



Direct co-liquefaction of vitrinite and inertinite-rich coal fines with plastic waste material

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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:	August 2024
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DECLARATION

I, Jacobus Arnoldus (Naldo) Meyer, hereby declare that this thesis entitled: "*Direct co-liquefaction of vitrinite and inertinite-rich coal fines with plastic waste material*", accepted in fulfilment of the requirements for the degree Doctor of Philosophy in Engineering with Chemical Engineering, is my own work, except where specified in the text, and has not been submitted at any other tertiary institution.

Signed at Potchefstroom on the 20th day of March 2024.



Jacobus Arnoldus Meyer

PREFACE

Format of thesis

The format of this thesis is in accordance with the academic rules of the North-West University (approved September 21st, 2017, with revisions on June 20th, 2019), where:

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Format of numbering and referencing

It should be noted that the formatting, referencing style, numbering of tables and figures, and general outline of the manuscripts were adapted to ensure uniformity throughout the thesis. The formats of manuscripts submitted and/or published adhere to the author guidelines stipulated by the editor of each journal and may differ from what is presented in this thesis. The headings and original technical content of the manuscripts were not modified from the submitted and/or published versions, and only minor spelling and typographical errors were corrected. The bibliography (reference list) is included at the end of each chapter.

Supplementary Information

Supplementary data, where applicable, have been included in the Supplementary Information section of each chapter.

LETTER OF CONSENT

The co-authors hereby give consent that Naldo J.A. Meyer may submit the following manuscript(s) as part of this thesis entitled: "*Direct co-liquefaction of vitrinite and inertinite-rich coal fines with plastic waste material*", for the degree Doctor of Philosophy in Engineering with Chemical Engineering":

Meyer, N.J.A.; Strydom, C.A.; Bunt, J.R.; Uwaoma, R.C. Direct Liquefaction of South African Vitrinite- and Inertinite-Rich Coal Fines. ACS Omega **2024**, 9 (10), 12272-12289.

<https://doi.org/10.1021/acsomega.4c00602>

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LIST OF OUTPUTS

Journal articles

Meyer, N.J.A.; Strydom, C.A.; Bunt, J.R.; Uwaoma, R.C. Direct Liquefaction of South African Vitrinite- and Inertinite-Rich Coal Fines. *ACS Omega* **2024**, 9 (10), 12272-12289.

<https://doi.org/10.1021/acsomega.4c00602>

Meyer, J.A.; Strydom, C.A.; Bunt, J.R.; Uwaoma, R.C. Pyrolysis products derived from co-processing of coal fines and microalgae. *Bioresource Technology Reports* **2022**, 19, 101128.

<https://doi.org/10.1016/j.biteb.2022.101128>

Uwaoma, R.C.; Schröer, B.J.; Strydom, C.A.; Bunt, J.R.; Matjie, R.H.; Mphahlele, K.; **Meyer, J.A.** Kinetics, thermodynamics, and thermal decomposition characteristics of co-pyrolysis of municipality solid waste residue hydrochar and <1.5 g/cm³ fraction of South African discarded fine coal. *Bioresource Technology Reports* **2022**, 18, 100998.

<https://doi.org/10.1016/j.biteb.2022.100998>

Conference proceedings

Meyer N.J.A.; Strydom C.A.; Bunt J.R.; Uwaoma R.C. Direct liquefaction of inertinite-rich coal fines using tetralin and benzene as solvent. (Proceeding not yet available)

Biennial Conference of the Southern African Coal Processing Society (SACPS) – The role of coal beneficiation towards a low carbon economy| Secunda, South Africa. August 2023. (Oral presentation)

Meyer N.J.A.; Strydom C.A.; Bunt J.R.; Uwaoma R.C. Pyrolysis products derived from co-processing of coal fines and microalgae. (ISBN: 978-8-8626-5029-8)

VENICE 2022 - 9th International Symposium on Energy from Biomass and Waste| Venice, Italy. November 2022. (Oral presentation)

Gaibie, S.; Hattingh, B.; Swart P.; Schmitz, W.; **Meyer J.A.**; Haripersad N. Valorisation potential of synthetic gypsum produced from Eskom's wet flue gas desulphurization (FGD) process. (Conference Proceedings ISBN: 978-0-6397-1934-4)

2022 CONFERENCE OF THE NATIONAL ASSOCIATION FOR CLEAN AIR| Kempton Park, South Africa. October 2022. (Scientific paper and oral presentation)

Gaibie, S.; Schmitz, W.; Hattingh, B.; Swart, P.; **Meyer, N.**; Haripersad, N. Evaluation of the product quality and market suitability of synthetic gypsum produced from Eskom's wet flue gas desulphurization (FGD) process. (ISBN: 978-1-7138-7230-6)

39th INTERNATIONAL PITTSBURGH COAL CONFERENCE – Clean Coal-based Energy/Fuels and the Environment| University of Pittsburgh, USA. September 2022. (Conference paper and oral presentation)

Meyer, J.A.; Strydom, C.A.; Bunt, J.R. The effect of microalgae as a binder on the characteristics of agglomerated coal fines.

11th RENEWABLE ENERGY POSTGRADUATE STUDENTS e-SYMPOSIUM| North-West University, South Africa. September 2020. (Oral presentation)

ACKNOWLEDGEMENTS

I would like to acknowledge and express my sincere gratitude to the following individuals who supported me throughout this study and played major roles in the development of this thesis:

- I am deeply grateful for the invaluable guidance, expertise, and unwavering support provided by my esteemed supervisors, Prof. Christien Strydom, Prof. John Bunt, and Dr. Romanus Uwaoma, throughout the duration of my study. Your contributions have been instrumental in shaping my academic journey, and I am truly thankful for your mentorship.
- I would like to express my sincere gratitude to the Coal Research Group and workshop personnel for their support and assistance.
- I am immensely grateful to my family and friends for their support, encouragement, and understanding throughout my journey.
- I extend my heartfelt gratitude to my parents, Thania and Allan Rowan, for their unwavering support throughout my academic journey. Your endless encouragement and belief in me have been invaluable, and I am deeply thankful for your constant guidance and love.
- The financial support of the National Research Foundation, SARChI Coal Research Chair, Centre of Excellence in Carbon-based Fuels, and North-West University is hereby acknowledged.

The work presented in this thesis is based on the research financially supported by the National Research Foundation (NRF) and South African Research Chairs Initiatives (SARChI) of the Department of Science and Technology (Coal Research chair Grant No. 86880). Any opinions, conclusions or recommendations expressed are that of the author(s), and no liability is accepted on the NRF's regard.

ABSTRACT

Direct coal liquefaction (DCL) stands as a promising process in the realm of energy production. This process is characterized by its ability to break down the complex macromolecular structure of coal using a solvent under moderate conditions. Direct liquefaction aims to yield liquid fuels with a targeted hydrogen-to-carbon ratio, which is achieved through hydrogenation reactions. Conversely, inadequate hydrogen availability can lead to the formation of undesirable residues. The co-liquefaction of coal with other feed materials have been examined extensively. Co-liquefaction involves the simultaneous treatment of various carbonaceous materials, including coal, biomass, and plastic waste, within a shared solvent or reaction medium. This innovative process capitalizes on the synergistic properties of diverse feedstocks, with the primary goal of increasing overall conversion efficiencies and generating valuable liquid products. Central to the success of co-liquefaction is a profound understanding of the intricate interactions between the heterogeneous components during the thermochemical conversion process.

In the initial phase of this study, the direct liquefaction of inertinite-rich coal fines was evaluated, alongside a comparison with a vitrinite-rich coal commonly utilized in coal-to-liquid processes. To discern the influence of mineral matter content, demineralization techniques were employed to eliminate the majority of inorganic constituents. The results revealed that the inertinite-rich coal demonstrated reduced liquefaction conversion values, attributed to a lower proportion of reactive macerals and increased levels of inorganic mineral matter. Notably, the liquefaction efficiency exhibited a strong correlation with the abundance of reactive macerals inherent in the parent coals. Interestingly, in the case of the inertinite-rich coal, the presence of inorganic mineral matter hindered the liquefaction process while promoting CO₂ gasification reactions of the resultant chars. Furthermore, CO₂ gasification experiments allowed for the determination of reactivities and apparent gasification activation energies of the coal chars, liquefaction residue chars, and pre-asphaltene and asphaltene (PAA) chars. Utilizing models such as the random pore model (RPM) and volumetric reaction model (VRM), these calculations shed light on the chemistry, reactivity, and kinetics of different chars during gasification. Overall, this investigation underscores the substantial disparities in liquefaction conversion values, product distribution, and composition, influenced by factors such as maceral composition, inorganic mineral matter content, solvent hydrogen-donor capabilities, and liquefaction reaction temperatures, with implications extending to CO₂ gasification reactivity of liquefaction solid residue chars.

In the subsequent phase of this study, polypropylene (PP) and low-density polyethylene (LDPE) were subjected to liquefaction experiments utilizing tetralin and benzene as solvents. This investigation delved into the impact of feed material and solvent selection on conversion values and the composition of liquid yields derived from liquefaction processes. Notably, variations in the molecular structure of polypropylene and low-density polyethylene exerted significant influence on conversion outcomes. Tetralin liquefaction experiments conducted at 450°C yielded conversion values of 97.0% for PP and 23.8% for LDPE, whereas benzene-liquefaction resulted in conversion values of 98.5% for PP and 97.5% for LDPE. GC-MS analysis of the liquid fractions derived from benzene liquefaction of PP and LDPE predominantly comprised alkanes and alkenes, indicative of the solvent's hydrogen-donor properties as evidenced by the presence of biphenyl in the liquid fraction. Overall, both PP and LDPE exhibited potential for substantial conversion to liquid products within the temperature range of 425–450°C. Particularly promising were the results from LDPE liquefaction using benzene,

which yielded higher conversion values (97.5%) accompanied by a significant fraction of oils rich in C₁₀–C₂₉ alkanes and C₁₀–C₁₉ alkenes. Remarkably, biphenyl constituted a substantial portion of the liquid fraction during the liquefaction of both PP and LDPE using benzene, suggesting that the dehydrogenation of benzene occurred. Further analysis using ¹H NMR revealed distinct differences between the liquid yields derived from LDPE and PP, with liquid fraction produced from the liquefaction of LDPE exhibiting a higher propensity for side chain cleavage due to its structural characteristics, resulting in the formation of diverse aliphatic compounds. Conversely, PP, with its methyl branches, demonstrated a tendency for cleavage, yielding smaller molecules or radicals that interacted with the solvent, leading to the generation of various benzene derivatives.

In the final phase of this study, co-liquefaction experiments were conducted utilizing a vitrinite-rich coal and inertinite-rich discard coal with polypropylene (PP) and low-density polyethylene (LDPE) as feed materials. Using tetralin, a hydrogen-donor solvent, and benzene, a hydrogen-poor solvent, allowed for a comprehensive assessment of liquefaction efficiency and the quantity and quality of derived products, comparing aromatic solvents with differing hydrogen-donor capabilities. Notably, tetralin co-liquefaction experiments involving the vitrinite-rich coal exhibited the highest carbon conversion values when co-processed with PP and LDPE reaching 83.3 and 80.8%, respectively. Conversely, overall conversion during tetralin liquefaction involving the inertinite-rich coal was lower, attributed to the differences in maceral composition between the coals. The co-liquefaction of the inertinite-rich coal with PP and LDPE showcased conversion values of 76.4 and 72.5%, respectively. Remarkably, experiments involving LDPE revealed significantly higher conversion values compared to predicted values, indicating synergistic effects between coal and plastic materials, influencing the product yields and overall conversion. Molecular structure disparities in the feed materials notably impacted conversion outcomes. GC-MS analysis of the liquid fractions derived from the co-liquefaction experiments of LDPE using benzene as the solvent revealed high yields of alkanes and alkenes, indicative of benzene's hydrogen-donor properties. ¹H NMR analysis of the liquid yields derived from the co-liquefaction using benzene revealed an abundant presence of tetralin and its derivatives, with LDPE derived liquids exhibiting higher aliphatic-to-aromatic proton ratios compared to PP. Remarkably, experiments conducted using benzene demonstrated a high presence of aliphatic protons in the liquid fraction. Alongside the formation of biphenyl, as determined using GC-MS, the results indicate that dehydrogenation of benzene occurred. Moreover, polypropylene and low-density polyethylene were found to facilitate hydrogen transfer in the co-liquefaction process, effectively converting inertinite-rich discard coal into liquid products when co-processed. Additionally, solid residue chars derived from inertinite-rich coal blends exhibited higher gasification reactivities compared to those containing vitrinite-rich coal. The results from this study indicate the potential of utilizing inertinite-rich coal fines and plastics such as PP and LDPE in co-liquefaction processes.

Keywords: Direct coal liquefaction, coal fines, plastic liquefaction, co-liquefaction, hydrogenation, benzene, tetralin.

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CHAPTER 1 INTRODUCTION

1.1. Background and motivation

Coal, a primary energy source in the 21st century due to its cost-effectiveness and widespread availability, plays a vital role in electricity generation, steel production, liquid fuel production, and various chemical processes.¹ However, despite its importance, the thermal processing of coal generates substantial residues, including dust and fines. South Africa, for instance, disposes of approximately 65 million tons of fine coal annually, with nearly 15 million tons classified as ultra-fine coal ($<150\text{ }\mu\text{m}$).² Unfortunately, these coal fines contribute to various environmental issues, such as acid mine drainage, air and water pollution, soil degradation, and the risk of spontaneous combustion when stored.^{2, 3} Nevertheless, these coal fines hold the potential to be a valuable resource through appropriate processing.

In parallel, the rise in plastic material usage and production has resulted in the disposal of approximately 1.12 million tons of waste annually in South Africa.⁴ As of 2018, 46.3% of plastic waste was collected for recycling, positioning South Africa as a leading player in mechanical recycling on the global stage. This initiative has not only created employment opportunities for thousands, but has also contributed significantly to reducing carbon emissions by preventing the release of around 246,000 tons of CO_2 emissions.⁴ Previous studies have identified the most commonly used and abundant polymers as high-density polyethylene (HDPE), low-density polyethylene (LDPE), polyvinyl chloride (PVC), polystyrene (PS), polypropylene (PP), and polyethylene terephthalate (PET), and are expected to constitute a significant portion of disposed solid municipal wastes at the end of their life cycle.^{5, 6} These materials are primarily composed of carbon and hydrogen (hydrocarbons), making most of them appropriate candidates for complementing coal fines in liquefaction processes.⁶⁻⁸

Direct liquefaction is a critical method for converting coal into liquid hydrocarbons such as liquid fuels and petrochemicals. This process, often referred to as coal-to-liquid (CTL) technologies, is particularly essential for countries like South Africa, which lack significant crude oil reserves.^{9, 10} An intriguing aspect of this liquefaction process is that after processing approximately a third of the feed coal constitutes liquefaction residues, which can be harnessed to also produce hydrogen and carbon monoxide (syngas) through gasification, effectively eliminating hazardous solid waste.⁹ During liquefaction processes, molecular breakdown occurs which leads to the formation of radicals that require hydrogen to form stable compounds. Hydrogen can be introduced into the reaction medium through solvents having hydrogen donor capabilities or by hydrogen gas. Studies have examined the impact of different solvents on coal liquefaction. For example, Frątczak *et al.* (2018)¹¹ investigated the use of model, petroleum-derived, and waste-derived solvents. The best results were achieved with light cycle oil (LCO) as the solvent. Niu *et al.* (2016)¹² explored the use of non-hydrogen-donor solvents in combination with high hydrogen-donor solvents like tetralin, and found positive effects on coal conversion and oil yield.¹² Solvents contribute to coal liquefaction by facilitating transport, heat transfer, and hydrogen donation.

Studies have shown that the addition of waste plastics to various coal types, such as lignite, bituminous, and sub-bituminous coal, can lead to synergistic effects during liquefaction.^{7, 8, 13, 14} However, it's worth noting that while coal can be effectively processed at temperatures between 375 and 450°C¹⁵, plastic materials tend to produce limited liquid products at these lower

temperatures. The optimal temperature range for plastic liquefaction is typically between 400°C and 450°C, with the best results observed at around 420°C.¹⁴ While direct coal liquefaction has received considerable attention, co-liquefaction of coal and waste materials has been less explored. Various waste types, including biomass, tires, and plastic waste, have been investigated. Notable studies have shown promising results. For instance, Singh and Zondlo (2017)¹⁶ demonstrated that coal co-liquefied with torrefied biomass, rich in lignin, promoted coal liquefaction, indicating the importance of temperature control. Khan *et al.* (2017)¹⁷ found that blending coal with waste tires at a 50:50 ratio yielded a maximum oil yield of 36%. Additionally, co-liquefaction of coal blended with polyethylene (PE) and polypropylene (PP) showed promising results, as these materials are known to facilitate liquefaction, promoting mass and energy transfer, and enhancing liquid hydrocarbon formation.^{8, 13}

The core focus of this study lies in the co-liquefaction of South African discard coal fines, which include both inertinite- and vitrinite-rich components, and waste plastic materials. This study investigates the co-processing and synergistic potential of these two resources during liquefaction. By exploring this field, the aim is to uncover novel approaches that can tackle both the environmental challenges and sustainability issues related to coal fines and plastic waste. Additionally, the co-liquefaction experiments introduce a new perspective on energy and resource utilization. It has the potential to reduce the overall cost of liquefaction processes and contributes to the production of hydrogen, a valuable energy carrier. This interdisciplinary approach bridges the gap between the coal and plastic industries and offers a sustainable solution to environmental and energy-related problems. Furthermore, this research expands the understanding of the co-liquefaction process by exploring the use of solvents, including tetralin, in combination with waste materials to further optimize coal liquefaction and enhance liquid yields and quality.

1.2. Aim and objectives

The aim of this study is to investigate the yield and composition of products derived during co-liquefaction of recycled polypropylene and polyethylene with inertinite-rich coal fines and vitrinite-rich coal (typically used in indirect coal liquefaction processes in South Africa) at different operating conditions. Additionally, the potential of plastic as a hydrogen source and to facilitate hydrogen transfer during co-liquefaction will be evaluated.

In alignment with this aim, the following objectives have been established:

Phase 1: Direct coal liquefaction

- Determine the conversion, product yield, and composition of the products derived from direct coal liquefaction of vitrinite-rich coal compared to inertinite-rich coal fines at different reaction temperatures.
- Evaluate hydrogen transfer and donation reactions during conversion using tetralin and benzene as solvents.
- Assess the catalytic and inhibitory effects of inorganic species during the liquefaction process by employing a demineralization treatment on the coals.
- Evaluate the potential of liquefaction residue chars for gasification purposes by conducting CO₂ gasification experiments and applying kinetic models to calculate apparent gasification activation energies.

Phase 2: Liquefaction of polypropylene and polyethylene

- Determine the conversion, product yields, and composition of the products derived from the liquefaction of polypropylene and polyethylene using tetralin and benzene as the solvents at different reaction temperatures.
- Evaluate the liquid products from fragmentation and chain scission reactions, and subsequent hydrogenation during liquefaction experiments.

Phase 3: Co-liquefaction of plastic materials with coals

- Determine the conversion, product yields, and composition of the products derived from the co-liquefaction of vitrinite-rich and inertinite-rich discard coal with polypropylene and polyethylene using tetralin and benzene.
- Assess possible synergistic and catalytic effects during co-liquefaction based on the conversion and composition of the products derived from co-liquefaction using tetralin and benzene as the solvent.
- Evaluate the potential of liquefaction residue chars for gasification purposes by conducting CO₂ gasification experiments.
- Identify the predominant factors influencing the yield and composition of the products during liquefaction processes.

1.3. Scope and thesis outline

Chapter 1 provides a comprehensive foundation for the thesis, starting with an overview that combines the background and motivation of the study. This section elucidates the context in which the research is situated and the driving factors that prompted this investigation. Following this, the chapter clearly articulates the aim and objectives of the study, outlining the specific goals and research questions that guide the inquiry. The scope of this chapter encompasses the theoretical and conceptual frameworks underpinning the research, setting the stage for detailed exploration in subsequent chapters. Finally, the chapter concludes with a thesis outline, offering a roadmap of the thesis's structure, summarizing the content and focus of each subsequent chapter, and demonstrating how each part contributes to the overall research objectives.

Chapter 2: The first part of this thesis offers an overview of coal production, coal discard (commonly known as coal fines) generation (**Section 2.1**), as well as plastic waste production and composition (**Section 2.2**). The objective was to provide a descriptive background on waste generation and its potential for use in thermochemical processing. A thorough discussion on the factors influencing the direct liquefaction of coal (**Section 2.4.2**) and plastic (**Section 2.5.2**) is presented to emphasize the effects of feedstock composition and process conditions on total conversion, product yield and composition, and oil quality. Subsequently, research and technologies concerning the co-liquefaction of coal with biomass and plastic are addressed, with emphasis on operating conditions, types of solvents, and the utilization of catalysts. This chapter provided insight into the valorization of waste materials through direct liquefaction and determined optimal process conditions (including temperature, pressure, and reaction times), solvent selection, and more.

Chapter 3: After identifying the coals predominantly used in direct liquefaction, a medium-rank C bituminous (vitrinite-rich) coal from the Highveld area was used as the standard. Additionally, a beneficiated fraction of this coal, constituting the same rank, was selected as the discard coal in this study, characterized by a high ash content and a higher inertinite and lower vitrinite content. In addition, both coals were subjected to a demineralization treatment to assess the influence of inorganic species during liquefaction. Direct liquefaction was conducted on the two coals and their respective demineralized fraction at 400, 425, and 450°C in the presence of a hydrogen-donor organic solvent (tetralin) and a hydrogen-poor organic solvent (benzene). This study provided insight into the optimal processing conditions and the effect of inorganic constituents during liquefaction experiments.

Chapter 4: The next step was to conduct direct liquefaction on plastic materials that primarily represent the composition of plastic wastes generated. Therefore, recycled low-density polyethylene and polypropylene were selected for liquefaction experiments conducted at 400, 425, and 450°C with tetralin and benzene as the solvents. The results from this study highlighted the optimal liquefaction temperatures and solvents for the two plastic types based on total conversion, oil yield, and quality.

Chapter 5: The results obtained from the previous two chapters (**Chapter 4** and **Chapter 5**) were used to identify the experimental conditions for the co-liquefaction of coal (including both raw coal fractions from **Chapter 3**) with plastics (LDPE and PP). The aim of this investigation was to obtain insights into the extent of secondary and synergistic reactions during co-liquefaction and the effect

of solvents and coal-to-plastic ratio on these reactions. The role of hydrogen derived from the plastic materials in the co-liquefaction experiments were evaluated based on the yields and composition of the products derived from two very different solvents, i.e., tetralin and benzene. The results from this study were used to evaluate the valorization of coal fines and waste plastic in co-liquefaction processes.

The conclusions of this thesis, mainly focused on the objectives outlined in **Section 1.2**, are summarized in **Chapter 6**. Additionally, recommendations for future work on discard coal liquefaction, plastic liquefaction, and co-liquefaction are discussed (**Section 6.2**).

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CHAPTER 2 LITERATURE REVIEW

2.1. Coal in South Africa

South Africa's coal industry is a cornerstone of the nation's energy and economic landscape, playing a pivotal role in the country's development. This section provides an overview of coal in South Africa, including its production, reserves, and significance in both national and global contexts.¹

Coal production in South Africa has remained relatively constant at approximately 250 million tons per year, with minor fluctuations.¹ The country's coal industry is dominated by five major mining companies, namely Anglo-American Thermal Coal, Exxaro Resources, Sasol Mining, BHP Billiton Energy Coal South Africa (Becs), and Glencore. Together, these companies account for over 80% of the country's annual saleable coal production, while numerous small and medium-sized producers contribute to the rest of the production.^{1, 2} South Africa holds about 3.5% of the world's coal resources, producing roughly 3.3% of the world's total coal output and exporting approximately 6% of global coal exports. This global significance underscores the critical role coal plays in the South African economy. Coal serves as the primary energy source for the country, supplying over 90% of its electricity and approximately 30% of its liquid fuel.¹⁻³ Furthermore, coal is an essential component of South Africa's chemicals and steelmaking industries, emphasizing its multifaceted importance.

Coal reserves are predominantly found in the Ecca deposits within the Karoo Supergroup.² These coalfields are concentrated in the north-eastern quarter of the country, encompassing regions such as Mpumalanga, Limpopo, KwaZulu-Natal, and the Free State. Some of the prominent coalfields include Ermelo, Highveld, Witbank, and Waterberg, among others. Notably, the Witbank and Highveld coalfields contribute about 75% of South Africa's total coal production.^{1, 2} However, these resources are finite and expected to be exhausted in the next century, prompting the need for long-term energy planning.

South Africa's coal varies in rank and carbon content, with bituminous coal being prevalent in Mpumalanga and Limpopo. These coal deposits often occur in thick seams, making them suitable for cost-effective mining. In contrast, KwaZulu-Natal primarily hosts anthracitic coal, which is found in thinner seams. South Africa has an estimated 66.7 billion tons of recoverable coal reserves, accounting for about 3.5% of the world's total. These substantial reserves underscore the country's coal wealth and its role in the global energy landscape.² With the fifth-largest recoverable coal reserves in the world, South Africa's energy landscape is undeniably dominated by coal. At the current production rate, South Africa is projected to have more than 50 years of coal supply left. While the country is exploring alternative energy sources, coal is expected to maintain its significant role in the foreseeable future.^{2, 3}

Dependency on coal-based energy in South Africa is unlikely to change significantly in the coming decades due to the limited availability of viable alternatives. The country is a net exporter of coal, with 24% of its coal production being shipped to international markets, while only 1% is imported. This further underscores South Africa's pivotal position in the global coal trade.

2.1.1. Coal uses

Coal serves as South Africa's primary energy source, with over 90% of the nation's electricity generation relying on it. Furthermore, coal contributes to approximately 30% of the liquid fuel production and roughly 70% of the country's overall energy demands (DoE, 2016).^{1, 2, 4} Beyond its role in the energy sector, coal plays a vital part in supplying raw materials to the South African chemicals industry and supplies 98% of carbon reductants needed for the metallurgical industry, supporting the production of iron, steel, and ferrochrome. In addition, it plays a crucial role in manufacturing over 200 major chemicals and more than 7,000 carbon-based products, including items like paints, plastics, fertilizers, explosives, and various food products.⁵ The three major coal-dominated processes are discussed below.

2.1.1.1. Electricity generation

The generation of electricity primarily relies on coal, which is pulverized and then combusted in boilers to generate the heat needed to convert water into steam. This steam propels turbines linked to generators, creating electric power. In a closed primary circuit, water circulates, and after losing its energy in the turbines, it condenses back into water and is reheated in the boiler. The resulting coal ash is transported to an external ash dam, and gaseous emissions (flue gas) exits through a chimney.

In South Africa, the electricity sector is predominantly controlled by Eskom, a government-owned utility responsible for a substantial portion of the nation's generation infrastructure and the national transmission grid. Eskom generates around 90% of South Africa's electricity and about 45% of Africa's total electricity consumption.^{2, 6} On a global scale, it ranks among the top utilities in terms of generating capacity and sales and operates one of the world's largest dry-cooled power stations. Eskom annually consumes more than 90 million tons of coal, with different power stations requiring varying coal grades, from higher grade coal (23 MJ.kg⁻¹) to lower grade options (16 MJ.kg⁻¹) for specific power plants.^{2, 6, 7}

2.1.1.2. Coal-to-liquid (CTL) technologies

Coal serves as the foundation for diverse products, not only in electricity generation but also in the production of liquid fuels and non-energy coal products such as chemicals. Sasol, a key player in the industry, leads the way in producing synthetic fuels and chemicals from low-rank coal and natural gas. Their synfuels plant in Secunda annually converts over 37 million short tons of coal into liquid fuels and various chemical feedstock.² Furthermore, Sasol is the largest chemical producer in South Africa, crafting approximately 4 million tons of products annually, including advanced materials, base chemicals, essential care chemicals, and performance solutions, all stemming from their unique Fischer-Tropsch technology.^{2, 8}

Coal-to-Liquids (CTL) and Indirect Coal Liquefaction are the core processes driving these achievements. CTL represents a process where coal is transformed into liquid hydrocarbon fuels through a series of steps including coal gasification, syngas cleaning, Fischer-Tropsch synthesis, and product workup.^{2, 3} Indirect Coal Liquefaction (ICL) takes a different approach. It first involves coal gasification to create syngas, which then serves as a versatile building block for a wide range of products. ICL includes two main routes, Fischer-Tropsch synthesis and Methanol synthesis. The FT process allows for the production of liquid fuels and various chemicals by reacting syngas over a

catalyst, while methanol synthesis can serve as an intermediate for different chemical products. These processes offer high-quality liquid fuels, and Sasol plays a pivotal role in meeting South Africa's fuel demand, supplying about 28% of the nation's annual fuel requirements.^{9, 10}

Indirect coal liquefaction provides South Africa with the means to harness its abundant coal resources and reduce reliance on imported oil. However, ongoing research and development efforts is needed in the area of direct coal liquefaction to enhance efficiency and mitigate environmental impacts, as both CTL and ICL are energy- and resource-intensive processes.

