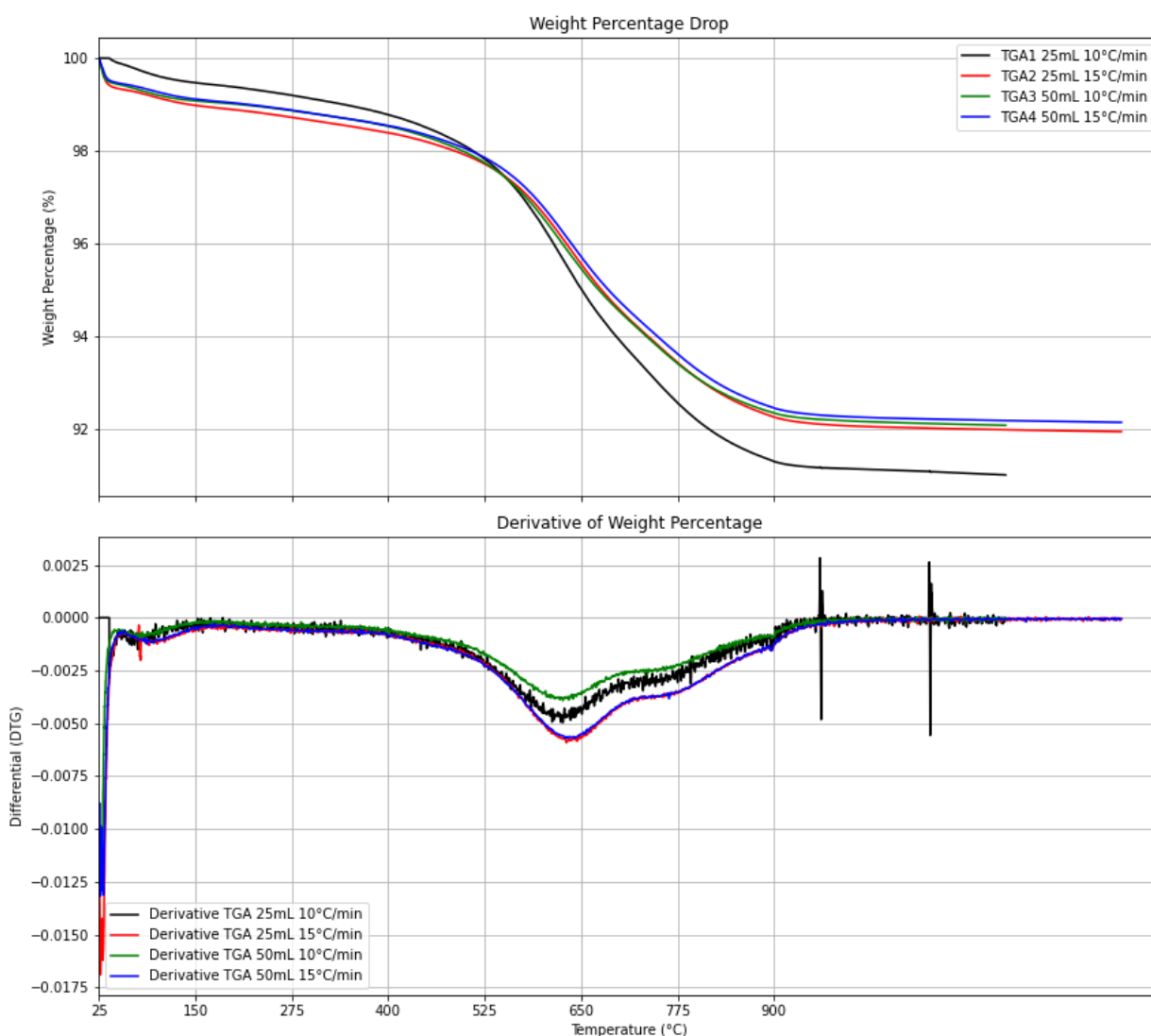
Figure 4.1: Weight loss and differential thermogravimetric analysis (DTG) for four different samples at different heating rates and flow rate

The weight loss across the four parallel samples is carefully analyzed over detailed temperature ranges (see figure 4.2) to assess differences in their response to heat treatment under varying conditions. These samples undergo similar heat treatments but differ in specific parameters such as heating rates and nitrogen purging speeds, which are critical to understanding their thermal behavior. As shown in table 4.1, the optimal conditions for these analyses involve a argon purge rate of 25 ml/min and a heating rate of 10°C/min. These settings are recommended because they provide clearer visibility of weight loss transitions, which helps in minimizing changes in chemical properties that could obscure the analysis. This approach ensures a more accurate assessment of how each sample decomposes and reacts to incremental heat increases

1. **Zone 1 (25°C to 200°C:** The weight loss is minimal, which suggests that there is a small amount of moisture and light volatile compounds in the petroleum coke. The slightly higher weight loss in Sample 2 could indicate a higher moisture content or more volatile compounds compared to other samples.

2. **Zone 2 (200°C to 500°C):** The weight losses in this zone are slightly more substantial. This range can correspond to the evolution of light hydrocarbons or the beginning of the breakdown of more volatile compounds of petroleum coke.

3. **Zone 3 (500°C to 700°C):** This zone shows a significant weight loss, which is typical for petroleum coke as it undergoes substantial thermal decomposition. The materials decompose into gaseous products such as carbon monoxide and carbon dioxide, and the difference in weight loss among the samples could indicate variation in their chemical structure or purity.

4. **Zone 4 (700°C to 900°C):** Weight loss continues but at a reduced rate compared to Zone 3, indicating that the rate of decomposition is slowing down. The remaining components are likely more thermally stable. the similarity in weight loss across samples suggest that these components are consistent in composition.

5. **Zone 5 (900°C and hold for 30 min):** The weight loss is relatively low, indicating the presence of very stable materials that only decomposes at very high temperature. This zone might represent the breakdown of the most refractory components of the coke or the approach towards a final ash content.

From the data (table 4.1), its evident that all the samples follow a similar trend, with the most significant decomposition occurring between 500°C and 700°C.

Table 4.1: Comparison of Samples across Different Zones with the change of weight percentage drop

	Zone 1 (WΔ%)	Zone 2 (WΔ%)	Zone 3 (WΔ%)	Zone 4 (WΔ%)	Zone 5 (WΔ%)
Sample 1	0.622	1.280	4.197	2.612	0.290
Sample 2	1.112	0.980	3.341	2.319	0.273
Sample 3	0.988	1.045	3.443	2.193	0.262
Sample 4	0.967	0.985	3.307	2.299	0.268
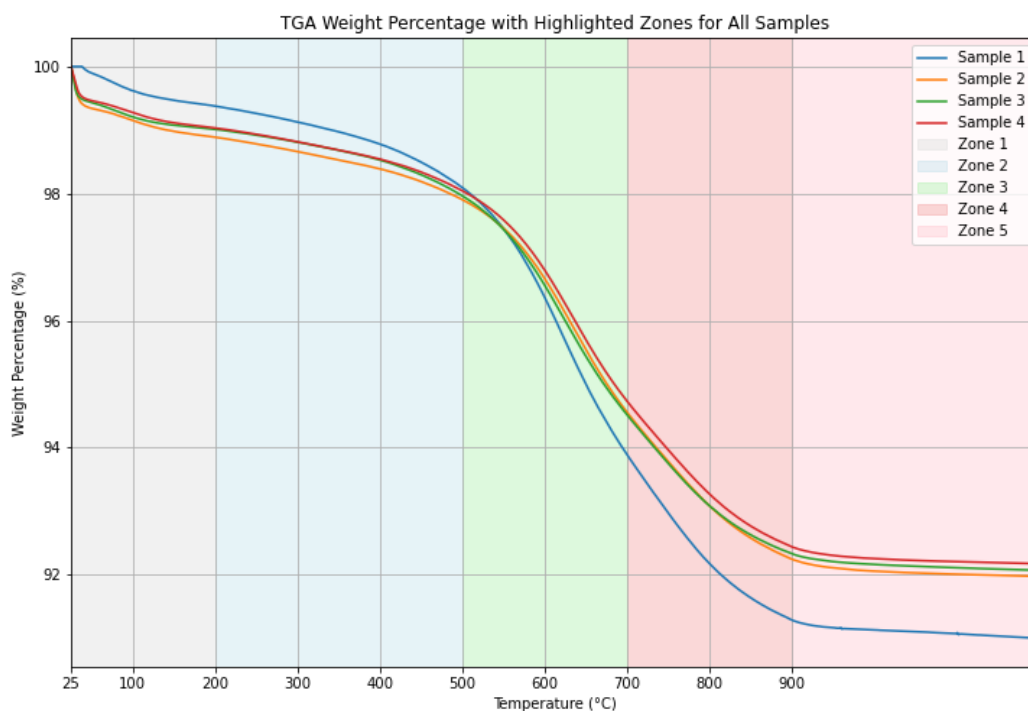
Figure 4.2: Weight Percentage drop divided into five different zones

4.1.2 Volatiles

For the sample with a mass of 12 mg, the lower amount of material available for analysis may result in less reliable signals. With a smaller sample size, there is a higher likelihood of variations in the composition and distribution of compounds within the sample. This variability can lead to less consistent results and increased uncertainty in the measurements obtained from TGA-MS analysis.

In contrast, the samples with a mass of around 35 mg provide more material for analysis, resulting in more stable and reliable signals. With a larger sample size, any variations in composition or distribution of compounds are likely to have less of an impact on the overall results. Additionally, having more material to analyze can help mitigate any potential errors or inconsistencies in the experimental process.

