



Faculty of Sciences

Department of Chemical and Forensic Science

**KINETIC ANALYSIS OF PYROLYSIS AND COMBUSTION OF BOTSWANA
MORUPULE COAL AND ITS BLEND WITH MUNICIPAL AND INDUSTRIAL WASTE
USING ISO-CONVERSIONAL AND MODEL-FITTING METHODS**

by

KGALALELO PHATSIMO KGATLANE

Student ID number: 20100113

BEd (Science) (UB)

A Dissertation/Thesis Submitted to the Faculty of Sciences in Partial Fulfilment of the
Requirements for the Award of the Degree of Master of Science in Chemistry of BIUST

Supervisor(s):

Dr Sebusi Odititse

Department of Chemical and Forensic Sciences

Faculty of Science, BIUST

odisitses@biust.ac.bw

Dr Isaac. N. Beas

Department of Natural Resources and Materials

Specialty Chemicals-BITRI

ibeas@bitri.co.bw

November 2023

TABLE OF CONTENTS

DECLARATION REGARDING THE WORK AND COPYRIGHT	viii
ABSTRACT	ix
DEDICATIONS	x
ACKNOWLEDGEMENTS	xi
LIST OF TABLES	iv
LIST OF FIGURES	vi
LIST OF ABBREVIATIONS AND SYMBOLS	xii
1 INTRODUCTION.....	1
1.1 Motivation	1
1.2 Objectives and research questions.....	4
2 LITERATURE REVIEW.....	5
2.1 Coal	5
2.1.1 Types of coals in Botswana	5
2.2 Polyolefins Plastics	5
2.3 Coal Pyrolysis.....	6
2.4 Coal Combustion	9
2.5 Fly Ash.....	11
2.5.1 Chemical and Physical Properties of Fly Ash	11
2.5.2 Classification and Utilization of Fly Ash.....	13
2.6 Liquefaction	13
2.7 Gasification	14
2.8 Coal & Plastic Waste.....	15
2.8.1 Coal and plastic waste pyrolysis	15
2.8.2 Coal and plastic waste combustion	17
2.9 Reaction Kinetics	17
2.9.1 Arrhenius Equation.....	19
2.9.2 Isoconversional Method	21
2.9.2.1 Kissinger-Akahira-Sunose.....	22
2.9.2.2 Ozawa-Flynn-Wall	22
2.9.2.3 Kissinger Method.....	23
2.9.3 Differential Analysis Methods	24

2.9.3.1	Friedman's isoconversional method.....	24
2.9.3.2	Master plot Method based on the Differential form.....	25
2.9.3.3	Vyazovkin.....	26
2.9.4	Model Fitting Method	26
2.9.4.1	Linear model-fitting method.....	27
2.9.4.2	Coats Redfern Method	29
2.10	Deconvolution analysis using bi-gaussian algorithm	29
2.11	Thermogravimetric Analysis Theory.....	30
2.12	Thermogravimetric-Mass Spectrometry Theory	31
3	MATERIALS AND METHODS	32
3.1	Sampling and Sample preparation	32
3.2	Thermogravimetric Analysis	33
3.3	Kinetic analysis	34
3.3.1	Kissinger Akahira Sunose	35
3.3.2	Kissinger method.....	35
3.3.3	Friedman.....	35
3.3.5	Linear model-fitting method.....	36
3.3.6	Coats-Redfern	36
3.4	Data Collection	36
3.5	Physicochemical Characterization of Coal.....	37
3.6	Thermogravimetric-Fourier Transform Infrared Spectrometry.....	38
3.7	Thermogravimetric-Mass Spectrometry	39
3.8	X-ray Fluorescence Spectrometry (XRF)	40
3.9	X-ray Diffraction Spectrometry (XRD)	41
4	RESULTS AND DISCUSSION	43
4.1	Thermogravimetric Analysis	43
4.1.1	Peak separation analysis of overlapping peaks by bi-Gaussian fitting	53
4.1.2	Thermal behavior of coal and plastic.....	57
4.1.3	Thermal behavior of fly ash	60
4.2	Evolved Gas Analysis	62
4.3	Fourier Transform Infrared Results	71
4.4	X- ray Diffraction Spectrometer (XRD) & X-ray Fluorescence (XRF) Results	72
4.5	Kinetic Analysis.....	77

4.5.1	KAS & OFW Results	77
4.5.2	Coats Redfern Results	94
4.5.3	Friedman Results	98
4.5.4	Vyazovkin Results	102
4.5.5	Model fitting (linear regression) results	104
4.5.6	Kissinger Results	107
5	CONCLUSION	109
6	FUTURE WORK	110
	REFERENCES.....	111
	APPENDIX.....	124

LIST OF TABLES

Table 2.1: Some of the kinetic models employed in solid state kinetics	19
Table 2.2: Parameters of equation 23 fitted to different reaction models	28
Table 3.1: Proximate and Ultimate analysis of Morupule coal samples [120]	38
Table 4.1: Mass loss and maximum temperature of decomposition of EM1, WM1 and S3-5 coals under inert atmosphere	45
Table 4.2: Mass loss and maximum temperature of decomposition of EM1, WM1 and S3-5 coals under air atmosphere	48
Table 4.3: Peak characterization of derivative conversion curves for EM1, WM1 and S3-5 coal pyrolysis at various heating rates of 5, 10, 15, 20 and 25 °C/min-1	51
Table 4.4: Peak characterization of derivative conversion curves for EM1, WM1 and S3-5 coal combustion at various heating rates of 5, 10, 15, 20 and 25 °C/min-1	52
Table 4.5: Peak temperature corresponding to local maximum at various heating rates for EM1 coal	54
Table 4.6: Peak temperature corresponding to local maximum at various heating rates of S3-5 coal	55
Table 4.7: Peak temperature corresponding to local maximum at various heating rates of WM1 coal	57
Table 4.8: The RSS of the heating rate and R2 correlation coefficient	57
Table 4.9: Thermogravimetric properties of HDPE plastic	59
Table 4.10: Thermogravimetric data of coal/plastic samples at 25 °C	59
Table 4.11: Thermogravimetric properties of fly ash	61
Table 4.12: Mineralogical composition of coals from XRD analysis	73
Table 4.13: XRF Composition of Morupule coal, Waterberg & Highveld coal	75
Table 4.14: XRF composition of HDPE plastic and fly ash	76
Table 4.15: Activation energies (E) and pre-exponential factor (A) for various conversion values of EM1 coal using OFW and KAS methods under inert atmosphere	82
Table 4.16: Activation energies (E) and pre-exponential factor (A) for various conversion values of WM1 using OFW and KAS methods under inert atmosphere	83
Table 4.17: Activation energies (E) and pre-exponential factor (A) for various conversion values of S3-5 coal using OFW and KAS methods under inert atmosphere	84
Table 4.18: Activation energies (E) and pre-exponential factor (A) for various conversion values of HDPE using OFW and KAS methods under inert atmosphere	85
Table 4.19: Activation energies (E) and pre-exponential factor (A) for various conversion values of fly ash using OFW and KAS methods under both inert and oxygen atmosphere	86
Table 4.20: Activation energies (E) and pre-exponential factor (A) for various conversion values of EM1 using OFW and KAS methods under oxygen atmosphere	87
Table 4.21: Activation energies (E) and pre-exponential factor (A) for various conversion values of WM1 using OFW and KAS methods under oxygen atmosphere	88
Table 4.22: Activation energies (E) and pre-exponential factor (A) for various conversion values of S3-5 using OFW and KAS methods under oxygen atmosphere	89
Table 4.23: Fitted kinetic parameters for pyrolysis of coal and coal/plastic mixture using coats redfern method	97
Table 4.24: Fitted kinetic parameters for combustion of coal and coal/plastic mixture using coats redfern method	97
Table 4.25: Kinetic parameters for pyrolysis of the HDPE plastic studied	98
Table 4.26: Kinetic parameters using the Friedman method for EM1, WM1 and S3-5 coals	101
Table 4.27: Kinetic parameters using the Friedman method for HDPE and coal mixture	101

Table 4.28: Activation energy of the three coals, plastic and coal mixture using the advanced integral Vyazovkin method	104
Table 4.29: Calculated kinetic parameters of coals and the coal mixture using Model Fitting method (linear regression)	106
Table 4.30: Kinetic parameters for pyrolysis of coal, plastic and coal mixture using Kissinger method.	108

LIST OF FIGURES

Figure 2.1: The coal pyrolysis process [29]	7
Figure 3.1: Thermogravimetric Analyser.....	34
Figure 3.2: Fourier transform Infrared Spectrometer Analyzer	39
Figure 3.3: Thermogravimetric Analyzer coupled to the Mass Spectrometer	39
Figure 3.4: X-Ray Fluorescence Spectrometer Analyser.....	40
Figure 3.5: X-Ray Diffraction Spectrometer Analyzer	42
Figure 4.1: TG (left) & DTG (right) of the EM1, WM1 and S3-5 pyrolysis at five different heating rates under inert atmosphere.....	44
Figure 4.2: Thermal behavior and DTG curve of WM1 coal at various heating rates under air atmosphere	47
Figure 4.3: Thermal behavior (left) and DTG curve (right) of EM1 coal at various heating rates under air atmosphere	47
Figure 4.4: Thermal behavior (left) and DTG curve (right) of S3-5 coal at various heating rates under air atmosphere	48
Figure 4.5: Conversion (left) and smoothed derivative conversion (right) curves for pyrolysis of EM1, S3-5 and WM1 coals at five various heating rates under inert atmosphere	50
Figure 4.6: Conversion (left) and smoothed derivative conversion (right) curves for pyrolysis of EM1, S3-5 and WM1 coals at five various heating rates under air atmosphere.....	52
Figure 4.7: TGA analysis of coal in (a) Oxygen atmosphere, and (b) Argon atmosphere.....	53
Figure 4.8: Deconvolution of reaction rate of EM1 coal at different rates (5, 10, 15, 20, 25 °C/min)	54
Figure 4.9: Deconvolution of reaction rate of S3-5 coal at different rates (5, 10, 15, 20, 25 °C/min).....	55
Figure 4.10: Deconvolution of reaction rate of WM1 coal at different rates (5, 10, 15, 20, 25 °C/min). ...	56
Figure 4.11: TG (left) and DTG (right) of the plastic at heating rates of 5, 10, 15, 20 and 25 °C/min under inert atmosphere.....	58
Figure 4.12: DTG profiles of the EM1, WM1 coal, plastic, and the mixture at an addition rate of 5 wt%	58
Figure 4.13: TG (left) and DTG (right) of various EM1 blends	60
Figure 4.14: TG (left) and DTG (right) of fly ash at heating rates of 5, 10, 15, 20 and 25 °C/min	61
Figure 4.15: Mass spectrum of gas release of EM1, WM1 and S3-5 coal under inert atmosphere	64
Figure 4.16: Mass spectrum of gas release of EM1, WM1 and S3-5 coal under oxygen atmosphere.....	65
Figure 4.17: Evolution of a) H ₂ , b) H ₂ O, c) CO, d) CO ₂ and e) CH ₄ during EM1, WM1 and S3-5 pyrolysis	66
Figure 4.18: Mass spectrum gas release of pyrolysis of EM1, WM1 and S3-5 coal mixtures with the HDPE plastic.....	68
Figure 4.19: Mass spectrum gas release of combustion of EM1, WM1, S3-5 coal mixtures with the HDPE plastic	69
Figure 4.20: Mass spectrum gas release of pyrolysis of fly ash.....	70
Figure 4.21: Mass spectrum gas release of combustion of fly ash.....	70
Figure 4.22: Infrared absorption profile of gas release of EM1, WM1 and S3-5 coal under air atmosphere	71
Figure 4.23: X-ray diffractograms of coal samples showing peaks used to identify individual major mineral components	72
Figure 4.24: X-ray diffractogram of fly ash.....	73
Figure 4.25: X-ray diffractogram of HDPE plastic.....	74

Figure 4.26: Kinetic plots for EM1 coal using a) OFW (left) and b) KAS (right) method under inert atmosphere.....	78
Figure 4.27: Kinetic plots for WM1 coal using a) OFW (left) and b) KAS (right) method under inert atmosphere.....	78
Figure 4.28: Kinetic plots for S3-5 coal using a) OFW (left) and b) KAS (right) method under inert atmosphere.....	79
Figure 4.29: Kinetic plots for the HDPE plastic using a) OFW (left) and b) KAS (right) method under inert atmosphere.....	79
Figure 4.30: Kinetic plots for the EM1 mixture using a) OFW (left) and b) KAS (right) method under inert atmosphere.....	80
Figure 4.31: Kinetic plots for all coals ran under oxygen atmosphere using OFW (left) and KAS (right) method	81
Figure 4.32: Kinetic plots for the fly ash using a) OFW and b) KAS method.....	82
Figure 4.33: Activation energy dependence on degree of conversion for pyrolysis of coal and plastic.....	91
Figure 4.34: Activation energy dependence on degree of conversion for the fly ash.....	92
Figure 4.35: Activation energy dependence on degree of conversion for the combustion of coal	93
Figure 4.36: Coats Redfern plots for EM1, WM1, S3-5 coals and EM1 mixture for the pyrolysis process	95
Figure 4.37: Coats Redfern plot of HDPE plastic.....	96
Figure 4.38: Coats Redfern plots for EM1, WM1, and S3-5 coals for the combustion process.....	96
Figure 4.39: Friedman plots of Morupule coal pyrolysis at different values of conversion	99
Figure 4.40: Friedman plots of HDPE plastic and coal mixture (EM1-5HDPE) at different values of conversion.....	99
Figure 4.41: E_a as a function of conversion for the coal at different values of conversion.....	100
Figure 4.42: E_a as a function of conversion for the HDPE plastic and coal mixture (EM1-5HDPE) at different values of conversion.....	100
Figure 4.43: The activation energy of the three coals in relation to conversion using the advanced integral Vyazovkin method	103
Figure 4.44: The activation energy of plastic and coal mixture in relation to conversion using the advanced integral Vyazovkin method.....	103
Figure 4.45: Kinetic curves for Model Fitting method (linear regression) for EM1, WM1 and S3-5 coals at different heating rates.....	105
Figure 4.46: Kinetic curves for Model Fitting method (linear regression) for HDPE and the coal mixture at different heating rates.....	105
Figure 4.47: Master plots for Model Fitting method (linear regression) for EM1, WM1, S3-5 and the coal mixture	106
Figure 4.48: Master plot for Model Fitting method (linear regression) for the plastic	107
Figure 4.49: Kissinger plots of EM1, WM1, S3-5, HDPE, and the coal mixture at different heating rates	108

DECLARATION REGARDING THE WORK AND COPYRIGHT

Candidate: KGALALELO PHATSIMO KGATLANE

Student ID: 20100113

Thesis Titled: **KINETIC ANALYSIS OF PYROLYSIS AND COMBUSTION OF
BOTSWANA MORUPULE COAL AND ITS BLEND WITH MUNICIPAL AND
INDUSTRIAL WASTE USING ISOCONVERSIONAL AND MODEL-FITTING
METHODS**

I, the **Candidate**, certify that the Thesis is all my own original work and that I have not obtained a degree in this University or elsewhere on the basis of any of this work.

(If the thesis is based on a group project, then the student must indicate the extent of her / his contribution, with reference to any other theses submitted or published by each collaborator in the project, and a declaration to this effect must be included in the thesis)

This dissertation/thesis is copyright material protected under the Berne Convention, the Copyright and Neighbouring Rights Act, Act. No. 8 of 2000 and other international and national enactments, in that behalf, on intellectual property. It must not be reproduced by any means, in full or in part, except for short extracts in fair dealing; for researcher private study, critical scholarly review or discourse with an acknowledgement, without the written permission of the office of the Postgraduate School, on behalf of both the author and the BIUST.



Signed:----- Date: -----10-11-23-----

Primary Supervisor (please write in caps or type)

Dr Sebusi Odisitse_____

I, the Candidate's **Primary Supervisor**, hereby confirm that I have inspected the above titled thesis and, to the best of my knowledge, it is based on the original work of the candidate.

Signed:---  ---

Date: 10th November 2023

ABSTRACT

Several mathematical tools for interpreting experimental data for non-isothermal heating protocols have been established. Such methods may generally be classified into two categories: model-fitting and model-free. Model-fitting methods have always been common because they can precisely identify the kinetic triplet (i.e., frequency factor $[A]$, activation energy $[E_a]$ and model). However, there are several issues with these methods, one of which is that they do not correctly predict the response model. As a result, these techniques have become less popular in favor of isoconversional (model-free) techniques that examine kinetics without relying on model assumptions. Isoconversional approaches on the other hand, do not compute a frequency factor or determine a reaction model, both of which are required for a complete and accurate kinetic analysis.

Critical analysis was done on the TGA data results from various models. Proximate and ultimate analysis of the coal from different active mining sites were performed following ASTM standard methods. Thermogravimetric-mass spectrometry studies were carried out for determining the evolved gas analysis during pyrolysis and combustion of Morupule coal. The municipal waste, high density polyethylene (HDPE) plastic was used in the coal-blending process at a 5wt% addition rate based on the literature point of view. Volatile and combustion products (H_2 , CO , CO_2 , H_2O , CH_4) were released based on their relative intensities. The pyrolysis behavior of the three kinds of Morupule sub-bituminous coal (EM1, WM1 and S3-5) were carried out under various heating rates with the temperature range 25-900 °C under both argon and oxygen atmosphere. The coal was washed with water to remove dirt and dried under static conditions. The samples were dried and pulverized to millimeter size with particle sizes of (0.6, 0.850, 1.0, 1.18 and 2.0 mm). Isoconversional and model fitting methods (Kissinger Akahira Sunose (KAS), Ozawa Flynn Wall (OFW), Kissinger, Friedman, Advanced integral Vyazovkin, linear regression and Coats Redfern) were applied to calculate the kinetic parameters of the coal, including activation energy and pre-exponential factor. The Arrhenius parameters from Friedman and advanced integral Vyazovkin showed a similar trend in the activation energy of the three coals. Among all the methods, advanced integral Vyazovkin method was considered to be best in order to evaluate kinetic parameters of coal pyrolysis. The mean activation energy calculated from the advanced integral Vyazovkin method was 155.77-284.59 kJ/mol for the three coals, the HDPE plastic, and the coal mixture.

DEDICATIONS

I dedicate this thesis to Jehovah God.

ACKNOWLEDGEMENTS

I would like to thank Botswana International University of Science and Technology, Department of Chemical and Forensic Science for giving me the chance to pursue my master's degree with them.

I would like to express my heartfelt gratitude to Botswana Institute for Technological Research and Innovation (BITRI), for funding my studies and allowing me to continue my studies while working.

I genuinely want to take a moment to thank you, Dr Odisitse for all the support and guidance you have provided during my studies. Am grateful for everything that you've done for me.

Thank you for being an incredible boss, Dr Beas. You have pushed me to challenge myself and grow, your continued support, guidance and persistent help had all made a massive contribution to the completion of this dissertation.

My heartfelt gratitude goes to my grandmother and my mother for all your support and for taking care of my son while I was busy with my studies.

LIST OF ABBREVIATIONS AND SYMBOLS

TGA: Thermogravimetric analysis

TG: Thermogravimetry

DTG: Differential Thermogravimetry

MS: Mass Spectrometry

EGA: Evolved Gas Analysis

XRF: X-ray Fluorescence Spectrometry

XRD: X-ray Diffraction Spectrometry

KAS: Kissinger Akahira Sunose

OFW: Ozawa Flynn Wall

ASTM: American Society for Testing and Materials

HDPE: High Density Polyethylene

$T_{\max}$: Temperature of maximum reaction rate

E_a : Activation Energy (kJ/mol)

R: Gas constant $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

R^2 : the degree of linear fitting

A: Pre-exponential factor

$f(\alpha)$: the reaction mechanism function

$g(\alpha)$: the integral form of reciprocal of reaction mechanism function

$k(T)$: reaction rate constant

α : extent of conversion

m: mass of samples

m_0 : initial mass of samples

m_f : final mass of samples

n : reaction order

t : time, s

m/z : mass to charge ratio

wt. %: Weight percentage

T : Temperature ($^{\circ}\text{C}$)

$^{\circ}\text{C}$: degrees Celsius

$^{\circ}\text{C}/\text{min}$: degrees Celsius/min

β : heating rate ($^{\circ}\text{C}/\text{min}^{-1}$)

CHAPTER 1

1 INTRODUCTION

The most widely available fossil fuel is coal. Reports show that it will remain accessible long after petroleum and natural gas wells have run dry [1]. It is a major contribution to fossil fuel energy sources and resources. It is the most important primary energy source for most countries' power generation and industrial processes and will remain so until at least 2030 [2]. Additionally, it is used as a fuel in the steel industry to extract iron from iron ore and in the production of cement. Because coal is comparatively cheaper than other fossil fuels like natural gas and oil, it remains vital in achieving a diverse and balanced energy source for developed and developing economies, providing 26% of global primary energy needs and 41% of global electricity generation [3]. But for coal to be used prudently and avert its associated pollution, it is imperative to understand each country or region's coal for energy generation purposes. Black lignite coals have been widely utilized to generate electricity and industrial steam in Botswana, Mozambique, Zambia, Zimbabwe, and Namibia [4]. Coal is anticipated to take position of petroleum as the world's primary source of energy in a few years due to its availability, global distribution, and affordability [5]. Since Botswana has a considerable amount of this domestic energy resource and an existing capacity for coal-based power production, such coals are anticipated to remain a vital energy source for both countries for several decades to come.

It is crucial to evaluate coal reactivity under specific reaction circumstances because of the heterogeneous nature of coal and the wide range of coal conversion methods available. Thermo-analytical methods such as thermogravimetry (TG), derivative thermogravimetry (DTG), differential scanning calorimetry (DSC), differential thermal analysis (DTA), and thermomechanical analysis (TMA) can be used to determine the combustion, gasification, pyrolysis, and characteristics of a fuel used in energy production.

1.1 Motivation

In Botswana and other nations across the world, black lignite coals have been extensively used for industrial and power steam generation. Since Botswana has a considerable amount of this domestic energy resource and an existing capacity for coal-based power production, such coals are anticipated to remain a vital energy source for both countries for several decades to come. Coal is

one of the energy assets estimated to be abundant in Botswana (200 billion tons) [6]. The Morupule Coal Mine is currently producing coal for local use, but Masama is producing for exports. The major consumers of the Morupule coal are the Botswana Power Corporation which uses it to generate electricity to supply throughout the country.

It is well established that gasification can improve power generation efficiencies from 35% for coal combustion to 45 and 55% [7]. Thus, carbon dioxide emissions into the atmosphere can be more easily recovered and also be minimized. In addition, Campoy *et al.* showed that a suitable combination of steam and temperature results in greater yields of H_2 and CO, calorific value, carbon conversion and gasification efficiency [7]. The systematic identification and study of the generation and evolution of CO_2 , H_2 , and CO throughout the conversion processes is necessary for the gasification optimization of high ash coals.

Keboletse *et al.* examined the suitability of Morupule coal for gasification technology and found more hydrogen flowing inside the reactor than other combustible gases [8]. CO followed this, while CH_4 was the least produced gas. Gasification kinetics of Morupule coal under atmospheric CO_2 isothermal temperatures of 900-1050°C in an efficient wire-mesh reactor, has been studied by Bikane *et al.*, who found that rates of response of gasification were substantially higher than those reported in the literature; with an activation energy of 320 kJ mol^{-1} as well as a pre-exponential factor of the order of 1010 s^{-1} [9]. A similar study of Morupule coal with thermogravimetry by Tabbiruka *et al.*, studied the thermogravimetric, calorimetric and chemical analytical characterization of Morupule coal and found an average heat of coal combustion of 27.3 kJg^{-1} , with a substantial amount of ashes after combustion [10]. Neither of the above two studies on Morupule coal is on pyrolysis, but because most of the use of coal involves pyrolysis, several researchers have studied pyrolysis kinetics of different coals in the world [11], [12] but not Botswana coal.

We have, thus, used the thermogravimetric-mass spectrometric (TG-MS) technique to examine the combustion and pyrolysis characteristics as well as kinetics of Botswana's black lignite coal. The results can contribute to a better understanding of Botswana's black lignite coal's combustion features and accurate pyrolysis systems design, and the optimization of operating conditions when used in Botswana and in countries that import coal from Botswana.

By 2050, the present rate of waste management is projected to result in the disposal of around 12 billion metric tons of waste into landfills or other natural resources [13]. Macro-, meso-, micro-, and nano-plastics can structurally break down into smaller particles over time as a result of improper waste plastic management, notably landfilling. Effective recycling methods for discarded plastic present a serious problem today for protecting the environment and natural resources. The Republic of Botswana is dealing with a number of environmental problems as a result of its fast growth. The volume of solid trash produced in the nation is among the most significant implications. Residents of Botswana are not aware of the threats associated with unregulated landfilling. Careless waste management and excessive littering have turned out to be serious problems in Botswana [14]. Suresh and Vijayakumar investigated current waste management practices in Gaborone from several perspectives in order to develop an improved waste collection system. According to their findings, management has to solve the problems in present waste management strategies to reduce the environmental issues brought on by waste generation in Gaborone [15]. Due to a lack of resources, municipal solid waste (MSW) is still a problem in transitional and developing countries like Botswana, where it is typically not given the utmost attention [16]. Lack of an efficient national waste policy implementation, unclear rules defining the obligations of generators and public authorities, and inconsistent and thorough solid waste management regulations all pose obstacles to Botswana's waste management practices. Due to these issues, there is concern about the growing practice of illegal waste disposal, which has resulted in mini-dumping sites all across the country and jeopardized the efforts of businesses involved in the tourist industry.

Therefore, there is a need today to develop and investigate alternative methods for plastic recycling. Co-pyrolytic methods are essential because they provide an efficient way of getting rid of waste and converting coal and polyolefins into higher-value fuel. Waste minimization, chemical recovery, and fossil fuel replacement are advantages of this approach to avoid resource wastage. [17], [18], [19].

1.2 Objectives and research questions

This project's primary purpose was to study kinetic analysis of pyrolysis and combustion of Botswana Morupule Coal and its blend with municipal and industrial waste in order to comprehend the degradation mechanism, the rate of reaction and the mechanism of reaction in order to gain some useful insight for enhancing the pyrolysis and combustion reactor's practical design and operation. Specifically, the project will:

- 1) Investigate the thermal degradation behavior of Morupule sub bituminous coal.
- 2) Characterize the physicochemical properties of raw coal samples i.e proximate and ultimate analysis.
- 3) Examine the distribution of the volatiles that were produced during pyrolysis and combustion of coal and coal mixture.
- 4) Investigate the interaction between coal and plastic waste during pyrolysis and combustion.
- 5) Fully characterize the coal which is imperative for the:
 - Identification of the chemical and mineralogical composition of coal.
 - Identification of the different functional groups of coal.
- 6) Assess the chemical changes that take place when fly ash is heated and to determine the actual UC content.
- 7) Determine the kinetic data for the pyrolysis and combustion processes for the three kinds of coal.

To the best of our knowledge, there has never been research done on such black lignite coal of Botswana.

The research questions addressed in this study were as follows:

- i. What are the chemical, physical and structural properties of Botswana coal and char?
- ii. What's the chemical composition of the evolved gas during pyrolysis, combustion, and what is the activation energy?
- iii. The relationship between the activation energy and the physical and chemical attributes of black lignite coal.
- iv. The relationship among size, evolved gas, and activation energy.

CHAPTER 2

2 LITERATURE REVIEW

This part includes the literature review survey to understand the prior and ongoing research pertinent to the current study. This covers pyrolysis, combustion, and reaction kinetics which are vital in understanding the black lignite coal of Botswana.

2.1 Coal

Coal is a physically and chemically heterogeneous blend of organic and inorganic materials. Organically, coal consists primarily of carbon, hydrogen, and oxygen, with lesser amounts of sulfur and nitrogen. Coal is made up of a variety of ash-forming substances that are spread all over it. Coal has a complex structure, and it is challenging to provide a precise quantitative description of the coal pyrolysis process, especially for coal that is mined in various parts of the world.

2.1.1 Types of coals in Botswana

There are various coalfields from different locations in Botswana, these include Tuli, Morupule and Moijabana, Pandamatenga, Eastern (Dukwi, Foley and Sese), Southeastern (Dutlwe, Letlhakeng) and Mmamabula [20]. Subbituminous coal is the only type of coal mined in Morupule coal mine. The coal field consists of four seams, namely:

- No. 4 seam - the Serowe Formation.
- No. 3 seam - the Lotsane Formation.
- No. 2 seam - The No. 2 Coal Seam Zone; and
- No. 1 seam - the Morupule Main Seam (“Morupule Seam”).

The coal seam is up to 17 m thick and at present only the lower section is mined as it is of higher quality than the rest of the coal seam.

2.2 Polyolefins Plastics

Polyolefins contain different types of polymers such as polypropylene (PP), polycarbonate (PC), polystyrene (PS), polyethylene terephthalate (PET), polyvinyl chloride (PVC), high density and low-density polyethylene (HDPE and LDPE), Polyacryl (PA) and others. They have different chemical structures with different amounts of carbon, oxygen and hydrogen content, their common

feature includes relatively high volatile content, viscosity, and heating value, but very low moisture and ash content.

For this study the high-density polyethylene is used, and this is a polymer whose monomer is ethylene. It is a thermoplastic with a very high strength to density ratio due to higher density and lower branching, which gives it stronger intermolecular forces and tensile strength than low density polyethylene. It is also one of the cheapest thermoplastics and fourth-largest commodity plastic material that accounts for about 15% of the global plastic consumption after polypropylene, low density polyethylene and polyvinyl chloride in terms of volume [21].

The most often used means of getting rid of waste in Botswana are dumpsites, landfilling and haphazard dumping [22]. Only a minor portion of the wastes are recovered through controlled scavenging in the landfill [23]. As a result, it has an adverse impact on the environment, contributing to methane emissions, air pollution, soil erosion, and other problems. Such activities also compromise lobbying attempts to attract investors and tourists to the nation. It also significantly shortens the time the landfill is operating. The operating time for the present landfill in Gaborone is expected to last another 20 years despite the fact that one landfill has already been closed due to operational capacity being surpassed.

2.3 Coal Pyrolysis

It is commonly recognized that coals may be used to produce a variety of valuable carbon-based products, including coal tars, petroleum pitch, and coal liquids produced through coal pyrolysis and coal liquefaction [24]. Coal pyrolysis has a crucial role in coal science and coal utilization technologies. Pyrolysis of coal is essential for coal beneficiation since it is the first step in coal conversion processes such as gasification, combustion, liquefaction, and carbonization [25]. Pyrolysis is also known as thermal cracking, thermolysis, and depolymerization [26].

To create the best working conditions, it is essential to comprehend the various stages of thermal decomposition while designing procedures for pulverized coal. It is crucial to emphasize both coal's chemical complexity and more efficient use in order to comprehend the pyrolysis process. Coal pyrolysis involves subjecting coal to high temperatures of 400-450°C in the absence of oxygen. The relative low temperatures of pyrolysis allow waste energy from the system to be used, avoiding the requirement for energy supply from other sources and making it a less expensive process than other energy conversion methods [27]. When oxygen or steam is present coal will

start burning and the process is no longer known as pyrolysis but rather referred to as combustion and gasification [28]. Gas, tar, and char are pyrolysis' primary byproducts. The amount as well as the composition of volatile material produced during pyrolysis, or the products of pyrolysis, are essentially dependent on the kind of coal, reaction temperature, pressure, heating rate, residence time, and particle size. Coal pyrolysis has a number of advantages, including the ability to turn char into energy, use the end products for managing solid waste as well as generating power in existing industrial boilers and furnaces using the in-product as fuel. Figure 2.1 below shows the basic coal pyrolysis process.

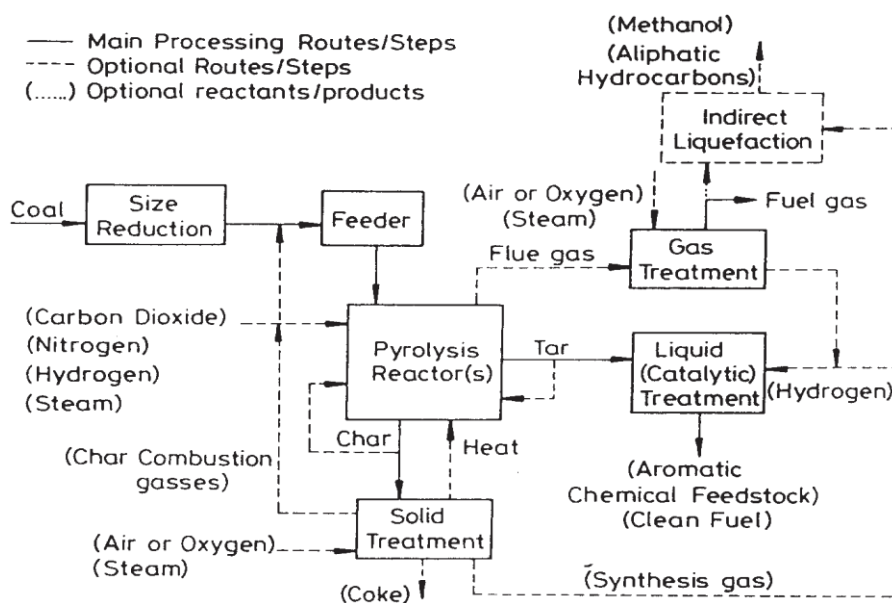


Figure 2.1: The coal pyrolysis process [29]

To better understand pyrolysis, various researchers used thermogravimetric analysis to study the thermal degradation of coal (TGA). Migliavacca *et al*, developed a thorough kinetic model that depicts how solid fuels devolatilize when subjected to pyrolysis conditions [29]. Vuthaluru and co-authors used a thermo-gravimetric study to evaluate the thermal behaviors of coal/biomass blends during pyrolysis [30], [31], [32], [33], [34]. Three biomass materials were analyzed by Vamvuka *et al*, for their primary devolatilization characteristics and kinetic parameters, the samples were pyrolyzed in a thermogravimetric analyzer under dynamic conditions either alone or in combination with Greek lignite [35]. Using combined TG-MS, Jayaraman *et al*, analyzed the pyrolysis and combustion characteristics of five coal samples from various sources. Based on their relative intensities and significance, the main combustion and volatile products release were

identified using online 3D measurements of MS [36]. Ruipu *et al*, used EGA-MS and in situ DRIFT to evaluate the co-pyrolysis properties of mixtures of Zhundong coal and corn stalk in order to investigate the release of the major small-molecule gas products and the effects of functional groups on the release of gas products, and concluded that the co-pyrolysis constituents of Zhundong coal and corn stalk interact with one another. Ma *et al* did a thorough investigation into the co-pyrolysis properties of blends made from Meihuajing bituminous coal and cow dung. Online mass spectrometry evolved gas analysis and kinetic analysis were used to examine the blends' gas evolution features and mass loss behavior [37]. Shi-Xin *et al*, employed a simultaneous thermogravimetric-mass spectrometric to analyze the pyrolysis characteristics and gas generation law of three coal samples and found that all three coal samples had similar pyrolysis characteristics and gas generation laws [38]. According to research by Wang *et al*, on the apparent activation energy of coal samples during pyrolysis, metal salts facilitate the devolatilization process with a lower activation energy. EGA-MS experiments were also used to examine the catalytic impact on the evolution of methane and hydrogen [39].

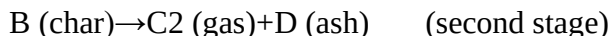
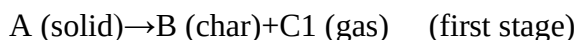
Kundu *et al*, employed thermogravimetric-mass spectrometry (TG-MS) to study the decomposition by pyrolysis of several metallurgical coals used in steel industries to better understand the coking mechanism during the carbonization of coking coals [40]. According to their experimental findings, the addition of resin to coal improved fluidity, poly-condensation process and the thermal cracking and aromatization. The findings revealed the mechanism and traits of gases evolved and, in some cases, also helped to resolve the differences between components with the same molecular weight. Seo *et al*, studied the coal pyrolysis features for Chinese coals in non-isothermal settings at various heating rates using thermogravimetric analysis and gas release measurements of the evolved species which showed that coal undergoes a series of complex chemical and physical changes during pyrolysis [41]. Yongkang *et al*, investigated the features, coal structure, and kinetics of five kinds of coal pyrolysis by a TGA system in a stream of Argon and Nitrogen with a heating rate of 20 K/min up to 1173 K and the results showed that the pyrolysis of five coals consists of three stages and that the second stage is the strongest pyrolysis stage [42].

Particle size is viewed by many researchers as a crucial factor that has an impact on pyrolysis. Firstly, the heating rates at various points along a radius inside a particle differ because of

restrictions on heat transfer. Additionally, the radius of the particle influences the residence time of evolved volatile matters and tars which in turn influences the rate of deposition of pyrolytic carbon [43]. Other investigators for example, Ozbas reported that at a heating rate of 10 K/min, the particle size of Elbistan lignite had basically no effect on pyrolysis [44]. Hanson *et al*, used different thermal analysis techniques to study the effect of particle size on coal pyrolysis and according to the findings the pyrolysis and gasification behavior was found not to vary significantly with particle size [45]. Gu˘ldoan *et al*, found that Mengen lignite coal particle size had almost no influence on the $T_{\max}$ (maximum decomposition temperature) values at the same heating rates [46]. Different coal types and the range of particle sizes utilized might be the cause of these conflicting test outcomes. For us, light differences demonstrate that particle size has almost no influence on mass loss and $T_{\max}$ during the pyrolysis. TGA data provide insights into coal's combustion behavior, volatile matter content, and emission profiles. This information is crucial for developing and implementing environmental regulations and policies related to air quality and emissions reduction. Improved combustion efficiency and cleaner burning contribute to meeting emission standards, avoiding fines, and improving public health.

2.4 Coal Combustion

Combustion is a complex process, and it involves gas-phase reactions between low temperature volatiles and oxygen as well as the combustion of char produced during the early stages of decomposition [47]. The following are two separate processes in charge of the thermal decomposition of coal and/or biomass in an oxidizing environment.



The combustion process of coal entails mass change with respect to temperature making it vital to understand the thermo-gravimetric analysis [48]. Calculating the kinetic parameters of the coal conversion process at various heating rates is done using the mass change versus temperature profile. Biswas *et al*, observed that in order to determine the ideal operating conditions, the design of the coal combustion process necessitates knowledge of the various stages of thermal degradation [49]. The combustion of coal is generally a combination of the two processes. One is when coal

undergoes pyrolysis or devolatilization because of thermal stress. The second is the slow process of heterogeneous combustion of the remaining char. The maximum mass loss occurs during the devolatilization stage (400 – 700 °C) of the coals where mainly H₂O, CO, CO₂, and a small amount of CH₄ are released in oxygen atmosphere.

A thorough understanding is needed on coal combustion behavior. Yu *et al*, employed EGA-MS to evaluate the gas release and combustion characteristics of blast furnace pulverized coal supplemented with sludge to explore the impact of the inorganic and organic components of sludge on the combustion process of blast furnace injection of pulverized coal. The results showed that the composition of sludge is mainly organic substances such as inorganic substances and lubricating oil; adding sludge can reduce the ignition temperature of pulverized coal and the temperature corresponding to the maximum combustion rate to improve the reactivity [50].

Kumar *et al*, investigated the combustion analysis of petroleum coke, coal and their blends. Thermogravimetric analysis of different characteristic parameters, such as ignition temperature, peak temperature, burnout temperature, and combustion efficiency, was used to assess the combustion performance of parent fuels and their mixtures. According to reported results petroleum coke has poor combustion characteristics compared to coal [51]. Mureddu *et al*, used thermogravimetric analysis, differential scanning calorimetry, and isoconversional kinetic techniques to characterize the air-blown combustion and oxy-combustion kinetics of several types of coal and biomass. The kinetic analysis results showed that the activation energy (E_a) varies with conversion values reflecting the kinetic complexity of the process [52].

Magalhaes *et al*, investigated the combustion behavior and kinetics of Turkish fuels using a thermogravimetric analyzer (TGA) coupled with a differential thermal analyzer (DTA), under three different heating rates, namely 15, 20, and 40 °C/min. The kinetic parameters and typical temperatures of each fuel were calculated using the Coats Redfern method [53]. Alonso *et al*, studied the combustion and pyrolysis behavior of Canadian coals using a thermogravimetric analyser. According to reported results, the coals' pyrolysis curves didn't match any distinctive feature of the related combustion profiles at all [54]. Sau *et al*, evaluated the thermogravimetric profile and kinetic characteristics of a specific grade of Indian sub-bituminous coal using a thermogravimetric analyzer. Samples were subjected to synthetic air atmospheres using heating rates of 2, 5 and 7 °C/min. DTG was employed to assess weight changes and weight loss rates for

computing the kinetic parameters [55]. Bryers investigated how inertinites affected coal's combustibility using samples of various ranks of coal collected from various geographic regions, such as China, North America, Australia, and Africa, which were petrographically and thermally analyzed. According to quantitative evaluation of the thermoanalytical combustion profiles, the inertinites are indeed slightly more reactive than vitrinite [47]. Borrego *et al*, studied the combustion characteristics of seven high-volatile bituminous coals and the results showed that at high temperatures (1100 °C) the burnout levels of the inertinite-richest coals were higher than those of medium-to-low inertinite coals [56]. This diversity calls for a further investigation into the understanding of the combustion characteristics and the kinetics of Botswana Morupule coal.