2.1.1.3. Metallurgical coal

Coking coal plays a crucial role in the manufacturing of iron, steel, and a variety of alloys, serving as a vital component in blast furnaces where it acts as both a reductant and an energy source. Globally, the second-largest market for coal is in blast furnaces, following thermal use. This application encompasses the production of iron for steelmaking and the manufacturing of ferroalloys. Despite limited reserves of coking coal in South Africa, primarily derived from the Limpopo coalfields, the country heavily relies on imported coking coal to meet the demands of its iron and steel industry.^{2, 4}

South Africa contributes to approximately 45% of the total crude steel output of the African continent, according to the World Steel Association.² Additionally, the nation is a notable exporter of ferroalloys, including ferromanganese, ferrochrome, and ferrovanadium.^{2, 4} Within South Africa, iron is produced from different furnace types, with 80% originating from blast furnaces, 6% from electric furnaces, and 14% from various other processes such as COREX (as reported by SAISI in 2016).² The Southern African coke industry manufactures two main types of coke: market coke, utilized by the ferroalloy sector, and metallurgical coke, employed in steel plants. Notably, there are four major coal users in South Africa for iron and steel production. Among these, ArcelorMittal's operations in Newcastle and Vanderbijlpark employ coking coal to produce coke. The ArcelorMittal operation in Saldanha utilizes the Corex process, directly using coking coal without conversion to coke.^{2, 5}

2.1.1.4. Other uses

Coal finds diverse applications, serving as a crucial fuel source in both industrial and commercial settings for steam generation, which is essential for providing heat and power. Within the industrial sector, coal is utilized by various entities such as pulp and paper manufacturers, food and tobacco industries (especially in sugar refining and breweries), cement manufacturers, brick and refractory producers, textile manufacturers, and mining operations.²

In many households throughout South Africa, coal is a preferred energy source. Its affordability makes it an appealing fuel option, especially for informal households, particularly those situated inland in proximity to coal mines.²

2.1.2. Production of coal fines

The South African coal mining industry is currently facing a significant challenge, as it disposes of more than 10 million tons of ultra-fine (<150 µm) coal annually.¹¹ This disposal practice stems from the perception that the cost of dewatering this ultra-fine coal outweighs its potential value. Paradoxically, the quality of this coal is often on par with or even superior to the run-of-mine (ROM) coal found in the mines.^{7, 11, 12} These discarded sulphur-containing ultra-fines contribute to various

environmental issues, including acid mine drainage, dust emissions, and spontaneous combustion.^{7, 13} Consequently, what should be considered a valuable resource is carelessly disposed of, exacerbating the environmental damage associated with the coal mining industry. In response to this issue, a collaborative effort led by the Water Research Commission (WRC) aimed to introduce cleaner production principles in the mining industry.¹⁴

Furthermore, coal mining in South Africa has remained relatively stable over the past two decades, yielding approximately 250 million tons annually. Within this production, about 60 million tons consist of fine coal discards, with 10 million tons classified as ultra-fines (<150 μm).¹¹ These fine coal byproducts have detrimental environmental consequences, including acid mine drainage, air pollution, and spontaneous combustion. Nevertheless, their quality is often comparable to run-of-mine (ROM) coal, with an average calorific value of 23 MJ.kg⁻¹, making them a viable fuel source for power generation, given the minimal heating value requirements of most power plants.^{7, 11} Typically, unprocessed fines are sold to power stations for use as a feedstock. However, their subpar quality, marked by their high moisture content, low calorific value, and high ash and sulphur content, often results in their disposal. Notably, the inorganic components in these fines vary within mined coal seams, with some minerals requiring substantial particle size reduction for separation.¹⁵ The coal macerals can be categorized into vitrinite, liptinite, and inertinite, with variations in hydrophobicity and friability affecting the generation of fines. High-rank coals tend to be more hydrophobic, while lower-rank coals contain higher oxygen contents and greater concentrations of humic acids, influencing their friability and consequently promoting fines generation.¹⁵

To address the dewatering and utilization of these ultra-fines, flotation is a widely adopted method, and various dewatering equipment, including screen-bowl centrifuges, horizontal vacuum belt filters, and thermal drying, are employed.¹⁵ Recent studies have indicated that thermal drying, capable of reducing surface moisture to 1%, is the most cost-effective dewatering method. Once beneficiated and dewatered, these ultra-fines can be blended with coarser coal for export markets.¹⁵ Conversely, un-beneficiated fines are of lower quality and are typically sold to local power stations as a feedstock. These ultra-fines exhibit an ash content of 45%, a particle size below 150 microns, and calorific values of below 14.6 MJ.kg⁻¹.⁷ The economic feasibility of thermal drying for these fines is limited due to their low value. Waste Energy Recovery and Management (WERM) has developed a patented process that uses solar energy to dry and recover ultra-fines from slimes dams. This approach involves periodic ploughing and stockpiling of the top layer of the dam, drying the ultra-fines to a moisture content of 12–18%. This process enables the conversion of ultra-fines into a valuable product, especially when blended with re-washed coarse waste rock to reduce overall moisture content.^{14, 16}

2.2. Plastic waste production: An overview

The surge in plastic production and consumption over the past decades is driven by the numerous advantages of plastics, including their lightweight nature, strength, durability, affordability, corrosion resistance, and low production costs.^{17, 18} Between 1950 and 2015, a staggering 8300 million tons of virgin plastics were produced worldwide, generating around 6300 million tons of plastic waste. Only 9% of this waste has been recycled, with 12% being incinerated, and 79% accumulating in landfills.^{19, 20} Annual global plastic production were estimated to be between 300 and 400 million tons for 2018 and 2019, with around 60 million tons produced within the European Union.^{20, 21} **Figure 2-1** highlights the global plastic usage per sector in 2019.²⁰

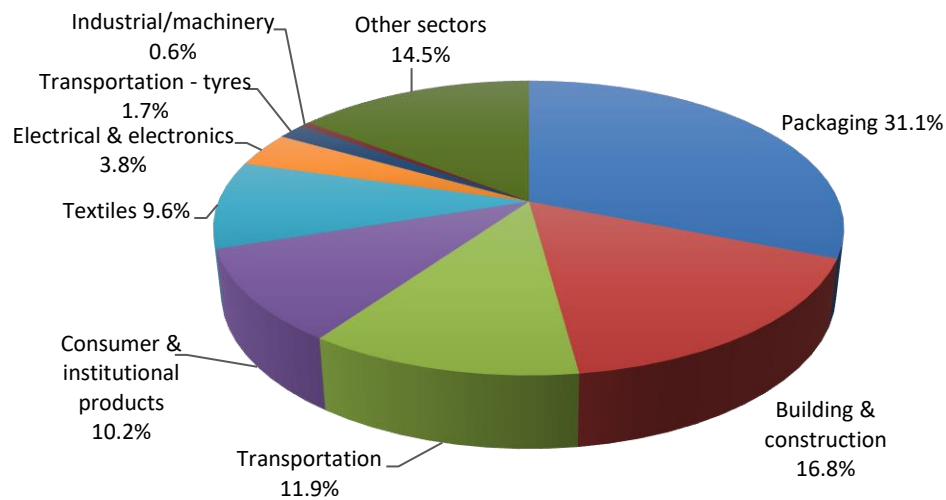


Figure 2-1. Global plastic usage per sector (in weight percentage) in 2019.

In the specific context of South Africa, between 2000 and 2017, approximately 13.7 million tons of plastics, valued at \$28.3 billion, were imported, constituting about 11.6% of Africa's total plastic consumption.²² It is estimated that the annual per capita plastic consumption in South Africa ranges from 30 to 50 kilograms. Given South Africa's population, this results in a total annual consumption of roughly 1.8 to 3 million tons, aligning with the annual production of approximately 2.4 million tons of plastic waste, which corresponds to about 41 kg per person.²²

The global plastic waste problem has proven challenging to manage sustainably. In Sub-Saharan Africa, plastic waste accounts for 13% of the total municipal solid waste.^{22, 23} Looking ahead to 2030, an estimated 29.9 million tons of plastic, twice the current amount, is expected to be imported into South Africa. Alarming statistics reveal that waste plastics make up about 12% of the municipal solid waste in South Africa, equating to 630,000 tons of mismanaged plastic waste annually, with 90,000 to 250,000 tons contributing to marine debris.²⁴ Over the past decade, it can be inferred that more than 6.3 million tons of waste plastics have been mismanaged in the country.^{24, 25} Waste plastics are predominantly disposed of within municipal solid waste (MSW) with minimal formal recycling, estimated at around 10%.¹⁷ Moreover, there is limited thermal/energy recovery from waste plastics through methods such as incineration, leading to the accumulation of waste plastics in dumpsites, waterways, and open burning.^{17, 26}

Despite the challenges, South Africa has made significant progress in managing plastic waste. In 2018, Plastics South Africa classified the country as a "mechanical recycling champion," boasting a 46% recycling rate for plastic waste, surpassing Europe's 31% rate.^{22, 27} To aid in the recycling of various plastic waste streams and prevent environmental pollution, voluntary producer responsibility organizations (PROs) like the PET Recycling Company (PETCO), Polystyrene Association of South Africa, Southern African Vinyls Association (SAVA), and Polyco have been established. These organizations focus on specific types of plastics, including polyethylene terephthalate (PET), polystyrene, polyvinyl chloride (PVC), and polypropylene, among others, and they operate under the umbrella organization Plastics South Africa.²²

Environmental pollution and human health challenges persist due to plastic waste mismanagement. The lightweight nature of items like plastic bags, packaging, and polystyrene facilitates their dispersion by the wind, ultimately leading to their presence in water bodies and contributing to marine litter. Projections indicate that by 2025, approximately 250 million tons of plastic will have entered the world's oceans, with over 1 million tons originating from African countries.^{17, 24} Furthermore, open burning is a common waste management practice in many African countries, particularly for plastics. Given the absence of effective solid waste sorting systems, mixed wastes, including plastics, are disposed of in dumpsites and set on fire. This practice releases hazardous substances into the environment due to the presence of plasticizers and flame retardants in the plastics, contaminating the air, soil, and food.^{17, 22, 28, 29}

To delve deeper into the discussion on plastics, it's essential to understand their composition. Previous studies have identified the most commonly used and abundant polymers as high-density polyethylene (HDPE), low-density polyethylene (LDPE), polyvinyl chloride (PVC), polystyrene (PS), polypropylene (PP), and polyethylene terephthalate (PET).^{18, 20, 30} **Figure 2-2** shows the estimated global plastic usage by polymer type (in million tons) for 2019.²⁰

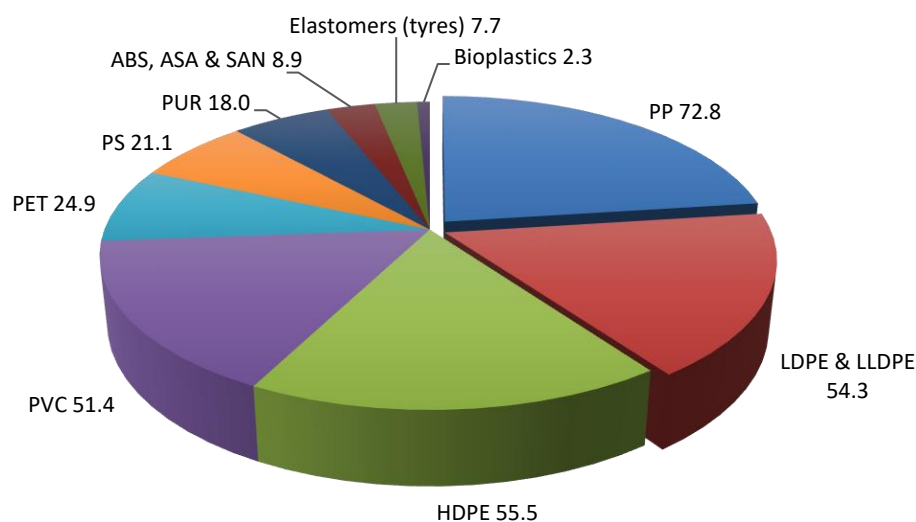


Figure 2-2. Global plastic usage by polymer type (in million tons) in 2019.

These plastic types are expected to constitute a significant portion of disposed solid municipal wastes at the end of their life cycle, warranting further exploration as discussed in the following section.^{17, 18, 20}

2.2.1. Potential plastic waste management and recycling practices

The escalating issue of plastic waste has prompted a critical need for effective management and recycling strategies to mitigate environmental and sustainability concerns. Plastics, known for their persistence in the environment and significant energy-intensive manufacturing process, pose a formidable challenge for waste management. Various processing techniques have emerged to address this challenge, each with distinct advantages and limitations. These techniques can be broadly categorized into plastic waste management and recycling practices, encompassing mechanical recycling and thermochemical conversion processes (**Figure 2-3**). This section highlights the details of some of these approaches, shedding light on their principles, applications, and ongoing efforts to harness plastic waste as a resource. Landfilling and biological conversion methods will not be discussed in this section.

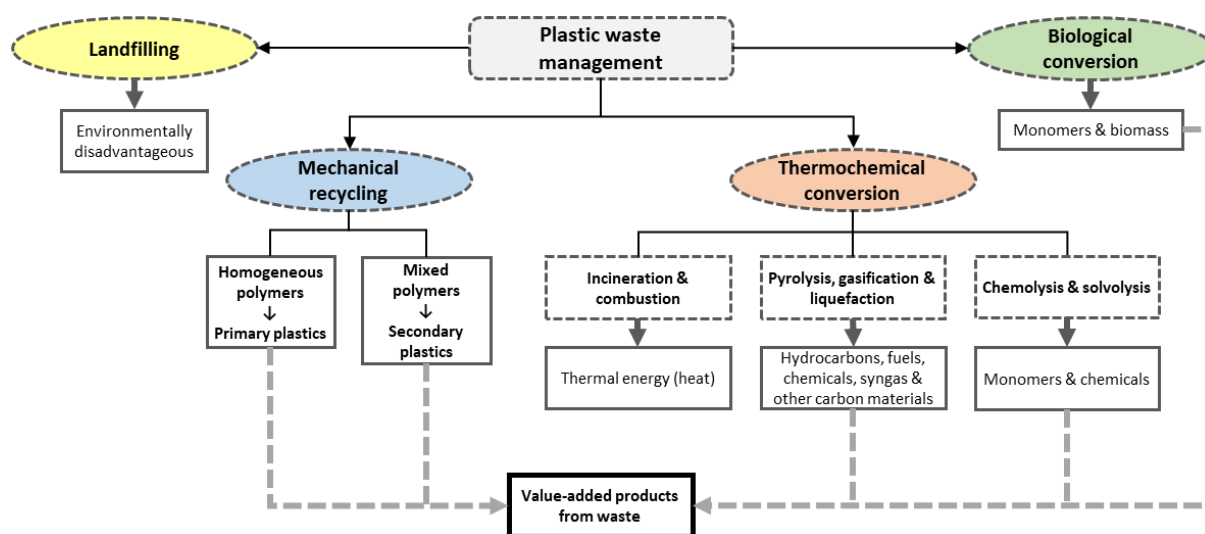


Figure 2-3. Potential waste plastic management and recycling practices.³⁰

2.2.1.1. Mechanical Recycling

Mechanical recycling is a widely adopted method for recycling plastics, particularly thermoplastics. It involves the physical transformation of plastics through processes like shredding, melting, and molding, which enables the creation of new products while retaining the polymeric structures.²⁹ In closed-loop recycling, or primary mechanical recycling, the recovered plastics have the same or similar chemical characteristics and properties as the original product.^{17, 29, 31} However, its effectiveness is limited when dealing with mixed plastic waste. This often results in down-cycling, where the quality of the recycled products, termed as secondary plastics, is lower than that of the original plastics.^{17, 29, 31} It is essential to note that mechanical recycling is less suitable for thermosets due to the breakdown of the polymer matrix at high temperatures. Additionally, the presence of specific intentionally added chemicals and their transformation products can impact the technical quality and marketability of the recycled plastics.

2.2.1.2. Thermochemical conversion and recycling approaches

Thermochemical conversion methods, which encompass pyrolysis, gasification, and hydrothermal processing or liquefaction, provide an innovative avenue for addressing the challenges of plastic waste management.^{30, 32-35} Thermochemical conversion processes are suitable for an input of mixed plastics. These processes use thermal energy to break or crack the chemical bonds in polymers,

leading to the creation of higher-value products, including fuels, chemicals, and nanocarbon materials.^{30, 32, 33, 35} Thermolysis involves the conversion of polymeric residue through heat treatment and simultaneous cleavage of organic compounds into valuable products, such as naphtha, hydrocarbons, or synthesis gas. This process is primarily applied to addition polymers.^{30, 36}

Chemical recycling, a promising avenue in plastic waste management, encompasses processes like gasification and depolymerization.²⁹ This transformation enables the production of substances that can serve as products or raw materials for new polymers. One of the chemical recycling methods, chemolysis (or solvolysis), is applied to depolymerize plastics using various combinations of chemistry, solvents, and heat, breaking them down into their constituent monomers, the fundamental building blocks of polymers.^{30, 33} In the subsequent step, potential contaminants are isolated from the monomers to ensure their purity. The purified monomers are then reintroduced into standard plastic production processes as a secondary raw material.^{29, 32, 33} This recycling approach allows for the production of plastics with qualities similar to those made from traditional fossil resources. Chemolysis encompasses the complete depolymerization of plastics using chemical reagents, resulting in the recovery of monomers that can be used to synthesize the original polymer or other polymers. This method, especially effective for polyesters, polyurethanes, polyacetals, and polyamides, requires plastics to be separated homogeneously (i.e., by resin type).³⁰ It involves solvolytic processes, such as hydrolysis, glycolysis, or alcoholysis to recycle and transform plastics into their basic monomers for subsequent repolymerization into new plastics. The notable advantage of this process is its ability to efficiently handle mixed plastic waste while maintaining the quality of the end products.

A subset of thermochemical conversion, waste-to-energy, offers the prospect of generating electricity and/or heat by either incinerating plastics or transforming waste plastics into fuel, typically through pyrolysis.^{29, 30, 32, 33, 35, 37} This approach presents a means of energy recovery from plastics, albeit with inherent drawbacks. The incineration process, while yielding thermal energy, also generates large volumes of gases and residues that may contain microplastics, hazardous additives, and toxic substances, requiring additional safety measures. For waste-to-fuel processes, the presence of metals and halogenated chemicals can have repercussions on yield, leading to the production of lower quality end-fuel products, and may pose technical challenges for thermal facilities and equipment.^{29, 30, 33}

Thermochemical conversion plays a vital role in addressing plastic waste, particularly when mechanical recycling proves less effective. Researchers are actively exploring innovative techniques to mitigate the environmental impact of plastic waste. These efforts encompass the production of liquid fuel and synthetic gas through pyrolysis and gasification, the utilization of microbial strains capable of breaking down polyethylene, incorporation of plastic waste into various construction materials, and the development of waste-to-energy and waste-to-fuel facilities.^{29, 30, 37, 38} Notably, the first African plant to convert plastic waste into synthetic fuel oil was established in Kenya, and waste-to-energy plants have been initiated in countries like Ethiopia.¹⁷

The comprehensive spectrum of plastic waste management and recycling practices underscores the importance of adopting a multi-pronged approach in addressing the plastic waste challenge, considering each technique's specific requirements and limitations. **Section 2.2.2** will encompass a descriptive overview of different thermochemical conversion processes.

2.2.2. Thermochemical processing of waste plastic

Plastic polymers, fundamentally derived from fossil fuels and petrochemicals, can undergo decomposition via thermochemical and catalytic pathways to yield green fuels and chemicals.³² Despite this potential, there is a notable gap in existing literature regarding the utilization of plastics for closed-loop waste-to-energy conversion. Addressing this knowledge deficit, **Section 2.5** will specifically delve into the liquefaction of plastic waste. Urgency surrounds the exploration of alternative and environmentally friendly methods capable of valorizing waste plastics, transforming them into value-added industrial products.³²

Striving toward this goal involves exploring the potential of waste plastics as a viable raw material for the production of alternative fuels and chemicals, focusing on thermochemical technologies such as pyrolysis, liquefaction, gasification, and chemolysis. Chemolysis is a type of depolymerization process, often termed solvolysis, that employs a combination of chemistry, solvents, and heat to disintegrate polymers into monomers—the elemental units of polymers. Subsequently, the ensuing step involves the isolation of potential contaminants from the monomers to facilitate their removal from the process.^{30, 32} **Figure 2-4** highlights the predominant products that could be derived from these processes (adapted from Yang *et al.* (2022)³⁰).

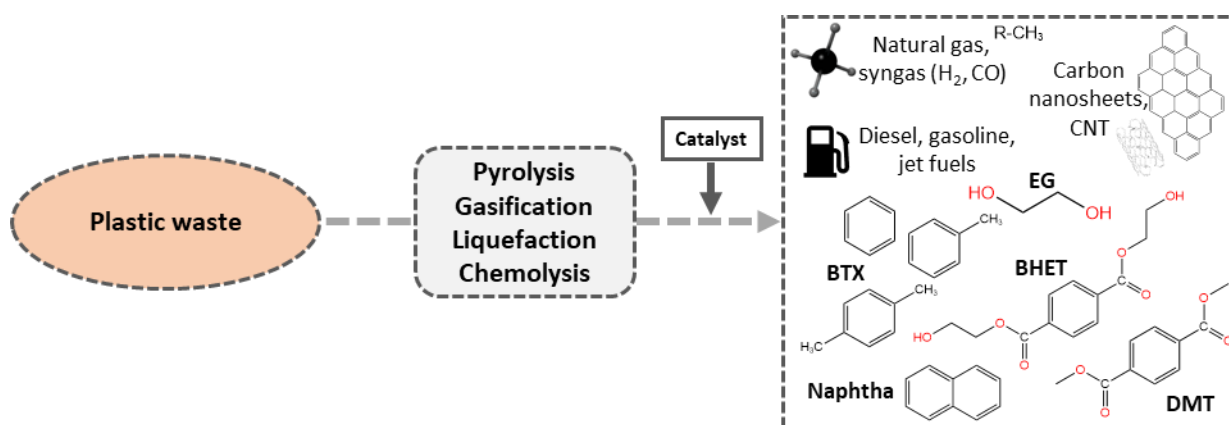


Figure 2-4. Value-added chemicals, fuels, and materials from thermochemical processes.

2.3. Overview of coal-to-liquid (CTL) processes

Historically, coal liquefaction technology has a significant legacy, with roots dating back to the early 20th century. One of the pioneers of coal liquefaction was Friedrich Bergius, who demonstrated the possibility of adding hydrogen to coal at elevated temperatures and pressures to produce distillate products. The Bergius process, proposed in 1913, is a technique for directly converting coal into liquid fuels through a hydrogenation process.³⁹ During World War II, advances were made to adapt coal liquefaction technologies to produce synthetic fuels and chemical feedstocks from coal. Notably, Germany utilized both direct and indirect liquefaction processes to support its war effort. By 1939, several hydrogenation plants were operating, producing millions of tons of liquid products, including high-quality aviation and motor fuels, aromatic chemical feedstocks, and liquefied gas. However, after World War II, the commercial viability of coal liquefaction processes faced various challenges, and widespread adoption was limited. The process was costly and required substantial infrastructure and energy inputs.⁴⁰

While the conversion of coal to liquid fuels is not practiced commercially in the United States, two countries, namely South Africa and China, have continued to invest in and develop coal liquefaction technologies. SASOL, a South African energy company, has been a pioneer in coal liquefaction. SASOL uses the Fischer–Tropsch process for coal-to-liquid conversion. Originally established in 1950 to develop and commercialize technology for synthetic fuels and chemical feedstocks, SASOL has continued to produce these products through an indirect process route via coal gasification.⁴¹ SASOL's success is attributed to the South African government's efforts to maintain the company as a vital entity in times of high oil prices. Today, SASOL (a private company) produces approximately seven million tons per year of synthetic fuels and chemical feedstocks. China has also invested significantly in coal-to-liquids technologies. They have developed a strong coal-to-chemicals industry based on methanol synthesis, resulting in products like olefins, monoethylene glycol, dimethyl ether, and aromatics.^{9, 41}

Coal-to-liquid (CTL) technologies are a group of processes that aim to convert coal into liquid fuels and chemical feedstocks. These processes are essential because they enable the transformation of solid coal into liquid hydrocarbons with a higher hydrogen-to-carbon ratio, making them more suitable for use as fuels and chemicals. There are three major methods of producing liquid fuels from coal, including pyrolysis, direct liquefaction (DCL), and indirect liquefaction (ICL).

2.3.1. Pyrolysis

Pyrolysis is a thermal process that aims to convert coal into gases, liquids, and condensable tar. This process involves heating coal to high temperatures, typically in the range of 400–800°C, in a controlled environment with limited oxygen supply or in an inert atmosphere. This causes the macromolecules of coal to break down into gases, liquids, and condensable tar. The residue product is a hydrogen-depleted char. During the heating process, coal releases volatile gases, which include methane, hydrogen, carbon monoxide, and various hydrocarbons. The gases, liquids, and tars produced in pyrolysis are typically further treated and refined to produce conventional liquid fuels.^{39,}

⁴² This method is characterized by the initial thermal generation of radicals from coal, and the resulting liquids are often depleted of heteroatoms when compared to the original coal or pyrolysis liquids. These liquids often contain a mixture of hydrocarbons and can be further refined to produce

conventional liquid fuels, such as gasoline and diesel. The solid residue or char that remains after pyrolysis is rich in carbon and depleted in hydrogen. This char can have various applications, including as a source of activated carbon.^{10, 42-44}

The primary advantage of pyrolysis is its ability to produce a wide range of products, including gases, liquids, and solids from coal. However, one of the main challenges is the need to further treat and refine these products to meet specific fuel or chemical quality standards. Additionally, the process consumes a significant amount of energy, as it involves high-temperature heating.

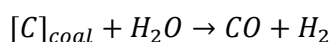
2.3.2. Direct Liquefaction (DCL)

Direct liquefaction processes are designed to convert coal into liquids without the need for intermediate steps. In this process, coal is mixed with a donor solvent that is able to provide ample molecular hydrogen to the reaction. The liquefaction process takes place at temperatures up to 500°C and hydrogen pressures up to 34.5 MPa. Catalysts are generally used during liquefaction processes.³⁹ This process breaks down the organic structure of coal and produces liquid hydrocarbons. After the reaction, the resulting mixture is separated to remove mineral matter and unconverted coal, leaving behind the liquid hydrocarbons.³⁹ This separation process is critical for obtaining high-quality products. The liquid hydrocarbons are further refined to meet specific product requirements. This may include additional processing steps to remove impurities and improve the fuel's properties.^{39, 45, 46}

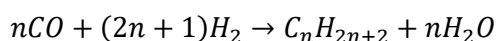
Direct liquefaction has the advantage of directly converting coal into liquid hydrocarbons, making it a more straightforward process compared to indirect liquefaction. However, it often requires high pressures and temperatures, along with a significant supply of hydrogen, making it energy intensive. The choice of solvent and catalyst is crucial in this process to achieve optimal conversion rates and product quality.^{9, 39, 46-48} In **Section 2.4**, direct coal liquefaction will be explored in more detail.

2.3.3. Indirect Liquefaction (ICL)

Indirect liquefaction processes operate in two stages.^{10, 39} In the first stage, coal is gasified to produce synthesis gas (syngas), which is a mixture of carbon monoxide and hydrogen. This typically involves heating coal in the presence of a controlled amount of oxygen or steam to produce carbon monoxide (CO) and hydrogen (H₂).^{10, 39, 42} The composition of the syngas can be adjusted depending on process conditions.



In the second stage, syngas is converted into liquid hydrocarbons. The specific method used for hydrocarbon synthesis, such as Fischer–Tropsch synthesis, methanol synthesis, or methanation, depends on the desired products and the catalysts employed.⁴² Fischer–Tropsch synthesis is the most well-known and widely used method for converting syngas into liquid hydrocarbons.



The resulting hydrocarbon products are then refined into the desired finished products. These processes are characterized by the production of water as a major by-product.^{10, 39} Fischer–Tropsch synthesis, in particular, is a versatile process that allows for the production of a wide range of hydrocarbons, including diesel, gasoline, and waxes. It is known for its ability to create high-quality,

clean-burning fuels from coal-derived syngas.¹⁰ In the ICL process, the production of water is a significant by-product, and this water must be managed and separated from the liquid hydrocarbons. The advantage of ICL processes is their flexibility and the ability to tailor the product slate to meet specific market demands. However, they typically require the integration of two distinct processes: gasification and hydrocarbon synthesis, which adds complexity to the overall system.^{10, 39, 42, 43}

In recent times, the primary commercial application of coal liquefaction is conducted in South Africa by Sasol, using the Fischer–Tropsch process. Sasol produces not only fuels but also high-value chemicals from coal. Despite ongoing research and development, coal liquefaction for the production of synthetic fuels and chemical feedstocks is not widely practiced commercially in many countries, except for countries like South Africa and China, which heavily rely on their domestic coal resources.^{2, 39}

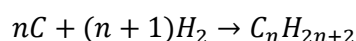
2.4. Direct coal liquefaction (DCL): An overview

Within the realm of energy production, the study of direct coal liquefaction emerges as a pivotal subject, encapsulating the intricate processes involved in converting coal into liquid hydrocarbons. This section serves as a comprehensive exploration into the scientific intricacies of direct coal liquefaction, delving into the nuances of process chemistry, reactions, and the myriad products that arise from this transformative process. Additionally, the investigation extends to a detailed analysis of the effect of process conditions and various influencing factors on liquefaction yield and the composition of resulting products. As we navigate through the scientific landscape, this thesis aims to unravel the complexities inherent to the conversion of coal to liquid fuels, shedding light on key variables that shape the efficiency and output of this crucial energy conversion process.

