



The effect of plastic addition on the mechanical and thermal properties of fine coal extrudates

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Thesis accepted in fulfilment of the requirements for the degree *Doctor of Philosophy in Chemical Engineering* at the North-West University

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Graduation:	June 2025
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PREFACE

Thesis format

The format of this thesis is in accordance with the academic rules of the North-West University, where rule **A.5.4.2.7** states: “Where a candidate is permitted to submit a thesis in the form of a published research article or articles, or as an unpublished manuscript or manuscripts in article format and more than one such article or manuscript is used, the thesis must still be presented as a unit, supplemented with an inclusive problem statement, a focused literature analysis, and integration and with a synoptic conclusion, and the guidelines of the journal concerned must also be included.”

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Format of numbering and referencing

The formatting, referencing style, numbering of tables and figures, and general outline of the manuscripts or chapters were changed to ensure uniformity throughout the thesis. The format of manuscripts which have been submitted and/or published adheres to the author guidelines as stipulated by the editor of each journal. The headings and original technical content of the manuscripts were not changed from the submitted and/or published scripts, and minor spelling and typographical errors were corrected therein.

Supplementary information

Relevant supplementary data, where necessary, were included in Appendices.

Preface

Nomenclature

The description of the nomenclature (notations/symbols, Greek symbols, and relevant abbreviations) were included in the text following the guidelines of the published and accepted papers, unless stated otherwise. It should be noted that notations/symbols and Greek symbols may vary between chapters, following the format of the published papers.

SOLEMN DECLARATION BY STUDENT

I, Carel Marais, declare herewith that the thesis entitled: “The effect of plastic addition on the mechanical and thermal properties of fine coal extrudates”, which I herewith submit to the North-West University is in compliance with the requirements set for a Doctor of Philosophy in Chemical Engineering degree, is my own work, has been text-edited in accordance with the requirements and has not already been submitted to any other university.



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25 November 2024

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STATEMENT FROM CO-AUTHORS

Letter of consent

To whom it may concern, the listed co-authors hereby give consent that **Carel Marais** may submit the following manuscript(s) as part of his thesis entitled: ***The effect of plastic addition on the mechanical and thermal properties of fine coal extrudates***, for the degree *Philosophiae Doctor in Engineering with Chemical Engineering*, at the North-West University:

Marais, C., Bunt, J.R., Leokaoka, N.T., Uwaoma, R.C. & Neomagus, H.W.J.P. Mechanical and Thermal Properties of Extrudates Produced from Discarded Coal Fines and Recycled Plastics as Binders. *Energy and Fuels*. **2023**, 37(8):5905–5916

Marais, C., Bunt, J.R., Leokaoka, N.T., Coetzer, R.L.J. & Neomagus, H.W.J.P. Slow Pyrolysis Products Derived from Extrudates Produced from Discard Coal Fines and Recycled Plastics as Binders. *ACS Omega*. **2024**, 9: 6627–6641

Marais, C., Bunt, J.R., Leokaoka, N.T., Neomagus, H.W.J.P., Okolo, G.N., Wagner, N. J., Meyer, J.A. Structural analysis and gasification reactivity of chars derived from the slow pyrolysis of extruded coal fines and recycled plastic. *Heliyon*. **2024**, 10(20):e39391

(This letter of consent complies with rules **A5.4.2.8** and **A.5.4.2.9** of the academic rules, as specified by the North-West University)

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LIST OF PUBLICATIONS

Journal articles

Marais, C., Bunt, J.R., Leokaoke, N.T., Uwaoma, R.C. & Neomagus, H.W.J.P. Mechanical and Thermal Properties of Extrudates Produced from Discarded Coal Fines and Recycled Plastics as Binders. *Energy and Fuels*. **2023**, 37(8):5905–5916

Marais, C., Bunt, J.R., Leokaoke, N.T., Coetzer, R.L.J. & Neomagus, H.W.J.P. Slow Pyrolysis Products Derived from Extrudates Produced from Discard Coal Fines and Recycled Plastics as Binders. *ACS Omega*. **2024**, 9: 6627–6641

Marais, C., Bunt, J.R., Leokaoke, N.T., Neomagus, H.W.J.P., Okolo, G.N., Wagner, N. J., Meyer, J.A. Structural analysis and gasification reactivity of chars derived from the slow pyrolysis of extruded coal fines and recycled plastic. *Heliyon*. **2024**, 10(20):e39391

Conference presentations

Marais C., Bunt J.R., Leokaoke N.T., Neomagus H.W.J.P., Grobler L. J., Uwaoma R.C. The co-pyrolysis and kinetic behaviour of extrudates produced from discard coal fines and recycled plastic binders at PYROLIQ II, Schloss Hernstein, Austria (oral and poster presentations on 11/05/2023)

Marais C., Bunt J.R., Leokaoke N.T., H.W.J.P. Neomagus, Coetzer R.L.J. The mechanical strength and co-pyrolysis characteristics of extrudates produced from discarded coal fines and recycled plastics presented at The South African Coal Processing Society (SACPS) Biennial Conference, Secunda, South Africa (oral presentation on 17/08/2023)

ACKNOWLEDGEMENTS

Isaiah 40:28-31

²⁸ Do you not know? Have you not heard? The Lord is the everlasting God, the Creator of the ends of the earth. He will not grow tired or weary, and his understanding no one can fathom. ²⁹ He gives strength to the weary and increases the power of the weak. ³⁰ Even youths grow tired and weary, and young men stumble and fall; ³¹ but those who hope in the Lord will renew their strength. They will soar on wings like eagles; they will run and not grow weary; they will walk and not be faint.

Throughout this study, I received tremendous amounts of support for which I am truly grateful. I want to thank everyone who helped me, even if it was only for a little bit of experimental work, writing advice, or a word of encouragement. I could not have done this without you. In particular I would like to thank the following:

1. Our Almighty God for giving me the talents and drive to finish this degree. Thank You for being my belief and hope and giving me trust that everything is following your plan when I could not see the way forward. I know that everything I have and will achieve is because of Your Grace alone.
2. Anke-Mari Wentzel, who brings out the best in me every single day. Thank you for all the love, support, and when needed, a few stern words. You carried me throughout this entire process and never stopped believing in me. I love you, and you mean more to me than I could ever describe.
3. Professor John Bunt, my supervisor since my honours project. From the first time we worked together in 2020 I knew I did not want to work with anybody else. Sir, your caring, understanding, and calm approach meant the world to me. Thank you for not only being a supervisor to me, but a true mentor. I will always remember how kindly and gracefully you handled everybody surrounding you.
4. My toughest reviewers, Ms. Nthabiseng Leokaoke and Professor Hein Neomagus, who provided me with an abundance of technical expertise and guidance. Your always honest feedback, not only on technical work, pushed me past my perceived limits. Thank you, I sincerely believe that I had the dream team of supervisors.
5. André Koekemoer and Professor LJ Grobler for your industrial knowledge and technical support.

Acknowledgements

6. My parents, Arno and Sibylie Marais, who never doubted me. Thank you for your never-ending love, time and support. I am proud to be your son, and I could not have asked for better role models.
7. Harry Marx, thank you for being my friend with which I was able to share this post-graduate journey. I could not choose a better friend.
8. Tannie René Bekker, for multiple long hours of lab work, patience, and guidance. You were always ready to help, even over weekends, and I really appreciated your immense care.
9. Every co-author, who brought expertise in their own field and helped me to elevate my work to much higher levels, thank you for your time, guidance and interest in my research.
10. Patria Men's Residence, the place that showed me what is possible when people work together for a goal greater than themselves. Thank you for all the memories, friendships, and life lessons. To the HC of 20/21, 21/22, and Tannie Rolien Roos, thank you for helping me find my voice. *Dulce et decorum est pro Patria mori. Patria in aeternum.*
11. The National Research Foundation (NRF) [Coal Research Chair Grant No. 86880] who financially supported this work. Opinions, findings and conclusions or recommendations expressed in any publication generated by the NRF supported research are that of the author(s) alone, and the NRF accepts no liability whatsoever in this regard.

ABSTRACT

Coal and plastics are significant sources of waste, not only in South Africa, but globally. During coal mining, coal fines are produced, and these fines are not widely used due to transportation and handling difficulties. The size of the coal fines needs to be increased to be integrated into most industrial processes. Multiple studies have investigated various potential agglomeration techniques and binders to improve the size of the coal fines. However, binders are often the most expensive part of agglomeration, therefore, waste streams as potential binders are being investigated. This study focusses on the extrusion, pyrolysis and gasification behaviour of discarded coal fines from the Highveld coalfield together with recycled waste low-density polyethylene (LDPE) and polypropylene (PP), respectively.

A twin-screw extruder with a 10 mm die and barrels heated to 220 °C was used to produce coal fine extrudates with varying plastic content (10, 25, 50, 75 and 100 wt.%) for both LDPE and PP. The 10% LDPE and 10% PP extrudates exhibited compressive strengths of 17.5 and 7.9 MPa before breaking, respectively. Extrudates containing more than 10% plastic did not break under load but merely deformed. All extrudates maintained similar compressive strengths after being submerged in water and absorbed less than 5% moisture after 24 hours in water.

The pyrolysis kinetics of the extrudates and raw materials were evaluated using Iso-conversional techniques (Kissinger–Akahira–Sunose, Starink, and Flynn–Wall–Ozawa) by means of Thermogravimetric analysis (TGA) under a nitrogen atmosphere, increasing temperature from ambient up to 900 °C. The extrudates exhibited lower activation energies and lower conversion temperatures, indicating synergy between plastic and coal fines during pyrolysis. Pyrolysis product yields and characteristics were further evaluated using Fischer Assay slow pyrolysis where the temperature was increased by 5 °C/min until the final pyrolysis temperature (520, 720, and 920 °C) was reached. The coal produced up to 83% char, whereas the main product derived from the plastics were overwhelmingly condensable liquids (< 90%). The small reactor volume and slow heating rate actively promoted condensable product formation. Both char and condensable product yields followed the additive model of the raw materials. Statistical models were developed which can estimate the pyrolysis product yield and characteristics using the composition of the original extrudate and the final pyrolysis temperature. The p-values indicate that temperature mostly interacts with the fine coal content, further supporting the observation that volatiles produced by the plastics leave the reactor before being exposed to higher temperatures. Furthermore, the condensable products derived from the PP containing extrudates have more components with higher boiling points than those produced from either coal or PP alone.

Abstract

Chars derived from extrudates containing 0, 10, 25, and 50 wt.% plastic were analysed using petrographic carbon form, surface area and porosity, and XRD carbon crystallite analysis. Chars produced at 920 °C were pulverised (75 - 150 µm) before undergoing CO₂ gasification at 800, 825 and 850 °C in the chemical-controlled regime. The chars' crystalline structure became more ordered with an increase in plastic content. Even with the more ordered structure, the gasification reactivity increased similarly with an increase in both LDPE and PP content in the original extrudates. Petrographic carbon form analysis showed an increase in crack and pore formation with an increase in plastic addition during all stages of the chars' evolution as the pyrolysis temperature increased. The low-pressure gas adsorption (LPGA) results report that maximum porosity occurred at 720 °C and decreased when the pyrolysis temperature further increased. This indicates that most of the pore growth occurred during pyrolysis and coalescence occurred during gasification. The volumetric reaction model (VRM) time factor showed a positive linear correlation with an increase in BET surface area, especially for the LDPE derived chars. Therefore, the observed reactivity increase with an increase in plastic content can be correlated to an increase in surface area.

The study suggests that the co-extrusion of recycled plastic with coal fines produces solid carbonaceous fuels with high hydrophobicity and mechanical strength compared to coal fines. The calorific value of the extrudates improves with an increase in plastic content since both LDPE and PP (46.5 MJ/kg) have calorific values more than double that of the coal fines. Additionally, the plastic content can be varied to vary the produced pyrolysis products. This alludes to the possibility that the fuel source can be adapted to suit a wide range of industries without causing large operational changes since the composition can be altered to be close to that of the fuel source currently in use. Furthermore, the gasification reactivity of the chars increased with an increase in plastic content. This allows processes to speed up the rate limiting char gasification step with the addition of plastic.

Keywords: coal fines, LDPE, PP, extrusion, mechanical strength, TGA, iso-conversional methods, Fischer Assay pyrolysis, CO₂ gasification

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TABLE OF ABBREVIATIONS

Abbreviation	Definition
A	Ash
BET	Brunauer–Emmett–Teller
BPE	Black polyethylene
BJH	Barrett–Joyner–Halenda
CP	Condensable products
CV	Calorific value
D-R	Dubinin–Radushkevich
FC	Fixed Carbon
FWO	Flynn-Wall-Ozawa
GC-MS	Gas chromatography mass spectrometry
GC	Gas Chromatography
GHG	Greenhouse gas
HDPE	High density polyethylene
HK	Horvath–Kawazoe
IRI	Impact resistance index
KAS	Kissinger-Akahira-Sunose
LDPE	Low density polyethylene
LPGA	Low pressure gas adsorption
M	Moisture
MFI	Melt flow index
MSW	Municipal solid waste
NRF	National Research Foundation
PET	Polyethylene terephthalate
PE	Polyethylene
PFI	Pulverised fuel injection
PP	Polypropylene
PSD	Pore size distribution
PS	Polystyrene
PVC	Polyvinylchloride
PW	Plastic waste
TGA	Thermogravimetric Analysis
TGMS	Thermogravimetric mass spectrometry
TCD	Thermal conductivity detector
RB	Richards Bay
ROM	Run off mine
RPM	Random pore model
SCI	Sasol chemical industries
SEM	Scanning electron microscope
SE	Standard error
SSF	Sasol Synthetic Fuels
VM	Volatile matter
VRM	Volumetric reaction model
WPE	White Polyethylene
WRI	Water resistance index
XRD	X-ray diffraction

CHAPTER 1: INTRODUCTION

1.1 Background and motivation

In South Africa, 77% of the energy needs are supplied through the usage of coal¹. The country uses 53% of the mined coal in electricity generation², which produces 91% of South Africa's generated electricity³. Furthermore, 33% of the country's mined coal is used to produce petrochemical products. The remaining mined coal is used in metallurgical processes (12%) and for domestic cooking and heating (2%)².

South Africa mines 250Mt of coal per annum⁴. During mining and operation, coal fines are formed. Coal with a particle size smaller than 1mm is classified as fine coal and it can be further classified as ultra-fine coal once the particle size is smaller than 0.15mm⁵. More than 12% of the country's mined tonnage is considered to be coal fines⁶. Coal fines are not accepted in most industrial processes, because of their transportation and handling difficulties. For coal to be used in fixed-bed gasification, the particle size should be 6mm or larger⁷. Furthermore, coal fines have a high moisture content, which decreases the heating value of the coal⁸.

Coal fines are historically discarded into slimes dams or unused underground workings⁶. Currently, approximately 38.8Mt of discard coal is dumped or stored in slimes dams annually⁹. These discarded coal fines are a direct cause of acid mine drainage³. Furthermore, when coal fines are improperly stored, dust build up can occur and become a safety hazard since the dust can spontaneously combust¹⁰. Thus, techniques to alleviate these problems are being implemented to use the discarded coal fines, instead of improper disposal. The agglomeration of coal fines to produce larger agglomerates that are easier to handle and have a lower moisture content can provide a financial opportunity⁶.

Binders are often incorporated in the coal agglomeration process to improve the characteristics of the agglomerate. Optimally, binders should improve the water resistance, strength, and heating value of the agglomerate¹¹. These binders should also be environmentally friendly. However, binders can often be the most expensive aspect of agglomeration⁸. To overcome financial and environmental problems, the binding properties of municipal wastes are being investigated⁵.

In South Africa, 46% of the 1.1 million tons of plastic waste was recycled during 2018, making the country one of the front runners in mechanical recycling. The recycling rate attained provided the country with an economic boost of R 2.3 billion and created a formal income of approximately 7800 employees and an informal income for more than 58,000 people¹². More

than 630,000 tons per annum of plastics are, however, not yet recycled and end up as municipal waste¹³. Most plastics have the characteristics of good binders, since they have a high heating value, along with good binding and water resistance attributes⁵.

The six main types of plastics are: high density polyethylene (HDPE), low density polyethylene (LDPE), polypropylene (PP), polystyrene (PS), polyvinylchloride (PVC), and polyethylene-terephthalate (PET)¹⁴. The calorific value of these plastics can be seen in Table 1-1^{15,16}.

Table 1-1: Plastic calorific value (air dry basis)

Plastic type	Calorific value (MJ/kg)
HDPE	44.8
LDPE	46.5
PET	23.0
PS	38.5
PVC	22.9
PP	46.5

In this study, the focus will be employed on the plastics that have the best attributes for fixed-bed gasification and are abundant in municipal waste. PET bottles are the most mechanically recycled product in Africa and not abundantly present in municipal waste¹³. PVC and PS are reported to be the two least abundant plastics in African municipal waste¹³. Both of these plastics have lower calorific values compared to HDPE, LDPE and PP. Furthermore, PVC releases hazardous chlorine gas during pyrolysis. If PVC is used, the hydrogen chloride gas (HCl) is driven off at low temperatures (mainly between 250 and 320 °C)¹⁷.

HDPE and LDPE are comprised mostly of polymerised alkanes with an $C_{2n}H_{4n+2}$ formula, where n represents the number of ethylene monomers in the polymer chain¹⁸. Since HDPE and LDPE have similar chemical structures and LDPE is more regularly available with a slightly higher calorific value, only LDPE will be evaluated in this study. On the other hand, PP has a high rigidity and hardness. Furthermore, PP has the highest calorific value of 46.5 MJ/kg¹⁵. Therefore, this study will focus on particle size upgrading via the extrusion of LDPE and PP with fine discard coal for utilisation in fixed-bed gasification.

There are several different methods to agglomerate coal which includes extrusion, pelletisation, and briquetting⁸. In this study the focus will be placed on hot extrusion since heat in conjunction with pressure can simultaneously be applied to activate the binder during agglomeration⁸. Since plastics need to be melted to activate the binder properties, both heat and pressure will be needed.

The extrudates need to adhere to mechanical strength standards to be utilised in industry. The extrudates will undergo various stresses and strains during transportation and handling¹⁹. Often, coal and agglomerates are stored in stockpiles that are exposed to the environment.

When exposed to water, the extrudates should not decay and maintain a compressive strength of at least 350kPa²⁰. Therefore, the extrudates require water resistant attributes²⁰. Furthermore, to be used in fixed-bed gasification, the extrudates need to have a compressive strength that is comparable to that of Run off mine (ROM) coal. It has been reported that ROM coal from the Highveld coalfield has a compressive strength of 14MPa²¹. If the extrudates possess the required mechanical strength, the thermal conversion processes of pyrolysis and gasification can be used to produce valuable chemical products, similar to that produced by run-of-mine (R.O.M) lump coal.

Pyrolysis is the thermal degradation of carbon containing materials in an inert environment at high temperatures and pressure²². These carbon-containing materials include biomass, coal, plastic etc. The process irreversibly breaks down larger molecules into smaller molecules²³. Coal pyrolysis can present multiple advantages, such as energy that can be converted from the produced char²³. Pyrolysis is also the first step in the coal gasification process, where the moisture and volatile matter of the coal is removed²⁴. Furthermore, the products derived from coal pyrolysis, like the produced char, can be used in boilers and furnaces that are currently operating. The pyrolysis of coal and plastic is also a desirable form of solid waste management²³.

Pyrolysis is one of the most robust chemical recycling technologies²³. As mentioned previously, it is not only coal that is efficiently pyrolyzed to produce valuable products²⁵. The various feed materials provide a varying quality of pyrolysis products. Therefore, the different products produced by the different materials need to be studied to better understand if these products are beneficial to the gasification process²³. Gasification is used to enhance the environmental properties of low-quality carbon-based fuels, such as coal. Gasification of the pyrolysis char is the step which produces synthesis gas from solid fuels²⁶. In South Africa, a fixed-bed dry bottom gasification process was developed by a joint venture between Sasol Technology and Lurgi²⁷. This fixed bed gasification technology is also used for heat and power generation. To improve the understanding of the how extrudates perform in a gasification reactor, the extrudates must undergo pyrolysis and gasification testing, and the products need to be characterised²⁶.

1.2 Problem statement

Both plastic and coal fines are waste products which cause environmental and ecological challenges. Therefore, alternative uses should be found for both coal fines and plastics. The hot extrusion of coal fines with various plastics as binders should be studied to determine if plastic bound extrudates would be acceptable for industrial use. Furthermore, the pyrolysis and gasification products derived from the extrudates need to be characterized. This is the

first study to report on the extrusion of coal fines and plastics. Previous studies conducted on the co-pyrolysis of coal and plastics were mainly focussed on powdered mixtures^{28–30} and using Northern hemisphere coals^{5,28,29,31,32}, whereas this study uses South African (inertinite rich) bituminous coal. Furthermore, no direct comparison was found in the literature between the synergic effect of coal and PP and that of coal and LDPE pyrolysis over a wide range of plastic concentrations, as will be conducted in this study. Multiple simultaneous reactions need to be accounted for when investigating the pyrolysis kinetics and thermodynamic parameters of carbonaceous material. It is difficult to obtain the mechanism for each reaction; therefore, iso-conversional methods can be used to estimate these parameters³³. Literature reports the use of multiple iso-conversional methods to determine kinetic parameters for both coal and plastics^{34,35}; however, limited use of these methods has been reported on the pyrolysis of mixtures of coal and plastics.

To understand the behaviour of plastics and coal when co-pyrolyzed, the derived products need to be investigated. Slow pyrolysis products and yields of extrudates produced from plastics and discarded coal fines have not yet been reported. Since both LDPE and PP will be used, the effects of the addition of these plastics on the yields and produced products will be compared. Products that need to be characterized include the produced char, condensable products, and gas.

Furthermore, the chars produced during pyrolysis need to be further investigated to understand how the increase in temperature and variance in plastic concentration affects the formation of the chars. All changes in the chars will also provide insight into changes in gasification behaviour. Previous studies that focused on the co-gasification of coal and plastic have not focused on the kinetic behaviours of the chars. To address this vacancy, the CO₂ gasification kinetics need to be determined and used in kinetic models such as the random pore model (RPM) and volumetric model (VM). By investigating the pyrolysis and gasification behaviour of the coal and plastic extrudates, this study endeavours to find a solution for the utilisation of both waste streams.

1.3 Aim and objectives

The aim of the study is to evaluate the extrusion of coal fines and plastics to determine the effect of varying plastic addition and plastic type on the mechanical properties of the produced extrudate. Additionally, this study aims to assess the effect of plastic addition on the produced products during thermal treatment.

The following objectives were set to reach the aim of the study:

- Characterize the Discard Materials:

Conduct a comprehensive characterization of the coal fines, LDPE (low-density polyethylene), and PP (polypropylene). This involves analysing their physical, chemical, and morphological properties to understand their composition and behaviour.

- Evaluate Mechanical Strength and Water Resistance:

Investigate the mechanical strength and water resistance of extrudates produced by blending fine coal discard with varying concentrations of LDPE and PP, respectively. This objective aims to assess how varying plastic concentrations affect the physical properties and durability of the resulting composite materials.

- Characterise Pyrolysis Products:

Analyse and characterize the pyrolysis products obtained from the extrudates. This involves determining the quantities along with compositional and structural properties of the solids, liquids, and gas produced during the pyrolysis process. The goal is to understand the thermal decomposition behaviour and potential applications of the resulting products.

- Determine Gasification Rate of Pyrolysis derived Chars:

Measure and establish the gasification rate of the pyrolysis chars derived from the extrudates. This objective focuses on assessing the reactivity of the chars during gasification, providing insights into their suitability for energy generation or other applications.

1.4 Project scope

1.4.1 Experimental procedure

This study was performed using coal fines from the Highfield coalfield. Recycled LDPE and PP (provided by Potchefstroom Plastic) were used as binders at different weight concentrations. To prepare the coal fines, the Highveld coal was sieved (<1 mm) and characterised. Since both the LDPE and PP melt during extrusion, it is not necessary to reduce the size of the obtained plastic pellets (± 5 mm). The LDPE and PP were characterised using the same tests as used for the coal fines. Extrusion was undertaken at 220°C which is above the melting point of LDPE and PP while still being below their onset of degradation temperature. The LDPE and PP concentration were each varied between 10, 25, 50, 75 and 100 %wt.

The mechanical strength testing of the produced extrudates were then evaluated. The extrudates underwent compressive strength-, impact resistance-, and water resistance tests to determine whether they have an acceptable mechanical strength. The extrudates that met the mechanical strength requirements were pyrolyzed. Pyrolysis of the extrudates were evaluated using thermogravimetric analyses (TGA) to determine the iso-conversional degradation kinetics as well as by using a modified Fischer Assay setup to evaluate the pyrolysis yields and products. The pyrolysis products were characterised, and the CO₂ gasification kinetics of the chars produced from the coal fines along with the 10, 25, and 50% plastic bound extrudates were explored.

1.4.2 Study outline

The following section provides an outline (Figure 1-1) of this study.

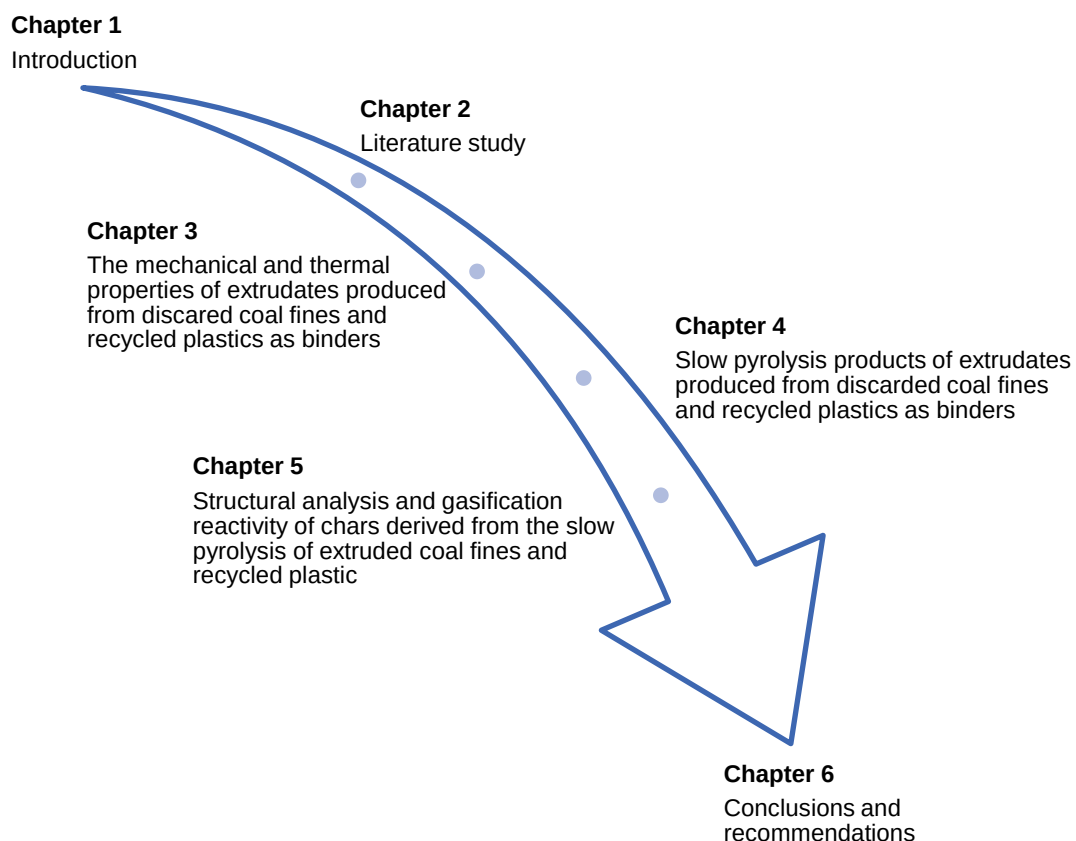


Figure 1-1: Study outline

In Chapter 1 the background and motivation behind this study is given. This chapter provides a brief discussion on coal, waste plastics, extrusion, mechanical strength, pyrolysis, and gasification. The problem statement, aim and objectives, and study outline are stipulated.

Chapter 2 provides a detailed literature study. The literature study investigated the consumption of coal as well as the production of waste plastics in South Africa. The environmental impact of coal and plastics are elucidated on, and the existing recycling techniques are explored. The possibility of combining coal fines and plastic waste to make valuable agglomerates that can be used industrially is examined. Different agglomeration techniques are discussed; however, since extrusion will be used in this study, it is discussed in detail. Furthermore, the mechanical strength standards that the extrudates need to adhere to for use in industry are given. The possible uses for the extrudates in industrial pyrolysis and gasification processes are investigated.

Three peer reviewed research articles were produced in this study which details all experimental methods and results obtained from this investigation. Chapter 3 presents the first article which discusses the extrusion of the coal fines and plastics along with the extrudates mechanical strength and thermal characteristics. The raw materials and extrudates were characterised using proximate analyses, ultimate analyses, and calorific value. Furthermore, the compressive strength and water resistance of the extrudates were measured, while the pyrolysis kinetic parameters were determined applying iso-conversional techniques using a TGA setup.

Chapter 4 is focused on the pyrolysis product yields and the characterization of each derived product during the slow pyrolysis of the extrudates and raw materials using a modified Fischer Assay setup. The yields, proximate analyses, and elemental analyses (for both char and condensable products) results were used to develop statistical models to predict these results. Gas chromatography mass spectrometry (GC-MS) analyses was used to indicate the composition of the condensable products while also providing simulated distillation estimations. Gas chromatography (GC) was used to determine the composition of the pyrolysis gas.

The evolution of the pyrolysis chars as the temperature increased was evaluated using XRD, SEM, BET along with the char morphology and petrography and is discussed in Chapter 5. Since the pyrolysis chars need to be produced at a higher or equal temperature to the gasification temperature, the chars produced at 920°C were selected for CO₂ gasification. The chars produced at 920°C are within the range where most coal gasification reactions occur (800 – 920°C)³⁶. Additionally, the CO₂ gasification kinetics of the chars produced at 920°C were determined and modelled using the Random Pore model (RPM) and the Volumetric Model (VM) in the chemically controlled regime.

Chapter 6 provides the final conclusions of the study. These conclusions were based on the results obtained and discussed in Chapter 3, Chapter 4, and Chapter 5. Recommendations for future research regarding the pyrolysis and gasification of the coal fines and waste plastic extrudates were made based on the conclusions formulated during this study.

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CHAPTER 2: LITERATURE STUDY

2.1 Introduction

The literature review begins with an examination of the production and consumption of coal in South Africa. The amount of waste produced by fine coal discards and plastics as well as the ecological damage caused by these waste products are elucidated on. Both coal and plastics are integrated into the modern lifestyles of South Africans, therefore, it is important to find a solution to manage the waste that both products produce.

Different plastic recycling methods are explored. Furthermore, to use coal fines (a waste product produced during coal mining) they need to be agglomerated. Various agglomeration techniques are reviewed, and the properties of waste plastics are investigated to determine whether any of the waste plastics would have suitable binder properties. The mechanical strength requirements for extrudates to be used industrially are investigated. Possible industrial processes in which these extrudates can be used are also reviewed. The possibility of using these extrudates in pyrolysis or gasification processes is explored by reviewing literature on the use of these processes for coal and plastic.

2.2 South African coal consumption and production

South Africa is greatly dependant on coal since it is crucial for the socio-economic development and the resource is widely used across the country¹. South Africa consumes the most coal of any African country south of the Sahara, and 77% of the country's energy needs are supplied by the utilisation of coal². This includes 91% of electricity generated in South Africa, as well as the production of 30% of the country's produced fuels³. Furthermore, coal is used in a wide variety of industries including metallurgical processes and domestic cooking and heating. Figure 2-1 illustrates the local consumption of coal in South Africa⁴.

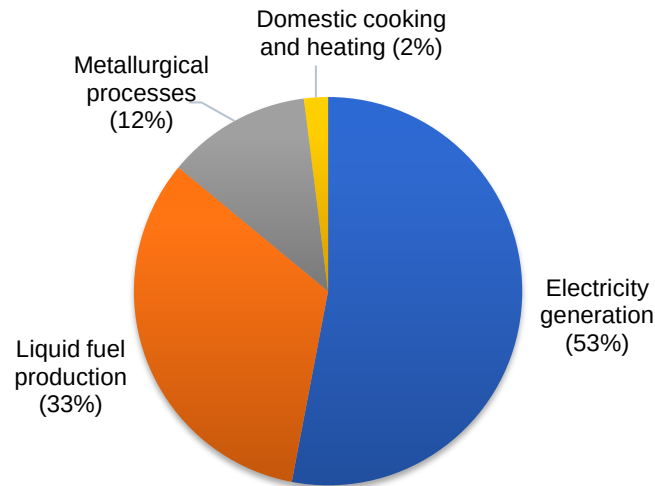


Figure 2-1: Coal consumption in South Africa⁴

Globally, South Africa is the 6th largest coal producer². The country mines 250Mt of coal per annum, which is approximately 3.3% of the global total³. The top 5 mining companies are responsible for supplying more than 80% of the country's coal market produce. These companies are Anglo American, Sasol, BHP Billiton, Exxaro, and Glencore Xstrata⁵.

27% of the saleable coal (approximately 68Mt per annum) is exported internationally⁶, making coal one of South Africa's largest export products. South Africa exports 61 billion rands worth of coal per annum⁷, which contributes to 6% of the global export revenue³. The large revenue generated from coal exports places it as the fourth most valuable mineral export in South Africa, only behind gold, diamonds, and platinum¹. South Africa produces a low-cost, low sulphur containing coal which is a favourable attribute in the international market⁸. Furthermore, South Africa is perfectly situated for international trade since the country is in between both the Pacific- and Atlantic oceans. This ideal placement allows South Africa to export coal to both Asia and Europe⁸.

South Africa has approximately 3.5% of the global coal reserves³. These reserves consists of 96% bituminous coal, 2% anthracite coal and 2% metallurgical coal⁸. The country's 19 official coal fields are spread out across 5 provinces: Free State, Gauteng, Limpopo, Mpumalanga and KwaZulu-Natal⁹. In the past, the main producers of coal were the Highveld, Witbank and Ermelo coal fields from the central basin⁸. Recently, South Africa has been more focussed on the Waterberg coalfields in the Limpopo province. The Waterberg coalfield makes up between 40 and 50% of the county's remaining coal reserves⁵.

The coal mining industry is dominated by the private sector⁸. More than 82 000 people are employed by the coal mining industry⁷. Even though the mining industry is mostly privately owned, the consumption of coal is dominated by Eskom, a state-owned company⁸. Eskom consumes 46% of the saleable coal in coal fired powerplants to produce electricity⁶ and employs around 50 000 people⁷. Even though greener sources of energy are constantly being developed, and given the slow pace at which progress is being made, it is predicted that South Africa will be dependent on coal for electricity generation for the next 50 years¹⁰.

The second largest consumer of coal is a privately owned company, Sasol⁸. Crude oil is normally used to produce petroleum products and since South Africa does not have large crude oil reserves, Sasol uses the country's abundance of low-grade coal to produce petroleum products⁶ using an indirect liquefaction process¹⁰. The process consists of a coal gasification step followed by the Fischer-Tröpsch synthesis process to produce liquid fuels and other petro-chemical products¹¹. The company is the biggest commercial manufacturer of petroleum products from coal⁸.

2.3 Highveld coalfield

The Highveld coalfield is situated just South of the Witbank coalfield; however, these coalfields are divided by the Smithfield Ridge⁵. The Highveld, Witbank and Ermelo coalfields currently produce 84% of South Africa's total coal production¹². The collieries of the Highveld coalfield contribute 22.7% of the country's saleable coal product¹³. Of the Highveld's saleable coal, Sasol Chemical Industries (SCI) and Sasol Synthetic Fuels (SSF) use 50 million tonnes of coal per year. Furthermore, the coalfield provides coal to the local Eskom power stations such as the Kriel, Matla and Tutuka power stations. Therefore, the Highveld coalfield is of extreme economic importance⁵.

The Highveld coalfield consists of five main coal seams¹⁴. Not all the seams are equally productive. The No. 4 seam is regarded as the most economic seam¹⁴. The No. 4 seam can be divided into an upper and a lower unit⁵ and spreads across the entire Highveld coalfield. This seam varies in depth. In the Kriel area the seam can be found around a depth of 15m, it then deepens to a depth of approximately 300m east of Standerton⁵. According to Hancox et al.⁵, 98% of South African coal is classified as medium rank C bituminous coal. This includes the Highveld's No. 4 seam which primarily consists of medium rank C bituminous coal⁵. The No. 4 seam generally consists of low-grade bituminous coal with a high ash content and a calorific value ranging from 18 to 25MJ/kg¹².

In 2005 it was estimated that the coalfields in South Africa have a recoverable coal reserve of 9 Gt. This reserve is rapidly approaching exhaustion. To extend the life of the remaining coalfields the utilisation of discarded coal fines is crucial. The usage of discarded coal fines is aligned with government policy and will increase the remaining coal reserves¹⁵. The Highveld coalfields are important for the sustainability and longevity of the South African synthetic fuel industry¹². It is therefore of the utmost importance that alternative methods of using discarded coal such as the agglomeration of coal fines, be investigated to increase the lifespan of the Highveld coalfield¹⁵.

2.4 Environmental impact

Both coal and plastic contribute immensely to the amount of waste generated in South Africa. The fly ash, bottom ash and dust, created from mainly coal fired powerplants, generate 96.1% of the country's hazardous waste¹⁶. Furthermore, in 2010 South Africa mismanaged 630 000 t of plastics, making South Africa the country with the 11th most mismanaged plastic country per annum in the world¹⁶. These are only two examples of the extent of wastes produced by coal and plastics. The full impact is discussed in detail in the following sections.

2.3.1 Environmental impact of coal

Across the world coal is the most used energy source¹⁷ since it is a widely available low-cost commodity¹⁸. Coal is used to provide 29% of the world's primary energy needs. However, the vast consumption of coal has become an increasing environmental concern¹⁸. Using coal to generate power is one of the primary causes of toxic gas and greenhouse gas (GHG) emissions across the globe¹⁹. Other worldwide issues including acid rain, acid mine drainage, groundwater pollution, fog and haze have been linked to the utilisation of coal¹⁸. South Africa is one of the largest consumers and producers of coal across the globe² and therefore greatly impacted by the various forms of pollution associated with coal⁹. Like many other countries that are reliant on fossil fuels, South Africa shows a noticeable divergence between official governmental commitments to reduce its carbon footprint, and measurable progress in reducing dependence on coal¹. South Africa has one of the most carbon intensive economies and produces approximately 480Mt of CO₂ annually³, making South Africa the 14th largest CO₂ emitting country globally²⁰. In 2023, South Africa was the 7th largest emitter of CO₂ through coal combustion, emitting 329.77 Mt²¹. The two largest consumers of coal in South Africa are Eskom and Sasol. These companies are responsible for 50% of the country's GHG emissions⁷ and when combined with road transport, produce 85% of the country's CO₂ emissions²². Between April 2023 and March 2024, Eskom produced an estimated 190.4 Mt of CO₂ emissions annually²³.

Additionally, coal contains sulphur and nitrogen elements that release SO_x and NO_x during combustion²⁴. This includes the release of nitrous oxide (N_2O), which has 298 times the global warming potential of CO_2 . In 2015, Eskom emitted a staggering 2919t of N_2O ³. South Africa mainly produces low rank coal²⁵ which emit higher concentrations of volatile matter²⁴. These gaseous emissions containing SO_x and NO_x are some of the main contributors to acid rain and smog formation²⁶. Not all companies are able to comply to the newly introduced legislation since companies like Eskom were operational before the introduction of emissions legislation and now need to install expensive gas emission control equipment²⁷. Emission mitigation strategies, although helpful, do not eliminate all the pollutants formed during the combustion of coal²⁶. During the residential combustion of coal, there are no emission mitigation strategies, which associates residential combustion with high gaseous emissions and poor environmental and health conditions²⁸. Furthermore, the ash produced during residential combustion is often dumped onto vacant land causing a leachate to seep into the ground³.

Mining practises used to extract the coal also result in threatening environmental problems²⁹. Opencast mines have large stockpile and disposal areas damaging the natural flora and fauna, additionally these mines cause erosion and an increase in fine particle matter into the air and surrounding waters³. Whereas underground mining causes various ecological problems such as surface ground disturbances, dust production, underground fires, and abandoned mining tunnels. Both mining methods are responsible for polluting surface and groundwater through bad mining practises³. One of the most threatening problems associated with mining is acid mine drainage which occurs when minerals in the coal, i.e. pyrite react with the oxygen trapped in rain water²⁹. The reaction produces sulphuric acid which seeps into the ground water²⁹. Mining activities break the supporting rock structure, which lead to the acid freely contaminating the groundwater below. The acid dissolves heavy metals, such as aluminium, which increase the toxicity of the groundwater, making the contaminated groundwater unfit for human consumption²⁹. Furthermore, the mining industry continuously pollutes not only the groundwater, but surface water by not following proper mining procedures³⁰.

Additionally, the South African coal mining industry discards 60Mt of coal fines per annum³¹ and these fines account for approximately 12% of the total South African mined coal³². Coal fines are coal particles with a diameter of less than 1mm³³. The low rank coal fines have a high sulphur and ash content and are generally considered as a waste product³¹. Industrial processes do not use coal fines due to handling and transportation difficulties³³. Coal fines consist of the same chemical and mineral structure as feed coal used in thermochemical processes, however, coal fines have a higher moisture content than feed coal which lowers the calorific value (CV) of the fines³². The production of coal fines during coal mining is

unavoidable¹. Since coal fines are considered to be a waste product the fines have historically been discarded in slime dams and unused underground mines³². These discarded coal fines are another contributor to the acid mine drainage crisis¹. Furthermore, if the produced coal fines are not properly stored, dust build up can occur leading to spontaneous combustion³¹. If the coal fines can be utilised a financial opportunity arises³². Furthermore, coal along with coal fines can be used in more environmentally friendly processes such as coal gasification which is at the forefront of clean coal technology currently³⁴.

2.3.2 Environmental impact of plastic

Plastic is the main priority in international waste management as highlighted in the recent discussions by the Conference of the Parties of Basel and during the Stockholm Convention³⁵. Emphasis is placed on the reduction of plastic consumption and on finding environmentally friendly waste management strategies³⁵. However, Dokl et al.³⁶ estimated that the global use of plastic is expected to increase from 464 Mt per annum in 2020 to 884 Mt per annum in 2050. The increase in plastic use is further accentuated with plastics extreme cost effectiveness³⁷. It is approximated that globally 8300Mt of plastics were consumed up to 2015. 6300Mt of the produced plastics were considered waste plastics and only 9% of waste plastics were recycled, 12% were incinerated, and 79% ended up in landfills. Due to the ability of plastics to withstand degradation, most of this waste will remain for centuries if it is not dealt with³⁵. In 2017 South Africa consumed approximately 1.8 Mt of plastic³⁸ and produced 1.14 Mt of plastic waste of which 0.63 Mt is classified as mismanaged waste³⁵. In 2015, South Africa was ranked as the country with the eleventh most mismanaged waste¹⁶. It is estimated that there are over 15 000 unofficial communal landfill sites. These sites do not meet the waste management requirements and are considered to be environmentally unsafe³⁹.

Traditional plastics are not biodegradable and cause problems decades after the initial pollution. Strong molecular bonds between carbon and hydrogen molecules prevent the degradation of plastics³⁷. In nature, the size of plastic particles are only reduced by harsh conditions such as direct sunlight or prolonged contact with water⁴⁰. When the size of the plastic particles become small enough, the small plastic particles are consumed by organisms and are integrated into the food chain. These inhaled and ingested plastics lead to general health problems including cardiovascular, neurological and carcinogenic conditions⁴¹.

Globally, the most popular and economical method of waste management is by landfilling. However, landfilling produces secondary pollutants such as the release of toxic gases and it produces acid leachate⁴². Furthermore, landfill fires are common. When waste, including plastic waste, is incinerated, more toxic gases are released which cause damage to the

environment and human health⁴³. Even though South Africa has added a fee that consumers have to pay to use plastic shopping bags, these plastic bags are the most widely spread of any form of plastic waste (PW)⁴⁴. South Africa consumes more than 8 billion plastic bags every year. Furthermore, plastic waste is light enough to easily blow off landfills, polluting the streets⁴⁴.

2.3.3 Recycling of coal wastes

Coal fines are not used industrially because of the transportation and handling difficulties which is associated with its small particle size³³. These small particles also contain a higher moisture content than ROM coal which lowers the CV of the particles³². Most industrial processes that use coal have a minimum size requirement, such as fixed bed gasifiers that can only use coal with a diameter larger than 6 mm³³. By agglomerating the coal fine particles, a larger agglomerate can be created which presents a financial opportunity.

These agglomerates still need to adhere to the mechanical strength standards to be utilised⁴⁵. To improve the mechanical strength of the agglomerates, binders are often added⁴⁶. Once these agglomerates are acceptable for industrial use, they can be used in a wide range of processes including gasification and power generation⁴⁵. The use of agglomerates in alternative processes such as the production of greener low smoke fuels, fluidized bed technology, methane production through solubilisation, and solid fuel production⁴⁷ would not only have a positive impact on the environment, but also prolong the lifespan of South African coal resources¹⁵. Using agglomerates along with ROM in coal gasification processes can produce a clean syngas. The syngas is used to generate electricity and to produce various chemical products. Coal gasification is currently becoming a leading competitor in clean coal technology³⁴.

2.3.4 Recycling of plastics

South Africa has a complicated standing in terms of waste management since the country has the eleventh most mismanaged waste globally¹⁶, but in complete contrast, South Africa is one of the frontrunners in plastic recycling. In 2018, South Africa recycled 46.3% of the 1.1Mt produced plastic waste⁴⁸, much higher than the average European country which recycled only 31.1%⁴⁹. This tremendous amount of recycled plastic prevented an additional 246 000 tonnes of CO₂ emissions, which is equivalent to one year's worth of emission produced by 51 200 vehicles traveling 30 000km per annum⁴⁸. Furthermore, from an economical standing, the plastic recycling industry is a tremendous asset since it provided 7890 formal jobs and an additional income to approximately 58 470 informal workers in 2018. The gathering and

recycling of plastics industry injects an estimated R2.3 billion into the economy per annum⁴⁹. Even though the recycling industry is making great environmental and economical strides, there is still room for much improvement. Approximately 70% of all recycled materials are sourced from landfills which is inadequate since this increases the extraction and cleaning costs and facilitates improper working conditions⁴⁸.

40 years ago, a worldwide plastic recycling campaign started and to this day only 14% of all the produced plastics, were recycled⁴⁰. A more robust recycling method is needed to cope with the condition of the plastic feed collected from waste sites. Another problem that the plastic recycling industry faces is that the recycled plastics' price is not competitive with that of newly produced plastic⁴⁰. This makes the traditional plastic recycling process financially difficult⁴⁰. The four main approaches to recycle plastic are primary recycling, mechanical recycling, chemical recycling, and energy recovery⁵⁰. Primary recycling refers to the direct recycling of the scrap material within the production line of a plant, without recycling any outside waste⁵⁰. Mechanical recycling is the most popular recycling method⁴⁰ and involves the separation of the different types of plastics and any contaminants to produce new plastic products with the help of melt extrusion⁵⁰. The intense sorting and cleaning of the various types of plastics is labour intensive and expensive³⁷. The six main types of plastics are high-density polyethylene (HDPE), low-density polyethylene (LDPE), polypropylene (PP), polystyrene (PS), polyvinylchloride (PVC), and polyethylene-terephthalate (PET)⁵¹. Not all plastics are easily recycled such as PS and PVC³⁵. Even though the plastic recycling rate is increasing, it is not keeping up with the production of plastics which results in more plastic waste entering the environment each year⁴⁰.