2.5 Fly Ash

Thermal power plants generate bottom ash (BA) and fly ash (FA), which are the two main types of coal ash. Fly ash accumulates in the filter section or on electrostatic precipitators positioned downstream from the main combustion section, while bottom ash is collected at the bottom of the boiler. About 80% of the ash generated by thermal power plants using coal is primarily made up of FA [57]. It is mainly made up of very small particles with a larger surface area, lighter fraction, and a high number of metalloids on the surface.

Tan, gray, and black are the possible shades of FA, depending on how much unburned carbon is present in the ash [58]. In comparison to the BA fraction, the FA fraction is more reactive chemically and has a finer texture (0.01-100 μ m).

The heavier and coarser BA fraction is ($>100 \mu$ m) a waste material that falls in the furnace bottom. They generally consist of bigger pieces of relatively inert material and are agglomerated ash particles that attach to the boiler walls or fall through the grate into an ash hopper at the bottom of the boiler because they are too large to be carried in the flue gases. The size of bottom ash particles ranges from fine gravel to fine sand, with very little of them being silt-clay sized. Both ashes are combined with water to create slurry, which is often delivered to ash ponds via pipelines made of iron alloy [59].

2.5.1 Chemical and Physical Properties of Fly Ash

Both dry sieving and wet sieving are used to check the fly ash's fineness. When a sample is sieved through a 45-micron sieve, the percentage of fly ash that is retained serves as a measure of the fly ash's fineness. Fly ash's fine texture has an impact on several significant physical variables. FA is

comprised of fine, glass-like particles that are often spherical in shape, hollow or solid, and typically amorphous (glassy) in nature. Much of the FA is made up of sphere-shaped particles, especially in the finer fractions. FA particles consist of smaller amorphous particles and crystals inside hollow, empty spheres called cenospheres. The majority (65–90%) of the particles in fly ash have sizes of less than 0.010 mm, giving it a silt loam texture [60].

FA mainly consists of SiO_2 (silica), Al_2O_3 (alumina), Fe_2O_3 (iron oxide), together with significant percentages of MgO (magnesium oxide), CaO (calcium oxide), Na_2O (sodium oxide), K_2O (potassium oxide). Additionally, it also includes considerable levels of trace elements including chromium, cobalt and mercury which are concentrated in the smaller ash particles [61]. Compared to bituminous/subbituminous ash, lignite FA has tremendous levels of CaO , Al_2O_3 , SiO_2 , SO_3 , and MgO . The FA is a mixture of amorphous and crystalline phases that differs from typical soil in terms of cation exchange capacity, specific surface area, electrical conductivity, bulk density, and moisture retention capacity. Most of the FA is made up of amorphous glass and a few crystalline phases. The crystallized forms of FA are composed of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), quartz (SiO_2), mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), aluminosilicate glass, anhydrite (CaSO_4), magnetite (Fe_3O_4), hematite (Fe_2O_3), ettringite ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$), opaline SiO_2 , chlorite, lime (CaO), , feldspars and spinel (FeAl_2O_4), depending on the mineralogy of the feed coal which is known as minerals [62].

Calcium is the most abundant cation in FA, followed by magnesium, sodium, and potassium. Due to the frequent formation of insoluble aluminosilicate complexes, the aluminum element's biological toxicity is greatly reduced. From an agricultural perspective, the FA contains macronutrients like potassium, phosphorus, calcium, sulfur, and magnesium as well as micronutrients like manganese, iron, zinc, cobalt, copper, molybdenum, and boron; the majority of which are the essential nutrients for plants. The main factor affecting the FA pH, which ranges from 4.5 to 12.0, is the sulfur content of coal. The CaO/SO_4 ratio or the amount of CaO are linearly proportional to the pH. According to Ainsworth and Rai, FA is classified as acidic if the Ca/S ratio is less than 2.5 and as alkaline if the Ca/S ratio is greater than 2.5 [63].

The FAs also contain radionuclides (^{238}U , ^{226}Ra , ^{232}Th , and ^{40}K), metalloid pollutants like mercury, arsenic, cadmium, lead, selenium, nickel, molybdenum, copper, and beryllium, and organic pollutants like polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated

dibenzofurans (PCDFs) and polycyclic aromatic hydrocarbons (PAHs) [64]. The presence of these elements in FAs is primarily determined by the kind of coal, FA particle size, combustion parameters, coal source, the presence of significant elements, condensation mechanisms, volatilization, and their relationship to the organic and inorganic components of the coal.

2.5.2 Classification and Utilization of Fly Ash

FA depending on the type of parent coal, combustion conditions, type of emission control devices storage and handling processes, and residue from coal combustion, exhibit a wide range of physico-chemical and mineralogical properties. FA is classified as class C and class F. Class C of FA is found in lignite or sub-bituminous coal and has a greater CaO content, while class F of FA has a lower CaO content and is found in bituminous coal. The amorphous and reactive water-soluble phases in FA, as well as the contents of silicon, calcium, iron, and magnesium oxides, are primarily used to categorize FA and identify its rational uses. Waste FA could be used in a variety of ways such as in concrete and cement manufacturing industries [65], an effective, inexpensive adsorbent to remove heavy metal ions from municipal solid waste leachate [66], removal of mercury and lead ions from waste water [67], and a chemical to ensure waste from industry and water treatment stay immobilized [68].

2.6 Liquefaction

The process of converting coal into a liquid fuel is known as coal liquefaction [69]. Pyrolysis, direct liquefaction, and indirect liquefaction are the three main processes used to turn coal into liquid fuels. A hydrogen-depleted char is left behind during the thermal process of pyrolysis, which involves heating coal to generate gases, liquids, and tars. Typically, more processing (refinement) is required to produce conventional liquid fuels from the gases, liquids, and tars. In direct coal liquefaction, coal that has been finely split is blended with a solvent and heated under pressure in a hydrogen-filled environment with a catalyst. The resultant liquids are often processed further to generate final products after being separated from ash and unconverted coal. There are two steps involved in indirect liquefaction. The first stage is gasifying coal in order to produce synthesis gas, which is a mixture of hydrogen and carbon monoxide. The primary byproduct of the second stage, which involves heating the synthesis gas in the presence of a catalyst to produce hydrocarbons, is water. The second phase that is most commonly considered is known as Fischer-Tropsch synthesis. Following refinement, the hydrocarbon product is transformed into the intended final products.

2.7 Gasification

The process through which coal is only partially burned is called coal gasification. It entails the reaction of solid coal with steam and air to produce gaseous byproducts that can be utilized as fuel gas, chemical feedstock, and other products. There are three steps that take place in a conventional gasifier: the pyrolysis and drying, combustion and gasification. Heat is applied in the drying and pyrolysis processes to drive out the water fed with the coal and moisture within the coal. A gas, tar, and char are then produced when the weak bonds in coal begin to break down. During combustion, the oxygen provided to the reactor reacts with the substances that are combustible to produce carbon dioxide and water. When these two products come into contact with char, they go through a reduction process that results in the production of carbon monoxide and hydrogen, which is the process of char gasification. In order to ensure a high carbon conversion rate in the gasifier, the system must maintain equilibrium between a sequence of endothermic and exothermic reactions.

Practical conditions under which these coal gasification processes take place are listed below:

1. The first step of coal gasification, known as devolatilization, yields syngas. This is followed by Char gasification and a few other secondary processes.
2. Pyrolysis, the process by which coal molecules break down at weak aliphatic and ether linkages, releases volatile matter, which includes all gases, tar (liquid hydrocarbons), and light gaseous hydrocarbons.



3. After pyrolysis, hydrogen is added to the tar molecules in the volatile matter through a process called hydrocracking. Through this process, methane is produced.

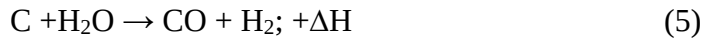


4. After that, tar is gasified to produce hydrogen and carbon monoxide.

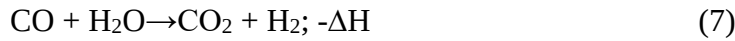


5. The char proceeds through the gasification and hydrogasification processes in the ways that are indicated below. Light alkane methane is produced when hydrogen gets added to a hydrocarbon during the hydrogasification process. Light alkane methane is produced when hydrogen gets added to a hydrocarbon during the hydrogasification process. (Eq.

(4)). Steam and carbon dioxide are then used to gasify the char, producing carbon monoxide and hydrogen.



6. Char combustion and water shift reactions are two other reactions that happen in a gasifier. (Eqs. (7) and (8)). When carbon monoxide is exposed to steam during the water shift reaction process, oxygen atoms from the water molecule attach to the carbon monoxide to generate carbon dioxide and hydrogen. (Eq. (7)). This is a means for raising the yield of hydrogen.



2.8 Coal & Plastic Waste

The efficient recycling of waste plastic represents a major obstacle to the preservation of the environment and natural resources. Therefore, it is crucial in today's era to investigate alternative methods of recycling plastic. Co-pyrolytic methods have lately received a lot of attention since they provide a viable way for disposing of and converting coal and polyolefins into better value fuels [18]. Several researchers have extensively studied the utilization of additives (tar, plastic, polyamide, oil vacuum residue) from synthetic polymers or petroleum precursors to partially replace coal in the production of coke and to improve the properties of the coal blends [70], [71], [72].

In trying to understand the physical and chemical interaction during the co-pyrolysis of HDPE plastic with black lignite coal of Botswana, TG-MS is employed to obtain information on the different events which take place during co-pyrolysis and the chemical composition of the evolved gases and also explain the different effects on the fluidity of the coal and the generation of the wall pressure during coking.

2.8.1 Coal and plastic waste pyrolysis

Melendi-Espina *et al*, evaluated the pyrolytic properties of mixtures comprised of coking coals and different plastics by analyzing the TG-MS evolution pattern of chosen evolving products

during their co-pyrolysis. According to reported results, the maximal evolution temperature was not significantly impacted by the addition of plastic waste, and hydrogen evolution profiles had similar shapes [73]. Melendi-Espina *et al*, investigated the pyrolytic decomposition of mixtures of different plastic wastes/coking coals by simultaneous thermogravimetry-mass spectrometry. The thermogravimetric parameters together with different characteristic ion fragments from selected libraries of evolving products during the co-pyrolysis process were monitored, such as hydrogen, CO₂, and aliphatic and aromatic hydrocarbons. The results showed that a synergistic effect between coal and individual residues has been found [74].

Nomura *et al*, investigated the effect of plastic addition on coal coking property. It was shown that during carbonization in coke ovens, bituminous coal and thermal decomposition byproducts of plastics interacted. To protect and preserve the environment and natural resources, plastic wastes with various structures and origins (electronic, municipal, agricultural, and automotive) have been considered as minor components of coal blends used to manufacture metallurgical coke [75]. Vivero *et al*, examined the thermal degradation of coal-plastic mixtures such as polyethylene terephthalate, polypropylene and high-density polyethylene using the thermogravimetric method. It was found that the structure and thermal behavior of semicokes as well as the thermoplastic features of coal are considerably impacted by the addition of plastic wastes to bituminous coal in quantities of 1, 2, and 5 wt.% [17]. Cai *et al*, used a thermogravimetric analyzer, to do investigations on the co-pyrolytic behavior of various plastics (polypropylene, low density polyethylene and high-density polyethylene), low volatile coal, and their blends with the plastic added at a rate of 5 wt.%. According to reported results there was a synergistic effect during the plastic and coal co-pyrolysis at the high temperature region [76]. García-Pérez *et al*, studied the thermal decomposition of petroleum residue, sugarcane bagasse and their blends under nitrogen using thermogravimetry at different heating rates (10, 20, 40 and 60 °C/min). It was found that when mixtures of petroleum residue and bagasse thermally decomposed, there was little to no interaction between the components in the solid phase under the analyzed experimental circumstances [77].

Chattopadhyay *et al*, studied the pyrolysis of pure biomass, polyethylene terephthalate (PET), polypropylene (PP), high density polyethylene (HDPE), plastic mixtures [HDPE+PP+PET], and biomass/plastic mixture using a thermogravimetric analyzer under a heating rate at 10 °C/min from

room temperature to 800 °C/min. The thermogravimetric results showed that biomass and plastic mixtures interacted significantly and had a synergistic effect during their co-pyrolysis at the high temperature region [78]. Sharypov *et al*, studied the thermal behavior of wood biomass and synthetic polymer mixtures in a rotating autoclave. A preliminary thermogravimetric examination reveals that biomass thermally degrades at a lower temperature than the investigated polyolefins. The origins of both biomass and plastic was greatly impacted by the co-pyrolysis products' distribution [79]. Burning plastic on its own can produce harmful emissions. However, by burning plastic and coal together, known as co-pyrolysis, some of these emissions can be reduced. This is because the coal reacts differently and burns more cleanly, resulting in fewer pollutants being released. Incorporating plastic waste into coal pyrolysis can help address plastic waste management challenges. By converting plastic waste into useful products, the environmental impact of plastic waste can be reduced.

2.8.2 Coal and plastic waste combustion

Boumanchar *et al*, did an investigation of thermal behaviours of biomass waste, biochar, coal, municipal solid waste and their mixtures using thermogravimetric analysis and differential scanning calorimeter techniques. The intention was to interpret the influence of mixtures on activation energy [80]. Rago *et al*, investigated the influence of torrefaction (300°C) on the combustion performances of blends of biomass-plastic wastes (Mango branches (MBr), newspaper (Np), LDPE) using thermogravimetric analysis. It was reported that synergies during waste char co-combustion with coal were influenced by the waste type, composition, and interactions that occurred during waste torrefaction [81]. Xinjie *et al*, utilized TGA to assess the combustion behavior of combining three feedstocks biomass, coal and polyethylene as a tri-fuel for various blend ratios. Their findings suggest that the tri-fuel combustion processes follow the diffusion model (D1 & D4) and can be categorized as three distinct stages based on the results of kinetic study. TGA analysis revealed that increasing the biomass-to-plastic blend proportion improves combustion properties by reducing ignition and burnout temperatures as well as by increasing the combustion stability indices [82].

2.9 Reaction Kinetics

According to literature, thermal decomposition data has been utilized to derive the kinetics of pyrolysis/devolatilization (reactions) since the early twentieth century [83]. Caballero & Conesa

in their study for mathematical considerations for non-isothermal kinetics in thermal degradation provided an overview of the most fundamental mathematical aspects involved in the kinetic study of thermal decomposition processes, particularly when TG-DTG was applied. The topics covered included handling raw data, introducing basic methods for filtering the data and obtaining smooth and accurate derivative thermogravimetric curves, comments on the proper mathematical model specification, and fitting data to a mathematical model. Errors were introduced in the kinetic analysis by temperature deviations from the preset control temperature program [83]. Álvarez *et al*, examined a large database of kinetic data for the most popular biomass by thermogravimetric analysis (TGA) and differential thermogravimetry (DTG). The kinetic parameters for the proposed two-stage reaction model were derived using model-based techniques with activation energy values for first and second stages in the range 1.75×10^4 – 1.55×10^5 J/mol and 1.62×10^4 – 2.37×10^5 J/mol respectively [84].

Non-isothermal thermogravimetric method has been applied to determine the chemical kinetic parameters [85]. According to Jiang *et al*, various methods are employed to evaluate the kinetic parameters from non-isothermal thermogravimetric analysis, and the most popular ones can be divided into two categories: model-fitting methods and model-free isoconversional methods [86]–[87].

Kinetic modelling of the pyrolytic behavior of coal is an important step in assessing the contribution of materials and their interactions during the devolatilization stage. Based on the review the understanding of the kinetics of co-pyrolysis of coal blends used in this study will be essential in the design of the reactor and operation of co-gasification processes and how the individual reactions from coal and biomass interact and affect each other. This study aim to examine the chemical kinetic performance of the Morupule Coal, together with the estimation of activation energy and pre-exponential factor and its influence on heating rate.

Table 2.1 below shows the differential and integral form of the most likely mechanism function.

Table 2.1: Some of the kinetic models employed in solid state kinetics

Code	Reaction Model	$f(\alpha)$	$g(\alpha)$
Reaction orders and geometrical contractions			
F1	First order	$1-\alpha$	$-\ln(1-\alpha)$
F2	Second order	$(1-\alpha)^2$	$(1-\alpha)^{-1}-1$
F3	Third order	$(1-\alpha)^3$	$[(1-\alpha)^{-2}-1]/2$
R2	Contracting area	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$
R3	Contracting volume	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$
Nucleation models			
P2	Power law	$2\alpha^{1/2}$	$\alpha^{1/2}$
P3	Power law	$3\alpha^{2/3}$	$\alpha^{1/3}$
P4	Power law	$4\alpha^{3/4}$	$\alpha^{1/4}$
P2/3	Power law	$2/3\alpha^{-1/2}$	$\alpha^{3/2}$
A2	Avrami-Erofeev	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
A3	Avrami-Erofeev	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
A4	Avrami-Erofeev	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	$[-\ln(1-\alpha)]^{1/4}$
Diffusion reactions			
D1	One-dimensional diffusion	$1/2\alpha^{-1}$	α^2
D2	Two-dimensional diffusion	$[-\ln(1-\alpha)]^{-1}$	$(1-\alpha)\ln(1-\alpha)+\alpha$
D3	Three-dimensional diffusion	$3/2(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$	$[1-(1-\alpha)^{1/3}]^2$

2.9.1 Arrhenius Equation

The overall rate of reactions is commonly described by the following equation.

$$\frac{d\alpha}{dt} = f(\alpha, T) \quad (1)$$

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (2)$$

Where $\frac{d\alpha}{dt}$ is the reaction rate, α is the conversion degree, $k(T)$ is the rate constant, t is the time, T is the temperature, and $f(\alpha)$ is the reaction model. When doing a kinetic study of a chemical process, the degree of conversion is frequently taken into account. The acquired TGA data is converted to the degree of conversion form. The processed TGA curve is used to determine the degree of conversion on equation (3) below.

$$\alpha = \frac{m_o - m_t}{m_o - m_f} \quad (3)$$

Where m_o is the original sample mass in mg, m_t is the actual mass recorded at a specific time t , and m_f is the final sample weight.

Using a linear heating rate $\beta = \frac{dT}{dt}$, where β is the heating rate (4)

We can rewrite Equation (2) as;

$$\frac{d\alpha}{dt} = \beta \frac{d\alpha}{dT} = k(T)f(\alpha) \quad (5)$$

The dependence of the rate constant will be described by the Arrhenius law;

$$k(T) = Ae^{\left(\frac{-E}{RT}\right)} \quad (6)$$

Where E is the activation energy, A is the pre-exponential factor and R is the gas constant.

$$\frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \exp\left(\frac{-E}{RT}\right) dT \quad (7)$$

$$Ae\left(\frac{-E}{RT}\right)f(\alpha)$$

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{dt} = \int_0^T k dt = \int_0^t Ae\left(\frac{-E}{RT}\right) dt \quad (8)$$

When the isoconversional principle is applied to the integral equation (8), integral isoconversional methods are developed.

2.9.2 Isoconversional Method

The International Confederation for Thermal Analysis and Calorimetry recently strongly recommended model free isoconversional methods, which have been demonstrated to be very beneficial for kinetics analysis [88]. These methods have been widely used to study the kinetics of chemical or physical processes and enable the establishment of strong explanations for the mechanisms behind a range of chemical reactions, including protein denaturation, crosslinking, renewable thermosets, polymer crystallization, glass transition kinetics, thermal and thermo-oxidative degradation, and glass aging [89], [90], [91]. Isoconversional methods entail carrying out a series of experiments at various temperature programs for non-isothermal data. The most popular methods are represented by the differential method and by the integral methods proposed by Ozawa–Flynn–Wall (OFW) [92] or Kissinger–Akahira–Sunose (KAS) [93] and Friedman method [94].

The activation energies as a function of conversion for a thermally activated solid-state reaction is computed from the isoconversional methods [95]. Model-free methods are the most dependable and popular due to their simplicity. Model-free approaches often report activation energies because they calculate the reaction activation energy ($E\alpha$) without making model assumptions. The OFW and KAS isoconversional methods could produce some significant errors when estimating activation energies, especially for processes with significantly different activation energies, as

these two methods were devised by integrating the Arrhenius equation under the assumption that activation energy would remain constant throughout the reaction [96].

2.9.2.1 Kissinger-Akahira-Sunose

The Kissinger Akahira Sunose method is said to be one of the best-known methods in applying the approximation of temperature integral to calculate kinetic parameters. In the KAS method, the kinetics of the reaction is described as:

$$\ln \frac{\beta}{T^2} = \ln \left[\frac{AR}{Eg(\alpha)} \right] - \frac{E}{RT} \quad (9)$$

The final equation is number 9, where T, A, R, β , and E are Temperature (K), frequency factor (min^{-1}), gas constant ($8.314 \text{ J/mol} \cdot \text{K}^{-1}$), heating rate (K/min), and activation energy (kJ/mol). Plotting $\ln \beta/T^2$ versus $1/T$ can be obtained after manipulation of the experimental data of different coal samples at different conversion values α whose slope give E.

2.9.2.2 Ozawa-Flynn-Wall

The Ozawa-Flynn-Wall method is an independently derived iso-conversional method for non-isothermal process [97]. Using Doyle's approximation [98];

$$\ln p(x) \cong -5.3305 - 1.052x \quad (20 \leq x \leq 60) \quad (10)$$

the kinetics of the reaction for OFW can be described by using equation (7) and (8) to obtain equation (11)

$$\frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \exp\left(\frac{-E}{RT}\right) dT \quad (7)$$

$$g(\alpha) = \int_{\alpha_0}^{\alpha} \frac{d\alpha}{f(\alpha)} = \int_{T_0}^T \frac{A}{\beta} \exp\left(\frac{-E}{RT}\right) dT = \frac{AE}{\beta R} \exp\left(\frac{-E}{RT}\right) \quad (8)$$

The linear equation of Ozawa-Flynn-Wall can be obtained by equation below:

$$\ln \beta = \ln \frac{AE}{Rg(\alpha)} - 5.331 - 1.052 \frac{E}{RT} \quad (11)$$

Where T, A, R, β , and E are Temperature (K), frequency factor (min^{-1}), gas constant (8.314 J/mol. K^{-1}), heating rate (K/min), and activation energy (kJ/mol)

$$\alpha = \frac{m_o - m_t}{m_o - m_f}$$

m_o : initial mass, m_t : mass at time t, m_f : final mass.

Plotting $\ln(\beta)$ versus $1/T$ at different conversion values α give E from the slope.

The OFW and KAS approaches are both linear, and their derivations both make use of an oversimplified temperature integral estimate. The techniques were developed with the presumption that the activation energy would remain constant during the reaction's course until it reached the conversion degree of interest. Below are schematic illustrations for the OFW and KAS isoconversional processes.

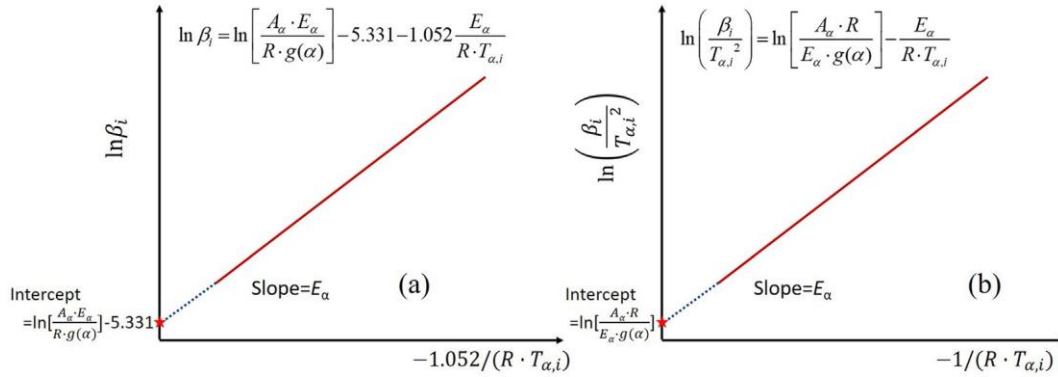


Figure 2.2: Detailed diagrams of the OFW and KAS isoconversional processes are shown below [100]

2.9.2.3 Kissinger Method

This approach allows estimation of the kinetic parameters of a solid-state reaction without taking the reaction mechanism into account. For non-isothermal conditions, Kissinger proposed a model-free method (not isoconversional) in which it is not necessary to estimate E_a for the progressive value of conversion (α) but rather assumes a constant E_a like other methods [93]. For a series of

measurements taken at various heating rates (β), this approach calculates the activation energy E_a and the pre-exponential factor (A) from a plot of $\ln\left(\frac{\beta}{T^2}\right)$ against $1000/T$, where T stands for the temperature at which the highest differential thermal analysis deflection occurs. The E_a and A are estimated by Eq. (12):

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{E_a}\right) - \frac{E}{RT} \quad (12)$$

2.9.3 Differential Analysis Methods

The most common differential isoconversional method is that of Friedman.

2.9.3.1 Friedman's isoconversional method

The following ordinary differential equation can be used to represent the rate of a thermally initiated solid-state reaction when using a linear heating approach [99];

$$\beta \frac{d\alpha}{dT} = Ae^{\left(\frac{-E}{RT}\right)} f(\alpha) \quad (13)$$

where A is the frequency factor, R is the universal gas constant, E is the activation energy, and $f(\alpha)$ is differential form of the conversion function.

One can get the following by taking the logarithm of both sides of the equation (13):

$$\ln\left(\beta \frac{d\alpha}{dT}\right) = \ln[Af(\alpha)] - \frac{E}{RT} \quad (14)$$

For a certain conversion and numerous experiments with various heating rates, the above equation becomes:

$$\ln\left(\beta_i \frac{d\alpha}{dT}\right)_{\alpha,i} = \ln[A\alpha f(\alpha)] - \frac{E\alpha}{RT\alpha_i} \quad (15)$$

where the non-isothermal experiment's ordinal number is indicated by the subscript i conducted at the heating rate β_i and the subscript (α) denotes the proportions determined by a certain conversion degree (α). For a given (α), activation energy (E_a) and $\ln[A\alpha f(\alpha)]$ can be obtained from the slope and intercept of the plot of $\ln[\beta_i(d\alpha/dT)_{\alpha,i}]$ versus $(-1/RT_{\alpha,i})$.

Advantages of Friedman method are as follows:

- i. The process is linear.
- ii. This method generates more accurate results than the integral methods.
- iii. It is not confined to the use of the heating rate's linear variation.
- iv. The method's application requires the derivative conversion data, which would make it noisy and numerically unstable.

2.9.3.2 Master plot Method based on the Differential form

There are various master plot approaches that use the differential, integral, or a combination of the two types of the kinetic equation [100]. Various kinds of master plots methods are equivalent to determining the kinetic mechanism function. Under non-isothermal conditions with a constant heating rate, for a solid-state reaction, the kinetic equation can be written as:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-E/(R.T)} f(\alpha) \quad (16)$$

Using equation (16) the following equation can be attained:

$$f(\alpha) = \frac{\beta}{A} e^{E/(R.T)} \cdot \frac{d\alpha}{dT} \quad (17)$$

Depending on the reference point at $(\alpha)=0.5$, equation (18) can be a resultant of equation (17):

$$\frac{f\alpha}{f(0.5)} = \frac{\left(\frac{d\alpha}{dT}\right)\alpha \cdot \exp[E\alpha/(R.T\alpha)] \cdot A0.5}{\left(\frac{d\alpha}{dT}\right)0.5 \cdot \exp[E0.5/(R.T0.5)] \cdot A\alpha} \quad (18)$$

where the conversion rate $(d\alpha/dT)_{0.5}$ corresponds to $(\alpha)=0.5$, $f(0.5)$, $E_{0.5}$ and $T_{0.5}$ reflect the kinetic mechanism function value, activation energy and temperature relative to $\alpha=0.5$.

Assuming $A\alpha/A_{0.5} \approx 1$ equation (18) can be reduced to the following form:

$$\frac{f\alpha}{f(0.5)} = \frac{\left(\frac{d\alpha}{dT}\right)\alpha \cdot \exp[E\alpha/(R.T\alpha)]}{\left(\frac{d\alpha}{dT}\right)0.5 \cdot \exp[E0.5/(R.T0.5)]} \quad (19)$$

Finite difference can be used to calculate the conversion rate $(d\alpha/dT)_\alpha$ as shown in the equation below:

$$\left(\frac{d\alpha}{dT}\right)_\alpha = \frac{\Delta\alpha}{T\alpha + \Delta\alpha/2 - T\alpha - \Delta\alpha/2} \quad (20)$$

The experimental data and the E values from the isoconversional techniques can be used to derive the right-hand side of Equation (19). Calculations of the values of $f(\alpha)/f(0.5)$ versus α generated from experimental data can be calculated according to equation (19). Luo *et al*, stated that when experimental master plot and various theoretical master plots are compared when employing the master plots method to estimate $f(\alpha)$, the theoretical $f(\alpha)$ that is closest to the experimental master plot is the best kinetic mechanism function [101].

2.9.3.3 Vyazovkin

The activation energy value that minimizes (E_a) , a function of the activation energy, can be determined using the Vyazovkin approach for a collection of temperature values acquired at the same conversion value (α) for n distinct heating rates [102].

$$\Phi(E_a) = \sum_{i=1}^n \sum_{j \neq i}^n \frac{J[E_a, T_i(t\alpha)]}{J[E_a, T_j(t\alpha)]} \quad (21)$$

2.9.4 Model Fitting Method

The model fitting methods are known for their simplicity in calculating the kinetic parameters directly from thermogravimetric data results (i.e., activation energy E_a , frequency factor A, and the reaction model $f(\alpha)$), some common kinetic models are listed in Table 1. If the models are fitted simultaneously to several data sets obtained under various temperature regimes, the model fitting methods can just be as reliable as the model-free isoconversional methods [88].

In contrast to isoconversional methods, model-fitting methods can identify multi-step reaction models that are appropriate for describing complex kinetics. However, a lot of significant difficulties that are not there when employing model-free methods are connected to this process. It has been recently demonstrated that the complementary use of the model-free method with the Isoconversional methods can be very useful to understand the solid-state reaction kinetics [103]. Model fitting can be achieved in a variety of approaches. They all entail reducing the difference between the reaction rate data calculated and tested experimentally. It is possible for the data to be

isothermal, to have a constant heating rate, or to combine the two. Minimization can be attained by utilizing linear and non-linear regression approaches.

2.9.4.1 Linear model-fitting method

Techniques for linear regression are used in linear model-fitting approaches. The rate equation should be transformed into a linear form before using such techniques. This can be easily done by rearranging a single-step rate shown below and taking the logarithm that makes a plot linear with respect to the reciprocal temperature.

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E}{RT}\right) f(\alpha) \quad (22)$$

There are several ways for performing linear model-fitting. The combined kinetic analysis is one effective example of such a method [104]. The entire kinetic triplet (E_a , A and $f(\alpha)$) has been proposed to be determined using the linear model-fitting from the simultaneous treatment of many kinetic curves acquired using various random temperature programs. The kinetic model is established in the general manner shown below.

$$f(\alpha) = c \alpha^m (1 - \alpha)^n \quad (23)$$

The values c , n , and m can be modified to accommodate a variety of ideal kinetic models developed under certain mechanistic assumptions as shown in Table 2.

Table 2.2: Parameters of equation 23 fitted to different reaction models

Symbol	$f(\alpha)$	Equivalent reduced Sestak-Berggren equation
R2	$(1-\alpha)^{1/2}$	$(1-\alpha)^{1/2}$
R3	$(1-\alpha)^{2/3}$	$(1-\alpha)^{2/3}$
F1	$(1-\alpha)$	$(1-\alpha)$
A2	$2(1-\alpha)[- \ln(1-\alpha)]^{1/2}$	$2.079(1-\alpha)^{0.806} \alpha^{0.515}$
A3	$3(1-\alpha)[- \ln(1-\alpha)]^{2/3}$	$3.192(1-\alpha)^{0.748} \alpha^{0.693}$
D2	$[- \ln(1-\alpha)]^{-1}$	$0.973(1-\alpha)^{0.425} \alpha^{-1.008}$
D3	$(3(1-\alpha)^{2/3})/(2[1-(1-\alpha)^{1/3}])$	$4.431(1-\alpha)^{0.951} \alpha^{-1.004}$

The following equation is the basis for the combined kinetic analysis [104].

$$\ln \left[\frac{d\alpha}{dt} \frac{1}{\alpha m (1-\alpha)^\eta} \right] = \ln(cA) - \frac{E}{RT} \quad (24)$$

It is necessary to simultaneously substitute kinetic data α and $d\alpha/dt$ versus T obtained at various temperature programs when evaluating the parameters of equation (24). The parameter values that produce the best linearity in a curve of the left-hand side of the above equation against the inverse temperature are believed to be the best fit ones. The coefficient of linear correlation, r , which is found by numerically optimizing the parameters n and m , is used to evaluate linearity. Considering that the kinetic data's relative experimental errors are bigger for low and high conversions, it is perhaps appropriate to limit analysis to the α range of 0.10-0.90 or 0.05-0.95. The values of E and $\ln(cA)$ would then be estimated from the slope and intercept of the linear plot once the values of n and m that maximize r have been identified. To determine whether the experimentally determined $f(\alpha)$ fits any of the ideal kinetic model values, the obtained values of n and m would then be verified to those values using (Table 2).

2.9.4.2 Coats Redfern Method

One of the old most popular model-fitting methods for evaluating solid-state kinetics for non-isothermal experiments is the Coats and Redfern method. This method makes use of the non-isothermal rate law's integral form [105],

$$g(\alpha) = \frac{AE\alpha}{\beta R} p(x) \quad (25)$$

Where $p(x)$ is the exponential integral which can be found in mathematical tables [106]. The following are main methods for evaluating the temperature/exponential integral.

1. Figuring out the numerical values of $p(x)$.
2. Changing the approximate form of $p(x)$ into one that can be integrated.
3. Using a series expansion to approximate $p(x)$.

Coats and Redfern approximated the temperature integral ($p(x)$), using the asymptotic series expansion and produced the equation below:

$$\ln\left(\frac{g(\alpha)}{T^2}\right) = \ln\left(\frac{AR}{\beta E_a}\right) - \frac{E_a}{RT} \quad (26)$$

Where $g(\alpha) = \frac{1 - (1 - \alpha)^{1-n}}{1-n}$ for $n \neq 1$ and $g(\alpha) = \ln(1 - \alpha)$ for $n = 1$, β is the linear heating rate, R is the universal gas constant ($8.314 \text{ J/mol} \cdot \text{K}^{-1}$), T is the temperature (K). The activation energy is obtained from the slope of the straight line. The pre-exponential factor (A) can be obtained through the intercept of Equation. (26). The reaction rate constant (k) was then achieved using Arrhenius's Equation. (6). The model that has the best linear fit is chosen.

2.10 Deconvolution analysis using bi-gaussian algorithm

The process of coal thermal decomposition is intricate and involves interrelated reaction pathways. Knowing all the stages and contributions in the pyrolysis process is essential. Deconvolution analysis makes use of the peak-fitting algorithm to identify digital signals in the chemical atlas. Through the use of appropriate mathematical algorithms, this method has been used for the kinetic study of complex processes.

Based on prior research [107]- [108], it has been determined that the Gaussian and Lorentzian functions are not ideal for analyzing asymmetric peaks. Instead, the bi-gaussian Weibull function is better suited for this task. By using this function, overlapping peaks in asymmetrical curves can be separated, leading to a more comprehensive understanding of pyrolysis reactions.

$$y = y_o + He^{-0.5\left(\frac{x-x_c}{w_1}\right)^2} \left(x < x_c \right)$$

$$y = y_o + He^{-0.5\left(\frac{x-x_c}{w_2}\right)^2} \left(x \geq x_c \right)$$

We are utilizing the reaction rate as input data and measuring the goodness of fit using the correlation coefficient R^2 and the residual sum of squares (RSS). The variables involved in this analysis are baseline offset (y_o), peak maximum height (H), independent variable (x), peak centre (x) left half width (w_1), and right half width (w_2). RRS is defined as:

$$RSS = \sum_i^N \left(y_i^{exp} - y_i^{th} \right)^2 = min$$

With y_i^{exp} and y_i^{th} are experimental and predicted result at different temperature and time, respectively the high fitting degree and small RSS show that the asymmetric bi-Gaussian function can be describe the deconvolution process.

2.11 Thermogravimetric Analysis Theory

Since the beginning of the 20th century, thermal decomposition data have been utilized to extract the kinetics of pyrolysis and devolatilization (reactions). TGA is a method where the mass of a material is measured as a function of temperature or time while the sample specimen is put through a controlled temperature program in a controlled environment [109]. The term "thermogravimetric (TG) thermogram" refers to the record of weight loss with regard to time or temperature. Differential thermogravimetric (DTG) thermograms are used to record the rate of weight loss (the first derivative with respect to time) as a function of time or temperature. For calculating devolatilization rates, thermogravimetric analyzers are utilized. A precise balance is used to hold a sample pan in a thermogravimetric analyser. The sample pan is placed in a furnace with a controlled atmosphere and heating temperature. Throughout the experiment, the sample's mass is constantly measured and recorded. TGA is frequently employed to evaluate the moisture and

volatile contents of coal, biomass, and other materials including sewage sludge, waste car tires, and medical waste. The kinetic analysis of biomass pyrolysis using TGA can be carried out with the help of a variety of heating methods: isothermal heating program [110], linear heating program [111] and stepwise linear heating program [112].

2.12 Thermogravimetric-Mass Spectrometry Theory

A well-known instrument in the study of solid fuel pyrolysis is thermogravimetry combined with mass spectrometry (TG-MS). It can offer comprehensive data in real-time on the many processes involved in co-pyrolysis as well as the properties of gas release in relation to temperature [113], [114], [115], [116]. Several researchers have conducted thermodynamic analysis from the perspective of gas changes generated by coal pyrolysis [117]- [118].

The kinds and quantities of gases released from the sample as a function of temperature are recorded concurrently with weight loss using mass spectrometry (MS) in conjunction with TGA through a vacuum-operated, heated line with quartz capillary tube. The MS system has been configured to generate the molecular weights (MW) of gases released during pyrolysis. All coals emit volatile substances when heated. The system detects gas fragments and reports their mass to charge ratio. A mass spectrum shows the ion current versus time for each detected MW or m/z . The amount of released gas directly influences the ion current's intensity. Any major peak or hump in the mass spectrum is considered to indicate the emission of a gas at that temperature, as opposed to background gases like He, which are represented by a flat MS spectrum with high intensity.

CHAPTER 3

3 MATERIALS AND METHODS

A brief description of experimental methods, characterization and evaluation techniques that were employed in this study are covered in this chapter.

3.1 Sampling and Sample preparation

The first stage in the sample handling methods an analyst does while analyzing populations is sampling. For the results of the analysis of the portion (sample) to fairly generalize the population from which it was chosen, a representative portion of the population of interest must be selected. Different coal types (S4-4, EM1, S3-9, WM1 and S3-5) and fly ash B coming from the power plant were used in this study. The coal samples were obtained from Morupule Coal Mine. The Morupule Coal Mine is a coal mine located on the outskirts of Palapye, Botswana, along the Serowe-Palapye road.

In a recent study by Nermark, coal from different mining sites were labelled as S3/9 (South main 3 development panel/ production panel number 9), S4/1 (South main 4 development panel/ production panel number 1), S4/4 (South main 4 development panel/ production panel number 4), EM1 (East main development panel 1/ production panel number 1), WM1 (West main development panel 1/ production panel number 1) and S3/5 (South main 3 development panel/ production panel number 5) [119].

They collected coal from the mining site and loaded it in the trucks which transport the raw coal to the conveyor belt. A jaw crusher and a sieve shaker with different sieves was used to separate the coal into different particles sizes of 0.6mm, 0.850mm, 1.0mm, 1.18mm and 2.0mm. The coal was washed with water to remove dirt and dried under static conditions. Coal was then characterized using a variety of analytical techniques, including thermogravimetric analysis coupled to the Mass Spectrometry (TGA-MS), thermogravimetric analysis coupled to the FTIR (Fourier transform Infrared Spectroscopy (TGA-FTIR)), X-ray fluorescence (XRF), and X-ray diffraction (XRD) [120]. SGS laboratories (SGS (Pty) Ltd) in South Africa performed both proximate and ultimate analyses on the raw coal samples. The American Society for Testing and Materials (ASTM) methodologies were used for proximate analysis. The HDPE plastic which is

the most common and abundant thermoplastic present in municipal waste was selected in this study and this plastic waste was collected from the BITRI (Nanomaterial's lab) in a dustbin. The plastic was pulverized using a ball miller and added to the coal (in an amount of 5, 10, 25, 50 and 66.7 wt.%) based on the literature point of view [17] [81].

3.2 Thermogravimetric Analysis

The thermogravimetry analysis of the coal samples, plastic waste and different coal/plastic mixtures were performed using a Mettler Toledo TGA/DSC3+ instrument. When using the technique, the sample was heated gradually while an inert gas was passed through it. Non-isothermal TG was applied in determining the chemical kinetic parameters in coal pyrolysis and combustion. The mass loss rate of coal was observed with temperature changes in a controlled atmosphere. The predicted mass loss was shown on a thermogravimetric (TG) curve as a function of time or temperature. A differential thermogravimetric (DTG) curve showed the rate of mass loss measured in relation to temperature or time. The ability to analyze the devolatilization of coal in both inert and oxidizing atmospheres was a key benefit of the thermogravimetry approach [121]. The analyses were carried out under 40 ml/min argon and oxygen flow at a heating rate of (5, 10, 15, 20 and 25 °C/min⁻¹) from room temperature to 900 °C when doing pyrolysis and combustion experiments for coal and coal blends. The HDPE plastic was heated from room temperature up to 600 °C at a heating rate of 25 °C/min⁻¹ using the same atmosphere and flow rate. Coal samples of around 15 mg were weighed and dispersed flatly on the 70µl alumina crucibles, which had flat bottoms. Each experiment was run three times under the same conditions to ensure reproducibility. The temperature at which the maximum release of volatile matter took place on the DTG curves ($T_{\max}$) was observed. To prevent temperature gradients across the sample and reduce the effects of mass transfer, a limited amount of sample and a slow heating rate were used.