The subsequent sections will delve into the role of process conditions and factors influencing the yield and composition of products in the liquefaction process.

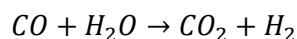
2.4.1. Process condition, chemical reactions, and products

The Bergius process, developed by Friedrich Bergius in 1913, is one of the most important methods of direct conversion of coal to liquids through hydrogenation. In this process, coal is blended with recycled heavy oil from the same process. The reaction takes place within the temperature range of 400–500°C under a hydrogen pressure of 20–70 MPa. A catalyst is often introduced into the mix. The following reaction was proposed to describe the process:³⁹



The primary objective of coal liquefaction is the production of substitutes for petroleum distillate fuels, specifically targeting a hydrogen-to-carbon atomic ratio of 1.8–2.5, with a focus on generating alternatives for gasoline and diesel fuel.⁴⁹ This goal is accomplished through the introduction of hydrogen and/or the removal of carbon and oxygen. The transformation of large aromatic rings in coal into smaller ones and/or liquid paraffinic hydrocarbons, resembling those found in petroleum products, occurs simultaneously with the elimination of carbon and oxygen, resulting in the formation of CO, CO₂, or H₂O. Undesirable by-products in direct coal liquefaction include water and gaseous hydrocarbons such as methane, ethane, and propane, which consume valuable hydrogen in the production of unintended products.⁴⁹

Hydrogen is derived from coal, petroleum, natural gas, and biomass through gasification, where the endothermic gasification process inevitably produces carbon dioxide. Carbon monoxide is subsequently converted into hydrogen through the water-gas shift reaction:³⁹



The direct coal liquefaction process essentially involves the hydrocracking of three-dimensional macromolecules in their aggregated forms. This process entails hydrogenation of aromatic structures, ring-opening, and final cracking into smaller saturated hydrocarbons. Coals, particularly low-rank coals, contain paraffins and numerous alkyl groups, and the liquefaction process involves dealkylation and cracking of alkyl chains. Concurrently, oxygen, nitrogen, and sulphur containing heteroatoms are removed through hydroelimination reactions, resulting in the production of pure hydrocarbons. Consequently, liquefaction products are refined into high-quality fuels resembling

petroleum-derived products. The chemical composition undergoes simplification due to intensive hydrotreatment and hydrocracking, leading to the loss of certain features.^{39, 42, 49}

Chemicals derived from coal should, to some extent, reflect the unique structure and function of the run-of-mine coal molecules. The low-temperature extract from solid coal is limited in yield, preserving the original molecular structure to a considerable extent. However, solubility limitations arise due to heteroatoms forming intermolecular bonds, restricting the extraction of components within a three-dimensional network of large aromatic units.⁴⁹ Destructive extraction and low-temperature pyrolysis enhance liquid yield by disrupting molecular associations and chemical bonds in the polymeric structure, albeit with the inevitable decomposition of some heteroatomic groups. Hydrogenation treatment further increases liquid product yield to over 90% through the hydrogenation and hydrocracking of C–C and C–X (X = other atoms) bonds. Consequently, the identities of coal chemicals progressively diminish during liquefaction.⁴⁹

Coal liquefaction generates C₁–C₃ gaseous hydrocarbons, naphthas, and middle distillates, serving as substitutes for petroleum. This combination constitutes the total distillate, accompanied by gaseous nonhydrocarbons (e.g., CO, CO₂, H₂S, NH₃) and residual oils, including vacuum gas oil, vacuum residue or heavy tar, and solid byproducts like unreacted coal and cokes. The vacuum gas oil is recycled as a solvent post-hydrogenation to restore hydrogen donor activity. The residual oil finds use as a coal tar substitute, particularly as a carbon source in coking processes.^{49, 50}

Aromatic hydrocarbons derived from coal liquefaction consist of various macromolecules such as five-, six-, and seven-membered aromatic rings, as well as condensed peri- and cata-type rings. Their industrial significance is attributed to the production of benzene, toluene, xylene, naphthalene, anthracene, xylene, and pyrene.⁴⁹ Conversion of large aromatic ring compounds is achievable through gas-, liquid-, and solid-phase carbonization. Mochida *et al.* (2014)⁴⁹ stated that primary liquefaction derived naphtha consists of 21–26% aromatic compounds and 40% naphthenic chemicals, with benzene, naphthalene, biphenyl, acenaphthene, and their derivatives as major constituents. Significant hydroaromatic compounds from coal liquefaction include indane, tetralin, and their alkylated derivatives. Hydrotreatment of naphtha results in 60–70% hydrogenation of aromatic hydrocarbons, significantly increasing naphthene content.⁴⁹ Lower temperatures (350–450°C) is favored for complete hydrogenation. Cyclic paraffins and their alkylated derivatives become the primary components in hydrotreated naphtha through hydrogenation of aromatic hydrocarbons, along with hydrogenated anthracene and phenanthrenes, which contribute to reduced boiling points.⁴⁹⁻⁵¹

Liquid products derived from coal also comprise of oxygen-containing chemicals like phenols, cresols, and naphthols, traditionally isolated from coal tar and essential for tar chemical industries. Direct coal liquefaction also yields these oxygen-containing chemicals, typically dominating heteroatom-containing compounds due to coal's higher oxygen content compared to nitrogen and sulfur.^{49, 51}

The conditions of single- and two-stage liquefaction processes typically involve a reaction temperature ranging from 400 to 460 °C at a pressure of 14 to 20 MPa. An iron-based catalyst, often sourced from materials like pyrite, limonite, or synthetic FeS₂, is commonly utilized, with the addition of sulfur for catalyst stabilization.⁴⁹ The Shenhua liquefaction process, is recognized as the world's first and still the only operating commercial-scale direct coal liquefaction process post-World

War II.⁵² This process operates in two stages, encompassing a hydrotreater for product refinement (naphtha and diesel). Operating at a high pressure of 19 MPa and a temperature of 455 °C for both reactors, it employs an iron sulfide catalyst. The main product undergoes hydrogenation to regenerate the circulating solvent and refine the products.^{49, 52}

2.4.2. Reaction mechanisms

Coal liquefaction is a complex process mainly influenced by temperature, affecting the covalent bonds within the coal structure. At temperatures around 300°C, covalent bonds in coal do not experience notable fragmentation by chain scission or bond dissociation; instead, the coal releases small amounts of gases, including hydrogen, methane, ethane, and H₂S, along with light hydrocarbons.⁵³ When compared to pyrolysis, coal liquefaction experiments at approximately 300°C leads to the release of gases. However, a key difference is observed during direct liquefaction, where coal tends to swell when heated in a suitable solvent, and substantial proportions can be extracted before covalent bond-cleavage reactions begin. The solubility of coal is often correlated with coal swelling, as solvents that promotes coal swelling also prove effective in extracting them.^{53, 54}

Fowler *et al.* (1988)⁵⁴ characterized the pyrolysis of various coal samples using Electron Spin Resonance (ESR) spectroscopy. They found that the characteristic onset temperatures (above 300°C) for covalent bond-cleavage reactions are rank-dependent. They also found that as temperatures rise above these onset temperatures, i.e., ESR spin population data of stable free radicals exhibit a gradual increase starting around 300–310°C, with a rapid escalation observed beyond 350–375°C. This pattern offers indirect evidence pointing to the initiation of significant bond cleavage reactions occurring at and above the temperature range of 350–375°C and the formation of free radicals.⁵⁴ Comparing these findings with data from direct coal liquefaction experiments shows that, at temperatures below 300–325°C, it is possible to extract a significant proportion of the coal mass. This extraction occurs before the onset of covalent bond cleavage, indicating that the weight loss at these temperatures primarily results from the solvent extraction of the more mobile and relatively low molecular mass compounds present in the coal. For middle-rank coals, weight loss at temperatures up to 350°C can be attributed to the extraction of smaller molecular mass and more soluble coal materials.⁵⁴ Notably, there is a significant temperature gap between the onset of bond cleavage and extensive depolymerization during liquefaction. Extensive coal depolymerization occurs at temperatures that are considerably higher than the onset of covalent bond cleavage. This suggests that multiple covalent bonds must be cleaved before larger molecular fragments attached to the solid matrix can be released as free radicals within the coal particles.^{53, 54}

Zhou *et al.* (2016)⁵⁵ suggested that modifications in the chemical reactivity of coal involves the restructuring of bonds. The most effective method for analyzing the chemical structure of coal, as proposed by Zhenyu (2014)⁵⁶, is to examine bond concentrations and suggested that the primary covalent bonds in coal can be expressed as C_{ar}–C_{ar}, C_{ar}–C_{al}, C_{al}–C_{al}, and C–X, with C representing carbon atoms. The subscripts (ar) denote aromatic bonded carbons, (al) signify aliphatic bonded carbons, and X encompasses heteroatoms, including oxygen (O), nitrogen (N), and sulfur (S).⁵⁵ The chemical structure of coal, in simple terms, can be considered as a combination of three primary functional groups: aromatic structures, bridging linkages between aromatic clusters (such as alkyl bridges, ethers, and esters), and oxygen functional groups. While these fundamental functional groups exist in all types of coal, their occurrences serve to distinguish one rank from another.⁵⁷

The bond dissociation energies (BDE) of aliphatic C–C bonds and aromatic C–C bonds differ, with aromatic carbons exhibiting high bond energy. Higher BDE's decrease the reactivity of coal during thermochemical conversion processes, as the fragmentation of aromatic structures require more energy and contributes to the low conversion values of high-rank coals. Coal liquefaction is usually favored when simple skeletal structures are present.⁵⁷⁻⁵⁹ **Table 2-1** summarizes covalent bond dissociation energies (BDE) for the molecules present in coal, as proposed by Speight (2012)⁴⁴, Ahamed *et al.* (2019)⁵⁷, Emelyanycheva *et al.* (2016)⁶⁰, and Shi *et al.* (2013)⁵⁹.

Table 2-1. Covalent bond dissociation energies (BDE) in the molecules in hydrocarbons present in coal^{57, 60}

Primary covalent bonds (single)	Bond classification	BDE (kJ.mol ⁻¹)
Ph–Ph	C _{ar} –C _{ar}	431.3
RCH ₂ –CH ₂ R	C _{al} –C _{al}	347.5
Ph–CH ₂ Ph	C _{ar} –C _{al} C _{ar}	339.1
RCH ₂ –OCH ₂ Ph	C _{al} –OC _{al} C _{ar}	335.0
PhCH ₂ –CH ₃	C _{ar} C _{al} –C _{al}	301.5
PhCH ₂ –CH ₂ CH ₂ Ph	C _{ar} C _{al} –C _{al} C _{ar}	288.9
PhCH ₂ –OCH ₃	C _{ar} C _{al} –OC _{al}	276.3
PhCH ₂ –CH ₂ Ph	C _{ar} C _{al} –C _{al} C _{ar}	238.7
PhCH ₂ –OCH ₂ Ph	C _{ar} C _{al} –OC _{al} C _{ar}	234.5
PhCH ₂ –OPh	C _{ar} C _{al} –OC _{ar}	213.5
PhCH ₂ –SCH ₃	C _{ar} C _{al} –SC _{al}	213.5
CH ₂ =CHCH ₂ –CH ₂ CH=CH ₃	C _{al} –C _{al} (unsaturated)	159.1

Ph = Phenyl group; R = Alkyl group; C_{ar} = Aromatic carbon; C_{al} = Aliphatic carbon.

Understanding these bond strength variations provides insight into the transformations that occur during coal liquefaction and its impact on the coal's macromolecular structure. In addition, the strength of chemical bonds plays a crucial role in predicting product formation, which is predominantly based on thermodynamics. It has been estimated that the thermal stability of hydrocarbons follows a specific order: paraffins (alkanes) < mono-olefin hydrocarbons (alkenes) < diolefin hydrocarbons (dienes) < naphthenes (cycloalkanes) < benzenes (aromatics) < condensed hydrocarbons (PAH's).⁶⁰

Decomposition reactions involve the absorption of heat, making them endothermic processes. Such reactions during thermochemical processing include cracking, dehydrogenation, dehydration, dealkylation, depolymerization, and dehydrocyclization. It has been established by various researchers that the reaction mechanisms (chain and radical interactions) during thermochemical conversion involves several key processes:^{60, 61}

Chain initiation: The chain initiation process is typically triggered by monomolecular decomposition, specifically C–C bond dissociation (as mentioned previously). In these reactions, a single molecule undergoes fragmentation, resulting in the formation of two free radicals. Although only a small fraction of the feed molecules undergo initiation, these reactions are crucial for generating the free radicals that drive subsequent decomposition reactions. In coal liquefaction, initiation often involves breaking the chemical bond between two carbon atoms (C–C covalent bond), as opposed to the bond between a carbon and a hydrogen atom.

Chain Transfer: During this stage, radicals formed during the initiation phase interact with the initial molecules, leading to the creation of new radicals. This process involves hydrogen abstraction, where a free radical removes a hydrogen atom from another molecule, transforming the second molecule into a free radical. This process is usually enhanced by hydrogen donation from organic solvents.

Molecule growth (Continuation of Chain): This stage encompasses various transformations of radicals based on process conditions. Radical decomposition and radical addition reactions that occur during the growth of a molecule. In radical decomposition reaction, a free radical is split into two molecules, with one being an alkene and the other a free radical. This process contributes to the production of aromatics and olefins such as vinylic and allylic hydrocarbons. Conversely, radical addition reactions involve a radical reacting with an olefin to form a larger, single free radical.

Chain Termination: The chain termination stage involves recombination and disproportionation reactions, leading to the elimination of free radicals. Recombination occurs when two free radicals combine to form a larger molecule, while disproportionation involves one radical transferring a hydrogen atom to another, resulting in the formation of an alkene and an alkane.

In the thermal cracking process, numerous chemical reactions occur, predominantly driven by free radicals and encompassing numerous reactions.

2.4.3. Factors affecting liquefaction conversion, and product yield and composition

The subsequent sections will explore the impact of various factors on the yields and composition of products during liquefaction processes. The behavior of coal during conversion processes is primarily influenced by several physicochemical properties of coal, including coal rank, maceral composition, chemical structure, mineral matter content, and pore structure. Additionally, the influence of process conditions, encompassing factors such as reaction temperature, heating rate, reaction time, pressure, solvent type, and atmosphere, on the liquefaction conversion process will be discussed.

2.4.3.1. Coal parameters: rank, organic composition, mineral matter content, and particle size

Coal primarily comprises of solid organic matter with an atomic hydrogen-to-carbon ratio ranging from 0.1 to 4.0.^{58, 62} The production of liquids from coal necessitates breaking down the chemical structure into lower molecular-weight compounds that exist in a liquid state under ambient conditions. In addition, this process involves the removal of heteroatoms, particularly O, N, and S, while increasing the hydrogen-to-carbon ratio. The outcome of this transformation includes the generation of saturated aromatic compounds and other hydrocarbons, contributing to the stabilization of the resulting liquids.⁵⁸ Various coal properties exert diverse and significant impacts on the coal liquefaction process. Extensive studies have been conducted on the chemical and physical characteristics of coal, highlighting their significance in the conversion of coal into liquid products. It has been established that the behavior of coal is predominantly affected by rank, petrographic composition, and inorganic constituents.⁶³

Coal rank and composition

The rank of coal, along with its vitrinite reflectance, serves as an indicator of its potential for producing liquid hydrocarbons.⁵⁸ Concerning its chemical composition, the macromolecular structure of coal forms a three-dimensional composite network consisting of clusters primarily composed of polycyclic aromatic, hydroaromatic, and heterocyclic clusters connected through short aliphatic and ether linkages, forming a cross-linked three-dimensional network. Aromatic rings are usually substituted with alkyl, phenolic hydroxyl, and ether groups. Various molecular models depicting the organic composition of coals at specific ranks have been reported.^{63, 64}

Bituminous coals are characterized by highly substituted, cyclical carbon structures consisting of one or more condensed rings (generally three to five rings), interconnected by alkyl or ether bridges (oxygen or sulfur), forming a macromolecular network. In low-rank coals, there is a higher proportion of oxygen groups. The sizes of structural units, bridges, and substituents vary relative to the coal rank. As the rank increases, functional groups decrease, and the ring system becomes more condensed. In bituminous coals, principal oxygen functional groups include phenolic or etheric groups, along with lesser amounts of carboxylic acids, esters, and carbonyls. On the other hand, lignite and subbituminous coals predominantly contain carboxylic groups.^{49, 63}

Optimal liquefaction yield occurs near the transition from brown coal to bituminous coal, typically within the carbon content range of 80–85%. However, a sharp decrease in oil yield is observed when the carbon content reaches 87–89% (medium volatile bituminous coals), while coals with carbon contents exceeding 90% (low volatile bituminous and anthracite) tend to be mostly unreactive.⁶³ When the carbon content of coals decreases below the optimal range, particularly in lower rank coals, the oil yield decreases. This is a result of an increased oxygen content, approaching 30 wt.% on a dry, mineral matter free (d.m.m.f.) basis. The oxygen reacts with carbon and hydrogen to form water and carbon dioxide during deoxygenation reactions. Additionally, lower rank coals, including lignites, brown coals, and subbituminous coals, require an additional hydrogen source for higher conversion levels. Although they liquefy more readily, the liquid hydrocarbon yield is limited due to increasing oxygen content, leading to the formation of water and carbon oxides. In addition, the moisture content needs to be low as it has to be removed during the hydrogenation step.⁶³

Despite a tendency for total liquid yield to decrease with decreasing rank, lower rank coals produce a higher fraction of low boiling point distillates. Subbituminous coal products, in particular, are more volatile, contain more saturated hydrocarbons, exhibit lower aromaticity, and possess higher hydrogen contents with fewer heteroatoms.⁶³ The composition of aliphatic and aromatic hydrocarbons is notably influenced by coal rank, with subbituminous coal and lignite producing around 50% of aliphatic hydrocarbons, while bituminous coal produces 21–23%. The rank of the coal plays a significant role in determining product composition, with higher-rank coals reflecting a more aromatic structure.⁶³

Mochida *et al.* (2014)⁴⁹ noted that the proportion of aliphatic and aromatic hydrocarbons is evidently influenced by coal rank. In direct liquefaction, subbituminous coals and lignites yielded approximately 50% aliphatic hydrocarbons in the oil fraction, whereas bituminous coals yielded between 21% and 23%. Aromatic hydrocarbons were the predominant products derived from bituminous coals, constituting 39–40% of the liquid yield, whereas in subbituminous coals and lignites, the fraction ranged from 29–36%. It is evident that low-rank coals tend to produce more aliphatic hydrocarbons. In addition, higher-rank coals produced significantly fewer C₁₄–C₁₈ hydrocarbons, whereas subbituminous coals and lignites produced a larger fraction of shorter aliphatic hydrocarbons. Thus, the coal rank played a decisive role in shaping the product composition, indicating a more aromatic structure in higher-rank coals.⁴⁹

The most crucial parameter for coal liquefaction is the degree of coalification. The coal rank, as indicated by vitrinite reflectance, can serve as a determinant of a coal's potential to produce liquid hydrocarbons.⁵⁸

Petrographic composition

Coal's intricate structure significantly influences processes such as pyrolysis, gasification, and liquefaction of coal. The primary macerals of coal, namely vitrinite, inertinite, and liptinite, each composed of distinct submacerals, contribute substantially to the complexity of the coal macromolecular structure. Therefore, investigating the macromolecular structure characteristics of coal macerals is valuable for gaining a more comprehensive understanding of coal's overall structural features and their impact on the conversion tendency and product yield during liquefaction.⁶⁴

The macerals within the vitrinite group, comprising over 80% of the organic content in most coals, and those within the liptinite group, are generally acknowledged to be much more reactive during liquefaction processes compared to inertinite macerals.^{58, 63, 64} However, coals rich in fusain, the predominant constituent of the inertinite group, are typically associated with the highest degree of conversion in liquefaction processes.^{58, 65} Fusain primarily consists of fusinite and semifusinite, constituting a range from 10–30% (by volume). The liquefaction yield is predominantly influenced by the quantity and characteristics of fusain, as they are generally deemed favorable for hydrogenation reactions.^{58, 65}

Keboletse *et al.* (2021)⁵⁸ stated that the estimated oil yields of the liquefaction products, based on weight, from different macerals are approximately 78–80% for liptinite, 6–10% for vitrinite, and 0–2% for inertinite during liquefaction. Vitrinite macerals readily dissolve, thereby aiding the conversion of coal into liquid products due to their inherent thermoplastic characteristics. These findings align with conclusions drawn by other researchers. For example, in hydrogen-transfer reactions with 9-fluorenone, varying reactivities were observed for different coal macerals, with liptinite (especially sporinite and cutinite) exhibiting the highest reactivity, followed by vitrinite, and then inertinite.^{53, 64} The elevated yields obtained from liptinites can be attributed to the presence of aliphatic structures, whereas inertinites tend to remain unreactive during the conversion processes. Both the liquid yield and the characteristics of the solid residue in coals under consistent rank conditions significantly depend on the maceral composition. Coals abundant in vitrinite and liptinite (formerly known as exinite) exhibit high hydrogen contents, and it has been observed that higher hydrogen contents tend to enhance liquefaction products.^{58, 64}

Inherent mineral matter in coal

Mineral matter in coal originates from inorganic elements associated with organic matter, pore water, and detrital minerals.^{40, 63} Recognized as intrinsic to coals, mineral matter is acknowledged as an active component in DCL, capable of catalyzing the transformation of organic matter during thermal processing.⁴⁰ For example, mineral matter is considered an internal diluent, minimizing coal particle agglomeration and enhancing the effective diffusion of hydrogen to bond rupture sites.⁶⁶ Similarly, the removal of some mineral matter by coal beneficiation (decreasing inorganic matter concentration) resulted in a significant reduction in total conversion and oil yield during liquefaction.⁶⁷ The conversion of coal to liquid products has been found to increase with higher mineral matter content and concentrations of iron and titanium in the coal.⁴⁰ However, mineral matter may have detrimental effects on direct liquefaction, including catalyst poisoning and ash-related issues. Moreover, mineral matter could play a negative role in donor extraction, leading to undesirable dehydrogenation of the solvent, adversely affecting oil yields.^{40, 68}

Organic matter and mineral matter coexist in the structure of coal. However, in terms of efficient coal utilization, mineral matter holds less value compared to organic matter. From a coal structure perspective, mineral matter can be considered a diluent, replacing useful organic matter with inert components that readily turn into ash upon combustion or gasification.^{40, 69} Additionally, mineral matter can lead to undesirable issues such as slagging, fouling, and corrosion in association with coal handling.⁴⁰ The occurrence of mineral matter in coal differs significantly. According to the classification method proposed by Ward (2002)⁶⁹, mineral matter in coals can be broadly categorized into three types:

1. Discrete mineral matter (crystalline and non-crystalline).
2. Exchangeable metallic species associated with the organic structure of the coal matrix.
3. Inorganic substances dissolved in the pore water of coal.

In high-rank coals, the discrete mineral matter is usually the most prevalent species, consisting primarily of silicates, carbonates, sulfides, and sulfates with varying chemical structures and molecular sizes.^{70, 71} Conversely, in low-rank coals, exchangeable metallic species are dominant, commonly existing in the form of carboxylates.⁷² The decrease in the concentration of metallic species with increasing coal rank is attributed to their structural association with oxygen-containing functional groups. These functional groups are typically more abundant in low-rank coals.⁴⁰ The presence of Ca (as humic acid salts) in low-rank coals accounts for up to 3% (by weight) of the total weight. During liquefaction, Ca-salts are transformed into CaO that reacts with CO₂, resulting in the deposition of CaCO₃ on reactor walls.^{58, 63} This phenomenon contributes to the unattractiveness of low-rank coals as feedstocks for direct liquefaction. Consequently, studies have shown that exchangeable metallic species in low-rank coals negatively impact the oil yield during direct liquefaction. The demineralization treatment of low-rank coals has been shown to enhance oil yield in direct coal liquefaction by removing these exchangeable metallic species.^{40, 70}

Kaolin stands out as a key clay mineral present in coals. In a study by Mukherjee and Chowdhury (1976)⁷³, the relationship between kaolin concentration and total conversion in direct coal liquefaction (DCL) was explored. The findings revealed a proportional increase in total conversion with the increasing content of kaolin in the coal. To delve deeper into the catalytic impact of kaolin, Gray (1978)⁶⁶ impregnated coals with pure kaolin. The results demonstrated a 21% increase in total conversion for the impregnated coal compared to the original coal. From these observations, it was deduced that the intrinsic clay minerals in coals possess the ability to fracture the coal matrix, thereby augmenting total conversion in DCL.

There are, however, conflicting views on the role of clay minerals during liquefaction. Some studies state that char-forming reactions are catalyzed by clay minerals and reduce conversion rates in certain liquefaction processes.⁷⁴ Gözmen *et al.* (2002)⁷⁵ employed a demineralization method to investigate the impact of clay minerals on liquefaction and found that the removal of clay through HF/HCl treatment left total conversion in liquefaction largely unaffected, but the oil and gas yields increased significantly (almost three-fold) compared to treatment with HCl alone (**Table 2-2**). This outcome suggests that eliminating clay is advantageous for direct liquefaction and strongly supports the notion that clay can promote char-forming reactions. This conclusion is more plausible and widely acknowledged because, in the process of adding kaolin to coal, kaolin can act as a dispersant, likely reducing agglomeration and improving mass transport properties within the system.^{40, 66} This

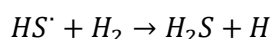
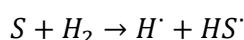
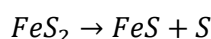
characteristic makes it challenging to definitively establish catalytic effects of mineral matter in coal during hydrogenation.

Table 2-2. Direct liquefaction results of two acid-treated coals, adapted from Gözmen *et al.* (2002)⁷⁵.