It is crucial that new recycling technologies are investigated and implemented. Chemical recycling technologies are promising, since multiple plastics can be recycled without an intense sorting process⁴⁰. Chemical recycling involves methods that lead to the depolymerization of the plastics. Plastics can be partially degraded to form valuable secondary products, or plastics can be fully degraded to monomers⁵⁰. LDPE, HDPE, and PP are thermoplastics that can be used in chemical processes such as pyrolysis to be converted to valuable petrochemical products such as liquids fuels⁵⁰. Energy recovery is another alternative plastic waste processing method that is being implemented since no sorting is required⁵⁰, however, incineration is not environmentally sound⁴⁰ since the practice releases toxic gases presenting a threat to the environment and human health⁴³. Clearly, the traditional recycling methods such as mechanical recycling and incineration are not effectively removing plastic pollution. Even though chemical recycling still has challenges to overcome, it may be the key to creating a closed recycling loop⁴⁰. To find an effective solution to the plastic recycling

problem, more robust recycling methods should be investigated⁴³. Since both coal fines and plastics can be reutilised through pyrolysis and gasification⁴⁰, the two waste streams can be combined to produce valuable products. This presents an opportunity to utilize two materials using one method. The addition of plastic provides a fuel source with a high heating value and a low ash and sulphur content, effectively providing a “greener” source of energy⁴⁷.

2.5 Coal agglomeration

Coal fines need to be agglomerated to be used in industrial processes such as fixed bed gasification³³. Once the coal fines have been agglomerated, the agglomerates need to meet all the consumer requirements while adhering to market standards⁵². For agglomerates to be used in fixed bed gasification, the agglomerates need to have a mechanical strength similar to that of ROM coal⁵³. There is a wide variety of different agglomeration techniques including briquetting, pelletisation, and extrusion. These techniques can be further differentiated when also considering binder addition or lack thereof⁴⁷. All these techniques as well as the agglomeration variables will be discussed in this next section.

2.4.1 Agglomeration techniques

- **Briquetting**

Coal briquetting has been around from the 15th century. In China, cow dung and clay were used as binders with coal fines and filled into a brick like mould by hand. The mould was allowed to air dry and produced weak low calorific briquettes used for domestic needs. Since then, the briquetting process has been industrialised and produce stronger briquettes using various mechanical methods⁴⁶. The two main methods of briquetting are by roller press or by producing individual briquettes using a die configuration. The roller press produces pillow-like briquettes using two rollers with built-in pockets. The coal fines are fed into the two rollers and high pressures are applied to produce the briquettes⁵². The die configuration produces briquettes by applying pressure to the material within the die. The high pressures produce a briquette in the specific shape of the die⁵⁴.

When using binders, a pre or post formation process might be needed if the binder requires a temperature variation to be activated. Depending on the binder used the formation treatment can either be a heating or cooling treatment⁴⁶. When coal fines are briquetted without using a binder, the briquettes produced are referred to as green briquettes. These green briquettes are more cost effective since no binder is added and no energy is spent on the activation process of the binder⁵⁴.

- **Pelletisation**

During pelletisation, a rotating pole forces coal and the added binder through a cylindrical open-ended die. The walls apply friction preventing the free flow of the mixture. The friction compresses the mixture while it is pressed forward. The densified mixture is pressed out of the die and is cut into individual pellets⁵².

- **Extrusion**

A mixture of coal fines and the binder is fed into the extruder chamber using a screw-feeder configuration⁴⁶. The screw feeder mixes the material while the extrusion chamber is kept at specified temperatures. This allows the binder to be activated during extrusion since the required heat can be applied. The rotating screws force the feed through a die. The diameter of the die is varied according to the product specification. As the extrudate leaves the die, a rotating knife cutter is used to cut the continuous extrudate into smaller pellet sized extrudates⁴⁶.

Extruders are used in a wide variety of industries and the geometry of the extruders can be varied depending on the required product⁵⁵:

- Different extruders have different screw configurations which are mostly varied between single and twin-screw configurations.
- The pitch and length of the screws vary.
- The screw length to diameter ratio is also varied.
- Depending on the amount of mixing required, kneading elements can be added to the screws. The angle and thickness of the kneading elements can be varied to improve mixing.

The following operational variables influence the final extrudates:

- The binder to solid ratio of the feed.
- Binder formulation.
- At lower screw speed, the feed material has a longer residence time which can give more time for larger granules to form. However, lower screw speed results in a higher mass being loaded into the screw configuration and will require more torque to produce extrudates.
- Higher material feed rates result in the formation of denser and stronger extrudates.

2.4.2 Agglomeration variables

Coal agglomeration is dependent on multiple variables including coal rank and oxidation, moisture content, mineral matter content, particle size, agglomeration temperature and

pressure, and binder addition⁵⁶. As the rank of the coal increases, the hydrophobicity of the coal increases as well. The hydrophobicity is directly correlated to the strength of the agglomerate formed; therefore, a coal of higher rank forms a stronger agglomerate⁵⁶. Since South Africa and specifically the Highveld coalfield consists of low-rank inertinite-rich bituminous coal, binders are often added to produce stronger briquettes⁵⁶.

Moisture can help to increase the strength of an agglomerate by increasing the cohesion and capillary forces between coal particles⁵⁷. However, a too high moisture content will enable the water to act as a lubricant between particles and lower the compressive efficiency during agglomeration, leading to the production of mechanically weaker agglomerates⁵⁸. If the moisture content of the agglomerate is too high, the agglomerate will not only lose its strength but also lose economical value by decreasing the calorific value⁵⁹.

Clays are one group of minerals that have the largest effect on agglomeration⁵⁶. Normally, when the mineral matter content of coal increases the compressive strength of the agglomerate also increases. This is especially true for clays. Kaolinite is a clay type that increases the plasticity of the coal and therefore it increases the compressive strength. However, the increase in mineral matter will cause an increase in ash production. When the ash yield of coal is high correlations show that the water resistance of that coal is lower. Therefore, a good balance in mineral matter is optimal to achieve a high compressive strength while retaining water resistance abilities and keeping a lower ash content³².

The particle size distribution of the feed material is one of the largest factors that influence the strength of the agglomerate⁶⁰. It is easier to agglomerate small particles than it is to agglomerate large particles⁵⁶. Coal particles with a diameter between 0.6mm and 0.8mm tend to produce strong agglomerates, and as soon as the particle size increases above 1mm, weak points start to form and the agglomerate becomes susceptible to cracks and breaks⁶⁰. With a wider range of particle sizes in an agglomerate, the smaller particles fill the unoccupied spaces between the larger particles⁵⁷. As the smaller particles fill the voids the interparticle attractive forces increase between the smaller and larger particles. The attractive forces reduce the distance between the particles and produce strong agglomerates. Therefore, the particle size needs to vary for both mechanical and economic incentives⁵⁶.

High temperatures are used during agglomeration to cure the agglomerate in order to increase the mechanical strength⁶¹. At higher temperatures the polymer binder deforms and forms permanent bonds between the particles, increasing the strength of the agglomerate. The mechanical strength of agglomerates increases up to when the degradation temperature of the sample is reached. When the temperature is too high the binder can decompose or

combust, nullifying the purpose of adding a binder⁵². Increasing the agglomeration temperature also increases the operational cost since the energy consumption of the process increases⁶². During extrusion the melt viscosity of the feed changes as the temperature changes. At higher temperatures the melt viscosity decreases thereby increasing the ease at which feed flows through the extruder⁶³. The extrusion temperature for LDPE and PP was found to be between 200 °C and 240 °C, varying only slightly between different reported studies^{64–66}.

The strength of an agglomerate is directly proportionate to the amount of forming pressure applied. When an inadequate amount of pressure is applied the contact between particles decreases and interparticle vacancies form within an agglomerate⁵⁷. With more space between particles the interparticle attractive force reduces producing weaker agglomerates⁵⁶. At higher pressures the size of interparticle spaces reduces and vacancies disappear increasing the interparticle attractive force. As the particles are more tightly packed, other forces like the Van der Waals and capillary forces increase and further increases the strength of the agglomerate⁵⁷.

Producing agglomerates without using a binder would be optimal since binders are normally the most expensive component in fine coal agglomeration⁴⁶. High-rank coal does not require binders to produce mechanically strong agglomerates⁵⁶. However, low-rank coals require external adhesive properties to produce strong agglomerates⁴⁶. South Africa mostly produces low-grade coal with a high ash content⁶⁷. Cheap binders are essential to agglomerate South African coal and many potential binders have been tested⁵³. For a binder to be classified as a good binder, it needs to meet the following criteria^{68,69}:

- Produces strong interparticle bonds.
- Has water resistant properties.
- The binder must be pollutant free and environmentally friendly.
- Binders should increase the heating value of the agglomerate.
- Be constantly available and economically feasible.
- The binder should not interfere with the process utilizing the coal.

2.6 LDPE and PP as binder

Plastics have many attributes that gives them the potential to be used as binders. In South Africa plastics are regularly available in both municipal waste and as recycled products since the country recycles 46.3% of its produced plastic waste⁴⁸. The use of waste materials as binders is an attractive option since binders are often the most expensive component of agglomeration⁴⁶.

Furthermore, plastics have high heating values and contain no discernible sulphur or ash. With the low sulphur content plastics reduce the SO₂ emissions while the low ash content reduces the amount of particulate matter emitted⁴⁷. These properties generally make plastics ideal for producing a high energy density fuel with minimal environmental impacts⁴⁷. The worst plastic to convert to fuel would be PVC, since preliminary heating is required to remove chlorine through HCl formation at 360 °C⁷⁰. Furthermore, it has a relatively low heating value (21.0 MJ/kg)⁷⁰ when compared to the other plastic types. On the other hand, LDPE and PP have the highest heating values (both have a heating value of 46.5MJ/kg) of all the plastic types and does not contain any toxic compounds like chlorine⁷¹. Since LDPE and PP have significantly higher heating values when compared to coal fines (21.9 MJ/kg⁷²), both increase the volumetric energy density of the agglomerate. However, plastics have a low density and will reduce the density of the formed agglomerate⁷³.

Both LDPE and PP consist almost completely of carbon and hydrogen making them ideal candidates to produce syngas during gasification⁷⁴. Furthermore, plastics contain mostly volatile matter (LDPE (99.8%) and PP (97.7%))⁷¹. When combining plastics with other feed material, the amount of plastic can be varied to produce the required amount of volatile matter⁴⁷. Furthermore, both LDPE and PP have shown that when used as binders, strong agglomerates can be produced^{72,73}. Massaro et al.⁷² also found that the addition of LDPE increased the water resistance of the agglomerates. Since polypropylene is also hydrophobic it does not absorb water⁷⁵ and should increase the water resistance of agglomerates.

Both LDPE and PP seem to be suitable binders since both plastics have the necessary binder properties described by Waters⁶⁹ and Zhang et al.⁶⁸. However, further investigation is still needed. Polymers have a high thermal expansion coefficient; therefore, as heat is applied the particles expand more than materials such as coal with a low thermal expansion coefficient. When these materials are combined the increase in temperature can lead to cracks, distortions, and the disintegration of the agglomerate⁷⁶. The thermal degradation of plastics was found to be between 438 and 521 °C, while that of coal has a wide range between 174 and 710 °C⁷⁷. Furthermore, since both LDPE and PP have an extremely high volatile matter content⁷¹, the effects of devolatilization on the integrity of the remaining char (mostly coal char) is unknown, and the structure could be compromised during pyrolysis and gasification. If the agglomerates are disintegrated into powder during gasification, the remaining powder could cause problems to existing fixed bed gasification processes which require a particle size above 6 mm³³.

2.7 Mechanical Strength

To solve the handling problems that coal fines present, the fines are agglomerated (hot extruded in this study). However, for extrudates to be used in industrial processes, the extrudates need to adhere to mechanical strength standards. During the handling and transportation, various strains and stresses are exerted upon the extrudates⁵². The extrudates will be stockpiled and transported in large containers where the bottommost extrudates will have to withstand a tremendous load⁷². To withstand the load, the compressive strength of the extrudates need to be at least 350kPa⁴⁵. For the extrudates to be used in fixed bed gasification each extrudate needs to have a similar compressive strength to that of ROM coal (14MPa)⁵³. However, Massaro *et al.* (2014) noticed that while working with briquettes produced from coal fines and LDPE that the briquettes no longer fractured once the LDPE concentration increased to 15%. Instead, the briquette deformed and flattened while staying in one piece and maintaining its strength due to the elastic properties of the LDPE.

Stockpiles are often exposed to the environment, therefore extrudates should be able to withstand exposure to water. The extrudates should maintain a maximum compressive strength above 350kPa after being exposed to water⁴⁵. Agglomerates have shown good water resistance properties when plastics like LDPE was used as a binder⁷². Plastic binders create a solid bridge matrix during agglomeration that is not influenced by the presence of water giving the agglomerate water resistance⁷².

The extrudates will be transferred and dropped from conveyor belts, rail cars, front end loaders etc. repeatedly. The extrudates need to be able to withstand the impacts to prevent damage from occurring⁷². To determine the impact resistance index (IRI) of the extrudates, the drop shatter test is performed on each extrudate.

2.8 Pyrolysis

2.8.1 Introduction to pyrolysis

Pyrolysis is a thermochemical process that decomposes carbonaceous materials in an inert environment while being exposed to high temperatures⁷⁸. The inert environment prevents any combustion of the feed material and enables the process to produce various products. The feed decomposes to produce char, condensable products, pyrolytic water, and volatile matter^{79,80}. Currently, pyrolysis is used to recycle a wide variety of waste materials⁸¹. The robust nature of pyrolysis has many benefits, and the produced products can be used in a wide variety of industries^{78,82}.

- Solid waste is renewed and used as an energy source.
- The pyrolysis products can be used in industrial furnaces as a viable fuel supply.
- The use of pyrolysis products is a greener alternative to many traditional fuels and emits less greenhouse gases.
- By using pyrolysis on waste streams, the process contributes to solid waste managing efforts.
- Electricity can be generated using the pyrolysis products.
- By manipulated process conditions, pyrolysis becomes more economical and productive, or potentially more environmentally friendly.
- Pyrolysis produces a wide range of products that can be used for different applications.

Pyrolysis is the first step in the gasification process wherein carbonaceous materials like coal are used to produce synthesis gas. The Fischer-Tröpsch process is then used to produce petroleum products from the synthesis gas (syngas)¹¹. As the wide variety of feed materials produce an even wider variety of pyrolysis products, the product yields and quality need to be evaluated. Evaluation of the pyrolysis products can determine whether the use of various feed materials would be beneficial to the gasification processes⁷⁸. In this study the focus is placed on the evaluation of coal and plastic pyrolysis (co-generation).

2.8.2 Coal pyrolysis

Coal pyrolysis occurs in an inert environment and at temperatures exceeding 400 °C⁷⁹. Coal is a complex substance and all the reactions occurring during pyrolysis are not yet completely understood⁸³. During coal pyrolysis multiple chemical reactions occur forming various products⁸⁴. Understanding all the reactions that occur during coal pyrolysis gets even more complicated since the qualities of the various coal types differ⁸⁵.

Coal pyrolysis is greatly dependent on the properties of the coal used⁸⁶. The effects of the properties of different coal samples on the pyrolysis reaction kinetics and products have been a point of focus in many recent studies⁸⁴⁻⁸⁷. The properties of a coal sample that have a significant impact on pyrolysis includes the coal rank, mineral matter content, petrography, and composition⁸⁷. Furthermore, it is not only the difference in coal properties that contribute to different pyrolysis yields and product characteristics, the pyrolysis operating conditions also influences the results⁸⁸. Changes in temperature has a large influence, while a multitude of other parameters like heating rate, pressure, catalysis addition, atmosphere, etc. also affects the product distribution and characteristics^{87,89}.

During coal pyrolysis the main products are char, tar, water, and gas^{79,80}. The char has a high heating value used for heating boilers or power generation. The tars are used in the petrochemical industry to produce liquid fuels like diesel, and the pyrolysis gas has high calorific values and is used to produce town gas and as fuel to heat up boilers⁸⁵.

2.8.3 Plastic Pyrolysis

The cost-effective nature and wide applicability of plastics has led to the dramatic increase in plastic product consumption⁹⁰. With the increase in production and consumption of plastic the role of recycling and re-refining plastic waste has become much more important⁹¹. Diesel has an energy content of 45.30MJ/kg and the average plastic energy content is between 80 and 90% of that of diesel with plastics like LDPE (46.52MJ/kg) and PP (46.50MJ/kg) even having a slightly higher energy content⁷¹. Plastic wastes are being reprocessed to produce petroleum products such as gasoline and other heavy oils. The high energy contents of plastic wastes enable them to be chemically repurposed to produce environmentally friendly and valuable products. Pyrolysis breaks down the plastic's macromolecular structure and produces smaller molecules in the range of gasoline like hydrocarbons⁹¹. Currently, pyrolysis is the main method of producing chemicals and fuels from plastic wastes⁹².

Extensive research has been conducted on the pyrolysis of plastics with similar findings being reported. Sogancioglu *et al.* (2017) found that the pyrolysis of both HDPE and LDPE waste produced mostly liquid and gaseous products (a combined average of 97.9% and 93.6% respectively) at temperatures varying from 300 °C to 700 °C. As the temperature increased the amount of char produced decreased and the amount of gas produced increased. At higher temperatures, the gas contained more aromatic compounds⁹⁰. Achilias *et al.*⁵⁰ reported results showing that HDPE, LDPE, and PP produced gas and oil products that consists mainly of aliphatic alkanes and alkenes when pyrolyzed at 450 °C. Furthermore, the LDPE produced a liquid containing hydrocarbons within the same range as commercial gasoline. Demibras (2004) experimented with the pyrolysis of municipal waste PE (760 °C), PP (760 °C), and PS (580 °C) and concluded that these waste plastics can also produce gasoline range hydrocarbons. The liquid product of the mixture of the waste plastics, pyrolyzed at 750 °C, contained naphtha, gasoline, and light gas oil.

Plastics mostly decompose into vapour that consists of a non-condensable gaseous product and condensable liquid and waxy product⁹³. Kříž *et al.*⁹⁴ reported that when pyrolyzing a mixture of waste plastics, the volatile matter content of the plastics (approximately 95.2 wt.%) are released at temperatures ranging between 340 °C and 430 °C. Most of the volatile matter is released around 380 °C⁹⁴. Depending on the temperature and plastic type used, the amount

of liquid and gas products vary⁹⁰. The liquid product consists of aliphatic hydrocarbons, aromatic hydrocarbons, and olefins ($C_9 - C_{35}$) and has similar properties to that of crude oil⁷¹. The liquid product is mainly a mixture comprising of three main types of products. The mixture contains a heavy naphtha fraction ($C_7 - C_{10}$), a gasoline fraction ($C_8 - C_{10}$) and a light gas oil fraction⁹¹. Most of the produced products are perfectly suited for further processing in the petrochemical industry⁴⁰. The type of liquid product produced greatly depends on the type of plastic used. PET and PS produce liquids and waxes with a higher aromatic content. Whereas HDPE, LDPE, and PP produce waxy liquids with a higher aliphatic and olefin content, and a lower aromatic content⁷¹. The gaseous products ($C_1 - C_4$) mainly consists of paraffinic hydrocarbons and olefins. The gaseous product has a high calorific value and can be directly used as fuel. Currently, plastic pyrolysis is attracting the attention of scientific and industrial communities since it is a promising versatile platform to convert plastic waste into valuable resources⁹⁵. However, plastics include a wide range of additives that are not considered to be environmentally friendly such as colorants, stabilisers, and antioxidants⁹⁰. The impact that these additives have on the pyrolysis products are still unclear and requires further investigation⁹¹.

2.9 Gasification

2.9.1 Introduction to gasification

Approximately 200 years ago, coal was converted into gaseous products for the first time in the United Kingdom⁹⁶. Since then, gasification has become a commercially proven technique to convert organic materials into valuable gaseous products⁹⁷. During gasification solid fuels reacts with mixture of gases which can include oxygen, air, carbon dioxide or steam at temperatures exceeding 700 °C. Different processes use different mixtures of steam and CO_2 depending on various factors such as the feed coal or gasifier used⁹⁸.

The reaction produces a gaseous product that can be directly used as an energy source, or it can be further processed to produce other gaseous fuels, liquid fuels, or chemicals⁹⁹. The gaseous product produced is referred to as syngas³⁴. The syngas contains a mixture of carbon monoxide, carbon dioxide and hydrogen and has a high heating value that can be used to produce energy through gas turbines and engines⁹³. The composition of the gaseous product is influenced by changes in the feed gas. Generally, the CO content of the syngas increases as the CO_2 content of the feed gas increases. When the steam in the feed gas increases, the yield of H_2 and CO_2 increases, while the yield of CO and CH_4 decreases⁹⁸. Other influences on the chemical composition of the syngas includes⁹⁹:

- coal rank,
- particle size of the coal,
- gasification agents used (air or oxygen), and
- the reactor conditions such as pressure, temperature, heating rate and residence time.

The manner in which the solid feed makes contact with the gaseous mixture determines what the type of gasifier is. There are four main types of gasifiers: molten bath, entrained flow, fluidised bed, and fixed bed¹⁰⁰. The Lurgi gasifier is the most significant commercially available fixed bed gasifier. It was developed in the 1930's in Germany. This dry-bottom system operates at high temperature (approximately 980 °C on lignite coals) and pressure (between 30 - 35 Atm.). Due to the high pressure, the feed needs to be coarse, or risk being blown out of the gasifier¹⁰⁰. These gasifiers are used to produce syngas for the Fischer-Tropsch process to produce hydrocarbons¹¹. The process was used in Germany during the second world war, but it was discontinued shortly afterwards due to unfeasible economics. However, Sasol adopted the process in the 1950's and now produces more than a third of South Africa's liquid fuels¹⁰⁰.

When gasification was firstly introduced, the technology gained the reputation of not being environmentally friendly since the process had various harmful impacts on the environment. Since then, the technology was improved and adapted to be able to operate efficiently under stern environmental regulations. One of the main advantages of gasification is that it is robust enough to be used to refine waste streams from various processes⁹⁷. Gasification has many advantages when compared to the combustion of solid wastes since it limits the amount of toxic gas including dioxins, SO_x, and NO_x being emitted¹⁰¹. Gasification still produces ash as a waste product; however, the waste can be disposed of in an environmentally friendly manner⁹⁷. A variety of suitable uses for the ash produced during gasification is being investigated. Possibilities include using the ash in plant fertilizers or as a neutralising or liming agent¹⁰².

2.9.2 Coal gasification

Across the globe, coal is the most used fossil fuel in a variety of industries including iron production, cement and concrete production, electricity generation and chemical production³⁴. However, coal emits CO₂, NO_x, SO_x, and other toxic gases during utilisation²⁴. The global demand for energy is increasing faster than the increase in the production of energy, while the energy industry is pressured to rapidly reduce their CO₂ emissions to prevent further global warming⁹⁹. For coal to be utilised in an environmentally friendly manner, clean coal

technologies need to be developed. Gasification technology is versatile and one of the cleanest ways to produce electricity and chemicals using coal as feedstock³⁴.

With a coal feedstock the gasification process can be divided into two parts. The first step is pyrolysis of the material where the volatile matter is discharged, and a char is produced. In the second step the char, containing mostly fixed carbon and mineral matter, is reacted with a mixture of gases to produce syngas. This step is the rate limiting step¹⁰³. Shahabuddin et al.⁹⁸ compared the gasification behaviour of bituminous coal char under steam, CO₂, and a mixture of the two gases. Gasification was completed at temperatures between 1000 and 1200 °C. The results showed that at 1000 °C and 10 vol% steam, gasification reaches an equilibrium, and if more steam is added the H₂, CH₄ and CO concentrations decreased while the concentration of CO₂ increased. At 1200 °C the yields of H₂ and CH₄ decreased compared to the yields of the char that underwent gasification at 1000 °C, resulting in a syngas with a higher heating value being produced at 1000 °C. The study also concluded that steam gasification resulted in an H₂-rich syngas while CO₂ gasification produced a CO-rich syngas. The syngas with the maximum lower heating value was achieved at 1000 °C with 10 vol% steam⁹⁸.

Sasol has 97 fixed bed gasifiers in operation and is the largest commercial user of this technology⁹⁷. After gasification the gaseous product is indirectly converted into liquid fuels using the Fischer-Tropsch process¹¹, making South Africa the largest producer of petroleum products from coal⁸. Since South Africa does not have an abundance in crude oil, Sasol uses coal to produce petroleum products⁶.

2.9.3 Plastic gasification

Thermal treatments to chemically recycle waste plastics are preferred alternatives to landfilling¹⁰⁴. Furthermore, the diminishing fossil fuel resources is creating new opportunities in the alternative energy market¹⁰⁵. Pyrolysis and gasification have shown tremendous potential to be used to produce valuable products including high energy gases and oils¹⁰⁴. These thermochemical processes have been developed and tested on pilot and demonstration scale. Gasification has been shown to be a robust process capable of operating using a wide range of plastics¹⁰⁶. One major advantage is that existing gasification technologies can be used in the gasification of plastics⁹². The gasification of coal with different waste materials has already illustrated that operation can continue without making large changes to the gasifier. The larger the ratio of coal to waste, the easier the transition is since coal acts as a stabiliser¹⁰⁷.

However, gasifying plastic does not come without its challenges. Plastics produce a relatively large condensable product fraction containing heavy hydrocarbons that could be undesirable in post process applications¹⁰⁵. Therefore, an extensive cleaning unit is needed to ensure the condensable products do not contaminate the syngas. Otherwise, higher temperatures or a catalyst is needed to crack the condensable products. Furthermore, the equipment needs to be able to handle the sticky nature of plastics⁹². Another possibility of reducing the amount of condensable products produced is to combine plastics with other feed materials such as wood or coal. The combined reactions of the plastics and other feedstock could lead to lower carbon losses and produce a syngas with a higher energy content¹⁰¹.

The syngas produced from plastics can be a valuable product if effectively cleaned. It can be used as an energy source or as raw material to produce fuels¹⁰⁶. One of the main components of the gas produced during plastic gasification is hydrogen. Plastics (including polyethylene and polypropylene) produce gases with a high hydrogen content during gasification¹⁰⁴. Hydrogen is an extremely useful gas since it has the potential for high efficiency power generation¹⁰⁵. Hydrogen is an important fuel since no CO₂ is released during its combustion¹⁰⁴.

Various literature studies have been reported on the gasification of waste plastic. Almost exclusively, the gasifying agent used was either steam or air¹⁰⁶. As the rate of steam injection increased, the amount of oil and solids produced decreased while the amount of gas produced increased. The amount of hydrogen produced increased as can be expected due to an increase in steam reforming reactions¹⁰⁴.

2.10 Summary

Coal is crucial for the socio-economic development in South Africa and the resource is widely used across the country¹. Both coal and plastic contribute immensely to the amount of waste generated in South Africa. In 2017 it was estimated that 54.2 Mt of general waste was generated in South Africa. Only 38.6% of the discarded waste was recycled, leaving 33.3 Mt of waste untreated. 12% of the countries annual municipal solid waste (MSW) consists of plastic waste. Furthermore, 630 000 tonnes of plastics are classified as mismanaged wastes³⁵. In South Africa, 12% of the coal mined tonnage are coal fines³². This amounts to 38.8Mt⁴⁷. The production of coal fines during coal mining is unavoidable¹ and the fines are considered to be a waste³².

Most industrial processes that use coal have a minimum size requirement, such as fixed bed gasifiers that can only use coal with a diameter larger than 6 mm³³. By agglomerating the fine coal particles, a larger agglomerate can be created which presents a financial opportunity.

Since both coal fines and plastics can be recycled through pyrolysis and gasification⁴⁰, the two waste streams can be combined to produce valuable products. This presents an opportunity to recycle two materials using one method. The LDPE and PP can act as binders to strengthen the coal agglomerates⁷². Furthermore, LDPE and PP have high calorific values and water resistant properties which increases the value of the agglomerates⁷¹.

For agglomerates to be used in industrial processes, the agglomerates need to adhere to certain mechanical strength standards. During the handling and transportation, various strains and stresses are exerted upon the agglomerates⁵². The agglomerates will be stockpiled and transported in large containers where the bottom agglomerates will have to withstand a vast load⁷². Therefore, the agglomerates need to undergo mechanical strength tests to ensure that they can be industrially utilised.

Pyrolysis is a thermochemical process that decomposes carbonaceous materials in an inert environment while being exposed to high temperatures⁷⁸. Currently, pyrolysis is used to recycle a wide variety of waste materials⁸¹. The robust nature of pyrolysis has many benefits, and the produced products can be used in a wide variety of industries⁷⁸.

Gasification is another robust process used to increase the value of carbon containing materials. During gasification solid fuels react with mixture of gases which can include oxygen, air, carbon dioxide or steam at temperatures exceeding 700 °C⁹⁸. The reaction produces a gaseous product that can be directly used as an energy source, or it can be further processed to produce other gaseous fuels, liquid fuels, or chemicals⁹⁹. The gaseous product produced is referred to as syngas³⁴. The combined reactions of the plastics and other feedstock such as fine coal could lead to lower carbon losses and produce a syngas with a higher energy content. However, this possible synergic effect has not been sufficiently studied and is not fully understood¹⁰¹.

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CHAPTER 3: THE MECHANICAL AND THERMAL PROPERTIES OF EXTRUDATES PRODUCED FROM DISCARD COAL FINES AND RECYCLED PLASTICS AS BINDERS

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ABSTRACT:

This study focuses on the extrusion of discard coal fines from the Highveld Coalfield together with recycled low-density polyethylene (LDPE) and polypropylene (PP) which are used as binders to produce agglomerates with better handling properties than the coal fines for industrial use. The binder content was varied between 5 and 100wt%. The barrels of the twin-screw extruder were kept at a temperature of 220 °C to melt the binders while forcing the mixture through a 10 mm die. The extrudates containing 10% or more binder were strong and homogeneous, while a 5% binder addition proved to be too low to produce homogeneous extrudates. The extrudates containing 10% LDPE and 10% PP showed compressive strengths of 17.5 and 7.9 MPa before breaking, respectively. The rest of the extrudates (>10% plastic addition) did not break but merely flattened as the plastic load increased. The compressive strength of all the extrudates showed no significant difference after being exposed to water. Furthermore, the extrudates absorbed less than 5% water after being submerged for 24 hours. Thermogravimetric analysis (TGA) of the extrudates was conducted under a nitrogen atmosphere up to 900 °C. Three iso-conversional methods, Kissinger-Akahira-Sunose (KAS), Starink, and Flynn-Wall-Ozawa (FWO), were used to determine the activation energy of the extrudates and raw materials. The lower activation energy and conversion temperatures found for the extrudates indicate a synergy between plastic and coal fines when the extrudates are pyrolyzed. Results from this study suggest that the co-extrusion of recycled plastic with coal fines will produce solid carbonaceous fuels with high hydrophobicity, heating value, and high mechanical strength compared to coal fines.

Keywords: coal fines, LDPE, PP, extrusion, mechanical strength, TGA, iso-conversional methods

3.1 Introduction

Coal is crucial for the socio-economic development in South Africa, and the resource is widely used across the country¹. Approximately 77% of the country's energy needs are supplied by coal², which includes 83%³ of the electricity generated and 30% of the country's produced fuels⁴. Globally, South Africa is the 6th largest coal producer² and mines approximately 250 Mt of coal per annum⁴. During mining and operation, coal fines (coal particles with a <1 mm diameter) are formed⁵ and account for approximately 12% of the total South African mined coal⁶. The South African coal mining industry currently discards 60 Mt of coal fines per annum⁷. Discarding coal fines causes environmental problems since acid mine drainage occurs when stored in slime dams¹, and improper storage can result in spontaneous combustion⁷. Industrial processes do not readily use coal fines due to handling and transportation difficulties⁵ as well as high ash yield, sulphur⁷ and moisture content⁶. From a financial incentive⁶, the use of coal fines would positively affect the environment and provide an additional source of coal available for utilisation⁸. To extend the life of the remaining coalfields, the utilisation of discarded coal fines is beneficial and aligned with government policy⁹.

To be used in industrial processes, coal fines need to be agglomerated to improve the handling of the material⁵. These agglomerates need to adhere to mechanical strength standards¹⁰ and must have water resistance properties¹⁰. In order to improve the mechanical strength of the agglomerates, binders are often added. These binders should be environmentally friendly; binders can often be the most expensive aspect of agglomeration¹¹. To overcome this problem, the binding properties of municipal wastes are continually being investigated¹².

South Africa has a complicated global standing in terms of waste management. Even though the country is one of the front runners in waste plastic recovery by recycling 46.3% of its 1.1 Mt of plastic waste annually¹³, the country is still however ranked the eleventh most mismanaged plastic waste practice globally (630 000 tons per annum)¹⁴. Plastic waste is continuously increasing and is an enormous environmental threat. Traditional plastics are not biodegradable and cause problems decades after the initial pollution¹⁵. The problem presented by plastic waste is further complicated because plastics are significantly cost-effective to produce¹⁵. Globally, the most popular and economical waste management method is via landfilling; however, landfilling produces secondary pollutants such as releasing toxic gases, acid leachate and spontaneous combustion¹⁶. When waste, including plastic waste, is incinerated, more poisonous gases are released, which cause damage to the environment and human health¹⁷. Polymers like polyethylene (PE) and PP experience decreasing quality during recycling and are unsuitable for monomer recovery. The lack of recyclability leads to

the exploration of blending plastics with other feedstock materials for application as a fuel source which can produce high-energy pyrolysis products or liquid fuels¹⁸.

Plastics have many good binder attributes, such as high heating values and no discernible sulphur or mineral content. From all the plastic types, LDPE and PP have the highest heating values (~ 46.5 MJ/kg) and do not contain toxic compounds like chlorine¹⁹. These plastics consist almost completely of carbon and hydrogen, making plastics ideal candidates for producing syngas²⁰. Furthermore, plastics contain mostly volatile matter, i.e., LDPE contains approximately 99.8%, and PP contains 97.7% volatile matter¹⁹. When combining plastics with other feed materials, the amount of plastic can be varied to produce the required amount of volatile matter necessitated for the Industrial application²¹.

Both LDPE and PP have shown that when used as binders, strong agglomerates can be produced^{12,22}. The authors are not aware of previous studies conducted on the extrusion of fine coal and plastic. Only one study has reported on the extrusion of plastics (LDPE and PP) together with a woodchip feedstock²³. The study used extrusion as a mixing method and indicated that none of the previous studies used sufficient agglomeration techniques that allowed for the simultaneous mixing and heating of the plastics with the respective feedstock, including coal, biomass and woodchips²³. Furthermore, Peng et al.²² investigated the palletisation of biochar and plastic, while Massaro et al.¹² investigated the briquetting of LDPE and coal fines. These studies all indicated that plastic usage as binders have significant industrial applications since plastics mostly have high energy densities, are hydrophobic, and produce durable agglomerates^{12,22,23}. Furthermore, Peng et al.²² found that waste plastics could be an economically feasible binder solution. Song et al.²³ increased the energy density of woodchips by extruding them with thermoplastics like LDPE and PP. Hence, this study is considered a novel study to understand the behaviour of discard South African coal fines when blended with these plastics and extruded¹⁸. By improving the understanding of the co-pyrolysis of extruded coal and plastic mixtures, the possible applications of this new fuel source in processes such as pyrolysis or gasification can be better evaluated.

Studies have reported on the thermogravimetric analyses (TGA) pyrolysis of plastic and coal mixtures by only mixing the raw powders^{24,25}. Furthermore, most available literature investigates the addition of low percentages of plastics (0 to 15 %) to coal blends^{12,24,25}. The low addition of plastic to the coal blends were investigated in order to find a suitable replacement for traditional fossil fuels without drastically changing current industrial processes^{12,24,25}. Low additions of plastics would prevent large changes to the fuel source composition since plastics consist almost exclusively out of volatile matter¹⁹. Sharypov et al.²⁶ and Sharma et al.¹⁸ both reported synergy between coal and plastics during pyrolysis as larger

plastic to coal addition ratios (1:1, 3:1, and 1:3) were investigated. Sharypov et al.²⁶ investigated the effect of PP on brown coal in an autoclave in an argon atmosphere and reported that the blends maximum degradation temperature remains close to that of the PP. Sharma et al.¹⁸ investigated mixtures of LDPE and Indian Ledo coal. The Ledo coal has lower activation energy than LDPE, and the blends reported higher activation energy than for both individual materials. These studies included larger ratios of plastic addition so that the fuel source can be applied to both waste management and energy production.

All the available studies in the literature use Northern hemisphere coal^{12,18,25–27}, and the thermal behaviour of South African (inertinite-rich) discarded coal fines and plastic blends have not yet been reported. Furthermore, no direct comparison was found in the literature between the synergic effect of coal and PP and that of coal and LDPE pyrolysis over a wide range of plastic concentrations, as has been conducted in this study. Multiple simultaneous reactions need to be accounted for when investigating the pyrolysis kinetics and thermodynamic parameters of carbonaceous material. It is difficult to obtain the mechanism for each reaction; therefore, iso-conversional methods are used to estimate these parameters²⁸. Multiple iso-conversional methods have been used to determine kinetic parameters for both coal and plastics^{29,30}; however, the use of these methods have not been reported on the pyrolysis of mixtures of coal and plastics.

This study investigates the extrusion of Highveld discarded coal fines with different ratios of recycled waste LDPE and PP as binders to produce extrudates suitable for industrial processes. The mechanical strength, as well as the thermal properties, were investigated, and three iso-conversional methods (KAS, FWO, and Starink) were utilized to determine the kinetic and thermodynamic properties of the extrudates during co-pyrolysis.

3.2 Methods

3.2.1 Materials

3.2.1.1 Coal fines

Inertinite-rich discard coal fines were sourced directly from the Highveld coalfield in South Africa. These fines were dried for a week, and all lumps were crushed using a manual roller and a ball mill. The moisture content of the coal fines after air drying was determined to be 4.8 wt.%. The fines were screened, and particles < 1 mm were used in this study³¹.

3.2.1.2 Plastic

Recycled LDPE and PP cylindrical pellets were obtained from Potch Plastic (Potchefstroom, South Africa) with a particle size of approximately 5 mm. Where fines are required for analyses of the plastic, a FRITSCH Variable Speed Rotomill PULVERISETTE 14 classic line was used to reduce the plastic particle size, and the particles were also sieved to < 1 mm.

3.2.2 Extrusion

Before attempting extrusion, the Melt flow index (MFI) of the plastics was determined. The MFI can be related to viscosity, shear strength, and the shear rate of the material³². The MFI indicated that the plastic melt would flow evenly with fine coal particles acting as obstructions. However, as the coal fines content increased, the mass flow decreased, and eventually, blockages occurred. The MFI results obtained are further discussed in [Appendix A1](#).

The extrudates were produced using a TX 32 laboratory-scale extruder supplied by CFAM Technologies (Pty) Ltd. Since the increase in coal particles decreased the mass flow during the MFI test, the pure plastics were extruded first, and then the coal content was only increased if a stable run was obtained at the previous set concentration. The run was considered stable if a homogenous product could be produced and no blockages occurred. The samples contained 100, 75, 50, 25, 10, and 5 wt.% of plastic pellets (5mm) mixed with discard coal fines (<1mm). A screw feeder fed the mixture into the co-rotating twin-screw extruder at a feed rate of 22.5 kg/hr. The screws rotated at a constant speed of 250 rpm while the extruder barrels were kept at 220 °C. The hot extrudates were pressed through a 10 mm die and quenched in a water bath to cool the extrudates.

As the coal concentration of the blends increased during extrusion, the flow became more restricted. A 5% plastic content no longer produced homogeneous products and caused blockages in the extruder. Only the homogeneous extrudates produced (100 to 10% plastic) are illustrated in Figure 3-1 and were used for the remainder of the experiments.

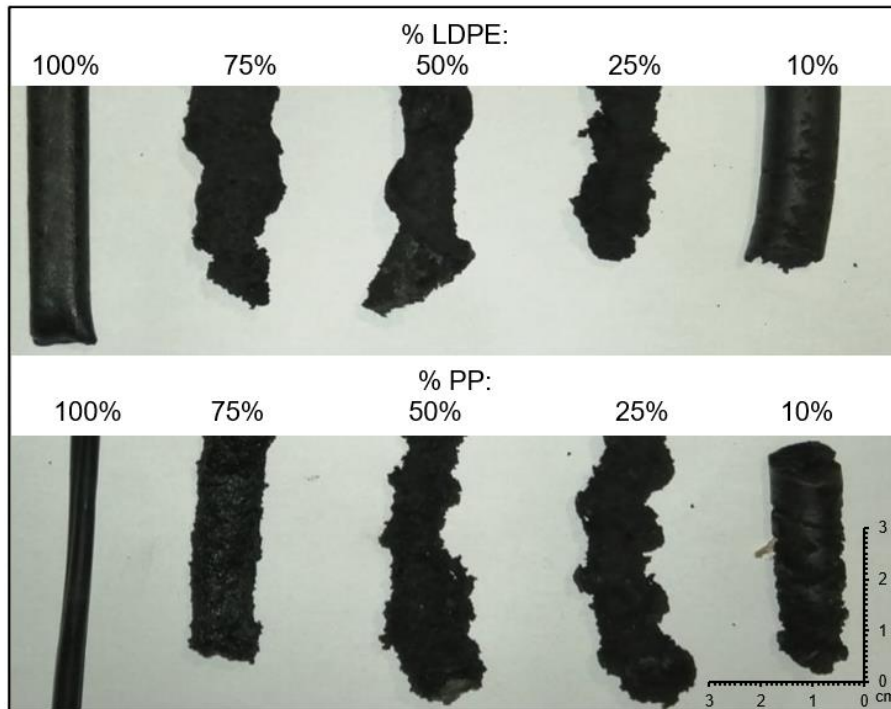


Figure 3-1: Extrudates containing various percentages of LDPE and PP

The extrudate strands were collected, dried, and then manually cut into 2 cm lengths using a table saw.

3.2.3 Chemical composition

3.2.3.1 Characterisation

The discard coal fines, LDPE, PP, and extrudates were characterised using proximate, ultimate and calorific value analysis. The proximate analyses and calorific value analysis were conducted at the North-West University along with the percentage carbon, hydrogen, and nitrogen. Bureau Veritas determined the percentage sulphur, and the percentage oxygen was determined by difference. The operating procedures used for these analyses are summarised in Table 3-1.

Table 3-1: Characterisation operating procedures

Description	Operating procedure
Proximate analyses	
Moisture (M)	ISO 11722: 2008
Volatile matter (VM)	ISO 1171: 2010a
Ash (A)	ISO 562: 2010b*
Fixed carbon (FC)	By difference
Ultimate analyses	
Carbon, Hydrogen, Nitrogen	ISO 29541: 2010
Sulphur	ISO 19579: 2006
Oxygen	By difference
Calorific value	ISO 1928: 2009b

*The ash yields of the coal and extrudates were determined using ISO 562: 2010b; the ash yields of the plastics were determined using the operating procedure described in Wong et al.³³.

3.2.4 Mechanical strength

3.2.4.1 Compressive strength

Compressive strength tests were conducted using a Lloyd LRX Plus Press. A single extrudate was placed between the two flat plates of the press, and the top plate applied a load onto the extrudate by extending downward at a rate of 5 mm/s. The maximum load at which the extrudate breaks or is permanently deformed is considered the maximum load. The LRX press provides two different graphs when the extrudate breaks and deforms (Figure 3-2a,b).

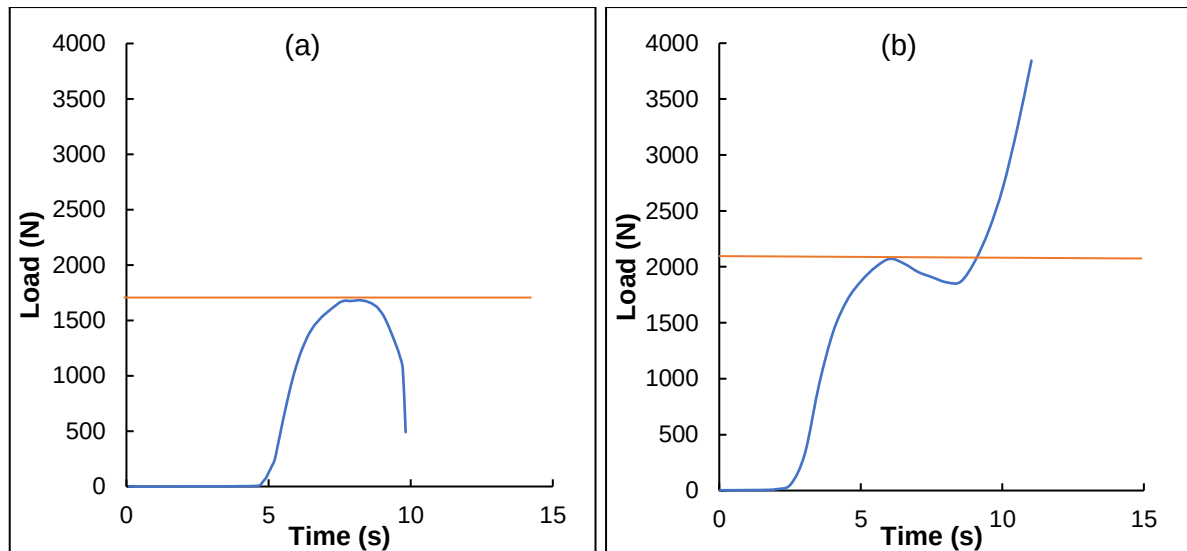


Figure 3-2: Compressive strength curves of a) breaking extrudates and b) deforming extrudates

When the extrudate breaks, a clear maximum peak can be recognised by the LRX press, and a breaking point is identified (Figure 3-2a); however, when the extrudate is deformed, a clear breaking point is not identified because the extrudate is slowly flattened and does not have a defined breaking point. The LRX press will thus show a slightly lower load when the deformation starts, and then the load will increase until the press reaches its maximum load since a breaking point was not identified (Figure 3-2b). The red line indicates the maximum load before breaking or deformation. The compressive strength of the extrudate was then calculated using Equation 3-1.

$$CS = \frac{L}{Ac \times 1000} \quad (3-1)$$

Where compressive strength is represented by CS (MPa), the maximum load applied by L (N), and the cross-sectional area is represented by Ac (cm²)³⁴.