Utilizing two distinct atmospheres, which is nitrogen and oxygen, using a constant gas flow of 75 mL/min, a two atmosphere TGA-MS was performed on a fly ash sample [122]. In this manner, the organic carbon (UC) was burned in the oxidizing environment while the inorganic carbon, bound water, and volatile substances were released during heating in the inert gas. Initially, a sample of fly ash was heated at a rate of 10 °C/min⁻¹ from ambient temperature to 110 °C. The sample was kept at 110°C for 15 min while the chamber was purged with nitrogen gas. The temperature was increased from 110 °C to 950 °C at a heating rate of 10 °C/min⁻¹. A temperature of 950 °C in the

nitrogen environment for 15 minutes was chosen as the isothermal segment. After that, the sample was cooled to approximately 150 °C in N₂ at a rate of 10 °C/min⁻¹. This cooling step was employed to enable the use of equivalent heating protocols in both inert and oxidizing environments. In order to generate an oxidizing atmosphere, the ambient gas was subsequently converted to oxygen (constant gas flow of 75 mL/min). The sample was held in an isothermal condition for 10 min in the oxygen, followed by heating to 950 °C at a rate of 10 °C/min⁻¹. The sample was maintained for 15 min at 950 °C in oxygen and finally cooled to room temperature.



Figure 3.1: Thermogravimetric Analyser

3.3 Kinetic analysis

Coal, plastic, and coal mixture samples were evaluated non-isothermally from several TGA thermograms. Non-isothermal runs were performed at different heating rates of 5, 10, 15, 20 and 25 °C/min⁻¹. Methods for kinetic analysis performed on these samples have already been described previously in Chapter 2. The following equations were employed to get the kinetics data or to model the process for combustion and pyrolysis.

3.3.1 Kissinger Akahira Sunose

The KAS method was also applied considering the following equation, whereas the plot of $\ln \frac{\beta}{T^2}$ versus $1000/T$ for a constant value of x should be a straight line whose slope can be used to evaluate the activation energy.

$$\ln \frac{\beta}{T^2} = \ln \left(\frac{AR}{g(\alpha)E} \right) - \frac{E}{RT} \quad (9)$$

In the FWO method, the kinetics of the reaction is described as:

$$\ln(\beta) = \ln \left(\frac{AE}{g(\alpha)R} \right) - 5.331 - 1.052 \frac{E}{RT} \quad (11)$$

Where T, A, R, β , and E are Temperature ($^{\circ}\text{C}$), frequency factor (min^{-1}), gas constant ($8.314\text{J/K}^{-1}\cdot\text{mol}^{-1}$), heating rate ($^{\circ}\text{C/min}$), and activation energy (kJ/mol).

3.3.2 Kissinger method

For a series of measurements taken at various heating rates (β), the Kissinger approach calculates the activation energy from a plot of $\ln \left(\frac{\beta}{T^2} \right)$ against $1,000/T$, where T stands for the temperature at which the highest differential thermal analysis deflection occurs. The E_a and A are estimated by Eq. (11):

$$\ln \left(\frac{\beta}{T^2} \right) = \ln \left(\frac{AR}{E_a} \right) - \frac{E}{RT} \quad (12)$$

3.3.3 Friedman

Friedman's suggested equation can be presented as:

$$\ln \left(\frac{d\alpha}{dt} \right) = \ln(Af(\alpha)) - \frac{E}{RT} \quad (14)$$

The activation energy (E) is calculated based on the slope of the curve $\ln(dx/dt)$ with respect to $1000/T$ with a constant rate of conversion.

3.3.4 Vyazovkin

The activation energy value that minimizes ($E\alpha$), a function of the activation energy, can be determined using the Vyazovkin approach for a collection of temperature values acquired at the same conversion value α for n distinct heating rates.

$$\Phi(E\alpha) = \sum_{i=1}^n \sum_{j \neq i}^n \frac{J[E\alpha, T_i(t\alpha)]}{J[E\alpha, T_j(t\alpha)]} \quad (21)$$

3.3.5 Linear model-fitting method

The following equation is the basis for the combined kinetic analysis.

$$\ln \left[\frac{d\alpha}{dt} \frac{1}{\alpha m(1-\alpha)\eta} \right] = \ln(cA) - \frac{E}{RT} \quad (23)$$

3.3.6 Coats-Redfern

Heat of activation ($E\alpha$) of different decomposition steps were calculated by the Coats-Redfern equation as follows:

$$\ln \left(\frac{g(\alpha)}{T^2} \right) = \ln \left(\frac{AR}{\beta E_a} \right) - \frac{E_a}{RT} \quad (26)$$

Where $g(\alpha) = \frac{1 - (1 - \alpha)^{1-n}}{1-n}$ for $n \neq 1$ and $g(\alpha) = \ln(1 - \alpha)$ for $n = 1$, β is the linear

heating rate, R is the universal gas constant ($8.314 \text{ J/K}^{-1} \cdot \text{mol}^{-1}$), T is the temperature (K). The activation energy is obtained from the slope of the straight line.

The pre-exponential factor (A) can be obtained through the intercept of Eq. (10). The reaction rate constant (k) was then achieved using Arrhenius's Eq. (2).

3.4 Data Collection

For the TG run, thermal data were gathered using TGA/DSC3+ STARe software with a data set size ranging from 2101 to 10501 points. The data were then exported as ASCII files each containing sample temperature T_s ($^{\circ}\text{C}$), time (s) Heat Flow HF (Wg^{-1}), weight (%) and reference

temperature T_r ($^{\circ}\text{C}$) at each data point. ASCII files were imported into OriginPro 2018 software to obtain worksheet formats which were further processed for Ozawa-Flynn-Wall (OFW) and Kissinger Akahira Sunose (KAS) methods. The initial stage in data analysis was to convert each original thermogram file with data points (temperature, and weight) to one with weight, temperature, and (conversion fraction) using equation (3). The conversion data points were ranging from 0.01-0.99. Microsoft Excel was used for the Coats-Redfern method. Other methods such as Friedman, Advanced Integral Vyazovkin, Kissinger, and Model fitting (linear regression) required the use of Thinks software [123].

3.5 Physicochemical Characterization of Coal

Nermark, investigated the physicochemical properties of the coal used in this study [119]. They sent the samples to SGS laboratories (SGS (Pty) Ltd) in South Africa to examine the proximate and ultimate analysis of the coal from different active mining sites following ASTM standard methods, as shown in Table 3.1. The parameters of moisture, volatile matter, ash, and fixed carbon (non-volatile organic matter) were all determined using proximate analysis. The fixed carbon was calculated by deducting the sum of the moisture, volatile matter, and ash percentages from a hundred. The three raw coal samples (EM1, WM1 and S3-5) yielded 22.4–23.8% of volatile matter, moisture content between 3.6-4.3%, and ash yield between 21.7-23.8% respectively. According to the results reported, Botswana coal has a high carbon content ranging from 56.4 to 60.7% and a relatively low total sulphur content ranging from 1.0 to 1.9%, indicating that the coal is classified as having low sulphur content as proposed by Chou. According to Chou, coal is typically referred to as having low sulphur (≤ 1 wt.% sulphur content), medium sulphur (≥ 1 to ≤ 3 wt.% sulphur content) and high sulphur coal (≥ 3 wt.% sulphur content) based on their sulphur content [124]. The oxygen content O_2 , was determined by subtracting the total percentage of C, H, N, S, carbonate, ash, and moisture content from one hundred per cent. The calorific value of the coal samples ranged from 21.8-22.6 MJ/kg, which indicates that heat was released during the complete pyrolysis process of the coal samples.

Table 3.1: Proximate and Ultimate analysis of Morupule coal samples [119]

	Raw Coal sample		
	WM1	S3/5	EM1
Proximate analysis (wt.%)			
Moisture ^[a]	3.7±0.2	4.3±0.1	3.6±0.1
Volatile matter ^[b]	22.4±0.3	22.9±0.2	23.8±0.3
Fixed Carbon ^[c]	50.0±0.4	51.2±0.2	48.2±0.2
Ash ^[d]	23.8±0.3	21.7±0.2	24.4±0.4
Ultimate analysis (wt.%)			
Carbon ^[e]	55.9±0.3	60.7±0.3	56.4±0.8
Hydrogen ^[e]	4.0±0.06	4.4±0.29	4.6±0.06
Nitrogen ^[e]	1.2±0.01	1.4±0.1	1.3±0.1
Oxygen (by difference)	8.1±0.2	8.9±0.2	8.0±0.6
Total sulphur ^[f]	1.6±0.1	1.0±0.1	1.9±0.2
Calorific value^[g]	21.8±0.07	22.6±0.1	22.3±0.2
(MJ/kg)			
Ao/c	0.14	0.15	0.14

[a] ASTM D3173-11, [125] [b] ASTM D3175-11, [126] [c] ASTM D5142, [127] [d] ASTM D3174-02, [128] [e] ASTM D5373-21, [129] [f] ASTM D4239, [130] [g] ASTM D5865-98a [131]

3.6 Thermogravimetric-Fourier Transform Infrared Spectrometry

A thermogravimetric analysis coupled to the Nicolet iS50 Thermo-Scientific Fourier transform infrared Spectrometer through a heated line was used to identify the different functional groups of coal. Experimental conditions were as follows: Resolution 4.0cm⁻¹, Scans 120, and the spectra was recorded in the wavenumber range of 400-4000 cm⁻¹.



Figure 3.2: Fourier transform Infrared Spectrometer Analyzer

3.7 Thermogravimetric-Mass Spectrometry

Experiments were performed using Mettler Toledo Thermogravimetric Analyzer (TGA/DSC3+) coupled with a quadrupole Hidden Analytical (HPR-20 EGA) Mass Spectrometry. The evolved gas from the thermogravimetry is coupled to the MS through a heated line with quartz capillary tube which is operated under a vacuum, where the MS detects the characteristic fragment ion intensity of the volatiles based on their mass to charge ratios. MS was set to detect gas products with a mass range of 1-300 a.m.u.



Figure 3.3: Thermogravimetric Analyzer coupled to the Mass Spectrometer

3.8 X-ray Fluorescence Spectrometry (XRF)

X-ray fluorescence spectroscopy or spectrometry is a method of elemental analysis, which assesses the presence and concentration of various elements by measuring the characteristic secondary radiation emitted from a sample that has been excited with an x-ray source. When compared to conventional chemical analysis techniques, the method is usually more rapid and precise. It is also efficient and reliable. The basis of XRF's elemental analysis is the hypothesis that when primary x-rays from a target tube strike a sample, the elements within it generate secondary (fluorescent) x-radiation (inversely related to the square of its atomic number) which is roughly proportional to the amount of that element present. Each element emits x-rays with a distinct wavelength and intensity when it is ignited. Long-wavelength, low-energy radiations are produced by low-atomic-number elements, whereas short-wavelength, high-energy radiations are emitted by high-atomic-number elements [132]. S8 Tiger Bruker X-ray Fluorescence (XRF) of model number 209955 was used to determine elemental composition of coal samples and fly ash.



Figure 3.4: X-Ray Fluorescence Spectrometer Analyser

3.9 X-ray Diffraction Spectrometry (XRD)

X-ray diffraction is a technique for analyzing the atomic or molecular structure of materials. It is non-destructive, and works most effectively with materials that are wholly, or part, crystalline. The technique is often known as x-ray powder diffraction because the material being analysed typically is finely ground down to a uniform state. It is used to inform about materials, such as the crystal orientations and defects. Determining the crystallinity of the elements depends critically on the diffraction angle [133]. The constructive interference of monochromatic x-rays with a crystalline substance is the basis of X-ray diffraction. A cathode ray tube generates the x-rays, which are then filtered to produce monochromatic radiation, focused by collimation, and directed at the sample. Atomic electrons in a crystal are made to vibrate when a monochromatic x-ray incidence occurs on it. With the same frequency as that of the frequency of the incident ray and are accelerated. Then, these accelerated electrons radiate in all directions at the same frequency as the incident x-rays. The emitted x-rays are in phase with one another if the incident radiation's wavelength is high in comparison to the crystal's dimensions.

Since the atomic dimension is almost equivalent to the x-ray wavelength the electrons' radiation is out of phase with one another. A diffraction pattern might occur from the constructive or destructive interactions between these radiations (i.e., maxima and minima) in certain directions [134]. It was used to characterize coal samples in terms of the minerals present and their relative abundance. Empyrean PANalytical X-ray Diffractometer of model number DY1740 was used to determine the mineral composition of the coal samples. The XRD was operated with Cu K α emission ($\lambda = 1.54105\text{\AA}$, 40 kV, 40 mA per sec). The analysis was carried out with a 2θ angle, and a scanning range used was $0^\circ - 100^\circ$ values. The phases were found using the X'Pert high score software, and the relative phase amounts (weight%) were estimated using the Rietveld method.



Figure 3.5: X-Ray Diffraction Spectrometer Analyser

CHAPTER 4

4 RESULTS AND DISCUSSION

In this chapter the results of thermal analysis are discussed in investigating the thermal behavior of coal, fly ash and plastic waste. Kinetic analysis of the pyrolytic and combustion behavior of coal, fly ash and plastic waste, structural and surface characterization of Botswana coal are covered.

4.1 Thermogravimetric Analysis

The results for the thermogravimetric (TG) and derivative thermogravimetric (DTG) for various heating rates are shown in Figure 4.1. The TG curves display the sample's percentage mass loss across the temperature range of 25–900 °C. The rate of mass loss depends on the temperature. All the peaks contained a strong peak which was attributed to the primary devolatilization process of coal between 350–550 °C, and the results are in good agreement with those found in the literature [135]. The primary devolatilization process proceeds fast with an increase in temperature up to 800 °C. It was observed that the greater the temperature, the bigger the mass loss because pyrolysis process is slow at low temperatures. The heating rate has no noticeable effect on the mass loss curve. Increasing the heating rate only changed the maximum temperature to a higher value, and the thermal profile of the decomposition remained unchanged. The first peak represents water release which occurred at temperature below 250 °C. The second region corresponded to the main decomposition stage of coal in the temperature range 300–700 °C. Major volatile matter occurred in this temperature range which formed gaseous products such as hydrogen, carbon dioxide, carbon monoxide and methane. This region is marked by a significant weight loss and complicated chemical reaction, such as release of tar and gaseous compounds and semi-char formation [136]. The last stage is observed above 700 °C where low decomposition rates occur.

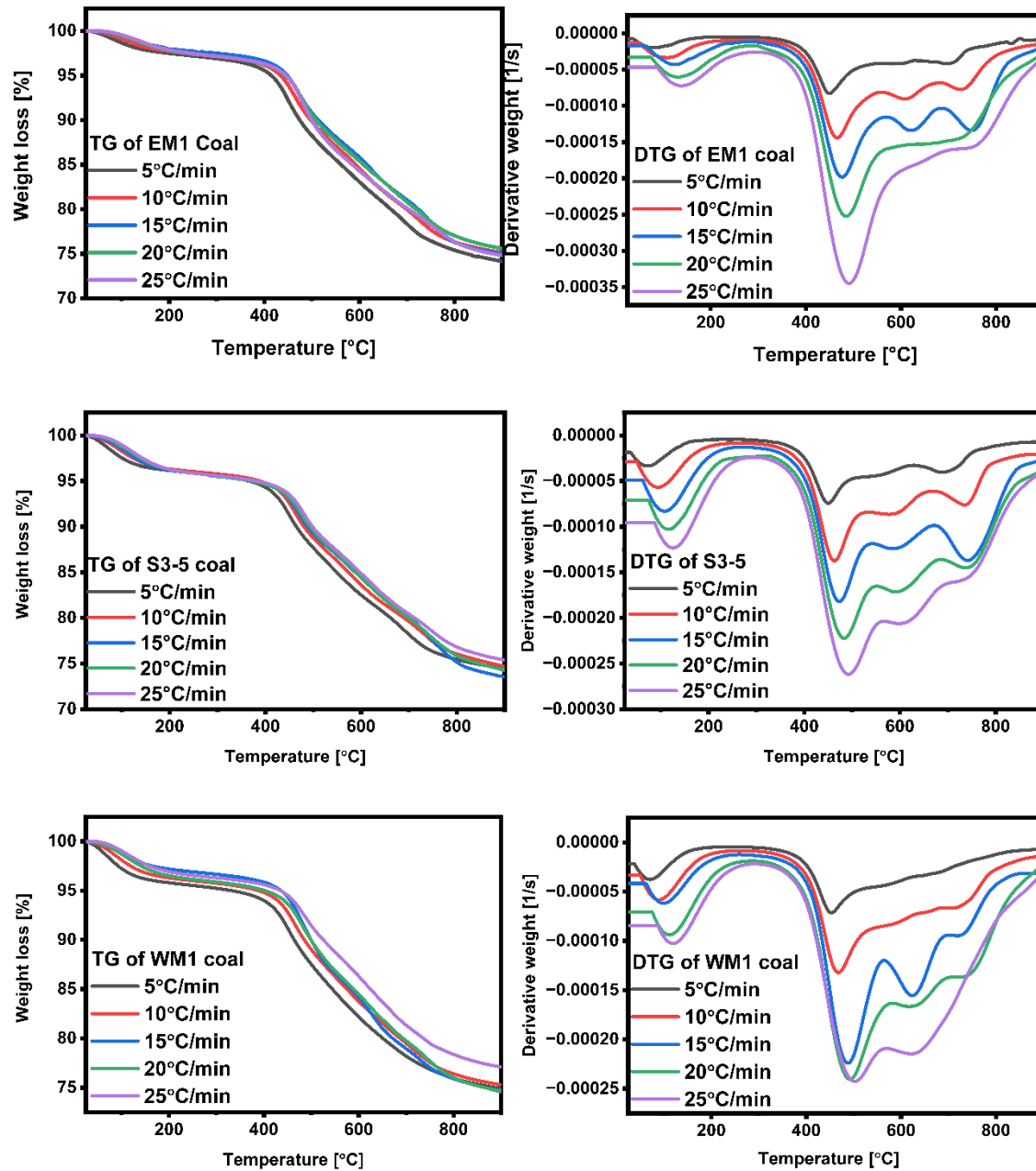


Figure 4.1: TG (left) & DTG (right) of the EM1, WM1 and S3-5 pyrolysis at five different heating rates under inert atmosphere

Table 4.1: Mass loss and maximum temperature of decomposition of EM1, WM1 and S3-5 coals under inert atmosphere

	EM1		WM1		S3-5	
$\beta/^{\circ}\text{Cmin}^{-1}$	Mass loss (%)	T_{max} ($^{\circ}\text{C}$)	Mass loss (%)	T_{max} ($^{\circ}\text{C}$)	Mass loss (%)	T_{max} ($^{\circ}\text{C}$)
5	25.7	448.3	24.8	452.9	25.1	450.7
10	24.8	465.7	24.5	467.9	25.1	463.3
15	24.9	475.9	25.1	487.4	26.2	473.7
20	24.1	485.0	24.8	490.8	25.2	482.8
25	24.8	489.6	22.5	503.4	24.2	492.0

Table 4.1 lists the TG properties of different heating rates of coals. The mass loss varied from 24.1 to 25.7% for EM1 coal and maximum reaction temperature rate (T_{max}) varied from 448.3 to 489.6 $^{\circ}\text{C}$ respectively, the mass loss of WM1 varied from 22.5 to 25.1% respectively, T_{max} varied from 452.9-503.4 $^{\circ}\text{C}$ and the mass loss of S3-5 was between 24.2 to 26.2% and the maximum decomposition temperature was between 450.7-492.0 $^{\circ}\text{C}$.

The TG and DTG thermograms of the decomposition of Morupule coal samples obtained at five different heating rates (5,10,15,20 and 25 $^{\circ}\text{C}$) under oxygen atmosphere are shown in Figures 4.2-4.4. The TG curves represent the percentage weight loss of the coal samples over the temperature range of 25-900 $^{\circ}\text{C}$. The rate of weight loss was temperature dependent, the higher the temperature, the greater the weight loss until all of the combustible mass is burned and the results agree with those of previous studies [137]. At around 350 $^{\circ}\text{C}$ the devolatilization process of WM1 coal (Figure 4.2) begins and rapidly increases the temperature up to 542 $^{\circ}\text{C}$ after which the weight of the samples decreases steadily and gradually as temperature rises. As the heating rate increased, the maximum decomposition temperature rate of WM1 was observed to shift towards higher temperature. The states of equilibrium attained by 5, 10, 15, 20 and 25 $^{\circ}\text{C}/\text{min}$ were 547, 590, 599, 624 and 636 $^{\circ}\text{C}$ respectively. The TGA results of WM1 coal revealed a relationship between percentage conversion and temperature.

For EM1 coal at all heating rates (Figure 4.3), the devolatilization process started at 370 °C and proceeded fast with increasing the temperature up to 477 °C for a heating rate of 5 °C/min, 515 °C for a heating rate of 10-20 °C/min, and 555 °C for a heating rate of 25 °C/min after which the weight of the samples dropped steadily with increase in temperature. At 5 °C/min the EM1 coal reached equilibrium at 550 °C much faster than the other heating rates. As the heating rate increased, the temperature of the maximum decomposition rate of EM1 coal changed towards higher temperature. The states of equilibrium attained by 5, 10, 15, 20 and 25 °C/min were 551, 593, 603, 609 and 653 °C respectively.

For S3-5 coal at all heating rates (Figure 4.4), the devolatilization process started at 380°C and proceeded fast with increasing the temperature between 478-566°C for all the heating rates after which the weight of the samples dropped steadily with increase in temperature. S3-5 coal at 5°C/min reached equilibrium at 561°C much faster than the other heating rates. As the heating rate increased, the maximum decomposition temperature rate of S3-5 coal changed towards higher temperature. The states of equilibrium attained by 5,10,15,20 and 25 °C/min were 561, 586, 605, 627 and 645 °C respectively. Figure 4.2 to 4.4 also shows the experimental DTG curves for the coal samples under oxygen atmosphere. The thermal decomposition reaction of EM1 coal in Figure 4.3 started at 340°C and continued until 561°C with a peak temperature at 474 °C for a heating rate of 5 °C/min, proceeded steadily until 605 °C with a peak temperature of 502 °C for 10 °C/min. EM1 coal's thermal decomposition reaction continued to 627 °C with a peak temperature of 507 °C for a heating rate of 15° C/min, continued to 642 °C with a peak temperature of 515 °C for 20 °C/min and lastly 701 °C with a peak temperature of 559 °C for a heating rate of 25 °C/min.

The one step thermal decomposition reaction of WM1 coal (Figure 4.2) began at 344 °C and continued until 562 °C with a peak temperature at 476 °C for a heating rate of 5 °C/min, proceeded steadily until 606 °C with a peak temperature of 502 °C for 10 °C/min, 637 °C with a peak temperature of 517 °C for 15 °C/min, 668 °C with a peak temperature of 530 °C for 20 °C/min and lastly 692 °C with a peak temperature of 541 °C for 25 °C/min.

The thermal decomposition reaction of S3-5 coal (Figure 4.4) started at 347 °C and continued until 565 °C with a peak temperature at 475 °C for a heating rate of 5 °C/min, proceeded steadily until 595 °C with a peak temperature of 490 °C for 10 °C/min, 630 °C with a peak temperature of 511

°C for 15 °C/min, 658 °C with a peak temperature of 534 °C for 20 °C/min and lastly 684 °C with a peak temperature of 555 °C for 25 °C/min. All the three coals showed an initial mass loss stage due to moisture evaporation primarily because of surface diffusion from oxygen gas between temperature ranges of 147-161 °C for all the heating rates. Mass losses in three stages occurred sequentially for WM1 and S3-5 coal compared to two mass losses in EM1 coal. Stages 2 and 3 mass losses are commonly caused by the burning of complex organic polymers, phenolic compounds, carboxyl groups, and organic carbon-containing compounds, whereas the final stage is predominantly caused by the combustion of the remaining carbonaceous material.

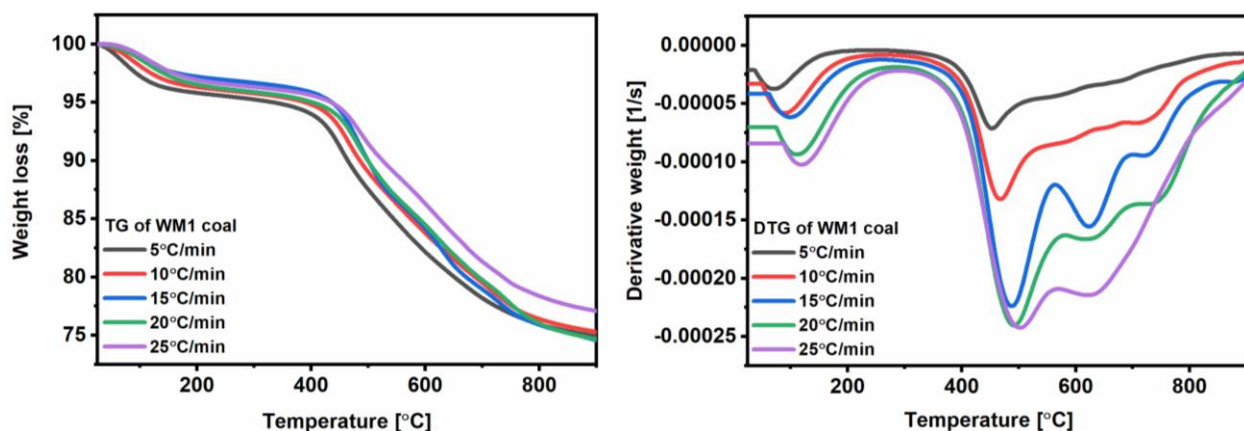


Figure 4.2: Thermal behavior and DTG curve of WM1 coal at various heating rates under air atmosphere

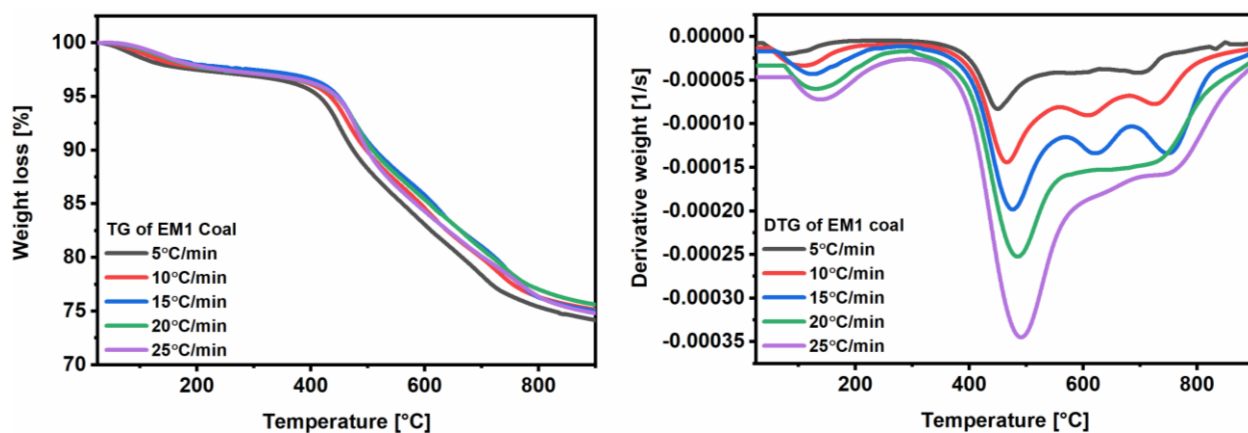


Figure 4.3: Thermal behavior (left) and DTG curve (right) of EM1 coal at various heating rates under air atmosphere

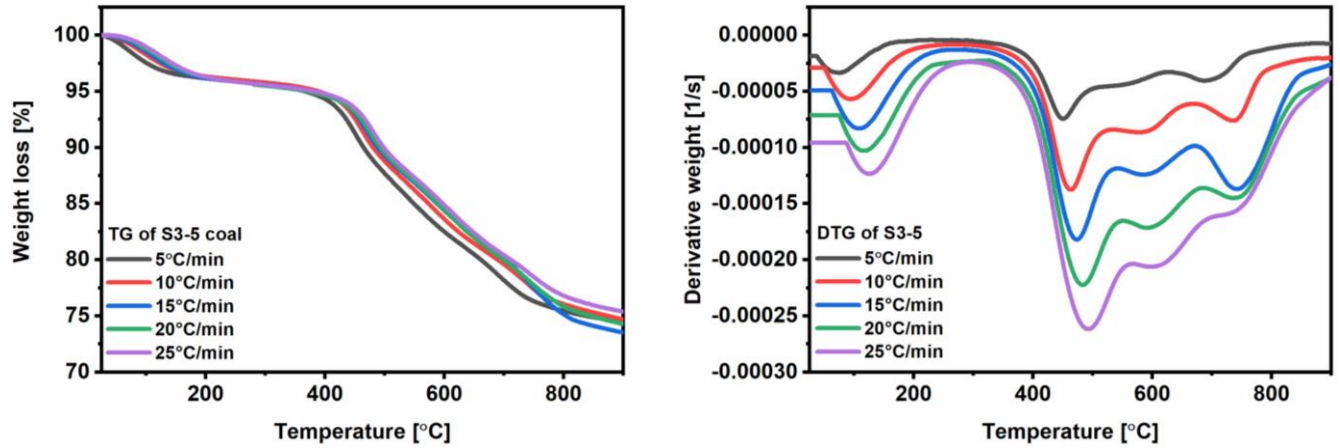


Figure 4.4: Thermal behavior (left) and DTG curve (right) of S3-5 coal at various heating rates under air atmosphere

Table 4.2: Mass loss and maximum temperature of decomposition of EM1, WM1 and S3-5 coals under air atmosphere

EM1			WM1		S3-5	
$\beta/^{\circ}\text{Cmin}^{-1}$	Mass loss (%)	$T_{\text{max}} (^{\circ}\text{C})$	Mass loss (%)	$T_{\text{max}} (^{\circ}\text{C})$	Mass loss (%)	$T_{\text{max}} (^{\circ}\text{C})$
5	25.9	448.6	25.0	453.0	25.6	448.9
10	24.9	466.5	24.7	468.7	25.3	462.9
15	24.9	475.3	25.2	488.4	26.4	472.7
20	24.3	484.0	25.4	490.9	25.6	482.6
25	25.1	491.0	22.9	501.9	24.5	492.4

Table 4.2 lists the TG properties of different heating rates of coals under air atmosphere. The mass loss varied from 24.3 to 25.9% for EM1 coal and maximum reaction temperature rate (T_{max}) varied from 448.6 to 491.0 °C respectively, the mass loss of WM1 varied from 22.9 to 25.4% respectively, T_{max} varied from 453.0-501.9 °C and the mass loss of S3-5 was between 24.5 to 26.4% and the maximum decomposition temperature was between 448.9-492.4 °C.

Figure 4.5 & 4.6 displays conversion graph as a function of temperature at various heating rates. The kinetic curves exhibited a typical sigmoidal shape. Since a high heating rate has a shorter degradation period at the exact same temperature and time setting, the temperature needed for the sample to attain the exact conversion is higher as the rate of heating increases. Figures 4.5 & 4.6 also represent the smoothed $\beta(d\alpha/dT)$ versus T curves of coal pyrolysis and coal combustion at different heating rates of 5, 10, 15, 20, and 25 °C/min⁻¹. It can be observed that the peak value of the derivative increases as the heating rate increases. The temperature at the peak derivative rises with the increasing heating rate. Conversion values between 0.1 to 0.9 were considered when calculating kinetic parameters. Table 4.3 & 4.4 provides details regarding the coal pyrolysis and coal combustion derivative conversion curve peaks.

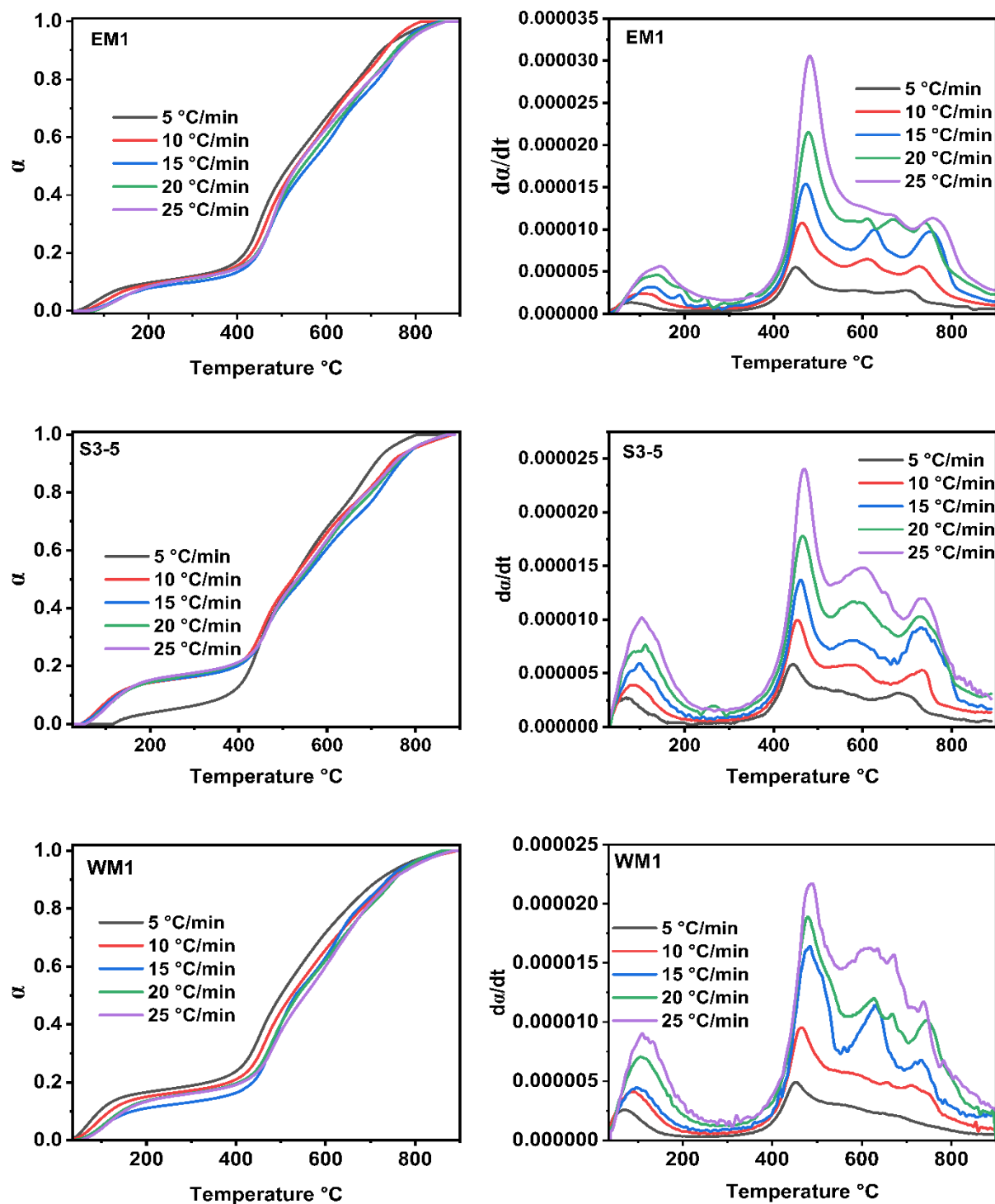


Figure 4.5: Conversion (left) and smoothed derivative conversion (right) curves for pyrolysis of EM1, S3-5 and WM1 coals at five various heating rates under inert atmosphere

Table 4.3: Peak characterization of derivative conversion curves for EM1, WM1 and S3-5 coal pyrolysis at various heating rates of 5, 10, 15, 20 and 25 °C/min-1

$$\beta \frac{d\alpha}{dT} |T|s^{-1}$$

$\beta/^{\circ}\text{Cmin}^{-1}$	EM1	WM1	S3-5
5	5.516×10^{-6}	4.881×10^{-6}	5.836×10^{-6}
10	1.077×10^{-5}	9.515×10^{-6}	9.906×10^{-6}
15	1.539×10^{-5}	1.633×10^{-5}	1.366×10^{-5}
20	2.145×10^{-5}	1.885×10^{-5}	1.773×10^{-5}
25	3.051×10^{-5}	2.175×10^{-5}	2.398×10^{-5}

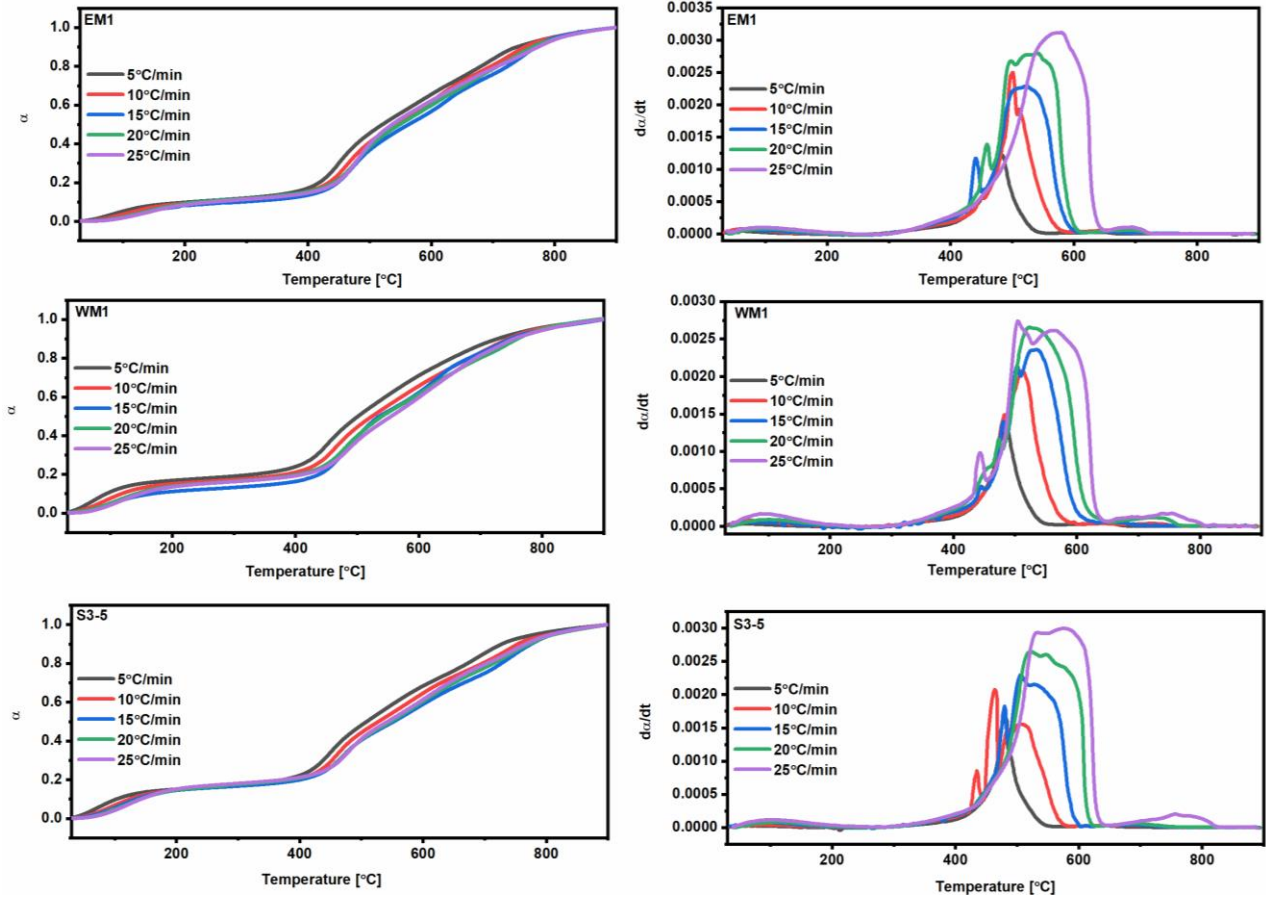


Figure 4.6: Conversion (left) and smoothed derivative conversion (right) curves for pyrolysis of EM1, S3-5 and WM1 coals at five various heating rates under air atmosphere

Table 4.4: Peak characterization of derivative conversion curves for EM1, WM1 and S3-5 coal combustion at various heating rates of 5, 10, 15, 20 and 25 °C/min-1

$$\beta \frac{d\alpha}{dT} |T|s^{-1}$$

$\beta/^{\circ}Cmin^{-1}$	EM1	WM1	S3-5
5	1.198×10^{-3}	1.371×10^{-3}	1.661×10^{-3}
10	2.476×10^{-3}	2.064×10^{-3}	2.080×10^{-3}
15	2.268×10^{-3}	2.359×10^{-3}	2.291×10^{-3}
20	2.774×10^{-3}	2.652×10^{-3}	2.653×10^{-3}
25	3.132×10^{-3}	2.745×10^{-3}	3.005×10^{-3}

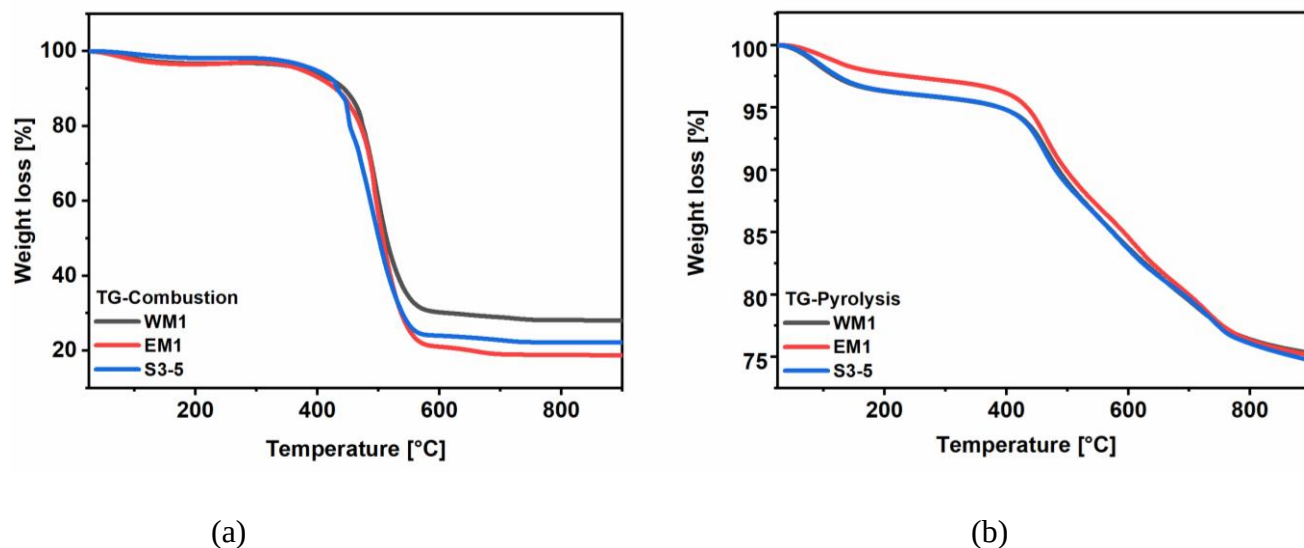


Figure 4.7: TGA analysis of coal in (a) Oxygen atmosphere, and (b) Argon atmosphere

It is logical to assume that two different oxidation processes have been observed in the oxygen atmosphere as shown in Figure 4.7 (a), the first one, most of the coal content oxidizes at low temperatures between 400 and 580 °C, perhaps because of the highly reactive aliphatic C-H concentration, and the second phase involves oxidizing the aromatic carbon at higher temperatures, between 590 and 700 °C. In the aliphatic oxidation process, weight loss ranges from 70 to 80 percent, while it is only 2 percent in the aromatic oxidation process. No combustion takes place during the TGA experiment when it is conducted in an inert environment; instead, pyrolysis, which releases volatile substances, takes place as shown in Figure 4.7 (b). The results obtained are in agreement with those of previous studies [138]. In comparison to coal burned in an inert environment (25%), all three types of coal burned under an oxygen atmosphere had a considerably greater volatile content (70–80%). Under inert atmospheres, below 200°C, moisture evaporation is seen, however under oxygen atmospheres, there is barely any observable water loss as most of the moisture in the coal was removed after drying it for 24 hours at 80°C in an oven.