Coal sample	Treatment	Conversion, %	Oil and gas yield, %
Gediz coal	None	89.7	12.2
	HCl	69.1	14.6
	HCl + HF	90.9	38.8
	HCl + HF + HNO ₃	17.6	10.2
Cayirhan lignite	None	74.2	30.0
	HCl	47.9	13.8
	HCl + HF	68.6	38.1
	HCl + HF + HNO ₃	10.4	5.5

Direct liquefaction experiments conducted at 400°C in a H₂ atmosphere with a reaction time of 30 minutes.⁷⁵

Another mineral component that can effectively catalyze the conversion of coal in direct liquefaction is pyrite, a common iron-containing mineral found in coal.^{40, 67} When pyrite is examined under petrographic microscopes, it becomes apparent that it is not evenly distributed within the coal particles.⁶⁶ However, advanced techniques and kinetic calculations have demonstrated that pyrite can be decomposed into pyrrhotite (Fe_{1-x}S) during direct liquefaction, and pyrrhotite is identified as the actual active substance required for coal hydrogenation.⁴⁰ The mechanisms responsible for the catalytic activity of FeS₂ under a hydrogen atmosphere are proposed to involve a series of reactions rather than a direct reaction of H₂ with FeS₂. One possible pathway can be described as follows.⁴⁰



Gözmen *et al.* (2002)⁷⁵ conducted direct liquefaction experiments on two high-sulfur coals that had been treated with HNO₃ to eliminate pyrite. The results, presented in **Table 2-2**, showed a significant reduction in total conversions, and oil and gas yields. This experiment strongly supports the catalytic role of pyrite in direct coal liquefaction. Moreover, a study revealed that pyrite can influence the re-hydrogenation process of the solvent. In the absence of pyrite, the solvent tended to dehydrogenate and subsequently lead to a shift in product distribution towards high-molecular-weight products.^{40, 76} Additionally, it was observed by researchers that pyrite enhanced coal pyrolysis by reducing the activation energy of pyrolysis and promoting the generation of more free radicals in DCL.^{76, 77}

Inorganic mineral matter contributes to the overall ash content in coals. Durie (1982)⁷⁸ suggested that the ash yield of coal should not exceed 10 wt%, considering that constituents prone to ash formation often exist as cations associating with carboxylic acid compounds in coal. The nature and quantity of these inorganic species can significantly influence the behavior of coal during thermal decomposition and facilitate the elimination of oxygen. Moreover, a high ash yield in coals has an adverse effect on the liquefaction process, negatively impacting reactor capacity. Additionally, a detrimental effect on the recoverable yield of distillable oil may be observed, as the added catalyst becomes deactivated in the presence of some mineral matter constituents.⁷⁸

In DCL systems, where coal particles are allowed to interact freely, agglomeration or caking behavior may occur when the coal particles transition through the liquid mesophase state. This caking

property has the potential to hinder effective hydrogen transfer to the sites of thermal bond rupture and hinder the diffusion of products to the surface. Moreover, this diffusion effect could dominate any catalytic effects of the inherent mineral matter.⁴⁰

Particle size of coal

Particle size plays a crucial role in the coal liquefaction conversion process. Small-sized particles have shorter diffusion distances for the solvent to access the core of the coal matrix to facilitate liquid product extraction. Larger sized particles lead to a more rapid depletion of the diffusing component compared to its diffusion into the particle. This is due to the extended distances that solvent molecules must travel to reach the core of the particles, resulting in reactions unrelated to solvent interactions, primarily occurring near the center of the particle. Consequently, this increases the number of reactions in the particle's central zones, leading to a higher concentration of coal-derived radicals. The presence of these free radicals contributes to the undesirable formation of stable, high-molecular-weight products through recombination reactions during liquefaction.^{10, 40, 79}

Research suggests that the extraction yields are higher for small-sized particles, attributed to their increased coal surface area. This characteristic enhances the solvent's ability to penetrate the coal structure easily, thereby increasing the efficiency of liquefaction.⁸⁰

2.4.3.2. Operating conditions

Temperature and heating rate

The mechanisms of direct coal liquefaction are intricate and not yet fully understood. Generally, the DCL process comprises two main steps: the breaking of the macromolecular structure of coal into radical fragments at elevated temperatures, and the subsequent stabilization and hydrogenation of these fragments to produce molecules with lower molecular weights.⁸¹ From a thermodynamic perspective, the reaction between coal and hydrogen leads to an increase in the production of aliphatic and alicyclic compounds at low liquefaction temperatures. As the temperature rises to medium levels, the production shifts towards gases and aromatics. However, at the high liquefaction temperatures, undesirable compounds such as coke and gas are generated.⁶⁷

Elevated temperatures lead to the thermal rupture of carbon-carbon linkages in coal molecules, promoting reaction rates. Temperature stands out as one of the most crucial factors influencing free radical formation and subsequent reactions. These reactions typically do not occur at low temperatures, and excessively high temperatures may lead to undesirable reactions and products.⁸¹ Therefore, for a specific set of reaction conditions, an optimal temperature exists. Shui *et al.* (2010)⁸² developed a reaction kinetic model for Shenhua coal liquefaction using a solid acid catalyst at temperatures ranging from 375 to 450 °C. They observed an increase in conversion from 46% at 375°C to 91% at 450°C for a 1-hour reaction, but noted considerable coke formation at 450°C.⁸² Flatman-Fairs and Harrison (1999)⁸³ showed that an increase in liquefaction temperature (from 380 to 400°C) improved oil yields by enhancing secondary cleavage reactions. However, when the temperature was increased to 450°C, the formation of coke through recombination reactions became evident. In a study by de Marco Rodriguez *et al.* (1998)⁸⁴, focusing on the direct liquefaction of a Spanish sub-bituminous coal in tetralin, they found a significant increase in the formation of free radicals with rising temperature. The optimal temperature for coal liquefaction, considering both conversion and product quality, was found to be around 425°C.⁸⁴

It has been demonstrated that the oil yields in a DCL process are influenced not only by the process temperature but also by the heating rate. Specifically, temperature-programmed liquefaction (TPL) has proven to be more effective compared to rapid heating rates for the liquefaction of low-rank coals.⁸⁵ The TPL process involves a low-temperature soak at 200 °C for 15 minutes, followed by slow heating rate (7 °C/min) to the final temperature, and concluding with a 30-minute soak at the final temperature (ranging from 300 to 425°C). By controlling the heating rate, coals can be efficiently liquefied with a controlled rate of pyrolytic cleavage of weak bonds, while minimizing the retrogressive crosslinking of radicals.⁸⁵ In a study by Song *et al.* (1992)⁸⁶, coal conversions achieved through the TPL process reached 77–81% at 400°C, compared to 71–72% in the rapidly heated liquefaction. Similar observations regarding the beneficial effects of TPL were reported by Huang and Schobert (2005)⁸⁷. In their study, conversion values of a low-rank coal in TPL processes generally exceeded those in single-stage liquefaction (SSL) and temperature-staged liquefaction (TSL). For instance, in the presence of ammonium tetrathiomolybdate (ATTM) as the catalyst and Wilsonville middle distillate as the solvent, conversion values at 400°C were 84.4, 89.5, and 90.9% for the SSL, TSL, and TPL processes, respectively.⁸⁷

Reaction times

It is generally accepted that coal conversion increases with higher temperatures and longer residence times during direct liquefaction processes.⁵¹ As stated by Rahman *et al.* (2015)⁵¹, it is crucial to emphasize that liquefaction conversion serves as an indicator of coal conversion rather than an indicator of coal liquid yield. Not all converted coal transforms into coal liquids, and typically, elevated temperatures and prolonged residence times result in higher selectivity to gaseous products. Gaseous products are not solely derived from coal but also from the cracking of the solvent. This was validated by Rahman *et al.* (2015)⁵¹. During a blank run with only solvent (hydrotreated industrial coal liquid) heated to 450 °C and maintained at that temperature for 0 minutes, a gas yield of 5 wt% was observed. During this study, it was also found that at the lowest liquefaction temperature of 350°C, the H/C molar ratio of the liquid fraction decreased with increasing residence time, whereas at the highest temperature of 450°C, the H/C molar ratio was unaffected by residence time. These observations can be attributed to differences in coal conversion. However, the molecular composition of the liquid fraction at 450°C was influenced by residence time, maintaining near-constant conversion. With an extended residence time, the products exhibited a slightly more aromatic nature, contained more heavy boiling material, and demonstrated a higher density and refractive index.

A prolonged residence time allows for increased hydrogen disproportionation, cracking reactions, and side reactions such as free radical addition. While increased cracking conversion may ultimately enhance coal conversion, it does not necessarily lead to an increase in liquid yield, as it may favor the formation of gas.⁵¹

Pressure and atmosphere

Maintaining high pressures during DCL processes offers several advantages. It ensures that the solvent and products remain in the liquid phase, prevents the accumulation of coke on reactor walls and catalyst surfaces by suppressing retrogressive recombination reactions, and facilitates hydrogenation by sustaining a high partial pressure of hydrogen. However, economic considerations often necessitate the use of lower H₂ pressure in liquefaction processes. With advancements in DCL

technologies, particularly in the development of more effective catalysts and solvents, the requirement for high pressure could be lowered to approximately 20 MPa, in the range of NEDOL, HTI, and Shenhua processes.^{9, 81, 88}

It has been demonstrated that, with a suitable solvent possessing a sufficiently high boiling point, coal liquefaction can occur under atmospheric pressure.⁹ However, in such cases, the majority of the products consist of heavy fractions, and the oil yield is typically around 10%. In the presence of a good donor solvent, coal liquefaction can proceed under relatively lower pressure, although significant improvements in coal conversions can be achieved by increasing the operating pressure. Once liquefaction reaches a certain degree, further increases in pressure have minimal effects on oil yields.⁸⁹ Supporting this statement, studies have shown that liquefaction yields remain almost unchanged as pressure increases from 14.7 to 18.6 MPa.⁹⁰ In a study by Cai *et al.* (2008)⁸⁵, total conversions only slightly increased from 25.4% to 26.1% as the process pressure was raised from 10 to 15 MPa.

Rahman *et al.* (2015)⁵¹ found that changing the atmosphere from H₂ to N₂ had only small effects on the liquid quality at 350°C. This can be explained by the stability of the H-H bond at low temperatures and in the absence of an appropriate catalyst. Similar findings were observed by other researchers, stating that a high conversion can be achieved under a nitrogen (N₂) atmosphere when using a good donor solvent during coal liquefaction⁸⁹. However, most DCL processes operate under a high-pressure hydrogen atmosphere. Assisted by the hydrogen-shuttling effects of liquefaction solvents, gaseous phase hydrogen can be transferred to the coal molecules and fragments. Hydrogen, acting as a capping agent, stabilizes fragments or free radicals to form liquid products and suppresses coke formation reactions in the process. It has been estimated that approximately 30% of the production cost for a DCL process is associated with hydrogen generation.⁹¹ Molecular hydrogen itself is a poor capping agent due to the stability of the H-H bond, but under high severity conditions and in the presence of an appropriate catalyst, H₂ molecules can be dissociated into reactive atomic hydrogen.

2.4.3.3. Solvent

In most DCL processes, the solvent plays a crucial role in stabilizing free radicals by donating hydrogen, promoting the cracking of coal macromolecules, and preventing the condensation and coking of radicals by diluting the intermediates.^{49, 53, 81, 86} This process ensures that the fragments remain as smaller molecules without recondensation or recombination reactions occurring that produce undesirable products. In addition, the solvent can promote heat and mass transfer for liquefaction reactions and act as a carrier of hydrogen by transporting it from the gas phase to the coal.^{49, 50, 81} Furthermore, the presence of a catalyst in the process allows for the re-hydrogenation of the dehydrogenated solvent back to the hydrogen donor state. Thus, hydrogenation, donation, and re-hydrogenation of the solvent are cyclically active to sustain the depolymerization of coal macromolecules.^{49, 81}

Once the coal macromolecules are liquefied or dissolved in the solvent, a solid catalyst can continue the hydrocracking process under hydrogen pressure, yielding distillate hydrocarbons. The liquefaction products exhibit various molecular interactions, particularly in the less soluble fraction, influencing their properties and reactivities. The liberation of these interactions proves beneficial for upgrading. The donor solvent can also be utilized in the second stage, where the liquefied coal and

the solvent fraction, originally derived from the coal in the primary liquefaction stage, undergo co-hydrogenation. This process further refines the liquefaction product and simultaneously regenerates the solvent into a hydrogen donor.^{49, 53}

During coal liquefaction experiments conducted in a flowing-solvent reactor it was observed that tetralin, a hydrogen-donor solvent, yielded approximately 10-12% higher conversion rates compared to 1-methylnaphthalene, a non-donor solvent.⁵³ Solvents were also categorized based on their hydrogen-donor ability and solvent strength, highlighting the distinction between these characteristics. In a comparison of hydrogen-donor solvents and solvent strength, it was found that effective hydrogen-donor solvents such as tetralin may not necessarily be as effective in dissolving coal-derived materials as some non-donor solvents like quinoline or phenanthrene. This suggests that both hydrogen-donor ability and solvent strength play crucial roles in the liquefaction process. Experiments involving various solvents, including tetralin, quinoline, a mixture of quinoline and phenanthrene, and hexadecane, revealed significant differences in conversion rates. Notably, at temperatures up to around 350°C, both quinoline and a quinoline-phenanthrene mixture showed higher conversion rates, extracting greater proportions of coal mass when compared to tetralin. However, at 450°C, non-donor solvents like quinoline and phenanthrene exhibited lower conversions, aligning with the behavior of 1-methylnaphthalene.⁵³

The extent of coal depolymerization is primarily temperature-dependent, with rapid char formation occurring at temperatures exceeding 450–470°C in gaseous mediums. Donor-solvent liquefaction, on the other hand, partially suppresses these fast, retrogressive reactions. Furthermore, retrogressive, char-forming reactions were observed during liquefaction, particularly for non-donor solvents, such as 1-methylnaphthalene, though the rate of these reactions appeared to be relatively slow.⁵³

Shui *et al.* (2010)⁸¹ suggested that coal liquefaction solvents can be categorized into four distinct types based on their effects on coal: specific, non-specific, degrading, and reactive solvents. Specific solvents like pyridine and NMP (N-methyl-2-pyrrolidone) can dissolve 20–40% of coal at 200°C. Non-specific solvents such as alcohol, benzene, ether, and acetone can only dissolve a trace amount of coal at 100°C. These solvents, acting as electron donors, involve a physical process of coal extraction, typically performed at low temperatures (below 200°C). Chemical extraction processes utilizing the other two categories of solvents are commonly conducted at higher temperatures. Degrading solvents, such as phenanthridine and anthracene oil, can extract over 90% of coal at 400°C. After extraction, the solvents can be almost completely recovered from the solution. Polymerization of coal fragments may occur in liquefaction with a degrading solvent, but this can be inhibited by the supply of high-pressure molecular hydrogen, which stabilizes the coal fragments facilitated by the solvent's hydrogen transferring and shuttling roles. Reactive solvents are those that can chemically react with coal during liquefaction, such as phenol. DCL solvents can also be classified as donor and non-donor solvents. Typical donor solvents include tetralin, tetrahydrofluoranthene, dihydroanthracene, etc., while common non-donor solvents include decalin, pyrene, fluoranthene, and anthracene, among others.⁸¹

Due to these varying properties, the effect of solvents on the DCL process can be significant. Mochida *et al.* (1990)⁸⁹ investigated the roles of four donor solvents, i.e. octahydroanthracene, dodecahydrotriphenylene, hexahydroanthracene, and tetrahydrofluoranthene, in the liquefaction of Australian brown coal under a N₂ atmosphere (1.0 MPa).^{89, 92} At 450 °C for 5 minutes and a solvent-

to-coal ratio of 1:1 (by weight), the yields of oil plus asphaltene were 40, 50, 40, and 35% for tetrahydrofluoranthene, octahydroanthracene, dodecahydrotriphenylene, and hexahydroanthracene, respectively. Interestingly, a mixture of tetrahydrofluoranthene and octahydroanthracene did not yield any noteworthy results. Dehydrogenation of the solvents was observed during these processes. Sakata *et al.* (1990)⁹³ examined the effects of non-donor solvents, where pure non-donor solvents such as pyrene and fluoranthene produced a lower oil yield compared to a donor solvent (tetrahydrofluoranthene). However, a high oil yield was achieved when tetrahydrofluoranthene and pyrene were mixed. Sakata *et al.* (1990)⁹³ believed that a non-donor solvent could swell the coal grains, facilitate the dispersion of the hydrogen donor solvent into coal, and dissolve coal-derived products to suppress retrogressive reactions. Additionally, hydrogen shuttling between donor and non-donor solvents would enhance hydrogen transfer processes. Many studies have also demonstrated the synergistic effects of solvent components in coal liquefaction, achieving a high oil yield with low hydrogen consumption.⁸¹

The selection of solvent in DCL processes significantly affects conversion rates, with hydrogen-donor solvents like tetralin generally leading to higher conversions. Solvent strength is another crucial factor, as some non-donor solvents demonstrate effectiveness in dissolving coal-derived materials. Additionally, temperature is a critical determinant, influencing the rate of retrogressive reactions, which can vary based on specific conditions and the concentration of reactive materials within the solvent.

2.4.3.4. Catalysts

Catalysts play a crucial role in nearly all developed DCL processes. While some processes claim to operate without catalysts, it's important to note that most coals inherently contain significant amounts of minerals like pyrite and iron oxides, which can act as catalysts in the DCL process. Iron-based catalysts, including pyrite (FeS_2), troilite (FeS), pyrrhotite (Fe_{1-x}S), iron oxide, iron sulfate, iron hydroxide, and other iron containing sources, have been extensively studied due to their cost-effectiveness and environmental compatibility.⁷⁷ Among these, pyrrhotite is widely acknowledged as the most active form of iron sulfide catalysts. Iron-based catalysts have the ability to enhance coal pyrolysis by significantly reducing the activation energy of pyrolysis.^{48, 77} Their primary role of catalysts during DCL processes is to facilitate the formation of activated hydrogen atoms and promote the secondary distribution of hydrogen atoms throughout the entire reaction system.⁹⁴

The use of iron-based catalysts and the utilization of tetralin as a solvent during liquefaction processes have been demonstrated to enhance the conversion of lignite and higher rank coals.^{48, 95, 96} The effectiveness of iron-based catalysts involves two dominant mechanisms. Firstly, these catalysts can cleave molecular hydrogen, generating free radicals that are both unstable and highly reactive, instigating swift hydrocracking. Secondly, iron-based catalysts facilitate the rapid dehydrogenation of tetralin, releasing hydrogen and initiating the subsequent fast hydrocracking process.^{48, 96} It has also been established that the presence of iron-based catalysts, coupled with tetralin as the hydrogen donor solvent, significantly promotes lignite conversion.⁴⁸

In scenarios lacking hydrogen, tetralin steps in as the hydrogen source for hydrocracking reactions during liquefaction, influenced by the catalytic impact of iron-based catalysts. While iron dominates, alternative catalysts have demonstrated notable conversion under specific conditions, often requiring elevated hydrogen pressures (13 MPa⁹⁷ and 20 MPa⁹⁸). Other noteworthy catalysts include

NaOH⁹⁷, [Bmim]Cl⁹⁹, Ni-B/SiO₂¹⁰⁰, and fumed silica¹⁰¹, displaying effectiveness under diverse circumstances. For instance, Ni-B/SiO₂ achieves efficient conversion at lower temperatures and pressures in methanol as a solvent.¹⁰⁰ During Shengli lignite liquefaction with NaOH/methanol it was observed that NaOH reacts with methanol, producing essential hydrogen for coal hydrogenation and achieving a remarkable 98% conversion.⁹⁷

While some catalysts exhibit good conversion, their activity often correlates with high hydrogen pressures. Iron-based catalysts generally outperform others, with non-conventional solvents and catalysts demonstrating potential for excellent/promising results. The comparatively lower activity of certain catalysts can be attributed to their limited hydrogen splitting capacities and diminished ability to extract hydrogen from tetralin or other solvents, aligning with the explanation of iron-based catalyst activity.

2.5. Direct plastic liquefaction (DPL)

The distinction between liquefaction and thermal pyrolysis lies in the presence of hydrogen-donating components, either in liquid or gas form, creating a difference in the depolymerization mechanism of plastic and plastic waste materials. Thermal liquefaction, or direct plastic liquefaction, involves the cleavage of polymer chains through reactions with a solvent. The solvent acts to break down the polymer into smaller chains and forms hydrogen ends, a process facilitated by a sufficient amount of solvent allowing intermolecular hydrogen transfer during the reaction.¹⁰² In a study by Jie *et al.* (2006)¹⁰³, the reaction of ethanol with polycarbonate suggested reactions at random positions along the polycarbonate main chain, resulting in two smaller fragments of the polymer chains. Conversely, thermal processing with a lower amount of solvent followed a free radical mechanism similar to thermal pyrolysis.¹⁰⁴ Serrano *et al.* (2007)¹⁰⁵ also suggested a radical approach in the degradation of high-density polyethylene (HDPE) using different types of solvents. The liquefaction of plastic typically involves introducing the feedstock and solvent into the reactor. This is followed by purging the reactor with an appropriate gas to create an inert or reactive atmosphere. Catalysts during plastic liquefaction are frequently used.¹⁰⁶

Prior to the liquefaction process, initial analyses are commonly conducted to determine the components present in the plastic, utilizing proximate and ultimate analyses. Proximate analysis provides information on the contents of ash, volatile matter, fixed carbon, and moisture in a feedstock. A high volatile matter content favors the conversion of plastics into liquid oil, while higher ash content results in increased char and gas formation.^{107, 108} On the other hand, ultimate analysis shows the elemental composition of the materials, i.e., carbon, hydrogen, oxygen, nitrogen, and sulphur content as weight fractions. It has been widely accepted that plastic materials are composed of high carbon and hydrogen contents with relatively low oxygen content.¹⁰⁶

2.5.1. Plastic types and thermal processing

The composition of plastic waste in municipal solid waste are predominantly comprised of low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET), and polyvinyl chloride (PVC).

2.5.1.1. Low-density polyethylene (LDPE)

LDPE is an addition polymer characterized by a highly branched structure, resulting in its lower density and less robust properties when compared to high-density polyethylene (HDPE). LDPE exhibits greater ductility and finds extensive use in applications such as plastic bags, stretch film, and plastic bottles, where structural strength and resistance to high temperatures are not critical. However, the significant volume of discarded LDPE poses serious environmental challenges and waste management issues, particularly as mechanical recycling is not a favorable option.¹⁰⁹

Various alternative processes have been investigated to convert LDPE waste into value-added products. While a limited number of studies have addressed the liquefaction of LDPE, noteworthy findings have been reported. Čolnik *et al.* (2021)¹¹⁰ conducted experiments liquefying LDPE at temperatures of 425 and 450°C in deionized supercritical water. Notably, a 95% oil/wax product was obtained at 450°C using a 15-minute reaction time, while complete conversion to oil was achieved after 30 minutes. Conversely, dos Passos *et al.* (2020)¹¹¹ performed an experiment at 350°C and 20

minutes reaction time (sub-critical state) in a water medium, resulting in approximately 1% liquid product. They explained that over 90% of the LDPE tested became solid residue due to the absence of heteroatoms in the polymer.

The importance of the supercritical state in LDPE degradation in water was highlighted by Wong *et al.* (2016)¹¹², revealing that LDPE degraded at a subcritical temperature of 300°C and produced a maximum liquid yield of 28.4% after 120 minutes. Furthermore, the degradation of LDPE was observed to yield up to 53% hydrocarbons within the C₆–C₈ range at 425°C and 15 minutes reaction time, with the oil yield gradually decreasing as reaction time increased.¹¹⁰

Feng *et al.* (1996)¹¹³ discovered that the liquefaction of PE using an HZSM5 zeolite catalyst or a Al₂O₃-SiO₂ catalyst resulted in high total conversion and oil yields at low hydrogen pressures (0.7 MPa, cold) or under nitrogen (1.4–4.1 MPa, cold). Their experiments on a waste plastic with various catalysts and solvents determined the optimum liquefaction temperature to be around 445°C. Notably, better yields were achieved from plastics alone when using waste oil or no solvent compared to tetralin, and the addition of several solid acid catalysts further improved yields. Simulated distillation analysis of the oil fractions revealed that higher hydrogen pressure led to improved oil quality and to a larger fraction of low-molecular weight distillates. Additionally, it was found that HZSM-5 catalyst outperformed the Al₂O₃-SiO₂ catalyst, providing higher quality oils that were also improved with increasing temperatures.

2.5.1.2. High-density polyethylene (HDPE)

HDPE, a thermoplastic polyolefin with minimal branching, exhibits relatively strong intermolecular forces due to the close packing of its linear polymer chains. This close packing enhances van der Waals forces, resulting in a material with high tensile strength, rigidity, and density compared to more branched polyolefins such as LDPE. It is chemically resistant and hydrophobic, making it suitable for applications like bleach bottles, toys, and pipes.¹⁰⁸ HDPE liquefaction yields a liquid with properties resembling diesel in viscosity, density, and heating value, dependent on processing conditions.¹¹⁴ Su *et al.* (2004)¹¹⁵ achieved a maximum liquid yield of 91.4% at 460°C in supercritical water after 1 minute, indicating high plastic conversion at elevated temperature and a short reaction time. Moriya and Enomoto (1999)¹¹⁶ obtained a similar yield of 90.2% at 425°C and 120 min. Higher liquid yield correlated with lower gas and solid residues (approx. 6% gas and negligible solid) for both conditions. Zhang *et al.* (2007)¹¹⁷ noted a decrease to 79% liquid yield at 530°C with a rise in residue to about 12%.

HDPE liquefaction using hydrogen gas achieved complete plastic conversion and up to 95% liquid yield.¹¹⁸ Yet, the process escalates operational costs due to expensive hydrogen gas.¹⁰⁷ Prior treatments, such as hydrothermal treatment, significantly increased liquid product yield, as evidenced by Sugano *et al.* (2009)¹¹⁹, who obtained nearly 99% oil. HDPE liquefaction is attractive, offering a calorific value comparable to gasoline.¹²⁰ Yuan *et al.* (2009)¹²¹ reported an HHV of 47.92 MJ/kg for HDPE oil, close to gasoline's 47.7 MJ/kg.¹²¹ Pei *et al.* (2012)¹²² found a calorific value of 51.02 MJ/kg, correlating with enriched hydrogen and carbon content.¹²²

During polyolefin degradation, different hydrocarbon percentages are produced: C₁–C₄ in gas yields, C₅–C₁₈ in the liquid fraction, and C₁₉–C₇₀ in solid products. Aguado *et al.* (2007)¹²³ obtained 35% in the C₅–C₁₈ range using HDPE in decalin solvent at 425°C, while Serrano *et al.* (2007)¹⁰⁵ achieved a

40% C₅–C₂₀ hydrocarbon fraction using 1-methylnaphthalene at 400°C. At 460°C in the supercritical state, 97.87% hydrocarbons within the C₄–C₁₂ range were achieved using acetone as the solvent.¹²⁴

2.5.1.3. Polypropylene (PP)

Polypropylene (PP), classified as a polyolefin alongside HDPE, LDPE, and polystyrene (PS), is a semi-crystalline, non-polar thermoplastic polymer widely utilized in commercial and industrial applications. As the second-largest polymer after polyethylene, PP finds extensive use in automotive, textiles, and consumer goods industries due to its low density, lightweight nature, exceptional heat resistance, and high durability. While resistant to organic solvents, its resistance reduces with rising temperatures.

Hwang *et al.* (2001)¹²⁴ achieved a substantial oil yield of approximately 96–98% through PP liquefaction at 450–470°C for a 30-minute reaction time in supercritical acetone as the solvent. Substituting the solvent with supercritical water at similar conditions, Chen *et al.* (2019)¹²⁵ obtained a comparable yield of 91% oil. In contrast, Seshasayee and Savage (2020)¹²⁰ reported a significantly lower oil amount, approximately 17%, at the same temperature and reaction time in supercritical water. The variance in liquid output is attributed to the solvent-to-plastic consumption ratio, possibly influenced by a synergetic effect at a specific biomass to PP ratio, as suggested by Pei *et al.* (2012)¹²². Subcritical water conditions for PP processing showed no quantifiable gas yield and no extractable oil product.¹²⁶ This is consistent with results from dos Passos *et al.* (2020)¹¹¹ with approximately 4% and 5% gas and oil, respectively, at 350 °C and 20 minutes. Hydrogen gas usage also resulted in substantial liquid yield, as reported by Williams and Slaney (2007)¹¹⁸, achieving up to 95% oil without solid residue at 500°C and 60 minutes. Feng *et al.* (1996)¹¹³, under slightly milder conditions (420°C) with tetralin solvent, obtained a lower total conversion of 83%.

The higher heating value (HHV) of liquefied polypropylene falls in the range of 46.2–49.3 MJ/kg, aligning well with gasoline's HHV.¹²⁵ Seshasayee and Savage (2020)¹²⁰, however, reported a lower calorific value of 40–45 MJ/kg for pure PP liquefaction. Research addressing environmental concerns regarding marine plastic waste and excess biomass production has explored co-liquefaction of plastic waste with varying biomass ratios.¹²⁶ Results indicate a decrease in the HHV value of the bio-oil product within the range of 32.5 MJ/kg to 34.5 MJ/kg as biomass is co-liquefied with plastic waste.^{126, 127} PP liquefaction produced a maximum of 97% hydrocarbons in the gasoline range (C₅–C₁₀) at 425°C and 120 minutes, with a lower percentage of C₅–C₁₀ hydrocarbons (approximately 20%) observed at a lower reaction time of 60 minutes.¹²⁵

2.5.1.4. Polystyrene (PS)

Polystyrene, a synthetic aromatic polymer formed through the polymerization of styrene monomers, displays versatility as a widely used plastic in both solid and foam structures. The solid variant finds applications in crafting car parts, medical devices, kitchen appliances, toys, and laboratory equipment. On the other hand, foam polystyrene, commonly known as expanded polystyrene (EPS), is employed in the production of surfboards, building insulators, food packaging, and child seats. Recognized for its lightweight composition and reduced thermal conductivity, EPS consists of over 95% air. However, the surge in plastic volume poses logistical challenges in the management of EPS waste.

Efforts to address this issue involved the liquefaction of polystyrene in supercritical toluene, revealing a remarkable oil yield of 97.9% at a processing temperature of 370°C and a 30-minute reaction time. The accompanying gas output remained minimal, accounting for less than 1% under these processing conditions.¹⁰⁶ Research conducted by Abdel-Raouf *et al.* (2013)¹²⁸ aligns with these findings, demonstrating high liquid yields during polystyrene liquefaction. Supercritical ethylcyclohexane and cyclohexane solvents produced liquid yields of 95.3% and 96.6%, respectively, at 300°C and a 60-minute reaction time, with gas outputs below 5%. The use of cyclohexane at higher temperatures and longer reaction times results in a decrease in liquid yield to approximately 87%, accompanied by an increase in gas yield to around 11%.¹²⁸

The choice of solvents in these processes enables milder operational conditions due to their low critical points, offering potential advantages in energy savings and reduced operational costs at an industrial scale. Ahmad *et al.* (2020)¹⁰⁷ highlighted that oil yields, having calorific values around 40.9 MJ/kg, are heavily influenced by the solvent to polystyrene ratio. The optimal weight ratio of 0.5:1 ethanol to polystyrene produced the highest calorific value, while an increase to 3:1 correlates with a gradual decrease to 34.93 MJ/kg. Seshasayee and Savage (2020)¹²⁰ noted that the higher heating value (HHV) is dependent on temperature, reaching a maximum of about 45 MJ/kg at 400°C. Notably, the liquefaction of polystyrene in water resulted in low yields of C₅–C₁₀ hydrocarbons, approximately 3–5%, at processing temperatures of 350°C and 425°C.