Overall, the sample mass plays a crucial role in the accuracy and stability of TGA-MS analysis. Larger sample sizes generally yield more reliable results, while smaller sample sizes may lead to greater variability and less accurate measurements. Therefore, it's important to consider sample mass carefully when conducting TGA-MS experiments to ensure the accuracy and reproducibility of the results. For most of the volatiles graphs there is a significant difference in generation of gases. Figure 4.3 below show how the weight drop and gas generation over given temperature.
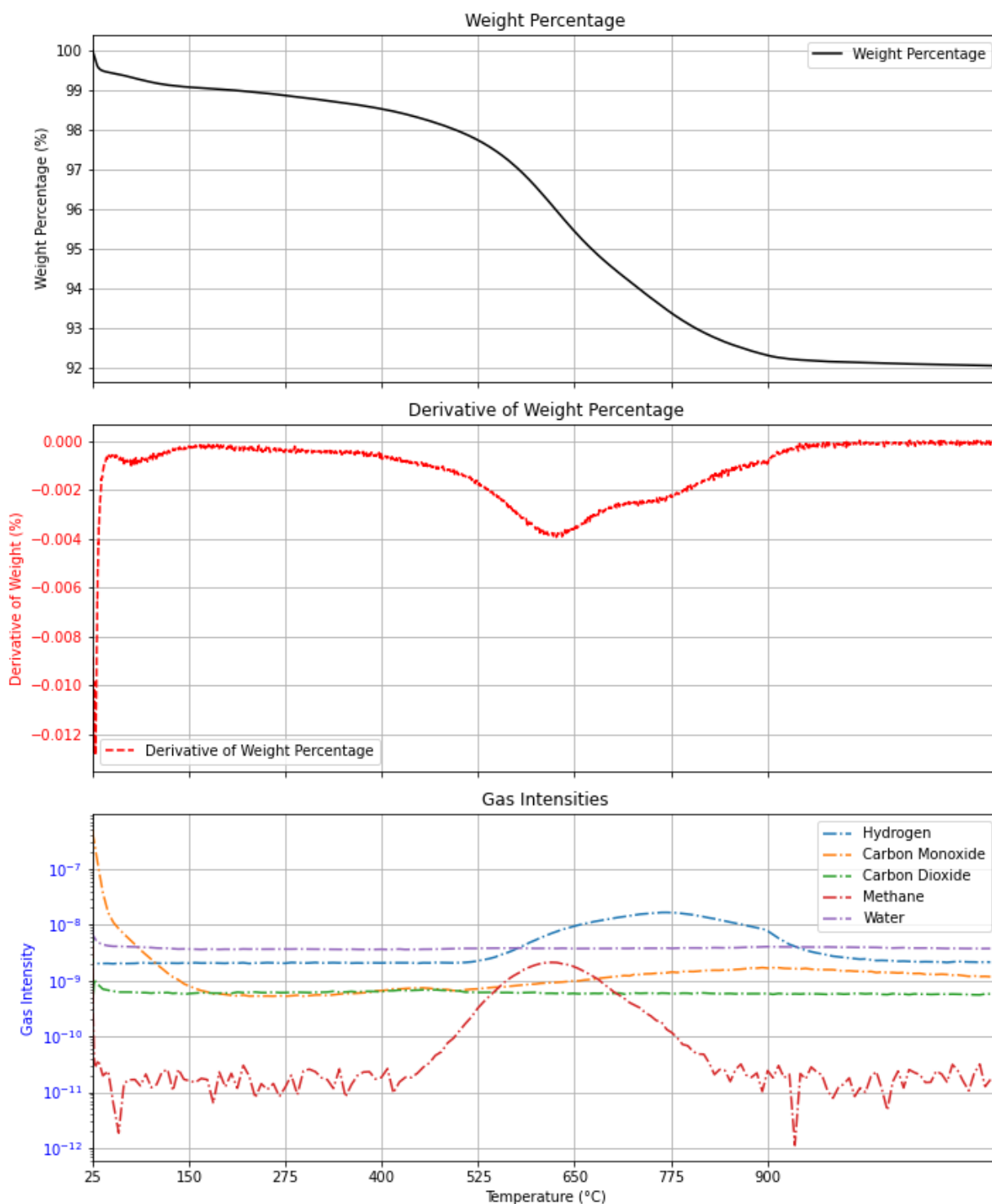
Figure 4.3: Comparison between the weight percentage drop, DTG and the gas generation for sample 3

Methane (CH$_4$)

Methane (CH$_4$) is the primary aliphatic product of petroleum coke and holds and significant importance. Its presence is characterized by fragmented ions with mass-to-charge ratios (m/z) of mainly 15 and 16 in the methane mass spectrum. However, the intensity of ions with m/z = 16 can be influenced by oxygen compounds such as H$_2$O, CO and CO$_2$. Notably, a pronounced peak around 800°C in the intensity curve of ions with m/z = 16 is attributed to CO$_2$, indicating the fragmentation of CO$_2$ compounds.

The absence of a high-temperature peak or tail beyond 550°C on the m/z = 15 curve sug-

gests that the peak at 800°C in the intensity-temperature curve of m/z = 16 is solely due to oxygen compound fragments, possibly from CO_2. Therefore, analyzing the fragment intensity-temperature relationship of m/z = 15 may be more effective in studying methane evolution[19].

The pyrolysis results demonstrate that methane generation initiates at approximately 450°C (m/z = 15) with a heating rate of 10°C/min, peaks around 630°C, and continues with decreasing rate until about 800°C. However, methane production ceases around 850°C to 900°C and have a low generation when the temperature is isothermal. Methane generation exhibits a broader and more intense peak compared to other aliphatic products, indicating a wider temperature range for its evolution.

The generation of methane (red curve), as depicted in Figure 4.3, exhibits a consistent pattern across all samples, despite variations in heating rate and flow rate. This pattern includes the initiation, peak, and subsequent decrease in methane generation occurring at approximately the same temperature range for all samples.

To summarize, the process of methane generation can be divided into three stages:

1. In the first stage (350-450°C), reactions occur where long-chained aromatic groups and alkyl groups undergo ether bond cleavage, yielding smaller methane molecules.

2. The second stage (500-550°C) involves the secondary cracking of relatively stable chemical bonds, such as methyl groups, to produce methane.

3. Finally, in the last stage, methane is generated through polycondensation reactions of aromatic molecules.

Water (H_2O)

In this study, the way water appears during petcoke pyrolysis happens in three main stages. At first, water that's already in the petcoke shows up, especially at lower temperatures below 100°C. Next, from 100°C to 400°C, water trapped between layers of clay minerals starts to emerge. Above 400°C, water created from the breakdown of oxygen-rich groups within the petcoke becomes more common [19].

Significantly, we see notable increases in water levels at 480°C and again at 800°C. The first increase in water, around 480°C, happens at the same time as methane starts to form, suggesting that both processes occur together. The second spike in water, at 800°C, happens as carbonate minerals like CaCO3 break down—something that typically happens between 700°C and 800°C. This matches with an increase in CO_2 observed at similar temperatures, as shown in figure 4.3. For a more detailed look at how water and carbon dioxide compare during this process, see figure 4.4.
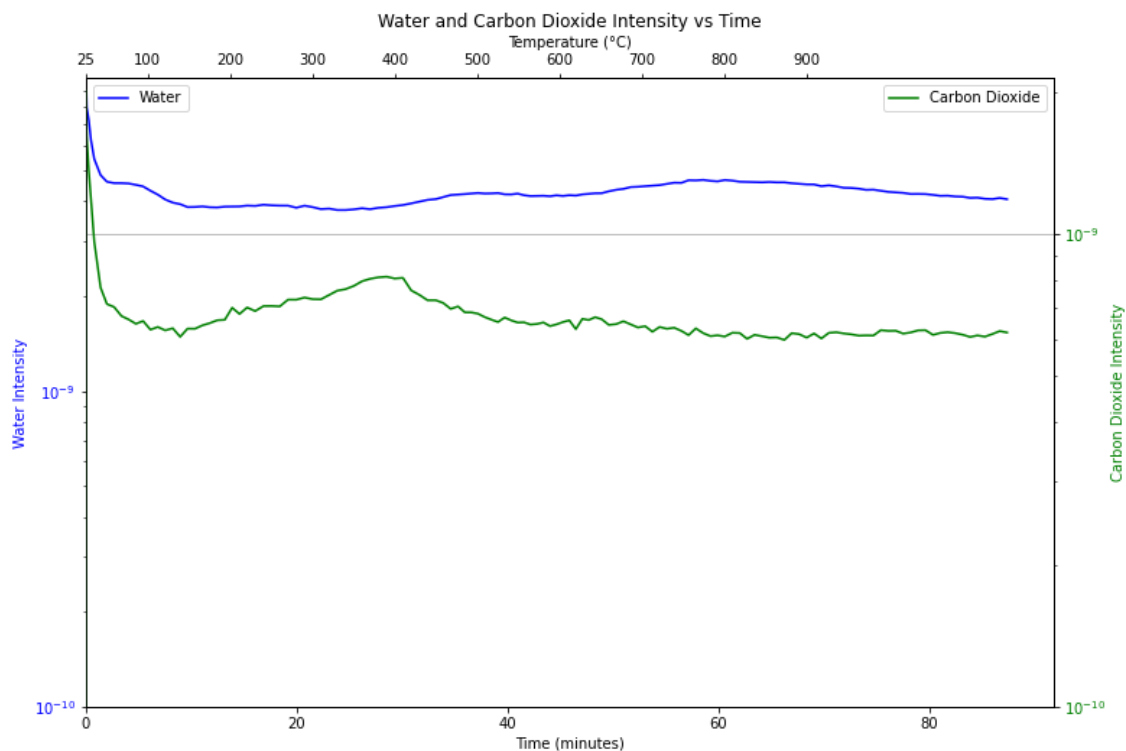
Figure 4.4: The comparison from water and carbon dioxide with a more focused graph

Carbon Dioxide(CO_2)

Throughout the pyrolysis process, CO_2 is produced from various sources, ranging from low to high temperatures. At lower temperatures, CO_2 comes from the release of CO_2 that was already present in the material. As the temperature goes up, CO_2 production increases due to the breakdown of certain chemical groups and bonds in the material.

An important source of CO_2 is the breakdown of carbonates. For instance, CaCO3 breaks down between 700°C and 800°C, and carbonates containing iron break down below 600°C. This breakdown significantly raises CO_2 levels, especially after 500°C.