4.1.1 Peak separation analysis of overlapping peaks by bi-Gaussian fitting

Bi-Gaussian function is used to separate the thermogravimetric curve at five various heating rates of 5, 10, 15, 20, and 25 °C/min in order to determine whether the pyrolysis process of Morupule coal of Botswana is dominated by a three-stage reaction or a four-stage reaction.

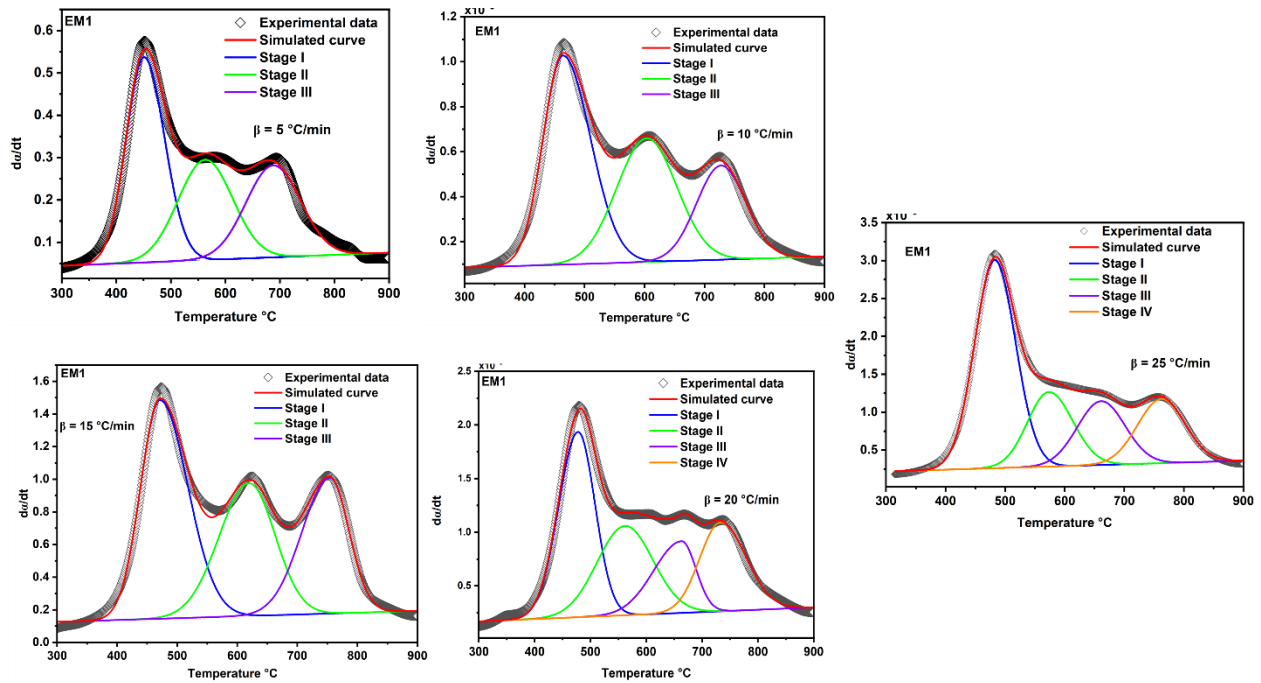


Figure 4.8: Deconvolution of reaction rate of EM1 coal at different rates (5, 10, 15, 20, 25 °C/min)

Table 4.5: Peak temperature corresponding to local maximum at various heating rates for EM1 coal

$\beta(^{\circ}\text{C}/\text{min})$	Stage I		Stage II		Stage III		Stage IV	
	T($^{\circ}\text{C}$)	da/dt	T($^{\circ}\text{C}$)	da/dt	T($^{\circ}\text{C}$)	da/dt	T($^{\circ}\text{C}$)	da/dt
5	454.47	4.27E-04	562.99	2.96E-04	681.54	2.72E-04	-	-
10	473.99	9.17E-04	603.48	6.89E-04	727.45	4.30E-04	-	-
15	471.03	0.0013	619.64	9.49E-04	742.29	8.18E-04	-	-
20	474.12	0.0014	561.75	0.0010	643.78	6.34E-04	739.32	8.58E-04
25	483.26	0.0023	576.56	9.33E-04	661.14	8.43E-04	761.71	8.43E-04

In many cases, the deconvolution method is utilized to enhance signal resolution and overcome overlapping peaks using a fitting algorithm that is mathematically appropriate. The simulation curve's accuracy can be improved theoretically by incorporating more pseudo-components.

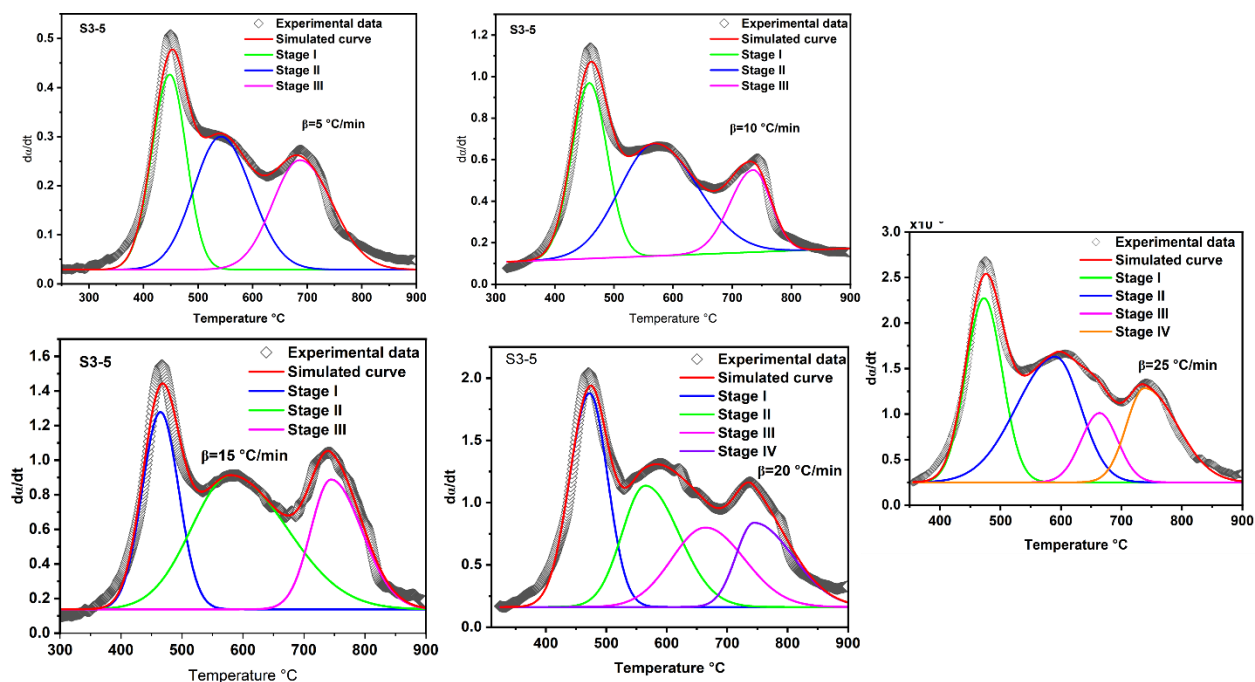


Figure 4.9: Deconvolution of reaction rate of S3-5 coal at different rates (5, 10, 15, 20, 25 °C/min)

Table 4.6: Peak temperature corresponding to local maximum at various heating rates of S3-5 coal

β (°C/min)	Stage I		Stage II		Stage III		Stage IV	
	T(°C)	da/dt	T(°C)	da/dt	T(°C)	da/dt	T(°C)	da/dt
5	445.88	3.14E-04	545.94	3.57E-04	693.80	3.05E-4	-	-
10	458.36	6.35E-04	578.85	8.94E-04	727.91	3.43E-04	-	-
15	464.74	8.57E-04	602.04	0.0015	758.18	7.89E-04	-	-
20	469.96	0.0013	578.05	0.0011	670.87	9.60E-04	771.54	7.97E-04
25	472.78	0.0015	572.68	0.0018	663.34	5.79E-04	757.56	0.0010

The thermal degradation of the three types of coal found in Morupule occurs in four stages (depending on the rate). These stages include primary pyrolysis (stage I), secondary depolymerization (stage II), and secondary repolymerization (stage III). Another stage (stage IV) is observed at high rates, which may involve depolymerization.

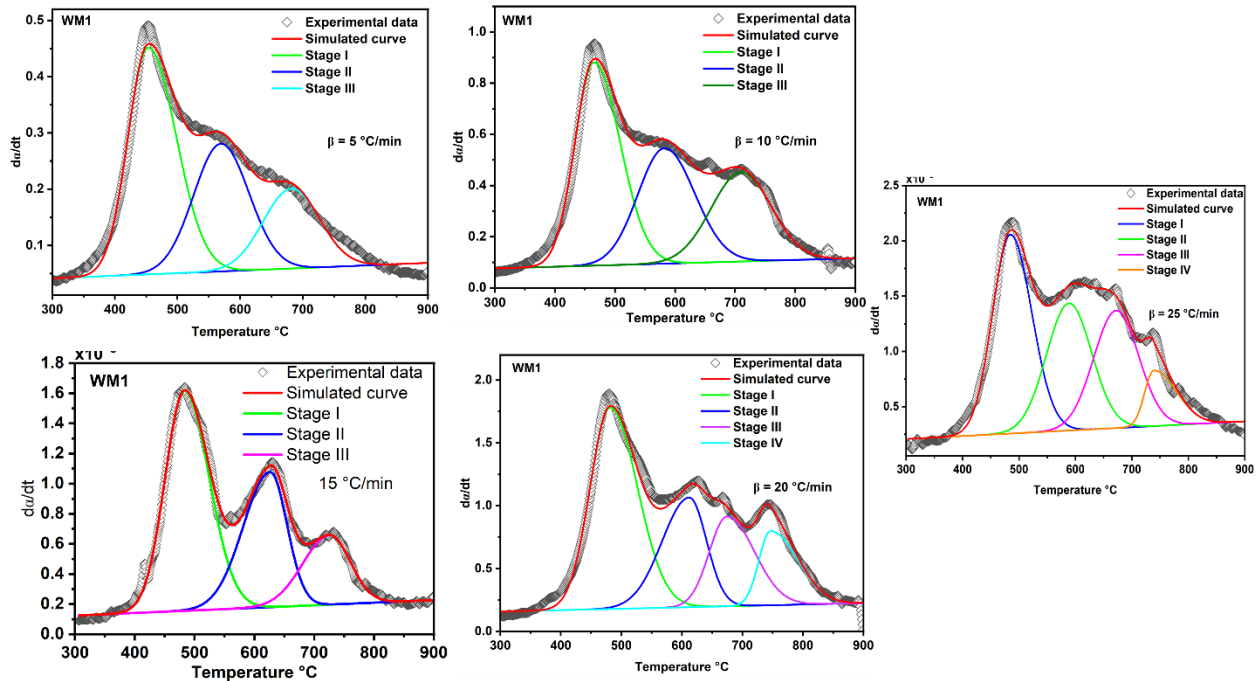


Figure 4.10: Deconvolution of reaction rate of WM1 coal at different rates (5, 10, 15, 20, 25 °C/min).

The process of coal pyrolysis can be divided into three distinct phases. The first phase, which occurs at room temperature (RT) and rises to the active thermolysis temperature (T) of 300 °C, is referred to as the dry degassing phase. During this phase, the shape of the coal remains largely unchanged, but dehydration occurs below 120 °C. The release of gases such as CH₄, CO₂, and N₂ is completed at around 200 °C.

The second phase takes place at approximately 600 °C and is primarily responsible for depolymerization and decomposition. Large amounts of volatile substances, including gas and tar, are generated, and released during this phase. Tar is discharged at its maximum quantity at around 450 °C, while gas is released at 450-600 °C. The gas has a greater calorific value and is mostly made up of CO, CO₂, and hydrocarbons. Tar is composed of fused ring aromatic and complex aromatic compounds. Bitumite starts to soften at around 350 °C, then melts and sticks together, and finally forms semi-coke at 600 °C. At 600-1000 °C, semi-coke is transformed into coke through polycondensation. In the secondary degassing phase, only a minimal amount of tar is emitted, and the majority of the volatiles are gases, including H₂ and some CH₄. The conversion

of semi-coke to coke releases a large amount of gas, causing the density of coke to increase and the volume to decrease, resulting in the formation of numerous cracks and fragments.

Table 4.7: Peak temperature corresponding to local maximum at various heating rates of WM1 coal

$\beta(^{\circ}\text{C}/\text{min})$	Stage I		Stage II		Stage III		Stage IV	
	T($^{\circ}\text{C}$)	$d\alpha/dt$	T($^{\circ}\text{C}$)	$d\alpha/dt$	T($^{\circ}\text{C}$)	$d\alpha/dt$	T($^{\circ}\text{C}$)	$d\alpha/dt$
5	463.10	3.89E-04	570.33	2.51E-04	681.81	1.60E-04	-	-
10	474.41	7.47E-04	586.83	5.33E-04	709.95	4.36E-04	-	-
15	489.91	0.0013	612.85	8.22E-04	717.30	4.59E-04	-	-
20	490.83	0.0015	598.93	8.02E-04	686.94	6.66E-04	766.85	4.74E-04
25	489.38	0.0015	588.56	0.0011	671.98	0.0010	757.63	3.55E-04

Table 4.8 below displays the RSS at various heating rates of 5, 10, 15, 20, 25 $^{\circ}\text{C}/\text{min}$ and the correlation coefficient of the three coals (EM1, S3-5, WM1), which confirms that the simulated curve aligns well with the experimental data. It is noteworthy that the thermal degradation temperature range for each reaction stage (I, II, III, IV) is approximately 450-550 $^{\circ}\text{C}$, 570-650 $^{\circ}\text{C}$, and 650-950 $^{\circ}\text{C}$, respectively.

Table 4.8: The RSS of the heating rate and R2 correlation coefficient

$\beta(^{\circ}\text{C}/\text{min})$	EM1		S3-5		WM1	
	RSS	R^2	RSS	R^2	RSS	R^2
5	8.89E-12	0.9951	1.68E-11	0.9861	1.37E-11	0.9893
10	2.40E-11	0.9964	4.74E-11	0.9895	3.96E-11	0.9916
15	5.86E-11	0.9948	1.10E-10	0.9896	6.12E-11	0.9949
20	6.28E-11	0.9974	2.05E-10	0.9857	1.57E-10	0.9914
25	5.34E-11	0.9985	2.45E-10	0.9889	2.05E-10	0.9915

4.1.2 Thermal behavior of coal and plastic

Figure 4.11 depicts the DTG curves of plastic waste, coal, and the mixture at a 5 wt% plastic addition rate. HDPE plastic mass loss happened in one step and had the smallest decomposition

temperature range. For both EM1 and WM1 coal, the evolution of volatiles from the plastic in the mixture toward a higher temperature is shown at a ratio of 95:5 (coal: plastic). This suggests that there is some kind of chemical interaction going on when plastic and coal are being pyrolyzed together at high temperatures. This agrees with previous studies [139]. Hydrogen transfer reactions are among the chemical processes that might happen, and if the additive is a hydrogen acceptor, they can cause fluidity to decrease [140]. A temperature lower than that of the plastic waste is where thermal degradation of coal begins, this is shown in Figure 4.12.

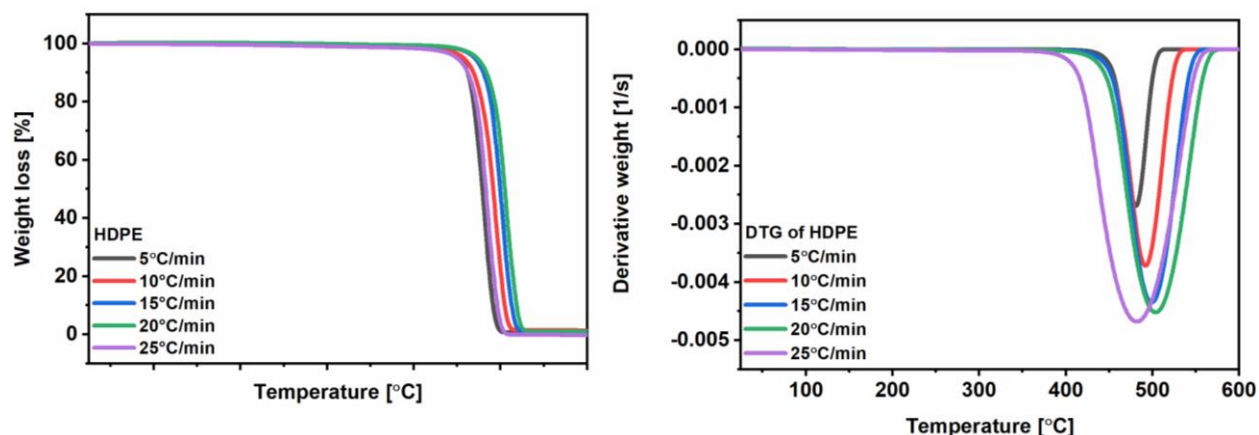


Figure 4.11: TG (left) and DTG (right) of the plastic at heating rates of 5, 10, 15, 20 and 25 °C/min under inert atmosphere

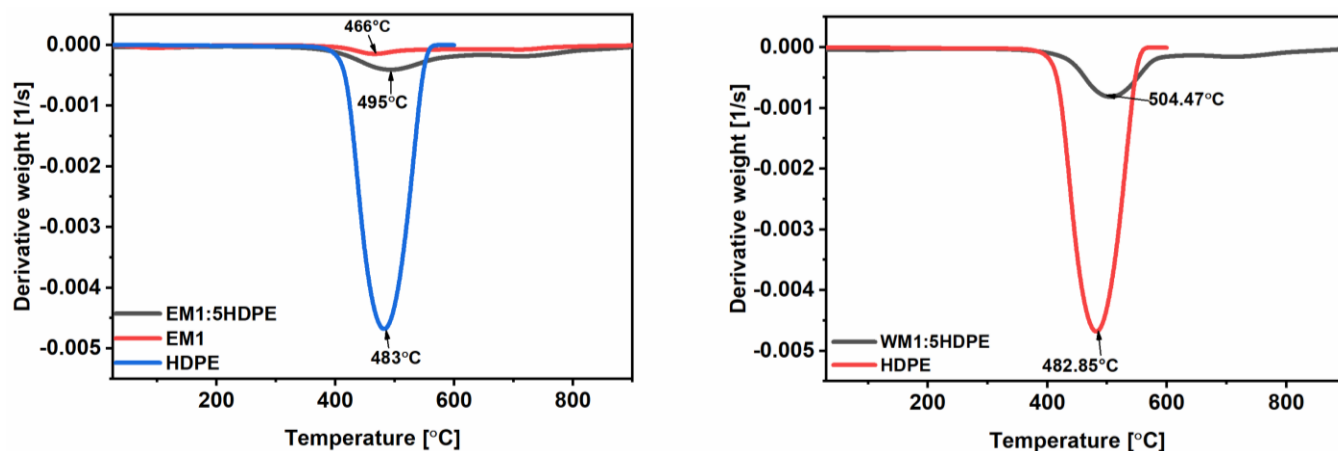


Figure 4.12: DTG profiles of the EM1, WM1 coal, plastic, and the mixture at an addition rate of 5 wt%

Table 4.9: Thermogravimetric properties of HDPE plastic

Heating rate (°C/min)	Mass loss (%)	T _{max} (°C)
5	99.4	480.2
10	98.7	492.2
15	99.3	500.5
20	99.2	503.5
25	99.0	483

Table 4.10: Thermogravimetric data of coal/plastic samples at 25 °C

	EM1	EM1:5HDPE	WM1:5HDPE
T _i	391	384	396
T _f	858	810	832
T _f -T _i	467	426	436
T _{max}	466	495	504.5

Table 4.9 shows the maximum temperature at which volatile matter is released (T_{max}, according to the DTG curves it occurred from temperature range of 480.2 to 503.5 °C at various heating rates, and the mass loss weight of HDPE plastic was between 98.7-99.4%

According to Figure 4.13 (b) before 400 °C, all of the mixtures of plastic and coal had no possibility of interacting with the coal since the plastic did not start decomposing at that temperature. The derivative weight of all mixtures as shown in Figure 4.13 (b) significantly rise in the negative direction up to 495 °C before beginning to decline. At around 500 °C, it achieves a value of (-0.0005 to -0.0035) for different mixtures. As the temperature increases, the plastic mixtures begin to decompose, resulting in a significant decrease in the derivative weight value. This was observed when coal and plastic were present in 90:10 and 33.3:66.7 proportions at a

value of (-0.00275 to -0.0035) respectively. The derivative weight becomes stable after 550 °C. The highest interaction during co-pyrolysis occurred at 495 °C, where coal and plastic were present in a 95:5 ratio. The derivative weight at this temperature was around (-0.00027). It can be attributed that during co-pyrolysis at high temperatures, 95:5, 90:10, and 33.3:66.7 have shown significant synergistic effects between coal and plastic.

The mechanism underlying the synergistic effect of coal and plastic during co-pyrolysis is unclear. A radical chain process, which includes the stages of radical initiation, chain propagation, and radical termination, is stated in the literature as the cause of thermal degradation of polyolefins. In a number of studies, the mechanisms of this process and the composition of the produced products were investigated [141]- [142].

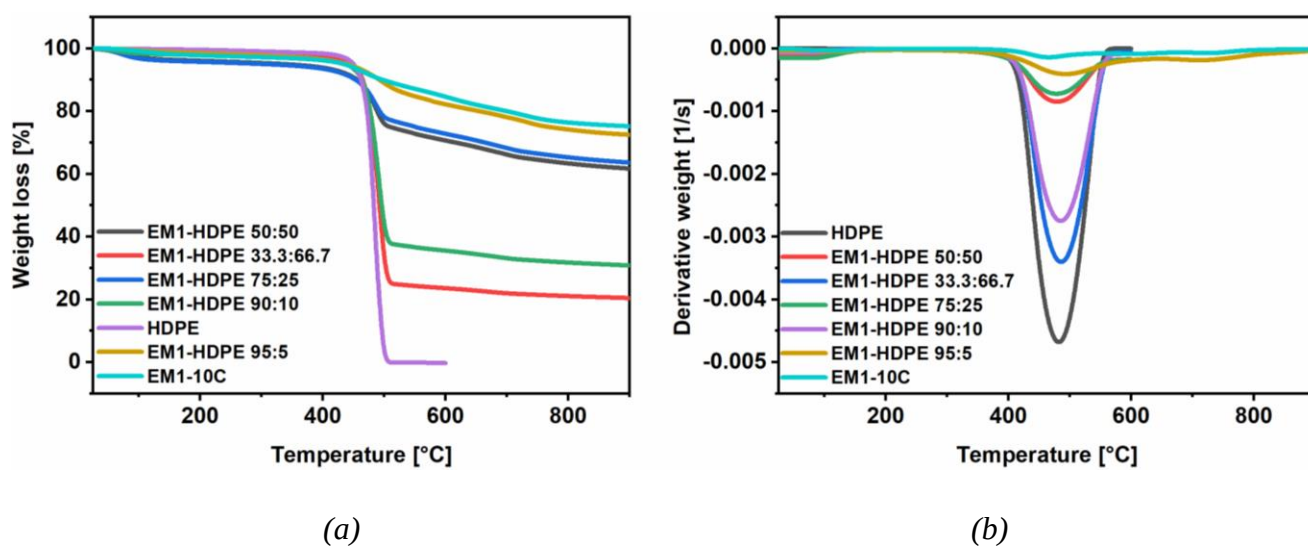


Figure 4.13: TG (left) and DTG (right) of various EM1 blends

4.1.3 Thermal behavior of fly ash

The two-atmosphere thermal analysis was first carried out in the inert atmosphere at temperatures between 25 and 950 °C, then transitioned to oxygen at temperatures between 150 and 950 °C using various heating rates of 5, 10, 15, 20, and 25 °C/min. As shown in Figure 4.14, peaks on the derivative curve reflect the temperatures at which specific reactions and weight loss occurs. From the derivative curve, peak temperatures in the non-oxidizing atmosphere were found to be 227.88 °C, 364.76 °C, and 459.24 °C and 757.24 °C in oxygen as oxidizing atmosphere for a rate of heating of 10 °C/min. It was found that the weight loss caused by the oxidation of carbon in oxygen was 4.344%.

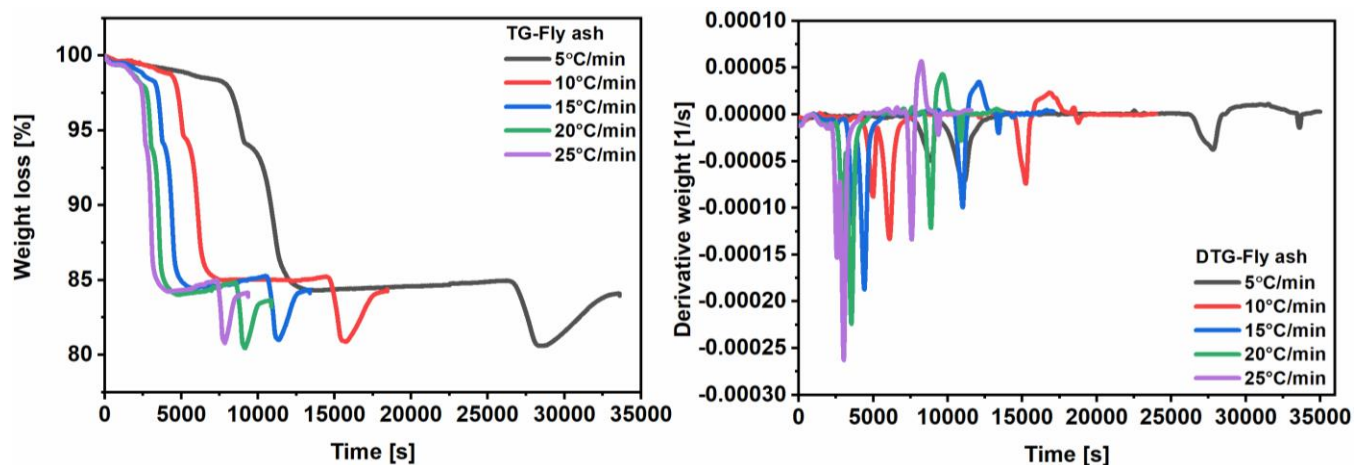


Figure 4.14: TG (left) and DTG (right) of fly ash at heating rates of 5, 10, 15, 20 and 25 °C/min

Table 4.11: Thermogravimetric properties of fly ash

Heating rate (°C/min)	Mass loss (%)	T _{max} (°C)
5	19.1	480.2
10	18.8	492.2
15	18.6	500.5
20	19.2	503.5
25	18.8	481.6

As shown in Table 4.11 the mass loss of fly ash varied from 18.6-19.2% and the T_{max} was between 480.2 to 503°C respectively.

4.2 Evolved Gas Analysis

Figure 4.15 illustrates graph measurements of combined mass spectrum (gas release) and thermogravimetry results to the corresponding temperatures of the three coal samples. The evolved gaseous products were dominated by light volatiles like H_2 ($m/z = 2$) and H_2O ($m/z = 18$), carbon oxides like CO ($m/z = 29$) and CO_2 ($m/z = 44$), and aliphatic hydrocarbons like CH_4 ($m/z = 15$). Other pyrolysis and combustion products could not be analysed (i.e char and pyrolysis oil). The main gases emitted during the pyrolysis process had molecular weight ranging from 2 to 64 and were at temperatures between 30 and 900 °C. A significant portion of hydrogen is emitted between 200 and 500 °C. The generated hydrogen gas is due to the greater amount of volatile substances in the coal sample. Similar kind of results were reported by pyrolysis of HSW coal (Western China) at a heating rate of 5, 10, 15, and 20 °C/min⁻¹ using TG-MS technique by Bai *et al.* [143] and using MS & FTIR studies by authors [144]- [145]. Figure 4.16 shows the mass spectrum of the gases evolved during combustion. Carbonization starts at around 450 °C, releasing carbon dioxide, carbon monoxide, and water. The combustion process of the three kinds of coals majorly produces CO_2 and H_2O gases.

The mass loss during TGA in inert conditions is typically lower than in oxidative conditions. Inert conditions refer to an environment where no oxygen is present, usually achieved by using an inert gas such as nitrogen, argon, or helium. The absence of oxygen restricts the oxidation reactions and subsequent carbon dioxide formation. During TGA on coal under inert conditions, the mass loss primarily occurs due to the release of volatile matter and moisture. The coal inherently contains a certain amount of moisture which evaporates as the temperature increases. Similarly, the volatile matter, including hydrocarbons, gases, and some organic compounds, are also driven off as the coal is heated. Without oxygen available, there is no combustion or oxidation occurring, resulting in a lower mass loss compared to oxidative conditions.

TGA under oxidative conditions, on the other hand, involves the presence of oxygen which facilitates the combustion or oxidation reactions of the coal. As a result, not only do the moisture and volatile matter release, but the carbonaceous components of the coal also undergo oxidation, leading to a greater mass loss. The carbon in the coal reacts with oxygen to form carbon dioxide (CO_2) and other gaseous by-products. This combustion process significantly contributes to the higher mass loss observed in oxidative conditions compared to inert conditions. Therefore, the

mass loss in inert conditions during TGA on coal is lower than in oxidative conditions due to the absence of oxygen. Inert conditions provide a suitable environment to study the thermal stability of the coal and the behaviour of its components without any oxidative reactions taking place. This information is valuable for understanding the properties of coal and its potential applications in various industrial processes.

The high mass loss observed during the Thermogravimetric Analysis (TGA) of EM1 coal can be attributed to its proximate composition. Proximate analysis is a standard method used for determining the composition and properties of coal. It involves the measurement of moisture, volatile matter, fixed carbon, and ash content parameters. EM1 coal, in particular, has a higher proportion of volatile matter, which is composed of hydrocarbons that can be vaporized at relatively low temperatures. Thus, when the coal is subjected to heating during TGA, the volatile matter is released as gases, resulting in a further mass loss. Consequently, the high mass loss observed in EM1 coal during TGA can be attributed to its higher volatile matter content.

Coal is a commonly used energy source containing varying amounts of sulfur, typically present in the form of organic sulfur compounds or pyritic sulfur. The pyrolysis or partial oxidation of coal can lead to the release of these sulfur compounds, which can react with oxygen present in the system, resulting in the formation of hydrogen sulfide (H_2S). Sulfur can exist in various forms, such as sulfides, sulfates, or organic sulfur compounds like thiols or sulfides. When these sulfur compounds come into contact with oxygen, they undergo oxidation reactions, which can involve the decomposition of larger sulfur compounds into smaller ones, ultimately leading to the formation of H_2S . Moreover, heat and moisture in an oxidative environment can further facilitate the conversion of sulfur compounds into H_2S . Higher temperatures can provide the necessary energy for chemical reactions, while moisture can catalyse these reactions. The exact mechanisms underlying the formation of H_2S from different types of coal are complex and can vary depending on the specific conditions and composition of the coal. However, the presence of sulfur compounds and the availability of oxygen and moisture are key factors that contribute to the generation of H_2S in an oxidative environment during the pyrolysis or oxidation of coal. Overall, understanding these processes is important for safely handling and utilising coal as an energy source.

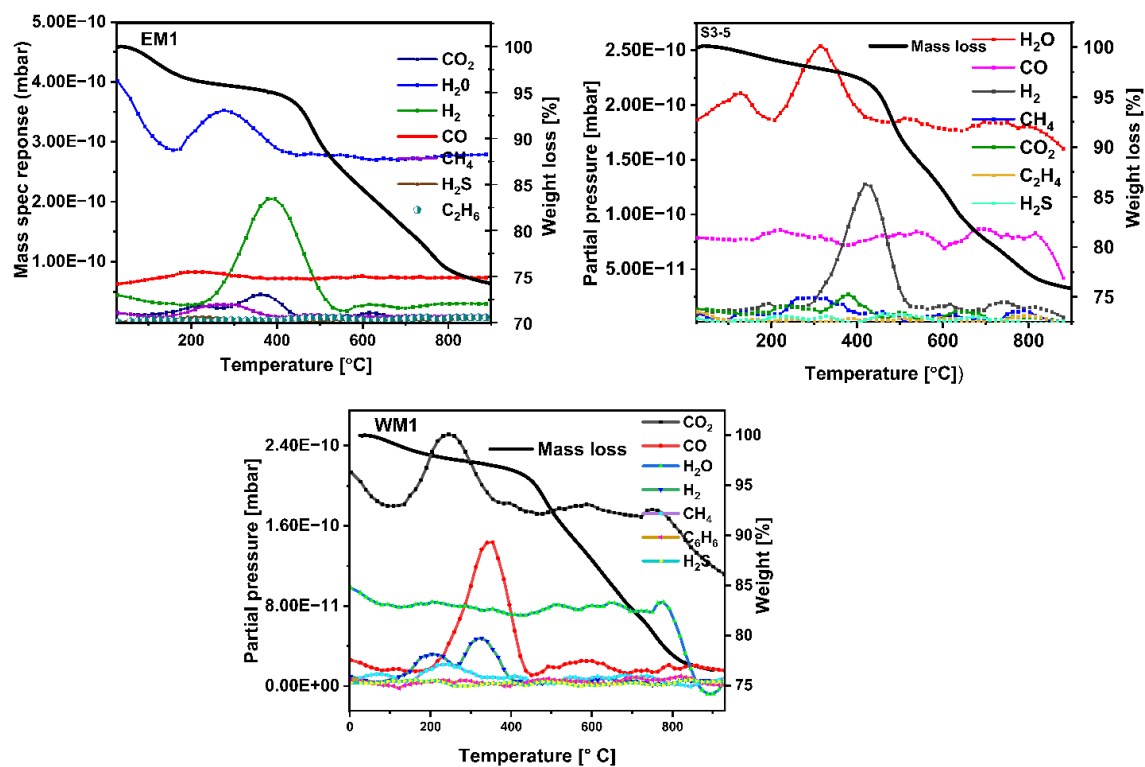


Figure 4.15: Mass spectrum of gas release of EM1, WM1 and S3-5 coal under inert atmosphere

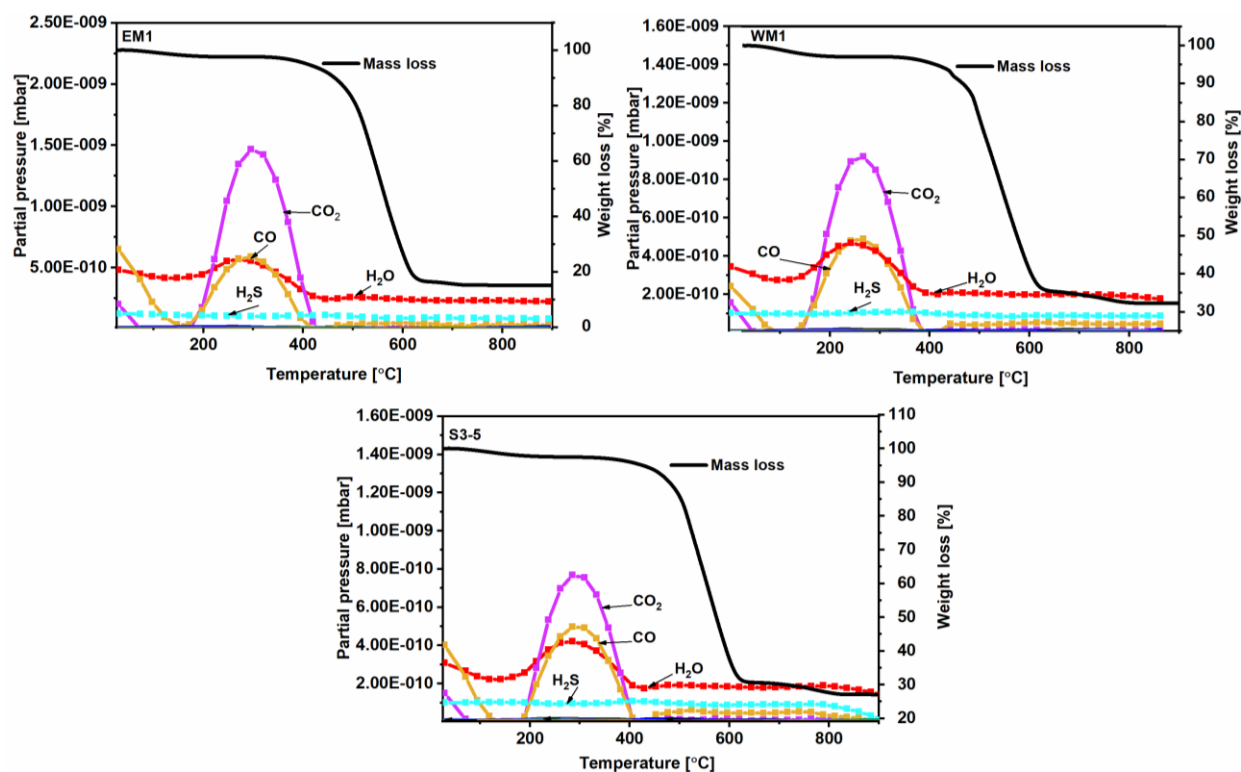


Figure 4.16: Mass spectrum of gas release of EM1, WM1 and S3-5 coal under oxygen atmosphere

The variation of H_2 content between the three kinds of coals (EM1, WM, S3-5) during pyrolysis is small. Hydrogen content from EM1 started to be generated around 250 °C, followed by WM1 at 280 °C and lastly S3-5 coal at 340 °C. WM1 and S3-5 reached their maximum value at about 700 °C. The value of S3-5 hydrogen was lower than that of other coals. The relative strength of H_2O followed by H_2 are higher than that of other three gas products as shown in Figure 4.17 (a and b). The H_2O temperature peak depicts the moisture of the samples. The peaks had a similar shape and appeared at a range of temperature 150-350 °C. The relative intensity of CO reached its first peak at around 160-210 °C and the second peak at around 500 °C. The temperature corresponding to the relative intensity of CO_2 is approximately between 300-400 °C for the second peak. Figure 4.17 (e) shows that EM1, WM1 and S3-5 coal start to generate CH_4 at around 250-420 °C.