2.5.1.5. Polyethylene terephthalate (PET)

PET, a commonly used thermoplastic polyester, displays outstanding mechanical and thermal properties, making it a prevalent choice in the production of clothing fibers, liquid containers, X-ray film, and magnetic recording tape. A significant portion of recycled PET finds application in beverage packaging and carpet manufacturing. However, the stable and minimally biodegradable nature of PET, coupled with its widespread use, has led to the accumulation of PET waste, necessitating disposal through conventional methods.¹²⁹

In response to the environmental challenges posed by PET waste, there is a growing interest in the liquefaction of PET as a means of converting it into valuable products. Seshasayee and Savage (2020)¹²⁰ investigated the liquefaction of PET using water under supercritical conditions (450°C, 25 MPa) for a duration of 30 minutes. The results revealed a maximum oil yield of 16%, with the majority (72%) remaining in solid form. The substantial solid yield is attributed to the low volatile content of PET, as determined through proximate analysis. Additionally, the aromatic character of PET contributes to the formation of a stable char structure, further enhancing the solid yield.¹⁰⁸ Similar findings were reported by Pedersen and Conti (2017)¹³⁰, with solid yields reaching up to 68.5%.¹³⁰ Liquefaction of PET at sub-critical conditions (300°C) resulted in a further reduction in oil yield, down to 9.1%, compared to processing at the supercritical state.¹³¹

Contrastingly, Williams and Slaney (2007)¹¹⁸ observed a higher oil yield during PET liquefaction using hydrogen gas. Their experiment yielded up to 27% oil at 500°C and a 30-minute reaction time, achieving an overall 59% conversion of the plastic. The higher heating value (HHV) of the liquid product obtained from PET processing falls within the range of 29–32 MJ/kg at temperatures ranging from 350°C to 450°C, with approximately 20% of the hydrocarbons generated falling within the gasoline range (C₅–C₁₀).¹²⁰ These studies indicate the potential of PET liquefaction as a promising

method for addressing PET waste-related environmental concerns and converting it into valuable resources.

2.5.1.6. Polycarbonate (PC)

Polycarbonate, an amorphous thermoplastic, is rapidly gaining prominence as one of the fastest-growing engineering plastics due to its distinctive properties. Its widespread applications in the engineering sector stem from its outstanding impact strength, toughness, favorable electrical properties, and dimensional stability. Additionally, polycarbonate exhibits excellent transparency, making it desirable for applications involving aesthetic features such as impact-resistant glass windows.

However, the conventional processing methods of polycarbonate waste, as documented in previous literature, often result in a substantial fraction of non-biodegradable solid products. To address this concern, converting polycarbonate into a value-added liquid product has emerged as a promising alternative. Pedersen and Conti (2017)¹³⁰ conducted research on polycarbonate liquefaction at 400°C for a 15-minute reaction time in supercritical water, reporting a significant oil yield of up to 99.8% with no detectable solid product. Zhao *et al.* (2018)¹³², employing a processing condition of 350°C and 60 minutes reaction time, disclosed a slightly lower oil yield of about 93%, accompanied by a minimal gas yield.

Shortening the reaction time to 20 minutes resulted in an observation of approximately 75% oil production from polycarbonate liquefaction, with a higher gas yield reaching up to 12%.¹¹¹ Notably, polycarbonate has the potential to generate bisphenol A (BPA), a substance known to be harmful to human health, prompting research to focus on BPA yield under different reaction conditions. Sato *et al.* (2005)¹³³ estimated a BPA yield of about 40% when polycarbonate was liquefied at 300°C in the presence of cyclohexanol. A similar yield was reported by Huang *et al.* (2011)¹³⁴ using water as the reaction medium at the same temperature. However, Jie *et al.* (2006)¹⁰³ observed a significant increase in BPA yield during liquefaction at the supercritical state, reaching a maximum of 90% when processing polycarbonate at 300°C in ethanol solvent.

In terms of thermal liquefaction, polycarbonate yields liquid products with a slightly lower higher heating value (HHV) of 29–33 MJ/kg compared to gasoline, attributed to the high oxygen content of the feedstock.¹²⁰ The hydrocarbons yield within the C₅–C₁₀ range shows a maximum of about 21% at 450°C. These findings highlight the potential for polycarbonate liquefaction to not only address waste-related concerns but also yield valuable liquid products with diverse applications.

2.5.2. Factors affecting the conversion, and product yield and composition during plastic liquefaction

2.5.2.1. Temperature and heating rate

Temperature plays a crucial role in determining the conversion efficiency of plastic waste into liquid and gas products and influencing the characteristics of the resulting yield. During the liquefaction process, the applied temperature impacts the kinetic energy available for breaking long-chain polymer bonds. Higher temperatures provide increased kinetic energy, accelerating the scission of polymer chains into smaller hydrocarbons, thus enhancing product yield. Conversely, low

temperatures lack the energy required for breaking polymer bonds, resulting in minimal or low overall conversion.

The literature reports the lowest liquefaction temperature for plastic as 162°C¹¹², while the highest recorded temperature is 550°C.¹¹⁷ The optimal processing temperature is heavily dependent on the polymer type, solvent, and catalysts used. Research indicates an increase in oil production with rising temperature up to a certain limit, beyond which the liquid yield begins to decline.^{107, 115, 117, 125} Ahmad *et al.* (2020)¹⁰⁷ studied polystyrene liquefaction in ethanol solvent at temperatures ranging from 290–370°C. Below 310°C, the oil yield is negligible, rising significantly from 43.4% to 84.7% between 330°C and 350°C, before stabilizing at 370°C. A similar temperature effect is noted by Zhang *et al.* (2007)¹¹⁷, using polyethylene in supercritical water, with a significant increase in oil yield from 520–530°C, followed by a decline due to secondary cracking reactions converting liquid products to gas.

The processing temperature range for each plastic type is commonly determined through thermogravimetric analysis (TGA). It's important to note that the difference in reaction environments during TGA and supercritical fluid processing may alter the degradation temperature range. Due to the superior qualities of supercritical fluids, the appropriate liquefaction temperature could be lower than that indicated by TGA.

The optimal liquefaction temperature for polystyrene is observed to be within 300°C to 400°C, achieving an oil yield exceeding 85%.^{107, 120, 128, 135, 136} PE liquefaction by various researchers suggests an optimum processing temperature of 425–460°C using organic and inorganic solvents.^{110, 115, 116, 124} Polypropylene shows a similar optimal processing temperature of 425–450°C with over 90% liquid yield.^{124, 125} However, these conclusions are drawn from a limited number of research papers, and the best processing temperature for PET is yet to be determined, as its current liquefaction yields an insignificant amount of oil (average value of 12.4%).^{111, 118, 120, 130, 131} Liquefaction of polycarbonate requires a lower optimum processing temperature of 300–350°C compared to other plastic types.^{132, 133}

The energy recovery from the liquefaction process can be calculated using the equation:¹²⁰

$$\text{Energy recovery (\%)} = \% \text{ oil yield} \frac{HHV_{oil}}{HHV_{initial plastic}}$$

For example, the liquefaction of PP in a water solvent shows an increase in energy recovery from 0.64–28.7% with a temperature increase from 350–425°C at a 30-minute reaction time. However, a further increase to 450°C results in a decrease in recovery to 12.5%. Liquefaction of PET exhibits a slightly different trend, with an increase in temperature from 350 to 400°C showing an insignificant change in energy recovery (about 7–9%). Higher energy recovery, up to 31.3%, is observed at 425°C, reaching a maximum of 33.4% at 450°C. In contrast, the energy recovery of polystyrene decreases from 87.7% to 34.4% with an increasing temperature from 350 to 450°C.¹²⁰

To assess the impact of heating rate on the oil yield in hydrothermal liquefaction (HTL), Seshasayee and Savage (2020)¹²⁰ conducted experiments on polypropylene (PP), polyethylene terephthalate (PET), polystyrene (PS), and polycarbonate (PC) at 425°C for 30 minutes. The experiments were initially performed in a 10 ml reactor and subsequently in a 4 ml reactor, where the smaller reactor

was expected to have a higher heating rate. By comparing the oil yields between the two reactors, the researchers aimed to analyze the effects of different heating rates. Their findings led them to conclude that variations in heating rate did not significantly impact the anticipated oil yields for any of the plastics.¹²⁰

2.5.2.2. Pressure

Two methods are used to study the impact of pressure in the liquefaction process: by monitoring the corresponding pressure due to elevated temperature or by adjusting the solvent quantity in the reactor. The pressure applied in plastic liquefaction varies widely, ranging from 0.7 MPa^{102, 113} to 32 MPa¹³⁷. The selection of the processing pressure is crucial and heavily relies on the type of solvents utilized. It is noteworthy that the critical points of solvents play a pivotal role, as surpassing into the supercritical phase alters fluid properties. Water, for instance, transitions from a polar to a non-polar solvent in the shift from subcritical to supercritical states. In the supercritical condition, water exhibits a low dielectric constant, rendering it less polar and capable of dissolving non-polar organic compounds into a single phase.^{115, 117, 120} Additionally, the Hansen solubility parameter can predict the compatibility between the components.

In the methanolysis liquefaction of PET plastic, conventional pressures range from 8.5 MPa to 20 MPa, slightly higher than methanol's critical pressure ($T = 240^{\circ}\text{C}$, $P = 7.87\text{ MPa}$), indicating a reaction in a supercritical condition. Kim *et al.* (2001)¹³⁸ depolymerized PET in a methanol solvent at 300°C , reporting a high dimethylterephthalate (DMT) yield of approximately 87% at 10 MPa pressure. Conversely, Yang *et al.* (2002)¹³⁹ demonstrated a significantly lower DMT yield of 61.33% at 11 MPa and 260°C . Similar results were obtained at a higher pressure, with PET liquefaction at 20 MPa using methanol resulting in up to 80% (DMT) at 120 min.¹⁴⁰ However, at 14.7 MPa, a maximum of about 97% DMT yield was achieved in a 60-minute reaction.¹⁴¹ The active ester linkages in PET interact effectively with supercritical methanol, facilitating the depolymerization process. Notably, pressure has a low influence on product yield once it surpasses the critical pressure of the solvent.¹³⁹

The impact of pressure on the liquefaction process of polystyrene was also investigated in various studies. Hwang *et al.* (2001)¹²⁴ reported up to 75.53% conversion of polystyrene feedstock at 3 MPa pressure using supercritical n-hexane solvent (critical point, $T = 234.5^{\circ}\text{C}$, $P = 3.03\text{ MPa}$). Increasing the pressure to 7 MPa showed minimal conversion improvement, reaching up to 84.64%. Jie *et al.* (2008)¹⁴² achieved a comparable output using supercritical toluene solvent (critical point, $T = 318.7^{\circ}\text{C}$, $P = 4.11\text{ MPa}$), where an increase in pressure from 4.5 MPa to 10.5 MPa raised the conversion by approximately 6%. Kwak *et al.* (2006)¹³⁷ liquefied polystyrene in water solvent, achieving full conversion at 32 MPa pressure. The utilization of methanol solvent at 10 MPa resulted in a conversion of up to 92%.¹⁴³ On the other hand, liquefaction of PS using ethyl cyclohexane at 5 MPa almost led to complete conversion.¹²⁸ The substantial dependence of PS conversion on the critical points of each solvent used is evident across a wide pressure range.

2.5.2.3. Solvent

The use of solvents in plastic waste liquefaction has garnered attention due to their ability to lower reaction temperatures. Solvents enhance mass and heat transfer during the reaction, reduce the viscosity of the liquid product, and result in a higher quality oil yield.¹⁰⁵ Water, being cost-effective, clean, non-harmful to humans, and serving as both reactant and catalyst in plastic processing, is the

most commonly used solvent and widely considered the preferable choice.¹⁴⁴ The effectiveness of water as a solvent depends on its state, whether subcritical or supercritical ($T = 374^{\circ}\text{C}$, $P = 22 \text{ MPa}$). Supercritical fluid, possessing higher density and better solute dissolution capabilities than subcritical solvents, offers distinct advantages.¹³⁹

Liquefaction using water as a solvent yields a liquid range between 0% and 90%, depending on the type of plastic and other processing conditions. The highest oil yield of 91.4% is achieved in the liquefaction of HDPE using water at supercritical conditions¹¹⁵, while subcritical water liquefaction results in over 90% solid yield with minimal oil.¹¹¹ A slight change in conditions can significantly alter product distribution, regardless of constant additional parameters. Similar trends are observed for PP liquefaction in water, with supercritical processing allowing up to 91% oil yield¹²⁵, while subcritical water liquefaction yields only around 27% oil.¹⁴⁵

Researchers have explored the use of various solvents to study their effects on plastic waste conversion. Besides water, organic solvents such as alcohols, alkanes, ketones, and aromatic solvents have been investigated, including their reaction mechanisms for clarity on polymer bond scission pathways. Notably, alcohol solvents like ethanol and methanol, with lower critical points ($T = 243^{\circ}\text{C}$, $P = 6.37 \text{ MPa}$ and $T = 240^{\circ}\text{C}$, $P = 7.87 \text{ MPa}$, respectively) compared to water (374°C , 21.77 MPa), allow for milder liquefaction conditions, leading to reduced energy consumption. Huang *et al.* (2011)¹³⁴ examined the selectivity of Bisphenol A (BPA) during polycarbonate liquefaction and found approximately 40% selectivity using water solvent at 300°C . Jie *et al.* (2006)¹⁰³, however, demonstrated higher BPA selectivity of 90% using ethanol at 290°C , achieved through random scission and ester exchange methods.

Supercritical water liquefaction of PC, around 400°C , results in the absence of BPA due to its instability, forming intermediate compounds that subsequently degrade into phenol, isopropylphenol, and isopropenylphenol compounds. Co-liquefaction of plastic with a specific solvent may create a synergistic effect. For example, polystyrene exhibits a maximum oil yield of 97.9% through liquefaction in toluene compared to other aromatic solvents.¹³⁶ Different solvents within the same group provide unique mechanisms when reacting with a type of plastic. Ke *et al.* (2005)¹³⁶ proposed the effect of secondary reactions of styrene on the formation of side products, with supercritical solvents of p-xylene and ethylbenzene showing 35–42% styrene conversion compared to benzene and toluene solvents, which exhibit 2.4–4.0% conversion in a closed system. Cyclohexane, ethyl cyclohexane, and ethanol as solvents produced an average liquid yield of 90.9%.^{107, 128, 135}

Researchers like Serrano *et al.* (2007)¹⁰⁵ have suggested selecting solvents based on their ability to donate hydrogen during the reaction. Solvents are classified based on the amount of weak C–H bonds compared to other types. Solvents with low hydrogen-donating capability, like 1-methylnaphthalene, contribute up to approximately 40% of hydrocarbons within the C_5 – C_{20} range during HDPE liquefaction. Poor hydrogen-donating solvents progress by slow hydrogen transfer, allowing the degradation of plastics into smaller hydrocarbons. In contrast, good hydrogen-donating solvents facilitate faster hydrogen transfer, preventing the formation of lower molecular weight hydrocarbons.¹⁰⁵ Brand *et al.* (2013)¹⁴⁶ emphasize the superior hydrogen-donor properties of supercritical alcohol compared to sub- and supercritical water. Supercritical alcohol generation of

hydrogen aids in breaking down feedstock, reducing oxygen content, suppressing repolymerization, and mitigating char/tar formation during the process.

2.5.2.4. Reaction time

Existing research on the liquefaction of plastic waste has affirmed the significant impact of reaction time on the transformation into liquid and gas products. Residence time, defined as the duration during which plastic reacts after reaching the desired temperature, aims to achieve complete conversion of plastic waste. In most reviewed literature, heating and cooling periods are typically disregarded in determining reaction time due to their minimal effect on yield. However, it is crucial to consider these aspects, as the heating process takes time, and reactions between plastics and the fluid in the reactor occur within this period.

The shortest reported reaction time for plastic liquefaction is 0 minutes, indicating that the process is completed immediately upon reaching the desired temperature, while the longest residence time extends to 24 hours.¹⁰⁶ Generally, an increase in reaction time contributes to a higher conversion of plastic waste into liquid and non-condensable gas. However, this parameter is constrained by the influence of temperature. At lower temperatures, oil and gas yield increases with prolonged reaction time up to a threshold, after which secondary reactions cause a decline in products. At high temperatures, rapid conversion occurs instantly, and extending the reaction time results in an invariant product distribution.

Studies by Ahmad *et al.* (2020)¹⁰⁷ on equivalent polystyrene to ethanol ratio at 350°C reveal a steep increase in oil yield from 56% to 83.3% within the first 45 minutes, with a marginal variation afterward. Chen *et al.* (2019)¹²⁵ compared residence time influence on the oil yield trend of polypropylene at different temperatures. At 425°C, oil production increased significantly from 25% to 91% as reaction time extended from 30 to 120 minutes. At 450°C, maximum oil yield is achieved within the first 30 minutes, with minimal fluctuation upon further extension of time.

The residue decreases due to conversion into liquid, and gas yield increases with prolonged processing periods. Reaction time in plastic liquefaction significantly affects energy recovery. For polypropylene (PP) at low temperatures (350°C and 400°C), energy recovery increases between 42% and 102% when reaction time extends from 30 to 60 minutes. At higher temperatures (425°C and 450°C), total energy recovery decreases by 3–14% with increased reaction time. In contrast, for PET, PC, and PS, increasing reaction time decreases energy recovery across all temperature ranges. For example, PC liquefaction at 350°C shows 47.7% energy recovery at 30 minutes, which reduces to approximately 24% at 60 minutes.

2.5.2.5. Solvent-to-plastic ratio

In addition to the choice of solvent, the ratio of solvent to plastic plays a crucial role in plastic liquefaction, as it affects the breaking of polymer bonds into smaller hydrocarbons, a process limited by the presence of solvents. According to literature findings, the lowest solvent to plastic weight ratio is 0.25:1 when using ethanol and polystyrene as feedstock¹⁰⁷, while the highest ratio used was 30:1, utilizing water with various plastic types as the initial material.¹⁴⁷ Liquefaction with a low amount of solvent follows a similar mechanism to thermal liquefaction.

A substantial amount of solvent favors random scissions and chain reactions.¹⁰⁴ Research indicates an increase in product yield with an increase in the solvent to plastic ratio during the liquefaction process. Ahmad *et al.* (2020)¹⁰⁷ achieved up to 86.4% oil from polystyrene processing at a 0.5:1 ethanol to plastic weight ratio. A further increase in the ratio to 4:1 showed only a slight increment in the oil yield to approximately 88%, employing cyclohexane as the solvent.¹³⁵ This showed that a higher amount of solvent enhances the liquefaction process. In contrast, Ahmad *et al.* (2020)¹⁰⁷ observed a decrease in liquid yield to 78.7% as the ratio increased from 0.5:1 to 3:1, indicating an optimum point. Beyond this optimum ratio, an increase in solvent leads to a decrease in oil production and an increase in gas yield due to the possibility of alkylation reactions.¹⁰⁷

A similar trend is noted in total product conversion at a higher solvent to plastic ratio. Jie *et al.* (2008)¹⁴² reported up to 76.2% conversion of polystyrene to oil and gas products at a 10:1 toluene to polystyrene weight ratio. The combination of adequate solvent and supercritical processing allows for higher conversion of plastics compared to conventional pyrolysis processes. The dissociation of PET into DMT is also influenced by the weight ratio of solvent to plastics. PET liquefaction in methanol solvent shows an increase in DMT yield as the weight ratio of solvent to plastic is raised from 3:1 to 6:1.¹³⁹ Further increase to 8:1 indicates a slower progress of DMT yield, reaching a maximum of 67%. Yang *et al.* (2002)¹³⁹ suggest that the optimal depolymerization ratio of PET is above 6:1 solvent to plastic ratio. This is supported by the research conducted by Kim *et al.* (2001)¹³⁸ with approximately 78% DMT yield at a 10:1 weight ratio.

Employing different ratios of solvent to plastic during liquefaction also affects the range of hydrocarbons produced in the product yield. Su *et al.* (2004)¹¹⁵ reported approximately 84% hydrocarbons within the C₇–C₁₈ range using a 2:1 solvent to plastic ratio for HDPE liquefaction. Conversely, increasing the weight ratio to 10:1 resulted in a decrease in hydrocarbon yield to approximately 75%. This was confirmed by Vicente *et al.* (2009)¹⁰⁴, albeit with a lower yield of 25% for hydrocarbons within the C₅–C₂₀ range. The variability in hydrocarbon yield is attributed to the use of different solvents.

2.5.2.6. Particle size

Exploring the impact of particle size on the product distribution is an additional aspect investigated in the plastic waste liquefaction process. Particle sizes are typically categorized into three groups: large, medium, and small. Large-sized plastic samples, typically measured in centimeters, have been studied by Kim *et al.* (2001)¹³⁸, who used 1 cm by 1 cm PET samples. They achieved a maximum DMT yield of 97.7% and an overall conversion of approximately 97% under specific processing parameters. Abdel-Raouf *et al.* (2013)¹²⁸ employed larger feedstock sizes, using chopped polystyrene with dimensions ranging between 2–4 cm, achieving over 95% styrene recovery and an overall plastic conversion of 96% under supercritical conditions.

Many researchers have focused on medium-sized samples, ranging from 2–6 mm in height and diameter, generating significant yields. Polystyrene liquefaction with dimensions of 2–3.3 mm led to nearly complete conversion, yielding up to 97.9% oil at temperatures ranging from 370 °C to 420°C.^{136, 137, 143, 148} The use of a broader plastic size range, from 2 mm to 5 mm, resulted in a slightly lower maximal oil yield of 86.4% at 350°C.¹⁰⁷ Hwang *et al.* (2001)¹²⁴ liquefied polypropylene plastic within the size range of 2.3 mm to 4.3 mm in supercritical acetone, achieving a 96% oil yield.

However, employing the same plastic dimensions in supercritical water yielded only 32% oil, highlighting the significant influence of the solvent type on oil yield.¹²⁰

Particle sizes less than 1 mm have also been examined. Aguado *et al.* (2007)¹²³ used HDPE with sizes <1 mm, achieving full conversion after a 420-minute reaction period. In contrast, Vicente *et al.* (2009)¹⁰⁴ conducted a similar liquefaction process with a shorter residence time of 300 minutes, obtaining a 99.8% conversion, indicating that particle size does not significantly impact plastic conversion. In conclusion, high conversion values and oil yields can be obtained regardless of the initial material's dimensions.

2.6. Co-liquefaction reviews and technologies

The growing concerns surrounding environmental sustainability have spurred increased research into innovative methods for waste management and resource utilization. Co-liquefaction, a process involving the simultaneous liquefaction of multiple feedstocks, has emerged as a promising avenue for addressing challenges related to both fossil fuel consumption and plastic waste disposal. This section of the literature review delves into the fundamentals of co-liquefaction, with a specific focus on the co-liquefaction of coal and plastic waste materials. By examining the synergistic effects and potential benefits of combining these diverse feedstocks, researchers aim to develop sustainable and efficient pathways for energy production, material recovery, and waste reduction.

Co-liquefaction involves the simultaneous treatment of different carbonaceous materials, such as coal, biomass, and/or plastic waste, in a common solvent or reaction medium. The process capitalizes on the complementary characteristics of the feedstocks, aiming to enhance overall conversion efficiencies and produce valuable liquid products. The key fundamentals of co-liquefaction lie in understanding the interactions between the diverse components during the thermochemical conversion process. The utilization of a common solvent, often water or organic solvents like alcohols or aromatic compounds, facilitates the blending of coal and other feedstocks, promoting efficient mass and heat transfer during the reaction. The co-liquefaction process typically operates at milder conditions compared to individual liquefaction processes for coal, thereby allowing for energy savings and improved process economics. Additionally, the synergistic effects arising from the co-processing of feedstocks contribute to a more favorable product distribution, including higher liquid yields and lower solid residues.

2.6.1. Co-liquefaction of coal and biomass

The co-liquefaction of coal with biomass, involving agricultural and forestry residues along with cellulosic waste materials, has attracted growing attention in research. This interest is fueled by rising concerns about greenhouse gas emissions and environmental issues associated with fossil fuels. An additional motivation for exploring co-liquefaction is the potential synergistic effects observed between biomass and coal during the process, as demonstrated by various studies.¹⁴⁹⁻¹⁵²

These investigations have demonstrated positive and synergistic outcomes in terms of enhanced yields and improved quality, such as a favorable H/C ratio in liquid products derived from coal. Particularly noteworthy are findings from studies conducted under milder temperature and pressure conditions. For instance, Matsumura *et al.* (1999)¹⁴⁹ explored co-liquefaction of biomass and coal in supercritical water at 673K (400°C) and 25 MPa, revealing beneficial effects due to *in situ* hydrogen generation from biomass during supercritical water gasification. This resulted in increased coal conversion and improved yields and quality of liquefaction products. Altieri and Coughlin (1987)¹⁵⁰ delved into the co-liquefaction of bituminous coal (Illinois No. 6) with lignin at 400 °C in tetralin, resulting in a substantial increase in benzene-soluble yield compared to coal alone. Similar synergistic effects were observed in the co-liquefaction of lignin and coal in research by Lalvani *et al.* (1991)¹⁵¹. Other co-liquefaction studies under different conditions were performed, such as those by Karaca and Bolat (2000)^{153, 154} on Turkish lignite with cellulose waste materials in tetralin, and Rafiqul *et al.* (2000)¹⁵⁵ on lignite with sawdust at 325°C. They concluded that improved total conversion and increased liquid quality by processing coal with waste materials could be obtained.¹⁵⁴

Furthermore, co-liquefaction of microalgae with coal, as studied by various researchers, demonstrated significant conversion and oil fraction yields, especially when utilizing catalysts.¹⁵⁶ Stiller *et al.* (1996)¹⁵⁷ investigated co-liquefaction of coal with various biomass materials at 350°C under 6.9 MPa hydrogen pressure (cold) in tetralin, revealing higher overall conversion and liquid yields compared to individual coal or biomass liquefaction.

The co-liquefaction of coal with biomass appears promising as it allows for the moderation of coal liquefaction reaction conditions. The synergistic effects between coal and biomass contribute to enhanced liquid product quality and yields. Despite these positive findings, the underlying mechanism behind the synergistic effects in co-liquefaction requires further clarification, emphasizing the need for continued research in this area.

2.6.2. Co-liquefaction of coal and plastic materials

In recent years, co-liquefaction research has gained much attention, focusing on the simultaneous treatment of coal and waste materials such as plastics. This approach aims to address environmental challenges associated with both fossil fuel utilization and plastic pollution. Studies have explored various combinations of coal and plastic waste, employing different solvents and processing conditions to optimize the co-liquefaction process. Investigations into the co-liquefaction of coal and plastic waste have demonstrated the potential for enhanced oil yields, improved energy recovery, and reduced residue generation. Researchers have examined the influence of parameters such as temperature, pressure, solvent type, and feedstock composition on the co-liquefaction outcomes.

Wang and Chen (2004)¹⁵⁸ focused on the direct liquefaction of various plastics (PE, PP, PS) and Chinese coal (Xianfeng lignite) at 410–450°C under 10 MPa H₂ pressure with a 60-minute reaction time in tetralin. Co-liquefaction experiments were conducted using a 1:1 coal-to-plastic ratio and a molybdenum-based catalyst (FAMo). They found that HDPE was the most challenging plastic to convert at relatively high temperatures (430°C), while LDPE, PP, and PS showed 100% conversions with oil yields of 69.4–79.9%. The co-liquefaction of coal–plastic mixtures showed synergistic effects, with approximately 98% conversion and high oil yields (over 70%). In addition, lower hydrogen consumption was observed when compared to the liquefaction of coal alone. The FAMo catalyst enhanced total conversion and oil yield (by approximately 10%) during co-liquefaction. It was also found that the conversion increased with a higher fraction of plastic in the mixture, indicating the role of plastic as a possible hydrogen donor solvent for coal liquefaction.

Feng *et al.* (1996)¹¹³ conducted a similar study focusing on medium and high-density polyethylene (MDPE and HDPE), and a waste plastic with a subbituminous coal (Black Thunder). In their research, various parameters such as catalyst type, temperature, gas, pressure, time, and solvent were systematically varied. Four types of catalysts were employed, namely a commercial HZSM-5 zeolite catalyst, and three synthesized in-house catalysts. The study found that for the direct liquefaction of plastics alone, solid acid catalysts like HZSM-5 or Al₂O₃-SiO₂ significantly enhanced oil and total conversion values. Temperature requirements varied, with PE requiring temperatures of 430°C or higher to obtain a 70% oil yield and 90% conversion, while PP exhibited excellent yields at 420°C. It was also found that the use of a waste oil as the solvent or no solvent yielded higher results compared to tetralin. Co-liquefaction experiments involving plastic-coal mixtures revealed optimal outcomes with tetralin or tetralin-waste oil mixtures as solvents. The presence of HZSM-5 or Al₂O₃-SiO₂-ferrihydrite catalysts increased oil yields and total conversion by approximately 10% at 460°C.

Regarding the co-liquefaction experiments conducted at 430°C, PP-coal mixtures showed substantial higher oil yields (~70%) and total conversion (>95%) compared to PE-coal mixtures (~40% oil yields and 70% total conversion). The results indicated that the solid acid catalysts, especially HZSM-5 zeolite, significantly improved oil yields during plastic liquefaction. Co-liquefaction of coal-plastic mixtures exhibited synergistic effects, leading to enhanced oil yields.

In the earlier work of Taghiei *et al.* (1994)¹⁵⁹, they studied the direct liquefaction of various plastics (PE, PP, and PET), mixed plastic waste, and the co-liquefaction with three different coals of varying rank (e.g., bituminous, subbituminous, and lignite). It was found that solid acid catalysts (like HZSM-5 zeolite) were highly active during plastic (HDPE, MDPE, PP, and PET) liquefaction, yielding 80–95% oil yields and total conversions of 90–100% at 420–450°C under 5.5 MPa H₂ pressure in tetralin and waste oil. Co-liquefaction of coal-plastic mixtures exhibited synergistic effects, with enhanced oil yields exceeding 80% during PE and lignite coal (3:1 ratio) liquefaction at 450°C and total conversions exceeding 90%. Co-liquefaction experiments of the bituminous coal with waste plastic reported oil yields and total conversion values exceeding the results obtained from the waste plastics and coal separately, indicating possible synergistic effects. Similar results were found when subbituminous coal was co-processed with waste plastics. The choice of solvents significantly affected liquefaction yields, with waste oil performing better than tetralin for plastics. In addition, it was found that the HZSM-5 catalyst was significantly more active during plastic liquefaction experiments conducted at moderate temperatures (420–430°C) compared to iron-based catalysts (including iron sulfides) which are effective in coal liquefaction. Iron-based catalysts become more effective at 450°C for plastic liquefaction. A later study by Huffman *et al.* (1995)³⁴ had similar outcomes during direct liquefaction of subbituminous coal (Black Thunder) with waste plastics, MDPE, HDPE, PP, and PET.