3.2.4.2 Water resistance

The water resistance properties of the extrudates were evaluated by two methods: (1) the extrudates were submerged in water for 2 hours, and directly afterwards the compressive strength of the extrudates was measured using the operating procedure as discussed in Section 2.4.1⁶; (2) the water absorbance of the extrudate provides a quantitative measure of its water resistance. Extrudates were submerged in water for 30 minutes, and the mass difference between the sample before and after being submerged was measured. The water resistance index (WRI) was determined using Equation 3-2.

$$WRI = 100 - \% \text{ water absorbed after 30 minutes immersion} \quad (3-2)$$

Extrudates need to obtain a WRI > 95% after 30 minutes of submersion to be deemed water-resistant¹⁰. This process was then repeated, and the samples' mass was recorded hourly until the extrudates achieved maximum water absorption.

3.2.4.3 Impact resistance

Each extrudate was dropped from a 2 m height onto a flat concrete floor. The extrudates were dropped for a maximum of 6 times or until the extrudate shattered into several small fractions. By counting the number of fractions (n) that the extrudate breaks into and the amount of drops necessary (N), the impact resistance index (IRI) was calculated using Equation 3-3. The IRI value of the extrudates should be higher than 50 to withstand the strains of industrial processes¹⁰.

$$IRI = \frac{100 \times N}{n} \quad (3-3)$$

3.2.5 Pyrolysis

3.2.5.1 Thermogravimetric analysis (TGA)

Before the samples were pyrolyzed, the extrudates were pulverised using a FRITSCH Variable Speed Rotomill PULVERISETTE 14 classic line, and all the samples were screened to <1 mm. The raw materials and extrudates were pyrolyzed using an SDT Q600 TGA. The samples were weighed, and ±15 mg was placed into a cylindrical alumina crucible. Each sample was kept under a constant nitrogen flow rate of 100 ml/min while the temperature increased from 25 to 900°C. The heating rate was varied at 10, 20, 30 and 40°C/min.

3.2.5.2 Kinetic analysis

Non-isothermal conditions were used at a constant heating rate for each experiment.

The decomposition rate ($\frac{dX}{dt}$) was defined using Equation 3-4.

$$\frac{dX}{dt} = f(X)k(T) \quad (3-4)$$

Where $f(x)$ is the conversion function, and $k(T)$ is the temperature dependant rate function^{29,30}. The degree of conversion (X) was determined using Equation 3-5.

$$X = \frac{m_0 - m_T}{m_0 - m_\infty} \quad (3-5)$$

Where m_0 and m_∞ are the initial and final sample mass, respectively. m_T represents the mass of a sample at a specific temperature. $k(T)$ is described by the Arrhenius equation^{29,30}.

$$k = A \exp\left(-\frac{Ea}{RT}\right) \quad (3-6)$$

Where A (s^{-1}), Ea ($J \cdot mol^{-1}$), and R ($J \cdot K^{-1} \cdot mol^{-1}$) are the pre-exponential factor, activation energy and ideal gas constant, respectively. By substituting the Arrhenius equation into Equation 3-4 and dividing by the heating rate β ($\beta = \frac{dT}{dt}$) Equation 3-7 is obtained³⁰.

$$\frac{dX}{dT} = \frac{A}{\beta} \exp\left(-\frac{Ea}{RT}\right) f(X) \quad (3-7)$$

When integrating Equation 3-7, Equation 3-8 is obtained.

$$g(X) = \int_0^X \frac{dX}{f(X)} = \frac{A}{\beta} \int_{T_0}^T \exp\left(-\frac{Ea}{RT}\right) dT \quad (3-8)$$

where

$$T = T_0 + \beta t \quad (3-9)$$

and T_0 is the initial experimental temperature³⁰.

The thermal degradation of carbonaceous material is complex since multiple reactions occur simultaneously and need to be accounted for. It is difficult to obtain the reaction mechanism for each individual reaction²⁸. Therefore, iso-conversional methods, including FWO, KAS, and Starink, were used to estimate the activation energy without knowledge of the reaction mechanisms. The integral in Equation 3-8 has no specific solution;

therefore, the iso-conversional methods simplify the equation using linearisation and approximate the solution using the constants S and B, as seen in Equation 3-10²⁸.

$$\ln\left(\frac{\beta}{T_X^S}\right) = C_s - \left(\frac{BEa}{RT_X}\right) \quad (3-10)$$

Where the value of S and B varies for each method. S = 0 and B = 0.457 for FWO; for KAS S = 2 and B = 1, and for Starink, S = 1.8 and B = 1.0037. The activation energy can be determined by plotting $\ln\left(\frac{\beta}{T^S}\right)$ versus $\frac{1}{T}$ and varying the heating rate. From the slope of the straight line, the activated energy can be obtained (calculated)^{28–30}.

3.3 Results and discussion

3.3.1 Chemical composition

The proximate analyses, ultimate analyses and calorific value results obtained in this study are reported in Table 3-2.

Table 3-2: Proximate analyses, ultimate analyses, and calorific value of the feed materials and extrudates (air-dry basis)

Proximate analyses					Ultimate analyses						Calorific Value
	%M	%VM	%A	%FC (by difference)	%C	%H	%N	%S	%O	Molar ratio C:H	(MJ/kg)
Feed Materials											
Recycled LDPE	0.3	97.7	1.6	0.3	83.4	14.6	0.1	0.1	0.0	0.5:1	46.2
Recycled PP	0.3	98.5	1.2	0.0	84.0	14.7	0.0	0.1	0.0	0.5:1	46.7
Coal fines	4.8	24.9	29.6	40.8	50.3	2.8	1.3	1.0	10.2	1.5:1	19.5
Extrudates											
10% LDPE	2.2	35.1	30.3	32.5	56.4	5.4	1.1	0.7	3.9	0.9:1	24
25% LDPE	1.7	45.5	26.9	25.8	62	7.4	0.9	0.6	0.5	0.7:1	28.6
50% LDPE	1.3	64.2	17	17.5	69.1	9.6	0.7	0.4	1.9	0.6:1	33.6
75% LDPE	0.9	75.1	10.1	13.9	73.5	11.2	0.5	0.4	3.4	0.5:1	39.8
100% LDPE	0.1	96.8	1.6	1.4	83.6	13.8	0.5	0.2	0.2	0.5:1	45.9
10% PP	2.5	36.7	29.4	31.4	57	5.3	1.1	0.6	4.1	0.9:1	24.7
25% PP	2.1	45.9	23.7	28.4	60.9	6.9	0.9	0.6	4.9	0.7:1	28.6
50% PP	1.3	64	15.7	19	68.6	9.4	0.7	0.4	3.9	0.6:1	33.9
75% PP	0.8	76.7	9.9	12.6	73.5	10.9	0.5	0.4	4	0.6:1	41.2
100% PP	0.1	98.6	1.3	0.0	83.9	14.5	0.1	0.1	0.0	0.5:1	46.6

3.3.1.1 Proximate analysis

It can be observed from Table 3-2 that the discard coal fines have moisture and volatile matter contents within the range of bituminous coal³⁵ typically mined in the Highveld coalfield³⁶. Compared to Run of mine coal (ROM) mined from the Highveld coalfield, the discard coal fines used in this study have a lower volatile matter content and higher moisture content than reported in previous studies. Matjie et al.³⁶ showed that ROM Highveld coals typically contain 30 - 34% volatile matter, 22.1 - 29.7% ash and 2.9 - 3.8% moisture.

LDPE and PP consist almost exclusively of volatile matter. Similar to the results obtained in this study, Diaz Silvarrey and Phan¹⁹ reported that pure LDPE and PP had 99.8 and 97.7% volatile matter content, respectively, with the remainder being fixed carbon. Furthermore, the plastics contain almost no moisture or mineral matter. As expected, when the plastic concentration in the extrudates increased, the volatile matter content increased and the moisture, ash yield and fixed carbon content decreased. All the extrudates showed a moisture content of less than 3%. Furthermore, the moisture content remained low and did not increase linearly towards the moisture content of fine discard coal as the plastic content decreased.

3.3.1.2 Ultimate analysis

LDPE and PP have a lower molar carbon to hydrogen ratio than coal fines. From Table 3-2, it can be observed that as the plastic content increased in the extrudates, the ratio of carbon to hydrogen decreased. Since plastic has a higher hydrogen content, the calorific value of the extrudates increased as the plastic content increased. Furthermore, the coal fines have a sulphur content below the maximum limit of export coal. The highest grade of Richard Bay (RB) export coal accepts a maximum sulphur content of 1%, while the lowest grade accepts coal with a sulphur content of 1.2%³⁷. Both LDPE and PP have sulphur contents of less than 0.2%. Therefore, as the plastic content increased in the blends, the sulphur content within the extrudates decreased even lower, further improving the extrudates' quality.

3.3.1.3 Calorific value (CV)

The recycled LDPE and PP calorific values agree with a study by Diaz Silvarrey and Phan¹⁹, who reported that both LDPE and PP had a calorific value of 46.5 MJ/kg. The calorific values of LDPE and PP are more than double compared to discard coal fines, which is due to the high hydrogen to carbon ratio³⁸, along with the low ash yield, low moisture, and high volatile matter content of the plastics compared to that of the coal fines³⁹. With this significant difference in calorific value between coal fines and plastics, the calorific value of the extrudates increased linearly with the increase in plastic content.

3.3.2 Mechanical strength

3.3.2.1 Compressive strength and water resistance

Both the dry and wet compressive strength results are discussed. Figure 3-3 illustrates the effect of the compressive strength test on the extrudates.

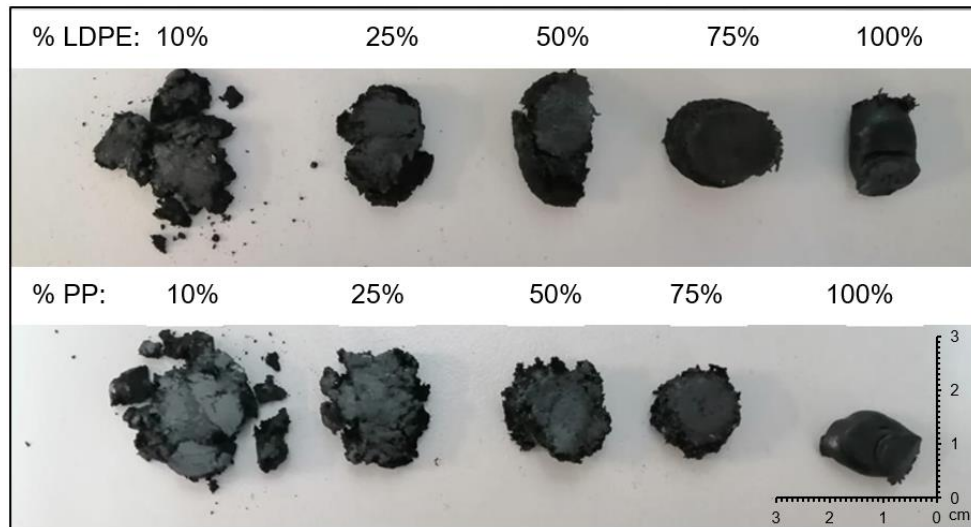


Figure 3-3: Extrudates after compressive strength analyses

Only the dry extrudates are depicted in Figure 3-3; however, both the dry and wet extrudates behaved the same when subjected to a large load. Thus, water exposure did not affect whether an extrudate was broken or deformed. As the plastic content increases, the extrudates start to deform instead of breaking when subjected to large loads. It can be observed that the 10% plastic bound extrudates were the only extrudates that broke when a large load was exerted on them. Thus, there is a distinct difference between an extrudate that breaks and one that deforms. When an extrudate breaks into smaller particles, the particles generally present problems in industrial processes. On the other hand, extrudates which deform (flattened in the case of >10% plastic bound extrudates) do not break into smaller particles and can still be used in industrial processes. Massaro et al.¹² reported similar plastic deformation when the LDPE content of the fine coal briquettes was increased to 15%. The measured compressive strength results of the extrudates are indicated in Figure 3-4.

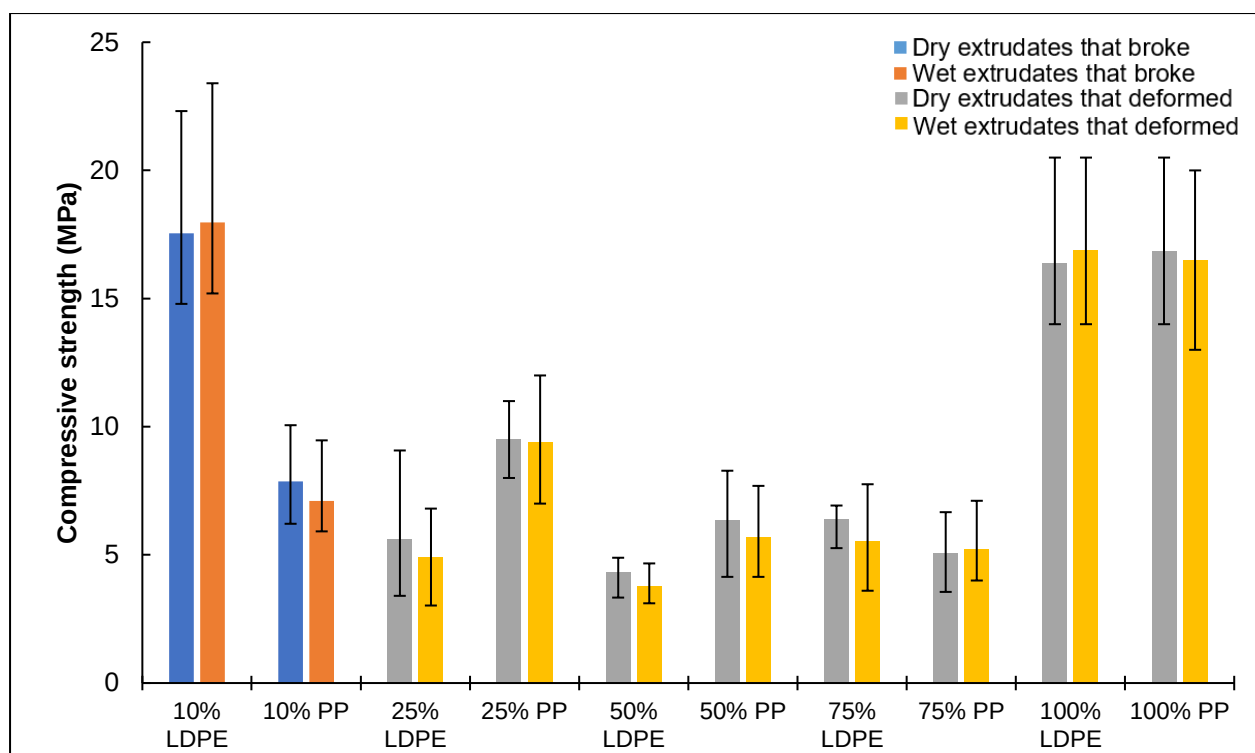


Figure 3-4: Compressive strength of breaking and deforming extrudates

The wet extrudates have a compressive strength that has no noticeable difference from that of the dry extrudates (Figure 3-4). The wet and dry extrudates containing 10% plastic had an average compressive strength far exceeding the 350 kPa minimum proposed by Richards¹⁰. This can be attributed to the good water-resistant characteristics of both LDPE and PP. It can also be seen that the average extrudate containing 10% LDPE had greater compressive strength than that of the extrudates containing 10% PP. The average extrudate containing 10% LDPE had a compressive strength that exceeded the 14 MPa compressive strength of ROM coal of the same dimension (10 mm), as reported by Leokaoke et al.⁴⁰. The higher compressive strength of the extrudates containing LDPE when compared to PP can be attributed to the Barus effect during extrusion, which results in additional swelling of plastics due to the remaining elastic energy when heated⁴¹. LDPE has more elastic energy, and the swelling could increase pressure during the extrudate formation within the die. Once the LDPE leaves the die, it swells more than the PP illustrating the Barus effect (Figure 3-1).

To compare the compressive strength of the deformed extrudates to that of the minimum acceptable strength proposed by Richards¹⁰ or to that of the ROM coal reported by Leokaoke et al.⁴⁰ would not be an adequate comparison since the deformed extrudates never broke under the load to form smaller pieces. Because these extrudates remained in one piece while being compressed, all these extrudates possess more than sufficient compressive strength to be used in industrial applications as feedstock. Furthermore, the deformation points for extrudates containing 100% plastic are much higher than that of the extrudates comprising of

coal and plastic mixtures. This is due to the physical structure of the extrudates, i.e., as the coal and plastic mixtures produce a much more rugged extrudate than the smooth extrudate produced by only plastic (Figure 3-1).

3.3.2.2 Water absorbance

All the extrudates showed excellent water resistance by maintaining their integrity and not disintegrating after 24 hours of submersion (Table 3-3). The extrudates containing 25% and higher PP remained floating in water for 24 hours, while only the extrudates containing 75 and 100% LDPE remained floating for the entire 24-hour period. This is explained by the higher specific gravity of LDPE (0.94 g/cm^3) compared to PP (0.91 g/cm^3). The specific gravity was measured at Potch Plastic, and the values obtained correspond to previously reported values in literature⁴².

Table 3-3: Visual effect of water submersion on extrudates

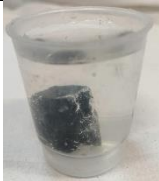
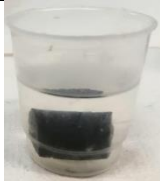
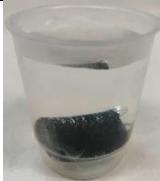
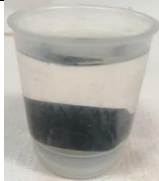
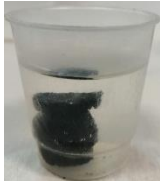
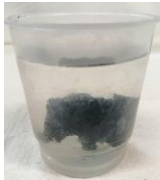
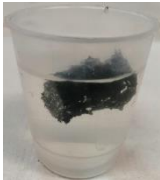
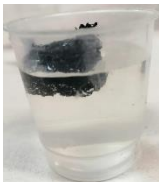
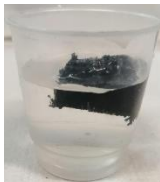
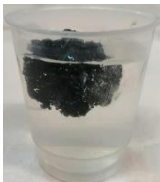
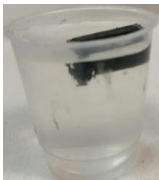
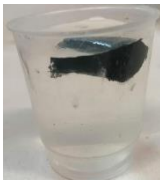
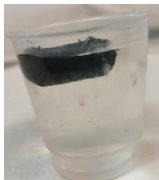
Plastic content	LDPE extrudates		PP extrudates	
	0 hours	24 hours	0 hours	24 hours
10 wt.%				
25 wt.%				
50 wt.%				
75 wt.%				
100 wt.%				

Figure 3-5 illustrates the percentage of water the submerged extrudates absorbed over 24 hours.

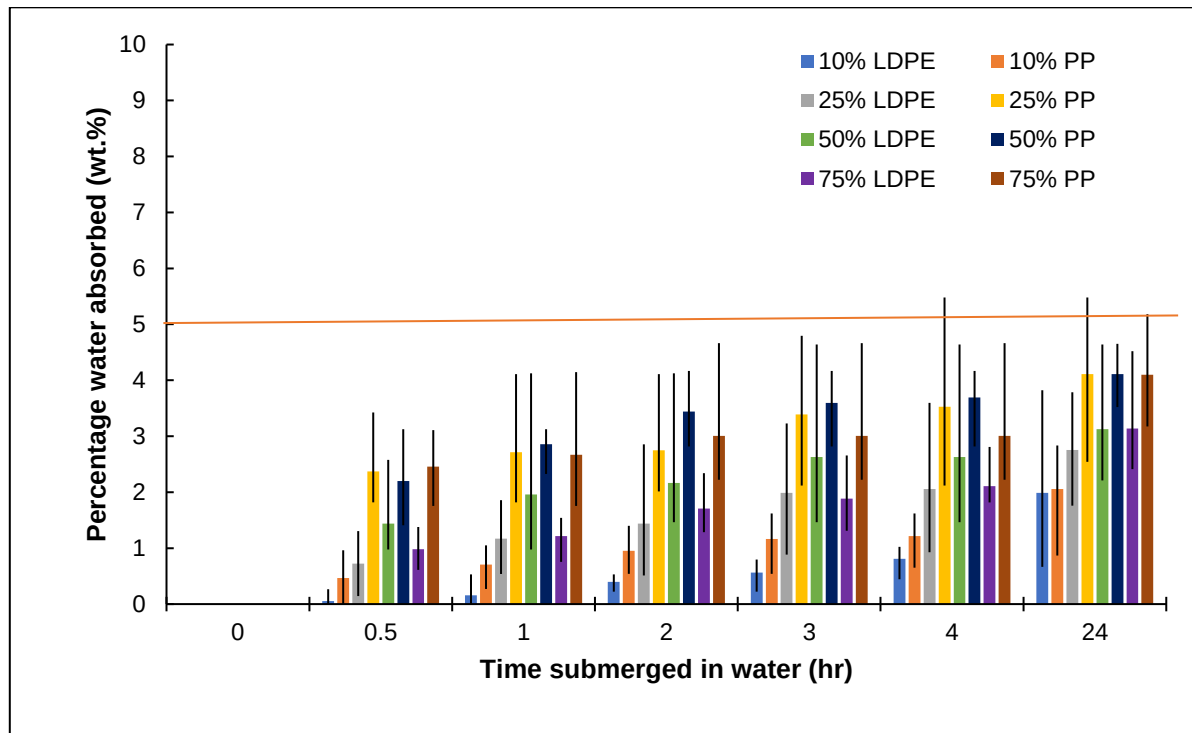


Figure 3-5: Water absorbance of extrudates

Even after 24 hours, the average water absorbance of all the extrudates tested remained under the absorbance limit of 5 wt.% specified for 30 minutes of submersion¹⁰, as indicated by the red line in Figure 3-5. The 100% plastic containing extrudates are not shown in Figure 3-5 since these extrudates absorbed no significant water as expected. For the remainder of the extrudates, the extrudates containing 10% LDPE absorbed the least amount of water (2.0 wt.% after 24 hours) and was closely followed by the extrudate containing 10% PP (2.1 wt.% after 24 hours). Generally, the 50% plastic-containing extrudates absorbed the most water due to the rugged surface of these extrudates, allowing more moisture to seep into cervices. The extrudate containing 50% PP had the highest absorbance of 4.1 wt.% water after 24 hours. The extrudates having a smoother surface (100 and 10% plastic) absorbed the least amount of water. The LDPE extrudates absorbed slightly less water at all the various plastic concentrations when compared to PP.

3.3.2.3 Impact resistance

None of the extrudates broke or shattered when dropped; therefore, all extrudates obtained a maximum IRI value of 600 and far surpassed the minimum IRI value of 50¹⁰. All the extrudates have a more than sufficient impact resistance to stay intact during conveyor belt transfers and other drops during handling¹⁰. The extrudates containing high concentrations of plastic (100,

75 and 50% plastic) did not even break when the extrudates were forcefully thrown onto the floor; however, the extrudates containing lower plastic concentrations (25 and 10% plastic) yielded very minor breakage as only small fractions broke off when forcefully thrown.

3.3.3 Pyrolysis

3.3.3.1 Thermogravimetric analysis (TGA)

Variation in heating rate influences the temperature at which decomposition occurs. As described in Uwaoma et al.³⁰, a higher heating rate causes the initial, maximum and final decomposition temperatures to slightly increase. Even though the decomposition temperatures are affected by the change in heating rate, the residual mass remains constant. This is expected when using a non-isothermal approach³⁰. The DTG-TGA results using a heating rate of 20 °C/min is exemplary of the behaviour of the results obtained at all the heating rates used in this study (10, 20, 30 and 40 °C/min). The mass loss and heat flow results of the samples using a heating rate of 20 °C/min are shown in Figure 3-6.

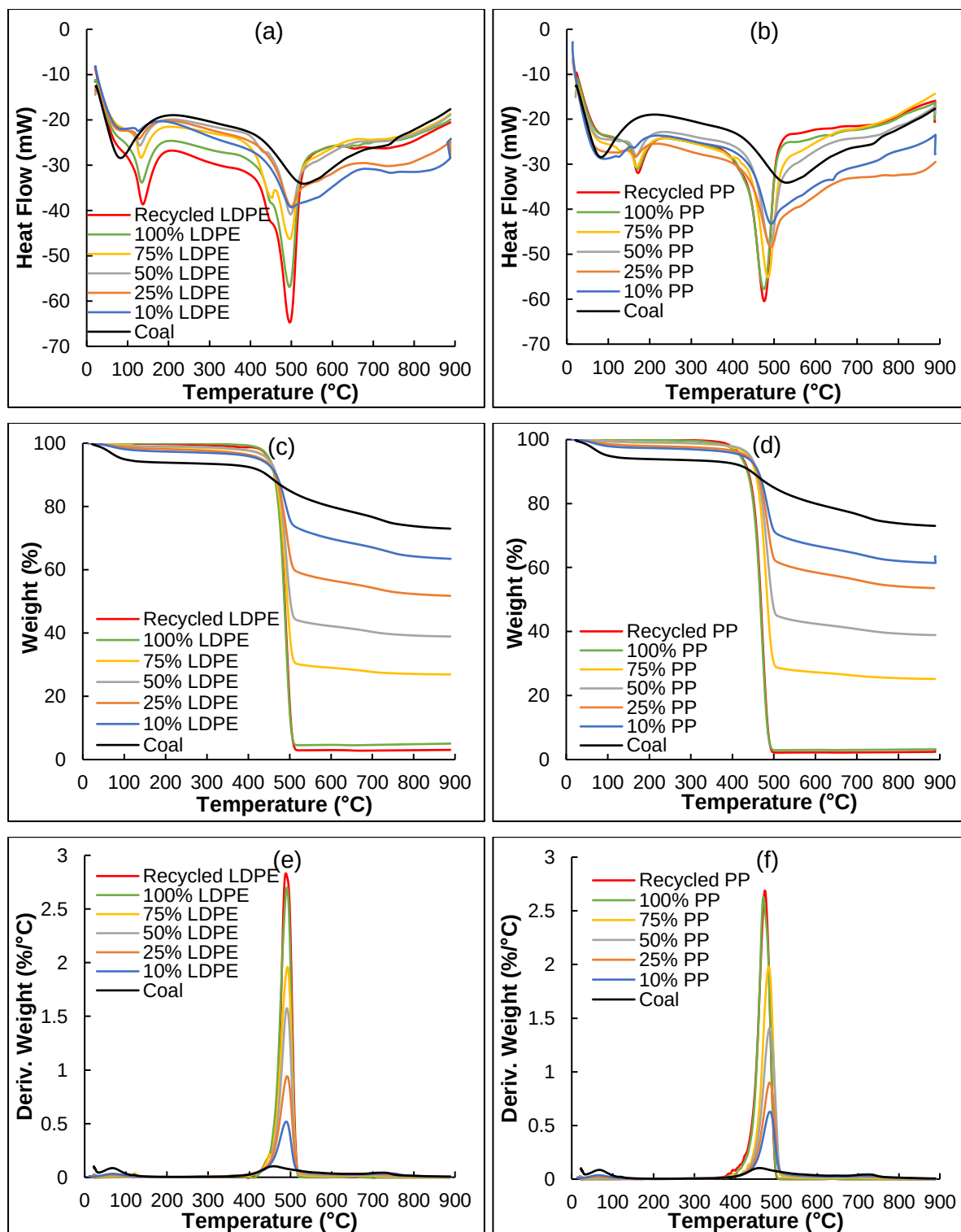


Figure 3-6: Heat flow (a, b), TGA (c, d) and DTG (e, f) of the LDPE and PP extrudates and the respective raw materials

The first heat flow peak at 100 °C indicates the moisture within the samples being driven off (Figure 3-6a,b). The proximate analysis indicated that LDPE, PP, and the extrudates have a lower moisture content than the coal fines; therefore, the increase in weight loss observed at 100 °C as the plastic content decreases is expected (Figure 3-6c,d). The onset of degradation

occurred around 325 °C for coal, whereas LDPE and PP had later onset temperatures but degraded within a narrower temperature range (Figure 3-6e,f). Since both plastics consist mostly of volatile matter, the total conversion increases as the weight concentration of plastic in the extrudates increases (Figure 3-6c,d). Therefore, the properties of fuel can be adapted to be used in various existing pyrolysis processes by altering the plastic content. The average pyrolysis parameters across the four different heating rates are illustrated in Table 3-4. Details of the influence of heating rate on the pyrolysis parameters is illustrated further in [Appendix A1](#).

Table 3-4: Pyrolysis parameters

	T_i (°C)	T_{max} (°C)	T_f (°C)	R_p (%/min)	R_v (%/min)	Mass Residue (%)
Coal	327.7	457.7	765.3	0.10	0.04	78.29
LDPE	386.4	489.3	519.5	2.88	0.19	3.25
PP	353.9	468.9	505.0	2.66	0.22	1.88
10% LDPE	343.8	488.3	774.6	0.59	0.06	63.37
10% PP	331.4	483.4	777.9	0.50	0.07	66.45
25% LDPE	357.6	490.6	775.3	0.95	0.09	53.16
25% PP	345.1	481.9	772.7	0.88	0.09	55.21
50% LDPE	353.8	490.2	730.2	1.69	0.12	36.47
50% PP	348.8	479.8	777.6	1.58	0.11	37.66
75% LDPE	352.5	490.6	754.3	2.02	0.13	27.00
75% PP	347.6	478.7	771.7	1.95	0.13	27.94

Table 3-4 presents the average onset temperature (T_i), maximum degradation temperature (T_{max}), final degradation temperature (T_f), lowest maximum decomposition rate (R_p), and lowest average decomposition rate (R_v).

It can be observed from Table 3-4 that the final degradation temperature of fine discard coal occurs above 760 °C, whereas LDPE and PP have final degradation temperatures below 520 °C. This is in accordance with Zhou et al.²⁵, who determined that 99% of LDPE decomposed between 426 and 526 °C and that 98% of PP decomposes between 399 and 507 °C. Das and Tiwari²⁹ found that the degradation onset and peak degradation temperatures of LDPE is higher than that of PP. The extrudates have a final degradation temperature c.a. 770 °C which can be attributed to the final degradation temperature of coal where mineral matter decomposition (carbonates)⁴³ and hydrogen abstraction occurs⁴⁴, since the plastics have decomposed at much lower temperatures.

The degradation of the coal and the plastics overlap, resulting in interactions between the degradation reactions of the coal and plastics within the extrudates. Synergy during the pyrolysis of blends of coal and plastic has been observed by various researchers^{18,24,26,27,45,46} and is attributed to the free radicals from the coal that participate during the degradation reactions of plastics which then results in an acceleration in the degradation of coal^{27,45}. The coal fines have a maximum degradation temperature (T_{max}) of 458 °C, and the LDPE had a

$T_{\max}$ of 489 °C. The remaining extrudates containing LDPE had similar maximum degradation temperatures than for the pure LDPE. LDPE decomposes in a narrow temperature range (386 – 520 °C) and provides a much larger derivative mass loss peak than for coal; therefore, even a low LDPE content will cause the maximum decomposition temperature to be the same as that of LDPE (Figure 3-6e). Sharma et al.¹⁸ found that the $T_{\max}$ of mixtures of coal and LDPE was slightly higher than that of the individual products; however, the study used Ledo coal and LDPE with similar maximum degradation temperatures. In this study, Highveld medium rank C bituminous discard coal reported a lower maximum degradation temperature than for the LDPE (Table 3-4) which could explain why the resulting maximum degradation temperature of the mixture is similar to that of the LDPE, and not higher.

Sharypov et al.²⁶ found that powder mixtures of coal and PP have maximum degradation temperatures close to that of PP. This study found that the extrudates have a maximum degradation temperature closer to PP than coal but is still higher than that obtained for both raw samples. The maximum degradation temperature of the 10% PP extrudate is the highest for the extrudates containing PP, and the maximum degradation temperature slightly decreases as the plastic content of the extrudates increases. The maximum degradation temperature of the extrudates is higher than that of the PP and coal samples separately; the right shift is visible in Figure 3-6f. This is an indication of synergy between coal and PP during the degradation of the extrudates.

As expected, coal has the highest residual mass, whereas plastics are almost completely devolatilised. This results in the coal having the lowest average decomposition rate (R_v) and lowest maximum decomposition rate (R_p). Therefore, the extrudates have increasing decomposition rates as the plastic concentration increases.

3.3.4 Kinetic analysis

3.3.4.1 Iso-conversional methods and activation energy

The KAS, Starink, and FWO methods were used to plot $\ln(\beta/T^2)$ against $1/T$, and the slope of the linear graph was used to calculate the activation energy. The activation energy at various degrees of conversion and the temperatures at which the conversion occurs for each of the samples are illustrated in Figure 3-7.

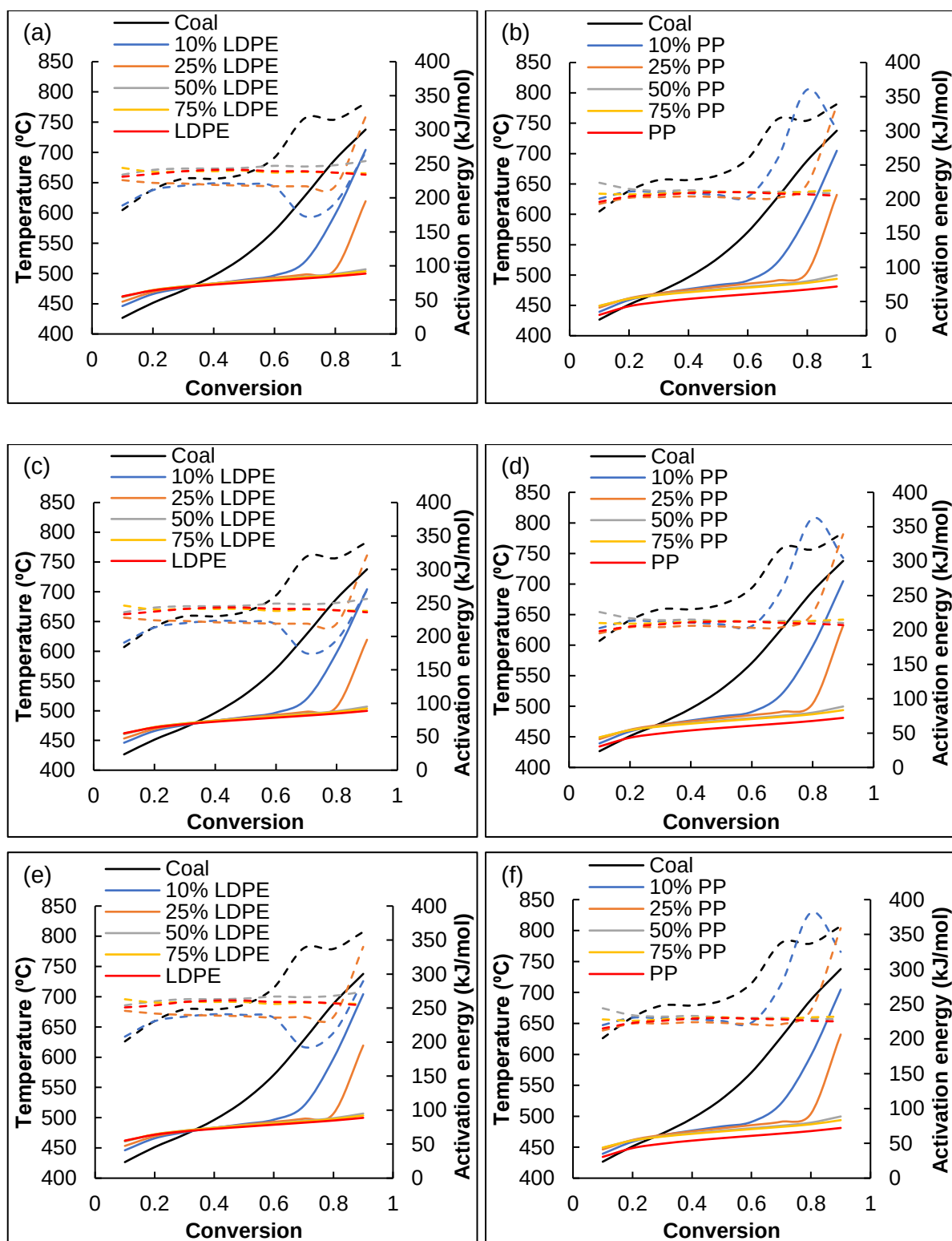


Figure 3-7: Temperature of conversion (solid line) and determined activation energy (dotted line) using the KAS (a, b), Starink (c, d), and FWO (e, f) methods.

The tabled values for the conversion temperature, showing activation energy and the corresponding R^2 values can be found in [Appendix A1](#). All the predicted activation energies had an R^2 value above 0.86. All three models showed similar values for the activation energies

of all the samples with only slight deviation. The KAS method was found to predict the lowest activation energy values, whereas the FWO method predicted the highest values. Coal has the highest activation energy variance across all three modes (182 - 362 kJ/mol), whereas LDPE (231 - 261 kJ/mol) and PP (196 - 230 kJ/mol) have small variances as conversion increases. Using the same iso-conversional methods, Uwaoma et al.³⁰ reported a similar activation energy range for the float fraction of bituminous discarded Highveld coal that ranged from 182 kJ/mol to 316 kJ/mol for a conversion range between 20 and 90%. These methods were also used by Das et al.²⁹, confirming that both plastics have only a slight increase in activation energy and that PP (136 - 173 kJ/mol) has a lower activation energy than LDPE (148 - 242 kJ/mol). Selecting the best model from the three used in this study is difficult since complex reaction mechanisms occur simultaneously during degradation²⁹.

As the conversion increases, the activation energy required for the coal sample increases, Uwaoma et al.³⁰ also observed an increase in activation energy as conversion increased. The activation energy for the plastics remains relatively constant and only slightly increases as conversion increases are observed (not significant). The extrudates containing both LDPE and PP exhibit similar activation energies to that of their respective plastics; however, at higher conversions the activation energy of the extrudates containing a lower plastic content starts to vary. The 10% and 25% PP bound extrudates deviate from the almost constant activation energy found for the PP, i.e., around 60% and 80% conversion respectively. Both of these extrudates show an increase in activation energy which shifts closer to that of the coal. This also includes an increase in conversion temperature above the final degradation temperature of the PP (505 °C). Therefore, the increase in activation energy can possibly be attributed to the remaining fine coal fraction of the extrudates once the PP has completely decomposed. The 50% and 75% PP containing extrudates do not show an increase in activation energy up to 90% conversion since the decreasing coal content results in the coal only having a negligible effect on the overall conversion. This is especially prominent since the coal only has 27% weight loss during degradation, while LDPE and PP have 97% and 98% weight loss, respectively (Figure 3-6c,d). An increase in activation energy for the 50 and 75% PP-containing extrudates would, therefore, only be observed between 90 and 100% conversion. The lack of an increase in the activation energy at higher concentrations of PP further confirms that the increase is caused by the remaining coal char fraction.

The 10% and 25% LDPE containing extrudates also deviate from the almost constant activation energy reported for LDPE. However, the activation energy of the 10% LDPE bound extrudates does not directly increase as is the case with the activation energies of the 10 and 25% PP, and 25% LDPE containing extrudates. The multiple complex reactions in which

chemical bonds are broken during pyrolysis can cause the activation energy to fluctuate as different reaction mechanisms are used¹⁸. Detailed investigations into reaction mechanisms are not included in the scope of this research. Therefore, it is recommended that a future study further investigates reaction mechanisms to clarify the decrease in activation energy observed in 10% LDPE containing extrudates compared to the increases observed in other extrudates. The deviances in activation energy of the 10% and 25% LDPE containing extrudates also occurs around 60 and 80% conversion respectively, and happens between 490 and 520 °C, once again at the final degradation temperature of the LDPE (520 °C). The rest of the extrudates follow the same trend as the 25% PP containing extrudate, but due to the low coal content, the increase in activation energy only occurs above 90% conversion.

In the temperature ranges where the degradation of the coal and the plastics overlap, the activation energy of the extrudates resembles that of the plastic and is not as high as that of the coal. This occurs for all the extrudates indicating that even a low plastic content can decrease activation energy and conversion temperature that would not occur if there was no synergy between the coal and the plastics. This results in the average activation energy of the extrudates being similar to that of the plastics, and it remains similar to the plastics even when the coal content increases. Miranda et al.⁴⁷ and Melendi-Espina et al.²⁴ reported that a blend of polymers would cause a decrease in the activation energy of the more stable polymers due to a transfer of hydrogen (free radicals) from the more stable polymers to the less stable polymers. The transfer of free radicals from the coal to the plastic during degradation has been reported as the reason for the observed synergy between the coal and plastics^{27,45,48}. Therefore, since coal has a higher activation energy, it can fulfil the role of the more stable component when mixed with plastics. Thus, during degradation, the transfer of free radicals from the coal to the plastics can cause the activation energy to be lower than expected and similar to that of the plastics rather than that of the coal. The lower activation energy results in a lower conversion temperature for the extrudates. Therefore, the synergy between the coal and plastic results in a degradation reaction that requires less activation energy than it would require if the coal and plastics were individually degraded. Hong et al.⁴⁵ also concluded that coal and polyethylene blends have a lower activation energy than the individual materials.

3.4 Concluding remarks

In this study, recycled waste plastics (LDPE and PP) were used as binders together with discard coal fines in producing extrudates having high mechanical strength, hydrophobicity, and high heating value. Both LDPE and PP served as excellent binders to extrudate coal fines. Moisture, ash, and sulphur content increased as the plastic content decreased. The increase in plastic content led to an increase in properties such as the ratio of hydrogen to carbon,

volatile matter, and calorific value. The 10% LDPE extrudate had the highest average compressive strength (dry = 17.5 MPa and wet = 18.0 MPa). All extrudates having a plastic content higher than 10% did not break but were merely deformed. Additionally, all the extrudates maintained their integrity after being submerged in water for 24 hours. The 50% PP bound extrudates absorbed the most water (4.1 wt.%), and the extrudates containing 10% LDPE absorbed the least (2.0 wt.%). All the produced extrudates have sufficient mechanical strength and water resistance to be used industrially. Depending on which properties are required during utilisation of the extrudates, the binder addition can be varied to significantly alter properties such as calorific value and volatile matter content. By incorporating recycled plastics, the coal fines were valorised into valuable extrudates. If the recycled plastics could be replaced with waste plastics, two waste streams would be reduced simultaneously to produce a new valuable fuel source.

The TGA results further demonstrated that both LDPE and PP have synergic interactions when pyrolyzed with fine discard coal. In addition, the synergy between coal fines and plastics was found to be prevalent across all ratios of mixtures. The extrudates containing PP had an increase in maximum degradation temperature compared to the PP and coal, respectively, indicating synergy between the two materials. Even with this increase in maximum degradation temperature, the iso-conversional methods found that the activation energies of all the extrudates were similar to that of the plastics and only increased when above the final degradation temperature of the plastics. Furthermore, the average activation energy of the extrudates resembled that of the plastics and is lower than that of the coal. The decrease in activation energy and temperature demonstrates the synergy obtained between coal and LDPE and coal and PP and could be attributed to free radical transfer from the coal. Since the decomposition of both LDPE and PP overlap with that of the coal fines, the use of waste plastics to improve the calorific value of coal during pyrolysis can be considered based on the findings reported in this study. The extrudate pyrolysis product yield and composition as well as the CO₂ gasification reactivity of the derived chars will be reported in future papers.

3.5 Supporting information

Additional information, tables, and figures regarding MFI, pyrolysis parameters and the kinetic analyses ([Appendix A1](#)).

3.6 Acknowledgements

This work was financially supported by the National Research Foundation (NRF) [Coal Research Chair Grant No. 86880]. Opinions, findings and conclusions or recommendations

expressed in any publication generated by the NRF supported research are that of the author(s) alone, and the NRF accepts no liability whatsoever in this regard. Prof LJ Grobler and staff at CFAM are also acknowledged for the provision of the extruder and operation of the machine.

3.7 Chapter 3 References

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CHAPTER 4: SLOW PYROLYSIS PRODUCTS DERIVED FROM EXTRUDATES PRODUCED FROM DISCARD COAL FINES AND RECYCLED PLASTICS AS BINDERS

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ABSTRACT:

The pyrolysis products derived from both coal and plastics have been extensively evaluated in literature, however, their co-pyrolysis product yields together with the characterization of the generated products have received less attention. Most studies use high heating rates with small particle sizes of mechanically mixed blends. This study aims to improve the understanding of the slow co-pyrolysis behaviour of extrudates produced from coal fines from the South African Highveld coalfield combined with recycled waste low-density polyethylene (LDPE) and polypropylene (PP), respectively. The fraction of plastic was varied between 10, and 100 wt.% during extrusion. The extrudates (10 mm diameter) underwent slow pyrolysis in a modified Fischer Assay setup by increasing the temperature (5 °C/min) under a nitrogen atmosphere to 520, 720, and 920 °C. The pyrolysis products (char, condensable products, water, and gas) were collected and characterised. The coal fines produced up to 83% char, whereas the plastics produced over 90% condensable products. The slow heating rate and small reactor volume favoured the production of condensable products, which increased with plastic concentration. The extrudates produced char and condensable product yields that fit the additive model of the raw materials. Statistical equations were developed to predict the pyrolysis yields and characteristics as functions of the coal and plastic composition. The equations accurately predict the char yield, condensable product yield, fixed carbon content, ash content, sulphur content of the chars, and the carbon and hydrogen contents of the chars and condensable products. GC-MS results indicate that the extrudates' condensable products consist mainly of alkanes and alkenes, similar to the plastics. Furthermore, the condensable products derived from PP and coal extrudates have fewer components with lower boiling points compared to the raw materials.

Keywords: coal, LDPE, PP, Fischer Assay, pyrolysis products

4.1 Introduction

South Africa's economy is highly dependent on coal¹, which is used to supply 30% of the produced fuels² and 83% of the generated electricity in the country³. During mining, coal fines (< 1 mm diameter) are produced⁴ (60 Mt per annum) and discarded⁵. Due to handling and transportation difficulties coal fines are not used in industrial processes⁴. Agglomeration can be used to improve the handleability and properties of the coal fines by increasing the size and lowering the moisture content of the coal fines⁶. Utilising coal fines provides financial opportunities⁷ and removes discarded waste from the environment⁸. The Highveld coalfield has particular value to South Africa's synthetic fuel production⁹.

Binders are often added to these agglomerates to improve the water resistance and mechanical strength of the agglomerates for industrial use⁶. Good binders are environmentally friendly; however, binders are often expensive⁶ and therefore, municipal wastes are regularly investigated for binding capabilities¹⁰. South Africa is the third largest consumer of plastics in Africa, resulting in 1.144 Mt of plastic waste in 2017¹¹. Plastic waste is continuously increasing, as plastics are cost effective products with multiple usages¹². Currently, waste is discarded in landfills since it is the least expensive solution¹³. Furthermore, some plastics (including polyethylene (PE) and polypropylene (PP)) cannot be recycled without decreasing the polymer quality¹⁴. Plastics, especially low-density polyethylene (LDPE) and PP have a high heating value, are hydrophobic, and contain negligible sulphur and mineral content, making them potential binders¹⁵. Currently, pyrolysis is the main method of producing chemicals and fuels from plastic wastes¹⁶. The high energy content of plastic wastes enables them to be chemically repurposed to produce environmentally friendly and valuable products. Pyrolysis breaks down the macromolecular structure of the plastic and produces smaller molecules in the range of gasoline-like hydrocarbons¹⁷. Furthermore, to alleviate the amount of plastic waste being discarded, alternative solutions, including combining plastics with other feedstock materials to create new fuel sources, are continuously explored¹⁴.