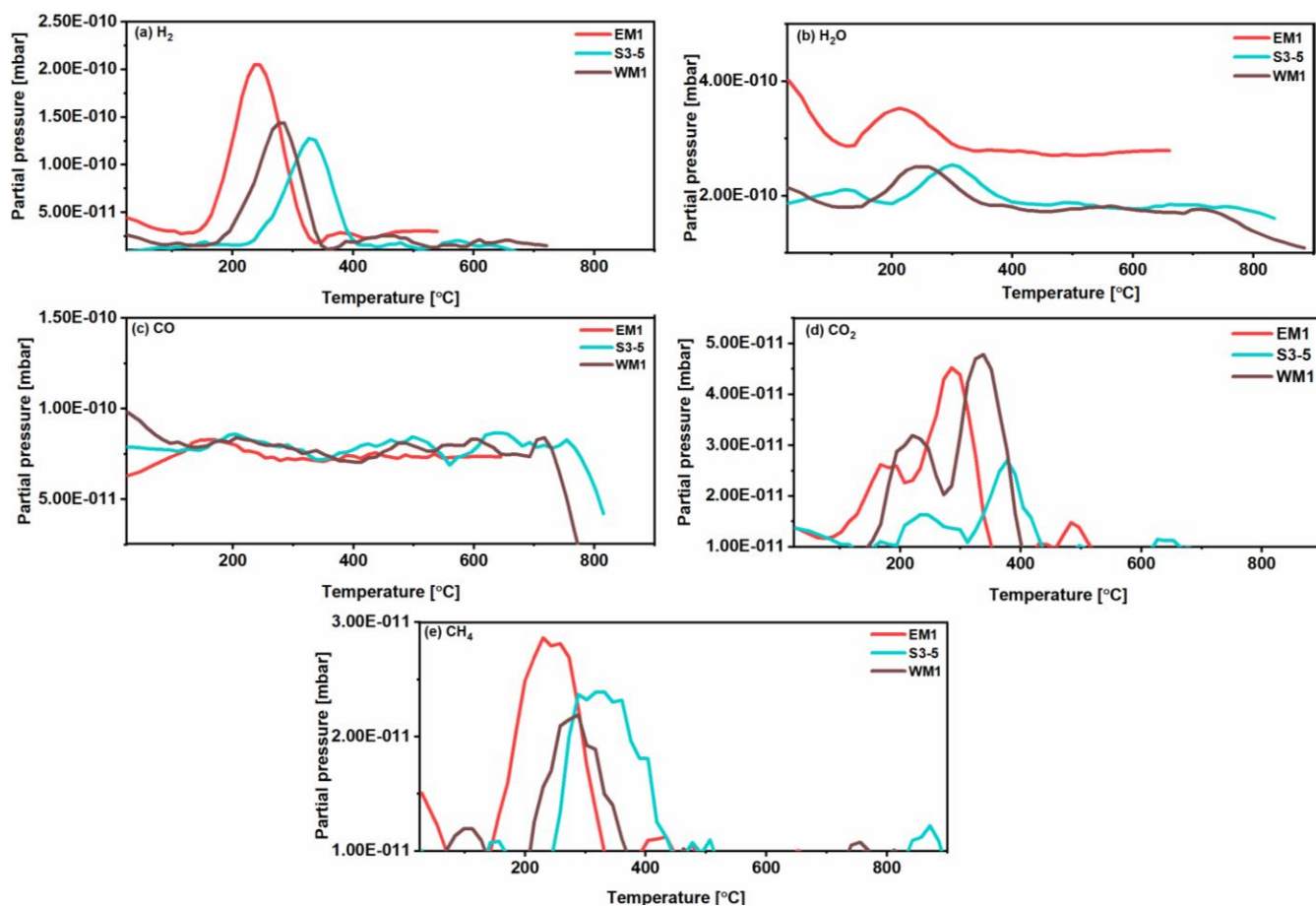


Figure 4.17: Evolution of a) H_2 , b) H_2O , c) CO , d) CO_2 and e) CH_4 during EM1, WM1 and S3-5 pyrolysis

The evolution of the hydrogen (m/z 2), water (m/z 18) and carbon monoxide (m/z 29) are the gaseous products produced in greater amount while CO_2 and CH_4 are produced in less amounts as displayed in Figure 4.18. Above $350^\circ C$ hydrogen is the most abundant product during the pyrolysis of the three kinds of coal and its mixture with the HDPE plastic. Greater amounts of hydrogen and carbon monoxide can be used to produce synthesis gas (syngas). Hydrogen results from the condensation of aromatic structures or the decomposition of heterocyclic compounds [146]. During the process of pyrolysis, volatile matter present in coal is released in the form of gas at low temperatures. This process is commonly referred to as devolatilization. The volatile matter comprises a variety of organic compounds, including hydrocarbons. As the temperature increases, these organic compounds break down, releasing gases such as methane (CH_4), ethane (C_2H_6), and other

hydrocarbons. In the devolatilization process, water vapor in the form of H_2O is also released. This water is generated from the moisture content present in the coal, which gets liberated as steam when heated. This is why even at high temperatures; the formation of H_2O is consistently observed during pyrolysis.

On the other hand, the formation of H_2 gas is limited to lower temperatures during pyrolysis. This gas is produced through hydrogenation or reduction reactions. The coal structure at lower temperatures has a higher concentration of active functional groups, such as carbonyl or carboxyl groups. Reacting with hydrogen (H_2) can reduce these functional groups to form H_2O .

Additionally, the release of H_2 gas can also occur through carbon-carbon bond cleavage processes at relatively low temperatures. However, as the temperature increases, the likelihood of carbon-carbon bond cleavage decreases, and the formation of H_2 becomes less prominent. In summary, coal pyrolysis consistently produces water (H_2O) due to moisture release at high temperatures. Meanwhile, hydrogen gas (H_2) formation mainly occurs at lower temperatures through hydrogenation reactions and carbon-carbon bond cleavage processes.

According to Figure 4.19, the evolution of the water (m/z 18) and carbon dioxide (m/z 44) are the gaseous products produced in greater amount during the combustion of the coal blends.

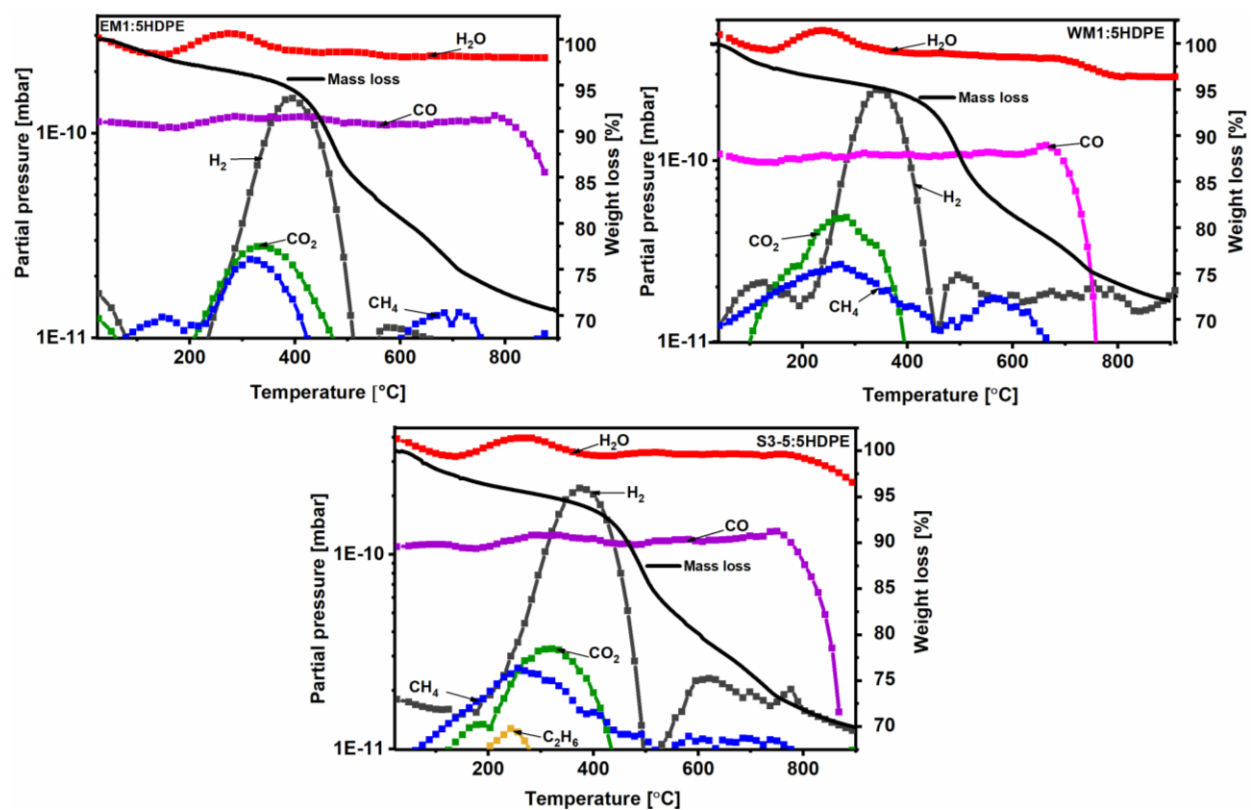


Figure 4.18: Mass spectrum gas release of pyrolysis of EM1, WM1 and S3-5 coal mixtures with the HDPE plastic

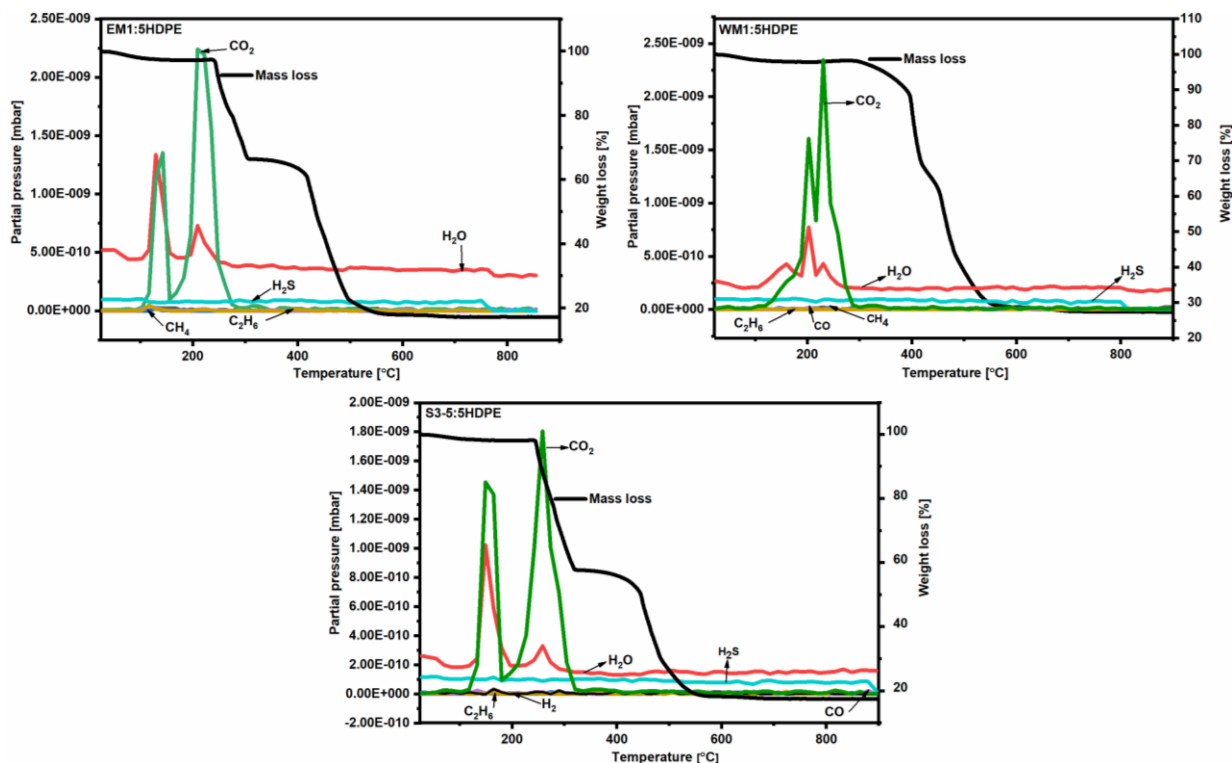


Figure 4.19: Mass spectrum gas release of combustion of EM1, WM1, S3-5 coal mixtures with the HDPE plastic

Following a thorough examination of the MS data, we concluded that, for the fly ash sample under investigation, only the spectrums for water H_2O (MW = 18), CO (MW = 28) and CO_2 (MW = 34) are observed at substantial intensities above the background under both pyrolysis and combustion conditions. The results of TGA-MS test are presented in Figure 4.20 and 4.21 for the fly ash heated to $T_{\text{max}} = 900^\circ\text{C}$.

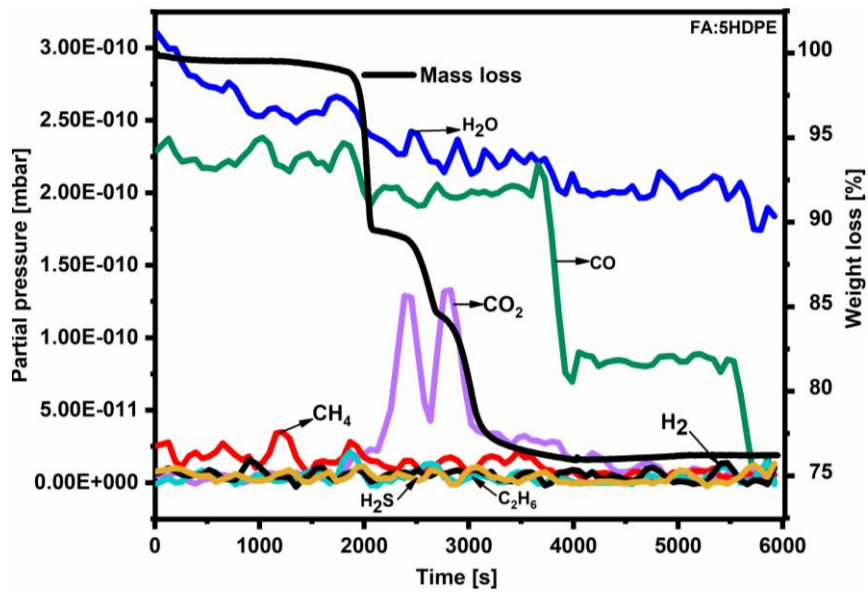


Figure 4.20: Mass spectrum gas release of pyrolysis of fly ash

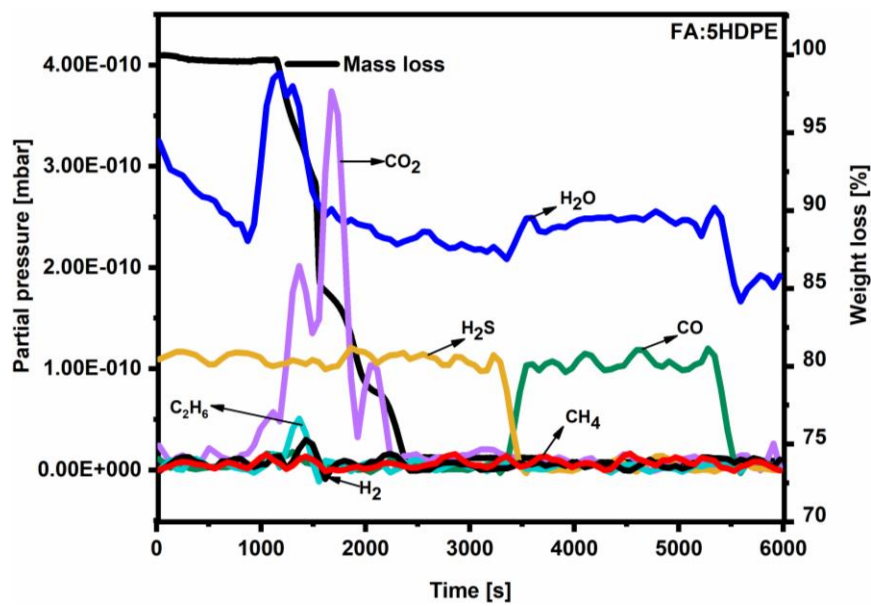


Figure 4.21: Mass spectrum gas release of combustion of fly ash

4.3 Fourier Transform Infrared Results

Figure 4.22 shows the FTIR results of WM1, S3-5 and EM1 combustion. The findings demonstrate that substantial amounts of CO₂ and CH₄ were emitted. The strongest infrared absorbance wavelengths of CO₂, CO, H₂O, and CH₄ were observed to be 2359 cm⁻¹, 1298 cm⁻¹, 3736 cm⁻¹, and 3014 cm⁻¹ respectively.

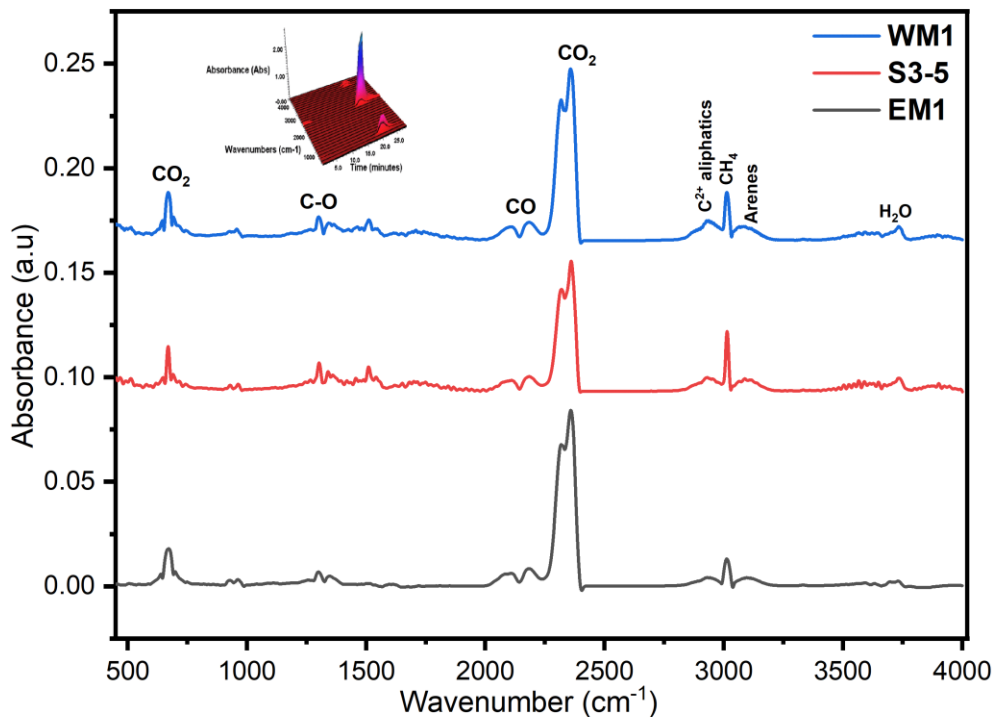


Figure 4.22: Infrared absorption profile of gas release of EM1, WM1 and S3-5 coal under air atmosphere

4.4 X- ray Diffraction Spectrometer (XRD) & X-ray Flourescence (XRF) Results

As shown in Figure 4.23 and Table 4.12, the coal samples are made up mainly of kaolinite with trace amounts of quartz, dolomite, and calcite. XRD measurement (Figure 4.25) was used to detect diffraction peaks of HDPE. A semi-crystalline peak intensity was observed. Anhydrite, calcite, and quartz are the dominant constituents of the fly ash.

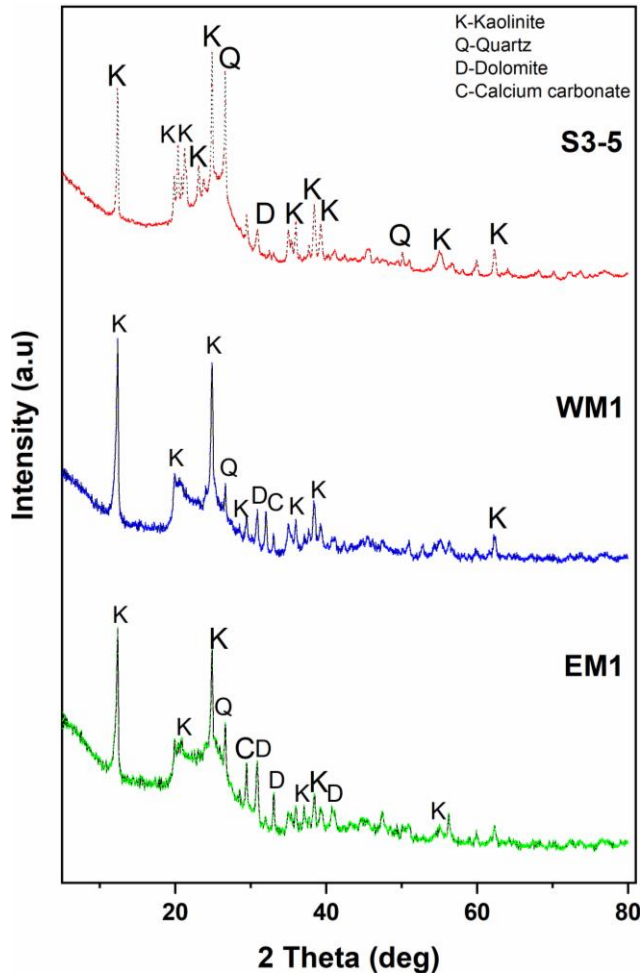


Figure 4.23: X-ray diffractograms of coal samples showing peaks used to identify individual major mineral components

Table 4.12: Mineralogical composition of coals from XRD analysis

	EM1 (%) dry basis	WM1 (%) dry basis	S3/5 (%) dry basis
Kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$)	54.2	51.4	51.7
Quartz (SiO_2)	21.6	32.1	33.5
Dolomite ($\text{CaMg}(\text{CO}_3)_2$)	14.9	9.7	7.9
Calcium carbonate (CaCO_3)	9.3	0	6.9

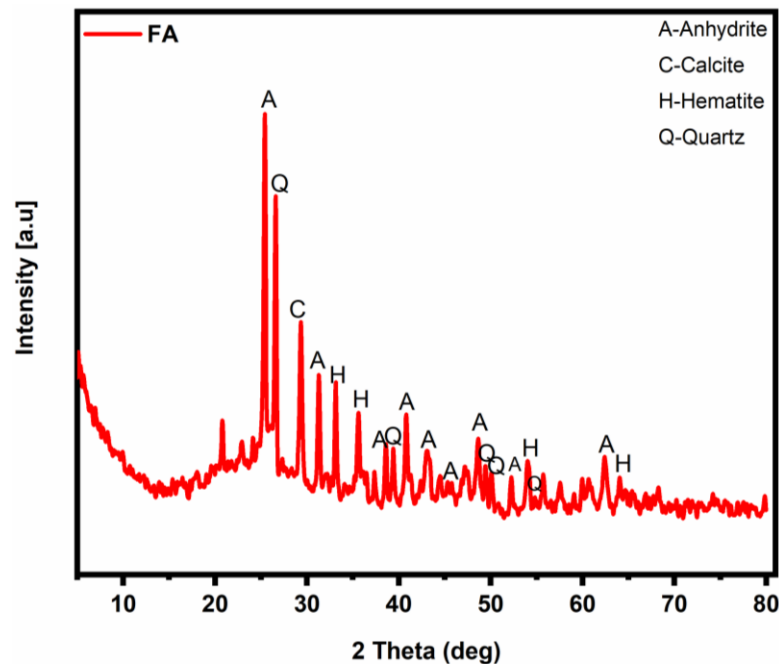


Figure 4.24: X-ray diffractogram of fly ash

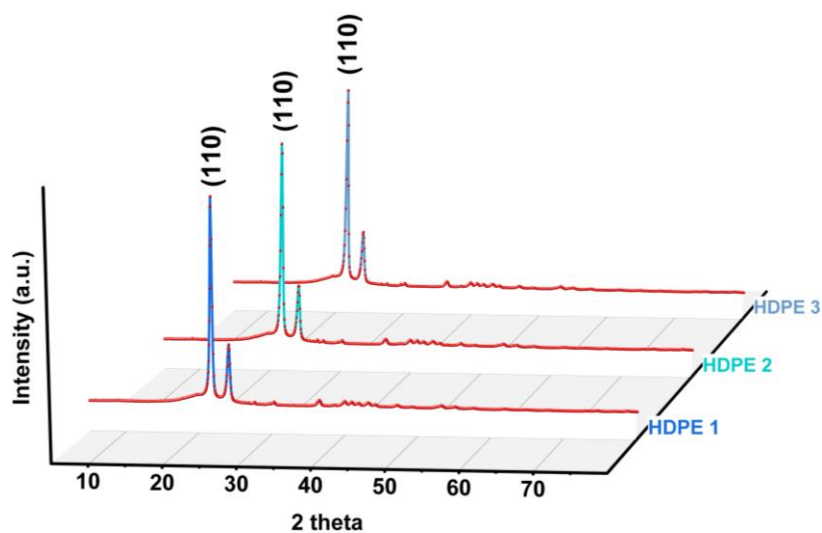


Figure 4.25: X-ray diffractogram of HDPE plastic

X-ray Fluorescence spectrometer was used to determine the elemental composition of coal ash. According to Table 4.13, silica (SiO_2 , 39.1-42.5%) and alumina (Al_2O_3 , 23.4-28.0%) are the dominant constituents of Morupule coal ash, with lesser but still considerable proportions of CaO , Fe_2O_3 and TiO_2 . Other oxides, like K_2O , Na_2O and MnO_2 , each make up less than 1%. The results correlate well with the previous studies [147]- [148]. TiO_2 dominated the HDPE plastic with lesser proportions of SiO_2 , Al_2O_3 , and CaO while fly ash was dominated by SiO_2 , Al_2O_3 , and CaO with lesser proportions of SO_3 and Fe_2O_3 according to Table 4.14.

Table 4.13: XRF Composition of Morupule coal, Waterberg & Highveld coal

Mineral Oxide	Botswana Morupule Coal			South Africa	
	EM1	S3/5	WM1	Waterberg coal	Highveld coal
SiO₂ (%)	42.5	39.1	41.2	57.3-58.8	46.79-58.25
Al₂O₃ (%)	27.7	23.4	28.0	25.8-27.9	21.22-27.05
Fe₂O₃ (%)	7.6	5.4	11.9	4.00-5.70	2.46-4.31
CaO (%)	10.1	12.6	8.2	3.80-10.1	5.70-13.27
MgO (%)	0.9	0.9	0.6	0.50-2.60	1.67-6.10
SO₃ (%)	5.7	6.05	4.6	1.30-2.80	4.47-6.10
TiO₂ (%)	3.3	5.2	3.5	1.10-1.40	1.15-1.54
K₂O (%)	0.5	1.09	0.6	0.40-1.10	0.35-1.13
Na₂O (%)	0.4	0.5	0.3	0.10-0.60	0.22-0.55
MnO₂ (%)	0.1	0.19	0.1	0.02-0.08	NF
P₂O₅ (%)	1.1	ND	0.6	0.28-0.68	0.07-1.17
SrO (%)	ND	ND	0.3	NF	NF

Table 4.14: XRF composition of HDPE plastic and fly ash

Mineral Oxide		
	HDPE	Fly ash
SiO₂ (%)	4.70	32.40
Al₂O₃ (%)	2.35	20.80
Fe₂O₃ (%)	0.52	6.78
CaO (%)	5.61	15.17
MgO (%)	NF	1.71
SO₃ (%)	0.69	7.98
TiO₂ (%)	20.4	NF
K₂O (%)	0.53	0.33
Na₂O (%)	0.58	NF
ZnO	0.41	NF
Cl	0.48	NF
MnO₂ (%)	NF	0.14
P₂O₅ (%)	NF	0.28
SrO (%)	NF	0.08

4.5 Kinetic Analysis

4.5.1 KAS & OFW Results

Non-isothermal kinetic analysis was done by the conventional model-fitting method such as Coats-Redfern model-fitting method, model fitting (linear regression) in addition to several isoconversional methods such as Ozawa-Flynn-Wall (OFW), Kissinger Akahira Sunose (KAS), Friedman and Vyazovkin method to investigate the relationship between activation energy and conversion.

The activation energy was calculated using the OFW method by applying equation (11). Figure 4.26a depicts linear graphs of $\ln(\beta)$ versus $1/T$ with slopes of $(-1.052E\alpha/R)$. Plots of $\ln(\beta/T_2)$ vs $1/T$ can be used using the KAS method to calculate the activation energy, according to equation (9). Figure 4.26b shows linear plots with slopes that produce $(-E/R)$ at increasing conversion degrees [149]. Due to poor correlation, data with conversion degrees below 0.25 and above 0.9 were excluded. Table 4.15-4.22 lists the calculated activation energies and pre-exponential factors of the OFW and KAS methods for all the three kinds of coals and the plastic. The mean activation energies calculated from the OFW and KAS methods for EM1 were 343.04 kJ/mol and 375.01 kJ/mol, the result of WM1 pyrolysis were 202.595 kJ/mol for OFW and 227.0388 kJ/mol for KAS, and the OFW mean activation energy for S3-5 coal was found to be 243.4875 kJ/mol and 270.1175 kJ/mol respectively for KAS.

The HDPE plastic had the mean activation energy of 245.735 kJ/mol for OFW and 271.2675 kJ/mol for KAS method. For the fly ash the calculated mean activation energy was found to be 354.2688 kJ/mol for the OFW method and 391.0713 kJ/mol for the KAS method. The activation energies determined using the OFW method were quite lower than those determined by the KAS method. These lines' parallelism is caused by the same reaction mechanism and kinetic behavior, according to reported studies [150]. The outcomes of the kinetic study demonstrated that activation energy is dependent on conversion. The standard errors were minimal. The correlation factors for OFW and KAS in the EM1 ranged from 0.8171 to 0.99967, WM1 curve's correlation factors was in the range of 0.88269-0.99719 and lastly S3-5 and HDPE's curves were within a narrow interval of 0.83159-0.99996 as shown in Figures 4.26-4.32. The fit ranges from $\alpha=0.25$ to 1.0 for both the KAS and OFW models, indicating that the kinetic data for all of the samples are well matched, and the findings were regarded acceptable. The activation energy estimations from the two

techniques are comparable. Compared to the other two coals, EM1 coal had significant activation energy for both models. In both situations, the activation energy values rise along with the conversion until a particular conversion level begins to fall. The reason for this was due to more elemental carbon present and less volatile matter, as observed in Table 3.1 and this agrees with previous studies [52].

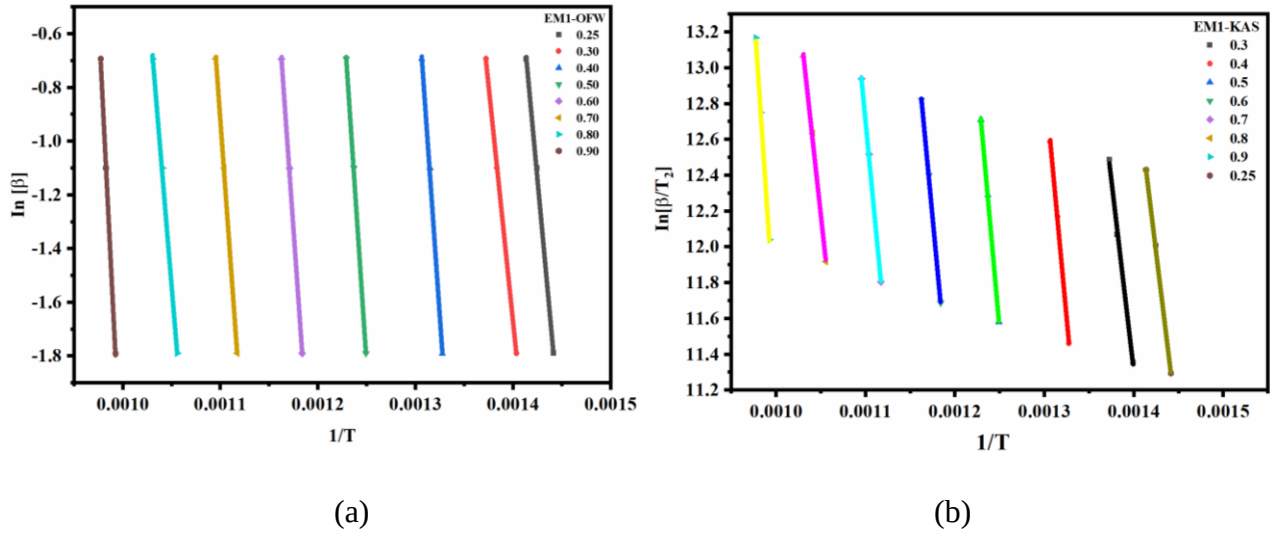


Figure 4.26: Kinetic plots for EM1 coal using a) OFW (left) and b) KAS (right) method under inert atmosphere

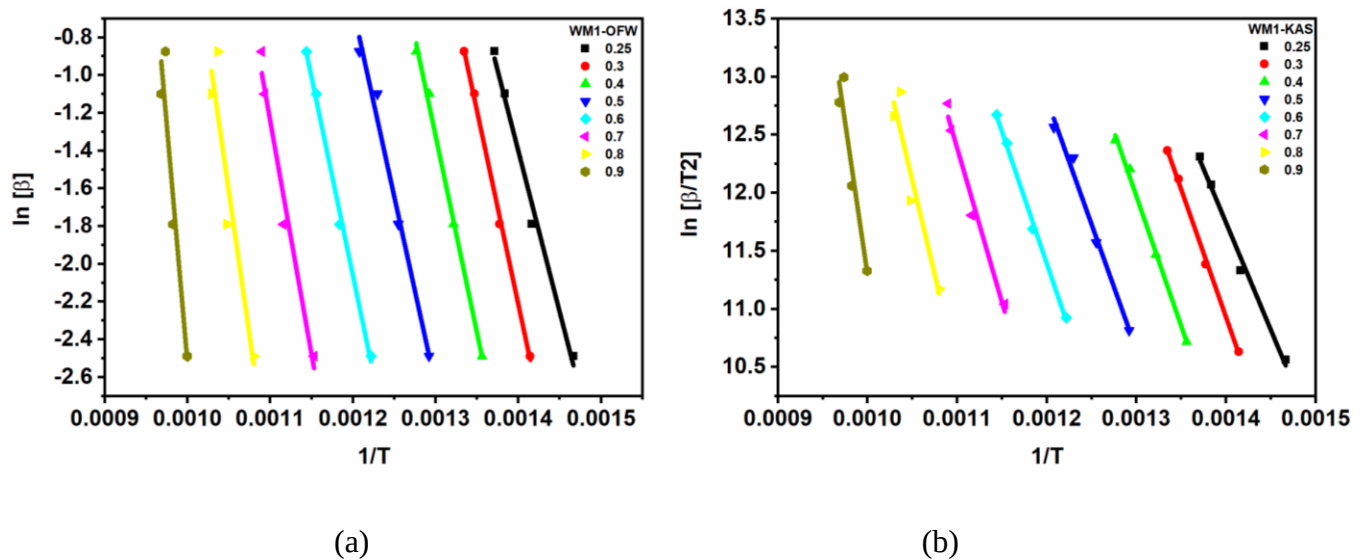
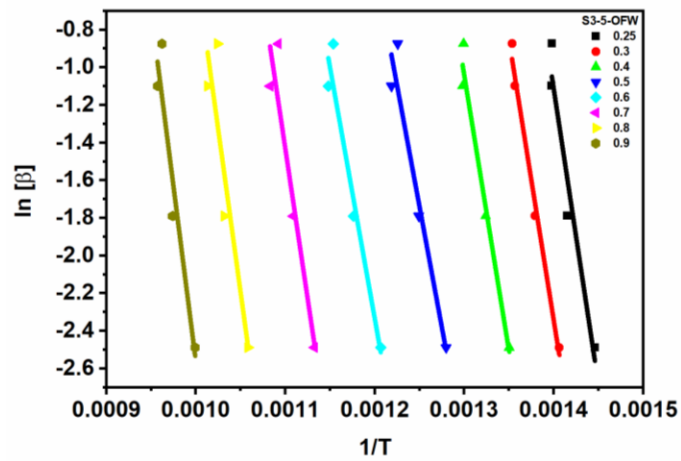
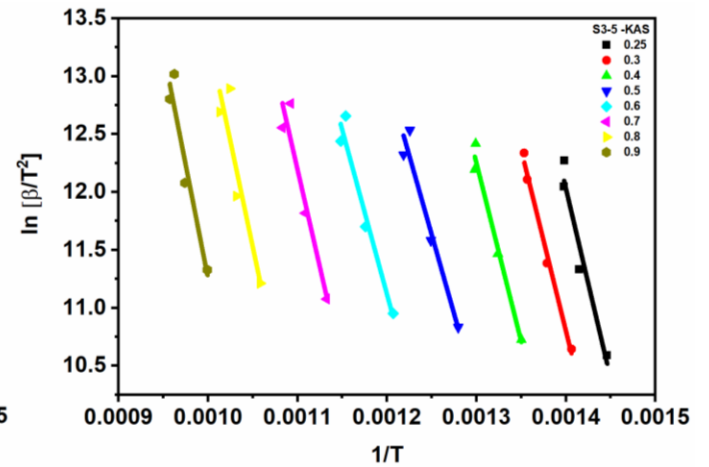


Figure 4.27: Kinetic plots for WM1 coal using a) OFW (left) and b) KAS (right) method under inert atmosphere

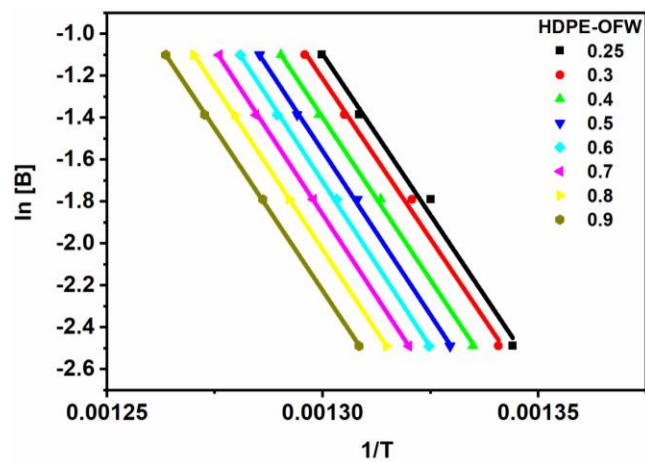


(a)

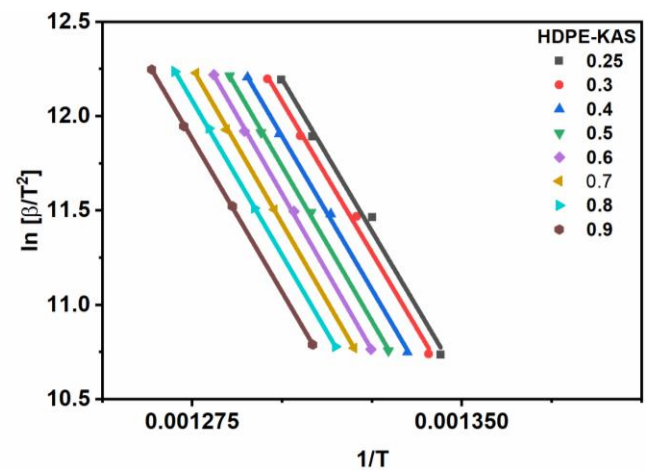


(b)

Figure 4.28: Kinetic plots for S3-5 coal using a) OFW (left) and b) KAS (right) method under inert atmosphere

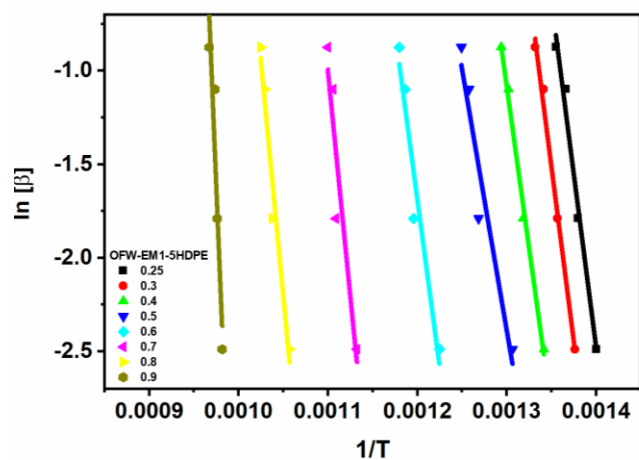


(a)

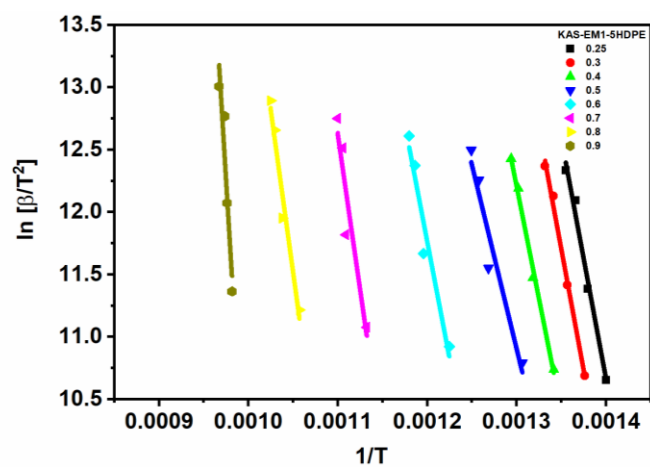


(b)