Wang and Chen (2002)¹⁶⁰ investigated the active sites of iron-based catalysts during co-liquefaction experiment conducted at 450°C using coal and low-density polyethylene (LDPE) in a 10 MPa H₂ atmosphere and tetralin as the solvent. Various iron-based catalysts were explored, including sulfur-promoted iron oxide, ferrous sulfide, ferrous sulfate, and pyrite. It was found that the sulfur-promoted iron oxide catalyst showed sulfate species as the active sites during co-liquefaction. Ferrous sulfate exhibited sufficient catalytic activity during co-liquefaction, also suggesting the active sites of the sulfate species. The study emphasized the importance of understanding the active sites of iron-based catalysts in the co-liquefaction of coal with LDPE.

Research conducted by Pinto *et al.* (2019)¹⁶¹ focused on the co-liquefaction of coal with carbonaceous wastes such as plastics (PE, PP, and PS), used tires, and biomass to produce liquid fuels. In addition, the coal was blended with 1 wt% molybdenum. Liquefaction tests were conducted in a H₂ atmosphere (3.45 MPa, cold), at 420°C using a reaction time of 60 minutes. The results indicated that waste materials enhanced the liquefaction process and subsequently improved liquid yields and oil quality. Coal blended with PS wastes led to the highest liquid yield (74%) and total conversion (88%). Furthermore, the addition of PE promoted the formation of linear alkanes (aliphatic components), whereas PS promoted the formation of aromatic compounds. It was found that tetralin enhanced liquid yields during the liquefaction of coal with plastics, while used tires led to higher solid yields.

It can be concluded that the choice of solvent and catalyst significantly influences liquefaction product yields, emphasizing the need for tailored conditions. In addition, the research by Wang and

Chen (2002)¹⁶⁰ highlighted successful co-liquefaction experiments involving coal and plastic waste mixtures. This study indicated synergistic effects between coal and plastic, resulting in increased oil yields and reduced hydrogen consumption. HZSM-5, FAMo, and iron-based catalysts have proven to enhance total conversion and oil yield.^{34, 113, 158, 159} The results obtained from Feng *et al.* (1996)¹¹³ emphasized the effectiveness of solid acid catalysts for plastics liquefaction, revealing synergistic effects in coal-plastic co-liquefaction. Similarly, the work by Huffman *et al.* (1995)³⁴ demonstrated the high activity of HZSM-5 zeolite catalyst for plastics liquefaction and co-liquefaction of coal with plastics. Additionally, Pinto *et al.* (2019)¹⁶¹ explored co-liquefaction of coal with various wastes, including plastics and used tires. The presence of plastics, especially polyethylene (PE), has been shown to improve liquid yields and conversions. And tetralin, a hydrogen-donor solvent, further enhanced the co-liquefaction process, indicating its potential for improving liquid yields.

2.7. Practical implications of co-liquefaction and chapter conclusions

While co-liquefaction holds promise, several challenges and opportunities need consideration for its successful implementation. The economic viability of large-scale co-liquefaction plants must be thoroughly assessed, considering factors such as feedstock availability, plant size, and return on investment. Optimization of process conditions, including temperature, pressure, and type of catalyst, is crucial to achieving maximum efficiency. Moreover, diverse feedstock combinations should be explored to assess the adaptability of co-liquefaction to different waste materials. The environmental impact of co-liquefaction processes, including the treatment of solid residues and potential emissions, must be carefully evaluated.

Future research in co-liquefaction should focus on refining and optimizing the process for enhanced economic and environmental performance. Exploring novel catalysts and solvents, as well as their interactions, may uncover synergistic effects that further improve liquid yields and overall efficiency. Research efforts should extend to investigating the potential of co-liquefaction of other waste materials beyond plastics and tires, broadening the applicability of this approach. The integration of co-liquefaction into a circular economy framework, where waste materials are continuously recycled and repurposed, holds significant promise. Collaboration between industry, academia, and governmental bodies is essential to drive innovation, address challenges, and facilitate the transition from laboratory-scale studies to large-scale implementation.

In conclusion, co-liquefaction represents a promising avenue for converting coal and plastic waste into valuable liquid fuels. This literature study provides a comprehensive understanding of the fundamentals of coal and plastic liquefaction, recent advancements, and challenges associated with co-liquefaction. The economic feasibility, environmental impact, and scalability of co-liquefaction processes should be carefully assessed to ensure the successful integration of this approach into waste management strategies. With continued research and development, co-liquefaction has the potential to contribute significantly to a sustainable and circular approach to waste utilization and energy production.

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CHAPTER 3 DIRECT LIQUEFACTION OF SOUTH AFRICAN VITRINITE- AND INERTINITE-RICH COAL FINES

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Journal: ACS Omega
Accepted: 29 January 2024
Published: 29 February 2024
DOI: 10.1021/acsomega.4c00602

Abstract

In this investigation, coal fines enriched with inertinite were used for direct liquefaction experiments. For comparison, a vitrinite-rich coal typically utilized in coal-to-liquid processes was also employed. To assess the impact of mineral matter content, demineralization was used to remove most of the inorganic constituents. The findings revealed that the inertinite-rich coal exhibited lower liquefaction conversions due to a reduced proportion of reactive macerals and elevated levels of inorganic mineral matter. These conversion values exhibited a strong correlation with the quantity of reactive macerals present in the parent coals. For the inertinite-rich coal, the presence of inorganic mineral matter impeded the liquefaction process but facilitated the CO₂ gasification reactions of the derived chars. To evaluate their potential in gasification processes, CO₂ gasification experiments were conducted and the reactivities and apparent gasification activation energies of both coal chars, liquefaction residue chars, and pre-asphaltene and asphaltene (PAA) chars were calculated. These calculations were carried out using the random pore model (RPM) and volumetric reaction model (VRM). The chemistry, reactivity, and kinetics of residue gasification conversion are not thoroughly understood, yet they hold significant importance in optimizing syngas production within gasification processes. The findings from this work highlight significant differences in liquefaction conversion values, product distribution, and composition. These differences are influenced by factors such as maceral composition, inorganic mineral matter content, hydrogen-donor capabilities of the solvent, and liquefaction reaction temperatures. Additionally, these variables affect the CO₂ gasification reactivity of liquefaction solid residue chars.

Keywords: Direct liquefaction; coal fines; macerals; demineralization; H-donor solvent; char CO₂-gasification; gasification kinetics.

3.1. Introduction

South Africa, one of the leading global coal producers and exporters, plays a crucial role in the world's energy demand. The coal beneficiation process, however, leads to substantial environmental detriments, notably the generation of disadvantageous residues such as dust and fines.^{1, 2} The accumulation of these fines raises grave ecological concerns, including but not limited to acid mine drainage (AMD), groundwater contamination, atmospheric pollution, and susceptibility to spontaneous combustion.¹ Consequently, the coal beneficiation operations in South Africa yield substantial amounts of coal fines, around 60 Mt per annum, which are disposed of in large stockpiles, thereby precipitating noteworthy environmental predicaments.³

Direct coal liquefaction (DCL) involves the breakdown of a coal's macromolecular structure through the addition of a solvent under moderate temperatures and pressures, yielding liquid fuels. The resulting residues from this process are typically used in coal-to-liquids (CTL) technologies.⁴ The purpose of this process is to produce hydrocarbon fuels having a hydrogen-to-carbon ratio of 1.8–2.5.⁵ This is achieved through the addition of hydrogen into the system to participate in hydrogenation reactions, subsequently removing carbon and oxygen, in the form of CO, CO₂, or H₂O, from the macromolecular structure of coal. During this process, large polycyclic aromatic hydrocarbons (PAHs) are converted into smaller aromatic and/or aliphatic compounds that predominantly constitute petroleum products. The process also produces undesired products like water and gaseous hydrocarbons, including methane, ethane, and propane, that consume costly hydrogen for the generation of non-targeted compounds.⁵

The DCL process is a specific approach that incorporates hydrogenation, leading to the dissolution of coal's organic structure into soluble products.^{4, 6} The fundamental concept of this process is widely recognized to follow the free radical mechanism. This mechanism involves the cleavage or cracking of coal molecules, yielding fragments which are commonly referred to as free radicals. These free radicals then undergo hydrogenation, facilitated by the presence of hydrogen, leading to the formation of lighter products such as oil and gas. Conversely, under conditions where the availability of hydrogen for donation is insufficient, the larger radicals tend to condense through undesirable repolymerization and recombination reactions, resulting in the formation of unwanted residues such as tars and cokes containing large, unreactive polycyclic aromatic structures.^{5, 7, 8} In addition to the solvent's most crucial role for hydrogen donation, the solvent acts as a carrier for coal particles and facilitate heat transfer.^{5, 8} This transformation of the macromolecular network occurs at moderate temperature and pressure, typically within the range of 400 to 455°C and at 69 to 172 bar, facilitated by the presence of a solvent.^{5, 6, 9} High pressures in coal liquefaction processes are applied to accelerate reactions, enhance solubility, allow cracking of molecules, minimize gas production, increase yields, and improve the quality of the resulting liquid products.¹⁰ The solubilized products, which is predominantly comprised of aromatic compounds, can be further upgraded using conventional petroleum refining methods, such as hydrotreating, to meet the final specifications of liquid products.^{6, 8, 11}

Coal liquefaction plays an important role in the production of liquid fuels and other petroleum products, particularly for countries lacking crude oil reserves like South Africa. Notably, liquefaction solid residues account for approximately one-third of the coal input, and their utilization is important in reducing the overall cost of the liquefaction process.^{7, 12} Managing the solid waste

generated by the chemical industry has gained much attention, with coal liquefaction residues representing about 25–30% of the feed coal.¹² The residues generated through liquefaction is comprised of not only unreacted coal macerals and intrinsic mineral components but also residual oil, as well as asphaltenes and pre-asphaltenes (PAA's).¹³ Employing thermal conversion through gasification presents an economically viable solution to improve the process output. Nevertheless, the high moisture contents of such feedstocks pose technical and conversion efficiency limitations on direct gasification. To address these challenges and enhance feedstock properties such as energy density and structural features, hydrothermal carbonization serves as a viable pretreatment method.¹² These residues contain significant amounts of carbon, hydrogen, inorganic substances, and spent catalysts. Increasing concerns are emerging regarding the disposal of residues and its detrimental environmental impact. Therefore, both economic and environmental considerations will encourage the recovery of higher-value, lighter products from direct liquefaction residues. The aspiration here is to produce valuable carbon products through residue conversion that can be effectively utilized.^{4, 13} Gasification of these residues offers the potential to produce syngas, a versatile intermediate used in the production of liquid fuels and chemicals through Fischer–Tropsch (FT) synthesis. Moreover, if hydrogen (H_2) is separated from the syngas, it can be re-used in the DCL process to hydrogenate the recycled solvent, thus reducing operational costs.¹⁴

In this investigation, coal liquefaction experiments of South African vitrinite and inertinite-rich coal were conducted in an autoclave reactor under an inert atmosphere utilizing tetralin as a hydrogen donor solvent at 400, 425, and 450°C. The product yield fractions were quantitatively and qualitatively examined using standard and advanced analytical techniques. In addition, the gasification reactivities of the coals and resultant residue chars were examined using thermogravimetric analysis (TGA). Proximate and ultimate analyses, Fourier-transform infrared spectroscopy (FTIR), surface area characterization, and X-ray diffraction (XRD) analyses of the residues were performed to characterize the properties of the residues and evaluate their roles during CO_2 gasification. These results will determine the potential uses of liquefaction solid residues in gasification processes. Furthermore, the effect of mineral matter contents during the gasification of the coal and liquefaction residue chars were evaluated by demineralization methods.

3.2. Experimental

3.2.1. Materials

Highveld inertinite-rich fine coal filter cake (IR) and a seam 4 vitrinite-rich (VR) coal from the Witbank coalfields (a typical coal used in coal to liquid processes in South Africa) were used as the raw feed material in this study. The pulverized ($-300\ \mu\text{m}$) samples were dried at 100°C for 24 hours to reduce the inherent moisture content in the samples. Both coals were classified as bituminous medium rank C coals. The coal samples were characterized using the methods summarized in **Table 3-1**.

Table 3-1. Characterization of the coal and demineralized coal samples.

Properties	Method of analysis	VR	VRD	IR	IRD
<i>Proximate analysis (wt.%, a.d.)</i>					
% Inherent moisture content	ISO 11722:1999	7.6	2.9	4.5	2.9
% Ash yield	ISO 1171:2010	12.4	0.7	28.3	1.1
% Volatile Matter	ISO 562:2010	31.8	35.8	23.8	29.2
% Fixed carbon	by difference	48.2	60.6	43.4	66.8
Fuel Ratio	FC/VM	1.5	1.7	1.8	2.3
Gross Calorific Value (MJ.kg^{-1})	ISO 1928:2009	25.4	29.6	20.3	28.5
<i>Ultimate analysis (wt.%, d.a.f.)</i>					
% Carbon Content	ISO 17247:2013	77.9	77.8	77.3	77.8
% Hydrogen Content	ISO 17247:2013	5.5	5.0	4.6	3.8
% Nitrogen Content	ISO 17247:2013	2.1	2.2	2.0	2.1
% Oxygen Content	by difference	13.7	14.4	14.9	15.4
% Total sulphur	ISO 19579:2006	0.7	0.6	1.2	0.8
O/C molar ratio		0.132	0.139	0.145	0.149
H/C molar ratio		0.842	0.759	0.706	0.586
<i>Maceral composition (vol.%)</i>					
	ISO 7404 – 3				
%Vitrinite		72.2	-	37.0	-
%Liptinite (exinite)		3.9	-	0.7	-
%Reactive Semifusinite		5.3	-	24.9	-
%Inert Semifusinite		8.7	-	15.7	-
%Fusinite + Secretinite		3.1	-	6.3	-
%Mineral matter (calculated)		6.8	-	15.4	-
Total Reactives (m.m.f.)		81.4	-	62.6	-
Total Inerts (m.m.f.)		18.6	-	37.4	-
Vitrinite classification content		Mod. high	-	Low	-
<i>Rank and vitrinite reflectance</i>					
Rank determination	ISO 11760	Med C	-	Med C	-
RoV max	ISO 7404 – 5	0.62	-	0.68	-

a.d. = Air-dried; d.a.f. = dry ash free; m.m.f. = mineral matter free.

Table 3-1 presents the results and methods used for proximate and ultimate analyses, calorific values, maceral composition, and rank determination. Demineralization experiments (as described in section 2.2) were conducted on the two coal samples to evaluate the effect of minerals during liquefaction experiments. The analysis results for the demineralized samples are also included in **Table 3-1** and are denoted as VRD (demineralized vitrinite rich coal) and IRD (demineralized inertinite rich coal).

X-Ray Fluorescence (XRF) spectroscopic analysis was conducted on the ash derived from the two raw coals using a PANalytical (Axios Max) WD-XRF spectrometer and is presented in **Table 3-2**. These

results are presented as elemental oxides on a loss on ignition free basis. From the normalized XRF data, the alkalinity index (AI) was determined using **Eq. 1**:

$$AI = \text{Ash yield} \times \left(\frac{Fe_2O_3 + CaO + MgO + Na_2O + K_2O}{SiO_2 + Al_2O_3 + P_2O_5} \right) \quad (1)$$

The provided expression for alkali index serves the purpose of providing insight into the catalytic effects of diverse minerals present in the coal ash when undergoing conversion processes. Within these expressions, the catalytic impact can be assumed through the alkali index which is established as the ratio between the cumulative weight percentages of inorganic elements (expressed as elemental oxides) exhibiting catalytic tendencies (K_2O , CaO , MgO , Na_2O , Fe_2O_3) and those with inhibitory tendencies (SiO_2 , Al_2O_3 , P_2O_5).¹⁵ Furthermore, the equation incorporates a factor involving the ash yield, multiplying it by this ratio, to accommodate coals with both high and low ash concentrations.

Table 3-2. Ash composition of the VR and IR coals presented as mineral oxides.

XRF results (wt.%, LOI-free basis)	VR	IR
SiO ₂	62.3	49.9
Al ₂ O ₃	25.5	27.9
CaO	3.0	7.3
Fe ₂ O ₃	3.2	4.6
K ₂ O	1.1	1.2
MgO	1.5	1.8
MnO	n.d.	0.1
Na ₂ O	0.1	0.3
P ₂ O ₅	0.1	0.8
TiO ₂	1.4	1.4
SO ₃	1.8	4.9
<i>Alkalinity Index (AI)</i>	1.3	5.4
SiO ₂ + Al ₂ O ₃ + Fe ₂ O ₃	91.1	82.3

3.2.2. Demineralization experiments

To consider the effect of inorganic minerals on the liquefaction process, acid treatment was conducted on the vitrinite-rich (VR) and inertinite-rich (IR) coal samples using concentrated hydrochloric acid (32%) and hydrofluoric acid (48%) to remove most of the inorganic components. Adapted from Strydom *et al.* (2011)¹⁶, a three-step, 24-hour treatment process was employed using a coal-to-acid weight ratio of 1-to-3. The treatment involved continuous stirring and subsequent filtration to isolate the acidic solution from the solid carbon-rich material. The sequence of acids used was HCl, followed by HF, and concluding with another round of HCl. Following the third treatment, the carbon-rich material underwent washing with Milli-Q water until reaching a pH level of at least 6. The demineralization method's efficiency was quantified by assessing the demineralization efficiency, E_d , expressed as a percentage. To determine the achieved demineralization efficiency, E_d , the following formula was employed:¹³

$$E_d = \left(\frac{A_0 - A_d}{A_0} \right) \times 100\% \quad (2)$$

Where, A_0 is the ash yield of the coal before demineralization, and A_d is the ash yield of the demineralized coal. The demineralization experiments yielded demineralization efficiencies of 94.4% and 96.1% for the vitrinite-rich (VR) and inertinite-rich (IR) coal samples, respectively.

3.2.3. Liquefaction experiments

The liquefaction experiments were carried out using a 600 mL stainless steel autoclave reactor (Parr Instruments, US), controlled using a 4848 controller from Parr. The feed materials were mixed with tetralin (1,2,3,4-Tetrahydronaphthalene for synthesis; $\geq 98\%$), a hydrogen-donor organic solvent, and benzene (ReagentPlus; purity $\geq 99\%$), a hydrogen-poor organic solvent, to a 1-to-3 weight ratio. An initial pressure of 0.2 MPa (2 bar) (absolute pressure), measured using a pressure display module integrated in the reactor controller, was applied by introducing an inert argon (AFROX, 99.999%) atmosphere. The temperature of the reaction vessel was increased to 450°C at 10 °C/min with an isothermal reaction time of 60 minutes. To ensure thorough mixing of the reacting materials and solvent during the experiment, the stirrer speed was set to 250 rpm. After the reaction period, the reaction vessel was cooled to room temperature using an internal cooling coil controlled by a solenoid valve module. Once the temperature attained room temperature, the gas fraction was collected in a 5 L Tedlar gas bag and set aside for analysis. The liquid and solid products were removed from the reactor vessel and separated using dichloromethane as the solvent and vacuum filtration to obtain the solid residue fraction. The dichloromethane was removed from the liquid yield using rotary evaporation. N-hexane was added to the liquid product and heated to 85°C for 60 minutes¹⁷. The solution was vacuum-filtered to further separate the liquid product into n-hexane soluble fractions as the oil yield and n-hexane insoluble fractions as the asphaltenes and pre-asphaltenes (PAA). The oil was isolated by removing the n-hexane using rotary evaporation. Three replicates of the liquefaction experiments were performed, and the standard deviations of the yields were determined to be less than 2%.

The following equations were used to calculate the weight percentages of the solid residues (W_{SR}), pre-asphaltene and asphaltene (W_{PAA}), liquid/oil residues (W_{liq}), and gas yield (W_{gas}):

$$W_{SR} = \left(\frac{m_{SR}}{m_{sol} + m_{feed}} \right) \times 100\% \quad (3)$$

$$W_{PAA} = \left(\frac{m_{PAA}}{m_{sol} + m_{feed}} \right) \times 100\% \quad (4)$$

$$W_{liq} = \left(\frac{m_{liq} - m_{PAA}}{m_{sol} + m_{feed}} \right) \times 100\% \quad (5)$$

$$W_{gas} = 100\% - W_{SR} - W_{liq} - W_{PAA} \quad (6)$$

Where m_{sol} and m_{feed} represent the mass (in grams) of the solvent and feed material, respectively; and m_{SR} , m_{PAA} , and m_{liq} represent the mass (in grams) of the solid residues, pre-asphaltene and asphaltene, and liquid/oil residues, respectively. All masses are presented on a dry and ash-free basis. The carbon conversions, C_{daf} , of the feed materials during solvent extraction were calculated on a dry, ash-free basis using the following equation and are presented as a percentage:

$$C_{daf} = \left[\frac{m_{feed} - m_{SR}}{m_{feed}} \right] \times 100\% \quad (7)$$

Carbon conversion values were calculated to determine the percentage of feed material that reacted to produce the liquid and gaseous products during liquefaction processes.

3.2.4. Characterization of feed materials and residues

3.2.4.1. Proximate analysis, ultimate analysis, and calorific values

The coal samples, demineralized coal samples, and solid residues were subject to proximate analysis, ultimate analysis, and calorific value determinations using the methods highlighted in **Table 3-1**; while the proximate analysis of the PAA products were approximated using thermogravimetric analysis (to follow in **Eqs. 13–16**). The results from the approximated proximate analysis were used to determine the approximate higher heating values (HHV) of the solid residues and PAA obtained from the liquefaction experiments using **Eq. 8**¹⁸:

$$HHV (MJ \cdot kg^{-1}) = 0.3536FC + 0.1559VM - 0.0078ASH \quad (8)$$

Where the fixed carbon content, volatile matter content, and ash yield are represented by *FC*, *VM*, and *ASH*, respectively.

3.2.4.2. CO₂ low-pressure adsorption analysis

The CO₂ low-pressure adsorption analysis, also known as CO₂-LPGA, was performed on the coal and demineralized coal samples, and their respective solid residues and PAA products using a Micrometrics ASAP 2010 instrument. The method of analysis is reported elsewhere.¹⁹ The micropore surface area of the samples were determined from the CO₂ adsorption data using the Dubinin-Radushkevich (D-R) method.^{19, 20} The maximum micropore volume, average micropore diameter, and pore size distribution (PSD) were calculated using the CO₂ adsorption data following the H-K method.^{19, 21, 22} These calculations were based on the entire isotherms within the reduced pressure ranges. The H-K method, a modification of the Kelvin equation, considers pore filling by the liquid phase of the adsorbate rather than the formation of a gaseous phase adsorbate layer. It also takes into account the dimensions of slit-shaped pores.^{19, 22} This method provides a realistic micropore PSD in the lower pressure range ($0.06 \leq P/P_0 \leq 0.07$). The purpose of the CO₂ low-pressure gas adsorption was to determine the surface area and porosity of the coal samples, demineralized materials, and their respective liquefaction solid residues and PAA.

3.2.4.3. FTIR spectroscopy

Fourier-transform infrared spectroscopy, FTIR, was employed for the characterization of solid materials and residues. A BRUKER ALPHA-P attenuated total reflection Fourier-transform infrared spectrometer (ATR-FTIR) was utilized for solid-state analyses. OPUS version 6.0 (BRUKER software) was used for spectrum acquisition and processing. The FTIR spectra were captured with a wavelength range of 4000–400 cm⁻¹.

3.2.4.4. X-ray diffraction (XRD)

Qualitative and quantitative XRD analysis were conducted on the coal and demineralized coal samples, and their respective solid residues and PAA to evaluate fractions of minerals and amorphous phases contained in the samples. Diffractograms were obtained for the different materials and products using a Malvern PANalytical Aeris diffractometer with a PIXcel detector and fixed slits with Fe-filtered Co-K α radiation. The phases were identified using X'Pert Highscore Plus software. The relative phase amounts (weight %) were estimated using the Rietveld method.²³ Curve-fitting manipulation was applied to obtain three Gaussian peaks that were used to fit XRD

patterns at around 20, 29, and 50°. These were assigned as γ , 002, and 100 bands, respectively.²⁴ When considering that the interlayer structure of coal has a uniform density, Hirsch (1954)²⁵ evaluated the molecular structure of pulverized coal using XRD analysis to determine the interlayer spacing (d_{002}), stacking heights (L_c), and average lateral sizes (L_a) of the crystallite structures (Eqs. 9–11):

$$d_{002} = \frac{\lambda}{2\sin\theta_{002}} \quad (9)$$

$$L_c = \frac{0.89\lambda}{\beta_{(002)} \cdot \cos\theta_{(002)}} \quad (10)$$

$$L_a = \frac{1.84\lambda}{\beta_{(100)} \cdot \cos\theta_{(100)}} \quad (11)$$

$$n = \frac{L_c}{d_{002}} \quad (12)$$

Where λ is the X-ray wavelength equal to 1.789 nm, and the diffraction angles, θ_{002} and θ_{100} , correspond to the 002 and 100 peak positions, respectively. The FWHM (full width at half maximum) of the 002 and 100 peaks are represented as β_{002} and β_{100} , respectively.²⁵ The stacking number of aromatic layers are signified by n in Eq. 12.^{24, 26}

3.2.4.5. Pyrolysis of solid fractions

Pyrolysis experiments of the coal, demineralized coal, and residues were conducted using an SDT Q600 TGA instrument from TA Instruments. The results show the relationship between mass loss and temperature as a result of decomposition and dehydration reactions on a mass loss (%) versus temperature (°C) plot and its derivative (%/°C) as a function of temperature in a differential thermal gravimetric analysis (DTG) plot. Approximately 15 mg (± 1 mg) of the sample was loaded in a 90 μ L alumina crucible and subject to thermogravimetric analysis. An inert environment was created using nitrogen (AFROX, 99.999%) with a constant flow rate of 100 mL/min. The samples were heated from 25–960°C with a linear heating rate of 20 °C/min.^{13, 27}

Additionally, moisture content ($MC_{approx.}$), ash yield ($ASH_{approx.}$), volatile matter content ($VM_{approx.}$), and fixed carbon content ($FC_{approx.}$) were approximated from the pyrolysis and gasification (Section 3.2.4.6) results with a <2% difference when compared to proximate results obtained using the ISO methods (ISO 11722; ISO 1171; ISO 562). The approximate proximate analysis was calculated using Eqs. 13–16:

$$MC_{approx.} = \frac{m_i - m_{180^\circ C}}{m_i} \times 100\% \quad (13)$$

$$ASH_{approx.} = \frac{m_{ash}}{m_i} \times 100\% \quad (14)$$

$$VM_{approx.} = \frac{m_{180^\circ C} - m_{char}}{m_i} \times 100\% \quad (15)$$

$$FC_{approx.} = \frac{m_{char} - m_{ash}}{m_i} \times 100\% \quad (16)$$

Where m_i , $m_{180^\circ C}$, m_{ash} , and m_{char} denotes the initial sample mass at 25°C, mass at 180°C, mass of the ash after full conversion, and the mass of the char prior to CO₂ gasification at 960°C, respectively. The approximate HHV's (in MJ.kg⁻¹) were calculated from these results using Eq. 8.

3.2.4.6. Char-CO₂ gasification and kinetics

CO₂ gasification experiments were conducted on the chars of the coal samples and demineralized coal samples, and their respective liquefaction solid residues and PAA's using an SDT Q600 thermogravimetric analyzer from TA instruments. The samples were heated to the desired isothermal reaction temperature (900, 930, and 960°C) at 20 °C/min in an inert atmosphere (as discussed in **Section 3.2.4.5**) to remove residual volatile contents before gasification tests. When the desired isothermal temperatures were reached, the atmosphere was switched to CO₂ with a of 30 mL/min flow rate until the reaction was completed and full conversion was reached. The reactivity at 50 and 90% ($R_{0.5}$ and $R_{0.9}$) conversion were calculated using **Eqs. 17** and **18**, where t is the time at conversion in minutes. The fractional carbon conversions (X), initial reactivities (R_i), and average final reactivities (R_{fa}) were evaluated using **Eqs. 19–21**.^{7, 13}

$$R_{0.5} = \frac{0.5}{t_{0.5}} \quad (17)$$

$$R_{0.9} = \frac{0.9}{t_{0.9}} \quad (18)$$

$$X = \frac{m_0 - m_t}{m_0 - m_{ash}} \quad (19)$$

$$R_i = \left. \frac{dX}{dt} \right|_{X=0.1} \quad (20)$$

$$R_{fa} = \frac{\sum_{X=0.9}^{X=0.7} \frac{dX}{dt}}{N} \quad (21)$$

Where X is the fractional carbon conversion, m_0 is the initial mass of the char before gasification, m_t is the mass of the char at reaction time (t), m_{ash} is the mass of the residual ash remaining after gasification occurred, and N in the number of data points.