Pyrolysis of these combined materials can produce high-energy liquid fuels and products¹⁴. Pyrolysis is a thermochemical process that decomposes carbonaceous materials in an inert environment, while being exposed to high temperatures¹⁸. The inert environment prevents any combustion of the feed material and enables the process to produce various products. The feed decomposes to produce char, condensable liquids (water, tars (for a coal feed)¹⁹, and waxes and oils (for a plastic feed²⁰)), and non-condensable gas¹⁹. Currently, pyrolysis is used to recycle a diverse range of waste materials²¹. The robust nature of pyrolysis has many benefits, and the produced products can be used in a wide variety of industries^{18,22}.

Sharypov et al.²³ investigated the yields of liquid products produced from the co-pyrolysis of coal and PP powders (blends of 1:1, 3:1, and 1:3) under an argon atmosphere up to 900 °C. It was found that liquid product yields with boiling points ranging between 100 and 180 °C were non-additive compared to the raw materials. The higher yield in components with boiling points between 100 and 180 °C corresponded with a lower yield in fractions with higher boiling points, indicating a hydrocarbon distribution change. Melendi-Espina²⁴ conducted thermogravimetric mass spectrometry (TGMS) on blends containing coking coal and 5% of various plastics (high-density polyethylene (HDPE), LDPE, PP, polystyrene (PS), polyethylene terephthalate (PET), and a plastic mixture). The two main gaseous products were methane and hydrogen. The addition of plastics increased the amount of hydrogen produced which promoted intermolecular re-arrangement and aromatic condensation. Furthermore, more aliphatic hydrocarbons were produced. Kříž et al.²⁵ investigated the co-pyrolysis of waste plastics (up to 20% addition) with coal from the Upper Silesian basin. The study indicated an increase in condensable product yields as the plastic content increased, while the char yield decreased, the gas and water yields remained constant. In another study, Kříž et al.²⁶ concluded that the gas produced from plastic and coal mixtures during single stage pyrolysis contained around 50 vol% hydrogen.

Most of the studies reported on the co-pyrolysis of coal and plastic used powder mixtures^{24,27,28}. Zhang et al.²⁹ investigated how the placement of low-rank Chinese coal relative to the HDPE (i.e. coal positioned above plastic, plastic positioned in between coal, etc.) would affect the co-pyrolysis yields and products. It was found that placing the coal particles on top of the HDPE particles improves the quality of the condensable products produced when compared to an evenly physical distributed mixture of particles. Furthermore, the available literature on the co-pyrolysis of coal and plastic mainly focuses on kinetic studies and is done using thermogravimetric analysers (TGA) for pyrolysis^{14,24,27,28}. Few studies have investigated the co-pyrolysis products and even fewer focused on characterising all the produced products. Wu et al.³⁰ investigated the fast pyrolysis products and yields of blends of low-rank coal combined with polyethylene without additives (WPE) and polyethylene with additives (BPE) (1:0, 9:1, 7:3, 1:1, 0:1). A wide range of synergistic effects in both the yields and product characterisation was reported when pyrolyzing 2 g blends and increasing the temperature from ambient to 450 – 600 °C using a fast-heating rate (20 °C/s).

To understand the slow co-pyrolysis of plastics and coal, the derived products also need to be investigated. This study investigated the Fischer Assay pyrolysis of extrudates produced from blends of Highveld discard coal fines and recycled waste LDPE and PP respectively. The pyrolysis product yields, and product characterizations were investigated using slow heating

rates from ambient to 520, 720, and 920 °C, respectively. Furthermore, the small reactor volume of the Fischer Assay retorts ensure a short residence time for the produced volatile matter, limiting further cracking and secondary reactions between the produced products, which occurs when using high heating rates³¹ and longer residence times³². Previous studies have focused on the co-pyrolysis of plastics and Northern hemisphere coal^{10,14,23–29}; the co-pyrolysis derived products and yields of extrudates produced from plastics and South African (inertinite-rich) discarded coal fines have not yet been reported. Since both LDPE and PP were used, the effects of the addition of these plastics on the yields and produced products were compared. Furthermore, this study characterized the char, condensable products, and gas produced to gain a better understanding of all derived slow co-pyrolysis products derived from the extrudates.

4.2 Methods

4.2.1 Materials

Extrudates containing mixtures of coal fines and recycled waste LDPE and PP were manufactured using a TX-32 lab-scale twin screw extruder provided by CFAM Technologies, at 220 °C. The coal fines were sourced from the Highveld coalfield (South Africa), air-dried and sieved to below 1 mm prior to extrusion³³. Cylindrical 5 mm recycled plastic pellets were procured from Potch Plastics, in Potchefstroom, South Africa, and extruded as is. Mixtures of coal fines and the individual plastics were made with 10, 25, 50, 75 and 100 wt.% plastic addition. The extrudates were pressed out of a 10 mm die and the long strands were cut to a length of 2 cm after cooling in a water bath at room temperature. Further detail on the extrusion method be found in Marais et al.¹⁵.

4.2.2 Pyrolysis experiments

The modified Fischer Assay Pyrolysis setup situated at the North-West University laboratories as described by Roets et al.³⁴ was used to pyrolyze the extrudates and can be seen in Figure 4-1. Pyrolysis was conducted by placing the extrudate sample in two stainless steel retorts that are flushed with nitrogen for 15 minutes to create an inert atmosphere at atmospheric pressure. The reactors are connected to round-bottom flasks filled with toluene and cooled within an ice bath where the produced condensable volatiles (tar, wax, oils, and pyrolytic water) are captured. The non-condensable volatile matter (gas) passes through the toluene and is entrapped using Restek Tedlar gas sampling bags. Between 20 and 30 g of extrudates with low plastic content (10 and 25% plastic) were used since this is the maximum amount that fits into the retort. The retorts have a small volume of 170 ml ± 10 ml based on the SANS

647 standard³⁵. As the plastic content increased (50, 75 and 100%) the sample mass had to be further reduced to between 10 and 20 g since the increase in temperature caused the plastics to swell and create blockages. The pyrolysis temperature was increased using a heating rate of 5 °C/min from ambient to 520, 720, and 920 °C, respectively. The oven was kept at the final pyrolysis temperature for 2 hours.

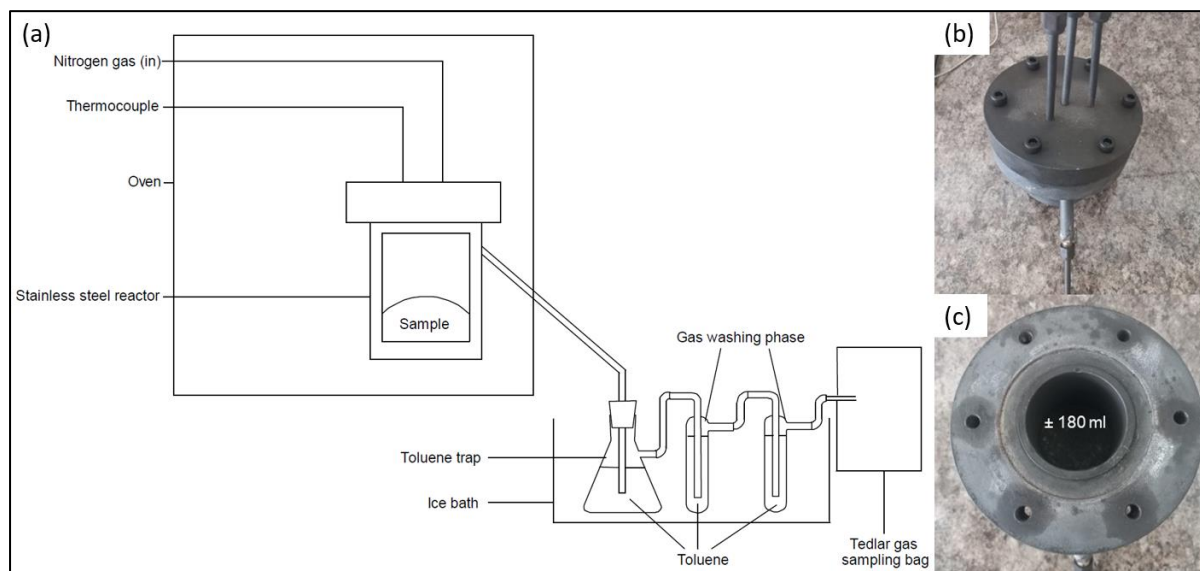


Figure 4-1: Modified Fischer Assay setup (a) Fischer Assay Schematic (b) closed reactor (c) open reactor

After pyrolysis, the char is collected from the cooled reactors and weighed. The reactor's piping is cleaned with toluene and the resulting mixture of toluene and liquid product is added to the toluene traps to ensure no loss in product. The pyrolysis water was separated from the condensable products and toluene using Dean and Stark Distillation, thereafter, the toluene was removed from the condensable products by rotary evaporation at 60 °C using a Büchi Rotavapor R II alongside a Büchi Vacuum pump V 700. The gas yield was determined by difference³⁴. The yield of the pyrolysis products produced from the extrudates were compared to the additive yields derived from the coal and plastics (Equation 4-1):

$$\text{Additive yield} = X_{\text{Coal}} \cdot Y_{\text{Coal}} + X_{\text{Plastic}} \cdot Y_{\text{Plastic}} \quad (4-1)$$

where X_{Coal} and X_{Plastic} are the fractions of the raw materials within the extrudate and Y_{Coal} and Y_{Plastic} are the pyrolysis product yields of the raw materials. Any deviance from the additive model would indicate interaction between the two raw materials during pyrolysis resulting in a synergistic effect³⁶.

4.2.3 Chemical characterisation

The pyrolysis chars and condensable products produced were evaluated using proximate, ultimate, and calorific value analyses. Proximate analyses were used to determine the moisture (%M, ISO 11722: 2008), volatile matter (%VM, ISO 1171: 2010a), ash (%A, ISO 562: 2010b), and fixed carbon content (%FC, by difference) of the chars. The chars and condensable products underwent ultimate analyses, determining the carbon, hydrogen, and nitrogen content using ISO 29541: 2010. The sulphur content of selected condensable products was measured using ASTM D5453; these selected samples were used to estimate the sulphur content of the remaining samples. ISO 19579: 2006 was used to determine the sulphur contents for all chars, and the oxygen content for both the condensable products and chars were determined by difference. The proximate and ultimate analyses results were used in the statistical analyses to create representative models, the detailed results can be found in [Appendix A2](#). Furthermore, the calorific value of both the chars and condensable products was measured using ISO 1928: 2009b. The characterisation of the raw materials from Marais et al.¹⁵ (proximate analysis, ultimate analysis, and calorific value) can be found in Table 4-1.

Table 4-1: Characteristics of the raw materials, air-dry basis¹⁵

	Proximate analyses				Ultimate analyses					Calorific Value
Sample	%M	%VM	%A	%FC (by difference)	%C	%H	%N	%S	%O	(MJ/kg)
Recycled LDPE	0.3	97.7	1.6	0.3	83.4	14.6	0.1	0.1	0.0	46.2
Recycled PP	0.3	98.5	1.2	0.0	84.0	14.7	0.0	0.1	0.0	46.7
Coal fines	4.8	24.9	29.6	40.8	50.3	2.8	1.3	1.0	10.2	19.5

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4.2.4 Statistical methodology

The extrudate composition, final pyrolysis temperature, product yields, proximate analyses, and ultimate analyses were used to develop statistical equations that can predict the yields and characteristics of the pyrolysis products as a function of the extrudate composition. The yields and characteristics were reported on a gram per gram extrudate basis. This was done to better illustrate how the composition of coal fines and plastics affect the pyrolysis characteristics. Since the plastics produce significantly more volatile matter than the coal fines during pyrolysis¹⁵, expressing the characteristics as gram per gram extrudate clearly indicates the weight of each property that will be produced at the end of a pyrolysis process. Therefore,

the proximate and ultimate analyses results (air-dried basis) were multiplied with their respective pyrolysis product yield (char and condensable product yields) to convert the characteristics to gram per gram extrudate before the statistical analyses was used to model these results. The yields and characteristics (air dried basis) can be found within [Appendix A2](#).

The statistical models fitted to the experimental data are of the following form:

$$y = \beta_1 C + \beta_2 L + \beta_3 P + \beta_{1T} C.T + \beta_{2T} L.T + \beta_{3T} P.T + \varepsilon \quad (4-2)$$

where y is the response (yields and characteristics), C, L, P are the Coal, LDPE and PP wt.% respectively, T is the final pyrolysis temperature ($^{\circ}\text{C}$), and $\beta_j, \beta_{jT}, j = 1, 2, 3$, are the regression coefficients to be estimated from the experimental data using least squares error minimization. The parameters $\beta_j, j = 1, 2, 3$, represent the linear effect of the components on the response. The variables $C.T, L.T$ and $P.T$ represents the interaction between the feed composition and the temperature, and the parameters $\beta_{jT}, j = 1, 2, 3$, the effect of the interaction on the response. The errors ε are assumed to be independent and identically distributed with mean zero and constant variance σ^2 . The predicted values are obtained as:

$$\hat{y} = b_1 C + b_2 L + b_3 P + b_{1T} C.T + b_{2T} L.T + b_{3T} P.T \quad (4-3)$$

where $b_j, b_{jT}, j = 1, 2, 3$, are the least squares estimates of the coefficients. The R^2 values are specified for each model. The significance of the coefficients is indicated by the p-value, which is the probability of a Type I error i.e., concluding that the variable has a statistically significant effect on the response, while the contrary is true. Therefore, the smaller the p-value, the higher the confidence in concluding that the variable has a significant effect on the response, for example, a p-value < 0.05 indicates that the variable in the model is significant at the 5% level or it is 95% confident that the variable has an effect on the response. All the statistical modelling was performed with Design Expert software (version 13)³⁷.

4.2.5 Chemical component analyses of the condensable products

An Agilent 7890 gas chromatograph equipped with a 5975C Triple Axis MSD detector was used to identify the chemical components of the pyrolysis condensable products. The gas chromatograph was fitted with a 30 m VF-5ht Ulti-metal column with a film thickness of 0.2 μm and an internal diameter of 0.25 mm. The injection volume of each sample was 0.2 μL with a split ratio of 5:1 using dichloromethane as solvent. Helium is used as a carrier gas and the temperature program for the heating of the GC oven is given in Table 4-2.

Table 4-2: GC oven temperature profile

	Setpoint temperature (°C)	Rate (°C/min)	Hold time (min)
T ₀	45	-	8
T ₁	100	2	-
T ₂	162	7	5
T ₃	300	7	-
T ₄	350	20	-

Simulated distillation curves were compiled to determine the boiling range distribution of the condensable pyrolysis products. Simulated distillation curves were compiled from GC-MS data using a modified method based on the Standard Test Method for Boiling Range Distribution of Petroleum Distillates (ASTM D7213)³⁸. The modification to the method involves the use of a 30-meter VF-5ht Ulti-metal high temperature GC column which is capable of detecting compounds in a boiling range of about 150 – 550 °C where a mass spectrometer is used as detector instead of a FID detector. The mass spectrometer as detector allows for the identification of the compounds. Similar to the original ASTM method, n-alkanes (C₁₀ – C₃₆) are used for calibration purposes.

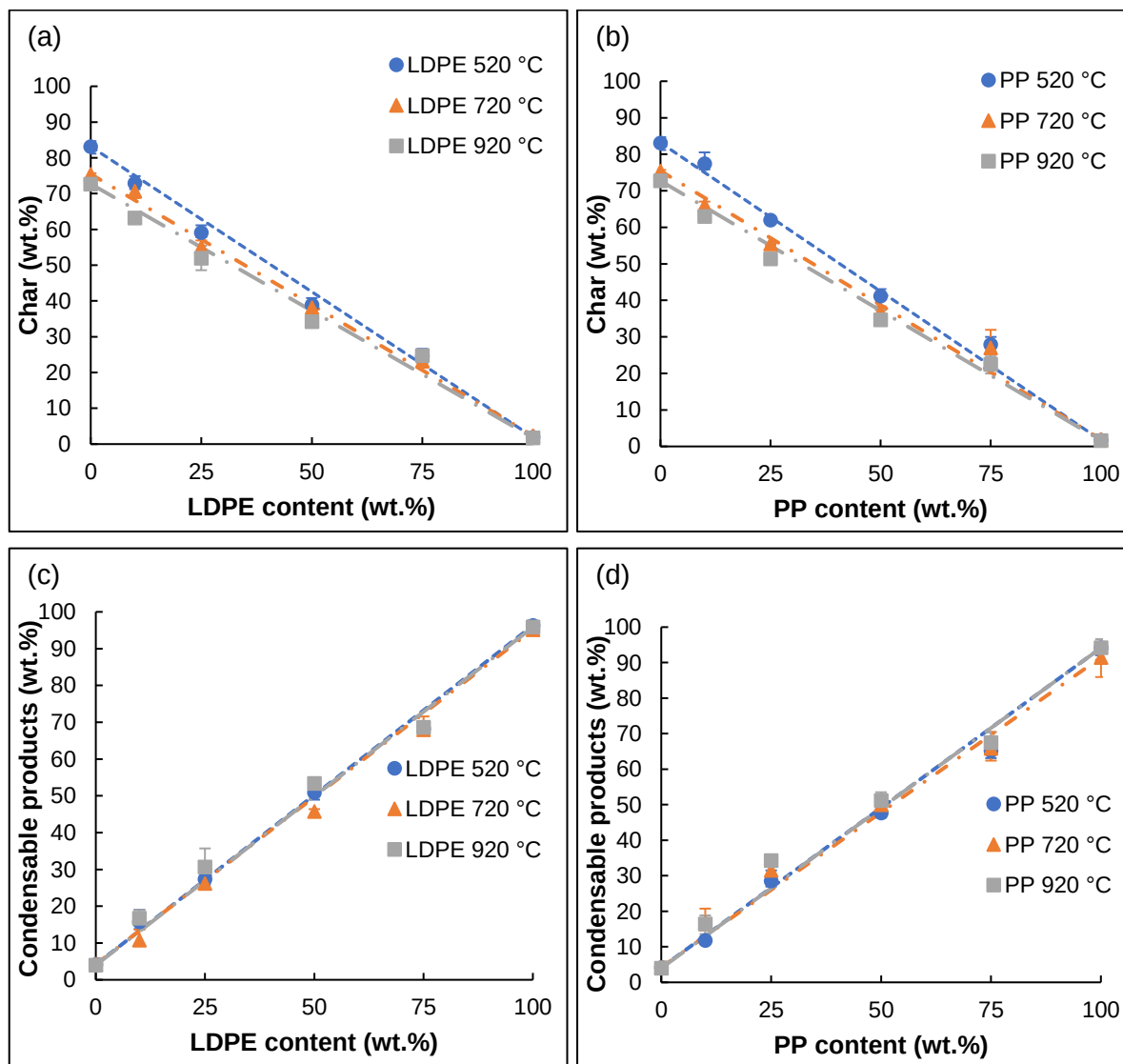
4.2.6 Composition analyses of the pyrolysis gas

The composition of the pyrolysis gas was determined using a Perkin Elmer Clarus 500 Gas Chromatograph (GC). 1 mL of each sample was injected using a capillary injector at 100 °C. Argon (99.999%) supplied by AFROX was used as carrier gas with a flow rate of 2 mL/min for 16 minutes and increased to 8 mL/min for the remainder of the run. The gases pass through and are separated by an Agilent J&W HP-PLOT/Q 30 m x 0.535 mm column, a VICI 10-port gas sampling valve, and the PerkinElmer Elite GC GS MSIEVE 30 x 0.53 mm column. The columns are kept in an oven at 40 °C. The separated gases are detected with a thermal conductivity detector (TCD) at a temperature of 100 °C for a total run time of 130 minutes. The GC was calibrated for C₂H₆, CH₄, H₂, CO₂, CO, N₂ and O₂. The results are analysed using TotalChrom Navigator software.

4.3 Results and discussion

4.3.1 Pyrolysis product yields

The pyrolysis product yields obtained from the experiments are compared to the additive model at final temperatures of 520, 720, and 920 °C as illustrated in Figure 4-2.



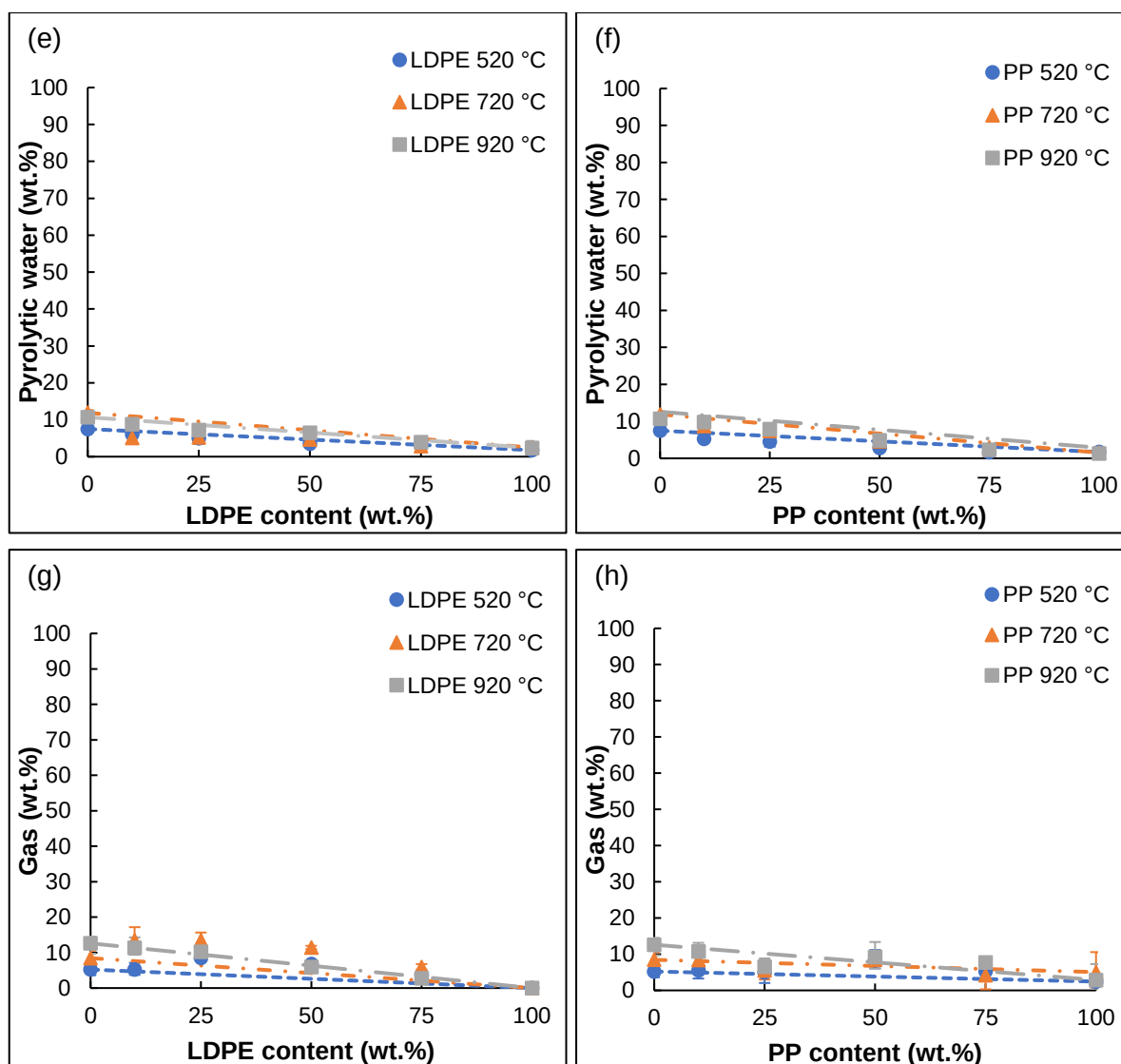


Figure 4-2: Product yields and predicted yields of extrudates containing LDPE (a) char, (c) condensable products, (e) pyrolysis water, (g) gas, and extrudates containing PP (b) char, (d) condensable products, (f) pyrolysis water, (h) gas. Where $- - -$, $- \cdot -$, and $-$, represents the additive model and $\bullet$, $\blacktriangle$, and $\blacksquare$ represents experimental datapoints at a final pyrolysis temperature of at 520, 720, and 920 °C, respectively

It can be observed that the pyrolysis products derived from coal are vastly different than those produced from LDPE and PP. During pyrolysis, only a fraction of the coal converts to volatiles while the most abundant product is the remaining char, whereas plastics mostly decompose into volatiles which consists of a non-condensable gaseous product and condensable liquid and waxy products³⁹. The proximate analysis (air-dry basis) of the raw material (Table 4-1) reveals why a large difference in pyrolysis products is observed. The difference in product distribution is due to the coal consisting mainly of fixed carbon and ash (70.4%), whereas the plastics consist almost exclusively out of volatile matter (LDPE – 97.7% and PP – 98.5%).

Therefore, the char yields generally decreased as the plastic content increased while the condensable product yields increased. The produced chars and condensable products of the extrudates can be predicted using the additive model with a deviance of less than 4%. Sharypov et al.²³ also reported a minimal product distribution deviance from the additive model (2%) when pyrolyzing various PP and coal blends under an argon atmosphere with a temperature increase from ambient to 900 °C.

The char content is more sensitive to a change in temperature than the condensable product content. The chars derived from the coal produced at 520 °C had a higher yield than those at 720 °C, and only a slight decrease in char content occurred from 720 to 920 °C. Previous studies on coal pyrolysis reported similar results and the increase in mass loss of the char is attributed to the increase in volatiles produced at higher temperatures⁴⁰. Furthermore, previous studies concluded that the char yield of coal decreased more from 520 to 720 °C than from 720 to 920 °C since most of the volatiles were already produced by 720 °C and only a small fraction of light gases were produced at high temperatures around 920 °C⁴⁰. The char yields obtained from the extrudates of both plastic types had a similar behaviour and decreased as the temperature increased, however as the plastic content increased the effect of an increase in temperature on the char yield decreased linearly. The small remaining fraction of char produced from the plastic ($\pm 2\%$) was negligibly affected by the increase in temperature.

The condensable product yields from the coal (4.0 – 4.2%) is much lower than that of the LDPE (95.1 – 96.3%) and PP (91.5 – 94.1%). The condensable product yields of the plastics remained similar with an increase in temperature. The lack of cracking due to an increase in temperature can be caused by the low heating rate used for the Fischer Assay setup (5 °C/min) along with a small reactor volume which allows the volatiles that are produced to leave the reactor before being exposed to higher temperatures and further cracking. The pyrolysis of polymers mainly consist of three common polymer chain reaction mechanisms including the scission of the polymeric chain, side group reactions, and recombination reactions⁴¹. Firstly, random scission occurs when polymers are pyrolyzed with a low heating rate which causes the dissociation of C-C bonds, breaking the large polymer chain into smaller polymer chains⁴². The random scission produces multiple smaller radicals with different molecular weights with further reactions often occurring through β -scissions⁴². The dissociation under low heating rate conditions results in the production of aliphatic paraffins and olefins⁴² since the produced radicals are stabilised through the inter- (produces paraffins) or intra-molecular (produces olefins) transfer of hydrogen⁴³. Parku et al.³¹ reported that the yields of condensable products at final pyrolysis temperatures between 450 to 525 °C remained similar during the

pyrolysis of PP in a 1 m long tubular reactor with a low heating rate (15 °C/min), however the gas yield did increase as the final pyrolysis temperature was increased to 600 °C resulting in a lower condensable product yield. Furthermore, Parku et al.³¹ reported that at elevated temperatures (600 °C) fast pyrolysis (180 °C/min) produced higher gas and light oil yields compared to slow pyrolysis, indicating the effect of heating rates on the final product yields.

The produced pyrolytic water of the extrudates is constantly slightly lower than the additive model. The total pyrolytic water yield is obtained at different temperatures and is a combination of surface moisture, inherent moisture within the carbon matrix and pyrolytic water produced from the dehydroxylation of clay minerals⁴⁴. The proximate analyses of the extrudates detailed in Marais et al.¹⁵ indicated that the extrudates showed a moisture content that was less than 3% and remained lower than the expected moisture content for blends of coal and plastic, which could explain the lack of moisture produced during pyrolysis. A temperature increase resulted in an increase in pyrolytic water production that was more prominent with a higher coal content. This can be expected since coal has a high mineral matter content which include clays. A larger increase in pyrolytic water production occurred from 520 to 720 °C than from 720 to 920 °C. The larger increase in water yields between 520 and 720 °C can be attributed to minerals such as kaolinite which releases water at temperatures between 450 to 700 °C^{45,46}. The smaller increase in pyrolytic water from 720 to 920 °C can be attributed to mineral dehydration reactions that occur above 700 °C⁴⁴.

Coal produced more gas than both LDPE and PP. During pyrolysis, the 100% LDPE sample is almost completely converted into liquid products and does not produce a measurable gas product, whereas the PP produces a small gas yield (2.4 – 5.1%). These results differ from previous studies that showed an increase in produced gas from plastics as the pyrolysis temperature increased^{31,47}, which could be due to the low reactor volume used in this study limiting the produced volatiles exposure to higher temperatures and further cracking. Kříž et al.²⁶ found that the addition of mixed waste plastics (15 and 20 wt.%) clearly increased the condensable product yield but had little effect on the amount of gas produced (between 11 and 13%) when using slow pyrolysis in a tubular reactor. The results reported by Kříž et al.²⁶ are similar to the findings of this study and can be attributed to similar low heating rates as used which could contribute to the lack of cracking and the observed lower gas yields.

4.3.2 Statistical analysis and chemical properties

Statistical models of the form in Equation (4-3) were developed to model the pyrolysis product yields (Equation 4-4, 4-5, 4-6, and 4-7), proximate analyses results (Equation 4-8, 4-9, 4-10, and 4-11) and ultimate analyses results (Equation 4-12, 4-13, 4-14, 4-15, 4-16, and 4-17) to

identify re-occurring trends. These equations indicate how the composition of the extrudates and final pyrolysis temperature (between 520 and 920 °C) impact the pyrolysis yields and characteristics. The equations are summarized in Table 4-3, together with the corresponding p, standard error (SE), and R^2 values.

Table 4-3: Statistical analysis equations estimating the pyrolysis yields, proximate analyses results, and ultimate analysis results

Analysis	Property	Linear mixture	p-values			Equation	SE	R ²
			CT	LT	PT			
Pyrolysis product yield	Char	0.0001	0.0001	NA	NA	$Char = 0.9712C + 0.0304L + 0.0367P - 3.0 \times 10^{-4}C.T$ (4-4)	2.5900	0.9908
	CP	0.0001	NA	NA	NA	$Condensable\ product = 0.0603C + 0.9328L + 0.9162P$ (4-5)	3.0300	0.9907
	Pyrolytic water	0.0001	0.0001	NA	NA	$Pyrolytic\ water = 0.0149C + 0.0179L + 0.0096P + 9.5 \times 10^{-5}C.T$ (4-6)	1.0800	0.8695
	Gas	0.0001	0.0076	NA	NA	$Gas = 0.0170C + 0.0190L + 0.0375P + 1.2 \times 10^{-4}C.T$ (4-7)	2.4100	0.6135
Proximate analyses	Ash	0.0001	NA	NA	NA	$Ash = 0.2823C + 0.0111L + 0.0176P$ (4-8)	0.9811	0.9899
	Fixed carbon	0.0001	NA	NA	NA	$Fixed\ carbon = 0.4149C + 0.0139L + 0.0142P$ (4-9)	1.6600	0.9871
	Volatile matter	0.0001	0.0001	NA	NA	$\sqrt{Volatile\ matter} = 0.0647C + 0.0067L + 0.0071P - 6.0E \times 10^{-5}C.T$ (4-10)	0.3129*	0.8801
	Moisture	0.0001	NA	NA	NA	$\sqrt{Moisture} = 0.0093C + 0.0037L + 0.0026P$ (4-11)	0.1720*	0.6267
Char ultimate analyses	Carbon	0.0001	0.0001	NA	NA	$Carbon = 0.5364C + 0.0148L + 0.0140P - 1.58 \times 10^{-4}C.T$ (4-12)	1.6400	0.9884
	Hydrogen	0.0001	0.0001	NA	NA	$\sqrt{Hydrogen} = 0.0305C + 0.0014L + 0.0013P - 3.3 \times 10^{-5}C.T$ (4-13)	0.1362*	0.9019
	Nitrogen	0.0001	0.0240	NA	NA	$\sqrt{Nitrogen} = 0.0159C + 0.0016L + 0.0035P - 8.5 \times 10^{-6}C.T$ (4-14)	0.2122*	0.6510
	Sulphur	0.0001	0.0028	NA	NA	$Sulphur = 0.0045C + 4.5 \times 10^{-5}L + 9.6 \times 10^{-5}P - 2.7 \times 10^{-6}C.T$ (4-15)	0.0488	0.9592
CP ultimate analyses	Carbon	0.0001	0.0367	NA	NA	$Carbon = -0.0168C + 0.782564L + 0.7686P + 8.7 \times 10^{-5}C.T$ (4-16)	2.3500	0.9924
	Hydrogen	0.0001	0.0338	NA	NA	$Hydrogen = -0.0052C + 0.1362L + 0.1343P + 1.5 \times 10^{-5}C.T$ (4-17)	0.3925	0.9900

*Given in square root unit. The yields, proximate analysis and ultimate analysis results are given in g/g extrudate. Where the linear mixture is the mixture of coal, LDPE and PP. C, L, and P represent the percentage weight of coal fines, LDPE, and PP within the extrudates, respectively. Furthermore, the condensable products are represented by CP and the maximum pyrolysis temperature (T) is given in °C. In [Appendix A2](#), the sensitivity of the equations to changes in the variables (X_s) were evaluated.

The p-values are given for each parameter in the model and the models were deduced given the significance of the variables. Specifically, if the p-value for a specific variable is > 0.05 the influence of the specific variable is not significant and is indicated as NA. However, the components C, L, and P make up the composition of the feed and, therefore, one p-value is given for the mixture. From Table 4-3, it can be observed that the composition of the extrudates is a significant factor in each of the produced equations. Since the raw materials have different characteristics, the significance of the composition was expected. The only interaction between temperature and the raw materials that was significant in most of the equations, is the interaction between temperature and the fine coal content.

The SE indicates the average deviation of the model from the experimental data points. Since the SE is provided in the same units as the experimental data, it is important to consider the SE relative to the range of experimental data or the mean. The developed equations for the char yield, condensable product yield, fixed carbon content, ash content, sulphur content of the chars, and the carbon and hydrogen content of the chars and condensable liquids have R^2 values above 0.9, indicating that the model correlates well with the experimental data.

The equations in Table 4-3 can be used to predict the product yields and characteristics after pyrolysis for specified values of feed composition and temperature. Furthermore, it can be used to generate response surface contour plots to interpret the effect of the feed composition and temperature on the product yields and characteristics. However, it is acknowledged that we can only quantify linear relationships between the components and products, due to the fact that there are no ternary experimental blends. For future work we recommend the inclusion of ternary blends to test for non-linear relationships. The contour plots can be found in [Appendix A2](#) along with tabulated values used to generate all the equations depicted in Table 4-3.

The statistical equations determined that the main contributor to the char yield and all the characteristics of the char (proximate analyses and ultimate analyses results) is the fine coal content, whereas the main contributors to the condensable product yield and its characteristics (ultimate analyses results) are the contents of LDPE and PP, respectively. Further investigation into the char characteristics indicated that both the fixed carbon and ash content remained relatively constant with an increase in pyrolysis temperature. The parameter in front of the composition (C, L, and P) is approximately the same as the fixed carbon content and ash content of each of the raw materials before pyrolysis¹⁵. This indicates that the mass of ash and fixed carbon within the samples remained constant and that the high temperatures removed mainly volatile matter and moisture. This is consistent with previous literature findings, however, since most studies report the results as a percentage weight of the char,

their findings will indicate an increase in ash and fixed carbon content due to the decrease in volatile matter and moisture content with an increase in pyrolysis temperature^{40,44}. The same trends can be seen in the raw proximate analyses results in [Appendix A2](#).

The carbon and hydrogen content (g/g extrudate) within the chars are much lower than those of the original extrudates¹⁵ and is due to the devolatilization occurring during pyrolysis⁴⁴. Furthermore, the increase in final pyrolysis temperature mainly lowers the carbon and hydrogen content of chars by interacting with the remaining fine coal content. There is no term involving temperature and plastics since the p-value indicates an insignificant effect, therefore the devolatilization due to an increase in final pyrolysis temperature can be mainly attributed to the remaining coal fine chars⁴⁴. Since devolatilization during pyrolysis is the first step in coal gasification, the devolatilized chars need to be further evaluated under a reactive atmosphere for possible gasification applications⁴⁸. Furthermore, the sulphur content of the chars remain low (below 1.15%) and similar to the original coal fines, making the chars suitable for gasification or combustion¹². The oxygen content remained lower than the original oxygen content of the coal fines, however, no model could be constructed to accurately describe the change in oxygen content and could be due to the fact that oxygen is traditionally determined by difference.

The hydrogen and carbon content within the condensable products are only slightly affected by the interaction between coal and the increase in final pyrolysis temperature and are mainly affected by the plastic content. This can be attributed to the volatiles derived from the plastics leaving the reactor and not experiencing further cracking. The fine coal only contributes to a very minor fraction of the total condensable product and therefore the effect of final pyrolysis temperature on the remaining coal char only slightly contributes to the condensable products.

The oxygen content of the condensable products was generally low. Shengyu et al.⁴⁹ pyrolyzed three different coals and found that the oxygen content released from the coal mainly contributed to the gas phase. In the current study the coal does not add much oxygen to the condensable product composition, additionally the oxygen content of the plastic is much lower than that of the coal, and since the plastic is the main contributor to the condensable product fraction, the oxygen content of the condensable products is mostly negligible. Furthermore, the sulphur content of the condensable products decreased with an increase in plastic content. Since, sulphur content is strictly regulated in fuel sources such as diesel (<0.001%)⁵⁰ to prevent SO_x emissions the decrease in sulphur content is essential if the condensable products were to be used as a fuel source. A statistical analysis was not performed on the oxygen and sulphur content of the condensable products since the oxygen content was mostly zero or slightly negative and the sulphur content was only experimentally

measured for certain samples while the rest was calculated. The sulphur content and oxygen content of the condensable products along with the formula used to predict the sulphur content can be found in [Appendix A2](#).

The equations describing the pyrolytic water yield, gas yield, moisture content, volatile matter content and the nitrogen content for the char have R^2 values between 0.61 and 0.9. The SE values of these equations are relatively large compared to the distribution range of the experimental data, resulting in lower R^2 values and indicating that the model does not correlate as accurately with the experimental data as the previously mentioned equations. Furthermore, the gas yields are determined by difference adding even more variance. However, even though these equations cannot precisely indicate the experimental yields or characteristics, the R^2 values indicate that these equations can still be used to identify trends within the data. No trend could be identified for the nitrogen content present in the condensable product yield, this could be because of the low nitrogen content, suggesting that the nitrogen content within the condensable products is not necessarily dependent on the coal fines content, plastic content, or temperature.

4.3.3 Calorific value (CV)

The calorific values (MJ/kg) of the pyrolysis chars and condensable products produced at different temperatures are compared to the raw materials in Figure 4-3.

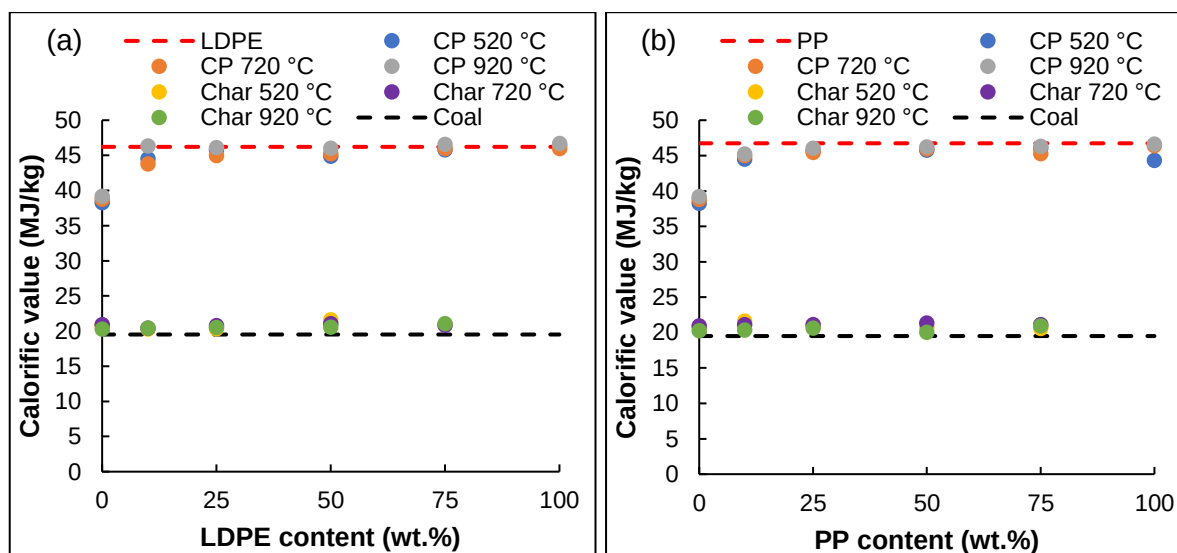


Figure 4-3: Calorific value of the pyrolysis chars and condensable products (CP) produced at different pyrolysis temperatures (a: LDPE, b: PP)

It is clear that the chars and condensable products divide into two groups. All condensable products derived from mixtures containing plastics have a calorific value close to that of the

plastics (44.3 – 46.6 MJ/kg). Parku et al.³¹ found similar high calorific values for the light condensable products and heavy condensable products produced during the slow pyrolysis of PP at various temperatures (450 – 600 °C) under atmospheric conditions. On the other hand, all coal-rich derived chars are only slightly above the calorific value of the coal (20.0 – 21.6 MJ/kg). The slightly elevated calorific value of the char compared to that of the coal further improves its suitability for utilisation in combustion processes, i.e. pulverised fuel (PF) applications or in pulverised fuel injection (PFI) applications applicable to blast furnace pig iron production.

The calorific value of the pyrolysis condensable products derived from coal is lower than the rest of the condensable products (38.3 – 39.2 MJ/kg). Therefore, it can be observed that the addition of plastic immediately raises the energy density of the derived condensable products. Furthermore, since the main pyrolysis product derived from the plastics is condensable products, a higher plastic content leads to an increase in condensable product production. The condensable products produced from plastic containing extrudates can be utilized as a valuable fuel source due to their high energy density.

4.3.4 Simulated distillation and GC-MS

The simulated distillation results are reported in Figure 4-4.

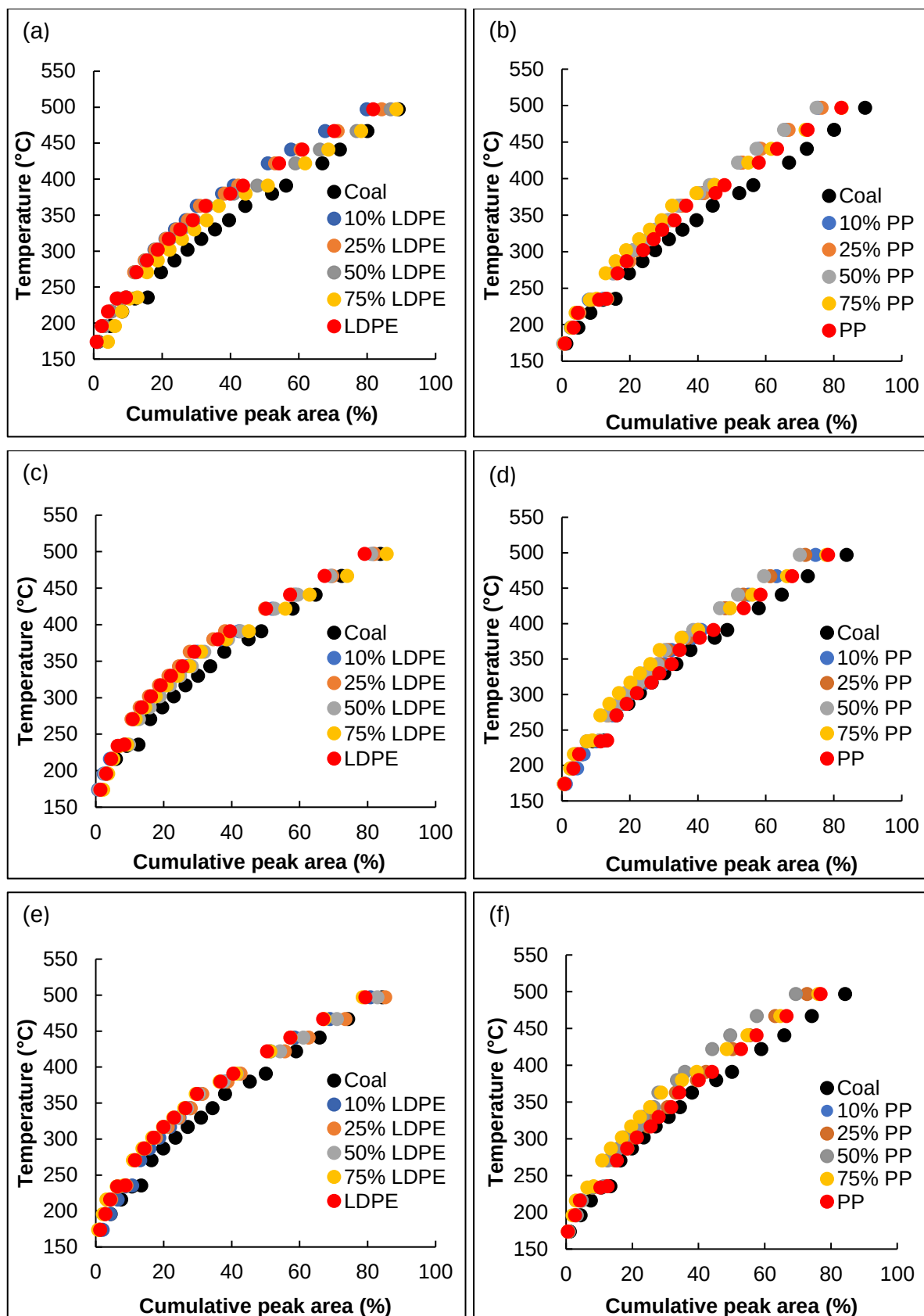


Figure 4-4: Simulated distillation of raw materials and extrudates containing LDPE (a) 520 °C (c) 720 °C (e) 920 °C and PP (b) 520 °C (d) 720 °C (f) 920 °C.