Figure 4.29: Kinetic plots for the HDPE plastic using a) OFW (left) and b) KAS (right) method under inert atmosphere



(a)



(b)

Figure 4.30: Kinetic plots for the EM1 mixture using a) OFW (left) and b) KAS (right) method under inert atmosphere

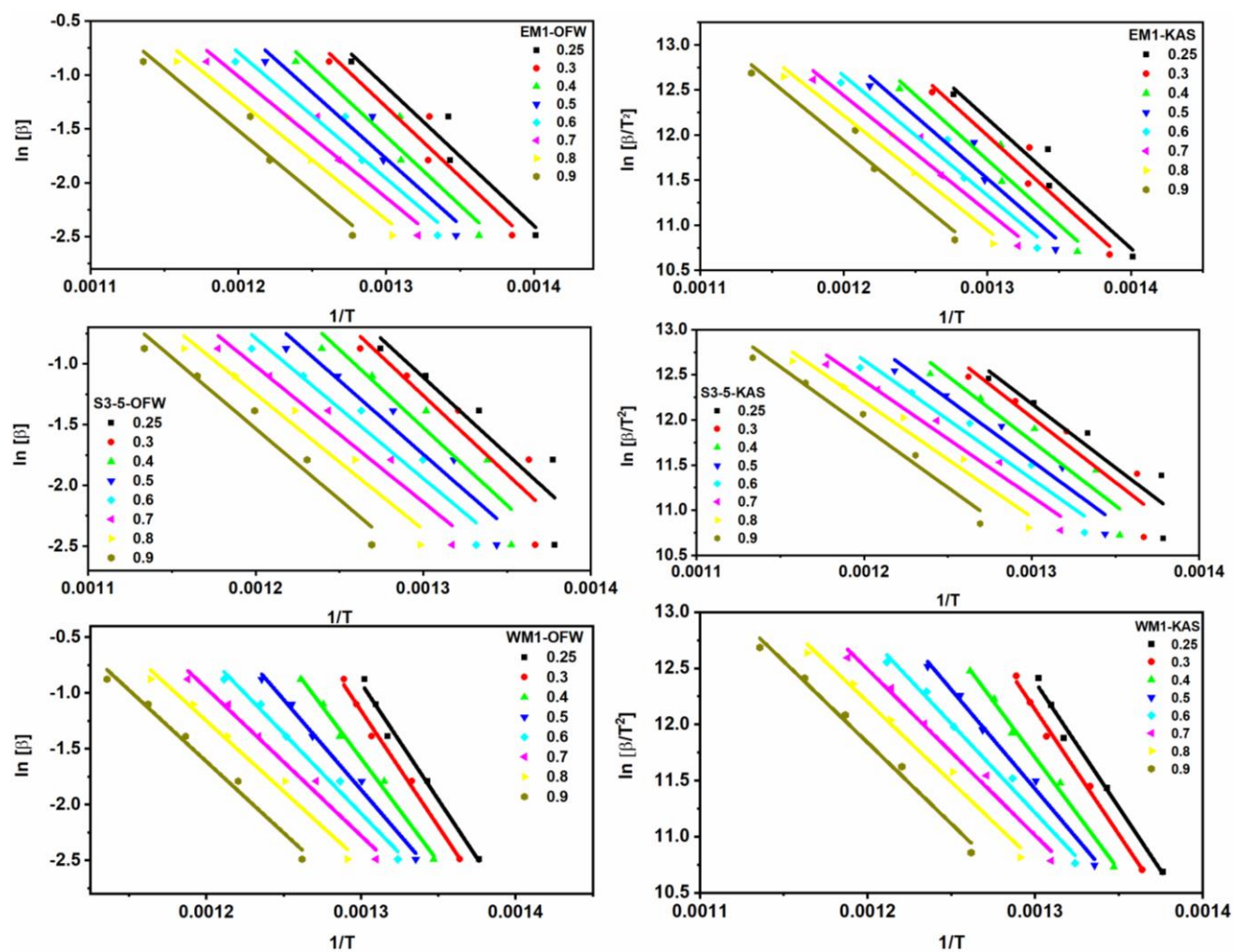


Figure 4.31: Kinetic plots for all coals ran under oxygen atmosphere using OFW (left) and KAS (right) method

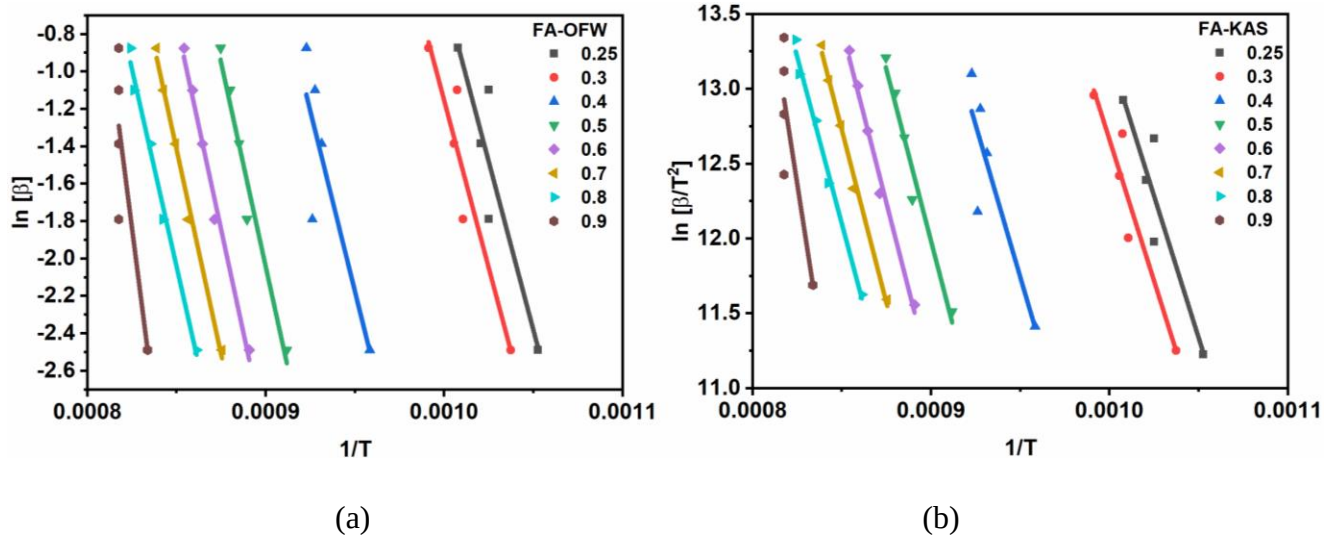


Figure 4.32: Kinetic plots for the fly ash using a) OFW and b) KAS method

Table 4.15: Activation energies (E) and pre-exponential factor (A) for various conversion values of EM1 coal using OFW and KAS methods under inert atmosphere

Conversion OFW				KAS		
	E (kJ/mol)	R^2	A (min^{-1})	E (kJ/mol)	R^2	A (min^{-1})
0.25	237.5	0.98324	3.5097E17	261.9	0.98467	5.9116E24
0.3	244.7	0.96953	6.67025E17	269.7	0.9721	1.23546E25
0.4	269	0.83793	9.43641E18	295.7	0.84948	2.26808E26
0.5	429.7	0.99965	1.07608E29	465.4	0.99967	7.25488E36
0.6	407.2	0.99956	1.35362E26	442.6	0.99959	9.1739E33
0.7	339.5	0.8171	2.0177E20	372.3	0.82928	1.09766E28
0.8	410.9	0.9638	1.27564E23	448.4	0.96623	1.13836E31
0.9	405.8	0.98634	3.65433E21	444.1	0.98739	3.60694E29
Average	343.04			375.01		

Table 4.16: Activation energies (E) and pre-exponential factor (A) for various conversion values of WM1 using OFW and KAS methods under inert atmosphere

Conversion	OFW			KAS		
	E (kJ/mol)	R ²	A (min ⁻¹)	E (kJ/mol)	R ²	A (min ⁻¹)
0.25	134.78	0.98995	1.83791E10	153.51	0.99129	9.77938E16
0.3	162.17	0.99788	1.04E12	182.7	0.99719	8.44716E18
0.4	164.69	0.99582	6.47869E11	185.88	0.99639	5.92954E18
0.5	157.98	0.98368	7.47742E10	179.49	0.98605	7.02759E17
0.6	165.99	0.9965	6.98465E10	188.68	0.99695	8.09917E17
0.7	195.61	0.97447	1.1867E12	220.61	0.97758	2.10984E19
0.8	241.11	0.88269	9.28065E13	269.4	0.89456	2.80104E21
0.9	398.43	0.90516	2.45139E21	436.04	0.91173	2.27527E29
Average	202.60			227.04		

Table 4.17: Activation energies (E) and pre-exponential factor (A) for various conversion values of S3-5 coal using OFW and KAS methods under inert atmosphere

Conversion	OFW			KAS		
	E (kJ/mol)	R ²	A(min ⁻¹)	E (kJ/mol)	R ²	A(min ⁻¹)
0.25	248.27	0.94689	7.15842E18	272.86	0.95107	1.24221E26
0.3	235.36	0.99024	2.69584E17	259.65	0.99108	4.48352E24
0.4	231.23	0.97704	3.47029E16	255.82	0.97918	6.07247E23
0.5	202.85	0.94275	6.39813E13	226.71	0.94896	9.76729E20
0.6	210.93	0.94805	3.84466E13	236.02	0.95379	7.15164E20
0.7	252.2	0.90824	2.00831E15	280.32	0.91706	5.98733E22
0.8	273.25	0.83159	3.28595E15	303.49	0.8463	1.31256E23
0.9	293.81	0.91621	5.69975E15	326.07	0.92404	2.95144E23
Average	243.49			270.12		

Table 4.18: Activation energies (E) and pre-exponential factor (A) for various conversion values of HDPE using OFW and KAS methods under inert atmosphere

Conversion	OFW			KAS		
	E (kJ/mol)	R ²	A(min ⁻¹)	E (kJ/mol)	R ²	A(min ⁻¹)
0.25	242.9	0.9923	1.32284E17	268.1	0.9948	2.55229E24
0.3	241.7	0.99584	1.16512E17	266.9	0.9987	2.2387E24
0.4	244.98	0.99902	2.19499E17	270.4	0.99934	4.36794E24
0.5	247.2	0.99941	3.34411E17	272.8	0.99918	6.82765E24
0.6	249.7	0.99954	5.17778E17	275.5	0.9993	1.08603E25
0.7	248.6	0.99979	4.29255E17	274.3	0.99746	8.98982E24
0.8	246.4	0.99996	2.92196E17	272.04	0.99774	6.06658E24
0.9	244.4	0.9999	1.98241E17	270.1	0.99932	4.09405E24
Average	245.74			271.27		

Table 4.19: Activation energies (E) and pre-exponential factor (A) for various conversion values of fly ash using OFW and KAS methods under both inert and oxygen atmosphere

Conversion	OFW			KAS		
	E (kJ/mol)	R ²	A(min ⁻¹)	E (kJ/mol)	R ²	A(min ⁻¹)
0.25	284.39	0.8517	3.57653E15	315.29	0.86448	1.56035E23
0.3	282.99	0.89357	2.04154E15	314.08	0.90334	9.10809E22
0.4	304.55	0.75374	2.03032E15	338.05	0.7731	1.22111E23
0.5	344.42	0.96475	3.4924E16	380.92	0.96793	2.96762E24
0.6	349.01	0.98766	2.822E16	386.21	0.98878	2.58469E24
0.7	346.82	0.99192	1.33339E16	384.24	0.99266	1.25157E24
0.8	333.56	0.9889	2.03475E15	370.64	0.99002	1.83567E23
0.9	588.41	0.71167	1.99109E26	639.14	0.72463	5.68755E34
Average	354.27			391.07		

Table 4.20: Activation energies (E) and pre-exponential factor (A) for various conversion values of EM1 using OFW and KAS methods under oxygen atmosphere

Conversion	OFW			KAS		
	E (kJ/mol)	R ²	A(min ⁻¹)	E (kJ/mol)	R ²	A(min ⁻¹)
0.25	101.87	0.93	2.63316E7	119.61	0.94335	9.3053E13
0.3	102.19	0.91907	2.75545E7	120.09	0.93447	1.0043E14
0.4	101.19	0.91332	2.39861E7	119.26	0.9302	8.90982E13
0.5	97.18	0.92436	1.31079E7	115.23	0.94013	4.65248E13
0.6	92.38	0.93628	6.24663E6	110.35	0.95057	2.07156E13
0.7	88.93	0.94624	3.5958E6	106.89	0.95904	1.14142E13
0.8	87.33	0.95031	2.62264E6	105.42	0.96257	8.31471E12
0.9	90.23	0.95185	3.35936E6	108.74	0.96357	1.18096E13
Average	95.16			113.20		

Table 4.21: Activation energies (E) and pre-exponential factor (A) for various conversion values of WM1 using OFW and KAS methods under oxygen atmosphere

Conversion	OFW			KAS		
	E (kJ/mol)	R ²	A(min ⁻¹)	E (kJ/mol)	R ²	A(min ⁻¹)
0.25	165.27	0.98711	6.69963E11	186.28	0.98871	5.9578E18
0.3	164.1	0.9922	5.21389E11	185.17	0.99319	4.66571E18
0.4	146.51	0.99338	2.81458E10	166.88	0.99439	2.0955E17
0.5	127.42	0.99124	1.32229E9	146.98	0.99282	7.75987E15
0.6	113.19	0.98735	1.39109E8	132.19	0.98993	6.71132E14
0.7	104.32	0.98407	3.35336E7	123.06	0.98759	1.43086E14
0.8	99.87	0.98273	1.52063E7	118.61	0.98678	6.20023E13
0.9	101.11	0.9842	1.41691E7	120.24	0.98798	6.21823E13
Average	127.72			147.43		

Table 4.22: Activation energies (E) and pre-exponential factor (A) for various conversion values of S3-5 using OFW and KAS methods under oxygen atmosphere

Conversion	OFW			KAS		
	E (kJ/mol)	R ²	A(min ⁻¹)	E (kJ/mol)	R ²	A(min ⁻¹)
0.25	99.95	0.83467	1.95475E7	117.65	0.86365	6.74125E13
0.3	102.06	0.84818	2.79608E7	119.99	0.87495	1.02333E14
0.4	101.12	0.89018	2.48049E7	119.21	0.91103	9.22144E13
0.5	95.63	0.93057	1.06759E7	113.59	0.94531	3.66735E13
0.6	91.21	0.94681	5.3089E6	109.11	0.95901	1.71579E13
0.7	88.38	0.95754	3.30546E6	106.32	0.96785	1.03703E13
0.8	88.21	0.96224	2.93282E6	106.36	0.97166	9.48798E12
0.9	92.41	0.95936	4.48302E6	111.07	0.96926	1.65652E13
Average	94.87			112.91		

Figure 4.33 shows both values calculated from the OFW and KAS methods, a sharp increase in activation energy for EM1 coal was observed from the 0.25 to 0.5 conversions to a value of 465.4 kJ/mol, and slowly decreased from 0.6 to 0.7, and increased to 0.8 conversion to a value of 448.4 kJ/mol. A gradual increase in activation energy is observed in WM1 coal from a value of 130 kJ/mol to a value of 425 kJ/mol at a conversion of 0.25 to 0.9. Activation energy of S3-5 decreased from 272-202 kJ/mol at a conversion of 0.25 to 0.5 and a sharp increase was observed from 0.5 to 0.9 to activation energy of 330 kJ/mol. For both values calculated from the OFW and KAS methods, HDPE's activation energy changed little from 0.25 to 0.3 conversions, a sharp increase was observed from 0.3 to 0.6 conversions to a value of 248 kJ/mol for OFW and 275 kJ/mol for KAS methods and lastly the activation energy decreased from 0.6 to 0.9 conversions to a value of

245 kJ/mol for OFW and 270 kJ/mol for KAS. According to Figure 4.34 an increase of activation energy was observed from a conversion of 0.25 to 0.5 for the fly ash, and a slow decrease in activation energy was observed from 0.5 to 0.8 conversions, lastly there was a sharp increase from 0.8 to 0.9 conversions to a value of 649 kJ/mol. Higher bond-energy reactions are occurring gradually at higher temperatures, resulting in higher activation energy. As shown in Figure 4.35, a significant decrease in activation energy was observed from a conversion of 0.3 to 0.8 in all the models during combustion studies of the three coal samples. The activation energies are not similar at different constant extends of conversion because most solid-state reactions are not simple one step mechanism & follow a complex multi-step reaction.

KAS and OFW methods were used to calculate the pre-exponential factor at different conversion fraction for pyrolysis. The results are shown in Table 4.15-4.22. EM1's pre-exponential factors for OFW and KAS methods varied from 3.51×10^{17} to 1.08×10^{29} and 5.91×10^{24} to 7.25×10^{36} /min, respectively. The pre-exponential factors for WM1 using OFW and KAS methods varied from 1.84×10^{10} to 2.45×10^{21} and 9.78×10^{16} to 2.28×10^{29} /min. S3-5's pre-exponential factors for OFW and KAS methods varied from 3.84×10^{13} to 7.16×10^{18} and 7.15×10^{20} to 1.24×10^{26} /min. HDPE's pre-exponential factors varied from 1.17×10^{17} to 5.18×10^{17} and 2.24×10^{24} to 1.09×10^{25} /min for OFW and KAS methods. The pre-exponential factors for the fly ash using OFW and KAS methods varied from 2.03×10^{15} to 1.99×10^{26} and 9.11×10^{22} to 5.69×10^{34} /min. For combustion studies, EM1's pre-exponential factors for OFW and KAS methods varied from 2.62×10^6 to 2.76×10^7 and 8.31×10^{11} to 9.31×10^{13} /min. Calculations of WM1 combustion using OFW and KAS methods varied from 1.52×10^7 to 6.70×10^{11} and 6.20×10^{13} to 5.96×10^{18} /min. The results of S3-5's pre-exponential factors for OFW and KAS methods varied from 2.93×10^6 to 2.79×10^7 and 9.49×10^{12} to 1.02×10^{14} /min.

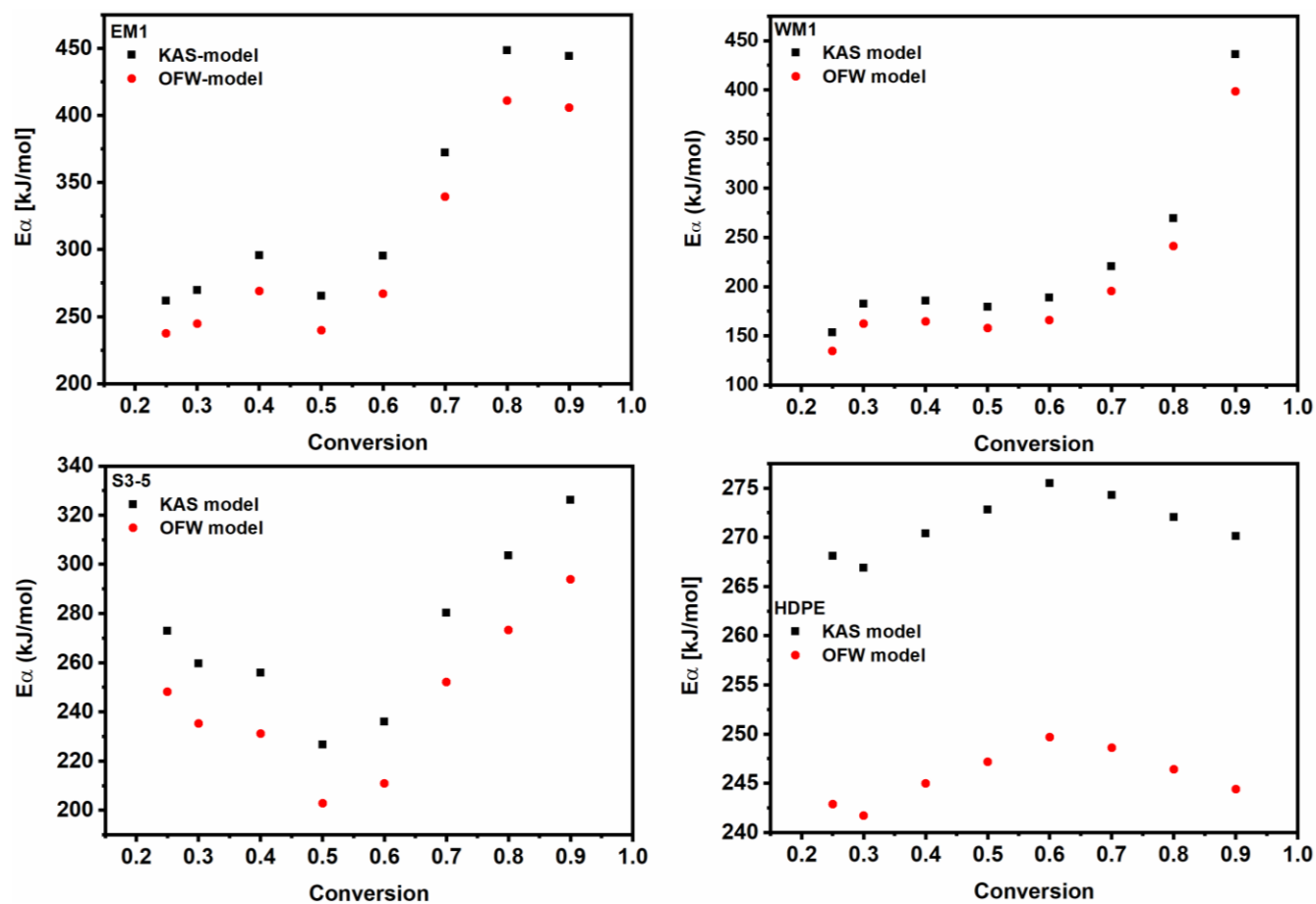


Figure 4.33: Activation energy dependence on degree of conversion for pyrolysis of coal and plastic

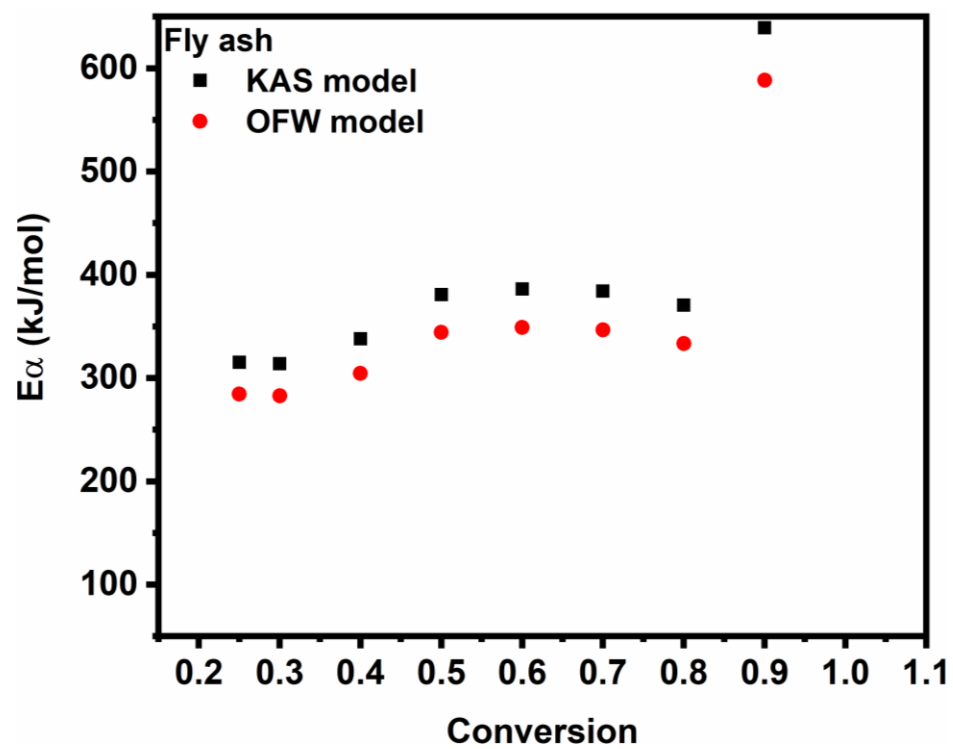


Figure 4.34: Activation energy dependence on degree of conversion for the fly ash

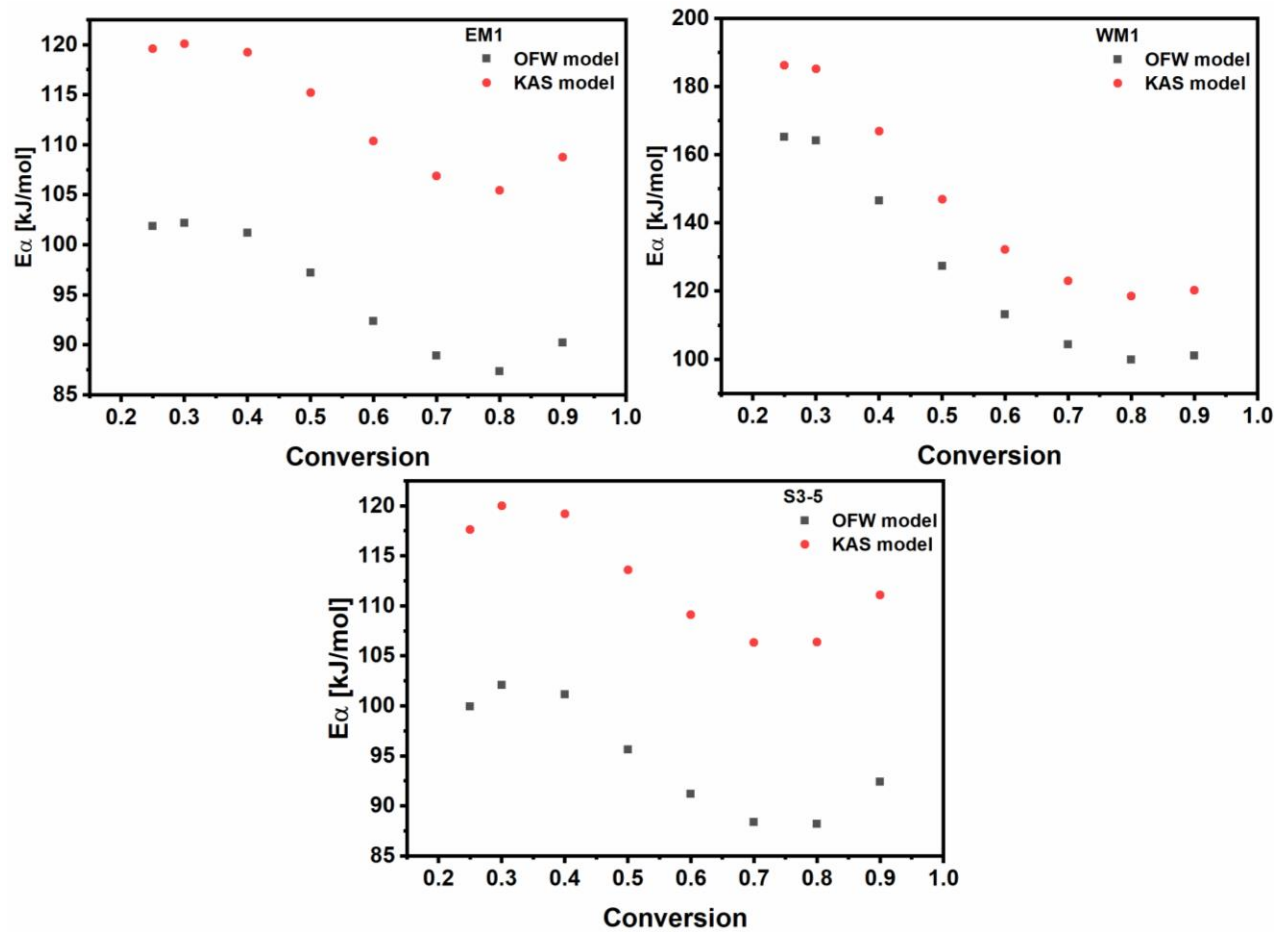


Figure 4.35: Activation energy dependence on degree of conversion for the combustion of coal

4.5.2 Coats Redfern Results

The kinetic parameters, that is the activation energies ($E\alpha$) of every decomposition step and the pre-exponential factor (A) were determined from TGA thermogram by Coats-Redfern method according to equation (26).

As shown in Figure 4.36-4.38, the correlation coefficient R^2 , was calculated using the least square method by plotting $\ln [g(\alpha)/T^2]$ against $1/T$ for the coal, plastic and coal/plastic mixture, where $E\alpha$ was obtained from the slope and A from the intercept. The data obtained are given in Table 4.23-4.25 for both the pyrolysis and combustion processes. In the subsequent decomposition stages, the activation energy $E\alpha$ rose, showing that the remaining substance is quite stable. The last decomposition step of a coal, plastic, and coal mixture always has a larger activation energy than the activation energy of the previous processes. At $n = 1$, the least square method provided the best fit for all phases of the decomposition process [151]- [152]. According to Table 4.23 and 4.24, $R^2 = 0.79493$ - 0.98506 for all coals and the plastic mixture ran under the pyrolysis process. Table 4.24 shows that R^2 for all coals ran under combustion process were in the range of 0.94132 - 0.98269 .

Three independent first-order reactions can be used to describe the pyrolysis process for the three coals and the coal mixture, however just one first order reaction should be used to explain the pyrolysis process for HDPE plastic with correlation factor at 0.98419 and activation energy of 372.7 as shown in Table 4.25. The combustion process for the three coals can be described as two independent first order reactions. From the slope of each line, the value of $E\alpha$ and A was obtained for different stages. According to Table 4.23, the activation energy of the three stages of EM1 pyrolysis was 52.2 kJ/mol for the first stage, 107.2 kJ/mol for the second stage, and 31.2 kJ/mol for the last stage. The result of WM1 pyrolysis was 23.9 kJ/mol, 107.8 kJ/mol, and 279.4 kJ/mol. Calculations of S3-5 pyrolysis were 24.7 kJ/mol, 135.2 kJ/mol, and 50.2 kJ/mol successively. The activation energy of the three stages of the coal mixture (EM1:5HDPE) pyrolysis was 13.5 kJ/mol, 66.5 kJ/mol, and 131.2 kJ/mol. The good correlation coefficient shows that the corresponding independent first order reaction model precisely matches the experimental data. Due to the covalent bond nature, the highest activation energy values suggested a high degree of stability. In theory, the higher the activation energy, the more stable the material.

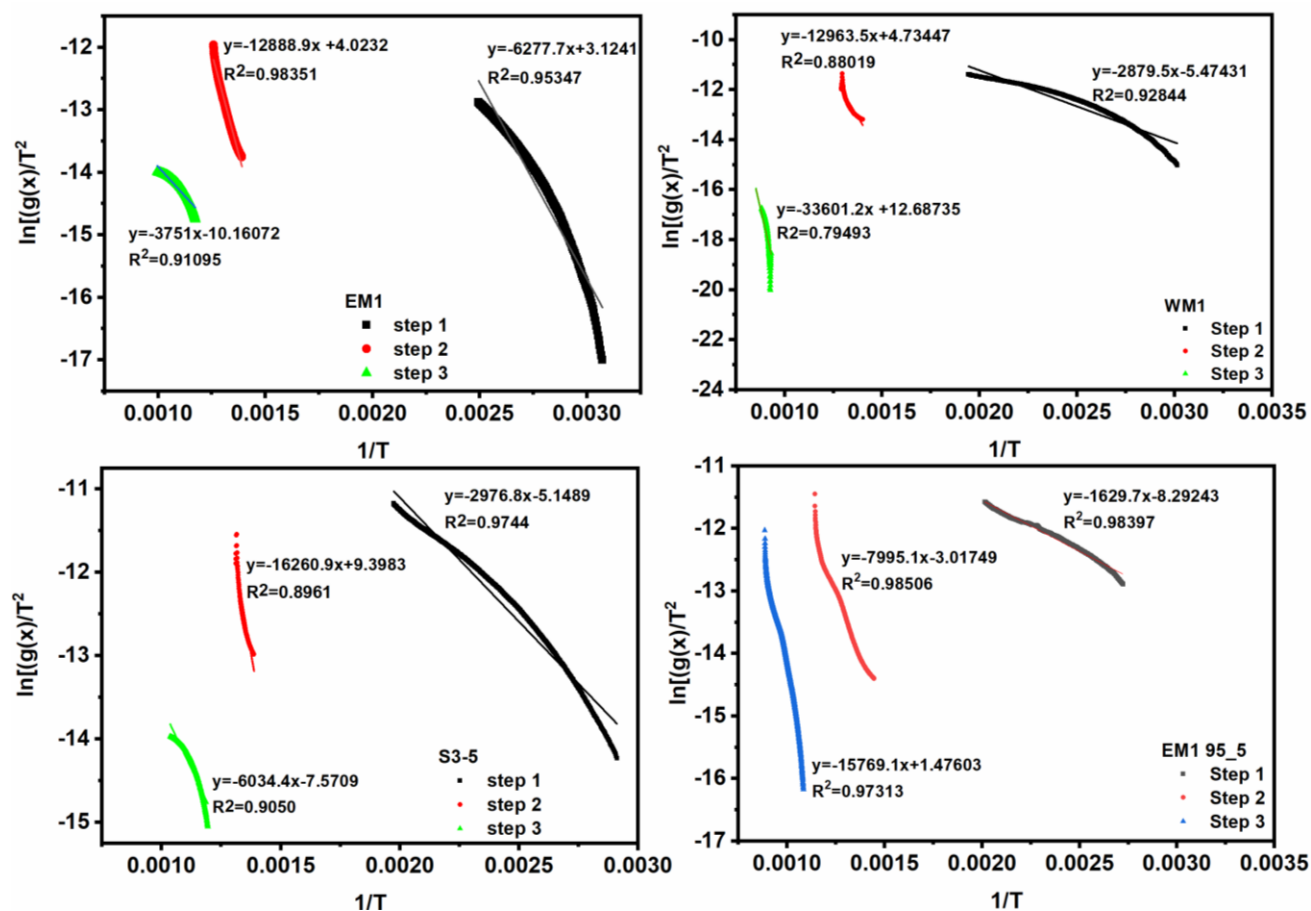


Figure 4.36: Coats Redfern plots for EM1, WM1, S3-5 coals and EM1 mixture for the pyrolysis process

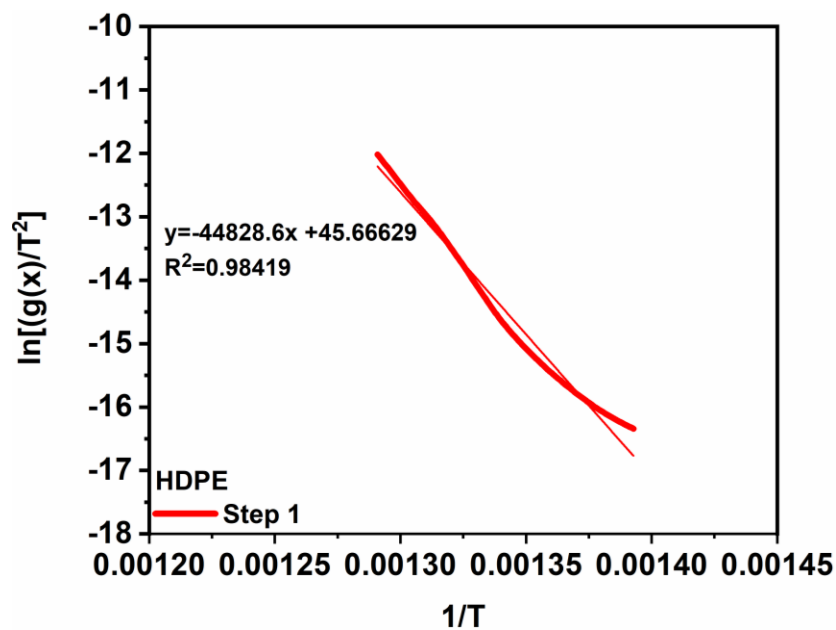


Figure 4.37: Coats Redfern plot of HDPE plastic

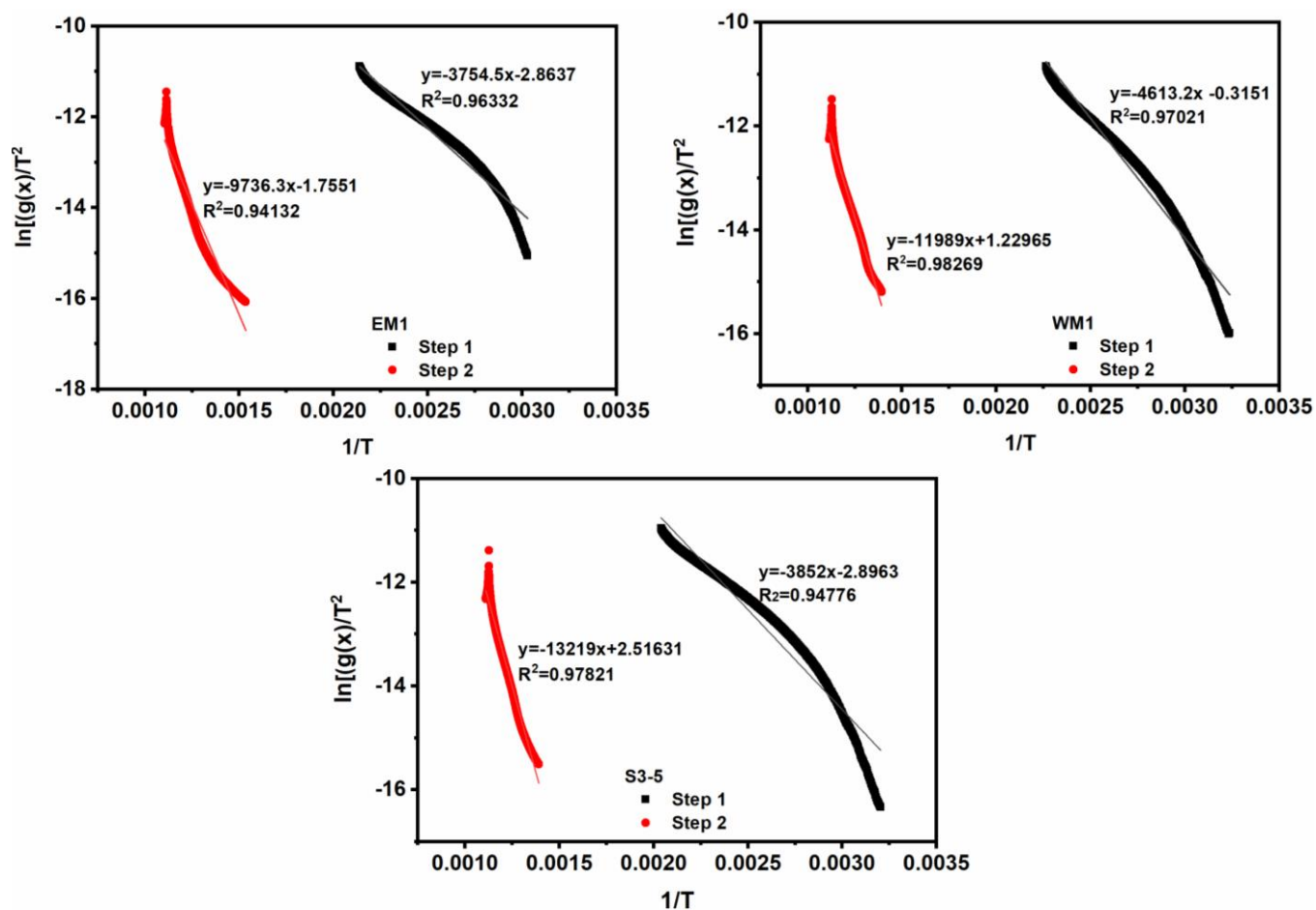


Figure 4.38: Coats Redfern plots for EM1, WM1, and S3-5 coals for the combustion process

Table 4.23: Fitted kinetic parameters for pyrolysis of coal and coal/plastic mixture using coats redfern method

Sample	Temperature (°C)	E (kJ/mol)	A (min ⁻¹)	R ²
EM1	27-289.83	52.2	5.95E+04	0.95347
	289.83-578.75	107.2	3.00E+05	0.98351
	578.75-898.75	31.2	6.04E-02	0.91095
WM1	30-275	23.9	5.03E+00	0.92844
	275-567.08	107.8	6.15E+05	0.88019
	567.08-900	279.4	4.53E+09	0.79493
S3-5	39-250	24.7	7.20E+00	0.9744
	250-564.47	135.2	8.18E+07	0.8961
	564.47-896.61	50.2	1.30E+00	0.9050
EM1: 5HDPE	30-250	13.5	1.70E-01	0.98397
	250-649	66.5	1.63E+02	0.98506
	650-900	131.2	2.87E+04	0.97313

Table 4.24: Fitted kinetic parameters for combustion of coal and coal/plastic mixture using coats redfern method

Sample	Temperature (°C)	E (kJ/mol)	A (min ⁻¹)	R ²
EM1	28-200	31.21	8.93E+01	0.96332
	312-681	80.95	7.01E+02	0.94132
WM1	32-173	38.35	1.40E+03	0.97021
	309-676	99.67	1.71E+04	0.98269
S3-5	36-224	32.03	8.86E+01	0.94776
	333-674	109.90	6.82E+04	0.97821

Table 4.25: Kinetic parameters for pyrolysis of the HDPE plastic studied

Sample	HDPE
E (kJ/mol)	372.7
A (min ⁻¹)	1.27E+24
R ²	0.98419

4.5.3 Friedman Results

Figure 4.39-4.40 shows a perfect linear relationship for all conversions considered. The kinetic parameters of the Friedman isoconversional method were calculated using a range of conversion from 0.05 to 0.65. From Figure 4.41-4.42, it can be observed that E_a depends on α : (1) From EM1 coal E_a gradually increases from 24 to 194 kJ/mol when α increases from 0.1 to 0.3; (2) E_a decreases from 194 to 166 kJ/mol in the α range between 0.3 and 0.4 and lastly the activation energy sharply increased from 180 to 261 kJ/mol between 0.5 to 0.8 conversions. For WM1 coal E_a sharply increases from 15 to 165 kJ/mol in the α range between 0 to 0.3; a slow decrease was observed between 0.4-0.5 conversions (i.e ranging between 154-152 kJ/mol), lastly E_a sharply increases from 163 to 503 kJ/mol in the α range between 0.6 and 0.9 conversions. Both EM1 and WM1 shows a similar trend in activation energy, this is in agreement with the results found in literature [153]- [154]. Furthermore, despite some minor changes, the activation energy of EM1 and WM1 increases with conversion generally. According to this finding, coal pyrolysis is not a single-step reaction with a constant activation energy. Therefore, if the entire process is to be detailed, coal pyrolysis should be separated into various stages. For S3-5 coal, there was a gradual increase of E_a from 9 to 220 kJ/mol when α was in the range of 0.1 to 0.3; E_a slowly decreased between 166 to 153 kJ/mol in the α range between 0.4 and 0.6, a sharp increase in activation energy occurred from 0.7-0.9 conversions (i.e ranging between 164-345 kJ/mol).