Two gasification reaction kinetic models were used to perform the kinetic modeling and calculation of kinetic parameters for the gasification process of the samples. These models include the random pore model (RPM) and the volumetric reaction model (VRM). The random pore model (RPM) considers a random distribution of pore sizes and orientations. Unlike other models, the RPM specifically accounts for the structural changes in the char as the reaction progresses. The liquefaction process affects the pore structure of the coal matrix, and these alterations have a significant impact on the advancement of the reaction. **Eqs. 22** provides the expression for the overall reaction rate using the random pore model (RPM).

$$\frac{dX}{dt} = \frac{r_s S_0 (1-X) \sqrt{1-\psi \ln(1-X)}}{(1-\epsilon_0)} \quad (22)$$

The intrinsic reaction rate, denoted as r_s , considers the impact of the operating conditions. S_0 and ϵ_0 are the pore surface area and solid porosity, respectively. To address variations in the char's structure during the progression of the gasification reaction, a dimensionless structural parameter (ψ) is introduced which is determined by char properties, as specified in **Eq. 23**.

$$\psi = \frac{4\pi L_0 (1-\epsilon_0)}{S_0^2} \quad (23)$$

Where, L_0 is the pore length. The RPM gasification conversion fraction (X) at the gasification reaction time, t , is determined using **Eq. 24**. Where the time factor (t_f) is evaluated using the random pore model.

$$X = 1 - \exp \left[-t_f t \cdot \left(1 + \frac{t_f t \psi}{4} \right) \right] \quad (24)$$

The structural parameter, ψ , can be estimated through linear regression using the dimensionless reduced time, $t/t_{0.9}$ (**Eq. 25**):

$$\frac{t}{t_{0.9}} = \frac{\sqrt{1-\psi \ln(1-X)}-1}{\sqrt{1-\psi \ln(1-0.9)}-1} \quad (25)$$

The activation energy, denoted as E_a , was determined by calculating the slope of the graphical representation of $\ln(t_f)$ plotted against T^{-1} . Concurrently, the lumped pre-exponential factor, denoted as k_{so} , was approximated from the intercept from the $\ln(t_f)$ versus T^{-1} plot.

$$\ln(t_f) = -\frac{E_a}{RT} + m \ln(y_{CO_2}) + \ln(k'_{so}) \quad (26)$$

The quality of fit (QOF) was evaluated by fitting the kinetic models and applying **Eq. 27**:

$$QOF(\%) = 100 \cdot \left(1 - \frac{\sum_1^N \frac{X_{cal} - X_{exp}}{X_{exp}}}{N} \right) \quad (27)$$

Where X_{cal} and X_{exp} are determined from the calculated and experimental conversion values obtained from the models, respectively. The number of data points used for the models are represented by N .

The volumetric (homogeneous) reaction model (VRM) assumes that gasification reactions take place homogeneously throughout the inner and outer surfaces of the reaction environment. The volumetric reaction model was proposed by Wen *et al.*²⁸:

$$X = 1 - \exp(-t_f t) \quad (28)$$

Where t_f is the time factor determined using the volumetric reaction model (VRM). The apparent activation energies determined using R_i , R_{fa} , $R_{t0.5}$ and $R_{t0.9}$ were calculated by plotting the $\ln$ of the reactivity value against $1/T$ (K^{-1}).

3.2.5. Characterization of liquid products from liquefaction experiments

3.2.5.1. GC-MS and calorific values of liquid products

Gas Chromatography-Mass Spectrometry (GC-MS) analyses were conducted to characterize the liquid products obtained from the coal liquefaction experiments. An Agilent 6890N gas chromatograph (GC) coupled with an Agilent 5975 mass detector was utilized for this purpose. The GC instrument was equipped with an Agilent 19091S column, with a length of 30 m, a diameter of 0.25 mm, and a film thickness of 0.25 μ m. The column temperature was programmed to increase at a rate of 5 $^{\circ}$ C/min until reaching 290 $^{\circ}$ C. Once the desired temperature was reached, it was maintained isothermally for 30 minutes to ensure complete evolution of all sample components. For peak identification, the National Institute of Standards and Technology (NIST) database was employed. This database served as a reference for identifying the peaks obtained during the GC-MS

analysis, aiding in the characterization of the samples. In addition, FTIR spectroscopic analysis was conducted using the method previously mentioned (**Section 3.2.4.3**).

3.2.6. Gas composition using gas chromatography.

For further gas analysis, a PerkinElmer Clarus 500 Gas Chromatograph was used, with two columns (Agilent J&W HP-PLOT/Q 30 m x 0.535 mm and PerkinElmer Elite GC GS MSIEVE 30 m x 0.53 mm) interconnected to the injector and detector via a VICI 10-port gas sampling valve from Valco Instruments. The detector (TCD, thermal conductivity detector) was set to 100°C, and the gas samples were injected using a capillary injector operating at the same temperature. Argon, supplied by AFROX with a purity of 99.999%, served as the carrier gas at an initial flow rate of 2 mL/min, increasing to 8 mL/min after 16 minutes. The oven temperature was set to 40°C, and the GC system was calibrated for CO₂, CO, H₂, CH₄, C₂H₆, O₂, and N₂ analysis. A 1 mL gas sample was injected, with CO₂ being separated out in the PLOT Q column, and a valve switch preventing it from entering the MSIEVE column. The concentration of each component was determined using the peak areas in the chromatogram. Data processing is conducted using TotalChrom Navigator software designed for the Clarus 500 GC.

The change in total pressure is attributed to the increase in partial pressures of the gases produced. By monitoring the change in pressure and knowing the initial pressure and the properties of the gases involved, the amount of gas produced may be quantified. Dalton's law was used to determine the partial pressures of the individual gas components together with the volume or molar percentage from gas chromatography. Dalton's Law states that the total pressure exerted by a mixture of non-reacting gases is the sum of the partial pressures of each individual gas: $P_{\text{total}} = P_1 + P_2 + \dots + P_n$, where P_{total} = Total pressure of the gas mixture, and $P_1, P_2, \dots, P_n$ = Partial pressures of individual gases in the mixture. Lastly, the ideal gas law ($PV = nRT$) was used to calculate the number of moles of each gas species in the mixture at a specific temperature (25°C) and pressure. From the number of moles of each gas the mass could be determined.

3.3. Results and discussion

3.3.1. Liquefaction product distribution

Initial liquefaction pressures, with tetralin as solvent, at the reaction temperatures of 400, 425, and 450°C ranged between 20 and 23 bar, 27 and 31 bar, and 38 and 40 bar, respectively. While the pressures of the experiments conducted using benzene as the solvent at 450°C ranged between 65 and 69 bar. At 450°C, the pressures at the end of the reaction period ranged between 43 and 48 bar using tetralin, and between 72 and 76 bar using benzene. **Table S3-5** highlights the partial pressures of the gas yields at the end of the reaction period and cooled down to 25°C. These pressures are directly proportional to the mass of the gases produced from the process. The reaction pressures obtained from tetralin liquefaction were lower than the typical pressures used in DCL processes which ranges between 69 and 155 bar.⁶ This is due to the initial volume occupation of the feed material and solvent. Higher reaction pressures can be obtained by increasing the amount of solvent used, or by increasing the initial argon pressure.

Tetralin, a hydrogen donor solvent, together with benzene, a hydrogen poor solvent, were used to evaluate the liquefaction effectiveness and product quantity and quality produced with two aromatic solvents with different hydrogen-donor capabilities. **Table 3-3** shows the product yields of the VR, VRD, IR, and IRD coal produced from liquefaction experiments conducted at 400, 425, and 450°C using tetralin. In addition, product yields of liquefaction experiment conducted in benzene at 450°C were included. The results from the experiments conducted at 425 and 400°C have shown low conversion values (5–10% conversion) and were excluded from this study. For tetralin liquefaction at 450°C, carbon conversion values of 81.0, 77.0, 50.9, and 61.7% were obtained from the VR, VRD, IR, and IRD coals, respectively. The overall conversion of the IR coal is lower than that of the VR coal by 30.9, 31.4, and 35.7% at 400, 425, and 450°C, respectively. Uwaoma *et al.* (2019)¹⁷ found similar conversion values during tetralin liquefaction of density separated fractions derived from Highveld coal fines. The difference between these conversion values can predominantly be ascribed to the different maceral compositions of the two coals. The fractions of reactive macerals, namely vitrinite and exinite, are significantly higher in the VR coal compared to the IR coal with vitrinite contents of 72.2 and 37.0%, and exinite contents of 3.9 and 0.7%; while reactive semifusinite contents were 5.3 and 24.9%, respectively (**Table 3-1**). Similar observations were also made by Yan *et al.* (2021)⁷ Inertinite macerals contain less aliphatic and oxygen-containing functional groups making the nature of the coal's macromolecular structure more aromatic.²⁹ The lower H/C molar ratio of the IR coal compared to the VR coal can be attributed to the higher degree of aromaticity (**Table 3-1**). The IR coal comprises of more inertinite that is difficult to convert during the liquefaction process and will most likely remain in the solid residue fraction. The results from **Table 3-3** support this statement. Higher oil yields derived from the liquefaction experiments of the VR coal are accompanied by higher carbon conversion at all temperatures. While the alkali indices for the IR coal are high and catalytic effects may be anticipated, the results show that the high ash yield in the IR coal inhibits liquefaction conversion reactions when compared to its demineralized counterpart, IRD. However, the VR coal resulted in higher conversion values than its demineralized counterpart, VRD, indicating that catalytic effects may be caused by its inorganic constituents. Certain minerals are known for their definite catalytic effects during gasification, while others are noted for their catalytic effects in liquefaction.^{10, 30} In addition, it is widely acknowledged that higher temperatures also promote the breakdown of coal macromolecules.^{10, 27, 31, 32} The resulting

fragments and radicals undergo hydrogenation through active hydrogen interactions, leading to the creation of oil or hydrocarbon gases. This process is contingent with the availability of ample active hydrogen atoms or hydrogen radicals, typically sourced from a hydrogen donor solvent such as tetralin.¹⁰ Consequently, increased temperatures elevate the production of oil and gas.

Liquefaction experiments performed at 450°C utilizing benzene, a H-poor aromatic solvent, exhibited inefficacy, resulting in lower conversion values (<22%) in contrast to the 400–450°C tetralin experiments. These findings underscore the necessity of a hydrogen-donating solvent in coal liquefaction, independent of coal's molecular composition. It's worth noting that supercritical conditions were achieved with both solvents. Consequently, the primary emphasis of this study will be on examining the liquefaction outcomes derived from experiments conducted with tetralin as the selected solvent.

Table 3-3. Liquefaction product distribution of experiments conducted at 400, 425, and 450°C with tetralin as the solvent; and at 450°C with benzene as the solvent.

Sample	Yield, weight % (d.a.f.)			Carbon conversion, % (d.a.f.)
	Solid residue	Liquid residue	Gas	
VR 450t	4.1	93.4	2.5	81.0
VRD 450t	5.5	91.8	2.6	77.1
IR 450t	9.0	89.0	2.0	50.9
IRD 450t	9.1	88.1	2.8	61.7
VR 425t	5.6	92.3	2.1	73.8
VRD 425t	7.5	90.3	2.3	69.1
IR 425t	10.7	88.0	1.3	42.4
IRD 425t	10.0	87.6	2.4	57.2
VR 400t	7.7	91.5	0.8	63.9
VRD 400t	10.5	88.4	1.1	56.7
IR 400t	13.3	85.7	1.0	28.2
IRD 400t	17.6	80.6	1.8	25.8
VR 450b	17.6	80.3	2.2	18.5
VRD 450b	19.2	78.8	2.0	21.1
IR 450b	15.0	83.9	1.1	17.7
IRD 450b	20.4	78.0	1.6	13.4

Feed materials = VR, VRD, IR, IRD; Liquefaction temperatures = 400, 425, 450°C; Solvent used: t = tetralin, b = benzene; feed-to-solvent = 25:75.

During solvent extraction using n-hexane to remove the pre-asphaltene and asphaltene (PAA) solid fraction from the liquid product yield, it was found that the yield of PAA's increased with rising reaction temperature (**Figure 3-1**). Notably, the PAA yield from the VR and VRD experiments remained relatively consistent, implying that ash constituents do not exert a significant influence during the catalytic breakdown of PAA molecules. In contrast, the IR PAA yields were lower compared to the PAA's from IRD liquefaction at all reaction temperatures. A lower hydrogen content in the IRD feed could result in products that are more aromatic in nature, supported by a lower H/C ratio of the solid and liquid yield. Another potential explanation could be that the inorganic minerals present in the IR coal act as catalysts for the decomposition of larger molecules, which typically result in the production of PAA. Alternatively, it is plausible that inorganic minerals inhibit recombination reactions that lead to the formation of PAA molecules. The IR liquefaction yields exhibited the lowest PAA yield across all temperature ranges. Asphaltenes are formally defined as materials insoluble in alkanes (such as n-pentane, n-hexane, and n-heptane) but soluble in aromatics such as benzene and toluene. Due to their bulky nature, they can be regarded as the nonpolar and

nonvolatile components in crude oil.³³ However, the extraction efficacy becomes apparent at higher temperatures (e.g., 85°C) due to the potential precipitation of polar compounds at lower temperatures, which might incorrectly contribute to the calculated PAA yield.

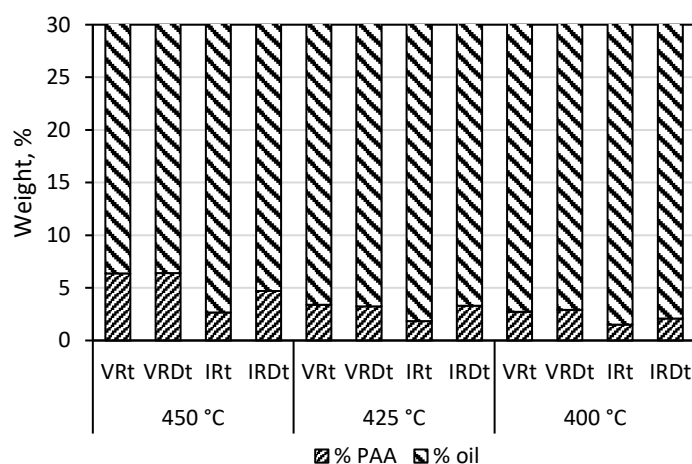


Figure 3-1. Pre-asphaltene and asphaltene yields from liquid products produced from tetralin liquefaction at 400 to 450°C.

3.3.2. Characterization of solid fractions obtained during liquefaction experiments

3.3.2.1. Physicochemical and structural characterization

Table 3-4 shows the approximated proximate analysis and calorific values of solid residues produced from tetralin liquefaction at 450°C. The volatile matter contents within the liquefaction solid residues are comparatively lower while the fixed carbon contents are higher compared to the original coal samples, and this observation becomes more pronounced as the liquefaction temperatures are increased (as shown in **Table 3-1**, **Table 3-4**, and **Table S3-1**). Nonetheless, when considering a dry-ash-free basis, the carbon and hydrogen contents of the residues exhibit only a minor increase compared to the original coal. Additionally, a significant portion of these residues can be transformed into syngas (CO and H₂) during the gasification process and further utilized in DCL plants.¹⁴ The low calorific values or HHV's of the VR and IR derived solid residues is a result of the high ash yields in the samples. Compared to the higher heating values of the solid liquefaction residues of the demineralized coal and residue samples, the HHV's of the residues increase as the liquefaction temperature rises. The proximate analysis and higher heating value results for the liquefaction experiments conducted at 425 and 400°C in tetralin, and 450°C in benzene are presented in **Table S3-1** in the supporting information section.

Table 3-4. Approximated proximate analysis, calorific values, and ultimate analysis of solid residues produced from tetralin liquefaction at 450°C.

Sample Identification	VR SR	VR PAA	VRD SR	VRD PAA	IR SR	IR PAA	IRD SR	IRD PAA
% Moisture content	1.5	3.6	2.7	3.7	0.8	3.1	1.9	4.5
% Ash yield	45.1	0.8	2.0	1.0	48.3	3.0	3.0	0.1
% Volatile Matter	11.3	38.0	13.1	38.5	14.1	31.1	11.8	37.9
% Fixed carbon (by calculation)	42.1	57.7	82.1	56.8	36.7	62.8	83.3	57.6
Fuel Ratio	3.7	1.5	6.3	1.5	2.6	2.0	7.1	1.5
Calorific values (MJ.kg ⁻¹)	17.0	-	33.6	-	15.9	-	33.6	-
HHV (MJ.kg ⁻¹) (Eq. 8)	16.5	27.3	31.9	27.1	14.9	27.9	31.9	27.5
% Carbon Content	82.0	-	87.4	-	82.9	-	88.5	-
% Hydrogen Content	3.6	-	3.8	-	3.8	-	3.7	-
% Nitrogen Content	2.6	-	2.4	-	2.2	-	2.0	-
% Oxygen Content (calculated)	10.8	-	5.9	-	9.4	-	5.0	-
% Total sulphur	1.0	-	0.5	-	1.7	-	0.8	-
O/C molar ratio	0.10	-	0.05	-	0.08	-	0.04	-
H/C molar ratio	0.52	-	0.52	-	0.54	-	0.49	-

* Approximated from thermogravimetric analysis. SR = liquefaction solid residue; PAA = pre-asphaltenes and asphaltenes.

Inertinites usually contain higher proportions of elemental carbon and lower proportions of elemental hydrogen compared to vitrinites and liptinites. Within this maceral group, fusinites, and semifusinites also show fossilized woody structure, but contain less hydrogen and more carbon than vitrinites.³⁴ Comparing the O/C and H/C molar ratio from **Table 3-1** and **Table 3-4**, it is clear that the residues produced from the liquefaction experiments had notably lower O/C and H/C values than their respective feed materials. This leads to the assumption that more aliphatic and polar structures reacted during liquefaction experiments.^{10, 27} H/C molar ratios decreased more in the residues produced from VR liquefaction compared to IR. This is consistent with literature indicating that H/C values and aromaticity for principle maceral groups decrease during pyrolysis and liquefaction processes in the order: liptinite > vitrinite > inertinite.³⁴ Gasification reactivities of these solid residue chars are expected to be relatively lower during CO₂ gasification, while higher activation energies (E_a) are required when compared to the raw feed materials (discussed in **Section 3.3.2.3**).

Figure 3-2 shows the IR spectra of the VR (**a**), VRD (**b**), IR (**c**), and IRD (**d**) coals; and their respective solid residues (SR) and pre-asphaltenes and asphaltenes (PAA) produced from tetralin liquefaction conducted at 450°C. No strong O-H stretching vibrations from intermolecular hydrogen bonding is observed in the 3400–3200 cm⁻¹ regions for all raw, SR, and PAA samples (**Figure 3-2a** to **Figure 3-2d**). However, strong O-H stretching vibrations of nonhydrogen-bonded or “free” hydroxyl groups of alcohols and phenols absorb strongly in the 3700–3584 cm⁻¹ region and can only be observed in the VR, VR SR, IR, and IR SR fractions.³⁵ No absorption peaks in these regions were observed in the PAA’s produced from the liquefaction of the VR and IR coals. Meanwhile, no hydroxy bands were observed in the spectra of the demineralized materials and their respective solid residues and PAA’s. The acid treatment (with HCl and HF) during demineralization may promote the reaction between H-X acids and alcohols to form alkyl halides (and H₂O, which is mostly removed during drying).¹⁶ It is also evident that no polar structures containing -C=O and -OH functional groups were removed from the liquid residues during the PAA separation process. This can be supported by absent C=O stretching and O-H stretching bands in the 1750–1650 cm⁻¹ and 3700–3200 cm⁻¹ regions of the PAA’s. The intensities of aliphatic sp³ C-H stretching bands at 2915–2840 cm⁻¹ of the solid residues (SR’s) are weaker than the corresponding signals of the coal samples (VR, VRD, IR, and IRD),

while no distinctive bands are observed in the spectra of the PAA's. From **Figure 3-2a** and **Figure 3-2c**, it follows that strong aromatic C=C stretching vibrations are observed near 1592 cm^{-1} and their intensities decrease in order: PAA > Raw > SR for the VR and IR fractions. The IR bands from VR, VRD, IR, and IRD in this region overlap with weak C=O stretching bands of carbonyl groups such as aldehydes, ketones, and esters in the $1960\text{--}1700\text{ cm}^{-1}$ region. The solid residues and PAA's appear to have no C=O stretching bands in this region.

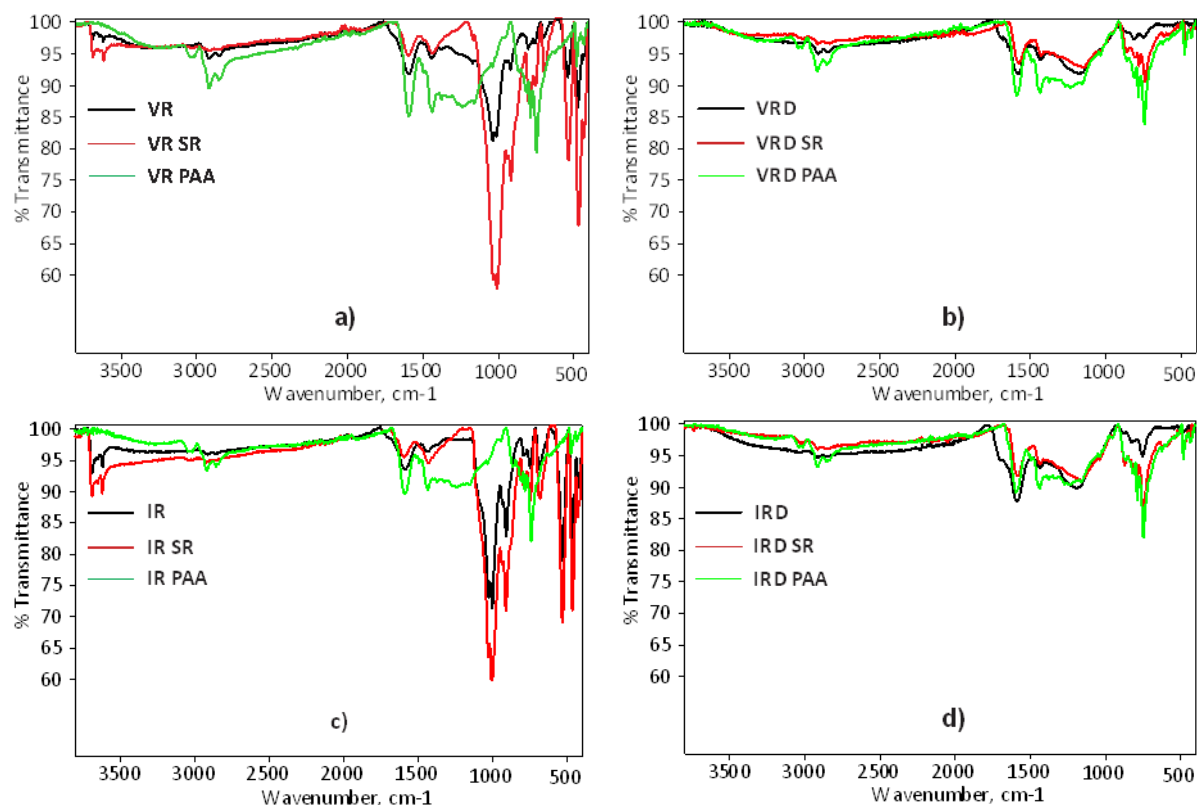


Figure 3-2. Infrared spectra of the solid feed materials, including solid residues and PAA's produced from tetralin liquefaction at 450°C , from a) VR Coal, b) VRD Coal, c) IR Coal, and d) IRD coal.

It can be deduced that more aliphatic components decompose to produce liquids and gases, and that the solid residues derived from the coals and demineralized coals were more aromatic in nature. Weak aromatic sp^2 C-H bands in the $3200\text{--}3000\text{ cm}^{-1}$ region indicate that macromolecular structures of the feed materials and solid residues are mostly made up of quaternary aromatic carbons, while the PAA's have bands in this area accounting for more C-H bonds. It can also be established that the PAA's have more aliphatic components because of stronger sp^3 C-H stretching bands in the $3000\text{--}2850\text{ cm}^{-1}$ region. The peak intensities of acyl and alkoxy C-O stretching bands at $1200\text{--}1000\text{ cm}^{-1}$ of the VR and IR coals are weaker than their respective SR's but have stronger aromatic C=O stretching bands near 1586 cm^{-1} . The results indicate that acyl and alkoxy C-O groups are less reactive during liquefaction experiments than carbonyl (C=O) groups; this includes cleavage of C-O-R linkages. No significant differences in this region were observed for the demineralized materials and their respective SR's and PAA's. These findings suggest that the organic structure of the coals was modified during the acid treatment process, as has been investigated by others.¹⁶

3.3.2.2. X-ray diffraction and CO₂ low-pressure adsorption analysis

The XRD results revealed that the demineralized samples (VRD and IRD) and their respective residue samples contained significantly high (> 98%) amorphous materials, while the PAA samples contained 100% amorphous materials – predominantly consisting of organic carbons.¹³ These results were not reported in this work. **Table 3-5** shows the XRD analysis results of the VR and IR samples with their respective solid residue products produced via tetralin liquefaction at 450°C. The samples contained high amounts of amorphous phases with some crystalline phases. The XRD results reveal that the most abundant crystalline minerals in the samples are quartz (SiO₂) and clay minerals like kaolinite (Al₂Si₂O₅(OH)₄) with minor amounts of dolomite, calcite, muscovite, and magnetite. The IR coal sample has a higher fraction of kaolinite compared to the VR coal sample. The decomposition of kaolinite (to meta kaolinite) generally occurs at around 450°C^{13, 19}, however, no changes in the diffractograms were observed that suggest the presence of meta kaolinite in the residue samples (VR SR and IR SR). It should also be noted that kaolinite and smectite peaks overlap and further tests would be necessary to distinguish between these.

Table 3-5. Relative mineral phase amounts (wt.%) of the coals and their solid residues produced at 450°C during tetralin liquefaction.

Mineral phases (%)	VR	VR SR	IR	IR SR
quartz	7.5	13.8	7.7	11.6
kaolinite	11.0	18.0	28.8	28.0
dolomite	-	0.1	4.4	4.7
calcite	-	<0.1	1.0	0.6
muscovite	1.0	1.2	3.1	2.7
magnetite	-	<0.1	0.5	0.6
smectite	2.8	-	-	-
pyrrhotite	-	<0.1	-	0.3
sepiolite	-	12.8	-	-
amorphous/organic carbon	77.7	54.0	54.4	51.4

The behavior of minerals during liquefaction depends on the specific mineral, the conditions of the liquefaction process, and the duration of exposure to high temperatures and pressures. The results, however, indicate that most minerals from the IR coal did not undergo major structural changes and remained stable under these liquefaction conditions.

Table 3-6. Structural parameters obtained by fitting XRD patterns from the feed materials, solid residues, and PAA.

Sample	d ₀₀₂ (Å)	L _c (Å)	L _a (Å)	n
VR	3.74	8.69	-	3.33
VR SR	3.53	11.06	-	4.13
VR PAA	3.49	19.52	26.46	6.60
VRD	3.61	15.21	53.37	5.22
VRD SR	3.42	42.36	34.91	13.38
VRD PAA	3.49	16.46	29.81	5.72
IR	3.67	12.23	-	4.33
IR SR	3.66	12.41	-	4.39
IR PAA	3.47	20.91	28.71	7.02
IRD	3.46	20.61	47.73	6.96
IRD SR	3.44	43.45	-	13.64
IRD PAA	3.49	20.84	41.53	6.98

Different structural parameters were calculated by fitting XRD patterns obtained from the different samples. The values of d₀₀₂ (Interlayer Spacing), L_c (Stacking Height of Graphitic Planes), L_a (Crystallite

Size), and n (Degree of Crystallinity) are presented in **Table 3-6**. These results provide insight into the structural changes that occur during coal liquefaction; and are indicative of the coal's crystalline structure, degree of graphitization, and overall maturity. These changes are highlighted by comparing the properties of the original feed materials (VR, VRD, IR, IRD), the solid residues chars (VR SR, VRD SR, IR SR, IRD SR), and the pre-asphaltenes/asphaltenes (PAA) obtained from the liquid fraction of the liquefaction experiments.