The CO_2 production curve shows several peaks, indicating different sources of CO_2. A peak at 400°C is mainly due to the breaking down of weak chemical bonds in the material (see figure 4.5). Another major peak at 800°C is linked to the breakdown of more complex molecules. There is also a smaller peak around 650°C, suggesting that other complex molecules are present.

Additionally, the simultaneous appearance of peaks for CO_2 and water at 800°C strongly indicates that carbonates are breaking down into CO_2 and water (see figure 4.3), which helps explain the detailed processes that produce CO_2 during pyrolysis [18].
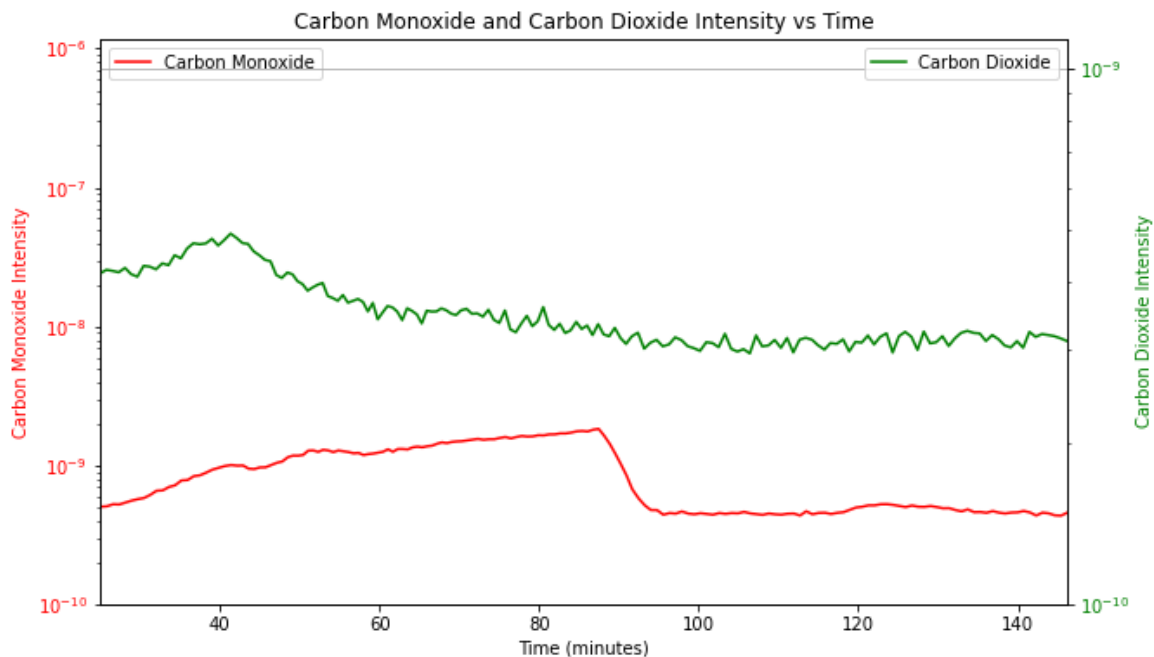
Figure 4.5: Carbon Monoxide and Carbon Dioxide Intensity vs Time with a heating of 10°C/min with start temperature at 25°C

Carbon Monoxide (CO)

The production of CO during petcoke pyrolysis follows a distinct pattern. Initially, there is minimal CO generation until the temperature surpasses 350°C. The production of CO peaks for the first time at around 400°C. Subsequently, the production rate of CO gradually declines. However, at higher temperatures, three minor peaks emerge at approximately 600°C, and 900°C, as depicted in Figure 4.3. This suggests that the formation of CO may be influenced by the decomposition of aliphatic–aliphatic ether structures or aliphatic–aromatic ether structures, as noted in previous studies[16]. However, as the temperature exceeds 700°C, the generation of CO is likely dominated by the Boudouard equilibrium reaction:

$$H_2O + C \rightarrow H_2 + CO \tag{4.1}$$

and

$$2CO \rightarrow CO_2 + C \tag{4.2}$$

Hydrogen (H_2)

During the thermal degradation process of petcoke, hydrogen (H_2) generation occurs primarily through polycondensation and dehydrogenation reactions involving aromatic structures and hydrogenated aromatic structures, particularly within the temperature range of 500 to 850 ° C, as shown in Figure 4.3. This temperature range is critical for inducing these reactions because of the high thermal energy present.

The generation of H_2 during petcoke pyrolysis is commonly conceptualized in two distinct phases:

First Phase (400-600°C): This phase initiates between 400 and 600°C and is attributed to polycondensation reactions among free radicals. During this stage, precursor molecules undergo chemical transformations, potentially leading to the formation of intermediate products rich in hydrogen content.

Second Phase (600-900°C): The subsequent phase occurs between 600 and 900°C, where a substantial amount of H_2 is produced. This increase in H_2 generation becomes more pronounced from 600°C onwards. Here, the primary mechanism involves polycondensation reactions, particularly during the late stage of pyrolysis. This phase is characterized by the condensation and dehydrogenation of aromatic structures, wherein compounds with fewer aromatic rings condense into larger aromatic structures. This process is often accompanied by the liberation of hydrogen molecules[4].

Sulphur Dioxide (SO$_2$)

During the thermal decomposition of petcoke, sulfur compounds such as sulfur dioxide (SO_2) are produced, along with other sulfur-containing compounds like hydrogen sulfide (H_2S), methyl mercaptan (CH_3SH), and thiophene[3]. These sulfur compounds can be measured using mass spectrometry (MS) fragments with specific mass-to-charge ratios (m/z), such as 64 for SO_2.

An intriguing observation is the presence of a low-temperature peak for sulfur compounds, including H_2S, CH_3SH, and thiophene, around 170°C. This is contrary to the typical decomposition temperature of pyrite, a common source of sulfur, which occurs around 600°C in an inert atmosphere[12]. This discrepancy suggests that the sulfur ions in these compounds may originate from the decomposition of organic sulfur rather than pyritic sulfur.

As the temperature rises, the intensities of MS fragments associated with sulfur compounds increase, indicating the generation of SO_2, CH_3SH, and H_2S during petcoke pyrolysis. Previous studies suggest that SO_2 formation may involve sulfur sourced from inorganic sulfur compounds like pyrite, reacting with external oxygen traces[3]. However, there's ongoing debate regarding the exact mechanisms and sources of SO_2 formation, with some proposing reactions between sulfur-containing intermediates and external oxygen as a plausible explanation[18].

Benzene and Toluene

Petroleum coke pyrolysis predominantly yields minimal aromatic compounds compared to the quantities of H_2O, CO, H_2, and CH_4. Consequently, the intensity curves of aromatic products exhibit noticeable noise due to their relatively lower abundance. However, qualitative analysis can still be conducted based on discernible trends in aromatic product evolution during pyrolysis. Major aromatic products generated during petcoke pyrolysis include benzene, toluene and their derivatives, arising from the degradation and cracking of large molecules[17].

Of particular note, the intensity curves of aromatic products and fatty hydrocarbons exhibit similar shapes and peak temperature positions, albeit with varying intensities. This similarity suggests that toluene and fatty products may result from a common chemical reaction triggered by the disruption of aliphatic bridge-connecting aromatic structures within large coke molecules[17].

In the context of analyzing gas intensity data from MS as part of TGA, the reliability of the data is critical. When the observation of benzene and toluene readings shows that the intensity is below 10^{-11}, such readings can be considered as noise rather than true signals.

The presence of noise can stem from various sources, including but not limited to:

1. **Background Noise:** The MS instrument has an inherent level of background noise that can be due to electronic or chemical sources, and low intensity signals can be lost within this noise floor.

2. **Sensitivity Limit:**Each MS instrument has a detection limit, which is the lowest of a substance that can be reliably distinguished from the absence of that substance. Readings below this limit cannot be confidently attributed to the presence of the gas being measured.

3. **Signal-to-noise Ratio (S/N):** This is a measure og the signal strength relative to the background noise. A low S/N ratio indicates that the signal is not significantly higher than the noise, making it unreliable.

4. **Statistical Variations:** At very low intensities, statistical fluctuations in the count of ions detected can lead to large relative variations in the measured intensity, which do not reflect changes in the actual concentration of the gas.

Given these factors, readings below a certain threshold, such as 10^{-11} in this case for benzene, toluene, and sulfur dioxide, will be ignored because they do not provide reliable information about the gas concentration. They could represent sporadic ions that are detected due to random fluctuations or background signals, rather than a true, stable presence of the gas in the sample.

4.2   Gas Generation

Following the targeted methodological adjustments, the thermal degradation of the petroleum coke was re-examined with a focus on the gas generation with different temperature mark, where an isothermal hold was anticipated to increase the generation of hydrogen, carbon monoxide, carbon dioxide or methane. However, the data did not indicate a substantial elevation in gas production during the isothermal phase compared to the continuous heating process employed in the initial run as shown in figure 4.6.

The weight percentage curves displayed a consistent trend with the previous analysis, with no notable shifts in the temperature zones corresponding to significant weight losses. Similarly, the derivative of weight percentage graphs, which pinpoint the rate of weight change, did not reveal any drastic deviations, maintaining a comparable profile throughout the temperature range.
Gas intensities for hydrogen, as well as for other gases such as carbon monoxide, carbon dioxide, and methane, were meticulously tracked through mass spectrometry. The expectation of a discernible increase in hydrogen release in the isothermal hold of 600 ° C was not met (more details are described in Section 4.2.1). Instead, the gas evolution pattern remained largely unchanged, following a trajectory similar to that in the first run.

This unexpected outcome could suggest that the petcoke's composition and the inherent pyrolytic behavior at 600°C are resilient to isothermal holds, or that the duration and conditions of the hold were not sufficient to significantly impact the gas production mechanisms. The gas intensity graphs, which were predicted to showcase a marked rise or sustained production peaks at the specific isothermal temperatures, mirrored the first run's results, confirming the resilience of the pyrolytic process to the altered temperature profile.