For HDPE plastic; E_a slowly decreased between 252 to 209 kJ/mol in the α range between 0.1 and 0.2, a sharp increase in activation energy occurred from 0.3-0.6 conversions (i.e ranging between 216-275 kJ/mol), and lastly there was a decrease from 261-241 kJ/mol in E_a between 0.7 and 0.9

conversions. From EM1:5HDPE coal mixture, E_a sharply increased from 110 to 311 kJ/mol the α range from 0.1 to 0.5, E_a decreased to 270 kJ/mol in the conversion range of 0.6, and lastly E_a sharply increased to 519 kJ/mol from 0.7-0.9 conversions. The average activation energies determined from Friedman methods were 164.26-304.32 kJ/mol, and the correlation coefficient factor (R^2) calculated for the three coals was between 0.7233-0.9856.

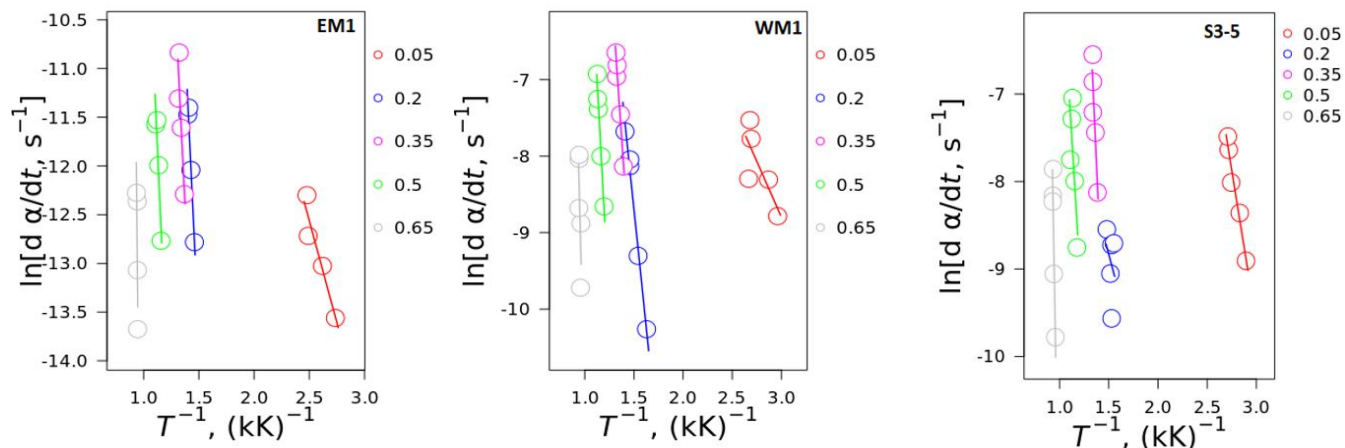


Figure 4.39: Friedman plots of Morupule coal pyrolysis at different values of conversion

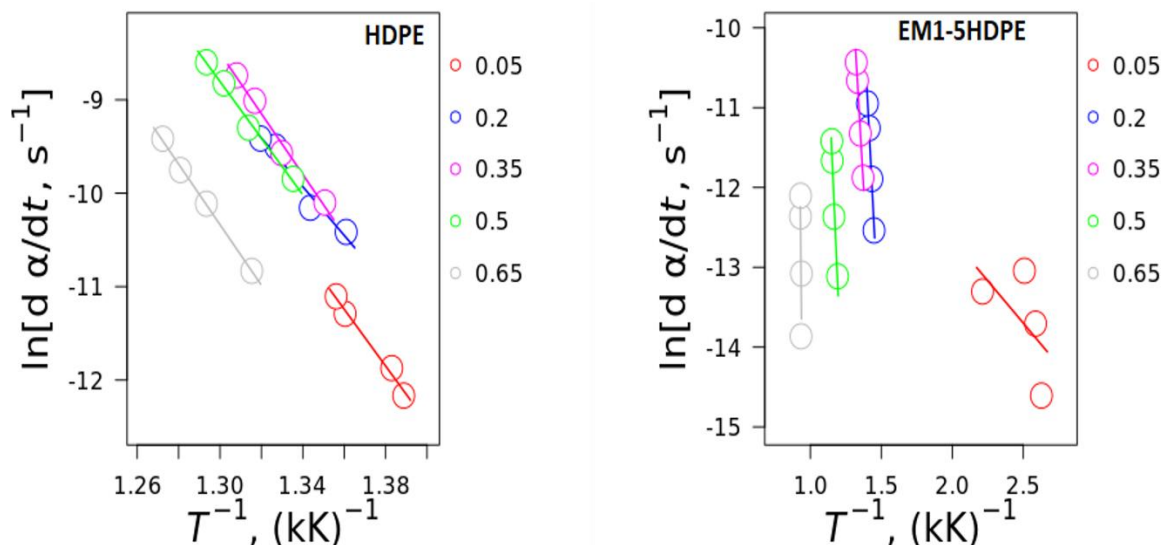


Figure 4.40: Friedman plots of HDPE plastic and coal mixture (EM1-5HDPE) at different values of conversion

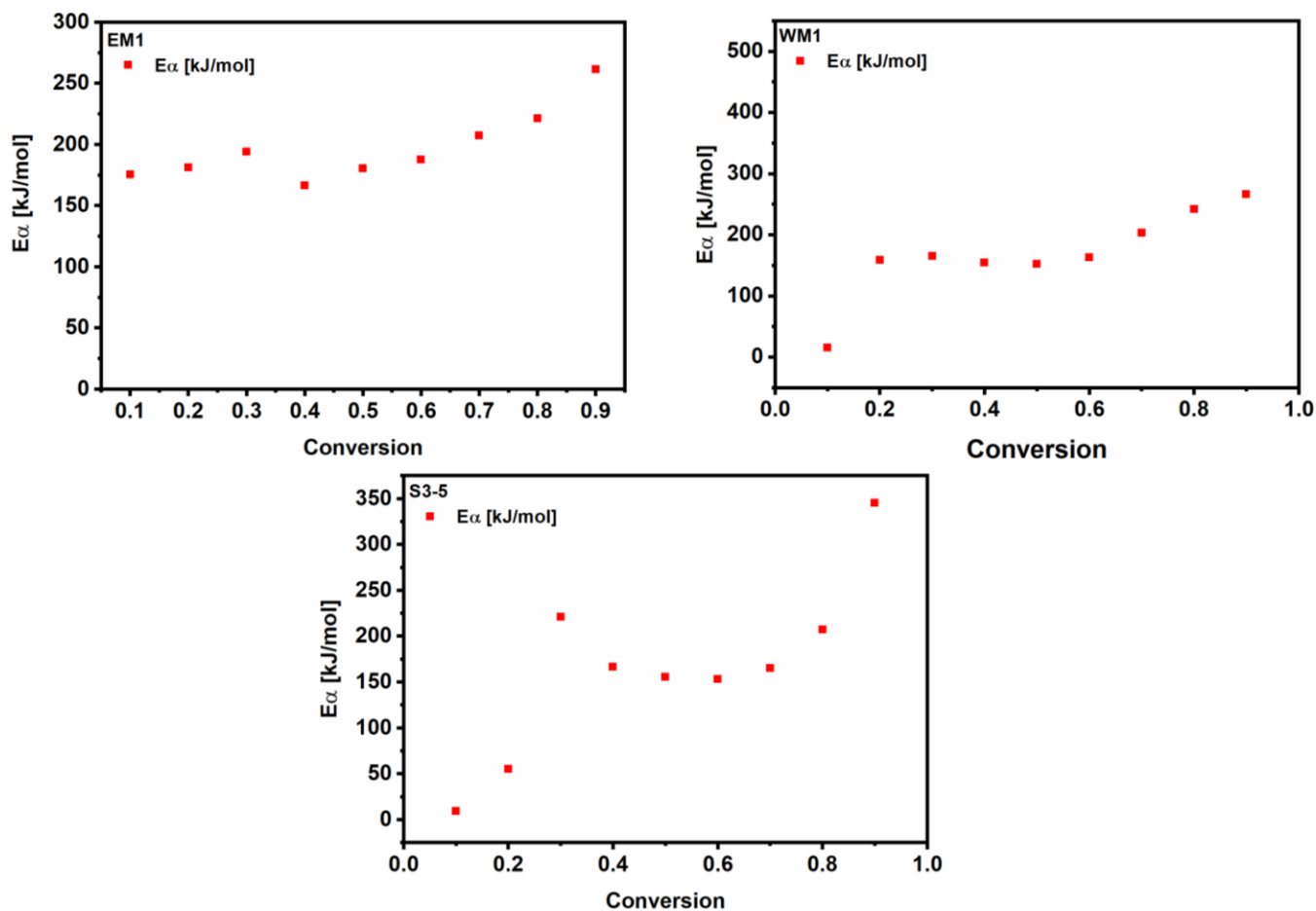


Figure 4.41: E_α as a function of conversion for the coal at different values of conversion

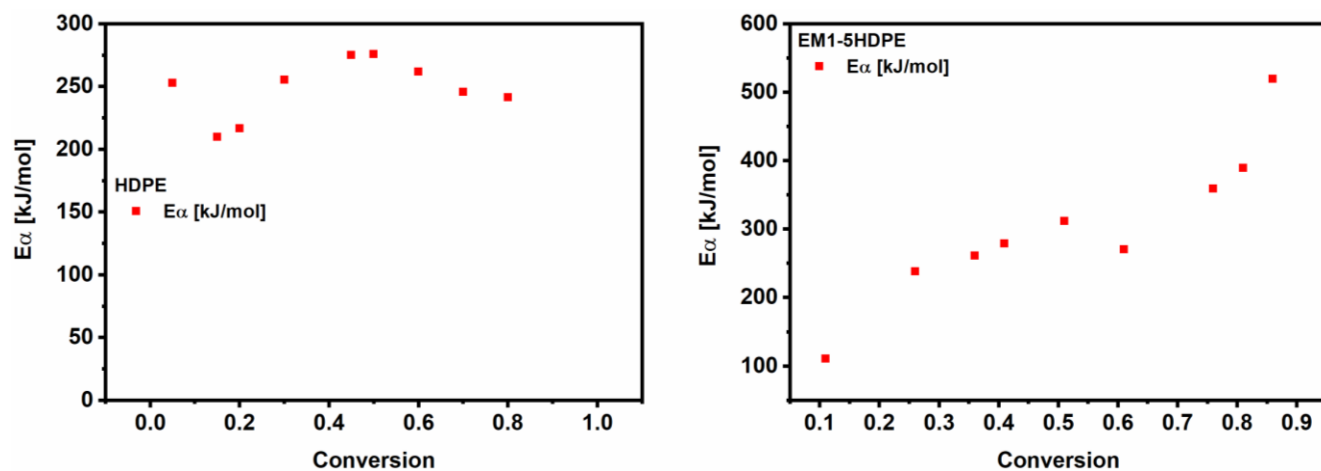


Figure 4.42: E_α as a function of conversion for the HDPE plastic and coal mixture (EM1-5HDPE) at different values of conversion

Table 4.26: Kinetic parameters using the Friedman method for EM1, WM1 and S3-5 coals

Conversion	EM1		WM1		S3-5	
α	E_a [kJ/mol]	R^2	E_a [kJ/mol]	R^2	E_a [kJ/mol]	R^2
0.1	175.27	0.9324	15.61	0.90251	9.29	0.69779
0.2	181.00	0.96395	158.82	0.98935	55.37	0.63013
0.3	207.52	0.95338	165.32	0.97648	220.79	0.92001
0.4	166.30	0.73182	154.30	0.97382	166.54	0.63521
0.5	146.49	0.7091	152.70	0.94381	155.72	0.71467
0.6	180.38	0.75641	163.27	0.96786	153.29	0.63077
0.7	207.10	0.88942	203.19	0.95182	164.93	0.57215
0.8	221.10	0.64359	242.11	0.79861	207.22	0.80935
0.9	261.47	0.88589	266.40	0.84592	345.15	0.89929
Average	194.07	0.8168	169.08	0.9165	164.26	0.7233

Table 4.27: Kinetic parameters using the Friedman method for HDPE and coal mixture

Conversion	HDPE		EM1-5HDPE	
α	E_a [kJ/mol]	R^2	E_a [kJ/mol]	R^2
0.1	252.68	0.9880	110.75	0.96186
0.2	209.86	0.99245	238.41	0.99476
0.3	216.54	0.95962	261.28	0.98425
0.4	255.43	0.96524	278.81	0.9274
0.5	275.12	0.99106	311.59	0.53342
0.6	275.72	0.99272	270.57	0.44727
0.7	261.81	0.99871	358.95	0.95135
0.8	245.59	0.98359	389.32	0.96132
0.9	241.33	0.99863	519.22	0.91317
Average	248.23	0.9856	304.32	0.8528

4.5.4 Vyazovkin Results

From Figure 4.43 & 4.44 it can be observed that the activation energy of EM1 coal increases from a conversion of 0.1 to 0.2 (i.e ranging between 167-203 kJ/mol), then decreases from 0.3 to 0.5 conversions (i.e ranging between 190-153 kJ/mol), and lastly there was a sharp increase in activation energy between conversions of 0.6-0.9 conversions (i.e ranging between 186-513 kJ/mol). For WM1 coal it can be observed that E_a increases from 0.1-0.3 conversion (i.e., ranging between 10-157 kJ/mol), a slight decrease was observed from 0.4-0.5 conversions (i.e., ranging between 151-149 kJ/mol) and lastly, the apparent activation energy shows an increasing dependence upon the conversion degree in the range 0.6-0.9 (i.e ranging between 160-496 kJ/mol). A sharp increase is observed from 0.1-0.3 conversions (i.e., ranging between 10-209 kJ/mol) for S3-5 coal. E_a further decreased from 0.4-0.7 conversions (i.e., ranging between 176-137 kJ/mol), and E_a slowly increased from 0.8-0.9 conversions (i.e., ranging between 229-280 kJ/mol). For the coal mixture a sharp increase is observed from 0.1-0.5 conversions (i.e., ranging between 72-304 kJ/mol), E_a slowly decreased to 259 kJ/mol at 0.6 conversion. Another increase in activation energy is observed from 361-476 kJ/mol between 0.8 to 0.9 conversions. A decrease in activation energy is observed from 0.1-0.2 conversions that is from 244-225 kJ/mol), E_a slowly increased from 0.3-0.5 conversions (i.e., ranging between 246-275 kJ/mol), a drop in activation energy to 266 kJ/mol was observed at 0.6 conversion and lastly an increase in E_a from 248-264 kJ/mol was observed between 0.7-0.9 conversions. The mean activation energy calculated from the advanced integral Vyazovkin method was 155.77-284.59 kJ/mol for the three coals, the HDPE plastic, and the coal mixture. Table 4.26 to Table 4.28 show that the two isoconversional models had very small differences in activation energy values, which ensured their validity.

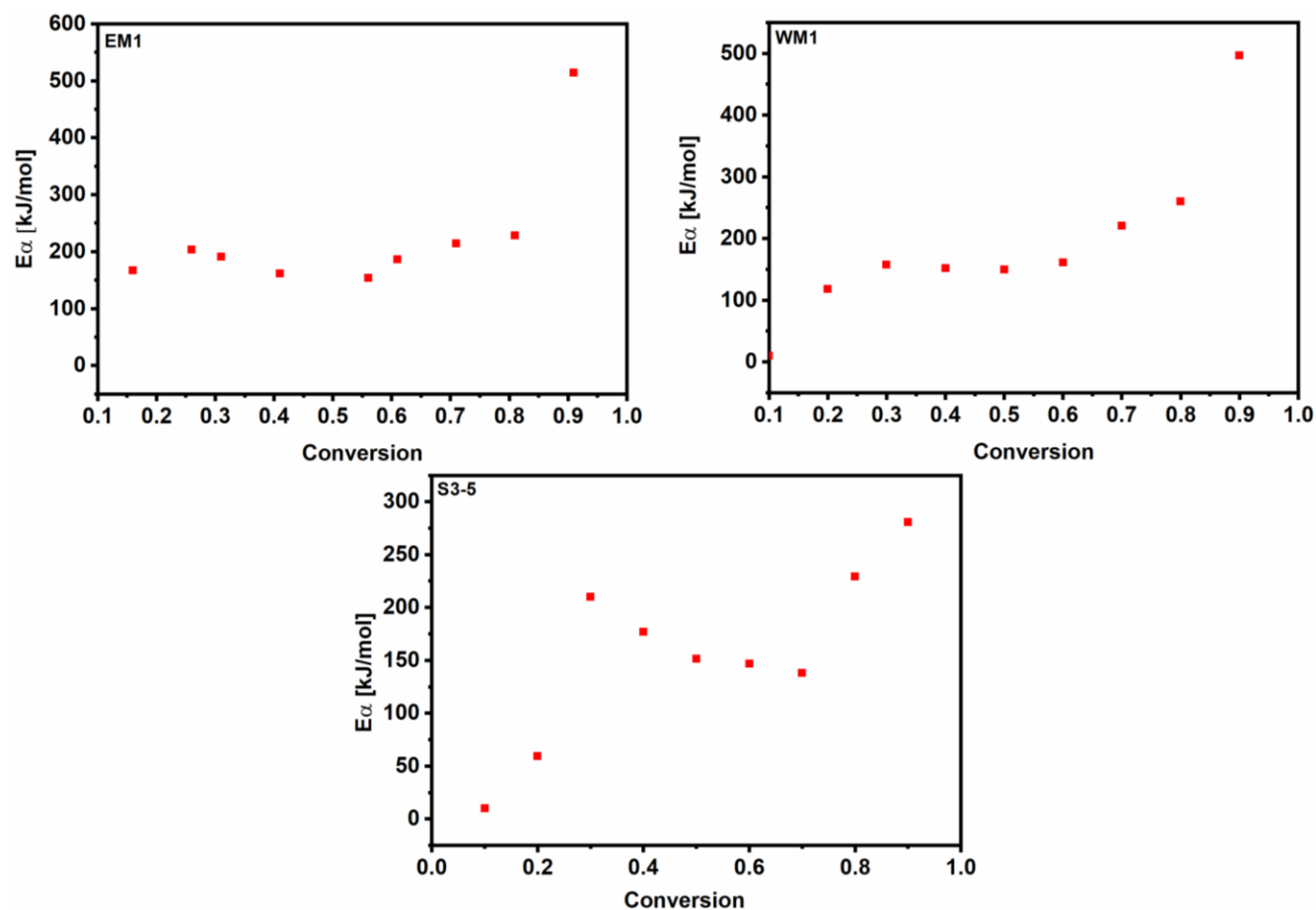


Figure 4.43: The activation energy of the three coals in relation to conversion using the advanced integral Vyazovkin method

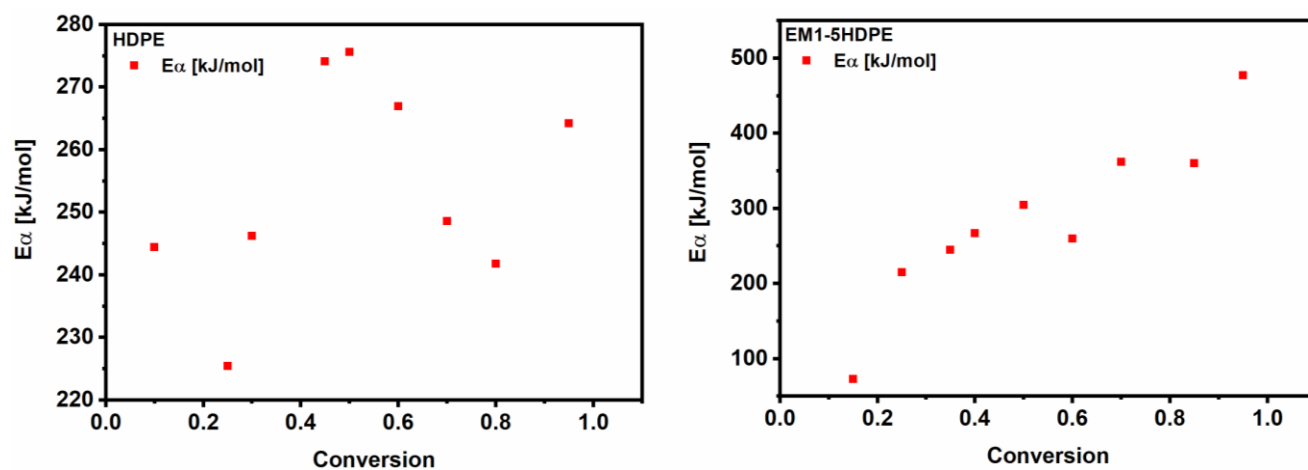


Figure 4.44: The activation energy of plastic and coal mixture in relation to conversion using the advanced integral Vyazovkin method

Table 4.28: Activation energy of the three coals, plastic and coal mixture using the advanced integral Vyazovkin method

Conversion	EM1	WM1	S3-5	HDPE	EM1-5HDPE
α	E_a [kJ/mol]	E_a [kJ/mol]	E_a [kJ/mol]	E_a [kJ/mol]	E_a [kJ/mol]
0.1	167.17	10.00	10.00	244.42	72.68
0.2	203.62	117.83	59.41	225.39	214.82
0.3	190.78	157.33	209.86	246.17	244.55
0.4	161.50	151.31	176.67	274.09	266.58
0.5	153.98	149.80	151.41	275.59	304.60
0.6	186.43	160.70	146.73	266.92	259.76
0.7	214.30	220.33	137.96	248.53	361.93
0.8	227.88	259.72	229.24	241.73	359.61
0.9	513.90	496.41	280.61	264.15	476.78
Average	224.40	191.49	155.77	254.11	284.59

4.5.5 Model fitting (linear regression) results

Figure 4.45-4.46 were used to derive the activation energy and pre-exponential factor from the intercept. The activation energy of the coals, plastic and the coal mixture varied between 167.9 to 302.6 kJ/mol and pre-exponential factor varied from 9.1 to 32.4 (1/s). The activation energy of the coal mixture (EM1:5HDPE) was low compared to the EM1 coal.

The master plot approach was used to calculate the kinetic mechanism function. The accurate determination of the kinetic mechanism function is extremely beneficial for future kinetic and thermodynamic investigations [155]. The experimental data plot of $f(\alpha)/f(0.5)$ was compared to that anticipated by several theoretical kinetic mechanism functions to accomplish this. [156]. According to the master plots in Figure 4.47-4.48 the calculated $f(\alpha)/f(0.5)$ values from the master plots method are in good agreement with the simulated ones. F3 model (third order reaction) was chosen to be the reaction mechanism function for the coal and the coal mixture while the A2 model (Avrami-Erofeev) was selected to represent the reaction mechanism for the HDPE plastic according to differential and integral form of the most probable mechanism function in Table 2.1.

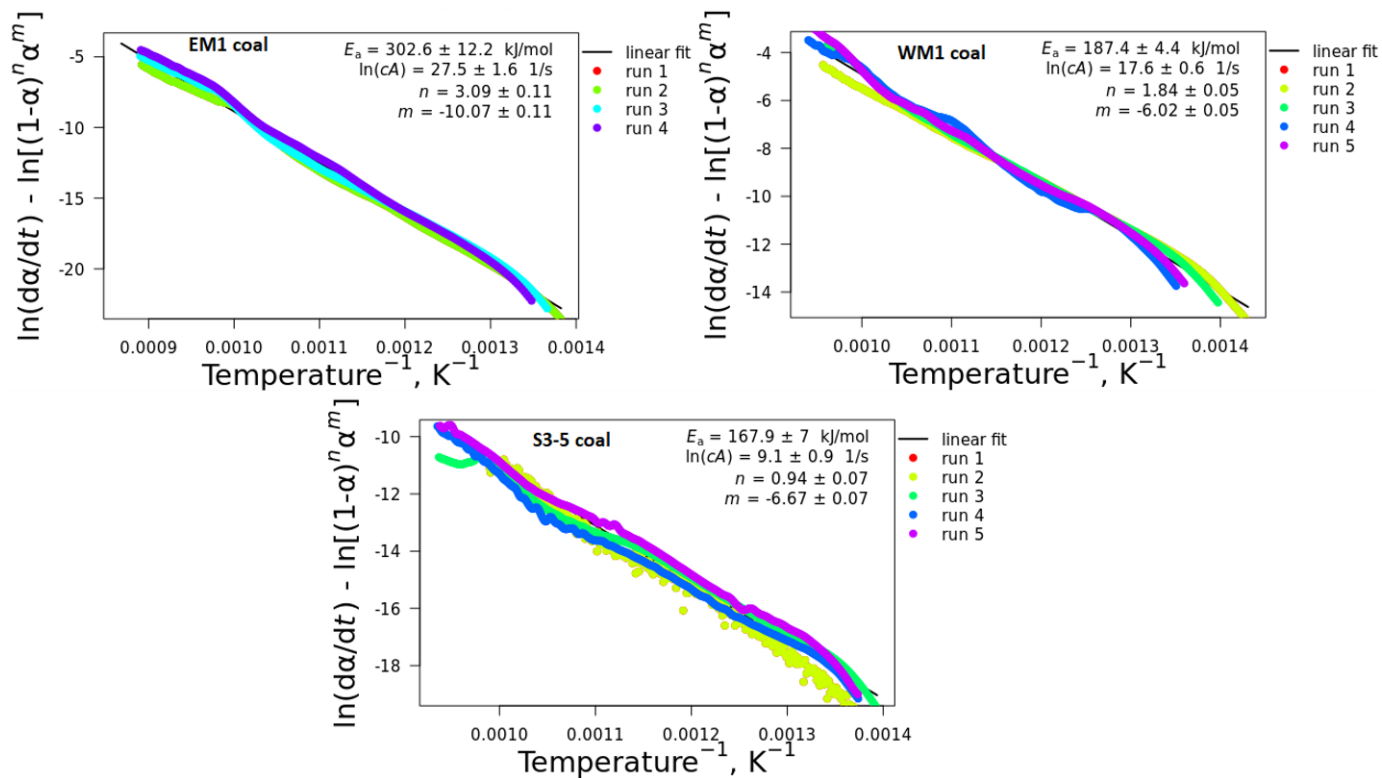


Figure 4.45: Kinetic curves for Model Fitting method (linear regression) for EM1, WM1 and S3-5 coals at different heating rates

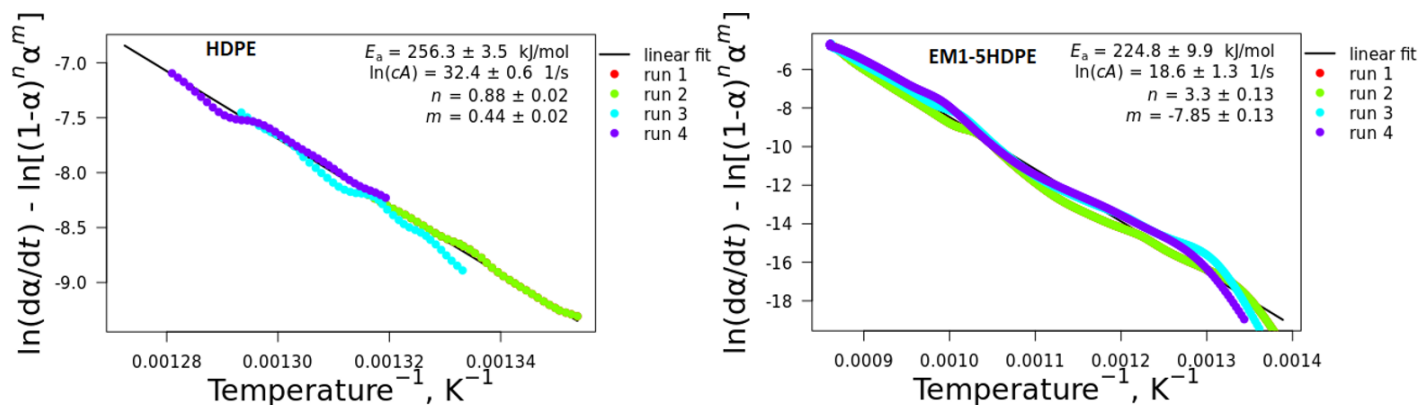


Figure 4.46: Kinetic curves for Model Fitting method (linear regression) for HDPE and the coal mixture at different heating rates

Table 4.29: Calculated kinetic parameters of coals and the coal mixture using Model Fitting method (linear regression)

Sample	E_a (kJ/mol)	A (1/s)	R^2
EM1	302.627.5	0.7734	
WM1	187.4	17.6	0.8108
S3-5	167.9	9.10.7011	
HDPE	256.3	32.4	0.9923
EM1-5HDPE	224.8	18.60.7621	

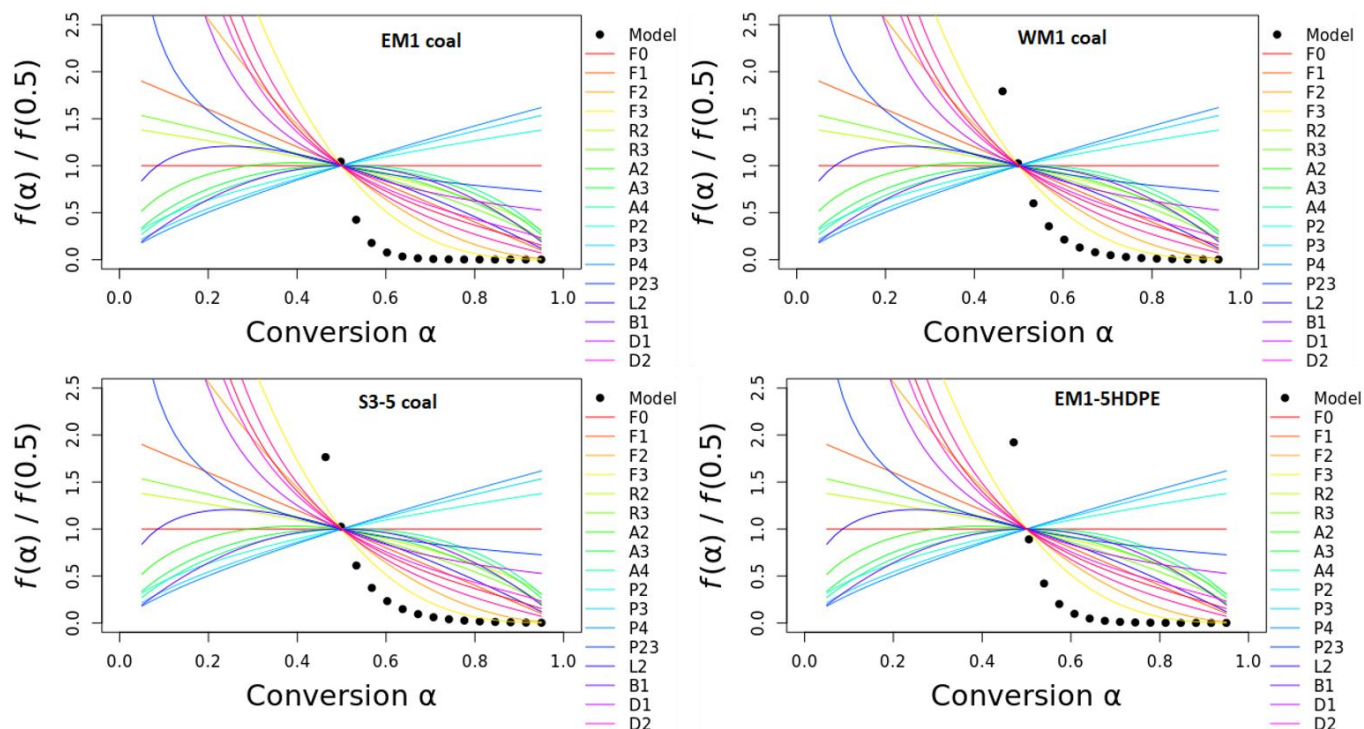


Figure 4.47: Master plots for Model Fitting method (linear regression) for EM1, WM1, S3-5 and the coal mixture

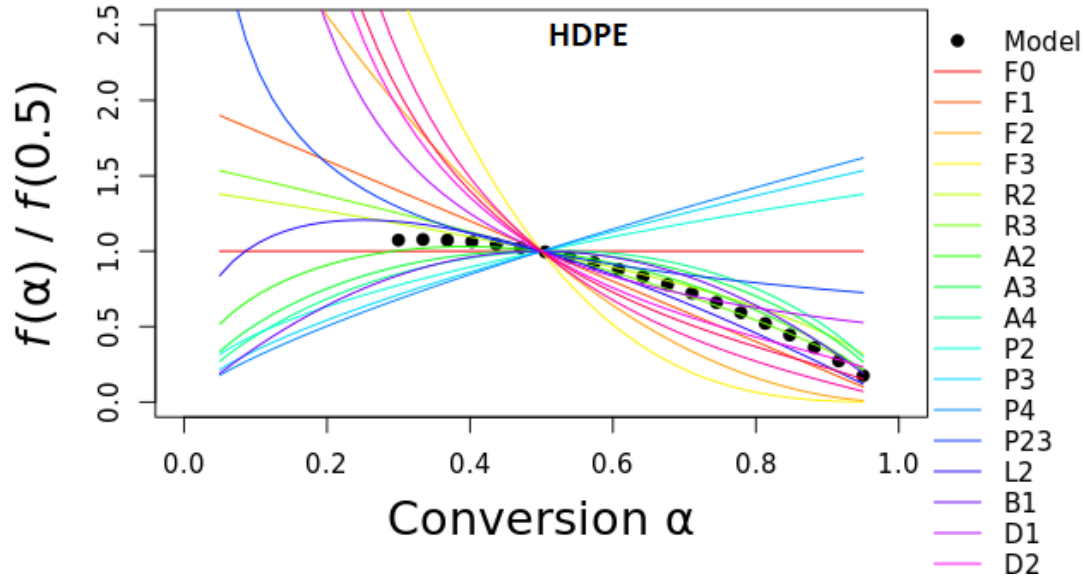


Figure 4.48: Master plot for Model Fitting method (linear regression) for the plastic

4.5.6 Kissinger Results

With various heating rates, the Kissinger method maintains a constant degree of conversion at the peak temperature (T_p). Figure 4.49 and Table 4.30 shows the kinetic parameters using Kissinger method which were found by linear regression line. The activation energy and pre-exponential factor extracted from the slope and intercept for EM1 were 196.85 kJ/mol and 10.19 1/s, respectively, for WM1 coal the activation energy and pre-exponential factor were 182.01 kJ/mol and 10.78 1/s, the calculations of activation energy and pre-exponential factor for S3-5 coal were 198.91 kJ/mol and 10.4 1/s. The Kissinger results for HDPE plastic were 295.97 kJ/mol for the activation energy and 16.6 1/s for the pre-exponential factor and lastly the coal mixture had an activation energy and pre-exponential factor of 298.12 kJ/mol and 17.21 1/s.

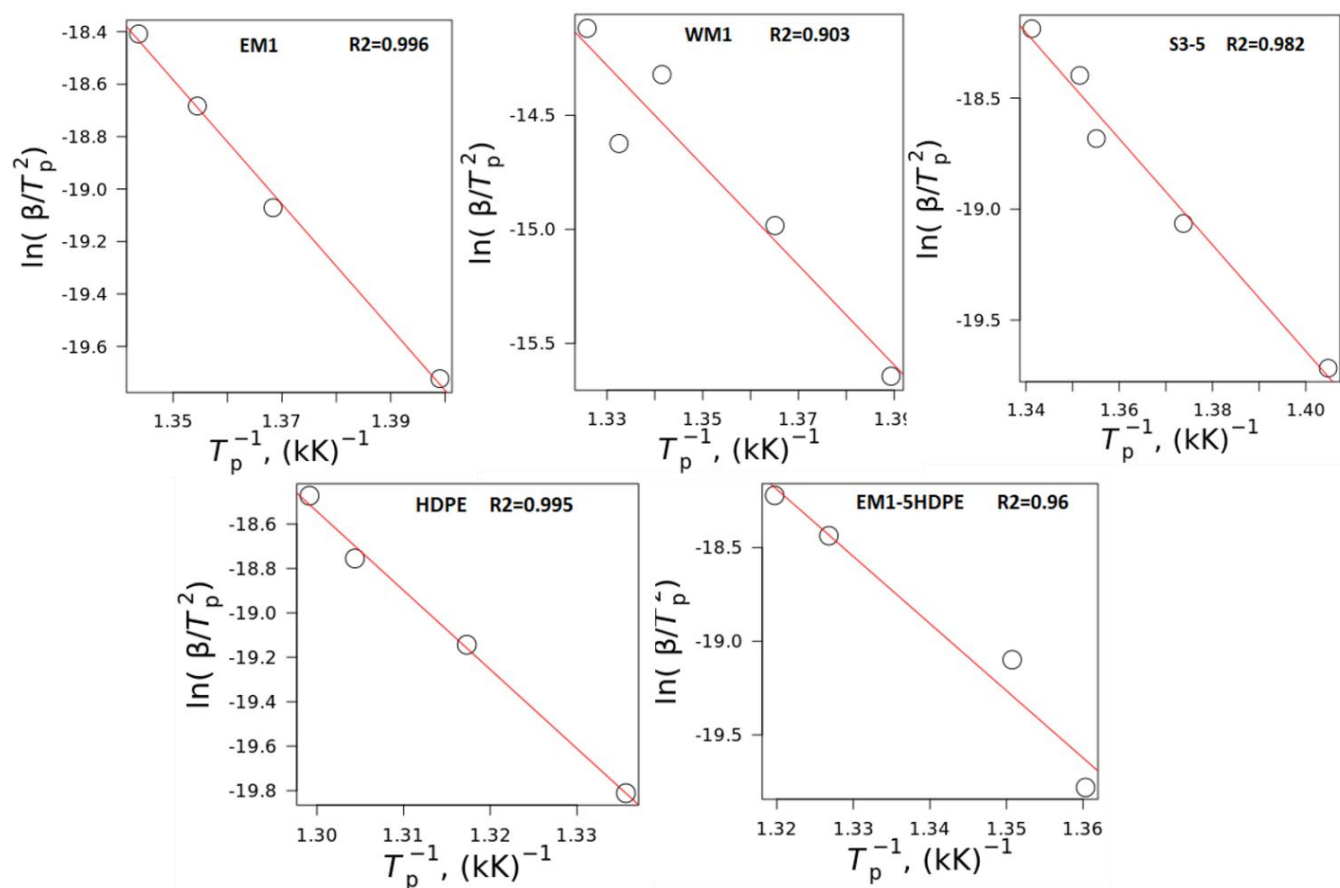


Figure 4.49: Kissinger plots of EM1, WM1, S3-5, HDPE, and the coal mixture at different heating rates

Table 4.30: Kinetic parameters for pyrolysis of coal, plastic and coal mixture using Kissinger method.

Sample	$E_a(\text{kJ/mol})$	$A(1/\text{s})$	R_2
EM1	196.85	10.19	0.99
WM1	182.01	10.78	0.903
S3-5	198.91	10.4	0.982
HDPE	295.97	16.6	0.995
EM1-5HDPE	298.12	17.21	0.96

CHAPTER 5

5 CONCLUSION

The pyrolysis and combustion of Morupule coal were performed using TGA/DSC3+ at five different heating rates of 5,10,15,20 and 25 °C/min. The influence of heating rate was examined. In this research kinetic study was presented where Arrhenius parameters were determined and compared through different methods of Kissinger, KAS, OFW, Friedman, Advanced integral Vyazovkin, model fitting (linear regression), and Coats Redfern. The heating rate affected the main pyrolysis process at temperatures ranging from 300-700 °C. From the experiments, it was found that with higher heating rates, the rate of coal thermal decomposition was increasing. The three raw coal samples (EM1, WM1 and S3-5) yielded 22.4–23.8% of volatile matter, moisture content between 3.6-4.3%, and ash yield between 21.7-23.8% respectively. According to the results reported, Botswana coal has a high carbon content ranging from 56.4 to 60.7% and a relatively low total sulphur content ranging from 1.0 to 1.9%, indicating that the coal is classified as having low sulphur content. Silica (SiO_2 , 39.1-42.5%) and alumina (Al_2O_3 , 23.4-28.0%) are the dominant constituents of Morupule coal ash, with lesser but still considerable proportions of CaO , Fe_2O_3 and TiO_2 .