It can be observed that the condensable pyrolysis products derived from coal contain more components with lower boiling points compared to that of LDPE. The condensable products of PP contain components with boiling points are more comparable to that of coal, however the condensable products of PP still contain more components with higher boiling points. The condensable products produced by the extrudates containing LDPE form components with boiling points that are in between the distillation fractions of the condensable products of the raw coal and LDPE. However, the condensable products of the extrudates containing PP form more components with higher boiling points than either the raw coal or PP. This indicates that the combination of coal and PP create more components with high boiling points when pyrolyzed compared to either of the raw materials individually. When investigating the mass loss of mixtures of PP and coal compared to the raw products, a previous study¹⁵ reported that the mixtures had elevated maximum degradation temperatures compared to the raw materials. The same interactions between the coal and PP that cause the maximum degradation temperature to increase could be the reason for the increase in the boiling points of the condensable products that are produced. Furthermore, it is well known that the free radicals of coal are transferred to the plastic during degradation when the degradation temperatures overlap^{15,28,51,52}.

The simulated distillation results were split into crude oil fractions according to the distillation ranges of the North American markets crude fractions⁵³ and are illustrated in Table 4-4 along with the corresponding GC-MS data. The boiling ranges were divided into kerosene (166 – 249 °C), diesel (249 – 343 °C), and vacuum gas oil (343 – 497 °C). Vacuum gas oil contains components with boiling points up to 538 °C, however, the boiling point of the largest alkane (C₃₆) used in the calibration of the GC-MS is 497 °C. The total in Table 4-4 represents the percentage area of all components with a boiling point below or equal to 497 °C. Furthermore, all individual components identified by the GC-MS with a confidence interval above 90% were divided into the respective boiling ranges. These components were sorted into four main groups (Alkanes, Alkenes, Aromatic compounds, Alicyclic compounds) and the remainder were classified as other. The GC-MS data is only semi-quantitative since the percentage area for each identified component is not calibrated. Furthermore, when calculating the sum of the area percentages of all the identified groups it will not equal the total given by the simulated distillation. This occurs since the percentage of each identified group is calculated as an area percentage of all components that were identified with a confidence interval above 90%, and not as a percentage of the total area as was used for the simulated distillation results. Since the GC-MS data is semi-quantitative, it was only used to identify trends.

Table 4-4: North American markets crude distillation fractions and GC-MS identified groups

Sample	Coal fines	%LDPE					%PP				
		10%	25%	50%	75%	100%	10%	25%	50%	75%	100%
		520 °C									
Kerosene	1 1 22 0	2 3 1 0	3 4 1 0	3 4 0 0	3 7 0 1	3 5 0 0	4 3 6 0	5 5 3 1	6 4 1 1	2 2 0 0	2 1 1 1
	17.3	10.5	10.7	10.6	13.8	10.6	13.6	14.5	13.8	11.3	14.3
Diesel	2 6 12 0	5 6 1 1	6 7 1 1	6 8 0 2	7 8 1 1	6 9 0 1	5 7 1 1	6 7 0 1	7 5 1 0	7 6 0 0	0 2 0 0
	22.3	16.4	17.8	18.8	19.2	18.4	18.0	18.0	17.5	18.0	18.8
>497 °C	9 5 14 2	30 19 0 2	36 16 1 4	33 15 2 4	36 11 1 4	32 13 4 3	27 5 1 4	25 9 3 1	8 13 3 0	36 18 2 0	3 8 0 9
	49.7	52.9	55.9	57.4	55.5	52.7	43.9	44.5	44.3	52.9	49.1
Total	11 12 48 2	37 28 3 4	45 27 2 6	42 28 2 6	47 26 2 6	41 27 4 4	37 16 9 6	36 21 6 2	21 22 4 2	45 27 2 0	4 11 1 10
	89.2	79.9	84.3	86.9	88.5	81.7	75.4	77.0	75.6	82.3	82.2
		720 °C									
Kerosene	1 0 23 1	2 4 0 0	2 4 1 0	3 5 0 0	3 6 0 0	3 5 0 0	2 3 9 0	2 3 2 0	4 4 0 1	2 2 0 0	4 6 0 2
	14.5	9.7	9.9	10.9	10.2	9.4	13.6	12.0	11.7	9.9	14.3
Diesel	6 7 13 0	5 7 1 2	5 7 0 1	4 8 0 1	6 8 0 1	5 9 1 1	5 4 2 1	5 2 3 2	5 3 0 1	5 4 0 0	6 5 2 0
	20.4	17.0	16.5	17.3	17.4	16.1	18.0	16.9	15.4	16.1	18.0
>497 °C	12 2 16 3	27 27 1 1	26 17 1 5	30 15 1 7	34 16 2 4	32 14 3 4	16 16 0 2	9 16 1 3	4 14 1 0	18 32 0 4	32 11 0 0
	50.6	54.9	53.5	52.8	58.0	53.6	43.9	42.7	43.0	51.8	46.0
Total	19 9 52 4	34 38 2 3	33 29 2 7	37 28 2 8	42 29 2 4	40 27 4 5	24 24 11 3	16 21 6 5	13 20 1 2	25 38 0 5	42 22 2 2
	85.5	81.6	79.8	81.0	85.6	79.1	75.4	71.6	70.0	77.8	78.3
		920 °C									
Kerosene	1 1 23 0	2 5 3 0	2 4 0 0	2 4 0 0	2 3 0 0	3 4 0 1	3 3 6 0	2 3 3 0	2 3 1 1	1 2 0 0	2 4 0 1
	14.5	11.7	10.0	9.8	9.5	9.8	13.1	13.1	11.8	9.2	13.6
Diesel	6 6 16 0	4 7 1 1	5 7 0 1	5 8 0 1	6 7 0 1	5 8 0 1	4 1 3 0	6 2 2 0	5 4 0 0	6 5 0 0	0 4 0 0
	19.9	16.0	17.9	17.0	16.5	16.6	17.4	17.6	14.7	16.2	18.1
>497 °C	19 2 12 0	28 17 0 5	31 22 1 2	31 25 0 1	28 32 1 1	30 11 0 5	32 7 1 0	9 11 3 3	2 21 0 0	15 34 0 0	15 4 0 15
	49.9	53.1	57.2	56.0	52.5	53.0	42.2	42.1	42.8	50.7	45.1
Total	25 8 52 0	34 29 4 6	38 33 2 3	38 36 0 2	36 42 1 2	37 23 0 6	39 11 10 1	17 16 8 3	9 29 1 2	21 41 0 0	18 12 0 17
	84.3	80.8	85.1	82.9	78.5	79.3	72.8	72.8	69.3	76.1	76.8

Compounds identified by the GC-MS were sorted into 4 main groups (■ - Alkanes, ■ - Alkenes, ■ - Aromatic compounds, and ■ - Alicyclic compounds)

Since the condensable pyrolysis products derived from coal contain more lighter components, these liquids contain the highest fraction of components in the boiling range of kerosene (15 – 17%) and diesel (22 – 23%). Furthermore, the coal derived condensable products had the highest total fraction of components with boiling points below 497 °C (84 – 89%). The condensable products of the LDPE and LDPE containing extrudates had the lowest fraction of components with boiling points in the range of kerosene (9 – 12%) and had a similar diesel fraction compared to the condensable products derived from PP and the PP containing extrudates (14 – 18%). Furthermore, when comparing the condensable products produced by the raw components, the condensable products produced from PP contained the lowest number of total components with boiling points below 497 °C (76 – 83%), and the extrudates containing PP produced condensable products with even fewer components that have boiling points below 497 °C (69 – 83%). This is a clear indication that extrudates containing coal and PP produce the largest fraction of condensable products with high boiling points.

The most prominent fraction is the vacuum gas oil fraction for both the condensable products of coal and plastics. This boiling range also correlates with that of light waxes (343 – 525 °C or $C_{21} - C_{40}$) when observing paraffin standards²⁰. The melted plastics within the heated extrudates can suppress the escape of volatiles produced from co-pyrolysis, resulting in cross-linking reactions between radicals from plastics and coal producing a large condensable product fraction with higher boiling points³⁰. Arabiourrutia et al.²⁰ reported a light wax fraction around 50% for pyrolysis waxes produced from both LDPE and PP at temperatures between 400 and 600 °C which correlates with the results reported in this study. However, Arabiourrutia et al.²⁰ on the other hand reported that an increase in pyrolysis temperature results in the production of more components with lower boiling points. This finding differs from the results obtained in this study, which can most likely be attributed to the continuous fluidised bed setup which operates at set operating temperatures used by the authors, compared to the Fischer Assay fixed-bed setup with a low heating rate used in this study.

When the pyrolysis temperature is increased from 520 °C to 920 °C using the Fischer Assay setup it resulted in a lower total yield of components below 497 °C for most of the condensable products. This could be an indication of heavier components with higher boiling points being produced at higher pyrolysis temperatures. Since the Fischer Assay setup uses a low heating rate the condensable liquids are removed from the retort and are captured in tar traps before being exposed to higher temperatures which would allow further cracking. Therefore, the increase in components with a boiling point above 497 °C most likely indicates the production of high boiling point condensable products from the remaining char fraction at higher temperatures.

The most prominent difference between the composition of produced condensable products from coal compared to that of the plastics is that condensable products derived from coal contain a larger fraction of aromatic components compared to either plastic type^{23,30}. Coal is a heterogeneous substance, and the condensable pyrolysis products contain a variety of aromatic components. The complex mixture of aromatic components have various functional groups (phenols, naphthalenes, benzenes, etc.) that are distributed and constitute a wide range of molecular weights⁵⁴. The increase in pyrolysis temperature results in a decrease in the fraction of components with a boiling point below 497 °C for the condensable product from the coal. Diesel has a combined fraction of benzene and naphthalene that equals more than 50% of the total fraction⁵⁵ indicating the importance of the higher aromatic content of the condensable products from coal compared to those from plastics. Both LDPE and PP can only be used as a blended fuel due to the lack of aromatic compounds⁵⁵.

The plastics produce condensable products with a much lower aromatic fraction. Furthermore, since the plastics are the main contributor to the condensable products produced from the extrudates, the extrudates only deliver a low aromatic fraction. A decrease in the aromatic fraction as the coal fraction decreases can clearly be seen in the PP containing extrudates; as for the LDPE containing extrudates, low aromatic fractions are reported as soon as LDPE is introduced. The immediate reduction of aromatic compounds with the addition of LDPE is supported by the results of Wu et al.³⁰, which reported a negative synergistic effect in the production of aromatic compounds and phenols with the addition of WPE and BPE to low-rank coal. This negative synergistic effect was attributed to the long aliphatic hydrogen chains from the PE attaching to the surface of the coal particles and preventing the breaking of C-C and C-O bonds responsible for the production of aromatics and phenols³⁰. The low aromatic fractions reported for condensable products from the extrudates are expected since the low heating rates during pyrolysis result in the production of olefins and paraffins from polymers⁴¹. Furthermore, most of the condensable products from plastic and coal extrudates contain mostly alkanes and are closely followed by alkenes. Cit et al.⁵⁶ also reported a higher fraction of alkanes compared to alkenes for the condensable pyrolysis products derived from both LDPE and PP.

Sharapov et al.²³ observed that the composition of the light hydrocarbons (boiling points below 180 °C) produced from the pyrolysis of coal combined with PE and PP, respectively consisted out of more linear alkanes and alkenes compared to cycloalkanes. This study reported similar findings with the alicyclic components making up a small fraction of the total composition of the condensable liquid product and can be attributed to the linear chemical structure of both LDPE and PP.

When investigating the boiling points of alkanes, the kerosene range contains $C_{10} - C_{13}$, diesel contains $C_{14} - C_{20}$, and vacuum gas oil (below 497 °C) has boiling points consistent with $C_{21} - C_{36}$. The condensable products of both plastics and corresponding extrudates have high alkane fractions within the vacuum gas oil range. This corresponds to compositional results of the pyrolysis oils, including waxes, reported from Mangesh et al.⁵⁵ which also mostly contained alkanes (above 50 wt.%). Furthermore, the high amount of alkanes in the vacuum gas oil range correlates to results from Wu et al.³⁰ that suggest that the addition of PE to low-rank coal inhibits the secondary cracking of $C_{13} - C_{20}$ alkanes which results in a large fraction of heavy condensable liquids (boiling point > 350 °C).

The alkenes with the same carbon number as their respective alkanes have similar boiling points and therefore the same carbon number ranges apply when dividing the alkenes into crude oil fractions. The largest fractions of alkenes were also reported in the vacuum gas oil range for all the condensable liquids. Diesel has a very small alkene content compared to the produced condensable products. Furthermore, most of the alkanes present in diesel have a carbon number between C_{11} and C_{20} . The increase in carbon number in the condensable liquids would result in higher CO and CO₂ emissions if used as fuel for combustion⁵⁵. Most of the condensable products from plastic pyrolysis are perfectly suited for further processing in petrochemical processes⁵⁷. Furthermore, a high alkene content has a wide variety of industrial applications as feedstock to produce organic chemicals and polymers⁴³.

4.3.5 GC gas analyses

The GC analyses results of the pyrolysis gas are illustrated in Figure 4-5.

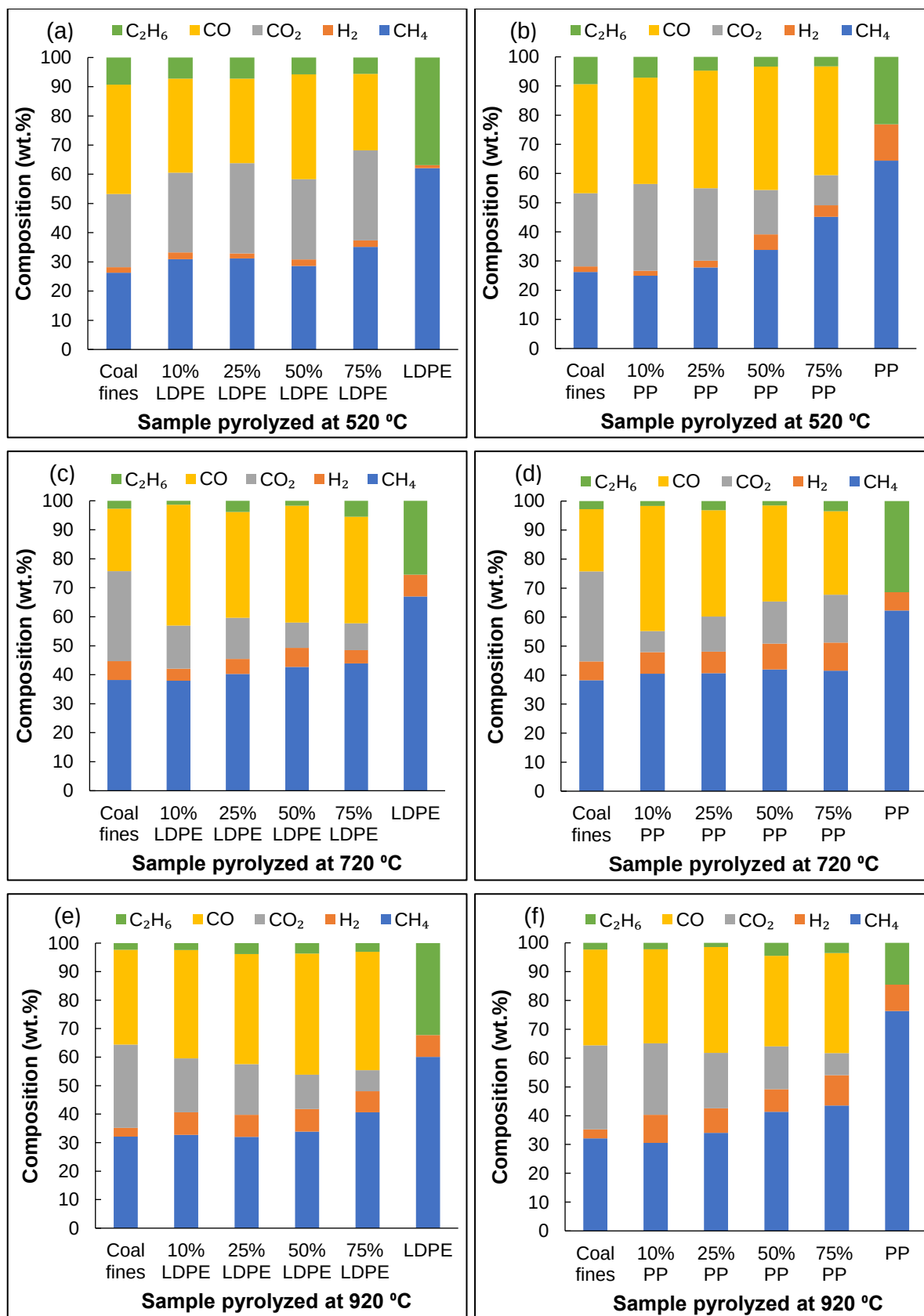


Figure 4-5: GC analyses of the pyrolysis gases from the extrudates containing LDPE (a) 520 °C, (c) 720 °C, (e) 920 °C and the extrudates containing PP (b) 520 °C, (d) 720 °C, and (f) 920 °C

The coal fines produce a gas that mainly consists of CO_2 , CO , and CH_4 . Both gases produced from LDPE and PP contain mostly CH_4 , the remainder consists of H_2 and C_2H_6 . According to Zhang et al.²⁹, the addition of high density polyethylene (HDPE) to low rank coal during pyrolysis resulted in an increase in $\text{C}_1 - \text{C}_4$ hydrocarbons and H_2 production, and a decrease in CO and CO_2 production. The prominence of H_2 and $\text{C}_1 - \text{C}_4$ hydrocarbons in the gas produced during the pyrolysis of HDPE was attributed to the combination of hydrogen and methyl radicals generated. The same mechanism can explain the prominence of CH_4 , H_2 , and C_2H_6 in the gas produced from pyrolysis of plastics in this study. Since both plastic types do not produce as much gas as the coal fines, the increase in plastic concentration mostly resulted in small changes in composition.

Melendi-Espina et al.²⁴ noted that CH_4 is the most prominent gaseous product of the pyrolysis of coal mixed with waste plastics above 450°C and also attributed it to dealkylation reactions. In this study, the CH_4 content of the pyrolysis gas increased as the plastic content increased at all temperatures. However, at 720°C , the CH_4 content was similar compared to the gas produced from the coal fines and only slightly increased with an increase in plastic content. Since almost all of the plastic is volatilized and left the reactor before 520°C , the gas composition produced by the extrudates changed to closely resemble the gas produced from the coal fines and can be attributed to the degradation of the remaining coal fines. Pretorius et al.⁴⁰ reported that the CH_4 content of the gas produced by coal, irrespective of rank, increased up to 720°C . This was attributed to the decomposition of methyl groups and methylene bridges. The pyrolysis gas of the coal fines in this study also had an increase in CH_4 content up to 720°C . Other trends identified in literature that were also prominent in the pyrolysis gas of the coal fines in this study include that the degradation of coal between 500 and 700°C increases the yields of CO and H_2 , whereas the hydrocarbon content (in this case C_2H_6) decreases⁵⁸. Furthermore, the degradation of mineral matter, such as ankerite, within the mineral matter of the coal fines produces CO_2 around 700°C ⁵⁹.

One prominent change that occurred to the composition of the gas as a result of plastic addition is that more CO was produced relative to the amount of CO_2 produced. This is due to the low oxygen content of the plastics relative to the coal¹⁵. The increased CO content was observed in all gases produced from the extrudates containing plastics when the final pyrolysis temperature was 720°C or higher. At 520°C , only the extrudates with high concentrations of PP produced a gas with a reduced CO_2 content, whereas the LDPE containing extrudates indicated no significant change in CO_2 . The delayed reduction of CO_2 relative to the CO content in the LDPE containing extrudates can be attributed to the lack of gas produced from the LDPE. When pyrolyzing coal with PE, Wu et al.³⁰ reported a decrease in CO and CO_2

production with an increase in PE. This is consistent with the findings from this study since the increase in CH₄ production results in a decrease in the combined CO and CO₂ content as the plastic content increases.

When the final pyrolysis temperature is increased from 720 to 920 °C, the CO₂ content of the gases produced from the coal fines and extrudates containing low plastic content (10% and 25%) does slightly increase. This is caused by further degradation of the mineral matter from the coal fines (dolomite and calcite)⁵⁹. Since the ash content decreases with increasing plastic content, the increase in CO₂ is less prominent at high plastic concentrations. Another reaction that occurs above 650 °C is the reaction between carbon and CO₂ to produce CO⁴⁰. The combined formation of CO and CO₂ at higher temperatures causes the CH₄ content to be reduced from 720 to 920 °C. The reduction is more prominent when the coal fines content is high⁴⁰.

Furthermore, the hydrogen content increased with an increase in temperature. Hydrogen, being a light gas, would be considered one of the most abundant products in terms of percentage volume as soon as plastics are introduced to the extrudates. This is consistent with results from Kříž et al.²⁶ indicating a H₂ content around 50 %v. The increase in H₂ content as the temperature increases is attributed to the further devolatilization and aromatisation of the remaining char. High temperatures are needed for the aromatic clusters present in coal to undergo dehydration reactions⁴⁰. Furthermore, since more H₂ is produced from the plastics, the H₂ content of the extrudates is mostly higher than that of the coal fines. Jung et al.⁶⁰ proposed the use of plastic derived pyrolysis gas as a potential heating source for a pyrolysis plant, thus, as the increase in plastic content results in an increase in H₂ and CH₄, the pyrolysis gas becomes a more viable heating source.

4.4 Concluding remarks

This study determined the slow pyrolysis yields and characterized the derived products of coal and plastic extrudates at various temperatures. Coal and plastic produce significantly different pyrolysis products, and when comparing the yields of the main pyrolysis products (char and condensable products) to the additive model of the raw materials, no significant deviation was observed. Furthermore, the increase in temperature did not result in a substantial increase in the cracking of condensable products into gaseous products. Therefore, it was concluded that the produced volatiles leave the Fischer Assay reactor before being exposed to higher temperatures due to the combination of the small reactor volume and the low pyrolysis heating rate. Both LDPE and PP have a narrow degradation temperature range and are responsible for the majority of the condensable products produced from the extrudates. The favoured

production of liquid products is further supported by literature, since low heating rates generally favour the production of liquid products instead of further cracking to produce higher gas yields, the opposite is true when using higher heating rates or longer residence times. All the condensable liquids from the extrudates containing LDPE or PP had high calorific values close to those of the original recycled plastics (± 46 MJ/kg).

Statistical equations were produced that utilize the extrudate composition and final pyrolysis temperature to predict the pyrolysis yields and characteristics of the main products. The equations were able to accurately predict the char yield, condensable product yield, fixed carbon content, ash yield, sulphur content of the chars, and the carbon and hydrogen content of the chars and condensable products with R^2 values above 0.9. Furthermore, the p-values indicate that temperature mostly interacts with the fine coal content which further supports the observation that the volatiles produced by the plastics leave the reactor before being exposed to higher temperatures.

The pyrolysis yields did not indicate much interaction between the coal and the plastics, however within the GC-MS and simulated distillation results some interactions were reported. The condensable products derived from the PP and coal extrudates had a larger fraction of components with higher boiling points than either of the raw materials which could be attributed the increase of maximum degradation temperature of the PP and coal mixtures reported in previous work. Furthermore, the condensable products of the LDPE and coal extrudates showed an immediate decrease in aromatic content even at low LDPE concentrations.

The gaseous product decreased as the plastic content increased since both plastics mainly produced condensable products. As the plastic content increased the CH_4 concentration increased. Furthermore, the low oxygen content of the plastics caused the production of CO_2 relative to CO to decrease with an increase in plastic content.

The extrudates could be used in a wide variety of industries since the pyrolysis product yields can be vastly altered by changing the ratio of plastic to coal. Furthermore, large amounts of condensable pyrolysis liquids were produced which can potentially be further processed to produce multiple different chemicals, fuels and polymers. Future work will investigate the char morphology and gasification reactivity of the chars produced in this study.

4.5 Supporting information

The tabulated pyrolysis product yields, ultimate analysis results, proximate analysis results along with the sensitivity analyses and contour plots of the statistical equations can be found in [Appendix A2](#).

4.6 Acknowledgements

This work was financially supported by the National Research Foundation (NRF) [Coal Research Chair Grant No. 86880]. Opinions, findings and conclusions or recommendations expressed in any publication generated by the NRF supported research are that of the author(s) alone, and the NRF accepts no liability whatsoever in this regard.

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CHAPTER 5: STRUCTURAL ANALYSIS AND GASIFICATION REACTIVITY OF CHARS DERIVED FROM THE SLOW PYROLYSIS OF EXTRUDED COAL FINES AND RECYCLED PLASTIC

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ABSTRACT:

The evolution of char resulting from the co-pyrolysis of recycled plastic and discard fine coal, along with the impact of varying plastic additions on the characteristics of the formed char and its subsequent gasification reactivity, remains unexplored. In this study, extrudates were produced using discarded South African Highveld coal fines, combined with either recycled low-density polyethylene (LDPE) or polypropylene (PP), respectively, and charred under a nitrogen atmosphere at three different temperatures (520, 720, and 920 °C). Co-gasification of plastic and coal provides an opportunity to reduce two waste streams simultaneously. The characteristics of the chars produced from the coal fines were compared to those produced from the extrudates formulated at varying plastic content (10, 25 and 50 wt.%), using petrographic carbon form analysis, surface area and porosity analysis, as well as XRD carbon crystallite analysis. Thermal fragmentation was observed to degrade the integrity of the extrudates when the plastic content exceeded 10%, therefore, the chars produced at 920 °C were pulverised (75 - 150 µm) before undergoing CO₂ gasification at 800, 825 and 850 °C in the chemical-controlled regime. Carbon crystalline analyses showed that the chars were more ordered with an increase in plastic content. However, even with the more ordered structure, the gasification reactivity increased similarly with an increase in plastic content for both the extrudate derived chars containing LDPE and PP. Petrographic carbon form analysis showed an increase in crack and pore formation with an increase in plastic addition during all stages of the chars' evolution as the pyrolysis temperature increased. The VRM time factor showed a positive linear correlation with an increase in BET surface area, especially for the LDPE derived chars ($R^2 > 0.7720$). Therefore, the observed reactivity increase with an increase in plastic content can be correlated to an increase in surface area. Results allude to the possibility of increasing gasification rates in Industrial gasifiers while reducing both coal and plastic waste. Further work should be conducted to minimise the thermal fragmentation

propensity of the plastic-containing fine coal bound extrudates to make the extrudates suitable for fixed bed gasification.

Keywords: coal, LDPE, PP, CO₂ gasification, BET, Carbon Form analysis

Nomenclature		
Symbol	Description	Units
A_0	Ash content	wt. %
d_{002}	Interlayer Spacing	Å
E_d	Demineralization efficiency	%
E_a	Activation Energy	kJ.mol^{-1}
L_a	Crystallite diameter	Å
L_c	Crystallite height	Å
k'_{s0}	Lumped pre-exponential factor	min^{-1}
N_{ave}	Average stacking number of aromatic layers	-
t	reaction real time	min
t_f	time factor	min^{-1}
QOF	Quality of fit	%
X	Conversion	-
β	Full Width at Half Maximum (FWHM) values	°
θ	peak position, X-ray diffraction angle	°
λ	X- ray wavelength	nm

5.1 Introduction

The main uses of coal in South Africa are for electricity generation and liquid fuel production, and these two industries account for approximately 90% of the domestic coal consumption¹. The Lurgi Fixed Bed Gasification technology is used to produce a variety of hydrocarbons from coal and employs the Fischer-Tropsch process for fuel production². This robust gasification process can be adapted to handle feedstock having a wide variety of properties², which is crucial, since there is mounting pressure to investigate the co-gasification of coal together with waste streams, thereby diversifying the energy mix and lowering the country's dependency on fossil fuels³. Coal fines are often discarded since its reduced size (<1mm) increases the difficulty of industrial handling and transportation⁴. Additionally these coal fines are not used in the Sasol lump coal gasification process as it requires particle diameters > 6 mm⁴. South Africa discards approximately 60 Mt of coal fines per annum⁵, and the use of these discarded coal fines in an agglomerated form within the fixed bed gasifier provides a financial opportunity for use in thermal applications⁶. Research aimed at enhancing the size of coal particles for industrial use, is currently exploring agglomeration processes involving municipal wastes and coal⁷.

South Africa has the eleventh most mismanaged plastic waste globally⁸. In a previous study, the extrusion of discarded coal fines from the Highveld Coalfield together with varying concentrations (10, 25, 50, 75, and 100 wt.%) of recycled waste LDPE and PP were investigated⁹. It was concluded that the extrudates (10mm diameter) had mechanical strength and water resistance properties that exceeds the standards for coal agglomerates, while iso-conversional methods determined that the addition of plastic lowered the overall activation energy required during pyrolysis⁹. The Fischer Assay slow pyrolysis products derived from the extrudates were investigated in a subsequent study, finding that the product yields of char, condensable products, water, and gas had little variance from the additive model; however, the product characteristics showed definitive interaction between the coal and plastic¹⁰.

Investigating the co-gasification of extruded waste plastic and discarded coal fines would be beneficial for maximizing the utilization of both waste streams. Coal gasification is a two-step process, including: (1) the devolatilization of the coal during pyrolysis; and (2) the subsequent reaction of the chars with multiple gases to produce syngas¹¹. Plastics yield minimal char, and their gasification is complex due to extensive cracking, and due to the abundant hydrocarbon chains (such as waxes and oils) being produced during pyrolysis^{10,12}. Since plastics produce almost no char¹⁰, the slow heterogenous gasification of chars is not as prominent during gasification as it is for coal. Given the robust nature of the Lurgi Fixed Bed gasifiers, fuel sources with widely different properties can be blended into the main coal fuel source². Therefore, the rate limiting char gasification step for these mostly coal containing fuel blends used by the Lurgi Fixed Bed Gasifiers is noteworthy. It is crucial to understand the effect that varying plastic content within the extrudates has on the formation and evolution of the chars as the final pyrolysis temperature is increased (step 1 in gasification).

Coal chars have been extensively analysed to better understand their characteristics and their evolution as the pyrolysis temperature increases^{13–16}. However, the properties of chars produced from coal and plastic extrudates have not received much attention. Wu et al.¹⁷ documented the char morphology resulting from premixed blends of white polyethylene (WPE) and coal, as well as black polyethylene (BPE) and coal, produced at 550 °C. The study employed a fast-heating rate of 20 °C/s, and microscope images revealed that blends with WPE generated larger pores on the char surface, suggesting an enhanced rapid escape of volatile matter during pyrolysis. Furthermore, the rough surface observed from the coal and BPE char can facilitate the interaction between the aliphatic radicals released from the BPE and the volatiles released on the surface of the coal¹⁷. Zhang et al.¹⁸ reported on the effect of the placement position of low-rank Chinese coal relative to a 5% addition of HDPE (i.e. HDPE placed below coal, HDPE placed in between coal, etc.) on the pyrolysis product yields and

characteristics when increasing the temperature to 800°C under an argon atmosphere. Fourier transform infrared spectroscopy illustrated that the intensity of the methylene peaks increased with the addition of HDPE. The X-ray diffraction (XRD) results reported that the introduction of HDPE increased the order of the carbon structure within the char samples, which increased the degree of graphitization¹⁸. Vivero et al.¹⁹ also identified increases in the intensity of the aliphatic peaks with the addition of plastics to coking coal during slow pyrolysis by using FTIR with diffuse reflectance mode.

Only a few studies have investigated the gasification of plastics with the addition of coal or biomass, and most of these studies focused on evaluating the product distribution and syngas composition^{3,12,20–24}. There is currently little available literature on the gasification kinetics of the co-pyrolysis of chars derived from coal and plastic blends. Zhang et al.²⁵ tested the CO₂ gasification kinetics of pulverized char derived from a semi-coke and a polyethylene film after it was heat treated. The addition of 20% polyethylene produced the highest CO₂ gasification reactivity. The reactivity of all of the blends that contained plastic (10 – 25%) was higher than that of the semi-coke alone, and the gasification reactivity could be adequately described by both the random pore model (RPM) and the volume reaction model (VRM)²⁵. Sahu et al.²⁶ also found that the CO₂ gasification reactivity and the syngas calorific value increased when HDPE was added to the high ash coal from the Jharia coalfield. The char became highly porous when HDPE was added, making it suitable for the Boudouard reaction. During TGA analysis from ambient up to 1000 °C, the gasification stage was best described with diffusional models²⁶.

Since changes in the structural and chemical properties of the chars produced during the pyrolysis step can affect the final gasification kinetics, this study aims to improve upon the understanding of the evolution of the chars derived during the co-pyrolysis of coal and plastic extrudates. This was done by increasing the final pyrolysis temperature from 520 to 920 °C, a temperature range similar to the pyrolysis temperature range of Lurgi fixed bed gasifiers (300 to 900 °C)^{27,28}, and varying plastic concentration. This was achieved by characterizing the produced chars using scanning electron microscope (SEM), surface area and porosity analysis, XRD (carbon crystallite analysis), and petrographic carbon form analyses. Since the addition of plastics during pyrolysis causes a significant increase in liquid product production¹⁰, only the gasification propensity of the pyrolysis chars with a lower plastic addition (0, 10, 25, and 50 wt.%) were investigated in this study. Furthermore, the CO₂ gasification kinetics of the pulverized chars produced at 920 °C were determined and modelled using the VRM. By enhancing the comprehension of the gasification kinetics of chars produced from coal and plastic extrudates, this study aims to contribute to the optimization of the utilization of both waste streams.

5.2 Methods

5.2.1 Samples

The chars produced from the slow pyrolysis of extrudates (diameter ± 10 mm) derived from discarded fine coal (< 1 mm) and recycled plastic were generated within a modified Fischer Assay setup. The extrusion and pyrolysis methods used are described in previous studies^{9,10}. Furthermore, in this paper only the chars produced from the raw coal fines and the extrudates containing lower plastic concentrations (10, 25, and 50 wt.% plastic) were selected and reported on for both the extrudates containing LDPE and PP, respectively. The final pyrolysis temperatures at which the chars were produced were 520, 720, and 920 °C. The chars were characterised to gain insight into their evolution with changes in temperature and plastic concentration. Depending on plastic concentration, the chars produced during pyrolysis did not remain in the original form of the extrudates (Figure 5-1).

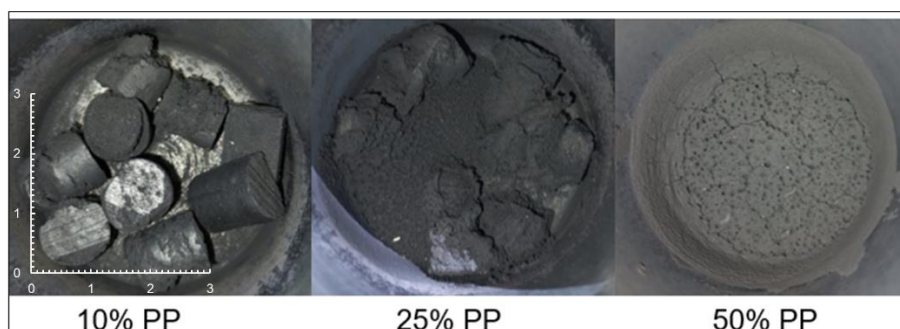


Figure 5-1: Chars produced using PP containing extrudates at 920°C

At higher plastic concentrations, char was found evenly spread around the reactor walls, which is a visual sign that swelling occurred during pyrolysis. With the increase in plastic content the swelling compromised the original structure of the extrudates. At 10% plastic addition, the chars remained in the shape of the extrudates after being exposed to the final pyrolysis temperature. The 25% plastic containing extrudates started to form a cake; however, the outline of the original shape of the extrudates within the cake can still be observed, whereas the 50% plastic containing extrudates formed a cake with no trace of the original individual extrudates. Visually, there was no noticeable change in swelling/caking behaviour with variation in the final pyrolysis temperature, or when comparing LDPE and PP addition. This suggests that the change in plastic content is responsible for the caking phenomena. All chars were found to be brittle and easily reduced to fines (even at 10% plastic addition). However, these chars were maintained in their original structure for all structural analyses performed.

5.2.2 CO₂ gasification experiments

To ensure gasification took place in the chemical-controlled reaction regime, the chars were crushed and sieved to between 75 µm and 150 µm and iso-thermal gasification temperatures below 900 °C were selected. An SDT Q600 TGA was utilized to gasify a sample of ±15 mg of the char produced during the Fischer Assay pyrolysis of the extrudates at 920 °C. The sample was heated (20 °C/min) under a constant nitrogen flow rate of 100 mL/min to the selected iso-thermal gasification temperature (800, 825, and 850 °C). Since the chars were previously pyrolyzed, insignificant mass loss occurred during heating, only removing any absorbed moisture or remnant volatile matter. The gasification of the chars commenced under a constant CO₂ flow rate of 100 ml/min at the selected gasification temperature until completion.

5.2.3 CO₂ gasification kinetics

The gasification kinetic parameters were modelled using the volumetric/homogenous reaction model (VRM) and the random pore model (RPM). These models provided similar results and the VRM model was selected to further discuss the gasification behaviour of the chars. The RPM method and the comparison between the RPM and VRM results can be found in the [Appendix A3](#). When using the volumetric reaction model, it is assumed that the sample contains enough voids that the reactions occur homogeneously throughout the solid phase. The VRM is described by Equation 5-1²⁹.

$$X = 1 - \exp(-t_f t) \quad (5-1)$$

where t_f is the time factor when using VRM and t is the reaction real time.

Arrhenius plots were constructed using Equation 5-2, and the slope of $\ln(t_f)$ versus T^{-1} was used to determine the activation energy (E_a) and the intercept was used to estimate the lumped pre-exponential factor (k'_{s0}) for both models³⁰.

$$\ln(t_f) = -\frac{E_a}{RT} + m \ln(y_{CO_2}) + \ln(k'_{s0}) \quad (5-2)$$

The VRM was evaluated using the quality of fit equation (Equation 5-3).

$$QOF(\%) = 100 \times \left(1 - \frac{\sum_1^N \frac{X_{cal} - X_{exp}}{X_{exp}}}{N} \right) \quad (5-3)$$

where the data points used for both models are represented by N . X_{cal} is the calculated conversion and X_{exp} the experimental conversion^{31,32}.

5.2.4 Physical-structural properties

5.2.4.1 SEM

The coal fines, extrudates, and chars were mounted on to pin-type aluminium stubs using double sided adhesive carbon tape. The loose excess particles were blown off using compressed air. The samples were examined using the backscatter mode. The chars and coal samples remained uncoated, whereas the extrudates required carbon coating to enhance conductivity. The images were taken at the North-West University using a Quanta 250 FEGSEM 20kV at a working distance of 10 mm.

5.2.4.2 Carbon form analysis

The chars were optically compared to the raw coal fines sample using a petrographic analytical method at the University of Johannesburg. The chars were prepared as polished block mounts using a Struers Tegraforce polisher, following the SANS 7404-2³³ procedure. A Zeiss Axiomager M2M reflected light microscope retrofitted with Hilgers Diskus Fossil components and software was used to perform the carbon form analysis, at a magnification of x500 under oil immersion. A semi-automated point counting stage was used, and the results are reported on a volume percentage (vol%). This petrographic method was previously applied by numerous researchers^{34,35}, and the categories included in the quantification of carbon form include: coal microlithotype (vitrite, inertinite, carbominerite, bi- and tri-macerals, and rock), devolatilized coal (porous, porous mixed, dense, cracked, and carbominerite), and char form (vitrite pores, porous mixed, dense vitrite, inertite, cracked, oxidised, carbominerite and rock). The nature of the coal fines presented quantification challenges similar to those previously encountered by Bunt et al.³⁴. Microphotographs of the samples were taken in reflected white light.

5.2.4.3 XRD

The XRD analysis was conducted by XRD Consulting and Analytical cc, and the samples (<75 μm) were prepared using a back-loading preparation method. A Malvern Panalytical Series diffractometer fitted with a PIXcel detector along with fixed slits with Fe-filtered Co-K α radiation was used to produce diffractograms. Different phases were distinguished using X'Pert Highscore plus software alongside PAN-ICSD. The percentage weight (wt.%) of each phase amount was approximated using the Rietveld method.

To investigate the carbon crystalline structures of the samples using the gaussian peaks, the mineral matter needed to be removed since the mineral peaks overlap and obstruct the measurements of the gaussian peaks. The samples were demineralized by immersing the samples for 24 hours in (1) hydrochloric acid (HCl, 37%, supplied by Sigma Aldrich), then for 24 hours in hydrofluoric acid (HF, 45%, purchased from Minema chemicals), and again into hydrochloric acid for a final 24 hours. The samples and acid mixtures (1:5 sample to acid weight ratio) are continuously agitated in each step. After the final acid wash was completed, the samples were rinsed with water until the pH of the filtrate was 6 or above. The demineralization efficiency (E_d) was determined using Equation 5-4³².

$$E_d = \left(\frac{A_0 - A_d}{A_0} \right) \times 100\% \quad (5-4)$$

Where A_0 is the original ash yield of the samples and A_d is the ash yield of the demineralized samples, respectively. The demineralization efficiency was calculated to be between 91.4% and 97.7% for all samples. The Braggs and Scherrer equations were used to determine the average carbon crystalline parameters (interlayer spacing (d_{002}), crystallite height (L_c), and crystallite diameter (L_a))³⁶ for the demineralized samples (Equations 5-5, 5-6, and 5-7). The average stacking number of aromatic layers (N_{ave}) was calculated using the crystalline parameters and the area below the 002-band and the γ side band (Equation 5-8)^{32,36}. Where the X-ray wavelength (λ) is equal to 1.789 nm.

$$d_{002} = \frac{\lambda}{2\sin(\theta_{002})} \quad (5-5)$$

$$L_c = \frac{0.89\lambda}{\beta_{002}\cos(\theta_{002})} \quad (5-6)$$

$$L_a = \frac{1.84\lambda}{\beta_{100}\cos(\theta_{100})} \quad (5-7)$$

$$N_{ave} = \frac{L_c}{d_{002}} + 1 \quad (5-8)$$

Additionally, the diffraction angles (θ_{002} and θ_{100}) and the full width at half maximum (FWHM) values (β_{002} and β_{100}) were correlated with the peak positions of 002 and 100, respectively.

5.2.4.4 Skeletal density

The Micromeritics Accupyc II 1340 Gas Pycnometer was used to measure the chars' skeletal density. The pycnometer uses the outlet pressure of 1.34 bar from a 10 cm³ sample container.

The sample was placed into the container ensuring that the container is at least 75% full (± 5 g) and then flushed with helium to degas the sample to a pressure of 10 $\mu\text{m Hg}$. The average of six skeletal density measurements, with a 95% confidence interval, was reported.

5.2.4.5 CO₂ and N₂-LPGA

A Micrometrics 3-Flex multiport surface area and porosity analyzer was utilized to measure the CO₂ and N₂ surface area and porosities of both the produced chars and the extrudates from which the chars originated. Prior to the CO₂ and N₂ low-pressure gas adsorption (CO₂– and N₂–LPGA) analyses the samples were degassed at 90 °C under vacuum conditions (10 $\mu\text{m Hg}$) for 12 hours. The CO₂ LPGA analyses were conducted in an ice-water bath, whereas the N₂ LPGA analysis was conducted using liquid nitrogen at -196 °C^{37,38}. The adsorption data was automatically collected by the Micromeritics Flex v6.02 software over a pressure range of $0 < P/P_0 \leq 0.033$ for CO₂, and $0 < P/P_0 \leq 0.995$ for N₂ adsorption analysis, respectively. For the surface area determination from N₂ LPGA analysis, the partial pressure range is limited to 0.30 when analysing coal since this range provides a multi-layer coverage of N₂ layers which gives a linear plot of $1/[Q(P_0/P - 1)]$ against (P/P_0) ³⁸. The N₂ surface area was evaluated using the BET method; in this case the D-R method was used to determine the micropore surface area. The adsorption pore diameter and volume were determined using the Barrett–Joyner–Halenda (BJH) method. The pore size distribution was calculated with the adsorption isotherm using the BJH method³⁸.

CO₂ LPGA surface areas were evaluated at a lower partial pressure range since the micropores are filled at substantially lower partial pressures due to significantly higher saturation vapour pressure of CO₂ at the analysis temperature of 0 °C³⁸. During CO₂ adsorption, the Dubinin–Radushkevich (D–R) and the Brunauer–Emmett–Teller (BET) isotherm models were used to determine the surface areas of the samples; furthermore, the maximum pore volume and pore width were determined by the Horvath–Kawazoe (HK) method³⁸. These calculations were performed using isotherm data with $P/P_0 \leq 0.033$. The N₂ surface areas of the samples were evaluated using the BET isotherm model. The adsorption pore diameter and volume were determined using the Barrett–Joyner–Halenda (BJH) method. Using the BJH pore size distribution (PSD) data from the N₂ LPGA adsorption and or desorption isotherm³⁸, the surface area, pore volume and porosity of the samples can be categorised into their micro-, meso-, and macropore contributions^{39–41}.

5.3 Results and discussion

5.3.1 Gasification

The CO₂ gasification conversion results obtained for the chars can be seen in Figure 5-2.

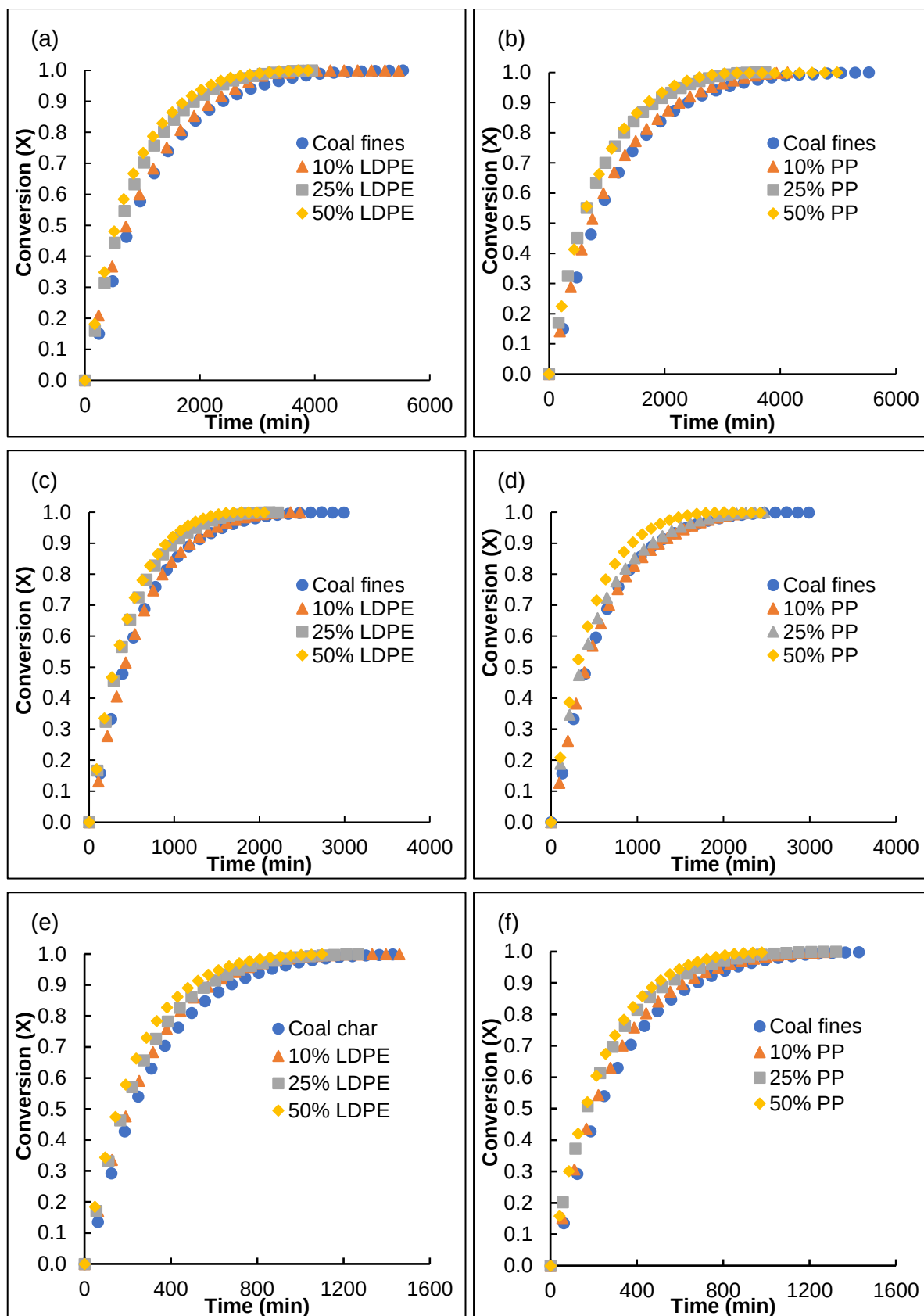


Figure 5-2: CO₂ gasification conversion of the chars produced from LDPE containing extrudates at (a) 800 °C, (c) 825 °C, and (e) 850 °C and the chars produced from PP containing extrudates (b) 800 °C, (d) 825 °C, and (f) 850 °C

It can be observed that, at every temperature, the gasification rate of the chars consistently increases with an increase in plastic content for both the chars derived from the LDPE and PP containing extrudates. Both Zhang et al.²⁵ and Sahu et al.²⁶ found that the gasification reactivity of the char increased when plastic was added to a coal source. Zhang et al.²⁵ also found that the reactivity of the chars increased with an increase in plastic content in the original blend up to 20% plastic addition, however, at 25% addition the reactivity no longer increased. In this study, the reactivities of chars produced from extrudates containing both LDPE and PP increased as the plastic content within the extrudates increased.