The consistency across runs, despite the methodological variations, could be instrumental in refining our understanding of the petcoke's thermal behavior. It emphasizes the robust nature of the pyrolysis process and the potential need for more drastic changes in the thermal profile or atmosphere composition to achieve a noticeable effect on hydrogen generation.
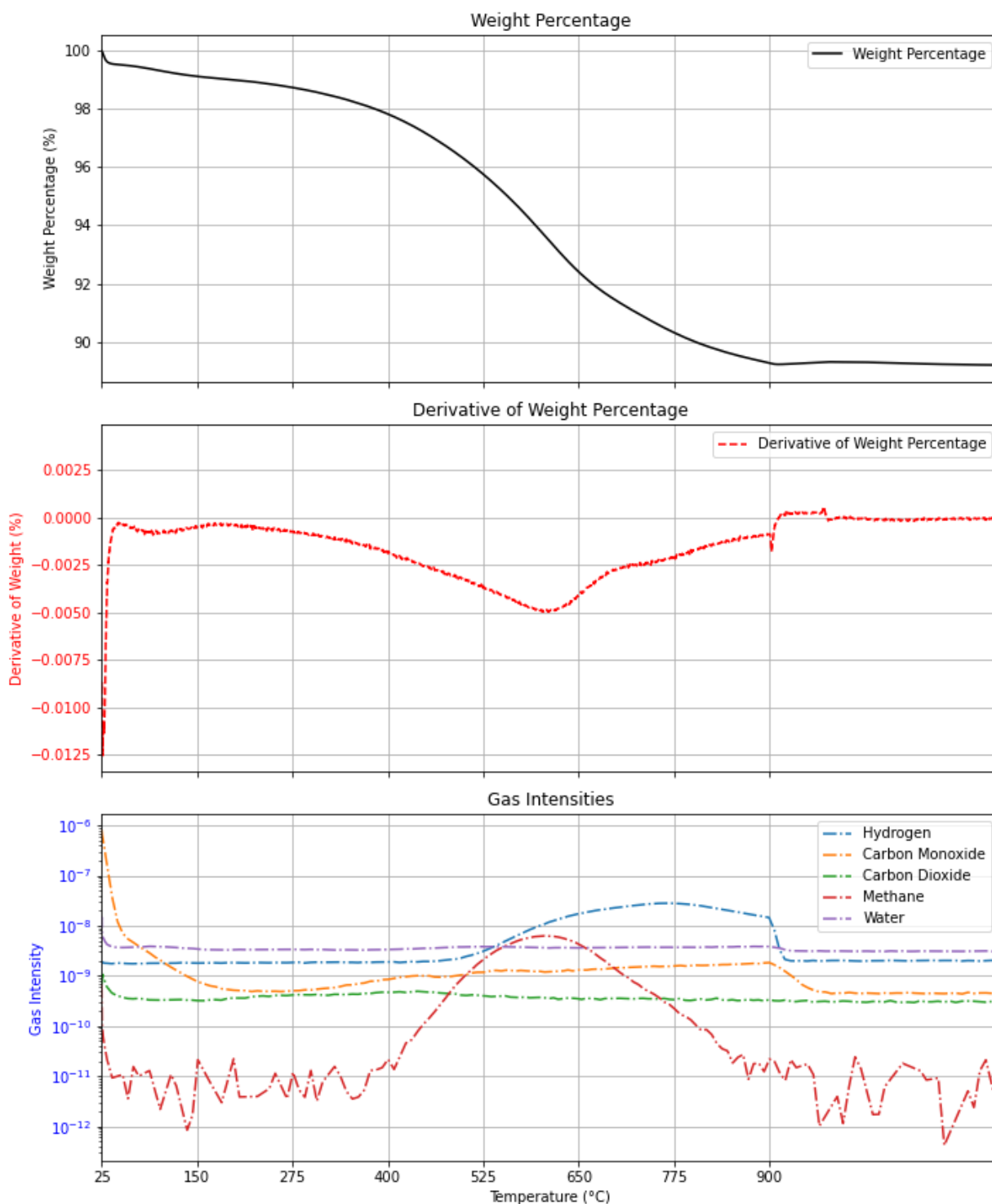
Figure 4.6: Comparison between the weight percentage drop, DTG and the gas generation for the run based on hydrogen generation where the focus was on hydrogen generation.

4.2.1 Hydrogen

The second run of TGA-MS analysis aimed to capitalize on the pronounced hydrogen production observed between 600°C to 800°C from the initial tests. Despite methodological refinements, including isothermal holds at these critical temperatures, the anticipated amplification of hydrogen evolution was not observed. This outcome prompts a reassessment of our understanding of the pyrolysis process and the conditions that favor hydrogen generation. Key findings from this run include:

1. **Isothermal Holds and Hydrogen Production:** The isothermal holds at 600°C and 800°C did not yield the expected increase in hydrogen release, suggesting that the conditions for enhancing hydrogen generation during pyrolysis may not solely be temperature-dependent. The reactions contributing to hydrogen production at these temperatures might have reached a kinetic limit under the given experimental conditions, implying a plateau effect.

2. **Reaction Kinetics Analysis:** The consistent hydrogen intensity across the temperature span could indicate that the reaction pathways for hydrogen evolution are not significantly extended or intensified by maintaining the temperature at the previously observed peak production points. This finding could reflect a balance between hydrogen generation and consumption within the sample matrix at these temperatures.

3. **Parameter Optimization:** Maintaining the heating rate and argon flow rate constant was crucial to focusing on the effects of temperature. The similarity in the results, regardless of these parameters, indicates that further optimization may be necessary, possibly in the form of dynamic temperature programming or adjusting other environmental conditions.

4.2.2 Carbon Monoxide And Carbon Dioxide

The Boudouard equilibrium reaction, which describes the balance between carbon monoxide, carbon dioxide, and carbon at high temperatures, was a central focus in this TGA-MS analysis. However, our results show no substantial increase in carbon monoxide or carbon dioxide production within the isothermal hold at 400 to 500°C for 30 minutes each. This suggests that the Boudouard equilibrium did not change significantly to enhance CO production under the tested conditions.

The generation of hydrogen, another gas of interest in petcoke pyrolysis, also did not exhibit a marked increase despite the adjusted methodological parameters. The expectation was that the isothermal holds would provide a window into the reactions contributing to hydrogen release, which might involve the reduction of water gas shift reaction, where CO reacts with water to form CO_2 and H_2. Given the unchanged levels of hydrogen, it appears that the conditions did not favor this reaction pathway either.

The data suggest a complex set of reactions during the pyrolysis process, where the Boudouard equilibrium's role in CO and CO_2 generation might be tempered by other concurrent reactions that include hydrogen formation. The presence of hydrogen could also indicate alternative reaction pathways, such as petcoke devolatilization or secondary reactions involving hydrocarbon fragments.

The absence of an increase in CO, CO_2, and H_2 generation, despite the tailored isothermal holds, indicates that the equilibrium state might have been maintained as in the previous run. This persistence of the equilibrium state suggests that the petcoke's pyrolytic behavior is governed by a balance of competing reactions, with no single reaction dominating the production of these gases under the given conditions. In this graph (figure 4.7), the x-axis shows time in minutes instead of temperature. This choice helps highlight how the gas levels change during specific times in the experiment, especially when we keep the temperature the same at 400°C and 500°C. This way, we can clearly see whether the amount of gas stays steady or changes when the temperature doesn't move.

The specific times when we hold the temperature at 400°C and 500°C aren't marked on the time axis. This is because the main point is to show what happens to the gas levels over time when the temperature is fixed. These steady temperature periods help us learn more

about the chemical reactions in a stable setting, which is very useful for situations where controlling the reaction conditions precisely is key.

In sum, while the Boudouard equilibrium provides a useful framework for understanding certain aspects of petcoke pyrolysis, it is clear that the full picture of gas generation during petcoke degradation is far more intricate, with multiple reactions occurring simultaneously and influencing each other.
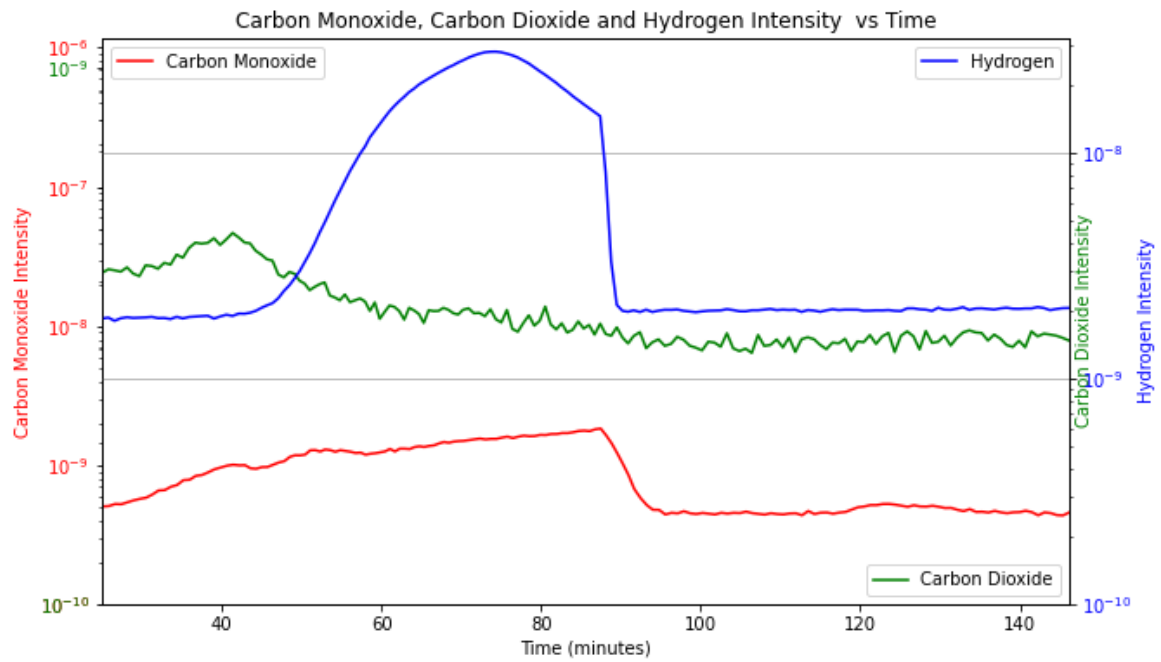

Figure 4.7: Carbon Monoxide, Carbon Dioxide and Hydrogen Intensity vs Time with a isothermal stop at 400 and 500°C

4.2.3 Methane

The latest tests aimed at understanding methane gas production during the heating of petroleum coke didn't reveal the significant increase that was anticipated. Even with precise temperature control around the critical points where methane is expected to start and peak in production, the results were similar to previous ones.