The Arrhenius parameters from Friedman and advanced integral Vyazovkin showed a similar trend in the activation energy of the three coals. However, among all the methods advanced integral Vyazovkin method was considered to be best in order to evaluate kinetic parameters of Morupule coal pyrolysis, since it is largely recognized as one of the most accurate method for evaluation of activation energy from TGA data. The average activation energy calculated from the advanced integral Vyazovkin method was 167-284 kJ/mol.

The Arrhenius equation was integrated, and the approximate temperature integral was used to generate the OFW and KAS methods. Such methods, particularly for various activation energy processes, might result in certain systematic inaccuracies in the estimation of the activation energies. The mean activation energies calculated from the KAS and OFW methods were 227.04 to 391.07 kJ/mol and 202.59 to 354.27 kJ/mol respectively. With the Coats Redfern method, where the ordinate ($\ln(g(\alpha)/T_2)$) and abscissa ($1/T$) axes are correlated, model-fitting issues are particularly obvious and violate a fundamental requirement of linear regression. All models would have

relatively excellent fits that is high correlation coefficient, despite the fact that they may be inadequate descriptors of the process. Coal was found to decompose at a lower temperature than the plastic. EM1 coal has a broader temperature range for organic matter devolatilization than plastic. For the three types of coal, the method by which gas is formed during pyrolysis is essentially the same. According to intensity distribution H_2 and H_2O dominated the evolved gaseous products, while CO , CO_2 and CH_4 were the lesser products. Greater amounts of hydrogen and carbon monoxide can be used to produce synthesis gas (syngas). Researchers and the coal industry can better understand coal pyrolysis and gasification dynamics and optimize process conditions using the kinetic parameters discovered in this work.

6 FUTURE WORK

The following recommendations are made for future work to improve on the present work:

- After deconvolution with bi-Gaussian, the kinetic parameters of the independent stages of three coal pyrolysis must be evaluated.
- Try using the Shuffled Complex Evolution algorithm for global parameter optimization through inverse modeling.
- Investigate the influence of co-pyrolysis on the quality of the resulting residue products.
- Discover more information about the interactions between coal and other municipal waste plastics (Polystyrene (PS), Polyvinyl Chloride (PVC), Polypropylene (PP), and Polyethylene Terephthalate (PET)).

REFERENCES

- [1] Podolski, W. F., Schmalzer, D. K., Conrad, V., Lowenhaupt, D. E., Winschel, R. A., Klunder, E. B., ... & Smith, F. L, "Energy resources, conversion, and utilization," *Coal Conversion*, vol. 27, p. 13, 2008.
- [2] Cloke, M., Wu, T., Barranco, R., & Lester, E, "Char characterisation and its application in a coal burnout model," *Fuel*, vol. 82, no. 15-17, pp. 1989-2000, 2003.
- [3] World Coal Institute, "www.worldcoal.org," 2007. [Online]. [Accessed 20 February 2023].
- [4] Paul Baruya and John Kessels, "Coal Prospects in Botswana, Mozambique, Zambia, Zimbabwe and Namibia," World Coal, 2014.
- [5] World Energy Council, "World Energy Resources:Coal," 2013.
- [6] Agarwal, A., & Dintwa, E, "Assessment Of Energy Demand And Supply Framework In Botswana," *International Journal of Engineering Research and General Science*, vol. 4, no. 6, 2016.
- [7] Campoy, M., Gomez-Barea, A., Vidal, F. B., & Ollero, P, "Air–steam gasification of biomass in a fluidised bed: Process optimisation by enriched air," *Fuel Processing Technology*, vol. 90, no. 5, pp. 677-685, 2009.
- [8] Kamogelo P. Keboletse, Thato Mongalenyane, Leungo Kelebopile, Philip Oladijo and Said Kutua, "Investigating the suitability of Morupule Coal for Coal Gasification Technology," *Materials Research Society*, pp. 2235-2245, 2018.
- [9] Bikane, K., Yu, J., Shankar, R., Long, X., Paterson, N., & Millan, M, "Early-stage kinetics and char structural evolution during CO₂ gasification of Morupule coal in a wire-mesh reactor," *Chemical Engineering Journal*, vol. 421, p. 127803, 2021.
- [10] Misael Silas Nadiye-Tabbiruka, Wilfred Ddamba, Kifilwe Tsheko, Zakarea Kenewang and Estella Judith Salamula, "Thermal-gravimetric, calorimetric and chemical analytical characterisation of coal," *International Journal of Materials Science and Applications*, pp. 325-330, 2014.
- [11] Xu, Y., Zhang, Y., Wang, Y., Zhang, G., & Chen, L, "Thermogravimetric study of the kinetics and characteristics of the pyrolysis of lignite," *Reaction Kinetics, Mechanisms and Catalysis*, vol. 110, pp. 225-235, 2013.
- [12] Matsuoka, K., Akiho, H., Xu, W. C., Gupta, R., Wall, T. F., & Tomita, A, "The physical character of coal char formed during rapid pyrolysis at high pressure," *Fuel*, vol. 84, no. 1, pp. 63-69, 2005.
- [13] Roland Geyer , Jenna R. Jambeck, and Kara Lavender Law, "Production, use, and fate of all plastics ever made DOI: 10.1126/sciadv.1700782," *Science Advances*, vol. 3, no. 7, 2017.

- [14] Gould, J. E., Humme, M. A., & Senior, R. L, "Proceedings of Workshop on "Waste" Recycling," in *Somarelang Tikologo*, 1995.
- [15] Shashidhar Suresh & Vinodhkumar Vijayakumar, "Waste Management in Botswana, Master Thesis," *Energy And Environmental Engineering, Department Of Management And Engineering, Linkoping University, Sweden*, 2011.
- [16] D. Mmereki, "Current status of waste management in Botswana: A mini-review," *Waste Management & Research*, vol. 36, no. 7, pp. 555-576.
- [17] L. Vivero, C. Barriocanal, R. Álvarez, and M.A. Díez, "Effects of plastic wastes on coal pyrolysis behaviour and the structure of semicokes," *Journal of Analytical and Applied Pyrolysis*, vol. 74, no. 1-2, pp. 327-336, 2005.
- [18] V.I Sharypov, N.G Beregovtsova, B.N Kuznetsov, L Membrado, V.L Cebolla, N Marin, and J.V Weber, "Co-pyrolysis of wood biomass and synthetic polymers mixtures. Part III: Characterisation of heavy products," *Journal of Analytical and Applied Pyrolysis*, vol. 67, no. 2, pp. 325-340, 2003.
- [19] N Marin, S Collura, V.I Sharypov, N.G Beregovtsova, S.V Baryshnikov, B.N Kutnetzov, V Cebolla, and J.V Weber, "Copyrolysis of wood biomass and synthetic polymers mixtures. Part II: characterisation of the liquid phases," *Journal of Analytical and Applied Pyrolysis*, vol. 65, no. 1, pp. 41-55, 2002.
- [20] "Global Energy Monitor," [Online]. Available: https://www.gem.wiki/Botswana_and_coal. [Accessed 16 October 2023].
- [21] Eylem Önal, Basak Burcu Uzun and Ayse Eren Pütün, "Bio-oil production via co-pyrolysis of almond shell as biomass and high density polyethylene," *Energy conversion and Management*, pp. 704-710, 2014.
- [22] Daniel Mmereki, Baizhan Li and Portia Tshagofatso Loeto, "Household Perceptions on Solid Waste Management Practices in Developing Countries: The Experience of the Northern Part of Botswana, Donga Area," *Environmental Research Journal*, vol. 6, pp. 246-253, 2012.
- [23] Kgosiésele, E., & Zhaohui, L., "An evaluation of waste management in Botswana: Achievements and challenges," *Journal of American Sciences*, vol. 6, pp. 144-150, 2010.
- [24] Chunshan Song and Harold H. Schobert, "Opportunities for developing specialty chemicals and advanced materials from coals," *Fuel Processing Technology*, vol. 34, pp. 157-196, 1993.
- [25] Luo Yongkang and Chang Liping and Xie Kechang, "Effects of Coal Structure on Its Pyrolysis Characteristics Under N₂ and Ar Atmosphere," *Energy Sources*, vol. 23, pp. 717-725, 2001.
- [26] Andrew O. Odeh, Samuel E. Ogbeide and Charity Okieime, "Coal pyrolysis: Comparative evaluation of the technical performance of two Southern Hemisphere demineralized bituminous coals," *Thermal science and engineering*, vol. 3, pp. 1-9, 2017.

- [27] Hawkins, Robert., Nilsson, J., Oglesby, Rebecca., & Day, Danny., "Utilization of Biomass Pyrolysis for Energy Production, Soil Fertility and Carbon Sequestration," *UN Commission on Sustainable Development Partnerships Fair–Partnership in New Technologies for Small Island Developing States*, 2007.
- [28] A. O. Odeh, "Pyrolysis: Pathway to Coal Clean Technologies," in *Pyrolysis*, Benin City, Nigeria, 2017.
- [29] Gabriele Migliavacca, Emilio Parodi, Loretta Bonfanti, Tiziano Faravelli, Sauro Pierucci, and Eliseo Ranzi, "A general mathematical model of solid fuels pyrolysis," *Energy*, vol. 30, no. 8, pp. 1453-1468, 2005.
- [30] H.B Vuthaluru, "Thermal behaviour of coal/biomass blends during co-pyrolysis," *Fuel Processing Technology*, vol. 85, no. 2-3, pp. 141-155, 2004.
- [31] Heinzl, T, Siegle, V, Spliethoff, H, and Hein, K R.G., "Investigation of slagging in pulverized fuel co-combustion of biomass and coal at a pilot-scale test facility," *Fuel Processing Technology*, vol. 54, no. 1/3, pp. 109-125, 1998.
- [32] Pedersen, L. S., Michelsen, H. P., Kiil, S., Hansen, L. A., Dam-Johansen, K., Kildsig, F., Christensen, J., & Jespersen, P, "Full-scale co-firing of straw and coal," *Fuel*, vol. 75, no. 13, pp. 1584-1590, 1996.
- [33] Ying Gang Pan, Enrique Velo, and Luis Puigjaner, "Pyrolysis of blends of biomass with poor coals," *Fuel*, vol. 75, no. 4, pp. 412-418, 1996.
- [34] Meesri, C. and Moghtaderi, B, "Lack of synergistic effects in the pyrolytic characteristics of woody biomass/ coal blends under low and high heating rates regimes," *Biomass & Bioenergy*, vol. 23, pp. 55-66, 2002.
- [35] Despina Vamvuka, Emmanouil Kakaras, Eleni Kastanaki and Panagiotis Grammelis, "Pyrolysis characteristics and kinetics of biomass residuals mixtures with lignite," *Fuel*, vol. 82, pp. 1949-1960, 2003.
- [36] Kandasamy Jayaraman, Mustafa Versan Kok and Iskender Gokalp, "Combustion mechanism and model free kinetics of different origin coal samples: Thermal analysis approach," *Energy* 204, pp. 2-9, 2020.
- [37] Meng Ma, Yonghui Bai, Xudong Song, Jiaofei Wang, Weiguang Su, Min Yao and Guangsuo Yu, "Investigation into the co-pyrolysis behaviors of cow manure and coal blending by TG–MS," *Science of The Total Environment*, vol. 728, p. 138828, 2020.
- [38] Zhang Shi-Xin, Li Chang-Rong, Huang Run, Xiao Yang-Wu, Mao Rui, Huang Jun and Zhou Cheng-Lin,, "Thermogravimetric study of the kinetics and characteristics of the pyrolysis of pulverized coal," *Material Research Express*, 2020.

- [39] Guanghua Wang, Zhiyong Ma & Qingdong Wang, "Effect of metal salts on the decomposition characteristics of Mengdong lignite," *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, vol. 42, pp. 246-257, 2020.
- [40] Niloy Kundu, Pinakpani Biswas, Prasenjit Bhunia, Rita Ghosh, and Supriya Sarkar, "Evolution characteristics of metallurgical coals for coke making through thermogravimetric-mass spectroscopic measurements," *Journal of Environmental Chemical Engineering*, vol. 9, no. 6, p. 106874, 2021.
- [41] Seo DK, Parka SS, Kim YT, Hwang J, and Yu TU, "Study of coal pyrolysis by thermogravimetric analysis (TGA) and concentration measurements of the evolved species," *Journal of Analytical and Applied Pyrolysis*, pp. 209-216, 2011.
- [42] Lu Yongkang, Chang Liping and Xie Kechang, "Effects of Coal Structure on Its Pyrolysis Characteristics Under N₂ and Ar Atmosphere," *Energy Sources*, vol. 23, pp. 717-725, 2001.
- [43] Lin, Y., Li, Q., Ji, K., Li, X., Yu, Y., Zhang, H., ... & Sun, L., "Thermogravimetric analysis of pyrolysis kinetics of Shenmu bituminous coal," *Reaction Kinetics, Mechanisms and Catalysis*, vol. 113, pp. 269-279, 2014.
- [44] K. Ozbas, "Effects of particle size on pyrolysis characteristics of Elbistan lignite," *Journal of Analytical Calorimetry*, pp. 641-649, 2008.
- [45] S. Hanson, J.W. Patrick, and A. Walker, "The effect of coal particle size on pyrolysis and steam gasification," *Fuel*, vol. 81, no. 5, pp. 531-537, 2002.
- [46] GÜldoğan, Y., Evren, V., Durusoy, T., & Bozdemir, T., "Effects of heating rate and particle size on pyrolysis kinetics of Mengen lignite," *Energy Sources*, vol. 23, no. 4, pp. 337-344, 2001.
- [47] R. W. Bryers, "Investigation of the reactivity of macerals using thermal analysis," *Fuel Processing Technology*, vol. 44, pp. 25-54, 1995.
- [48] C.G. Thomas, M.E. Gosnell, E. Gawronski, D. Phont-anant, & M. Shibaoka, "The behaviour of inertinite macerals under pulverised fuel (pf) combustion conditions," *Organic Geochemistry*, vol. 20, no. 6, pp. 779-788, 1993.
- [49] S. Biswas, N. Choudhury, P. Sarkar, A. Mukherjee, S.G. Sahu, P. Boral, and A. Choudhury, "Studies on the combustion behaviour of blends of Indian coals by TGA and Drop Tube Furnace," *Fuel Processing Technology*, vol. 87, no. 3, pp. 191-199, 2006.
- [50] Wang Yu, Zou Chong, Li Jianyun, Liu Zhiwei, Zhao Junxue and Wang Wei'an, "Combustion performance of blast furnace pulverized coal mixed with metallurgical sludge," *Engineering Science and Technology*, 2020.

- [51] Pritam Kumar, and Barun Kumar Nandi, "Assessment of combustion characteristics of high ash Indian coal, petroleum coke and their blends for cement industry using TGA," *Cleaner Chemical Engineering*, vol. 5, pp. 2772-7823, 2023.
- [52] Mauro Mureddu, Federica Dessì, Alessandro Orsini, Francesca Ferrara, and Alberto Pettinau, "Air- and oxygen-blown characterization of coal and biomass by thermogravimetric analysis," *Fuel*, vol. 212, pp. 626-637, 2018.
- [53] Duarte Magalhaes, Feyza Kazanc, Juan Riaza, Sevgi Erensoy, Ozde Kabakli, and Hannah Chalmers, "Combustion of Turkish lignites and olive residue: Experiments and kinetic modelling," *Fuel*, pp. 868-876, 2017.
- [54] M.J.G Alonso, A.G Borrego, D Alvarez, W Kalkreuth, and R Menéndez, "Physicochemical transformations of coal particles during pyrolysis and combustion," *Fuel*, vol. 80, no. 13, pp. 1857-1870, 2001.
- [55] Deepak Chandra Sau, Amit Banerjee, Sanchita Chakravarty, Pragyan Senapati, Rabiranjana Murmu, and Harekrushna Sutar, "Thermal Decomposition Behavior and Kinetic Study of Jamadoba Coal and Its Density Separated Macerals: A Non-Isothermal Approach," *Advances in Chemical Engineering and Science*, vol. 11, no. 3, pp. 203-227, 2021.
- [56] Angeles G. Borrego, Diego Alvarez, and Rosa Menendez, "Effects of Inertinite Content in Coal on Char Structure and Combustion," *Energy & Fuels*, pp. 702-708, 1997.
- [57] V. C. Pandey, Phytomanagement of Fly Ash, Lucknow: Department of Environmental Science, Babasaheb Bhimrao Ambedkar University, India, 2020.
- [58] Kassim, T. A., & Williamson, K. J., Environmental Impact Assessment of Recycled Wastes on Surface and Ground Waters: Concepts; Methodology and Chemical Analysis (Vol. 5), Springer Science & Business Media., 2005.
- [59] Amr S. Meawad , Darinka Y. Bojinova, & Yoncho G. Pelovski, "An overview of metals recovery from thermal power plant solid wastes," *Waste Management*, vol. 30, no. 12, pp. 2548-2559, 2010.
- [60] A. C. Chang, L. J. Lund, A. L. Page, & J. E. Warneke, "Physical Properties of Fly Ash-Amended Soils," *Journal of Environmental Quality*, vol. 6, no. 3, pp. 267-270, 1977.
- [61] Adriano, D. C., Page, A. L., Elseewi, A. A., Chang, A. C., & Straughan, I., "Utilization and disposal of fly ash and other coal residues in terrestrial ecosystems: a review," *Journal of Environmental quality*, vol. 9, no. 3, pp. 333-344, 1980.
- [62] Moreno, N., Querol, X., Andrés, J. M., Stanton, K., Towler, M., Nugteren, H., ... & Jones, R, "Physico-chemical characteristics of European pulverized coal combustion fly ashes," *Fuel*, vol. 84, no. 11, pp. 1351-1363, 2005.

- [63] Ainsworth, C. C., & Rai, D., "Chemical characterization of fossil fuel combustion wastes: Final report," Pacific Northwest Lab., Richland, WA (USA); Electric Power Research Inst, Palo Alto, CA, 1987.
- [64] C. Papastefanou, "Radioactivity of coals and fly ashes," *Journal of radioanalytical and nuclear chemistry*, vol. 275, no. 1, pp. 29-35, 2008.
- [65] Gao, X., Wang, W., Ye, T., Wang, F., & Lan, Y., "Utilization of washed MSWI fly ash as partial cement substitute with the addition of dithiocarbamic chelate," *Journal of environmental management*, vol. 88, no. 2, pp. 293-299, 2008.
- [66] Mohan, S., & Gandhimathi, R., "Removal of heavy metal ions from municipal solid waste leachate using coal fly ash as an adsorbent," *Journal of hazardous materials*, vol. 169, no. 1-3, pp. 351-359, 2009.
- [67] Somerset, V., Petrik, L., & Iwuoha, E., "Alkaline hydrothermal conversion of fly ash precipitates into zeolites 3: the removal of mercury and lead ions from wastewater," *Journal of environmental management*, vol. 87, no. 1, pp. 125-131, 2008.
- [68] G. Dirk, "Pulverised fuel ash products solve the sewage sludge problems of the wastewater industry," *Waste Management*, vol. 16, no. 1-3, pp. 51-57, 1996.
- [69] "Energy Education," [Online]. Available: https://energyeducation.ca/encyclopedia/Coal_liquefaction. [Accessed 21 10 2023].
- [70] Mohammad Ishaq, Imtiaz Ahmad, Mohammad Shakirullah, Mohammad Arsala Khan, Habib ur Rehman, & Ali Bahader,, "Pyrolysis of some whole plastics and plastics–coal mixtures," *Energy Conversion and Management*, vol. 47, no. 18-19, pp. 3216-3223, 2006.
- [71] P. Straka, J. Náhunková, & Z. Brožová,, "Kinetics of copyrolysis of coal with polyamide 6," *Journal of Analytical and Applied Pyrolysis*, vol. 71, no. 1, pp. 213-221, 2004.
- [72] M. Ahmaruzzaman, & D.K. Sharma,, "Non-isothermal kinetic studies on co-processing of vacuum residue, plastics, coal and petrocrop," *Journal of Analytical and Applied Pyrolysis*, vol. 73, no. 2, pp. 263-275, 2005.
- [73] Melendi-Espina, Sonia & Díez Díaz-Estébanez, Maria & Alvarez, R., "Evolution of volatile products of coal and plastic wastes during co-pyrolysis," in *International Conference on Coal science and Technology (ICCS&T 2011)*, Oviedo (Spain), 2011.
- [74] S. Melendi-Espina, R. Alvarez, M.A. Diez and M.D. Casal, "Coal and plastic waste co-pyrolysis by thermal analysis–mass spectrometry," *Fuel Processing Technology*, vol. 137, pp. 351-358, 2015.
- [75] Seiji Nomura, Kenji Kato, Tomoyuki Nakagawa, and Ikuo Komaki,, "The effect of plastic addition on coal caking properties during carbonization,," *Fuel, Volume 82, Issue 14,,* pp. 1775-1782,, 2003,.

- [76] Junqing Cai, Yiping Wang, Limin Zhou, and Qunwu Huang,, "Thermogravimetric analysis and kinetics of coal/plastic blends during co-pyrolysis in nitrogen atmosphere," *Fuel Processing Technology*, vol. 89, no. 1, pp. 21-27, 2008.
- [77] M García-Pérez, A Chaala, J Yang, and C Roy,, "Co-pyrolysis of sugarcane bagasse with petroleum residue. Part I: thermogravimetric analysis," *Fuel*, vol. 80, no. 9, pp. 1245-1258, 2001.
- [78] Chattopadhyay, Jayeeta & Kim, Chulho & Kim, Raehyun & Pak, and Daewon., "Thermogravimetric characteristics and kinetic study of biomass co-pyrolysis with plastics," *Korean Journal of Chemical Engineering*, pp. 1047-1053, 2008.
- [79] V.I. Sharypov, N. Marin, N.G. Beregovtsova, S.V. Baryshnikov, B.N. Kuznetsov, V.L. Cebolla, and J.V. Weber,, "Co-pyrolysis of wood biomass and synthetic polymer mixtures. Part I: influence of experimental conditions on the evolution of solids, liquids and gases," *Journal of Analytical and Applied Pyrolysis*, vol. 64, no. 1, pp. 15-28, 2002.
- [80] Imane Boumanchar, Younes Chhiti, Fatima Ezzahrae M'hamdi Alaoui, Mohamed Elkhouchi, Abdelaziz Sahibed-dine, Fouad Bentiss, Charafeddine Jama, & Mohammed Bensitel,, "Investigation of (co)-combustion kinetics of biomass, coal and municipal solid wastes," *Waste Management*, vol. 97, pp. 10-18, 2019.
- [81] Rago, Y. P., Collard, F. X., Görgens, J. F., Surroop, D., & Mohee, R, "Co-combustion of torrefied biomass-plastic waste blends with coal through TGA: Influence of synergistic behaviour," *Energy*, vol. 239, p. 121859, 2022.
- [82] Liao Xinjie, Surjit Singh, Haiping Yang, Chunfei Wu, & Shihong Zhang,, "A thermogravimetric assessment of the tri-combustion process for coal, biomass and polyethylene," *Fuel*, vol. 287, p. 119355, 2021.
- [83] Caballero, J. A., & Conesa, J. A., "Mathematical considerations for nonisothermal kinetics in thermal decomposition," *Journal of analytical and applied pyrolysis*, vol. 73, no. 1, pp. 85-100, 2005.
- [84] A. Álvarez, C. Pizarro, R. García, J.L. Bueno, & A.G. Lavín,, "Determination of kinetic parameters for biomass combustion," *Bioresource Technology*, vol. 216, pp. 36-43, 2016.
- [85] Heireche, L., & Belhadji, M, "The methods Matusita, Kissinger and Ozawa in the study of the crystallization of glasses. The case of Ge-Sb-Te alloys," *Chalcogenide Letters*, vol. 4, no. 2, pp. 23-33, 2007.
- [86] Guozhan Jiang, Daniel J. Nowakowski, and Anthony V. Bridgwater,, "A systematic study of the kinetics of lignin pyrolysis," *Thermochimica Acta*, vol. 498, no. 1-2, pp. 61-66, 2010.
- [87] Nicolas Sbirrazzuoli, Luc Vincent, Alice Mija, and Nathanael Guigo, "Integral, differential and advanced isoconversional methods Complex mechanisms and isothermal predicted conversion–time curves," *Chemometrics and Intelligent Laboratory Systems*, vol. 96, p. 219–226, 2009.

- [88] Sergey Vyazovkin, Alan K. Burnham, José M. Criado, Luis A. Pérez-Maqueda, Crisan Popescu, and Nicolas Sbirrazzuoli,, "ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data," *Thermochimica Acta*, vol. 520, no. 1-2, pp. 1-19, 2011.
- [89] Sergey Vyazovkin and Nicolas Sbirrazzuoli,, "Isoconversional Kinetic Analysis of Thermally Stimulated Processes in Polymers," *Macromolecular Rapid Communications*, vol. 27, pp. 1515-1532, 2006.
- [90] Sergey Vyazovkin and Nicolas Sbirrazzuoli,, "Mechanism and Kinetics of Epoxy-Amine Cure Studied by Differential Scanning Calorimetry,," *Macromolecules*,, pp. 1867-1873, 1996,.
- [91] Nathanael Guigo, Alice Mija, Luc Vincent and Nicolas Sbirrazzuoli, "Chemorheological analysis and model-free kinetics of acid catalysed furfuryl alcohol polymerization," *Physical Chemistry Chemical Physics*, pp. 5359-5366, 2007.
- [92] T. Ozawa, "A new method of analyzing thermogravimetric data," *Bulletin of the chemical society of Japan*, vol. 38, no. 11, pp. 1881-1886, 1965.
- [93] H. E. Kissinger, "Reaction Kinetics in Differential Thermal Analysis," *Analytical Chemistry*, vol. 29, no. 11, pp. 1702-1706, 1957.
- [94] H. L. Friedman, "Kinetics of thermal degradation of char-forming plastics from thermogravimetry. Application to a phenolic plastic," *In Journal of polymer science part C: polymer symposia*, vol. 6, no. 1, pp. 183-195, 1964.
- [95] Junmeng Cai & Sibinuer Alimujiang, "Kinetic Analysis of Wheat Straw Oxidative Pyrolysis Using Thermogravimetric Analysis: Statistical Description and Isoconversional Kinetic Analysis," *Industrial & Engineering Chemistry Research*, vol. 48, no. 2, pp. 619-624, 2009.
- [96] P. Šimon, "Isoconversional Methods," *Journal of Thermal Analysis and Calorimetry*, vol. 76, pp. 123-132, 2004.
- [97] A. Khawam, "Application of solid-state kinetics to desolvation reactions," *University of Iowa*, 2007.
- [98] C. D. Doyle, "Estimating isothermal life from thermogravimetric data," *Journal of Applied Polymer Science*, vol. 6, no. 24, pp. 639-642, 1962.
- [99] Vyazovkin, S., & Wight, C. A., "Isothermal and nonisothermal reaction kinetics in solids: in search of ways toward consensus," *The Journal of Physical Chemistry A*, vol. 101, no. 44, pp. 8279-8284, 1997.
- [100] Vikul Vasudev, Xiaoke Ku, and Jianzhong Lin,, "Kinetic study and pyrolysis characteristics of algal and lignocellulosic biomasses," *Bioresource Technology*, vol. 288, p. 121496, 2019.

- [101] Laipeng Luo, Zhiyi Zhang, Chong Li, Nishu, Fang He and Xingguang Zhang, "Insight into master plots method for kinetic analysis of lignocellulosic biomass pyrolysis," *Energy*, vol. 233, p. 121194, 2021.
- [102] A. Khawam, Application of solid-state kinetics to desolvation reactions, The University of Iowa, 2007.
- [103] Ammar Khawam & Douglas R. Flanagan, "Complementary Use of Model-Free and Modelistic Methods in the Analysis of Solid-State Kinetics," *The Journal of Physical Chemistry B*, vol. 109, pp. 10073-10080, 2005.
- [104] Pérez-Maqueda, L. A., Criado, J. M., & Sanchez-Jiménez, P. E, "Combined kinetic analysis of solid-state reactions: a powerful tool for the simultaneous determination of kinetic parameters and the kinetic model without previous assumptions on the reaction mechanism," *The journal of physical chemistry A*, vol. 110 , p. 12456–12462, 2006.
- [105] Coats AW & Redfern JP, "Kinetic Parameters from Thermogravimetric Data," *Nature*, vol. 201, pp. 68-69, 1964.
- [106] Gautschi W and Cahill WF, Exponential integral and related functions. In M. Abramowitz and I. Stegun (eds), Handbook of mathematical functions with formulas, graphs, and mathematical tables,, Washington, DC: National Bureau of Standards, 1964.
- [107] Vyazovkin, S., Burnham, A. K., Favergeon, L., Koga, N., Moukhina, E., Pérez-Maqueda, L. A., & Sbirrazzuoli, N., "ICTAC Kinetics Committee recommendations for analysis of multi-step kinetics," *Thermochimica acta*, vol. 689, p. 178597, 2020.
- [108] B. Janković, "The kinetic modeling of the non-isothermal pyrolysis of Brazilian oil shale: Application of the Weibull probability mixture model," *Journal of Petroleum Science and Engineering*, vol. 111, pp. 25-36, 2013.
- [109] Junmeng Cai, Di Xu, Zhujun Dong, Xi Yu, Yang Yang, Scott W. Banks & Anthony V. Bridgwater, "Processing thermogravimetric analysis data for isoconversional kinetic analysis of lignocellulosic biomass pyrolysis: Case study of corn stalk," *Renewable and Sustainable Energy Reviews*, vol. 82, pp. 2705-2715, 2018.
- [110] Jankovic BZ, and Jankovic MM, "Pyrolysis of pine and beech wood samples under isothermal experimental conditions. The determination of kinetic triplets," *Cellulose Chemistry & Technology*, vol. 47, pp. 681-97, 2013.
- [111] Wu W, Cai J, and Liu R., "Isoconversional Kinetic Analysis of Distributed Activation Energy Model Processes for Pyrolysis of Solid Fuels," *Industrial & Engineering Chemistry Research*, vol. 52, pp. 14376-83, 2013.

- [112] Varhegyi G, Bobaly B, Jakab E and Chen H., "Thermogravimetric study of biomass pyrolysis kinetics. A distributed activation energy model with prediction tests," *Energy & Fuels*, vol. 25, pp. 24-32, 2013.
- [113] Avid B, Purevsuren B, Born M, Dugarjav J, Davaajav Y, and Tuvshinjargal A., "Pyrolysis and TG analysis of shivee ovoos coal from Mongolia," *Journal of Thermal Analysis and Calorimetry*, vol. 68, pp. 877-885, 2002.
- [114] Diaz-Faes E, Barriocanal C, Diez MA and Alvarez R, "Applying TGA parameters in coke quality prediction models," *Journal of Analytical and Applied Pyrolysis*, vol. 79, pp. 154-160, 2007.
- [115] Jayaraman K, and Gokalp I., "Gasification characteristics of petcoke and coal blended petcoke using thermogravimetry and mass spectrometry analysis," *Applied Thermal Engineering*, pp. 10-19, 2015.
- [116] Saikia BK, Boruah RK, Gogoi PK, and Baruah BP, "XRD and FT-IR investigations of sub-bituminous Assam coals," *Fuel Processing Technology*, pp. 196-203, 2009.
- [117] Zou, C., Ma, C., Zhao, J., Shi, R., & Li, X., "Characterization and non-isothermal kinetics of Shenmu bituminous coal devolatilization by TG-MS," *Journal of analytical and applied pyrolysis*, vol. 127, pp. 309-320, 2017.
- [118] Liu, J., Jiang, X., Shen, J., & Zhang, H., "Pyrolysis of superfine pulverized coal. Part 1. Mechanisms of methane formation," *Energy conversion and management*, vol. 87, pp. 1027-1038, 2014.
- [119] Nermark Fiona, "Application of subcritical and supercritical fluids in coal extraction and analysis," *Lund University*, 2022.
- [120] Guijian Liu, Pengyue Yang, Zicheng Peng, Guiliang Wang, and Wei Zhang, "Comparative study of the quality of some coals from the Zibo coal field," *Energy*, vol. 28, pp. 969-978, 2003.
- [121] M.A. Serageldin, & Wei-Ping Pan, "Coal: Kinetic analysis of thermogravimetric data," *Thermochimica Acta*, vol. 71, no. 1-2, pp. 1-14, 1983.
- [122] Mohebbi, M., Rajabipour, F., & Scheetz, B. E., "Evaluation of two-atmosphere thermogravimetric analysis for determining the unburned carbon content in fly ash," *Advances in Civil Engineering Materials*, vol. 6, no. 1, pp. 258-279, 2017.
- [123] D. N. V. Muravyev, 2016-2022. [Online].
- [124] C.-L. Chou, "Sulfur in coals: A review of geochemistry and origins," *International Journal of Coal Geology*, pp. 1-13, 2012.
- [125] ASTM International (2003), ASTM D3173-11 Standard Test Method for Moisture in the Analysis Sample of Coal and Coke 1.

- [126] ASTM International (2007), ASTM D3175-11 Standard Test Method for Volatile Matter in the Analysis Sample of Coal and Coke, West Conshohocken.
- [127] ASTM International (2013), ASTM D5142 Standard Practice for Proximate Analysis of Coal and Coke 1.
- [128] ASTM International (2002), ASTM D3174-02 Standard Test Method for Ash in the Analysis Sample of Coal and Coke from Coal.
- [129] ASTM International (2014), ASTM D5373 - 21 Standard Test Methods for Determination of Carbon, Hydrogen and Nitrogen in Analysis Samples of Coal and Carbon in Analysis Samples of Coal and Coke.
- [130] ASTM International (2008), ASTM D4239 Standard test methods for sulfur in the analysis sample of coal and coke using high-temperature tube furnace combustion methods.
- [131] ASTM International (2007), ASTM D5865-98a A standard test method for gross calorific value of coal and coke.
- [132] A. D. Karathanasis, and B. F. Hajek, "Elemental Analysis by X-Ray Fluorescence Spectroscopy," in *Methods of Soil analysis*, 1996, pp. 161-223.
- [133] Suryanarayana C and M.G. Norton, "X-ray diffraction: a practical approach," *Springer Science & Business Media*, 2013.
- [134] S. Sharma, "Physics Wave Online Education," 24 May 2020. [Online].
- [135] Misael Silas Nadiye-Tabbiruka, Wilfred Ddamba, Kifilwe Tsheko, Zakarea Kenewang and Estella Judith Salamula, "Thermal-Gravimetric, Calorimetric and Chemical Analytical Characterisation of Coal," *International Journal of Materials Science and Applications*, vol. 3, no. 6, pp. 325-330, 2014.
- [136] S. Sharma and A. K. Ghoshal,, "'Study of kinetics of co-pyrolysis of coal and waste LDPE blends under argon atmosphere",' *Fuel*, vol. 89, no. 12, pp. 3943-3951, 2010.
- [137] Muhammad F. Irfan, Muhammad R. Usman,& K. Kusakabe, "Coal gasification in CO₂ atmosphere and its kinetics since 1948: A brief review," *Energy*, vol. 36, no. 1, pp. 12-40, 2011.
- [138] Aviv Hassid, Mathias Klinger, Steffen Krzack and Haim Cohen, "TGA-DSC Combined Coal Analysis as a Tool for QC (Quality Control) and Reactivity Patterns of Coals," *ACS Omega*, vol. 7, no. 2, pp. 1893-1907, 2022.
- [139] Jayeeta Chattopadhyay, Chulho Kim, Raehyun Kim, and Daewon Pak, "Thermogravimetric characteristics and kinetic study of biomass co-pyrolysis with plastics," *Korean Journal of Chemical Engineering*, vol. 25, no. 5, pp. 1047-1053, 2008.

- [140] A Domínguez, C.G Blanco, C Barriocanal, R Alvarez, & M.A Díez,, "Gas chromatographic study of the volatile products from co-pyrolysis of coal and polyethylene wastes," *Journal of Chromatography A*, vol. 918, no. 1, pp. 135-144, 2001.
- [141] Davis, A., Derbyshire, F. J., Finseth, D. H., Lin, R., Stansberry, P. G., & Terrer, M. T, "Catalytic hydrogenation of coals in the absence of solvent: 1. Compositional changes of an hvA bituminous coal by chemical analysis and reflected fluorescent light microscopy," *Fuel*, vol. 65, no. 4, pp. 500-506, 1986.
- [142] Bockhorn, H., Hornung, A., Hornung, U., & Schawaller, D., "Kinetic study on the thermal degradation of polypropylene and polyethylene," *Journal of Analytical and Applied Pyrolysis*, vol. 48, no. 2, pp. 93-109, 1999.
- [143] Hongcun Bai, Ning Mao, Ruihan Wang, Zhuangmei Li, Meilin Zhu, & Qiang Wang, "Kinetic characteristics and reactive behaviors of HSW vitrinite coal pyrolysis: A comprehensive analysis based on TG-MS experiments, kinetics models and ReaxFF MD simulations," *Energy Reports*, vol. 7, pp. 1416-1435, 2021.
- [144] Bin Zhou, Lei Shi, Qingya Liu, & Zhenyu Liu, "Examination of structural models and bonding characteristics of coals," *Fuel*, vol. 184, pp. 799-807, 2016.
- [145] Yu-Gao Wang, Xian-Yong Wei, Sheng-Kang Wang, Zhan-Ku Li, Peng Li, Fang-Jing Liu, & Zhi-Min Zong, "Structural evaluation of Xiaolongtan lignite by direct characterization and pyrolytic analysis," *Fuel Processing Technology*, vol. 144, pp. 248-254, 2016.
- [146] Van Heek, K. H., & Hodek, W., "Structure and pyrolysis behaviour of different coals and relevant model substances," *Fuel*, vol. 73, no. 6, pp. 886-896, 1994.
- [147] Makgato, S. S., & Chirwa, E. M. N., "Waterberg coal characteristics and SO₂ minimum emissions standards in South African power plants," *Journal of environmental management*, vol. 201, pp. 294-302, 2017.
- [148] Matjie, R. H., Li, Z., Ward, C. R., Bunt, J. R., & Strydom, C. A, "Determination of mineral matter and elemental composition of individual macerals in coals from Highveld mines," *Journal of the Southern African Institute of Mining and Metallurgy*, vol. 116, no. 2, pp. 169-180, 2016.
- [149] Damartzis, T., Vamvuka, D., Sfakiotakis, S., & Zabaniotou, A, "Thermal degradation studies and kinetic modeling of cardoon (*Cynara cardunculus*) pyrolysis using thermogravimetric analysis (TGA)," *Bioresource technology*, vol. 102, no. 10, pp. 6230-6238, 2011.
- [150] Heydari, M., Rahman, M., & Gupta, R., "Kinetic study and thermal decomposition behavior of lignite coal," *International Journal of Chemical Engineering*, 2015.
- [151] Masoud, M. S., Ghareeb, D. A., & Ahmed, S. S., "Synthesis, characterization, spectral, thermal analysis and computational studies of thiamine complexes," *Journal of Molecular Structure*, vol. 1137, pp. 634-648, 2017.

- [152] Emara, R., Masoud, M. S., & Abboudy, S, "Optical, electrical, thermal and kinetic studies for some pyrimidine ligands and their complexes," *Journal of Non-Crystalline Solids*, vol. 597, p. 121873, 2022.
- [153] Jingchong Yan, Hanren Jiao, Zhanku Li, Zhiping Lei, Zhicai Wang, Shibiao Ren, Hengfu Shui, Shigang Kang, Honglei Yan, & Chunxiu Pan, "Kinetic analysis and modeling of coal pyrolysis with model-free methods," *Fuel*, vol. 241, pp. 382-391, 2019.
- [154] Jingchong Yan, Qitong Yang, Li Zhang, Zhiping Lei, Zhanku Li, Zhicai Wang, Shibiao Ren, Shigang Kang, & Hengfu Shui,, "Investigation of kinetic and thermodynamic parameters of coal pyrolysis with model-free fitting methods," *Carbon Resources Conversion*, vol. 3, pp. 173-181, 2020.
- [155] Varma, A. K., Lal, N., Rathore, A. K., Katiyar, R., Thakur, L. S., Shankar, R., & Mondal, P., "Thermal, kinetic and thermodynamic study for co-pyrolysis of pine needles and styrofoam using thermogravimetric analysis," *Energy*, vol. 218, p. 119404, 2021.
- [156] Gotor, F. J., Criado, J. M., Malek, J., & Koga, N. , "Kinetic analysis of solid-state reactions: the universality of master plots for analyzing isothermal and nonisothermal experiments," *The journal of physical chemistry A*, vol. 104, no. 46, pp. 10777-10782, 2000.
- [157] M. F. I. T. U. O Kural, Coal, Turkey: Resources, Properties, Utilization, Pollution. v 494, pp 337-351, 1994.

APPENDIX

List of papers

- I) Thermogravimetric-mass spectrometry study of pyrolysis of Botswana-Morupule coal: kinetic parameters determination using iso-conversional and model fitting methods
Kgalalelo P. Kgatlane, Sebusi Odisitse, Casper Gate , James Darkwa, Isaac N. Beas
Reaction Kinetics, Mechanisms and Catalysis, **136**, pages 2343–2358 (2023),
<https://doi.org/10.1007/s11144-023-02459-z>