The VRM estimated the gasification conversion of the produced chars and was compared to their experimental conversions at various temperatures as demonstrated in Figure 5-3.

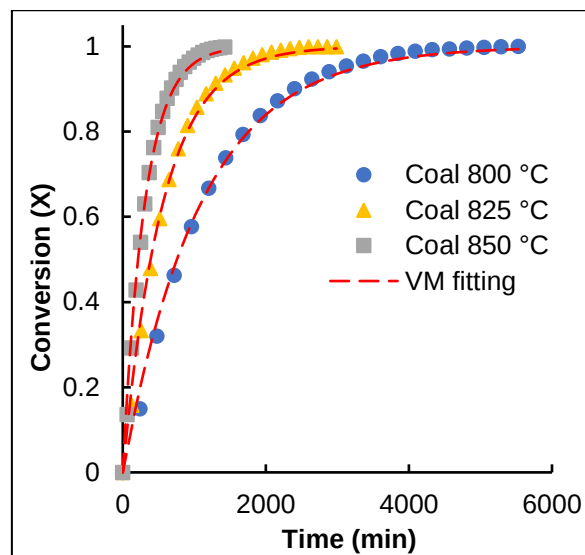


Figure 5-3: The experimental gasification conversion of coal char compared to the estimated VRM conversions.

The remainder of the modelled conversion results compared to the experimental gasification conversion graphs can be found in the [Appendix A3](#). The VRM time factors and the quality of fit for each char type at all three temperatures are summarized in Table 5-1.

Table 5-1: Gasification reactivity parameters

Char	Gasification temperature (°C)	$t_{f\text{VRM}}$ (min ⁻¹)	QOF _{VRM} (%)
Coal fines	800	9.2E-04	97.9
	825	1.8E-03	97.9
	850	3.2E-03	97.7
10% LDPE	800	1.0E-03	98.8
	825	1.8E-03	97.1
	850	3.5E-03	98.0
25% LDPE	800	1.2E-03	98.6
	825	2.2E-03	98.4
	850	3.9E-03	98.7
50% LDPE	800	1.3E-03	99.1
	825	2.4E-03	98.5
	850	5.0E-03	97.9
10% PP	800	9.9E-04	98.3
	825	1.8E-03	98.1
	850	3.7E-03	98.2
25% PP	800	1.2E-03	99.1
	825	2.0E-03	99.6
	850	4.2E-03	99.4
50% PP	800	1.3E-03	98.8
	825	2.4E-03	99.1
	850	4.5E-03	98.5

The VRM obtained a QOF > 97%. Zhang et al.²⁵ also reported that the VRM and RPM adequately described the gasification reactivity of polyethylene and semi-coke derived chars.

Therefore, the VRM time factor parameter accurately correlates with the changes in reactivity and consistently increased with an increase in temperature, similar to the results of previously reported results for South African bituminous coals^{30,32}. When comparing the time factor of the chars at the same gasification temperature, it increased with an increase in plastic content. At the same plastic content, chars produced from PP and LDPE containing extrudates had similar time factor values, indicating that there is no significant difference in the gasification reactivity when comparing the addition of different plastic types.

The prominent increase in reactivity obtained with an increase in plastic content is somewhat unexpected considering that Marais et al.¹⁰ previously reported that the pyrolysis char yield can overwhelmingly be attributed to the coal fines since the plastics consist almost exclusively of carbon and hydrogen (C and H), thereby yielding high quantities of volatile matter during thermal treatment. Furthermore, the reported carbon and hydrogen content of the chars were

similar, and the char yield followed the additive model and did not indicate interaction between the plastics and coal.

The kinetic parameters were determined using the VRM for each char sample. The respective activation energies, pre-exponential factors, and average quality of fit (for all three reaction temperatures) are presented in Table 5-2.

Table 5-2: Gasification kinetic parameters

Char	R ²	E _a (kJ.mol ⁻¹)	k' _{s0} (min ⁻¹)
Coal Fines	0.9997	254	2.0.E+09
10% LDPE	0.9980	248	1.2.E+09
25% LDPE	0.9995	241	6.2.E+08
50% LDPE	0.9971	267	1.3.E+10
10% PP	0.9939	265	8.0.E+09
25% PP	0.9807	241	6.7.E+08
50% PP	0.9998	249	1.8.E+09

The VRM estimated activation energies ranged between 241 and 267 kJ/mol for all the derived chars. These activation energies are slightly higher than the activation energy values of previously reported Highveld coal char which were between 163 and 243 kJ/mol^{42–44}. Since all the chars have relatively similar activation energies, the changes in activation energy cannot be the only reason for the sequential increase in reactivity observed with an increase in plastic content. Zhang et al.²⁵ found that the addition of plastic to semi-coke did result in changes in activation energy, however, the lower activation energies reported did not necessarily correspond to the fastest reactivities obtained. Therefore, the study also concluded that changes in activation energy is not solely responsible for the observed change in reactivity²⁵.

Arrhenius plots were derived from the VRM time factors obtained at all three gasification temperatures. The natural logarithm of the time factors was plotted against T^{-1} for all of the samples as shown in Figure 5-4.

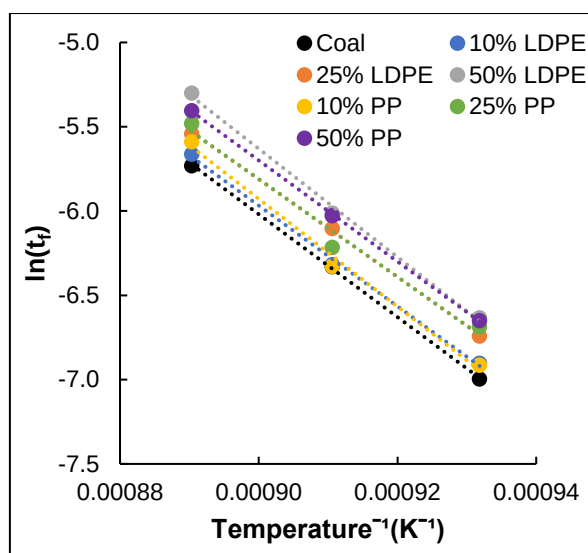


Figure 5-4: Arrhenius plot for charred samples

Since there is no change in slope for each sample, all the reactions occurred within the same regime. If the regime shifted to the pore diffusion-controlled regime, the activation energy at higher temperatures would have decreased significantly and induced a change in slope. Additionally, the gasification reaction was conducted below 1000 °C (generally low temperatures for gasification) and no shift in slope was observed as shown in Figure 5-4, therefore, the chemically controlled regime accurately describes the experimental conditions⁴⁵. The almost parallel lines should indicate similar activation energies⁴⁶, thus, changes in activation energy cannot be the reason for the observed increase in reactivity as the plastic content increases (see Figure 5-1). To better understand the difference in gasification reactivities observed from the different chars, the changes in evolution of the chars during pyrolysis were further investigated.

5.3.2 Physical-structural properties

5.3.2.1 SEM

To qualitatively understand the characteristics of the produced chars, the raw coal fines and extrudates were first examined using SEM as shown in Figure 5-5.

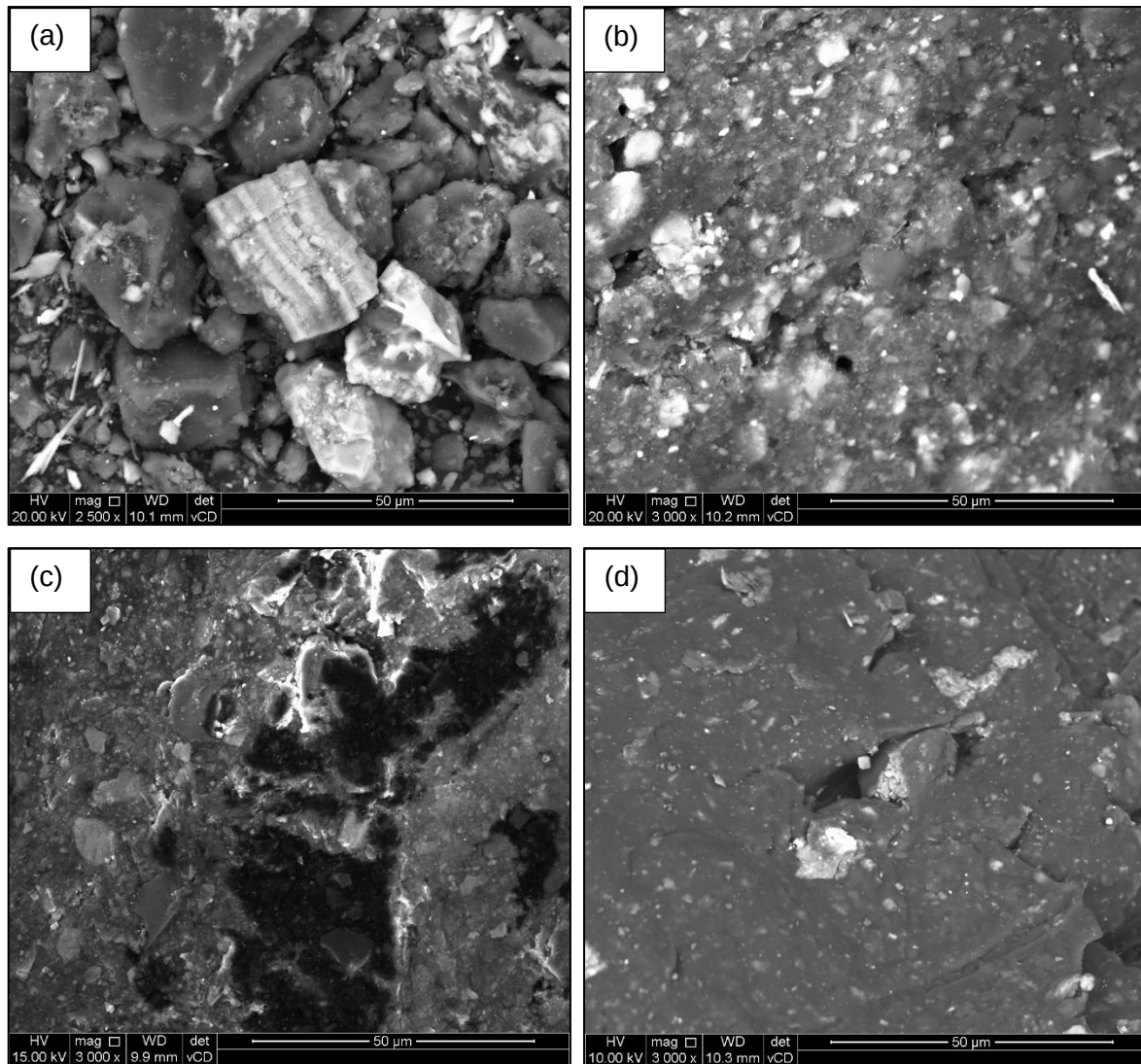


Figure 5-5: SEM micrographs of the (a) coal fines and LDPE containing extrudates (b) 10% LDPE, (c) 25% LDPE, and (d) 50% LDPE (scale bar 50μm)

It can be observed that as soon as plastic is added, the surface is smoother, and the coal particles are surrounded by plastic. The coal particles are evenly spread out indicating that adequate mixing occurred during extrusion. Additionally, as the plastic content increased the spacing between the coal particles increased and the smooth surface of the plastic became more prominent. Zhang et al.²⁵ observed the evolution of the char during pyrolysis of polyethylene and semi-coke. The SEM images indicated that the coal was still imbedded in the molten plastic until around 500 °C, whereafter the plastic is fully degraded. The same degradation was found in a previous study^{9,10}. Since all the plastic has already degraded for the chars produced at the lowest pyrolysis temperature (520 °C), no distinct differences between the char derived from the coal fines and the chars produced from the extrudates were observed through the SEM analyses.

5.3.2.2 Char form analysis

During pyrolysis, the devolatilization of the reactive macerals coincides with the morphological and molecular structural changes of the reactive carbon particles to produce char¹⁴. The photomicrographs in Figure 5-6 shows the evolution of the coal fine chars without any plastic addition as the pyrolysis temperature is increased.

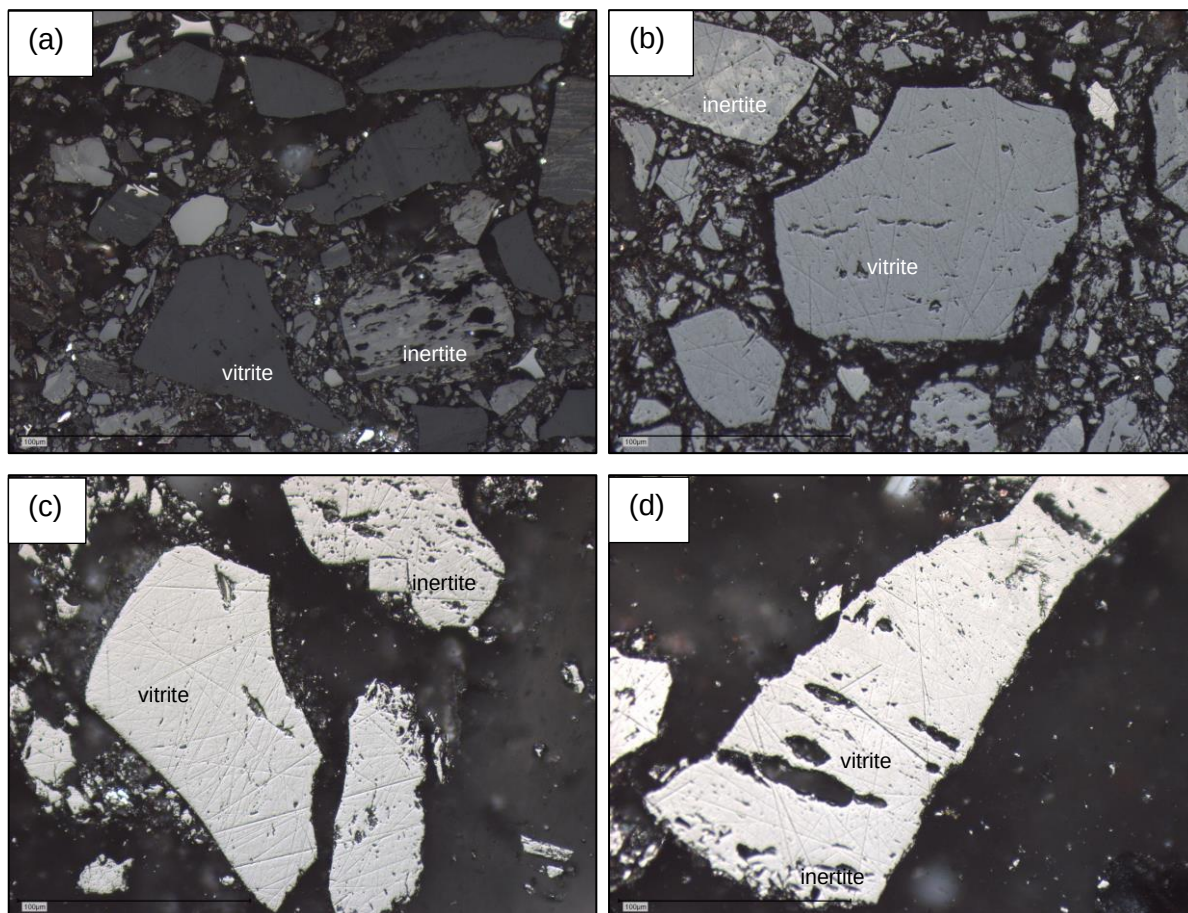


Figure 5-6: Photomicrographs of pyrolysis at different temperatures (a) raw coal fines, (b) pyrolysis at 520 °C, (c) pyrolysis at 720 °C, and (d) pyrolysis at 920 °C (scale bar 100µm)

The coal fines (Figure 5-6(a)) contain vitrite and inertite and combinations thereof, typical of South African medium rank C bituminous coal fines. As the coal fines underwent pyrolysis, the colour of the vitrite and inertite lightened with an increase in temperature and the release of volatile components¹⁴. At 520 °C, the vitrite is slightly darker in shade than the inertite (Figure 5-6(b)), and all particles show signs of early devolatilization. At 720 °C, the vitrite and inertite particles having the shade of light grey to white are classified as chars. The shade of the vitrite and inertite lightens further at 920 °C indicating that the char underwent further evolution between 720 and 920 °C. The chars derived from the plastic and coal extrudates underwent comparable changes in colour as the pyrolysis temperature increased. To gain

insight into the petrographically observable changes, the carbon forms were classified and quantified (Figure 5-7).

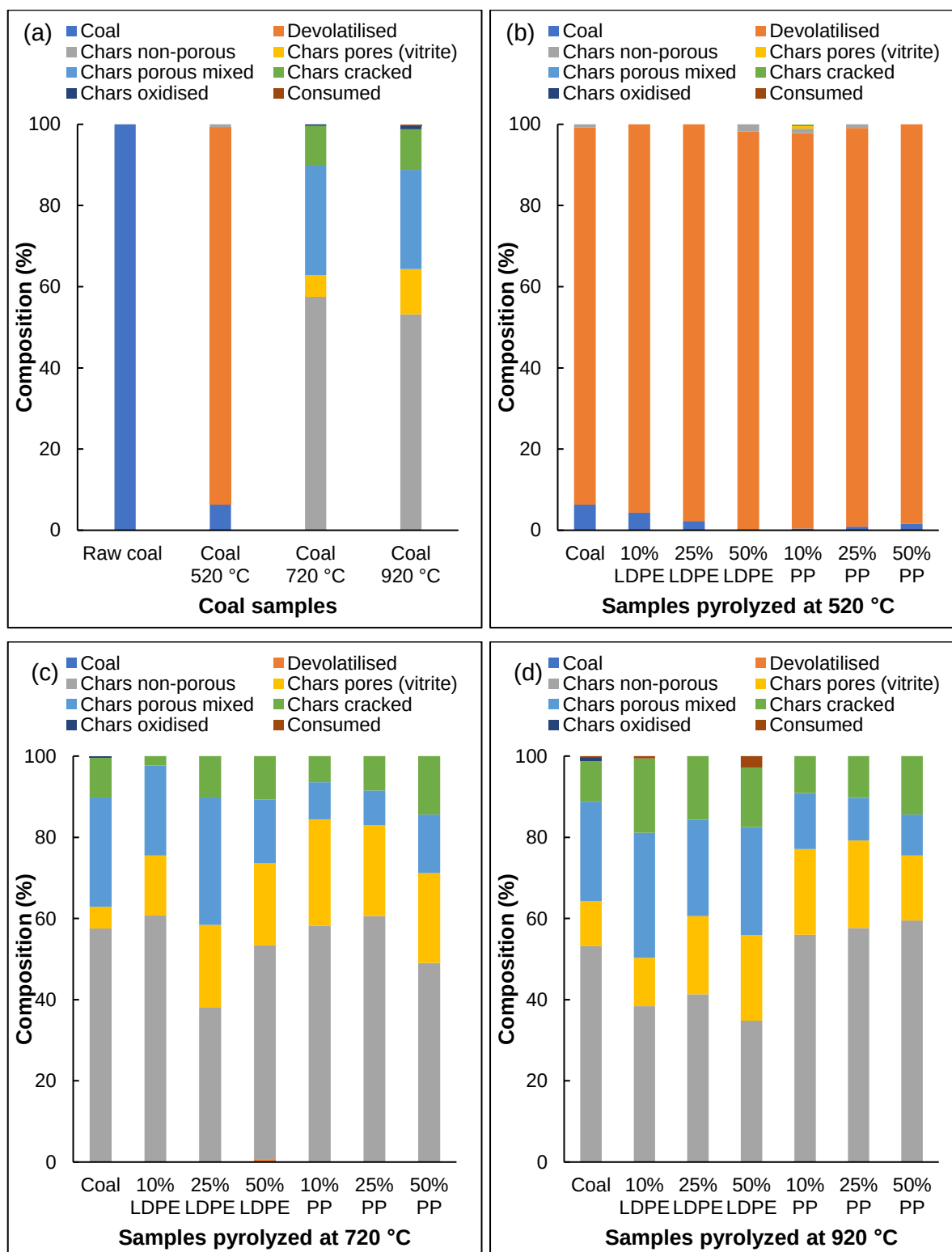


Figure 5-7: Classification and quantification of the carbon forms present in (a) the coal sample pyrolyzed at different temperatures, (b) samples pyrolyzed at 520 °C (c) samples pyrolyzed at 720 °C and (d) samples pyrolyzed at 920 °C.

Figure 5-7(a) confirms the progression observed in Figure 5-6. Devolatilised coal particles exhibit changes from coal particles due to being partially heated. Under reflective light microscope, devolatilised coal has a lighter grey colour when compared to coal particles, but individual macerals can still be identified³⁵. Devolatilised coal becomes progressively lighter with increased heating and eventually form chars, which appear white irrespective of the starting maceral³⁵. The coal sample forms mainly devolatilized coal at 520 °C and consists mainly of chars at 720 °C and 920 °C. The pyrolyzed extrudates showed the same broad char category development. However, differences were observed when evaluating the quantity of material exhibiting pores and cracks. At 520 °C, the samples mostly consist of devolatilised coal, however, the largest portion of the particles has yet to show any signs of pore or crack formation. A small portion of pyrolyzed sample produced from the coal fines is yet to devolatilize (6.3%), this portion decreases with an increase in LDPE content. The 50% LDPE containing extrudates pyrolyzed at 520 °C had no observed non-heated particles or remnant coal present. All the pyrolyzed samples that contained PP showed little coal microlithotype particles (<1.6%) with most particles having been devolatilized. This indicates that addition of plastic accelerated devolatilization at 520 °C.

Furthermore, at 520 °C, the amount of devolatilized coal particles with crack formation derived from the pyrolyzed coal fines (14.5%) is slightly higher than that produced from the extrudates derived from a 10% plastic content (LDPE – 10.6% and PP – 12.3%). The amount of devolatilized material containing cracks was higher at 25% and 50% plastic addition, where 50% PP contained the most cracked devolatilized coal (17.3%). Cracking can be attributed to an increase in mechanical or thermal stress⁴³. Since these samples were extruded before pyrolysis, cracking due to mechanical stress is possible. However, the 10% plastic containing samples had to overcome the highest resistance during hot extrusion, since there was only limited molten plastic to ease the flow of material through the extruder. Therefore, if mechanical stress was the main contributor to the crack formation, the 10% plastic containing extrudates would have exhibited the highest amount of cracking. Since the cracks increased with increasing plastic content, it can be deduced that thermal stress during pyrolysis is possibly the main cause of crack formation. Due to most of the plastics being degraded in a short temperature range⁹, the increased volume of volatile matter trying to escape in a short timespan can cause increased stress on the remaining char particles, which could explain the increase in the observed cracking with an increase in plastic content. Furthermore, as the plastic content increased, the amount of devolatilized coal containing pores increased, with the char derived from the 50% containing plastic extrudates producing the most porous particles observed (LDPE – 20.0% and PP – 16.4%). Wu et al.¹⁷ made similar observations

when pyrolyzing polyethylene with coal at 550 °C and attributed the more prominent pore formation to the rapid release of volatiles from the polyethylene.

At 720 °C all the samples have converted to chars (as indicated by the white colouration). Once again, the amount of cracking increased with increasing plastic content, and 50% plastic addition resulted in the most chars forming pores or cracks. The char produced from the coal fines show slight signs of oxidation, which can most likely be attributed to the higher oxygen content present within the coal fines compared to the other plastic-containing samples⁹. A similar slight oxidation effect can also be observed for the char derived from the coal fines produced at 920 °C.

At 920 °C the chars derived from the LDPE containing extrudates produced more signs of cracks and pores than the chars derived from the coal fines and the chars from the PP containing extrudates. The chars derived from the 10% and 50% LDPE containing extrudates even contained slight traces of consumed char, once again suggesting that the addition of LDPE accelerated the char formation. Chars derived from PP-containing extrudates showed similar amounts of non-porous char than the char produced from the coal fines, however, the amount of cracking increased with an increase in plastic content. Particles containing cracks have an increased surface area⁴³, increasing potential active reaction sites which could contribute to the measured increase in gasification rate with an increase in plastic content.

5.3.2.3 XRD

The relative mineral phase composition of the char samples can be found in the [Appendix A3](#). The mineral phase composition of the chars produced from plastics and coal did not show significant deviance to what was observed in chars produced from raw coal. This was expected since both LDPE and PP have an almost insignificant ash fraction (< 2%) compared to the 29.6% ash yield fraction obtained for the raw coal^{9,10}. The structural parameters of the chars using carbon crystallite analysis were calculated (Table 5-3).

Table 5-3: Structural parameters of the demineralized chars produced from the coal fines, LDPE containing extrudates, and PP containing extrudates

Sample	Pyrolysis temperature (°C)	d_{002} (Å)	L_c (Å)	L_a (Å)	N_{ave}
Coal fines	0	3.45	9.72	49.68	3.82
Coal fines	520	3.51	11.49	23.90	4.27
10% LDPE	520	3.53	11.12	36.36	4.15
25% LDPE	520	3.53	10.59	34.19	4.00
50% LDPE	520	3.52	11.05	36.17	4.14
10% PP	520	3.53	10.91	22.00	4.09
25% PP	520	3.54	11.11	33.65	4.14
50% PP	520	3.52	10.74	33.24	4.05
Coal fines	720	3.62	11.29	29.02	4.12
10% LDPE	720	3.58	10.49	40.90	3.93
25% LDPE	720	3.58	10.54	30.89	3.95
50% LDPE	720	3.55	10.21	39.41	3.88
10% PP	720	3.56	10.37	31.57	3.91
25% PP	720	3.59	10.10	39.36	3.81
50% PP	720	3.58	10.34	37.97	3.89
Coal fines	920	3.59	10.75	34.16	4.00
10% LDPE	920	3.58	10.74	46.56	4.00
25% LDPE	920	3.62	11.40	37.22	4.15
50% LDPE	920	3.58	10.69	41.03	3.98
10% PP	920	3.58	10.99	37.00	4.07
25% PP	920	3.58	11.04	38.92	4.08
50% PP	920	3.58	11.03	50.79	4.08

It can be observed that the interlayer spacing (d_{002}), crystallite height (L_c), the stacking number of aromatic layers (N_{ave}) of all the chars generally increased when compared to the raw coal sample, whereas crystallite diameter (L_a) of the chars was lower than that of the raw coal fines. These structural changes are due to the carbon crystallites' exposure to high temperatures which cause the disordered carbon present in the raw coal to become more ordered and better orientated in the produced chars³⁶.

When comparing the chars produced at different temperature, the interlayer spacing increased with an increase in temperature and at 720 and 920°C the spacing was relatively similar. The carbon crystallites are more intensely annealed at higher temperatures which increases the interlayer spacing as the disordered carbons of the char are becoming more ordered and orientated³⁶. Zhang et al.¹⁸ noted a slight decrease in interlayer spacing when increasing the HDPE content which was co-pyrolyzed with low-rank Chinese coal, however, in the case of this study the change in interlayer spacing with the addition of plastic was found to be insignificant when compared to the effect of temperature.

Additionally, the crystallite height and stacking number of the chars produced from the coal decreased with an increase in temperature; this is in line with previous findings of crystallite condensation where the carbon crystallite size increases in diameter but decreases in height³⁶. Yet, the chars produced from the coal and plastic containing extrudates did not behave the same. The char stacking number and crystallite height of the chars produced from the plastic and coal extrudates decreased more significantly between 520 and 720 °C than was the case for the chars derived from the coal fines; but, instead of decreasing further with increasing temperature, as was the case for the stacking number and crystallite height of the char derived from the coal fines, these values increased at 920 °C. Therefore, the crystallite height and stacking values calculated for the chars produced from the extrudates containing plastic at 720 °C had lower calculated values than for any of the other chars, even the chars produced from the coal fines at 920 °C.

The crystallite diameter was also found to increase with an increase in temperature for the chars produced at 920 °C, having the largest crystallite diameter for the chars and closest to that of the raw coal fines. Generally, the chars produced from the extrudates had a larger crystallite diameter than for the chars produced from coal at the same pyrolysis temperature. Furthermore, the chars produced from the extrudates containing PP seems to have a general increase in crystallite diameter as the PP content within the extrudates increased. The char produced from the LDPE containing extrudates have a clear increase in crystallite diameter compared to char produced from the coal at the same pyrolysis temperature, however, there is no gradual increase as the LDPE content in the extrudates further increased. The increase in crystallite diameter indicates a more ordered char with higher degrees of graphitization³². This increase in order due to the addition of plastics to coal during pyrolysis was also reported by other studies^{18,25}.

At 920 °C, the crystallite height and stacking number of the chars produced from the extrudates containing PP are higher than that of the char derived from the coal fines, indicating an increase in skeletal density, order, and degree of graphitization when PP is added to the original sample¹⁸. It has been theorized that the additional graphitization could be a result of free radicals from the plastic that are absorbed onto the char during pyrolysis, thereby enhancing condensation of aromatic rings¹⁸. Therefore, comparing the chars produced from the extrudates to the chars produced from the coal at 920 °C, the increase in crystallite diameter found, together with the increase in crystallite height for PP containing extrudates, is not expected to increase the gasification reaction rate, in contrast, it should decrease it since it is known that the growth of crystallite size is associated with a reduction of carbon active sites which halts the gasification rate⁴⁷. Thus, the addition of plastic to coal does not change

the carbon crystallite structure in such a way as to promote gasification propensity. However, the reactivity increased with an increase in plastic content, indicating that other changes also occurred to the structure of the char when plastic was added, which positively affected the gasification rate.

5.3.2.4 CO₂ and N₂ LPGA results

During gasification, char-CO₂ reactions mostly occur via the surface area provided by the mesopores and macropores⁴⁸, however, these mesopores develop from micropores in the early stages of char conversion⁴⁹. Therefore, understanding the differences in micropore properties can help to better understand the differences in gasification reaction rates. The micropore properties of the extrudates and derived chars were evaluated using CO₂ adsorption and are presented in Table 5-4.

Table 5-4: CO₂ adsorption micropore properties of the extrudates and derived chars

	Pyrolysis temperature (°C)	Micropore surface area (m ² /g)	Surface area (m ² /g)	Maximum pore volume (cm ³ /g)	Pore width (Å)	Porosity (%)
Method		D-R	BET	HK	HK	
Coal	-	91	72	2.9E-02	3.79	5.41
10% LDPE	-	51	40	1.5E-02	3.92	2.61
25% LDPE	-	47	37	1.4E-02	3.92	2.38
50% LDPE	-	35	28	1.0E-02	3.94	1.75
10% PP	-	57	45	1.7E-02	3.90	3.22
25% PP	-	50	39	1.5E-02	3.93	2.44
50% PP	-	30	24	8.5E-03	3.98	1.36
Coal	520	117	90	3.7E-02	3.77	6.84
10% LDPE	520	123	92	4.0E-02	3.67	7.82
25% LDPE	520	115	86	3.8E-02	3.69	7.25
50% LDPE	520	121	91	4.0E-02	3.70	7.63
10% PP	520	124	93	4.0E-02	3.72	7.64
25% PP	520	122	92	4.0E-02	3.70	7.64
50% PP	520	128	96	4.2E-02	3.68	8.11
Coal	720	173	128	5.9E-02	3.51	12.36
10% LDPE	720	170	125	5.9E-02	3.45	12.36
25% LDPE	720	172	126	5.9E-02	3.45	12.50
50% LDPE	720	172	126	6.0E-02	3.44	12.56
10% PP	720	176	129	6.0E-02	3.48	12.59
25% PP	720	176	129	6.1E-02	3.46	12.76
50% PP	720	172	127	6.0E-02	3.46	12.55
Coal	920	162	126	5.4E-02	3.67	10.55
10% LDPE	920	177	135	6.0E-02	3.61	12.03
25% LDPE	920	178	137	6.2E-02	3.54	12.84
50% LDPE	920	181	138	6.3E-02	3.53	12.94
10% PP	920	180	135	5.9E-02	3.68	11.47
25% PP	920	185	137	6.0E-02	3.69	11.65
50% PP	920	179	134	5.9E-02	3.68	11.38

Before pyrolysis, the extrudates and coal fines have the lowest micropore surface areas, BET surface areas, maximum pore volumes and porosities when compared to their derived chars. As the plastic content in the extrudates is increased, the amount of micropores decreased, most likely being filled by non-permeable melted plastic during hot extrusion. Furthermore, the extrudates and coal fines have a larger pore width than for their respective derived chars, due to the formation of smaller new pores formed at high temperatures.

When comparing the properties of the micropores from the chars produced at different temperatures, the chars produced at 520 °C had the lowest surface area, maximum pore volume, and porosity. This is due to the release of volatile matter and reactions occurring to the carbon structure leaving more porous chars at higher temperatures⁵⁰. Generally, the

difference in properties observed for the micropores present in the chars produced at 520 °C when compared to those produced at 720 °C is much larger than the difference observed between the chars produced at 720 and 920 °C since less volatiles are released at higher temperatures^{10,27}.

At 720 °C, the micropores present in the chars produced from the coal fines are almost identical to those produced from the extrudates. However, the chars produced from the coal fines behave slightly differently when compared to the chars derived from the extrudates when increasing the temperature from 720 to 920 °C. At 920 °C, the micropore surface area, maximum pore volume, and porosity of the chars produced from the coal fines is lower than it is at 720 °C. This is most likely due to the micropores being further developed and coalescing into mesopores, without substantial formation of new micropores to replace them. Since micropores have a small size range, once the pore starts to grow it is a relatively fast transition to a mesopore⁴⁹.

However, the extrudates containing LDPE produce chars that exhibit a slight increase in micropore surface area, maximum pore volume, and porosity from 720 to 920 °C, implying that the formation of new micropores was more than sufficient to replace the micropores that grew into mesopores. Furthermore, the CO₂ adsorption properties of the chars derived from the LDPE containing extrudates increased with an increase in LDPE content, indicating that an increase in LDPE content actively improves micropore formation between 720 and 920 °C.

The extrudates containing PP produced chars at 920 °C that still had increased micropore surface area, maximum pore volume, and porosity when comparing it to the chars produced from the coal fines, yet all of these properties did not increase when compared to the chars produced at 720 °C. Furthermore, the increase in PP content within the extrudates did not result in a continuous increase in the previously mentioned properties as was observed with the extrudates containing LDPE. Therefore, LDPE appears to be more efficient at producing micropores at 920 °C even though the addition of PP still clearly improves the micropore formation of the produced chars. The improvement in pore formation was also reported by Sahu et al.²⁶, who found that the addition of HDPE to high ash Indian coal produced a char with a larger surface area and CO₂ adsorption capacity than that of coal alone.

The pyrolysis of both LDPE and PP containing extrudates improved upon the micropore formation of the chars produced at 920 °C, which can definitively be a contributor to the increased gasification reactivity⁴⁹ observed in Figure 5-1. The N₂ adsorption pore properties are presented in Table 5-5.

Table 5-5: N₂ adsorption pore properties and skeletal density of the extrudates and derived chars

	Temperature (°C)	BET surface area (m ² /g)	Adsorption pore diameter (Å)	Skeletal density (g/cm ³)	Adsorption volume (cm ³ /g)	Adsorption Total Porosity (cm ³ /cm ³)
Method		BET	BJH		BJH	
Coal	-	6.74	43.92	1.65	2.13E-02	3.52E-02
10% LDPE	-	0.06	558.36	1.44	0.05E-02	0.08E-02
25% LDPE	-	0.13	74.13	1.36	0.09E-02	0.12E-02
50% LDPE	-	0.11	70.11	1.19	0.07E-02	0.09E-02
10% PP	-	0.07	101.87	1.51	0.07E-02	0.10E-02
25% PP	-	0.05	112.67	1.35	0.06E-02	0.07E-02
50% PP	-	0.09	204.70	1.17	0.16E-02	0.18E-02
Coal	520	3.82	58.32	1.72	1.18E-02	2.02E-02
10% LDPE	520	13.82	51.86	1.77	2.99E-02	5.28E-02
25% LDPE	520	9.80	84.44	1.75	2.59E-02	4.52E-02
50% LDPE	520	9.73	88.54	1.77	2.80E-02	4.94E-02
10% PP	520	11.14	61.52	1.75	2.51E-02	4.38E-02
25% PP	520	8.83	75.34	1.75	2.17E-02	3.80E-02
50% PP	520	14.20	58.05	1.77	3.01E-02	5.34E-02
Coal	720	4.86	447.41	1.93	1.18E-02	2.28E-02
10% LDPE	720	71.11	23.07	1.93	6.04E-02	11.67E-02
25% LDPE	720	68.45	28.32	1.98	4.85E-02	9.58E-02
50% LDPE	720	45.62	107.57	1.99	3.17E-02	6.30E-02
10% PP	720	72.68	20.83	1.98	7.08E-02	14.05E-02
25% PP	720	42.25	123.06	1.97	2.66E-02	5.24E-02
50% PP	720	42.63	119.70	1.96	2.72E-02	5.32E-02
Coal	920	3.70	435.88	2.08	1.18E-02	2.45E-02
10% LDPE	920	7.36	200.97	2.19	2.94E-02	6.44E-02
25% LDPE	920	14.95	50.80	2.20	3.18E-02	6.99E-02
50% LDPE	920	16.63	45.66	2.22	3.15E-02	7.01E-02
10% PP	920	9.21	132.68	2.14	2.63E-02	5.63E-02
25% PP	920	8.90	205.21	2.15	3.55E-02	7.62E-02
50% PP	920	11.35	79.58	2.01	2.39E-02	4.79E-02

Table 5-5 shows that the extrudates containing either plastic type has a very low surface area, adsorption volume, and total porosity. This is due to the melted plastics filling most of the existing cracks and pores of the coal fines, and plastics are by nature non-porous. In Figure 5-2(b – d) the plastic can be seen covering the fine coal particles. Since most of the pores are filled with plastic during extrusion, there is no obvious trend when observing the average pore diameter of the few remaining open pores. Furthermore, the skeletal density of the extrudates decreases linearly as the plastic content increases, since both LDPE and PP have a lower skeletal density than that of the coal fines⁹. The chars derived from the extrudates all have

higher surface areas, skeletal densities, adsorption volumes, and porosities when compared to the properties of the chars produced from the coal fines pyrolyzed at the same temperature.

The increase in skeletal density is most likely a further indication of a more ordered carbon structure. This should also be a sign of decreasing reactivity since a more ordered carbon structure containing larger carbon crystallites is evident and thereby, limiting the amount of available reaction active sites⁴⁷. However, the reactivity of the chars still increase even with an increase in skeletal density, which can be attributed to the increase in other structural properties like surface area when comparing the coal char to the chars derived from the extrudates.

Zhou et al.⁵¹ reported that PP almost completely degrades (98%) in a narrow temperature range between 399 and 507 °C and that LDPE similarly degrades (99%) between 426 and 526 °C. A previous study found similar results with a final degradation temperatures of 505 °C for PP and 520 °C for LDPE⁹. Therefore, when pyrolyzed at 520 °C, both plastics have largely degraded producing large amounts of volatile matter (dependent on the concentration within the extrudate) which contributes to the formation of pores. The pores produced from the extrudates generally have more than double the surface area, adsorption volume, and porosity when compared to the those of the chars produced from the coal fines, whereas the average pore diameter is in a similar range (between 50 and 90 Å). This indicates that the chars produced from the extrudates are more meso-porous.

At 720 °C, the difference in properties of the pores produced by the extrudates when compared to those of the chars produced from the coal fines become even more pronounced, especially the difference in surface area. The lowest surface area recorded for the chars produced from the extrudates at 720 °C is 42.25 m²/g (25% PP); this is almost 10 times the surface area of the chars produced from the coal fines (4.86 m²/g). The average pore diameter of the char derived from the coal fines (447.41 Å) is almost four times larger than the average diameter of the nearest char produced from the extrudates. This can be an indication that the existing pores of the coal fines grew due to thermal stress⁴⁹ without developing new pores, whereas the chars produced from the extrudates developed new pores and this is why the average pore diameter is much lower. The continuous development of new pores from the extrudates is confirmed by the increase in micropore volume and porosity (Table 5-4).

Figure 5-8 shows the pore size distribution of the N₂ adsorption porosity, helping to evaluate the contributions of the micro-, meso-, and macropores to the overall porosity of the samples and the produced chars.

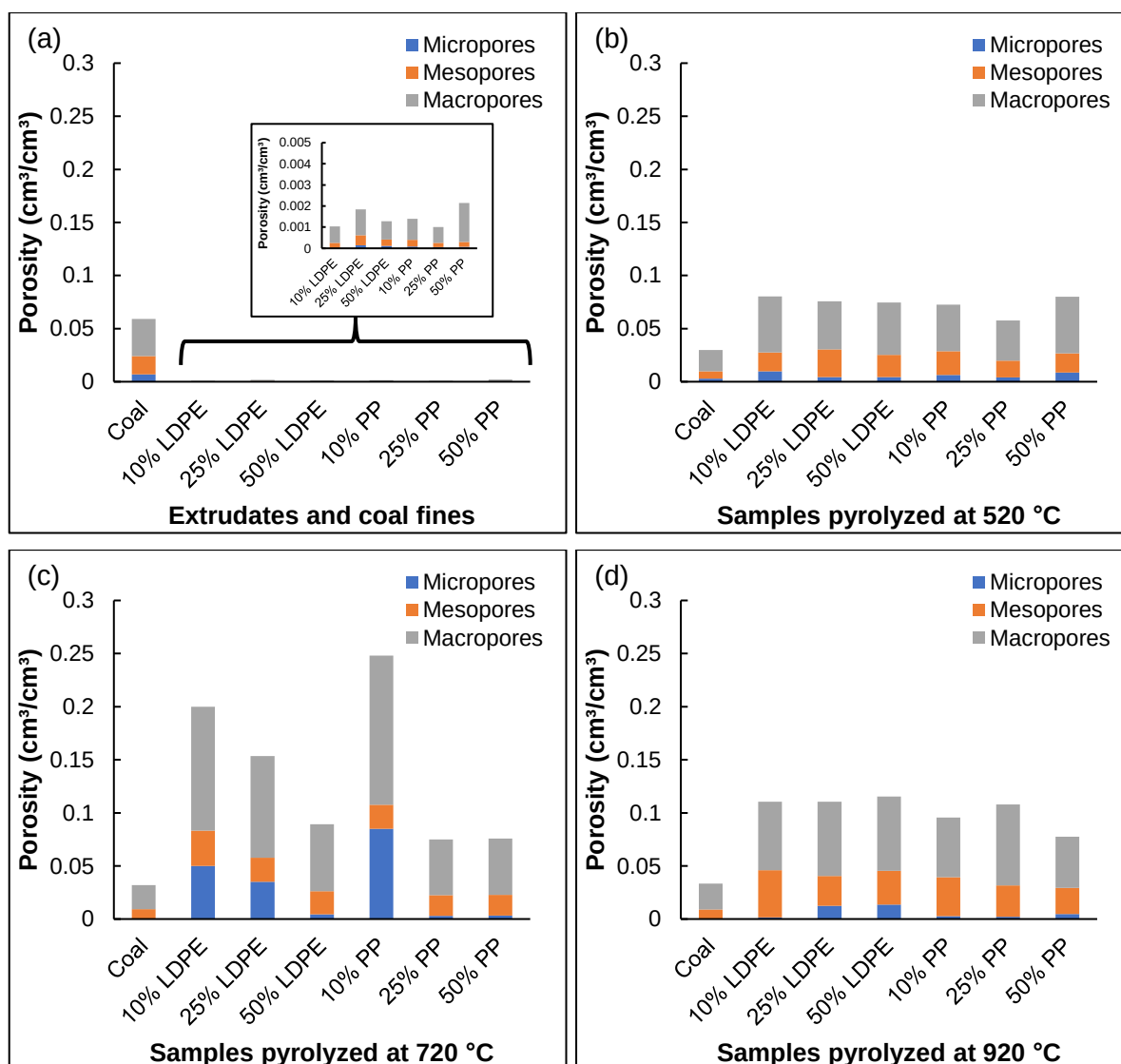


Figure 5-8: The overall porosity of the (a) coal fines and extrudates, and the produced chars pyrolyzed at (b) 520 °C, (c) 720 °C, and (d) 920 °C

It can be seen from Figure 5-8 that the largest contributor to the overall porosity are macropores, since the increased diameter increases the pore volume. The mesopores generally contribute the second most, and the small diameter of the micropores contributing the least. However, at 720 °C, the micropores significantly contribute to the porosity of the extrudates containing a lower plastic content (10% LDPE, 25% LDPE, and 10% PP). This increased microporosity could be because the extrudates tend to maintain their structures best at lower plastic concentrations during pyrolysis (Figure 5-1) which possibly entraps the volatile matter within the structure. The entrapment of the volatile matter within the structure exposes the char to the volatile matter for longer periods which can lead to increased interactions and the possible production of micropores. Another possibility is that there is more coal relative to the plastic content, which results in more intense contact when the plastic is volatilized. These

micropores are consumed by the evolution of larger pores during pore coalescence when pyrolyzed at 920 °C, however, the porosity of the chars produced from the extrudates is still considerably higher than that for the chars derived from the coal fines. The increase in porosity provides more surface area and increase the availability of reaction active sites. Most of the gasification reactions occur based on the surface area of the mesopores and macopores⁴⁸.