This suggests that simply controlling the temperature may not be the key factor influencing methane production. Other aspects such as the specific type of petroleum coke used or the substances within it might play a bigger role in this process than previously assumed.

The temperature range examined, specifically from 450°C to 630°C, might not be the only important factor for enhancing methane release. It's possible that within this range, temperature alterations don't significantly impact the gas production rate. Alternatively, the rate at which the coke is heated could have a greater effect on methane release than the precise temperature points used in the tests.

Since methane levels remained consistent across different experiments (figure 4.6 and 4.8), it appears that the experimental approach of holding the sample at targeted temperatures did not have the expected impact on methane production. Future investigations may require a broader examination of temperature ranges, varied heating rates, or changes in the coke's composition to fully understand the variables that control methane production during pyrolysis.

These findings add to the collective knowledge about thermal decomposition of petroleum coke. They highlight the complexity of the process and the necessity of exploring a range of factors, beyond just temperature, to enhance the predictability and efficiency of gas production from pyrolysis.

4.2.4 Weight Loss

In the recent test run that included an isothermal hold at 600°C for petroleum coke, the results indicate that there was no significant change in weight loss across all samples compared to previous tests as shown in figure 4.9. Despite the focus on this particular temperature, which follows the most active stage of weight reduction, the weight loss percentage remained consistent with earlier findings.

From the results, it seems that the isothermal hold didn't lead to any additional degradation that was significantly different from the normal progressive increase in temperature. This could mean that the majority of reactive components in the petroleum coke had already degraded before reaching the isothermal stage. As such, the hold at 600°C mainly served to provide a clearer picture of the reactions that occur at a steady temperature after the major weight loss stages.

Given these observations, it can be concluded that the isothermal hold at 600°C did not introduce new thermal degradation behaviors for the petroleum coke samples tested. This suggests that the primary reactions affecting weight loss occur before this temperature is reached, and that maintaining the temperature at this point does not further contribute to weight loss.

For future analysis, it may be beneficial to explore different temperature ranges for isother-
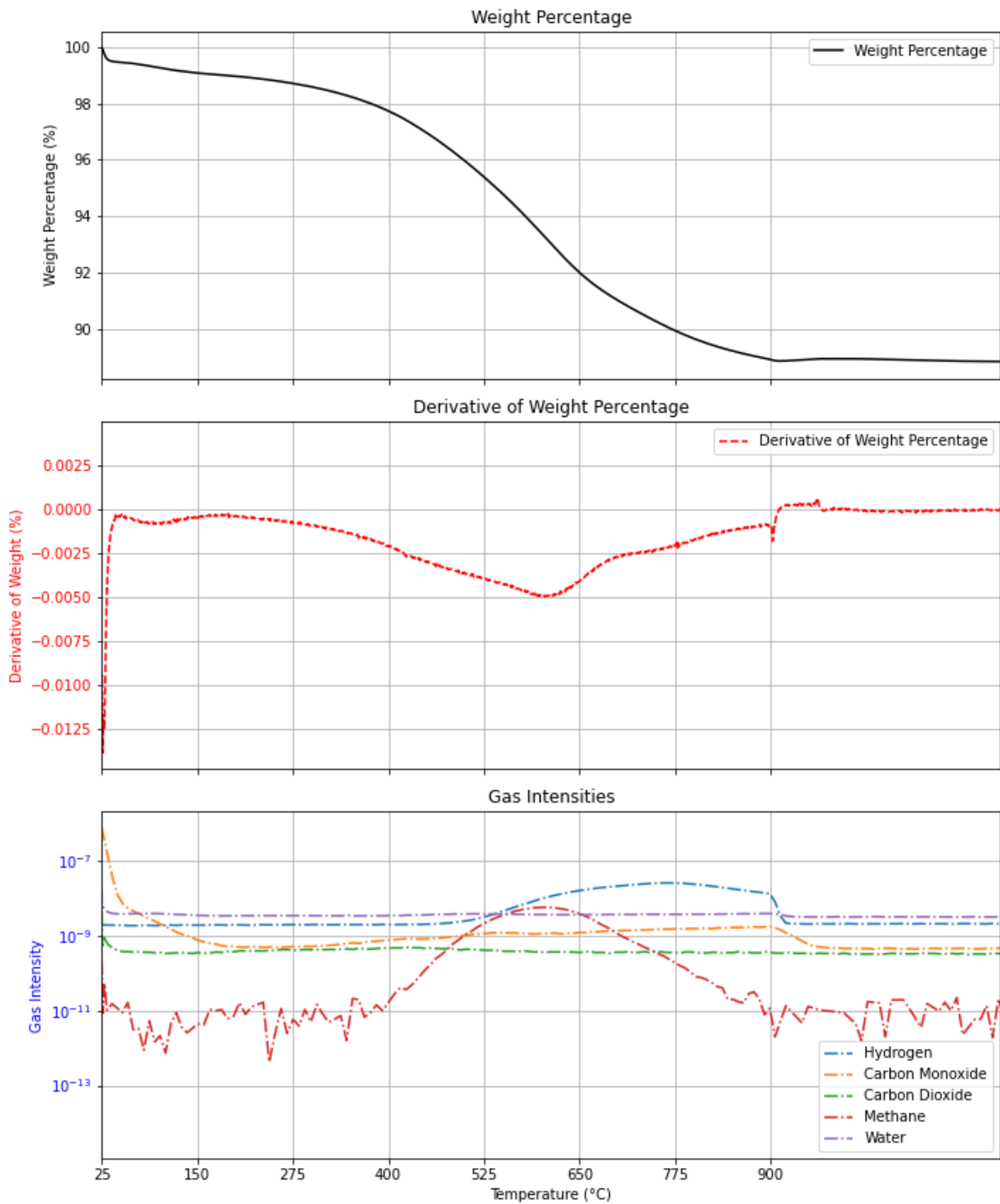
Figure 4.8: Comparison between the weight percentage drop, DTG and the gas generation for the run based on hydrogen generation where the focus was on methane generation.

mal holds or to investigate other modifications in the test protocol. Adjustments such as varying the atmosphere within the TGA, using different petroleum coke samples with varying properties, or applying catalysts could provide new insights into how to influence the thermal degradation process and weight loss of petroleum coke.

Comparing the weight loss data of the petroleum coke samples across the defined temperature zones highlights the uniformity in the behavior of most samples, with Sample 4 serving as a

Figure 4.9: Weight Percentage drop divided into five different zones where there been an isothermal hold at different degrees.

focal point to investigate any differences due to an isothermal hold at 600°C, see table 4.2 for detailed data.

- **Zone 1 (25-200°C):** The weight loss across Samples 1 to 3 is very similar, all just above 1%. This small weight loss suggests that these samples have a similar moisture content and light volatiles that are released at low temperatures. S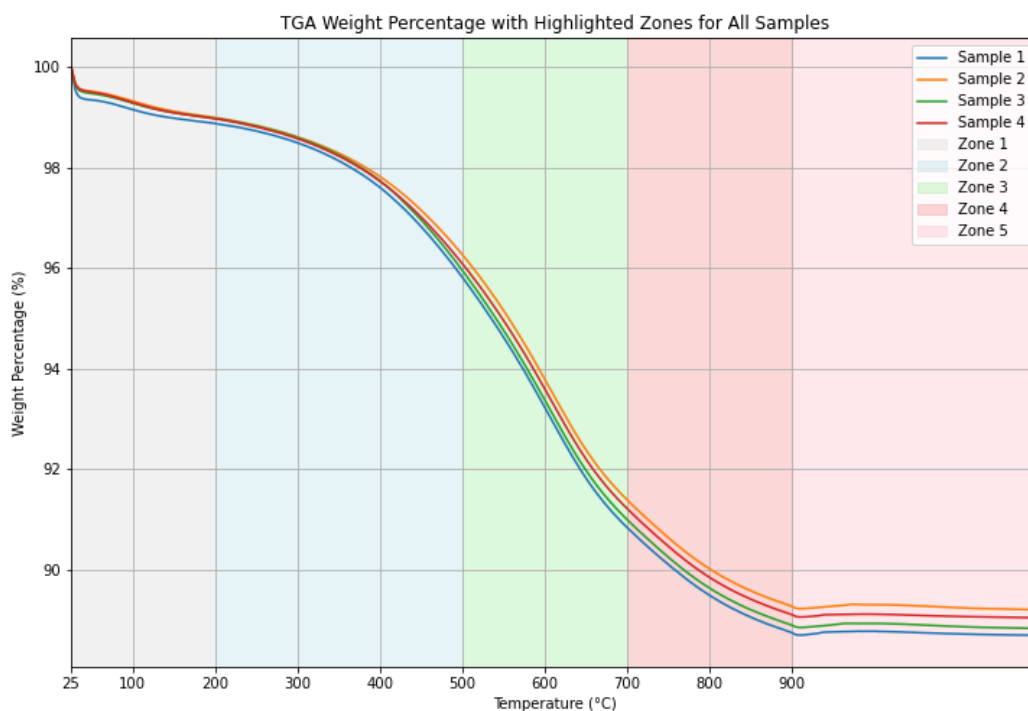ample 4 shows a marginally higher weight loss, which could indicate either a slight difference in composition or an experimental variation.

- **Zone 2 (200-500°C):** Here, the weight loss for Samples 1 to 3 ranges from approximately 2.7% to 3.0%, suggesting a consistent release of volatile components such as heavy hydrocarbons. Sample 4 has a slightly lower weight loss compared to Sample 1 but remains within a similar range to Samples 2 and 3, indicating that the behavior in this zone is fairly consistent across all samples.

- **Zone 3 (500-700°C):** In the primary pyrolysis zone, all samples exhibit a weight loss around 4.9%. This indicates a uniform thermal degradation process, where Sample 4 aligns with the others, showing that the isothermal hold at 600°C did not significantly alter the weight loss pattern in this zone.

- **Zone 4 (700-900°C):** The weight loss in this zone is about 2.1% for all samples. This suggests that the residual carbonaceous material left after the primary pyrolysis is breaking down at a similar rate, with Sample 4 demonstrating no unusual deviation from this trend.

- **Zone 5 (Above 900°C):** All samples show a very minimal weight loss, less than 0.1%, which is expected as most of the reactive components have already been decomposed in earlier stages.

The data points to the conclusion that the thermal behavior of Sample 4 closely mirrors that of the other samples, suggesting that the isothermal hold applied in this particular case did not lead to a discernible difference in the weight loss during TGA analysis. This could indicate that the reactions contributing to weight loss are not significantly impacted by maintaining the temperature at 600°C for an extended period, or that the underlying mechanisms of weight loss are governed by factors that were not altered by the modified experimental approach in Sample 4.

Table 4.2: Comparison of Samples across Different Zones with the Change in Weight Percentage Drop, Sample 1 represent section 4.2.1, sample 2: section 4.2.2, sample 3: section 4.2.3 and sample 4: section 4.2.4.

	Zone 1 (WΔ%)	Zone 2 (WΔ%)	Zone 3 (WΔ%)	Zone 4 (WΔ%)	Zone 5 (WΔ%)
Sample 1	1.129	3.046	4.970	2.091	0.058
Sample 2	1.012	2.715	4.868	2.119	0.073
Sample 3	1.027	3.011	4.948	2.099	0.070
Sample 4	1.035	2.869	4.864	2.110	0.065

4.3 Gas Generation at Lower Heating Rate

The experiment was set up to see if heating petroleum coke slowly at 5 °C per minute would make more gas generation like, hydrogen, carbon monoxide, carbon dioxide and methane during certain temperature holds. However, the results didn't show much change in gas generation compared to previous tests where the heat was turned up continuously.

When looking at the weight percentage graphs, which show how much of the sample's weight is left as it heats up, there was no big change at temperatures where the weight typically drops a lot as shown in figure 4.10 and in figure 4.6 for the previous run. The rate of weight change also stayed similar across the temperatures tested, showing no unexpected shifts.
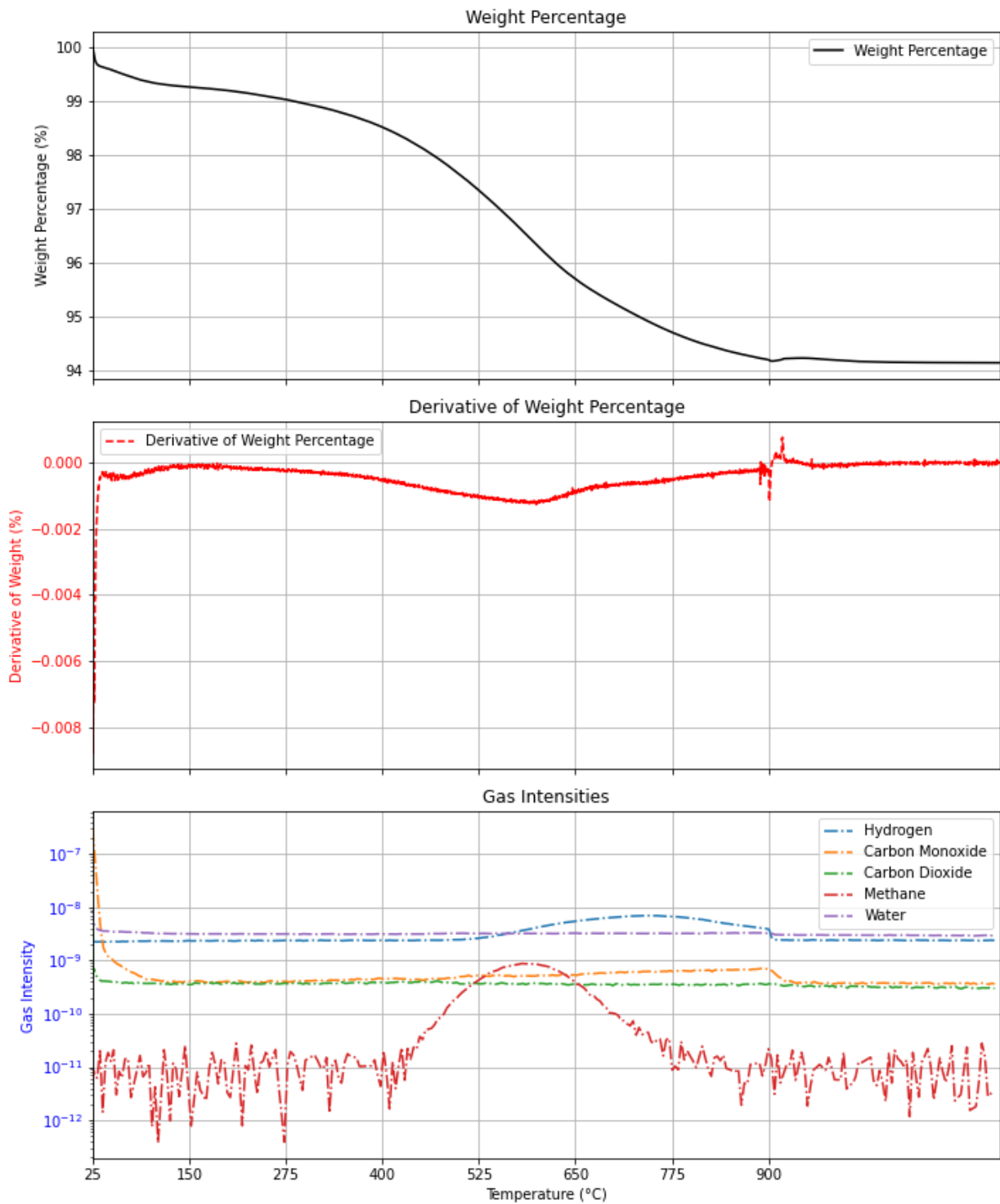
Figure 4.10: Comparison between the weight percentage drop, DTG and the gas generation for the run based on hydrogen generation at a heating rate of 5°C/min

4.3.1 Hydrogen

Here the focus was the same as the run before, increasing the hydrogen generation by using isothermal hold at 600 ° C and 800 ° C, the result did not meet the expectations. The test heated the sample at 5 ° C per minute at these temperatures, hoping to see a significant rise in hydrogen levels, but this did not happen. In figure 4.12 its compared both the hydrogen and methane test, (methane results discussed in section 4.3.3).

Here are the breakdowns of the key observations:

- **Hydrogen Production During Isothermal Holds:** Holding the temperature steady at 600°C and 800°C didn't lead to the boost in hydrogen production that was anticipated. This suggests that just controlling the temperature at these points isn't enough to significantly enhance hydrogen production.

- **Understanding the Reaction Processes:** The data showed that the hydrogen levels stayed pretty much the same throughout these temperature holds. This could mean that the processes that make hydrogen in this experiment happen at a steady rate that doesn't change much, even when the temperature is held constant at the peaks where hydrogen release initially spikes.

To further investigate why these adjustments didn't have the expected effect, it might be helpful to explore different experimental setups or delve deeper into the chemical reactions happening in the sample during heating. This could provide new insights into how to better control and maximize hydrogen production from petroleum coke during pyrolysis.

4.3.2 Carbon Monoxide and Carbon Dioxide at Lower Heating Rate

The goal of this experiment was to see how controlling the temperature very carefully affects the production of carbon monoxide, carbon dioxide, and hydrogen. The temperatures used, 400°C and 500°C, were chosen because they are important for a chemical balance called the Boudouard equilibrium, which predicts how these gases interact at high temperatures. Figure 4.11 shows that it has more or less the same generation of gas in both Carbon monoxide, Carbon dioxide and Hydrogen.
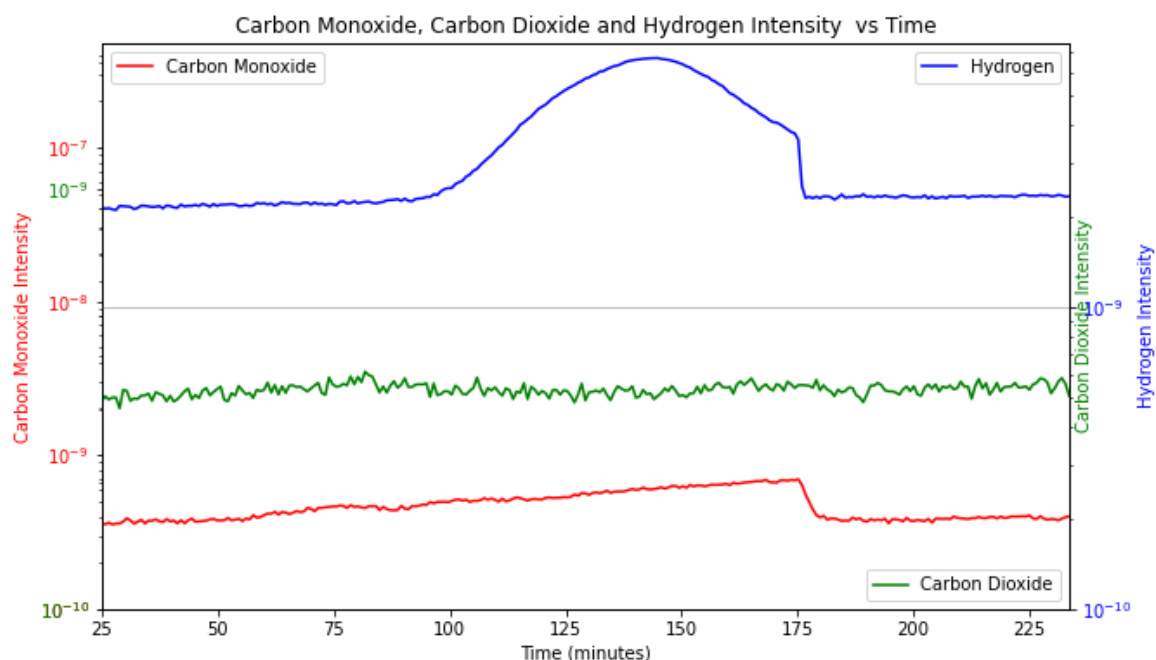

Figure 4.11: Carbon Monoxide, Carbon Dioxide and Hydrogen Intensity vs Time with a isothermal stop at 400 and 500°C with a heating rate of 5°C/min

Observations from the experiment:

- **Carbon Monoxide and Carbon Dioxide Levels:** The idea was that keeping the temperature steady at these points would increase the production of carbon monoxide and dioxide. However, we didn't see a big increase in these gases, which suggests that the experimental conditions might not have changed the expected balance enough, or other reactions were also happening.