When the chars are pyrolyzed at 920 °C, the surface area is greatly reduced when compared to chars produced at 720 °C. This can be attributed to the collapse of the carbon skeleton of coal, which is known to collapse at higher temperatures thereby reducing the available surface area⁵². Therefore, from 720 to 920 °C the shift most likely occurs where pore growth is no longer dominant, and pore coalescence is more prominent.

Even though the surface area of the chars produced from the extrudates decreases from 720 to 920 °C, the surface area, adsorption volume, and porosity of these chars are still clearly higher than the char produced from the coal. The increase in these properties observed when comparing the coal char to the chars of the extrudates produced at 920 °C provides a larger reaction zone for the CO₂ gasification reaction to occur, resulting in higher reactivities. This is demonstrated by plotting the time factor of the VRM against the BET surface area (Figure 5-9).

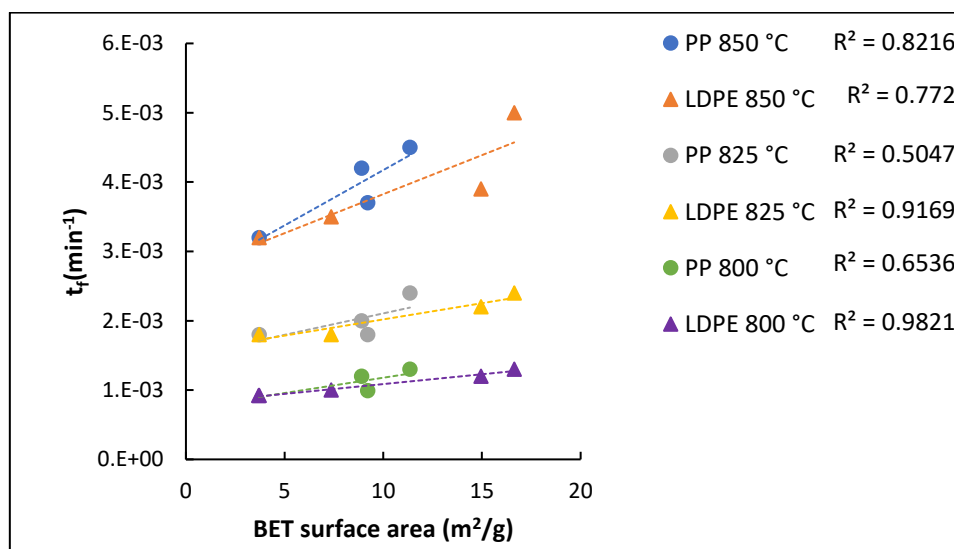


Figure 5-9: BET Surface area compared to the volumetric time factor for the gasification of the chars pyrolyzed at 920 °C.

A positive linear correlation was found for both the chars derived from LDPE and PP extrudates, however, the chars derived from the LDPE obtained better R² values, indicating a stronger linear correlation. Even though the surface area of the chars derived from PP

extrudates is much higher than that of the coal, the 25% PP derived char had a slightly lower surface area than the 10% PP derived char, whereas the chars derived from the LDPE extrudates had a continuous increase in surface area with increase in LDPE content (Table 5-5). Since the surface area can be positively correlated to the VRM time factor, it can directly be correlated to the increase in reactivity. Additionally, most of the gasification reactions occur based on the surface area of the mesopores and macropores⁴⁸, of which the chars produced from the extrudates had increased mesopore and macropore porosity when comparing the chars produced from the coal at 920 °C (Figure 5-9). Therefore, the increase in meso- and macropores can be correlated to the increase in measured gasification reactivity observed with increasing plastic content.

5.4 Conclusions

The pyrolysis chars derived from extrudates containing plastic and coal showed an increase in gasification reactivity with an increase in plastic content for both LDPE and PP containing extrudates. At similar plastic content, the reactivities of the chars derived from LDPE and PP were similar, indicating that there was no significant difference in reactivity when different plastics were used.

With increasing pyrolysis temperature, the chars produced from the extrudates containing plastic continuously demonstrated higher degrees of pore and crack formation when compared to the chars produced from the coal fines. Even though the XRD analysis of the carbon crystalline structure indicated that the addition of plastic lead to the production of more ordered chars and increasing crystallite size, the addition of plastic to the raw extrudate also resulted in more abundant pore formation, which lead to a net increase in gasification reactivity. Changes in activation energy was not responsible for the increase in observed reactivity, since all the pulverized chars had similar activation energies ranging between 241 and 268 kJ/mol.

The LPGA results reports that maximum porosity occurred at 720 °C and decreased when the pyrolysis temperature further increased. This indicates that that pore coalescence mainly occurs during gasification and that most of the pore growth occurred during the pyrolysis stage. At 920 °C the chars produced from the extrudates demonstrated an increase in meso- and macro-porosity, compared to the char derived from the coal. The volumetric reaction model (VRM) adequately describes the gasification kinetics of the pulverized chars. The VRM time factor showed a positive linear correlation with an increase in surface area, especially with for the LDPE containing chars ($R^2 > 0.7720$). Therefore, the reactivity increase observed with an increase in plastic content can be correlated to an increase in surface area.

It can be concluded that pyrolysis of the extrudates containing plastic and coal fines formulated a fuel source that has an increased gasification rate. Therefore, the gasification of plastics and coal fines has the prospect of reducing two major waste streams while potentially increasing gasification rates which could increase production rates for industrial fixed bed gasification. Since thermal fragmentation during pyrolysis was found to destroy the integrity of the chars formed from the extrudates at plastic additions >10%, further work should be conducted with the addition of suitable binders to minimise the thermal fragmentation propensity of the plastic-containing coal bound extrudates in order to make the extrudates suitable for the fixed bed gasification application.

5.5 Supporting information

The RPM experimental method and the comparison between the RPM and VRM along with the XRD mineral phase distribution can be found in the [Appendix A3](#).

5.6 Acknowledgements

This work was financially supported by the National Research Foundation (NRF) [Coal Research Chair Grant No. 86880]. Opinions, findings and conclusions or recommendations expressed in any publication generated by the NRF supported research are that of the author(s) alone, and the NRF accepts no liability whatsoever in this regard.

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CHAPTER 6: CONCLUSIONS AND RECOMMENDATIONS

6.1 Concluding remarks

In this study, extrusion of recycled waste plastics (LDPE and PP) together with discarded coal fines produced extrudates that possess a high mechanical strength, have hydrophobic properties, and with an increase in plastic content, the calorific value increases. The 10% LDPE bound extrudate had the highest compressive strength, even higher than the reported compressive strength for ROM coal. These extrudates maintained their integrity after being submerged in water and the compressive strength of the 10% LDPE bound extrudate remained unchanged after being submerged (dry = 17.5 MPa and wet = 18.0 MPa). Furthermore, with the increase in plastic addition (< 10%) the extrudates no longer broke under large loads but merely flattened. All the extrudates could withstand being submerged in water for 24 hours and absorbed less than 5% moisture.

The calorific value of the plastics far exceeded that of the coal fines, furthermore; the TGA pyrolysis experiments demonstrated that plastics produced mostly volatile matter. TGA pyrolysis experiments exhibited signs of synergistic interactions across all coal fines and plastic blend ratios for both LDPE and PP containing extrudates. The iso-conversional techniques illustrated that even with a small addition of plastic the activation energy of the extrudates were similar to that of the plastics and not as high as the activation energy needed to pyrolyze the coal fines. **The observed decrease in activation energy and degradation temperature illustrated the synergy prevalent between coal and plastics during pyrolysis. This could possibly be attributed to free radical transfer from the coal.** Furthermore, the activation energy of the extrudates only increased at higher temperatures past the degradation temperature of the plastics, indicating that the increase in activation energy experienced at higher temperatures is solely due to remaining coal fines.

Fischer Assay slow pyrolysis of the extrudates and raw materials was conducted by increasing the temperature using a heating rate of 5 °C/min from ambient to 520, 720, and 920 °C, respectively. It was found that the coal fines predominantly produced char, whereas the plastics almost exclusively produced condensable products (> 90%). The additive model of the char and condensable product yields produced from the raw materials accurately described the yields of the extrudates. It was concluded that the combination of a low heating rate and small reactor volume allowed the volatiles produced during pyrolysis to escape before the temperature increased significantly. This resulted in no significant decrease in condensable products or increase in gas yields with an increase in final pyrolysis temperature.

Both LDPE and PP have a narrow degradation temperature range and the production of mainly condensable products with the use of low heating rates is supported by literature.

The condensable products produced from the extrudates containing plastics showed high calorific values similar to those of the plastics (± 46 MJ/kg). Furthermore, although the condensable product yield followed the additive model and showed minimal interaction between the coal fines and plastic, the GC-MS analysis of the condensable products derived from the pyrolysis of coal fines and PP extrudates revealed a greater presence of components with higher boiling points compared to those obtained from either raw material alone. The pyrolysis of coal fines and PP extrudates also indicated that the maximum degradation temperature elevated when the two raw materials are combined. Furthermore, the condensable products from the LDPE containing extrudates also indicated interaction between the raw materials since even when a small amount of LDPE is added the aromatic content immediately dropped.

Statistical models were produced to predict the pyrolysis product yield and characteristics using the extrudate composition and the final pyrolysis temperature. The char yield, condensable product yield, fixed carbon content, ash yield, sulphur content of the chars, and the carbon and hydrogen content of the chars and condensable products were accurately described with the produced equations having R^2 values above 0.9. Furthermore, the p-values indicated that final pyrolysis temperature mostly effected the fine coal content and not the plastic content. This further supports observations that volatiles produced by the plastics left the reactor before being exposed to higher temperatures.

Since the plastics mainly produce condensable products, the gas yield decreased with an increase in plastic content. However, even though plastics are responsible for a smaller fraction of the gas yield, the addition of plastic lead to noticeable changes. With an increase in plastic content the CH_4 content of the gas increased, furthermore, the plastics contain low amounts of oxygen, resulting in the decrease in CO_2 production compared to CO production.

The evolution of the chars produced from the coal fines and the extrudates containing up to 50% plastic with an increase in final pyrolysis temperature (520 to 920 °C) were evaluated to understand any changes in CO_2 gasification reactivity. The structural properties of the chars were evaluated using SEM, petrographic carbon form analysis, surface area, porosity analysis, and XRD carbon crystallite analysis. The chars derived from the extrudates containing 75 and 100% plastic were not evaluated since the char yield is only a very small fraction of the overall yield. Thermal fragmentation was observed to degrade the integrity of the extrudates when the plastic content exceeded 10%, therefore, the chars produced at 920

°C were pulverised (75 - 150 µm) before undergoing CO₂ gasification. Carbon crystalline analyses showed that the chars, crystalline structure were more ordered with an increase in plastic content. However, even with the more ordered structure, the gasification reactivity increased with an increase in plastic content for both the extrudate derived chars containing LDPE and PP. Crack and pore formation increased with the increase in plastic content at all pyrolysis temperatures. LPGA results indicate that maximum porosity occurred during pyrolysis at 720 °C, which indicates that most of the pore growth occurred during pyrolysis and coalescence occurred during gasification. Furthermore, the VRM time factor showed a positive linear correlation with an increase in BET surface area, especially for the LDPE derived chars ($R^2 > 0.7720$). Therefore, the observed reactivity increase with an increase in plastic content can be correlated to an increase in surface area.

The combination of plastics and coal fines could potentially be used as a fuel source during pyrolysis. The increase in calorific value and decrease in oxygen and sulphur content when increasing the plastic content within the extrudates are additional benefits improving the fuel value. These extrudates could be considered as a robust fuel source since the properties can be adapted by changing the plastic addition and the large amounts of condensable products produced can potentially be further processed to produce valuable petrochemical products. Finally, the addition of plastics increased the gasification reactivity of the produced chars, speeding up the rate limiting step during gasification.

6.2 Contributions to science

The following contributions were made during this study:

- (i) Discarded coal fines were extruded using recycled waste plastics (LDPE and PP, respectively) with varying ratios of coal and plastics.
- (ii) The mechanical strength of these extrudates were classified and compared to industrial standards.
- (iii) Previous TGA co-pyrolysis studies on coal and plastics almost exclusively focussed on mechanically mixed blends and northern hemisphere coal, where this study was conducted on South African discarded inertinite-rich coal fines. Furthermore, iso-conversional techniques were used to measure the impact of plastic addition on the activation energy.
- (iv) The Fischer Assay slow pyrolysis of the extrudates was experimentally conducted and the product yields were measured, and each product was extensively characterized.

- (v) The extrudates were pyrolyzed at different final pyrolysis temperatures (520, 720, and 920 °C) and the effect of an increase in final pyrolysis temperature on pyrolysis yields and product characteristics from the extrudates was reported.
- (vi) Statistical equations were developed to predict the pyrolysis product yields and characteristics of the extrudates using the composition and final pyrolysis temperature.
- (vii) The CO₂ gasification kinetics of chars produced from coal fines and plastic extrudates were investigated and modelled using the VRM, demonstrating that an increase in plastic content result in increased reactivity.
- (viii) The physical structure of the chars produced from extrudates containing plastics and coal fines were characterized by petrographic carbon form analysis, surface area and porosity analysis, and XRD carbon crystallite analysis, giving insights into why the reactivity increases with an increase in plastic content.
- (ix) Since both LDPE and PP were extruded with coal fines individually, the effect of the 2 different plastic types and addition was directly compared throughout the extrusion, pyrolysis, and gasification experiments.

6.3 Recommendations for future studies

This study was completed using recycled waste LDPE and PP as binders with the view to compare the effects that the utilization of different plastic types has on the extrusion, pyrolysis, and gasification behaviour together with discard coal fines. Detailed investigations into reaction mechanisms were not included in the scope of this research. Therefore, it is recommended that a future study further investigates reaction mechanisms to clarify the decrease in activation energy observed in the TGA pyrolysis results obtained for the 10% LDPE containing extrudates compared to the increases observed in other extrudates of different composition.

To further improve the knowledge of co-processing different plastic types with coal fines, the co-processing of other plastic types like PS, PVC, PET, and HDPE should be investigated. Furthermore, this study aimed to understand the effect of the co-processing of coal fines with individual waste plastics, however, to avoid a rigorous sorting process the co-processing of coal fines with mixed waste plastics should be investigated. It is important to understand the effect that each individual plastic contributes when co-processing, however, plastics are known to have synergic effects between each other and therefore it is essential to further investigate the synergy of mixed plastics. If mixed waste plastics can be co-processed with

coal fines, two waste streams have the potential to be converted into valuable products without an intense sorting process.

Additionally, although the extrudates showed good mechanical strength, once thermal stress was exerted on them during slow pyrolysis all the plastics that glued the coal fines together was degraded. Therefore, the resulting chars were easily compressed, and their compressive strength was too low to be recorded by the LRX press. Thus, it would be worthwhile to investigate possibilities of improving the compressive strength after pyrolysis. These possibilities should include the addition of other waste products that could possibly act as the glue once the plastic is degraded. Furthermore, the binders should not drastically increase the ash content since this will be working against the advantage that plastic has of having almost no ash. Furthermore, the chars derived from the extrudates showed promising signs of swelling, which could be an indication of coking. Since coking coal is a sought-after product the coking properties of the chars derived from the extrudates should be further examined.

Slow pyrolysis caused the plastics to overwhelmingly produce condensable products. However, during fast pyrolysis when the sample is immediately exposed to a preheated oven, the pyrolysis products produced from the discard coal fines and plastic extrudates might not follow the additive model. The form of the extrudates could entrap volatiles and may lead to further cracking due to additional residence time at high temperatures. Furthermore, the entire sample will be exposed to higher temperatures which could produce vastly different pyrolysis products when being compared to slow pyrolysis products. Fast pyrolysis of plastic and coal extrudates should be further investigated.

For this fuel source to progress, an economic analysis of the production of the extrudates should be conducted. South Africa has vast supplies of discarded coal fines and plastics are separated into their respective types at landfill disposal sites. Therefore, doing an economic analysis in South Africa and comparing the fuel source to the traditionally used coal could provide interesting insights into whether the production of this combined fuel source is economically viable.

APPENDIX A1: SUPPORTING INFORMATION FOR – CHAPTER 3 – THE MECHANICAL AND THERMAL PROPERTIES OF EXTRUDATES PRODUCED FROM DISCARD COAL FINES AND RECYCLED PLASTICS AS BINDERS

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Before attempting extrusion, the Melt flow index (MFI) of the plastics was determined. The MFI can be related to viscosity, shear strength, and the shear rate of the material²⁸. The CEAST MFR at Potch Plastics was used to test the MFI of these samples. The plastic is melted in a vertical heating chamber and pressed through the capillary die by a piston connected to a weight according to ASTM D1238 and ISO 1133. The weight of the plastic that leaves the die is measured after 5 minutes and the results reported in g/10min.

Since the plastics will be extruded together with coal fines, the ASTM method was adapted to include coal fines, and the mixtures underwent the test under the same conditions as the pure plastics. Because the coal fines vitrinite component does not melt at these relatively low temperatures, the particles only obstructed the plastic melt flow. This test proved that the plastic would still flow in the extruder even if coal particles were blocking the flow. At 100% plastic content, the results for both LDPE and PP were similar to the industry standard for recycled plastics (0.44 g/min for LDPE and 9.6 g/min for PP). Both plastics showed that the mass flow decreased as the coal concentration increased. No flow was recorded at 50% LDPE, while the flow of the PP only stopped at 25% PP content. The melt flow is smooth when pure plastic passes through the die however, as the coal concentration increases, the melt flow becomes more rugged (Figure A1-1).

Appendix A1

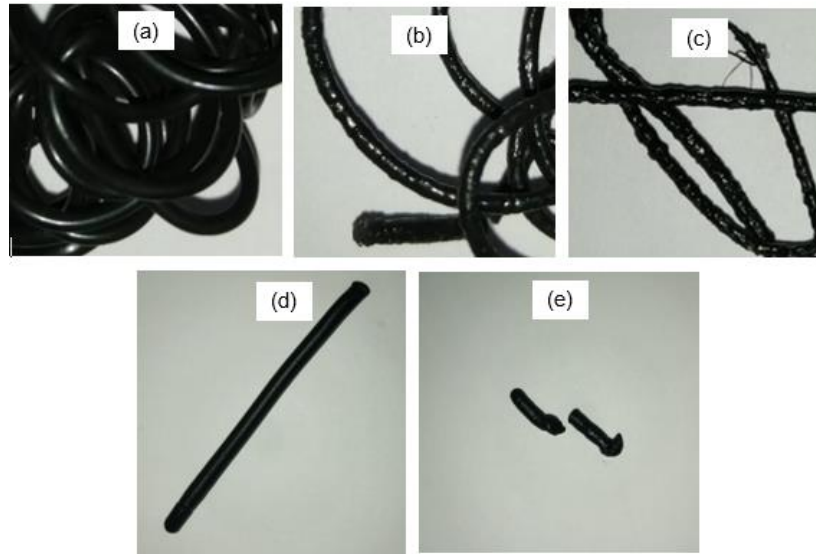


Figure A1-1: Melt flow of (a) 100% PP (b) 75% PP (c) 50% PP (d) 100% LDPE (e) 75% LDPE

The influence of heating rate on the pyrolysis parameters presented in Table 3-3 in Chapter 3 can be found in Table A1-1.

Table A1-1: Influence of heating rate on pyrolysis parameters

Sample	Heating rate	T _i (°C)	T _{max} (°C)	T _f (°C)	R _p (%/min)	R _v (%/min)	Mass Residue (%)
Coal	10	285.0	443.3	744.3	0.10	0.03	77.98
	20	315.3	455.7	744.3	0.10	0.03	78.39
	30	355.1	462.6	775.0	0.10	0.04	78.59
	40	355.3	469.1	785.0	0.10	0.04	78.21
10% LDPE	10	290.1	474.0	744.3	0.67	0.06	61.45
	20	345.0	485.3	779.5	0.55	0.04	64.48
	30	365.0	493.4	788.2	0.51	0.06	65.43
	40	375.0	500.3	786.3	0.63	0.07	62.12
25% LDPE	10	350.0	474.8	750.6	0.97	0.08	54.28
	20	360.1	488.3	769.0	0.96	0.08	52.52
	30	360.0	496.9	789.3	0.95	0.09	52.96
	40	360.3	502.6	792.1	0.91	0.09	52.88
50% LDPE	10	329.8	475.9	718.6	1.69	0.11	37.03
	20	360.1	488.3	722.9	1.72	0.12	36.76
	30	360.2	495.5	734.0	1.66	0.13	36.57
	40	365.1	500.9	745.4	1.69	0.12	35.51
75% LDPE	10	345.0	475.8	715.9	2.12	0.13	26.94
	20	355.0	488.8	783.5	2.04	0.13	29.03
	30	355.0	496.4	770.6	1.95	0.13	28.31
	40	360.1	501.5	783.5	1.99	0.14	25.87
LDPE	10	340.1	474.9	508.8	3.06	0.18	1.76
	20	385.1	488.0	519.9	2.96	0.19	2.02
	30	400.2	494.7	520.9	2.79	0.19	4.99
	40	420.2	499.6	528.6	2.71	0.21	4.22
10% PP	10	300.0	472.1	748.0	0.63	0.10	63.43
	20	305.0	479.2	772.6	0.47	0.06	67.47
	30	355.2	488.1	791.1	0.46	0.06	67.33
	40	365.2	494.0	799.8	0.44	0.06	67.57
25% PP	10	320.0	465.2	751.8	0.92	0.13	55.66
	20	350.1	479.7	770.8	0.90	0.08	54.33
	30	350.0	487.9	781.8	0.87	0.06	55.76
	40	360.3	494.7	786.6	0.84	0.08	55.09
50% PP	10	345.0	463.8	770.8	1.66	0.11	40.16
	20	345.1	477.8	772.3	1.59	0.11	36.93
	30	350.1	485.9	782.8	1.58	0.12	35.83
	40	355.1	491.8	784.6	1.50	0.11	37.73

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75% PP	10	340.1	462.8	756.9	2.04	0.13	27.93
	20	340.1	476.4	764.5	1.95	0.13	27.57
	30	350.1	484.7	771.8	1.90	0.13	27.83
	40	360.3	490.8	793.6	1.89	0.13	28.41
PP	10	325.0	453.4	495.3	2.77	0.34	2.56
	20	350.1	467.3	504.8	2.67	0.18	1.75
	30	370.0	474.7	508.1	2.70	0.19	0.14
	40	370.3	480.1	511.7	2.49	0.19	4.31

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The conversion temperatures presented in Figure 3-7 in Chapter 3 can be found in Table A1-2.

Table A1-2: Conversion temperatures

	Coal	LDPE	PP	10% LDPE	25% LDPE	50% LDPE	75% LDPE	10% PP	25% PP	50% PP	75% PP
X	Temperature (°C)										
0.1	426.6	462.1	434.4	446.1	453.3	460.7	461.7	439.4	446.4	449.0	449.4
0.2	451.3	471.8	448.6	465.9	469.2	472.4	472.5	458.9	461.7	461.1	460.8
0.3	472.0	477.4	455.6	475.9	477.4	478.7	478.5	469.3	469.8	467.8	467.1
0.4	496.4	481.5	460.6	483.2	483.4	483.5	483.0	476.9	475.6	472.7	471.6
0.5	527.9	485.0	464.6	489.5	488.3	487.4	486.8	483.6	480.7	476.9	475.5
0.6	570.9	488.4	468.4	496.7	493.1	490.9	490.4	490.9	485.6	480.7	479.2
0.7	627.9	491.7	472.1	519.2	498.2	494.8	493.8	521.0	491.2	484.7	482.9
0.8	688.3	495.3	476.1	597.7	506.7	499.2	497.8	598.2	504.3	489.7	487.0
0.9	737.8	499.8	481.1	704.2	619.4	506.9	503.6	704.7	632.1	499.7	493.7

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The activation energy values that are graphically presented in Figure 3-7 in Chapter 3 and the average activation energies can be found in Table A1-3.

Table A1-3: Activation energies

KAS	Coal	10% LDPE	25% LDPE	50% LDPE	75% LDPE	LDPE	10% PP	25% PP	50% PP	75% PP	PP
X	Ea (kJ/mol)										
0.1	182	189	226	234	244	231	201	193	224	208	196
0.2	212	211	222	241	238	235	211	202	215	207	204
0.3	228	218	221	243	239	239	210	203	212	208	206
0.4	228	221	219	243	239	241	209	204	213	210	209
0.5	235	220	218	244	240	241	206	203	211	211	210
0.6	259	216	217	247	237	239	203	201	210	210	210
0.7	317	173	217	246	238	239	259	202	211	209	208
0.8	315	192	217	248	237	237	360	222	210	211	207
0.9	339	267	319	254	236	234	302	337	208	213	205
AVG	257	212	231	244	239	237	240	219	213	210	206
Starink											
X	Ea (kJ/mol)										
0.1	184	191	228	236	246	233	203	195	226	210	198
0.2	214	213	224	243	240	237	213	204	217	209	205
0.3	230	220	223	245	241	241	212	204	214	210	208
0.4	230	223	221	245	241	243	211	206	215	212	211
0.5	237	222	220	246	241	243	208	205	213	213	212
0.6	261	218	219	249	238	241	205	203	212	212	212
0.7	319	175	219	248	240	241	261	204	213	211	210
0.8	317	195	219	250	239	239	362	224	212	213	209
0.9	341	269	321	256	238	236	305	339	210	215	207
AVG	259	214	233	246	241	239	242	221	215	212	208

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FWO											
X	Ea (kJ/mol)										
0.1	201	208	246	254	263	251	220	212	244	228	215
0.2	231	231	242	260	258	254	230	222	234	226	223
0.3	248	237	240	263	259	259	230	222	232	228	226
0.4	248	241	239	263	259	261	228	224	233	230	229
0.5	255	240	238	264	259	261	226	223	231	231	230
0.6	280	236	236	267	256	259	223	221	230	229	229
0.7	338	193	237	266	258	259	279	221	230	229	228
0.8	337	214	237	268	257	257	381	241	229	231	226
0.9	362	290	340	274	256	254	325	359	228	232	225
AVG	278	232	251	264	258	257	260	238	232	229	226

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The R^2 values for the activation energies presented in Figure 3-7 in Chapter 3 can be found in Table A1-4.

Table A1-4: R^2 values

KAS	Coal	10% LDPE	25% LDPE	50% LDPE	75% LDPE	LDPE	10% PP	25% PP	50% PP	75% PP	PP
X		R^2									
0.1	0.9990	0.9983	0.9990	0.9979	0.9985	0.9950	0.9765	0.9950	0.9985	0.9993	0.9997
0.2	0.9933	0.9993	0.9996	0.9993	0.9998	0.9968	0.9962	0.9985	0.9998	0.9999	1.0000
0.3	0.9806	0.9996	0.9998	0.9997	0.9998	0.9971	0.9983	0.9986	1.0000	0.9998	0.9999
0.4	0.9491	0.9997	0.9996	0.9997	0.9997	0.9969	0.9992	0.9989	0.9999	0.9999	0.9999
0.5	0.9271	0.9996	0.9993	0.9997	0.9999	0.9963	0.9991	0.9989	0.9999	0.9999	0.9999
0.6	0.8936	0.9993	0.9995	0.9999	1.0000	0.9969	0.9989	0.9987	1.0000	0.9998	1.0000
0.7	0.8609	0.9866	0.9991	0.9999	0.9998	0.9963	0.9952	0.9984	1.0000	0.9999	0.9998
0.8	0.8960	0.9476	0.9971	0.9999	0.9998	0.9968	0.9667	0.9826	0.9999	1.0000	0.9999
0.9	0.9503	0.9880	0.8830	0.9993	0.9998	0.9970	0.9718	0.8874	0.9991	0.9999	0.9997
Starink											
X		R^2									
0.1	0.9990	0.9983	0.9990	0.9979	0.9986	0.9950	0.9769	0.9951	0.9985	0.9993	0.9997
0.2	0.9934	0.9993	0.9996	0.9993	0.9998	0.9969	0.9963	0.9985	0.9998	0.9999	1.0000
0.3	0.9809	0.9997	0.9998	0.9997	0.9998	0.9971	0.9983	0.9987	1.0000	0.9998	0.9999
0.4	0.9499	0.9997	0.9996	0.9997	0.9997	0.9969	0.9992	0.9990	0.9999	0.9999	0.9999
0.5	0.9282	0.9996	0.9993	0.9997	0.9999	0.9963	0.9991	0.9989	0.9999	0.9999	0.9999
0.6	0.8951	0.9993	0.9995	0.9999	1.0000	0.9970	0.9989	0.9987	1.0000	0.9998	1.0000
0.7	0.8626	0.9869	0.9991	0.9999	0.9998	0.9963	0.9953	0.9984	1.0000	0.9999	0.9998
0.8	0.8973	0.9487	0.9972	0.9999	0.9998	0.9969	0.9671	0.9829	0.9999	1.0000	0.9999
0.9	0.9509	0.9882	0.8844	0.9993	0.9998	0.9971	0.9722	0.8886	0.9992	0.9999	0.9997
FWO											
X		R^2									
0.1	0.9992	0.9986	0.9991	0.9982	0.9987	0.9957	0.9804	0.9959	0.9987	0.9994	0.9997

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0.2	0.9944	0.9994	0.9997	0.9994	0.9998	0.9973	0.9968	0.9987	0.9998	0.9999	1.0000
0.3	0.9835	0.9997	0.9998	0.9998	0.9998	0.9975	0.9986	0.9989	1.0000	0.9998	0.9999
0.4	0.9566	0.9997	0.9997	0.9997	0.9998	0.9973	0.9993	0.9991	0.9999	0.9999	0.9999
0.5	0.9376	0.9997	0.9994	0.9998	0.9999	0.9968	0.9992	0.9991	1.0000	0.9999	0.9999
0.6	0.9075	0.9994	0.9996	0.9999	1.0000	0.9974	0.9991	0.9989	1.0000	0.9998	1.0000
0.7	0.8760	0.9893	0.9992	0.9999	0.9999	0.9968	0.9959	0.9986	1.0000	0.9999	0.9998
0.8	0.9082	0.9570	0.9976	0.9999	0.9998	0.9973	0.9702	0.9853	0.9999	1.0000	0.9999
0.9	0.9562	0.9898	0.8958	0.9994	0.9998	0.9974	0.9755	0.8991	0.9993	0.9999	0.9998

APPENDIX A2: SUPPORTING INFORMATION FOR – CHAPTER 4 – SLOW PYROLYSIS PRODUCTS DERIVED FROM EXTRUDATES PRODUCED FROM DISCARD COAL FINES AND RECYCLED PLASTICS AS BINDERS

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The Fischer Assay pyrolysis product yields of the extrudates and the raw materials at various final degradation temperatures are tabulated in Table A2-1.

Table A2-1: Pyrolysis yields at various final degradation temperatures

Sample	Temperature (°C)	Char (wt.%)	Condensable products (wt.%)	Water (wt.%)	Gas (wt.%)
Coal Fines	520	83.2 ± 1.4	4.1 ± 0.8	7.5 ± 0.5	5.2 ± 1.3
Coal Fines	720	75.4 ± 0.4	4.2 ± 1.2	11.9 ± 0.7	8.4 ± 2.0
Coal Fines	920	72.7 ± 0.7	4.0 ± 1.9	10.7 ± 1.0	12.6 ± 1.9
10% LDPE	520	72.9 ± 1.8	15.7 ± 2.9	6.1 ± 0.3	5.3 ± 1.7
10% LDPE	720	70.7 ± 2.7	10.8 ± 4.0	5.0 ± 1.6	13.5 ± 5.2
10% LDPE	920	63.2 ± 0.6	16.7 ± 2.3	8.8 ± 1.1	11.4 ± 2.9
25% LDPE	520	59.2 ± 1.8	27.4 ± 2.0	5.0 ± 2.1	8.5 ± 0.5
25% LDPE	720	55.1 ± 2.5	26.1 ± 1.6	5.3 ± 2.2	13.5 ± 3.1
25% LDPE	920	51.9 ± 3.5	30.7 ± 5.1	7.2 ± 0.5	10.2 ± 0.7
50% LDPE	520	38.9 ± 2.2	50.8 ± 1.8	3.5 ± 1.3	6.8 ± 1.2
50% LDPE	720	38.2 ± 2.1	45.7 ± 0.9	4.7 ± 1.8	11.4 ± 0.7
50% LDPE	920	34.2 ± 0.1	53.4 ± 0.3	6.4 ± 0.0	6.0 ± 0.2
75% LDPE	520	24.6 ± 2.8	68.2 ± 2.5	3.4 ± 0.5	3.7 ± 0.2
75% LDPE	720	23.2 ± 2.7	67.9 ± 5.1	2.8 ± 1.3	6.0 ± 1.1
75% LDPE	920	24.8 ± 0.5	68.6 ± 0.8	3.9 ± 0.6	2.7 ± 0.3
100% LDPE	520	2.0 ± 0.2	96.3 ± 1.2	1.8 ± 1.6	<0.1 ± 0.0
100% LDPE	720	2.4 ± 0.1	95.1 ± 9.4	2.5 ± 1.1	<0.1 ± 0.0
100% LDPE	920	1.8 ± 0.4	95.8 ± 1.9	2.4 ± 1.9	<0.1 ± 0.0
10% PP	520	77.4 ± 2.7	11.7 ± 0.5	5.3 ± 0.3	5.5 ± 2.0
10% PP	720	66.1 ± 1.0	16.8 ± 3.4	8.8 ± 1.5	8.4 ± 3.4
10% PP	920	63.0 ± 1.3	16.4 ± 2.6	9.8 ± 1.4	10.8 ± 2.1
25% PP	520	62.0 ± 0.0	28.5 ± 2.6	4.5 ± 1.4	4.9 ± 2.9
25% PP	720	55.5 ± 0.3	31.5 ± 1.7	7.4 ± 0.5	5.6 ± 2.3
25% PP	920	51.4 ± 0.7	34.3 ± 2.1	7.9 ± 1.9	6.5 ± 3.3
50% PP	520	41.2 ± 2.0	47.7 ± 0.9	2.8 ± 1.0	8.3 ± 1.8
50% PP	720	36.9 ± 1.1	50.0 ± 1.9	4.6 ± 0.4	8.5 ± 1.3
50% PP	920	34.7 ± 2.2	51.1 ± 2.4	4.9 ± 0.5	9.3 ± 3.7
75% PP	520	27.9 ± 2.0	65.1 ± 3.4	1.7 ± 0.3	5.3 ± 1.9
75% PP	720	27.0 ± 3.4	65.8 ± 3.4	3.0 ± 0.7	4.2 ± 3.0
75% PP	920	22.5 ± 2.4	67.5 ± 2.5	2.3 ± 0.6	7.7 ± 1.1
100% PP	520	1.7 ± 0.5	94.1 ± 4.5	1.7 ± 0.4	2.4 ± 4.5
100% PP	720	2.0 ± 0.5	91.5 ± 4.5	1.5 ± 0.4	5.1 ± 4.5
100% PP	920	1.7 ± 0.3	94.1 ± 3.2	1.3 ± 0.6	2.9 ± 3.0

*Standard deviation of each pyrolysis product at each temperature was calculated from multiple repeats

The ultimate analyses results of the chars produced from the extrudates and the raw materials at various pyrolysis temperatures is tabulated in Table A2-2.

Table A2-2: Ultimate analyses results (air-dry basis) of the pyrolysis chars

Sample	Temperature (°C)	%C	%H	%N	%S	%O
Coal fines	520	55.8 ± 1.00	1.6 ± 0.05	1.5 ± 0.13	0.7 ± 0.04	5.2 ± 1.01
Coal fines	720	57.8 ± 1.00	0.1 ± 0.05	1.1 ± 0.13	0.8 ± 0.04	0.7 ± 1.01
Coal fines	920	57.4 ± 1.00	0.0 ± 0.05	0.9 ± 0.13	1.0 ± 0.04	0.0 ± 1.01
10% LDPE	520	54.1 ± 1.00	2.0 ± 0.05	1.3 ± 0.13	0.7 ± 0.04	6.5 ± 1.01
10% LDPE	720	56.1 ± 1.00	0.8 ± 0.05	1.0 ± 0.13	0.9 ± 0.04	0.9 ± 1.01
10% LDPE	920	57.1 ± 1.00	0.1 ± 0.05	0.6 ± 0.13	1.0 ± 0.04	0.0 ± 1.01
25% LDPE	520	54.3 ± 1.00	1.8 ± 0.05	1.4 ± 0.13	0.8 ± 0.04	6.9 ± 1.01
25% LDPE	720	56.2 ± 1.00	0.6 ± 0.05	0.9 ± 0.13	0.9 ± 0.04	0.9 ± 1.01
25% LDPE	920	55.0 ± 1.00	0.0 ± 0.05	0.6 ± 0.13	1.1 ± 0.04	2.5 ± 1.01
50% LDPE	520	55.9 ± 1.00	1.8 ± 0.05	1.4 ± 0.13	0.6 ± 0.04	6.6 ± 1.01
50% LDPE	720	57.3 ± 1.00	0.6 ± 0.05	1.0 ± 0.13	0.8 ± 0.04	1.1 ± 1.01
50% LDPE	920	55.7 ± 1.00	0.0 ± 0.05	1.2 ± 0.13	0.8 ± 0.04	0.5 ± 1.01
75% LDPE	520	54.6 ± 1.00	2.0 ± 0.05	1.3 ± 0.13	0.7 ± 0.04	5.0 ± 1.01
75% LDPE	720	55.7 ± 1.00	0.4 ± 0.05	1.1 ± 0.13	0.8 ± 0.04	0.5 ± 1.01
75% LDPE	920	55.7 ± 1.00	0.0 ± 0.05	1.2 ± 0.13	0.7 ± 0.04	4.9 ± 1.01
LDPE	520	47.3 ± 1.00	0.6 ± 0.05	0.2 ± 0.13	0.6 ± 0.04	8.4 ± 1.01
LDPE	720	45.2 ± 1.00	0.3 ± 0.05	0.1 ± 0.13	0.6 ± 0.04	6.8 ± 1.01
LDPE	920	43.7 ± 1.00	0.1 ± 0.05	0.0 ± 0.13	0.8 ± 0.04	0.0 ± 1.01
10% PP	520	55.1 ± 1.00	2.2 ± 0.05	1.4 ± 0.13	0.7 ± 0.04	0.0 ± 1.01
10% PP	720	55.5 ± 1.00	0.5 ± 0.05	1.0 ± 0.13	0.8 ± 0.04	2.3 ± 1.01
10% PP	920	54.0 ± 1.00	0.0 ± 0.05	0.8 ± 0.13	1.2 ± 0.04	2.8 ± 1.01
25% PP	520	55.9 ± 1.00	1.9 ± 0.05	1.6 ± 0.13	0.8 ± 0.04	4.0 ± 1.01
25% PP	720	55.2 ± 1.00	0.5 ± 0.05	0.9 ± 0.13	1.0 ± 0.04	3.8 ± 1.01
25% PP	920	55.0 ± 1.00	0.0 ± 0.05	1.0 ± 0.13	1.1 ± 0.04	1.7 ± 1.01
50% PP	520	55.3 ± 1.00	1.8 ± 0.05	1.5 ± 0.13	0.7 ± 0.04	4.4 ± 1.01
50% PP	720	55.6 ± 1.00	0.3 ± 0.05	0.9 ± 0.13	0.7 ± 0.04	1.8 ± 1.01
50% PP	920	54.1 ± 1.00	0.0 ± 0.05	1.2 ± 0.13	0.6 ± 0.04	3.0 ± 1.01
75% PP	520	54.8 ± 1.00	1.4 ± 0.05	3.3 ± 0.13	0.8 ± 0.04	3.5 ± 1.01
75% PP	720	54.2 ± 1.00	0.5 ± 0.05	3.7 ± 0.13	0.9 ± 0.04	0.0 ± 1.01
75% PP	920	52.6 ± 1.00	0.0 ± 0.05	4.1 ± 0.13	0.7 ± 0.04	2.7 ± 1.01
PP	520	27.5 ± 1.00	0.5 ± 0.05	0.1 ± 0.13	0.7 ± 0.04	10.8 ± 1.01
PP	720	24.7 ± 1.00	0.3 ± 0.05	0.0 ± 0.13	0.2 ± 0.04	8.5 ± 1.01
PP	920	22.0 ± 1.00	0.1 ± 0.05	0.0 ± 0.13	0.4 ± 0.04	5.6 ± 1.01

*The standard deviation was calculated for each sample repeated and triplicate and the average of the standard deviations was used.

The ultimate analyses results of the condensable pyrolysis products produced from the extrudates and the raw materials at various pyrolysis temperatures is tabulated in Table A2-3.

Table A2-3: Ultimate analyses results (air-dry basis) of the condensable pyrolysis products

Sample	Temperature (°C)	%C	%H	%N	%S	Predicted %S	%O
Coal fines	520	83.1 ± 1.0	11.3 ± 0.3	4.6 ± 1.5	0.96 ± 0.03		0.00 ± 0.95
Coal fines	720	81.2 ± 1.0	9.7 ± 0.3	4.0 ± 1.5	1.79 ± 0.03		3.37 ± 0.95
Coal fines	920	82.2 ± 1.0	8.9 ± 0.3	2.3 ± 1.5	4.37 ± 0.03		2.24 ± 0.95
10% LDPE	520	83.7 ± 1.0	13.4 ± 0.3	2.6 ± 1.5		0.29	0.00 ± 0.95
10% LDPE	720	82.3 ± 1.0	13.0 ± 0.3	4.1 ± 1.5		0.53	0.00 ± 0.95
10% LDPE	920	81.6 ± 1.0	13.1 ± 0.3	4.1 ± 1.5		1.20	0.00 ± 0.95
25% LDPE	520	80.8 ± 1.0	13.4 ± 0.3	5.7 ± 1.5		0.13	0.00 ± 0.95
25% LDPE	720	82.2 ± 1.0	13.6 ± 0.3	3.9 ± 1.5		0.23	0.00 ± 0.95
25% LDPE	920	83.8 ± 1.0	14.0 ± 0.3	1.7 ± 1.5		0.51	0.00 ± 0.95
50% LDPE	520	83.5 ± 1.0	13.7 ± 0.3	2.8 ± 1.5		<0.1	0.00 ± 0.95
50% LDPE	720	83.7 ± 1.0	14.3 ± 0.3	1.9 ± 1.5		0.10	0.00 ± 0.95
50% LDPE	920	81.7 ± 1.0	13.6 ± 0.3	4.4 ± 1.5	0.19 ± 0.03	0.20	0.00 ± 0.95
75% LDPE	520	84.4 ± 1.0	14.9 ± 0.3	0.3 ± 1.5		<0.1	0.26 ± 0.95
75% LDPE	720	84.5 ± 1.0	15.0 ± 0.3	0.4 ± 1.5		<0.1	0.00 ± 0.95
75% LDPE	920	84.3 ± 1.0	14.9 ± 0.3	0.7 ± 1.5		<0.1	0.00 ± 0.95
LDPE	520	84.3 ± 1.0	15.0 ± 0.3	0.7 ± 1.5		<0.1	0.00 ± 0.95
LDPE	720	85.0 ± 1.0	14.2 ± 0.3	0.2 ± 1.5		<0.1	0.54 ± 0.95
LDPE	920	81.6 ± 1.0	14.1 ± 0.3	4.2 ± 1.5	<0.1 ± 0.03		0.00 ± 0.95
10% PP	520	80.2 ± 1.0	12.6 ± 0.3	6.9 ± 1.5		0.27	0.00 ± 0.95
10% PP	720	83.8 ± 1.0	13.4 ± 0.3	2.3 ± 1.5		0.53	0.00 ± 0.95
10% PP	920	84.2 ± 1.0	13.5 ± 0.3	0.7 ± 1.5		1.21	0.42 ± 0.95
25% PP	520	81.4 ± 1.0	13.2 ± 0.3	2.3 ± 1.5		0.12	2.96 ± 0.95
25% PP	720	80.6 ± 1.0	13.0 ± 0.3	0.6 ± 1.5		0.23	5.5 ± 0.95
25% PP	920	83.9 ± 1.0	13.9 ± 0.3	1.8 ± 1.5		0.50	0.00 ± 0.95
50% PP	520	81.0 ± 1.0	13.7 ± 0.3	5.3 ± 1.5		<0.1	0.00 ± 0.95
50% PP	720	82.7 ± 1.0	14.0 ± 0.3	3.3 ± 1.5		<0.1	0.00 ± 0.95
50% PP	920	82.5 ± 1.0	13.8 ± 0.3	0.4 ± 1.5	0.27 ± 0.03		3.03 ± 0.95
75% PP	520	83.8 ± 1.0	14.6 ± 0.3	1.6 ± 1.5		<0.1	0.00 ± 0.95
75% PP	720	84.3 ± 1.0	14.6 ± 0.3	1.1 ± 1.5		<0.1	0.00 ± 0.95
75% PP	920	84.9 ± 1.0	14.7 ± 0.3	0.3 ± 1.5		<0.1	0.00 ± 0.95
PP	520	83.8 ± 1.0	14.9 ± 0.3	1.3 ± 1.5		<0.1	0.00 ± 0.95
PP	720	84.7 ± 1.0	15.0 ± 0.3	0.3 ± 1.5		<0.1	0.00 ± 0.95
PP	920	83.6 ± 1.0	14.4 ± 0.3	1.2 ± 1.5	<0.1 ± 0.03	<0.1	0.77 ± 0.95

*The standard deviation was calculated for each sample (repeated and triplicate) and the average of the standard deviations was used. The predicted %S was calculated using Equation A2-1 which accounts for variance in condensable products yields of the coal compared to the plastics:

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$$Predicted \%S = \frac{X_{Coal} \cdot YCP_{Coal} \cdot S_{Coal} + X_{Plastic} \cdot YCP_{Plastic} \cdot S_{Plastic}}{(X_{Coal} \cdot YCP_{Coal} + X_{Plastic} \cdot YCP_{Plastic})} \quad (A2-1)$$

where X_{Coal} and $X_{Plastic}$ are the fractions of the raw materials within the extrudate and YCP_{Coal} and $YCP_{Plastic}$ are the condensable product yields of the raw materials, and $S_{Plastic}$ and S_{Coal} are the sulphur content of the condensable products from the raw materials (wt.%).

The proximate analyses results of the chars produced from the extrudates and the raw materials at various pyrolysis temperatures is tabulated in Table A2-4.