- **Hydrogen Production:** We also looked at whether hydrogen production would go up, especially from reactions where carbon monoxide and water vapor turn into hydrogen and carbon dioxide. But, like carbon monoxide and dioxide, the hydrogen levels didn't really change, showing that these reactions weren't the main activity during the experiment.

- **Complex Reaction Dynamics:** The results show that bringing out the volatiles and gases involves many different chemical reactions. Although the Boudouard equilibrium helps us understand some of these reactions in theory, the real-life chemical reactions during pyrolysis seem to be affected by a mix of different processes.

- **Equilibrium Stability:** Even with the changes in how we ran the experiment, like holding the temperature steady, the amount of gas generated did not really vary. This might mean that the conditions inside the experiment naturally balance out, preventing large changes in gas generations.

4.3.3   Methane Generation at Slower Heating Rate

In the latest tests, petroleum coke was heated at a slower rate of 5 degrees per minute to see if it affects methane gas production differently compared to the previous faster rate of 10 degrees per minute. However, the results were very similar across both heating rates and when the test where hydrogen was the focus, see figure 4.12.
Here's what the findings show:

- **Consistent Methane Levels:** The amount of methane gas produced didn't change significantly with the adjustment in heating rate. This suggests that the difference in heating speeds from 10 degrees to 5 degrees per minute doesn't greatly influence methane production.

- **Temperature's Role:** The focus was on heating the coke to specific temperatures thought to potentially increase methane production, particularly between 450°C and 630°C. Controlling the temperature this precisely didn't yield a noticeable difference in methane output.

- **Considering Other Factors:** Since adjusting the heating rate and precise temperature control did not deliver the expected changes, it appears that other elements may have a more substantial impact on methane production. This could involve the specific characteristics of the petroleum coke or other experimental conditions.

Figure 4.12 shows both the hydrogen and methane test which shows there is almost none difference in hydrogen and methane generation compared to figure 4.10.
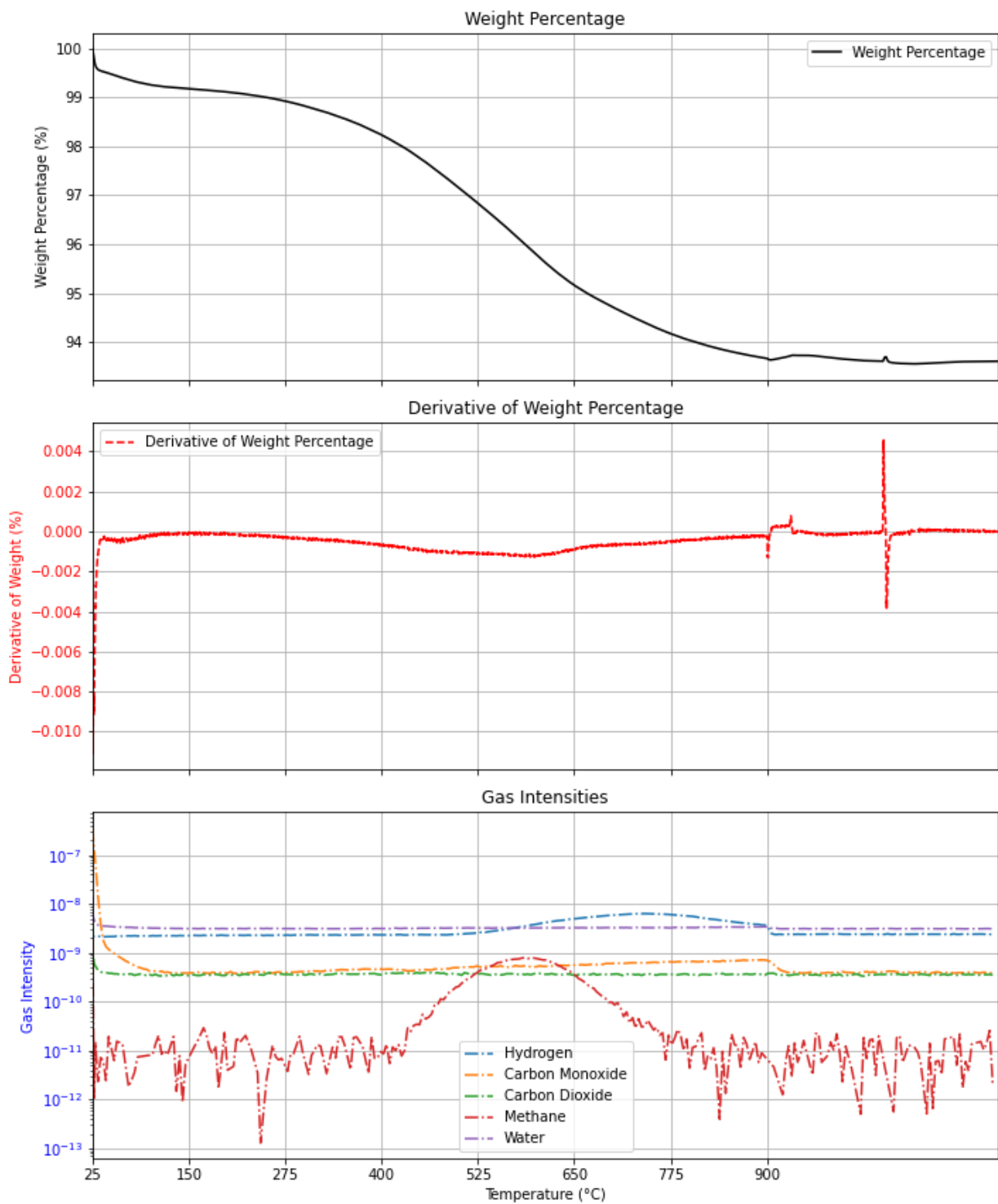
Figure 4.12: Comparison between the weight percentage drop, DTG and the gas generation for the run based on hydrogen and methane generation at a heating rate of 5°C/min

4.3.4 Weight Loss at Lower Heating Rate

The experiment where the focus was to look more into the weight loss at a lower heating rate, the temperature were held steady at 600 °C for the petcoke. There wasn't much difference in how much weight loss was lost compared to earlier test. This temperature was chosen because its usually where a lot of weight loss, but the result were pretty much the same as before.

Just as in section 4.2.4 the isothermal hold at 600 °C did not introduce new behaviours in the thermal degradation and the important changes happens before 600°C . So, keeping the temperature at 600 °C just showed what happens at this temperature after most of the big changes have already happened. Looking at figure 4.13 we see that it very familiar to the one where the heatng rate was 10 °C per minute (figure 4.9)
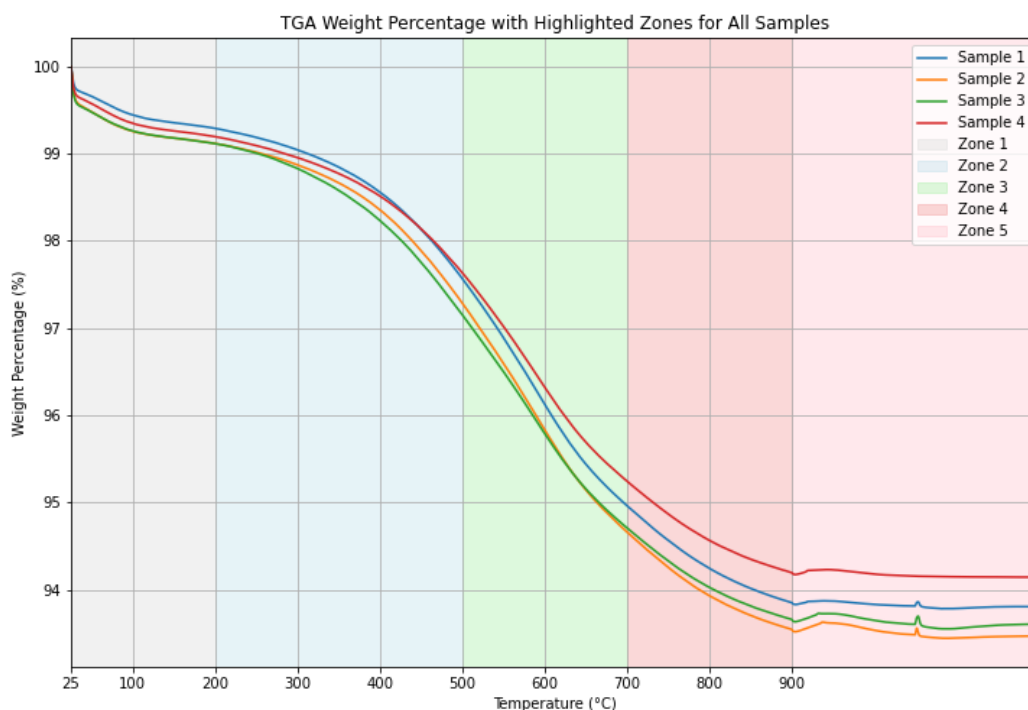

Figure 4.13: Weight Percentage drop divided into five different zones where there been an isothermal on 600 degrees and a heating rate at 5°C per minute.