Table A2-4: Proximate analyses results (air-dry basis) of the pyrolysis chars

Sample	Temperature (°C)	%M	%VM	%A	%FC (by difference)
Coal fines	520	0.8 ± 0.2	13.9 ± 0.3	34.5 ± 0.9	50.8 ± 0.9
Coal fines	720	0.8 ± 0.2	4.3 ± 0.3	38.7 ± 0.9	56.1 ± 0.9
Coal fines	920	1.4 ± 0.2	1.5 ± 0.3	39.4 ± 0.9	57.8 ± 0.9
10% LDPE	520	2.0 ± 0.2	14.4 ± 0.3	33.3 ± 0.9	50.3 ± 0.9
10% LDPE	720	1.7 ± 0.2	3.4 ± 0.3	38.7 ± 0.9	56.7 ± 0.9
10% LDPE	920	1.2 ± 0.2	2.4 ± 0.3	40.0 ± 0.9	56.4 ± 0.9
25% LDPE	520	1.4 ± 0.2	14.7 ± 0.3	33.5 ± 0.9	50.4 ± 0.9
25% LDPE	720	1.4 ± 0.2	3.7 ± 0.3	39.0 ± 0.9	55.9 ± 0.9
25% LDPE	920	1.4 ± 0.2	2.3 ± 0.3	39.3 ± 0.9	56.9 ± 0.9
50% LDPE	520	1.1 ± 0.2	14.2 ± 0.3	32.6 ± 0.9	52.1 ± 0.9
50% LDPE	720	2.2 ± 0.2	6.9 ± 0.3	37.1 ± 0.9	53.7 ± 0.9
50% LDPE	920	1.1 ± 0.2	1.6 ± 0.3	40.7 ± 0.9	56.6 ± 0.9
75% LDPE	520	1.7 ± 0.2	12.1 ± 0.3	34.8 ± 0.9	51.5 ± 0.9
75% LDPE	720	1.6 ± 0.2	5.3 ± 0.3	39.9 ± 0.9	53.2 ± 0.9
75% LDPE	920	1.3 ± 0.2	2.5 ± 0.3	36.2 ± 0.9	60.0 ± 0.9
LDPE	520	1.5 ± 0.2	13.9 ± 0.3	41.4 ± 0.9	43.1 ± 0.9
LDPE	720	1.9 ± 0.2	9.4 ± 0.3	45.2 ± 0.9	43.5 ± 0.9
LDPE	920	2.7 ± 0.2	6.5 ± 0.3	52.6 ± 0.9	38.2 ± 0.9
10% PP	520	0.6 ± 0.2	13.6 ± 0.3	34.5 ± 0.9	51.3 ± 0.9
10% PP	720	0.8 ± 0.2	2.4 ± 0.3	39.1 ± 0.9	57.7 ± 0.9
10% PP	920	0.7 ± 0.2	1.5 ± 0.3	40.5 ± 0.9	57.2 ± 0.9
25% PP	520	1.4 ± 0.2	13.7 ± 0.3	34.5 ± 0.9	50.4 ± 0.9
25% PP	720	0.6 ± 0.2	5.1 ± 0.3	38.0 ± 0.9	56.2 ± 0.9
25% PP	920	0.6 ± 0.2	2.5 ± 0.3	40.6 ± 0.9	56.3 ± 0.9
50% PP	520	0.7 ± 0.2	13.4 ± 0.3	35.6 ± 0.9	50.3 ± 0.9
50% PP	720	1.1 ± 0.2	3.4 ± 0.3	39.5 ± 0.9	55.9 ± 0.9
50% PP	920	0.2 ± 0.2	2.2 ± 0.3	40.8 ± 0.9	56.8 ± 0.9
75% PP	520	1.0 ± 0.2	13.2 ± 0.3	35.2 ± 0.9	50.6 ± 0.9
75% PP	720	2.0 ± 0.2	5.7 ± 0.3	38.8 ± 0.9	53.5 ± 0.9
75% PP	920	1.0 ± 0.2	3.5 ± 0.3	38.8 ± 0.9	56.7 ± 0.9
PP	520	3.6 ± 0.2	19.0 ± 0.3	56.9 ± 0.9	20.5 ± 0.9
PP	720	2.5 ± 0.2	8.1 ± 0.3	63.8 ± 0.9	25.6 ± 0.9
PP	920	3.8 ± 0.2	10.5 ± 0.3	68.1 ± 0.9	17.6 ± 0.9

*The standard deviation was calculated by repeating the proximate analyses of the coal analysis 5 times and this was used for each sample.

Appendix A2

The statistical analysis equations along with the sensitivity of the equations to changes in the respective variables at average conditions are illustrated in Table A2-5.

Table A2-5: The sensitivity of the statistical analysis equations

Analysis	Property	Equation	Sensitivity			
			C _s	L _s	P _s	T _s
Pyrolysis product yield	Char	$Char = 0.9712C + 0.0304L + 0.0367P - 3.0 \times 10^{-4}C.T$ (4-4)	7.5518	0.3038	0.3669	-1.5000
	CP	$Condensable\ product = 0.0603C + 0.9328L + 0.9162P$ (4-5)	0.6031	9.3275	9.1616	NA
	Water	$Pyrolytic\ water = 0.0149C + 0.0179L + 0.0096P + 9.5 \times 10^{-5}C.T$ (4-6)	0.8335	0.1785	0.0964	0.4750
	Gas	$Gas = 0.0170C + 0.0190L + 0.0375P + 1.2 \times 10^{-4}C.T$ (4-7)	1.0125	0.1901	0.3753	0.5850
Proximate analyses	Ash	$Ash = 0.2823C + 0.0111L + 0.0176P$ (4-8)	2.8229	0.1112	0.1758	NA
	Fixed carbon	$Fixed\ carbon = 0.4149C + 0.0139L + 0.0142P$ (4-9)	4.1487	0.1386	0.1415	NA
	Volatile matter	$\sqrt{Volatile\ matter} = 0.0647C + 0.0067L + 0.0071P - 6.0E \times 10^{-5}C.T$ (4-10)	0.2147*	0.0675*	0.0708*	-0.3000*
	Moisture	$\sqrt{Moisture} = 0.0093C + 0.0037L + 0.0026P$ (4-11)	0.0925*	0.0373*	0.0261*	NA
Char ultimate analyses	Carbon	$Carbon = 0.5364C + 0.0148L + 0.0140P - 1.58 \times 10^{-4}C.T$ (4-12)	4.2267	0.1484	0.1397	-0.7900
	Hydrogen	$\sqrt{Hydrogen} = 0.0305C + 0.0014L + 0.0013P - 3.3 \times 10^{-5}C.T$ (4-13)	0.0674*	0.0144*	0.0125*	-0.1700*
	Nitrogen	$\sqrt{Nitrogen} = 0.0159C + 0.0016L + 0.0035P - 8.5 \times 10^{-6}C.T$ (4-14)	0.0977*	0.0156*	0.0348*	-0.0427*
	Sulphur	$Sulphur = 0.0045C + 4.5 \times 10^{-5}L + 9.6 \times 10^{-5}P - 2.7 \times 10^{-6}C.T$ (4-15)	0.0644	0.0005	0.0010	0.0134
CP ultimate analyses	Carbon	$Carbon = -0.0168C + 0.782564L + 0.7686P + 8.7 \times 10^{-5}C.T$ (4-16)	0.4582	7.8258	7.6862	0.4350
	Hydrogen	$Hydrogen = -0.0052C + 0.1362L + 0.1343P + 1.5 \times 10^{-5}C.T$ (4-17)	0.0563	1.3620	1.3400	0.0750

*Given in square root unit. C_s, L_s, and P_s indicate the influence of the addition of 10% of the respective components at 720 °C (average temperature) on the yields and characteristics. When using C_s, L_s, and P_s, the variable that is increased by 10% results in a 10% reduction in the remainder of the mixture, for example, when looking at an extrudate consisting out of coal and LDPE, a 10% increase in coal content will result in a 10% decrease in LDPE content. Therefore, for this example the total change in the properties will be the result of L_s subtracted from C_s. Furthermore, T_s indicates the influence of a 100 °C increase in final pyrolysis temperature when the extrudate contains 50% plastic and 50% coal fines (neither LDPE or PP has a significant interaction with temperature, therefore it does not matter which plastic is selected when evaluating the effect of temperature on any of the yields or characteristics). C_s is the largest for any char related property and L_s and P_s are larger for any condensable product related property, illustrating that coal is the main contributor to the char and the plastics the main contributors to the condensable products.

The sensitivity of the equations to changes in composition at the average temperature can be observed in the contour plots presented in Figures A2-1 to A2-14.

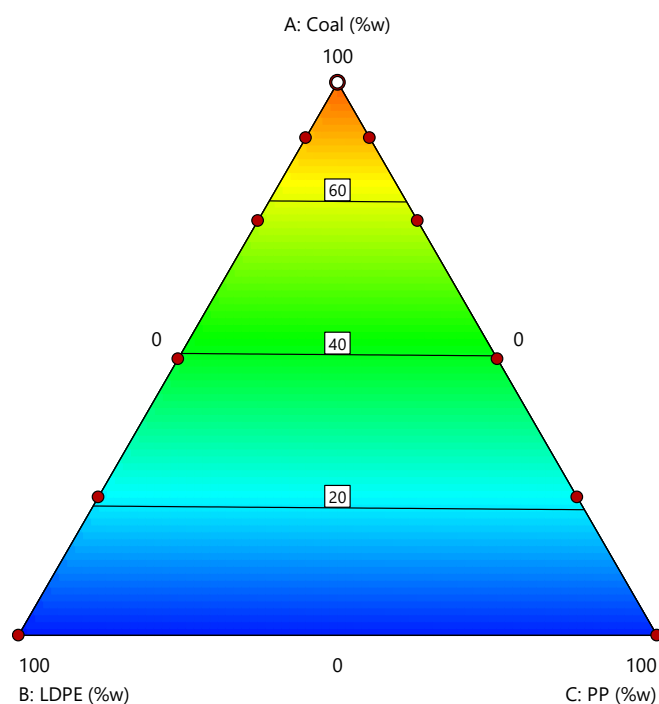


Figure A2-1: Predicted contours of the char yield (g/g extrudate) as a function of extrudate composition at a final pyrolysis temperature of 720 °C

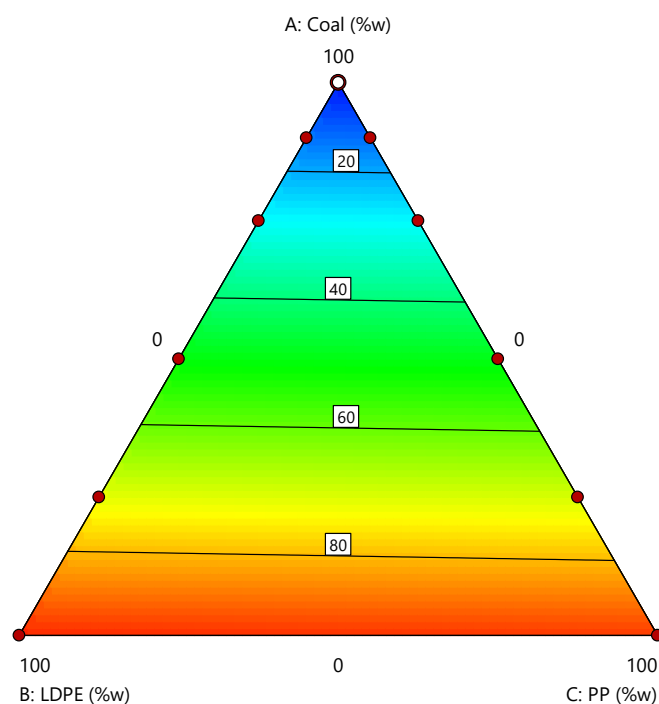


Figure A2-2: Predicted contours of the condensable product yield (g/g extrudate) as a function of extrudate composition at a final pyrolysis temperature of 720 °C

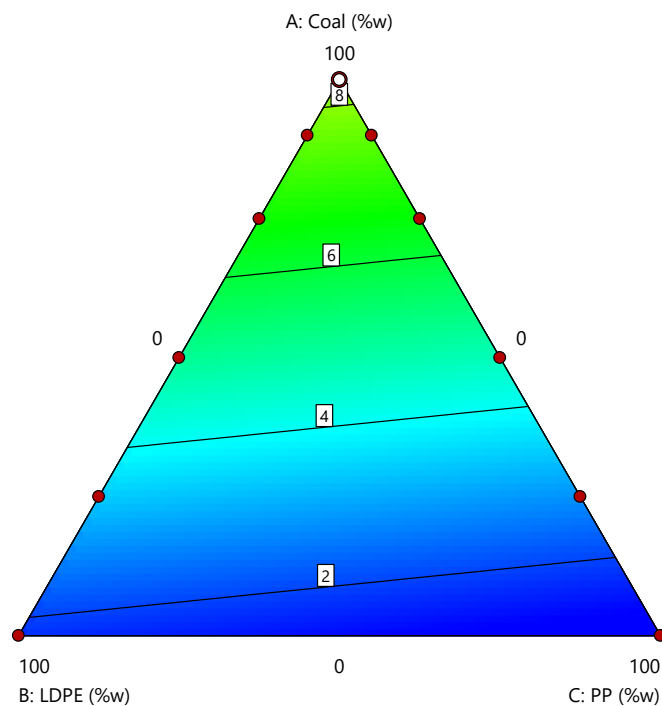


Figure A2-3: Predicted contours of the pyrolytic water yield (g/g extrudate) as a function of extrudate composition at a final pyrolysis temperature of 720 °C

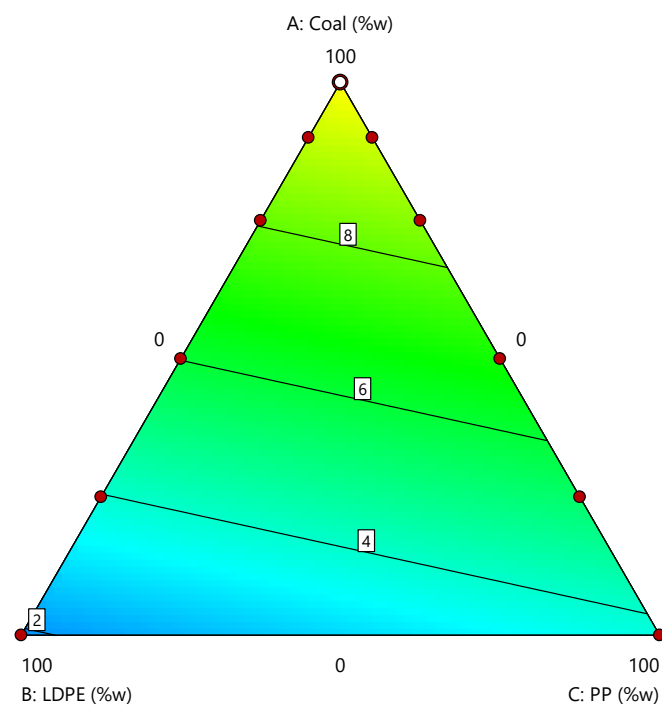


Figure A2-4: Predicted contours of the gas yield (g/g extrudate) as a function of extrudate composition at a final pyrolysis temperature of 720 °C

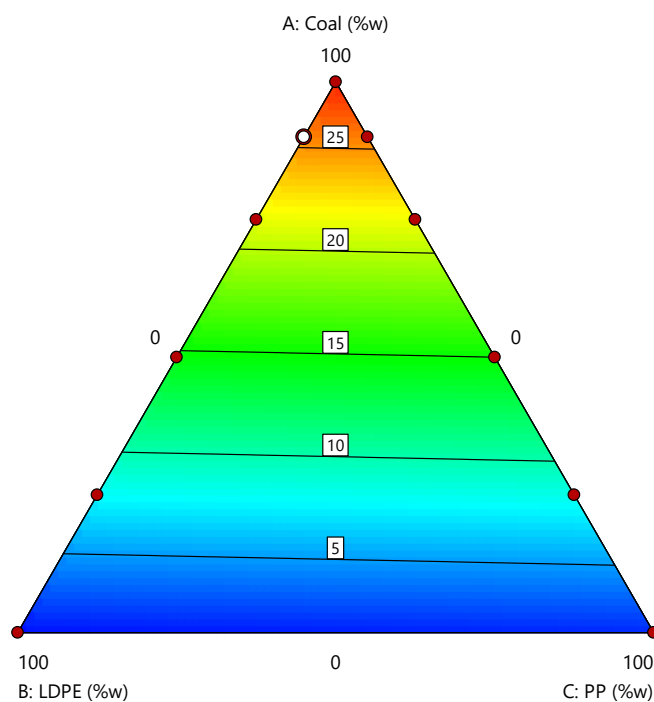


Figure A2-5: Predicted contours of the ash content (g/g extrudate) of the char as a function of extrudate composition at a final pyrolysis temperature of 720 °C

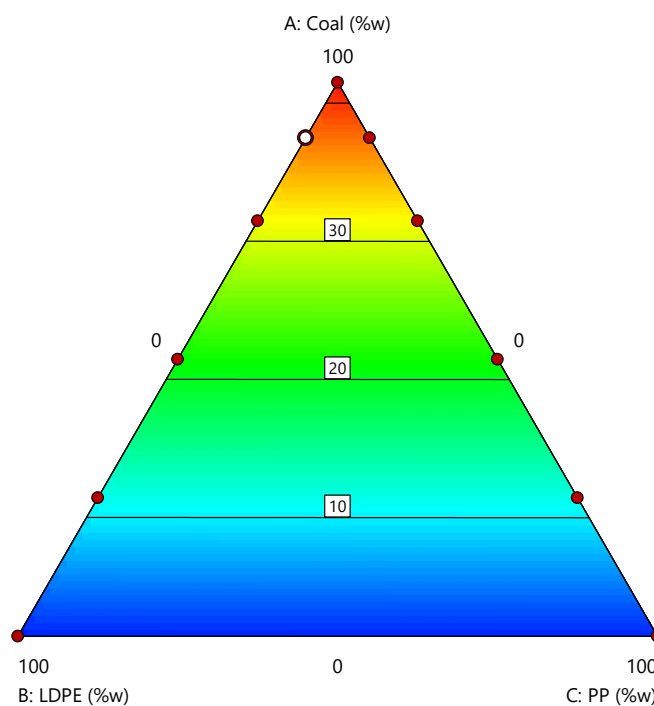


Figure A2-6: Predicted contours of the fixed carbon content (g/g extrudate) of the char as a function of extrudate composition at a final pyrolysis temperature of 720 °C

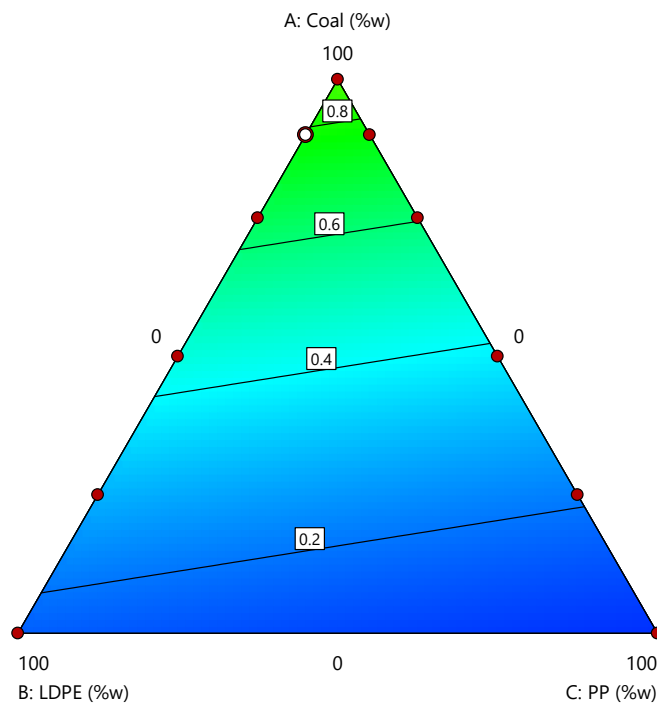


Figure A2-7: Predicted contours of the moisture content (g/g extrudate) of the char as a function of extrudate composition at a final pyrolysis temperature of 720 °C

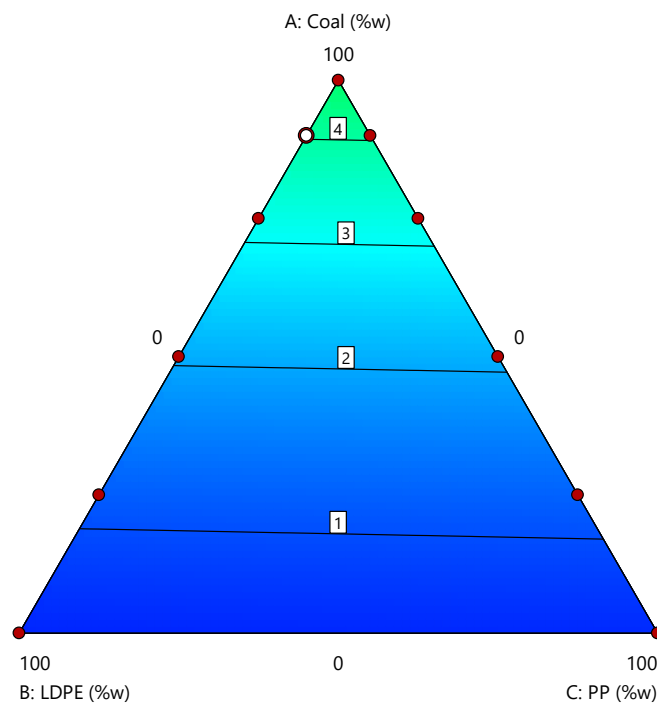


Figure A2-8: Predicted contours of the volatile matter content (g/g extrudate) of the char as a function of extrudate composition at a final pyrolysis temperature of 720 °C

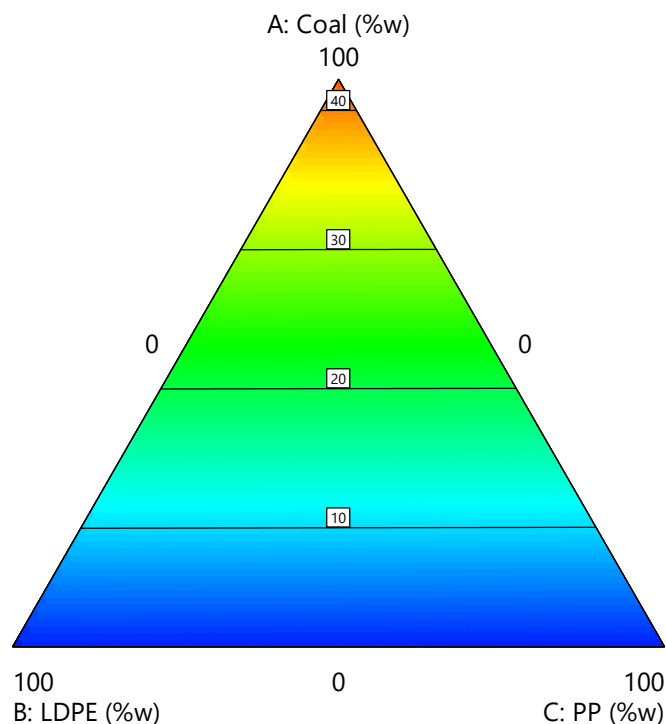


Figure A2-9: Predicted contours of the carbon content (g/g extrudate) of the char as a function of extrudate composition at a final pyrolysis temperature of 720 °C

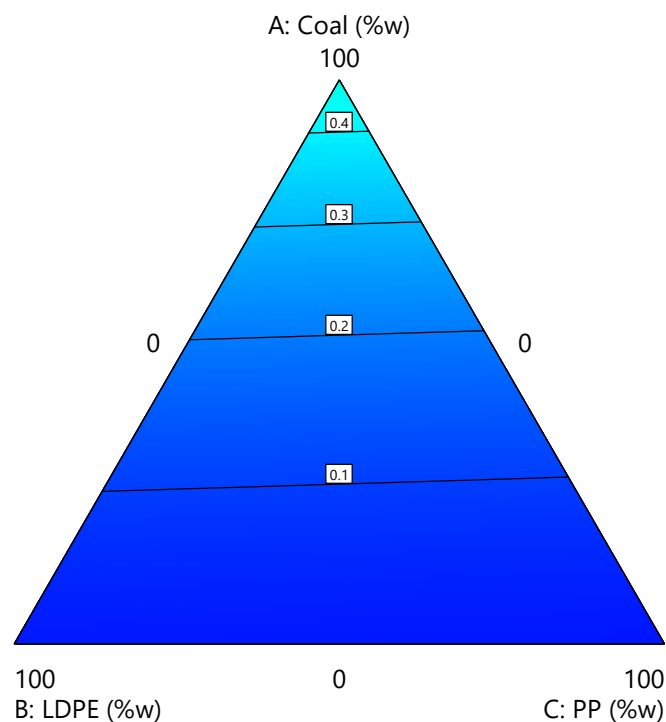


Figure A2-10: Predicted contours of the hydrogen content (g/g extrudate) of the char as a function of extrudate composition at a final pyrolysis temperature of 720 °C

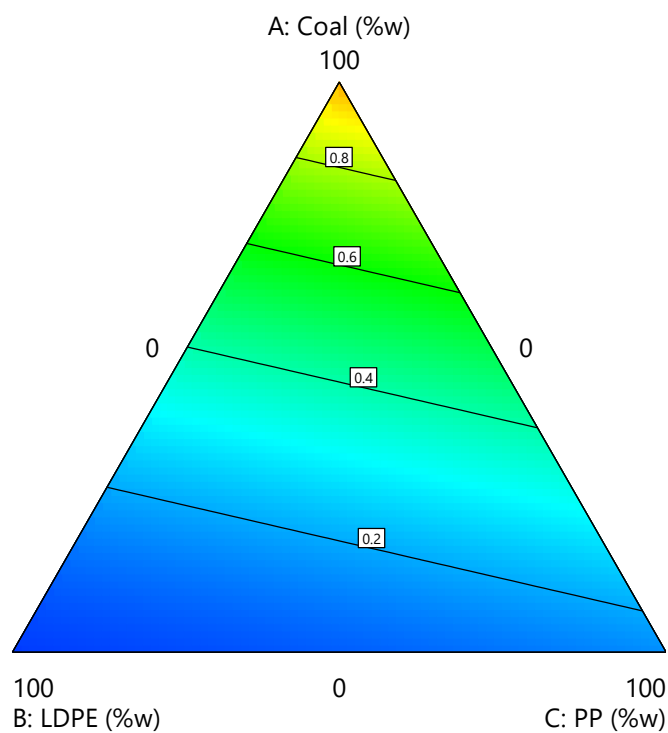


Figure A2-11: Predicted contours of the nitrogen content (g/g extrudate) of the char as a function of extrudate composition at a final pyrolysis temperature of 720 °C

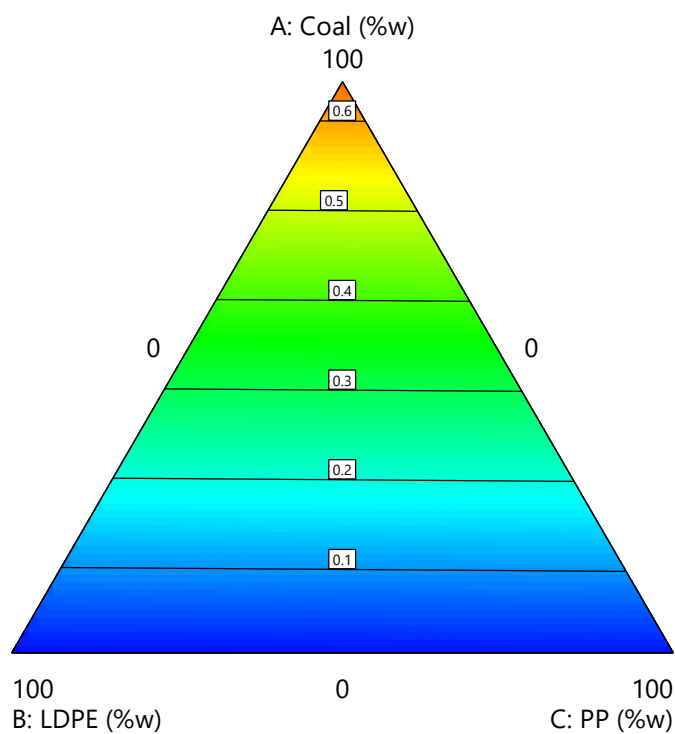


Figure A2-12: Predicted contours of the sulphur content (g/g extrudate) of the char as a function of extrudate composition at a final pyrolysis temperature of 720 °C

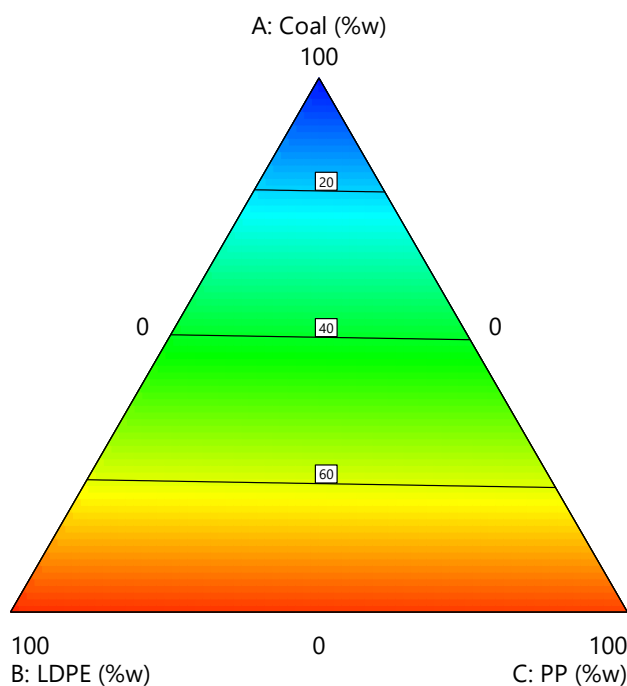


Figure A2-13: Predicted contours of the carbon content (g/g extrudate) of the condensed product as a function of extrudate composition at a final pyrolysis temperature of 720 °C

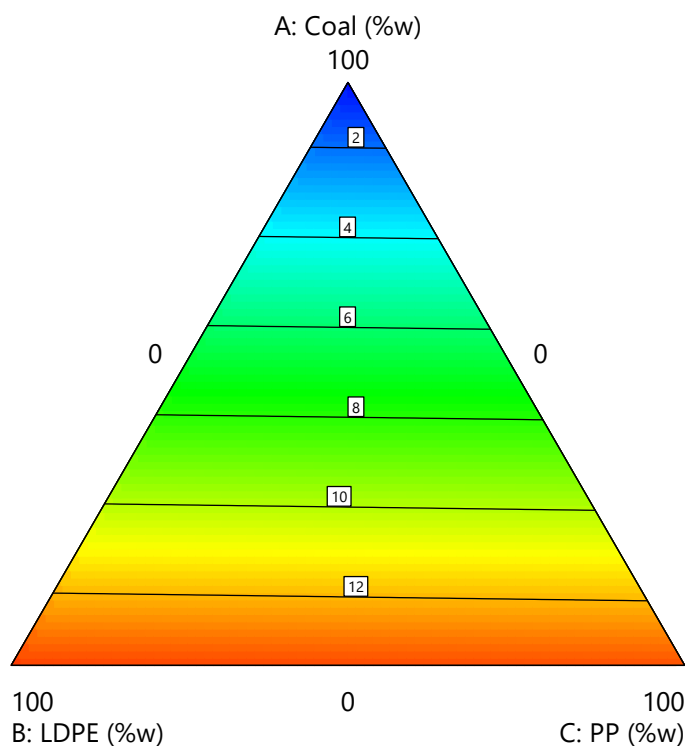


Figure A2-14: Predicted contours of the hydrogen content (g/g extrudate) of the condensed product as a function of extrudate composition at a final pyrolysis temperature of 720 °C

APPENDIX A3: SUPPORTING INFORMATION FOR – CHAPTER 5 – STRUCTURAL ANALYSIS AND GASIFICATION REACTIVITY OF CHARS DERIVED FROM THE SLOW PYROLYSIS OF EXTRUDED COAL FINES AND RECYCLED PLASTIC

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Nomenclature		
Symbol	Description	Units
E_a	Activation Energy	kJ.mol^{-1}
k'_{s0}	Lumped pre-exponential factor	min^{-1}
r_s	Intrinsic reaction rate	m.min^{-1}
S_0	Initial Surface area	$\text{m}^2.\text{m}^{-3}$
t	reaction real time	min
t_f	time factor	min^{-1}
QOF	Quality of fit	%
X	Conversion	-
ε_0	Initial porosity	-
ψ	Dimensionless structural parameter	-

A3-1: Random pore model (RPM) experimental method

The RPM considers the random pore orientation and size distribution¹⁻³. This model provides an explanation for the changes in the char's surface as the reaction proceeds, including pore growth and the formation of overlapping pores which reduces the available surface area^{2,3}. The RPM is given by Equation A3-1^{3,4}.

$$\frac{dX}{dt} = \frac{r_s S_0 (1 - X) \sqrt{[1 - \psi \ln(1 - X)]}}{(1 - \varepsilon_0)} \quad (\text{A3-1})$$

Where r_s is the intrinsic reaction rate, and the dimensionless structural parameter (ψ) is described by Equation A3-2.

$$\psi = \frac{4\pi L_0 (1 - \varepsilon_0)}{S_0^2} \quad (\text{A3-2})$$

L_0 is the total length per unit volume and ε_0 , and S_0 are the initial porosity and surface area, respectively. The RPM gasification conversion is provided by Equation A3-3.

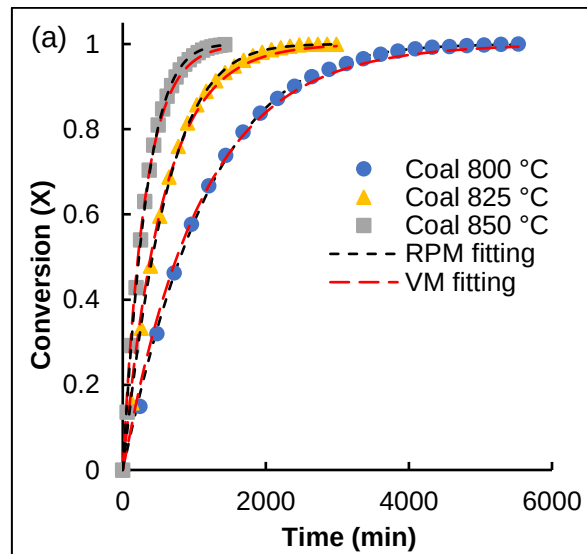
$$X = 1 - \exp \left[-t_f t \left(1 + \frac{t_f t \psi}{4} \right) \right] \quad (A3-3)$$

Where t_f is now the time factor when using the RPM and t is still the reaction real time. The structural parameter can be estimated by linear regression using the dimensionless reduced time, $t/t_{0.9}$ (Equation A-4)⁵.

$$\frac{t}{t_{0.9}} = \frac{\sqrt{1 - \psi \ln(1 - X)} - 1}{\sqrt{1 - \psi \ln(1 - 0.9)} - 1} \quad (A3-4)$$

A3-2: Comparison between RPM and VRM

The char gasification was modelled using both the RPM and VRM. These models provided similar kinetic parameters and quality of fit results as presented in Figure A3-1, Table A3-1, and Table A3-2. When the structural parameter (Ψ_{RPM}) is equal to zero (Table A3-2), the RPM reduces exactly to the VRM. Since the structural parameter is very close to zero, the VRM and RPM provide similar results, and both models deliver satisfactory QOF-values for all chars. Therefore, the simpler VRM model was used to further discuss the gasification kinetics of the chars.



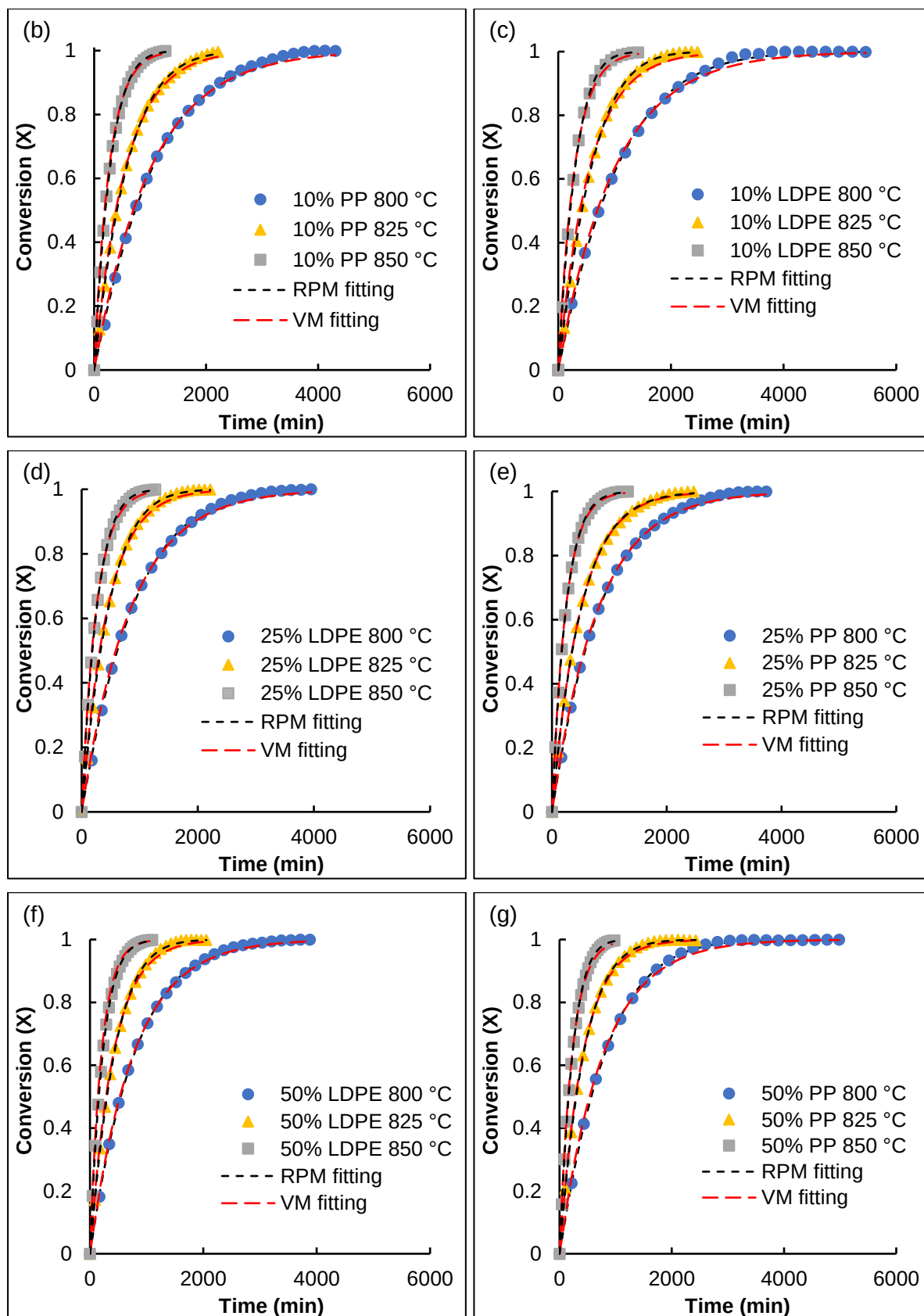


Figure A3-1: The experimental gasification conversion compared to the estimated RPM and VRM conversions of the chars produced from the extrudates containing (a) coal, (b) 10% LDPE, (c) 10% PP, (d) 25% LDPE, (e) 25% PP, (f) 50% LDPE, (g) 50% PP.

Table A3-1: Gasification kinetic parameters

Char	Reactivity model	R ²	E _a (kJ.mol ⁻¹)	k' _{s0} (min ⁻¹)
Coal Fines	R _{RPM}	0.9999	253	1.6.E+09
	R _{VRM}	0.9997	254	2.0.E+09
10% LDPE	R _{RPM}	0.9856	244	6.4.E+08
	R _{VRM}	0.9980	248	1.2.E+09
25% LDPE	R _{RPM}	1.0000	242	6.4.E+08
	R _{VRM}	0.9995	241	6.2.E+08
50% LDPE	R _{RPM}	0.9954	252	2.1.E+09
	R _{VRM}	0.9971	267	1.3.E+10
10% PP	R _{RPM}	0.9955	262	4.9.E+09
	R _{VRM}	0.9939	265	8.0.E+09
25% PP	R _{RPM}	0.9878	245	9.5.E+08
	R _{VRM}	0.9807	241	6.7.E+08
50% PP	R _{RPM}	0.9996	253	2.3.E+09
	R _{VRM}	0.9998	249	1.8.E+09

The reactivity values, reaction times, time factors for the RPM and VRM, the dimensionless structural parameters of the RPM, and the quality of fit for each char type at all three temperatures are summarized in Table A3-2.

Table A3-2: Gasification reactivity parameters

Char	Gasification temperature (°C)	$t_{f\text{ RPM}}$ (min ⁻¹)	Ψ_{RPM}	QOF _{RPM} (%)	$t_{f\text{ VRM}}$ (min ⁻¹)	QOF _{VRM} (%)
Coal fines	800	8.0E-04	0.47	99.0	9.2E-04	97.9
	825	1.5E-03	0.51	99.0	1.8E-03	97.9
	850	2.8E-03	0.49	98.9	3.2E-03	97.7
10% LDPE	800	9.0E-04	0.34	99.2	1.0E-03	98.8
	825	1.5E-03	0.77	99.1	1.8E-03	97.1
	850	3.0E-03	0.47	99.3	3.5E-03	98.0
25% LDPE	800	1.1E-03	0.29	99.4	1.2E-03	98.6
	825	2.0E-03	0.36	99.5	2.2E-03	98.4
	850	3.6E-03	0.26	99.6	3.9E-03	98.7
50% LDPE	800	1.2E-03	0.18	99.5	1.3E-03	99.1
	825	2.2E-03	0.36	99.5	2.4E-03	98.5
	850	4.4E-03	0.15	99.7	5.0E-03	97.9
10% PP	800	9.0E-04	0.33	99.2	9.9E-04	98.3
	825	1.6E-03	0.32	99.0	1.8E-03	98.1
	850	3.3E-03	0.28	99.3	3.7E-03	98.2
25% PP	800	1.2E-03	0.17	99.5	1.2E-03	99.1
	825	2.0E-03	0.06	99.6	2.0E-03	99.6
	850	4.0E-03	0.12	99.7	4.2E-03	99.4
50% PP	800	1.2E-03	0.38	99.7	1.3E-03	98.8
	825	2.2E-03	0.22	99.7	2.4E-03	99.1
	850	4.1E-03	0.32	99.7	4.5E-03	98.5

A3-3 Mineral phase composition

The relative mineral phase composition of the raw coal and char samples is provided in Figure A3-2.

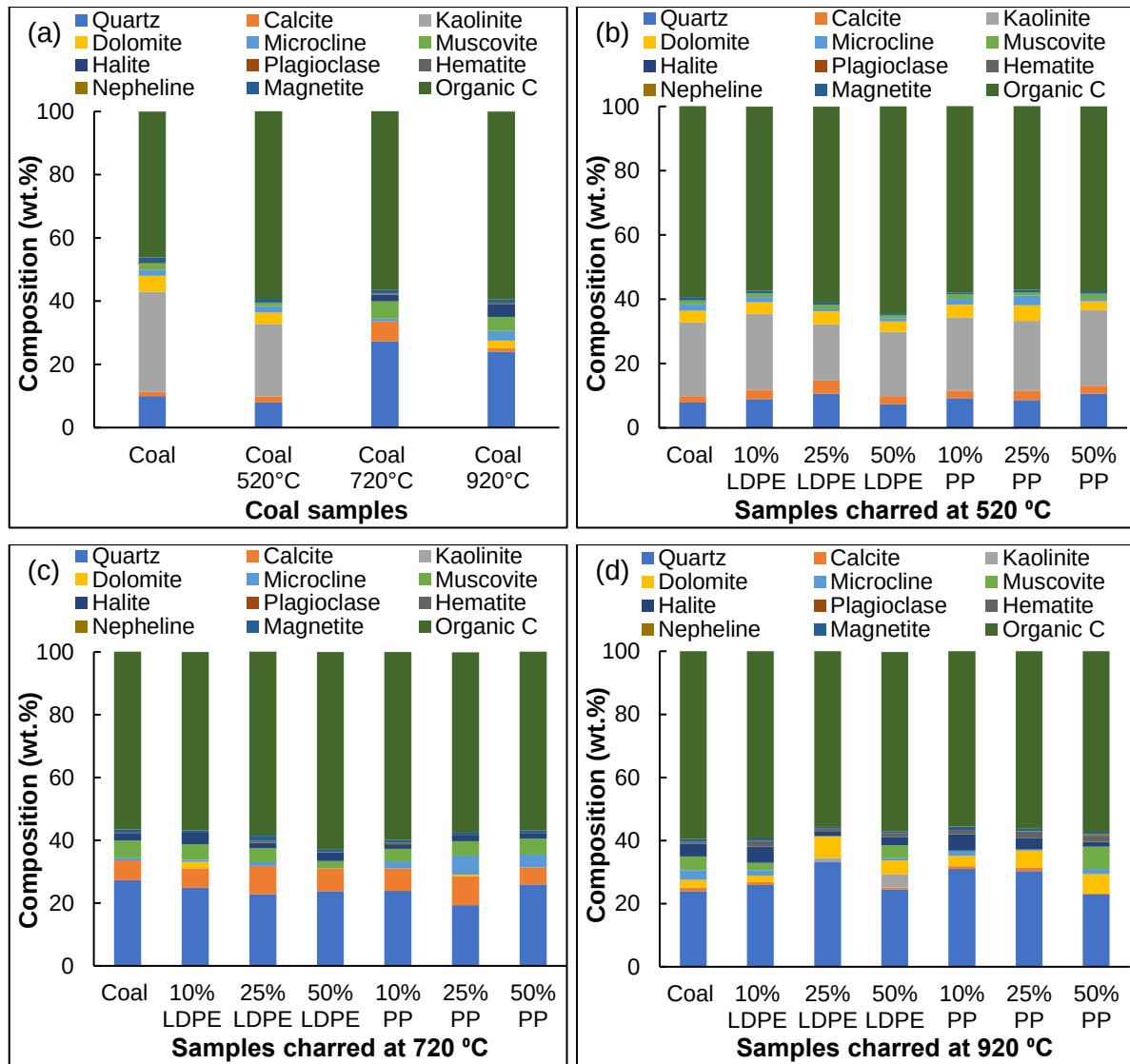


Figure A3-2: Mineral phases of (a) the raw coal compared to the char produced from coal at 520, 720 and 920 °C, (b) chars produced at 520 °C, (c) chars produced at 720 °C and (d) chars produced at 920 °C

Figure A3-2(a) indicates that the organic carbon is the most abundant in the raw material and in all of its produced chars. The organic carbon content increases when charred due to the release of volatile matter and moisture content. The most prominent mineral phase in the raw coal and the char produced at 520 °C is kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), however, the chars produced at higher temperatures have almost no kaolinite present. This is due to the dehydroxylation of kaolinite between 450 and 700 °C to produce metakaolinite⁶. Metakaolinite does not appear in the mineral phase XRD analysis due to its amorphous layered structure preventing it from producing crystalline XRD diffraction lines^{7,8}. Since there is no metakaolinite shown in the mineral phases, the other minerals appear more abundant resulting in the appearance of quartz being the most prominent mineral phase at higher temperatures.

The mineral phase composition of the chars produced from plastics and coal did not show significant deviance to what was observed in chars produced from raw coal. This was expected since both LDPE and PP have an almost insignificant ash fraction (< 2%) compared to the 29.6% ash yield fraction obtained from the raw coal^{9,10}.

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