Here is a look at how the weight loss in different temperature zones for all the samples as displayed in table

- **Zone 1 (25-200°C):** All samples lost about the same small amount of weight, which means they probably all had similar moisture and light stuff that burns off easily. Sample 4 lost a little less, which might mean it's a bit different or just a normal variation in the test.

- **Zone 2 (200-500°C):** The weight loss here was between about 1.7% and 1.9% for all samples, which shows they're pretty consistent in losing heavier stuff at these temperatures. Sample 4 lost a bit less, but it's still in the same range as the others.

- **Zone 3 (500-700°C):** This zone, where a lot happens, showed all samples losing about 2.4% to 2.6% of their weight, so the temperature hold didn't really change anything special for Sample 4 or the others.

- **Zone 4 (700-900°C):** Each sample lost about 1.1%, showing that whatever's left after the big changes is breaking down at the same rate for everyone.

- **Zone 5 (Above 900°C):** Very little weight was lost by all samples, under 0.08%, because most of the reactive reactions was already gone.

Table 4.3: Comparison of Samples across Different Zones with the Change in Weight Percentage Drop. Sample 1 represents section 4.3.1, sample 2: section 4.3.2, sample 3: section 4.3.3 and sample 4: section 4.3.4.

	Zone 1 (WΔ%)	Zone 2 (WΔ%)	Zone 3 (WΔ%)	Zone 4 (WΔ%)	Zone 5 (WΔ%)
Sample 1	0.709	1.718	2.607	1.113	0.048
Sample 2	0.882	1.827	2.626	1.119	0.078
Sample 3	0.884	1.958	2.446	1.051	0.056
Sample 4	0.804	1.557	2.391	1.049	0.056

4.4 Comparing The Different Experiments

4.4.1 Experiment Overview

- First Run (10°C/min heating rate, no isothermal hold): This experiment set the baseline, showing standard gas production and weight loss profiles for petroleum coke up to 900°C.

- Second Run (10°C/min heating rate with isothermal holds at critical temperatures): Isothermal holds at 600°C and 800°C were introduced to potentially enhance gas generation, particularly hydrogen, but the results did not differ significantly from the first run.

- Third Run (5°C/min heating rate with similar isothermal holds): The heating rate was reduced to see if a slower approach could differently affect gas production or promote more distinct changes during the holds.

4.4.2 Observations

Gas generation

According to the figures 4.3, figure 4.6, and figure 4.10, any larger peaks in gas generation can be observed. The comparison is small but there is some;

- **Hydrogen:** Despite expectations, lower heating rates and strategic isothermal holds did not significantly increase hydrogen production in any of the runs but it has its biggest intensity peak in experiment 2. The reaction conditions at the holds (600°C and 800°C) were likely not sufficient to enhance the hydrogen-releasing reactions beyond their typical behavior observed at higher heating rates.

- **Carbon Monoxide and Carbon Dioxide:** Intended modifications to affect the Boudouard equilibrium (400°C and 500°C holds) did not yield significant changes in CO or CO_2 production and had similar pattern across all experiments. This suggests that the equilibrium or other reaction pathways might be more resilient to such experimental changes or that additional factors beyond temperature manipulation are necessary to alter these gas productions significantly.

- **Methane:** Consistency in methane production across different heating rates and isothermal conditions indicates that methane generation is not heavily influenced by the slower progression of temperature or by holding temperatures at supposed peak generation points. Still the highest peak was in experiment 2.

Weight loss Patterns

- **Experiment 1** showed a certain range of weight loss across different temperature zones. The observed pattern suggests that the petcoke used here exhibited typical

thermal behavior, with a steady reduction in weight as temperatures increased. This could be indicative of a balanced reaction to the thermal conditions applied, aligning with expected norms for petcoke gasification (Experiment 1 has a total weight loss ranging from 7.826% to 9.001%).

- **Experiment 2** exhibited the highest total weight loss among the three experiments. This suggests that the petcoke in this experiment responded more actively to the thermal conditions. The increased weight loss could be due to a variety of factors such as differences in the thermal stability or chemical composition of the petcoke used. This experiment might have involved petcoke that degrades more readily under similar conditions, resulting in greater gas production and weight loss (Experiment 2 shows an increased total weight loss, ranging from 10.787% to 11.294%).

- **Experiment 3** demonstrated the least weight loss, which might suggest that the petcoke used was more resistant to thermal decomposition or had a lower reactivity under the applied conditions. This could indicate a type of petcoke that maintains its structural integrity to a higher degree, possibly due to a higher content of thermally stable materials or a composition that does not easily break down under the applied thermal conditions (Experiment 3 demonstrates the least total weight loss, ranging from 5.857% to 6.532%.

Reaction Dynamics

The experiments show that many different reactions happen together when petroleum coke is heated to break it down. Changing how fast the heating happens or pausing the temperature didn't make any single reaction stand out more than others. The overall pattern of how gases form and how the material breaks down stayed the same as what was first seen.

Chapter 5

Conclusions

The series of experiments using Thermogravimetric Analysis-Mass Spectrometry (TGA-MS) to study how petroleum coke from Vianode breaks down under heat have provided clear insights into its behavior during heating. These experiments have been crucial for understanding how changes in temperature, air control, and the size and type of samples can affect how petroleum coke breaks down when heated.

The first set of experiments laid the groundwork by monitoring how the weight of the coke changed and what gases were released at different temperatures from 25°C up to 900°C. The major findings were that a lot of weight is lost, especially between 500°C and 700°C, which matches up with large amounts of gases like carbon monoxide, carbon dioxide, and methane being released. These gases mainly come from the breakdown of complex hydrocarbon materials in the coke. This phase of the research highlighted how important it is to control the size of the coke samples and the flow of argon gas to get reliable and consistent results. It also showed that keeping a close watch on the temperature is key for detecting gases effectively.

The second round of experiments tested whether holding the coke at specific temperatures (600°C and 800°C) for longer times would make it release more gas. However, the expected increase in gases such as hydrogen, carbon monoxide, and methane did not happen. The findings suggested that the natural properties of petroleum coke might limit how much it reacts, meaning that simple temperature holds might not be enough to significantly enhance gas production. More complex changes might be needed, such as using different air compositions or adding substances that help along the reactions (catalysts).

The third set of tests, which involved heating the coke more slowly at a rate of 5°C per minute and using temperature holds like before, aimed to see if a slower increase in temperature affected gas production. Like the previous experiments, no significant changes were noted in the amount of gas produced or in how the weight of the coke decreased. This confirmed that the way petroleum coke breaks down is quite stable and doesn't change much with just moderate adjustments to how it is heated.

The analysis of how much weight petcoke loses when heated shows different behaviors across three experiments. Experiment 1 had a moderate weight loss (7.826% to 9.001%), suggesting this type of petcoke works well for regular gasification methods. Experiment 2 showed the most weight loss (10.787% to 11.294%), which means this petcoke might burn more easily and produce more gas, but it needs to be handled carefully. Experiment 3 had the smallest weight loss (5.857% to 6.532%), indicating a petcoke that doesn't break down as quickly and is good for slower, more controlled heating. These differences show why it's important to choose the right type of petcoke for specific gasification processes to make them more efficient and environmentally friendly.

Future Research:

Future studies could benefit from pushing the boundaries of the temperature ranges and heating rates used in the experiments. While previous tests have generally not exceeded 900°C, exploring higher temperatures could provide new insights into the stability and breakdown of more refractory components of petroleum coke. This could help identify new stages of gas evolution or decomposition reactions that occur beyond the conventional temperature limits. Additionally, experimenting with rapid heating rates, possibly exceeding 15°C/min, might reveal transient phenomena or short-lived intermediates that are not detectable at lower heating rates.

Adjusting the atmospheric conditions during pyrolysis, such as introducing oxygen, steam, or other reactive gases, could help in understanding the oxidative or other chemically influenced degradation processes. Utilizing catalysts or other chemical agents is another promising area. Catalysts could potentially lower the activation energy required for certain reactions, leading to different yields or types of gases. Research could focus on various catalysts that influence specific reaction pathways, thus providing more control over the gas compositions produced during pyrolysis.

Combining TGA-MS with other analytical methods such as gas chromatography-mass spectrometry (GC-MS) could enhance the detailed analysis of gases and volatiles. GC-MS would allow for the separation, identification, and quantification of individual compounds, offering a deeper understanding of the chemical processes occurring during petcoke gasification. This could be particularly useful for identifying minor but critical components that might influence overall reaction pathways.

A more detailed kinetic analysis could be crucial for future research. This would involve not just varying the temperature holds but also systematically studying how these holds at different temperatures influence the kinetics of gas production. Incorporating isothermal holds at strategic temperatures based on initial TGA data could help in understanding the kinetics of complex reactions during petcoke decomposition.

The impact of how petroleum coke is prepared and presented for pyrolysis could also be a valuable study area. This could include examining the effects of particle size, distribution, and the homogeneity of the samples on the pyrolysis behavior and gas yields. Understanding these factors could lead to more standardized methods for preparing petcoke samples for TGA-MS analysis, potentially leading to more consistent and reproducible results..

In conclusion, while the experiments showed consistent behaviors in how petroleum coke breaks down, they also highlighted that to really enhance our understanding and control of this process, we need to think beyond simple tweaks. A more comprehensive approach that considers a wider range of changes to the experimental setup is necessary. This could lead to significant advances in how we understand and optimize the gasification of petroleum coke, helping develop cleaner and more efficient technologies for using this resource.

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