The d_{002} parameter reflects the interlayer spacing within the coal structure. It is noticeable that this parameter decreases in the solid char residues (VR SR, VRD SR, IR SR, IRD SR) compared to the feed materials (VR, VRD, IR, IRD). The d_{002} values decrease from 3.74 Å in VR to 3.53 Å in VR SR and from 3.61 Å in VRD to 3.42 Å in VRD SR, while IR SR and IRD SR also show decreases in d_{002} compared to their parent coals. This decrease suggests a compaction and reduction in the interlayer spacing during coal liquefaction, and that the coal's crystalline structure becomes more ordered and compact as a result of the liquefaction process. Such compaction is often associated with the removal of volatile matter and the rearrangement of carbon atoms, leading to higher carbon content and increased maturity. Demineralization significantly affects the coal structure, as indicated by the larger d_{002} values in demineralized samples (VRD and IRD) compared to their parent coals (VR and IR), suggesting an expansion of the crystalline structure due to the removal of mineral impurities. The crystallite size (L_c) of inertinite is larger than that of vitrinite macerals in coals.³⁶ These values generally increase in liquefaction solid residues, reflecting a growth of crystallites and the stacking height of graphitic planes, and is indicative of a higher degree of graphitization during liquefaction. The results are consistent with literature.^{7, 26} The L_a parameter represents the crystallite size within the coal structure. The results show that the crystallite size (L_a) tends to increase in the solid char residues compared to the feed materials. This increase in crystallite size indicates that the coal's macromolecular structure becomes more ordered and extended during liquefaction. Larger crystallites are associated with higher degrees of crystallinity and increased graphitization, which is a sign of enhanced structural maturity. Similar results were found by other authors.^{7, 26}

The solid char residues (SR) reflect the structural compaction and enhanced graphitization (and recombination reactions) that occurs during liquefaction, while the PAA fractions demonstrate the retention of structural order and crystallinity in the soluble components formed during the process. Furthermore, during coal maturation, molecular chains reconnect into larger macromolecular chains, leading to increased maturity and aromaticity in both VR and IR. The shedding of aliphatic side chains and oxygen functional groups results in a more orderly arrangement of coal macromolecules, leading to fewer lattice defects in carbon atoms and a structure closer to graphitization, which shows the decrease of d_{002} and the increase of L_a and L_c . These structural changes may influence the gasification reactivities of the samples by affecting the accessibility of reactive sites and the overall reactivity of the carbonaceous material.

Table 3-7 presents the CO₂ low-pressure adsorption analysis results of the coal samples, their solid residues, and PAA's. It appears that the liquefaction process generally reduces the surface area. For example, VR has a higher BET surface area (90.1 m²/g) compared to VR SR (42.6 m²/g). Similarly, IR has a higher BET surface area (36.5 m²/g) compared to IR SR (32.6 m²/g), suggesting a decrease in surface area after liquefaction. Similar to the BET surface areas, the D-R micropore surface areas tend to decrease in the solid residues compared to the parent coal samples after liquefaction. For example, VR has a higher D-R micropore surface area (112.5 m²/g) compared to VR SR (55.0 m²/g),

indicating a reduction in micropore surface area. Similarly, IR has a higher D-R micropore surface area ($85.8 \text{ m}^2/\text{g}$) compared to IR SR ($41.9 \text{ m}^2/\text{g}$). In addition, the liquefaction process generally leads to a decrease in pore volume in the solid residues compared to the parent coal samples. For instance, VR has a higher H-K pore volume ($3.55 \text{ cm}^3/\text{g} \times 10^2$) compared to VR SR ($1.61 \text{ cm}^3/\text{g} \times 10^2$), indicating a reduction in pore volume after liquefaction. Similarly, IR has a higher H-K pore volume ($2.76 \text{ cm}^3/\text{g} \times 10^2$) compared to IR SR ($1.15 \text{ cm}^3/\text{g} \times 10^2$), suggesting a decrease in pore volume due to liquefaction. VRD and IRD also follow these trends. The median pore width values appear to increase slightly from the parent coal samples to their solid residues.

Table 3-7. CO₂ low-pressure adsorption analysis of the coal and demineralized coal samples, and their respective liquefaction solid residues and PAA's produced at 450°C.

Sample	BET surface area, m^2/g	D-R micropore surface area, m^2/g	H-K Pore Volume, $\text{cm}^3/\text{g} (\times 10^2)$	H-K Median pore width, Å
VR	90.1	112.5	3.55	3.84
VR SR	42.6	55.0	1.61	3.95
VR PAA	1.9	15.2	0.18	4.67
VRD	96.7	120.1	3.80	3.84
VRD SR	59.3	66.8	1.86	4.03
VRD PAA	1.3	16.2	0.17	4.69
IR	69.5	85.8	2.76	3.80
IR SR	32.6	41.9	1.15	4.02
IR PAA	2.1	18.7	0.24	4.63
IRD	93.4	116.2	3.81	3.77
IRD SR	55.2	62.7	1.67	4.09
IRD PAA	1.4	16.5	0.15	4.70

BET = Brunauer-Emmet-Teller; D-R = Dubinin-Radushkevich; H-K = Horvath-Kawazoe.

Coal liquefaction tends to reduce the surface area, micropore surface area, and pore volume of the solid residues compared to the parent coal samples. This suggests that the liquefaction process results in a reduction in porosity and available surface area for gasification reactions in the solid residues. Consequently, the solid residues from coal liquefaction may exhibit lower gasification reactivities compared to the original coal samples, primarily due to the alteration of their porous structure during the liquefaction process. These changes encompass the breakage of carbon-carbon bonds, the removal of specific functional groups, and the consequent widening of existing pores. Moreover, these reactions may lead to the loss of micropores, resulting in an increase in the average pore size. Additionally, smaller pores have the propensity to coalesce or merge into larger ones during conversion, ultimately contributing to an overall expansion in average pore width.

3.3.2.3. Thermogravimetric analysis: pyrolysis, CO₂ gasification, and kinetics.

Figure 3-3 illustrates a standard thermogravimetric analysis graph for coal, detailing its behavior during pyrolysis and CO₂ gasification. This curve can be divided into three distinct phases: the dewatering stage below 180°C, the pyrolysis stage in a nitrogen (N₂) atmosphere from 180–960 °C, and the isothermal gasification stage at 960°C.

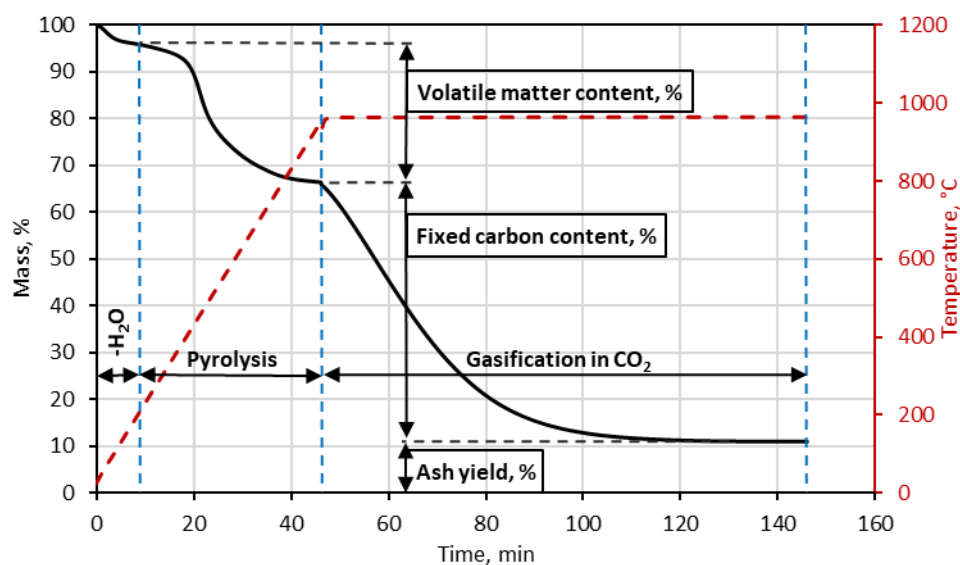


Figure 3-3. Thermogravimetric analysis: Mass loss profile during pyrolysis under N₂ and isothermal CO₂ gasification

In **Figure 3-4a-d**, pyrolysis curves are presented for the following coal samples: a) VR, b) VRD, c) IR, and d) IRD. These curves also depict the amounts of solid residues and PAA's obtained during liquefaction experiments conducted at 450°C, utilizing tetralin as the solvent.

Table 3-8 presents results from the CO₂ gasification experiments at 960°C on the vitrinite-rich (VR) and inertinite-rich (IR) coals, their demineralized variants (VRD and IRD), as well as the solid char residues (VRSR, VRDSR, IRSR, and IRDSR) and the PAA (asphaltenes and pre-asphaltenes) removed from liquid fractions obtained from liquefaction experiments at 450°C in tetralin. Various parameters, such as $t_{0.5}$ (time for 50% conversion), $R_{0.5}$ (reactivity at 50% conversion), $t_{0.9}$ (time for 90% conversion), $R_{0.9}$ (reactivity at 90% conversion), R_i (initial reactivity), and R_{fa} (average final reactivity) for CO₂ gasification, have been determined.

VR SR, VRD SR, and IRD SR chars exhibit higher reactivities at 50% conversion ($R_{0.5}$) compared to their parent coal chars, i.e., VR, VRD, and IRD. This indicates that the liquefaction process produces char residues with enhanced gasification reactivities. This trend did not hold for the IR SR char and its parent coal (IR) char. The VRD (demineralized VR) char exhibits lower $R_{0.5}$ values compared to VR char, while similar results were obtained for the IRD (demineralized IR) and IR chars. VRD and IRD chars display lower initial reactivities (R_i) compared to the VR and IR chars. In this context, the presence of inorganic minerals appears to have a catalytic effect on the initial carbon conversion reactions and that the removal of inorganic minerals through demineralization can inhibit gasification reactions.³⁷

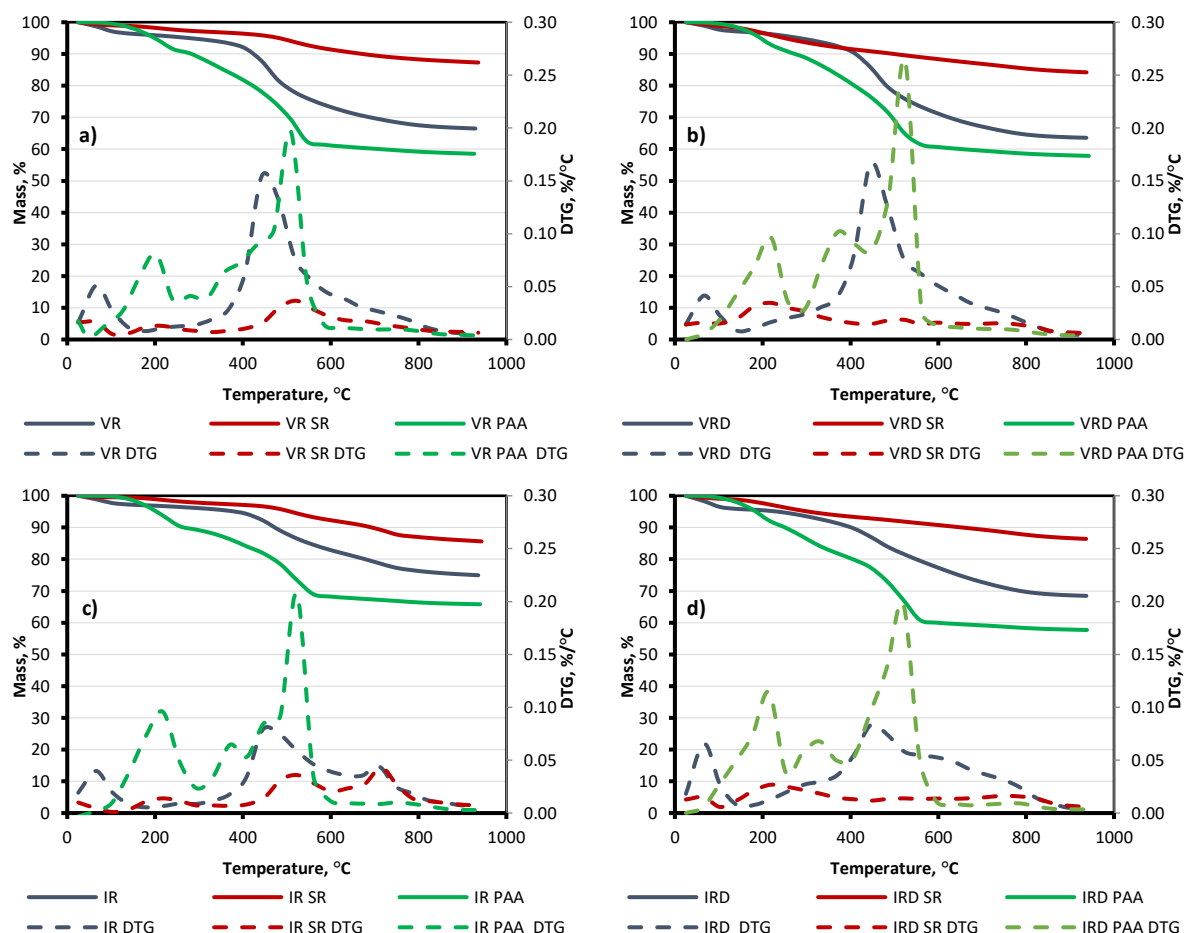


Figure 3-4. Pyrolysis curves are presented for the following coal samples: a) VR, b) VRD, c) IR, and d) IRD, with their respective solid residues and PAA's obtained during liquefaction experiments conducted at 450°C, utilizing tetralin as the solvent.

Furthermore, a more pronounced catalytic effect can be observed on the initial carbon conversion of the IR coal, characterized by a higher ash yield, when compared to the VR coal. A higher R_i value indicates a higher initial reactivity, meaning that the chars are more reactive at the beginning of the reaction than at 50% and 90% conversion. Nevertheless, this phenomenon was not evident for the demineralized materials, where the initial reactivities were lower than the reactivities observed at 50% and 90% conversion. Sakawa *et al.* (1982)³⁷ found that CO_2 gasification rates were higher in coals with higher inertinite contents but also expressed that higher inertinite contents were generally accompanied by high alkali indices.³⁸

However, the catalytic effect of inorganic minerals in the IR coal appears to outweigh the inherently lower reactivity of inertinite-rich macerals, leading to a higher R_i in the IR coal. The data indicates that, despite the inherently higher reactivity of vitrinite-rich macerals in VR coal, the higher ash yield and the catalytic effect of inorganic minerals in IR coal result in a more pronounced increase in initial reactivity (R_i) in the IR coal. This suggests that the catalytic effect of inorganic minerals can be particularly influential in enhancing the initial stages of carbon conversion reactions during gasification.³⁸ Lower L_c values of chars, indicative of smaller crystallite sizes and stacking height of graphitic planes, generally suggest that the accessibility of active sites is enhanced resulting in higher reactivities during gasification, whereas larger crystallite sizes are not favored during gasification.^{32,}

³⁶ When comparing the L_c values of VR SR (11.1 Å) and IR SR (12.4 Å) lower overall reactivities of the

IR SR char were observed. However, the reactivities of the solid residue chars obtained from the demineralized coal samples do not correlate with this trend, where R_i , $R_{0.5}$, $R_{0.9}$, and R_{fa} of IRD SR ($L_c = 43.5 \text{ \AA}$) is significantly higher than VRD SR ($L_c = 42.3 \text{ \AA}$). These results can be supported by the inhibiting or hindering effects of mineral matter in the IR coal sample and solid residue.^{31, 32, 37} This hindering effect can particularly be observed at the end of conversion – highlighted by lower R_{fa} values during char gasification reactions of the IR compared to the VR coals.

The gasification reactivity of coal generally decreases as the carbon content increases, corresponding to higher coal maturity. Various factors contribute to the variations in gasification reactivity, including the influence of pyrolysis conditions on the distinct mineral matter contents of the coals. Several char properties crucial for gasification, like surface area, porosity, chemical composition, and active site presence, are altered during pyrolysis and are influenced by the initial coal properties. The initial characteristics of the coal are thus unavoidably influenced by the chemical and physical processes that occur during the intermediate pyrolysis stage. In fact, the findings indicate that the pyrolysis step primarily determines the gasification reactivity of the char materials.³⁴ The mass loss curves from the CO_2 gasification experiments of the VR, VRD, IR, and IRD coal samples, and their respective liquefaction solid residues (produced at 450°C) at 900, 930, and 960°C are presented in **Figure S3-2**.

Table S3-2 shows the CO_2 gasification reactivities of solid residues produced from tetralin liquefaction at 425 and 400°C , and benzene liquefaction at 450°C . From these results the initial reactivities, R_i , of the liquefaction residue chars were mainly affected by liquefaction temperature. While the R_i of the residues derived from the VR coal increased at higher temperatures, i.e., the R_i of the residues derived from the IR coal decreased at higher liquefaction temperatures. Notably, the VRD solid residues and IRD solid residues showed the highest R_i values at 425°C .

Proximate analysis results indicate a higher fraction of fixed carbon content is achieved at higher liquefaction temperatures (**Table 3-4** and **Table S3-1**). Similarly, the fuel ratios of the liquefaction residues increased, indicating that volatile hydrocarbons are more prone to react during the liquefaction process. In general, vitrinite macerals contain a higher fraction of volatile matter compared to inertinite macerals because inertinite macerals have undergone a more advanced stage of coalification. This means that a larger portion of inertinite is composed of solid, carbonaceous material with a higher fixed carbon content compared to vitrinite macerals.³⁴

Table 3-8. CO_2 gasification reactivities at 960°C of the coal and demineralized coal samples, and their respective solid residues and PAA's produced from tetralin liquefaction at 450°C .

Reactivities	VR			VRD			IR			IRD		
	Raw	SR	PAA	Raw	SR	PAA	Raw	SR	PAA	Raw	SR	PAA
$t_{0.5}, \text{min}$	18.3	12.9	408.1	28.8	15.6	335.0	14.5	20.9	291.3	14.6	11.3	243.1
$t_{0.9}, \text{min}$	41.3	44.4	814.7	52.8	44.3	631.2	40.1	69.2	605.2	28.5	23.5	508.0
$R_{0.5}, \text{min}^{-1} \times 10^2$	2.73	3.88	0.12	1.74	3.21	0.15	3.44	2.39	0.17	3.42	4.43	0.21
$R_{0.9}, \text{min}^{-1} \times 10^2$	2.18	2.03	0.11	1.71	2.03	0.14	2.24	1.30	0.15	3.16	3.84	0.18
$R_i, \text{min}^{-1} \times 10^2$	2.29	4.92	0.12	1.21	2.86	0.14	4.38	3.77	0.24	2.71	3.21	0.24
$R_{fa}, \text{min}^{-1} \times 10^2$	1.37	0.89	0.09	1.43	1.09	0.12	1.22	0.65	0.11	2.43	2.65	0.13

Raw – feed materials; SR – Solid residues; PAA – Pre-asphaltene and asphaltene.

The random pore model (RPM) and the volumetric reactive model (VRM) were applied to the obtained CO_2 gasification results to determine parameters such as time factors (t_r) and structural parameters (Ψ) using **Eqs. 24** and **28**, respectively. The accuracy of the two models was assessed

using uncertainty parameters. These parameters, namely the quality of fit (QOF), determined from **Eq. 27**, and the error sum of square (ESS), were derived from the model fitting process. The summary of the RPM and VRM derived time factors (t_f), structural parameters (Ψ), quality of fit (QOF), and error sum square (ESS) at different temperatures for the VR and IR coals, as well as their respective solid residue chars and PAA's, is presented in **Table S3-3**. QOF values obtained from the RPM varied from 98.9–99.8 for the VR coal chars, and 98.1–99.7 for the IR coal char. Lower values were obtained using the VRM. The Random Pore Model considers a pore structure characterized by random overlap, resulting in a reduction in the available reaction area. This model can predict the maximum reactivity value as the reaction progresses because it simultaneously considers the effects of pore growth during the initial gasification stages and the destruction of pores due to the coalescence of adjacent pores.³⁹

The structural parameters, Ψ , of the VR chars were found to increase from 4.9–6.5 with increasing isothermal temperature (900–960°C). Similarly, the structural parameters of the IR chars increased with isothermal temperature, ranging from 0.23 to 0.77. The structural parameters obtained from the VR coal char indicate that pore growth occurred during the early stages of the gasification process ($\Psi > 2$) and that increased surface areas are expected during further carbon conversion. Whereas the values from the IR coal char indicate that pore coalescence was favored during the early stages of the gasification process ($\Psi < 2$), and surface areas are expected to decrease during further carbon conversion. As expected, the time factors, t_f , obtained from the coal chars and their liquefaction residue chars increased with increasing isothermal temperature. Similar results on South African bituminous coals were observed by other researchers.^{13, 26, 40} Structural parameters of the VR SR and IR SR chars were found to be 0.00 at all isothermal temperatures, which implies that both the random pore model and volumetric reaction model can be used to estimate the apparent activation energies of the chars during gasification (QOF values were the same for these materials). In addition, pore coalescence is expected to be mostly favored during the early stages of gasification. The VRM implies that that chemical reactions takes place simultaneously at all sites within the particle and the reaction surface linearly decreases with increasing char conversion.³⁹ This is supported by the lower average final reactivities obtained from the CO₂ gasification of the liquefaction solid residue chars, as presented in **Table 3-8**.

The E_a values estimated from the gasification reactions of all PAA's were difficult to calculate and values obtained from the different reactivity parameters and t_f values were inconsistent (**Table S3-3**). R^2 values derived from the reactivities at different isothermal temperatures were also low. This can be a result of significantly low gasification reactivities where model-fitting becomes difficult. From **Table S3-3**, the structural parameters, Ψ , of the PAA chars were expected to be higher compared to their parent coal derived chars, as per definition, larger structural parameters are indicated by low surface areas and smaller porosities.¹² This was true for the gasification reactions at 960°C for the IR coal char ($\Psi = 0.77$; BET = 69.5 m²/g) and IR PAA ($\Psi = 7.59$; BET = 2.1 m²/g); and for the VR coal char ($\Psi = 6.47$; BET = 90.1 m²/g) and VR PAA ($\Psi = 17.39$; BET = 1.9 m²/g). The structural parameters obtained from the VR and VRD coal chars, and their respective PAA's, were found to be inconsistent with this trend at gasification reactions conducted at 900 and 930°C.

Using the values of R_i , $R_{0.5}$, R_{fa} , t_f (RPM), and t_f (VRM) from the char CO₂ gasification results of VR, VR SR, IR, and IR SR, Arrhenius plots were constructed to estimate the apparent activation energies (E_a , kJ.mol⁻¹) and lumped pre-exponential factors (k_{so} , min⁻¹) from **Eq. 26**. These results are presented in

Table 3-9. The results from the demineralized coals and their liquefaction residue chars and PAA's are summarized in **Table S3-4**.

Table 3-9. Apparent activation energies (E_a , $\text{kJ}\cdot\text{mol}^{-1}$) and lumped pre-exponential factors (k_{so} , min^{-1}) calculated using the different reaction reactivity models from CO_2 gasification experiments of VR and IR, and their respective solid residue fractions produced from tetralin liquefaction at 450°C .

Sample	Reactivity model	R^2	Slope	Intercept	E_a ($\text{kJ}\cdot\text{mol}^{-1}$)	k_{so} (min^{-1})
VR	R_i	0.985	-21203.9	13.38	176.3	$6.5\text{E}+05$
	$R_{t0.5}$	1.000	-24220.8	16.04	201.4	$9.2\text{E}+06$
	$t_{f(RPM)}$	0.992	-22174.8	14.16	184.4	$1.4\text{E}+06$
	$t_{f(VRM)}$	1.000	-24280.4	16.58	201.9	$1.6\text{E}+07$
	R_{fa}	1.000	-24374.8	15.48	202.7	$5.3\text{E}+06$
VR SR	R_i	0.952	-20524.1	13.69	170.6	$8.8\text{E}+05$
	$R_{t0.5}$	0.982	-27809.7	19.35	231.2	$2.5\text{E}+08$
	$t_{f(RPM)}$	0.986	-28282.3	20.04	235.1	$5.1\text{E}+08$
	$t_{f(VRM)}$	0.986	-28281.5	20.04	235.1	$5.1\text{E}+08$
	R_{fa}	0.998	-27138.4	17.30	225.6	$3.3\text{E}+07$
IR	R_i	0.998	-13044.8	7.46	108.5	$1.7\text{E}+03$
	$R_{t0.5}$	0.999	-22582.9	14.95	187.8	$3.1\text{E}+06$
	$t_{f(RPM)}$	0.996	-20712.7	13.66	172.2	$8.6\text{E}+05$
	$t_{f(VRM)}$	0.999	-23729.3	16.30	197.3	$1.2\text{E}+07$
	R_{fa}	1.000	-26385.1	16.99	219.4	$2.4\text{E}+07$
IR SR	R_i	0.978	-13282.3	7.52	110.4	$1.8\text{E}+03$
	$R_{t0.5}$	0.999	-20688.5	13.05	172.0	$4.7\text{E}+05$
	$t_{f(RPM)}$	0.999	-20047.0	12.84	166.7	$3.8\text{E}+05$
	$t_{f(VRM)}$	0.999	-20097.7	12.88	167.1	$3.9\text{E}+05$
	R_{fa}	0.999	-23737.3	14.21	197.4	$1.5\text{E}+06$

The natural logarithm of R_i , $R_{t0.5}$, and R_{fa} were plotted against $1/T$ (K^{-1}) to approximate the values for E_a and k_{so} .

Estimated from the random pore model, the apparent activation energies of the gasification reaction were $184.4 \text{ kJ}\cdot\text{mol}^{-1}$ for the VR char, $235.1 \text{ kJ}\cdot\text{mol}^{-1}$ for the VR SR char, $172.2 \text{ kJ}\cdot\text{mol}^{-1}$ for the IR char, and $166.7 \text{ kJ}\cdot\text{mol}^{-1}$ for the IR SR char. The E_a values obtained from the char gasification reactions indicate lower overall apparent activation energies for the IR coal compared to the VR coal. However, a higher E_a was obtained for IR using R_{fa} parameters, indicating that more energy is needed to convert the char fraction between $X = 0.7$ and 0.9 . These values are inversely proportional to the char CO_2 gasification reactivities obtained from the IR and VR coal samples. Other researchers have established that chars with a higher gasification reactivity usually have lower apparent activation energies.^{13, 26} However, the reported E_a estimated from all parameters of the solid residue chars indicate that IR SR char had significantly lower E_a values (accompanied by lower gasification reactivities) compared to VR SR char, but comparable values to the IR char.

3.3.3. Characterization of liquid yields from liquefaction experiments

3.3.3.1. FTIR spectroscopy of liquid yields

The FTIR spectra of the liquid/oil products produced from tetralin liquefaction of VR, VRD, IR, and IRD coals at 450°C are presented in **Figure 3-5**. Pre-asphaltenes/asphaltenes (PAA's) were removed prior to FTIR spectroscopic analysis. The FTIR spectra of the liquid products from benzene liquefaction are presented in **Figure S3-4**. The FTIR spectra of the two solvents used, namely tetralin and benzene, are presented in **Figure S3-5**.

Relevant FTIR wavenumbers (cm^{-1}): 3052 and 3016 (sp^2 C-H stretch, aromatic); 2925 and 2857 (sp^3 C-H stretch, methylene/ CH_2); 1596, 1493 and 1451 (C=C stretch, aromatic); 1068 (C-O stretch, alkoxy); 781 and 741 (out-of-plane sp^2 C-H bend, ortho disubstituted aromatics); 618 (sp^2 C-H bend, methylene/ CH_2); 475 (out-of-plane ring bending).

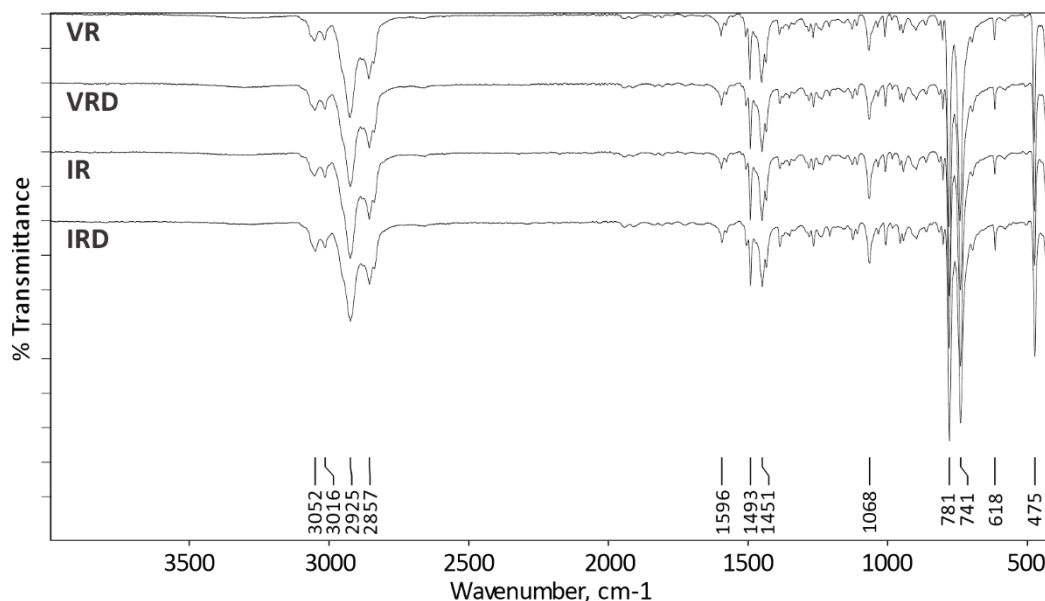


Figure 3-5. FTIR spectra of liquid/oil residues obtained from tetralin liquefaction conducted at 450°C on the VR, VRD, IR, and IRD coals.

Aromatic sp^2 C-H bands in the 3200–3000 cm^{-1} region indicate that the molecular structures of the liquid residues are similar to that of tetralin, signifying aromatic structures with connected methylene groups (methylene C-H stretch, 2925 and 2857 cm^{-1}). Bands with slightly higher intensities at 1596 cm^{-1} indicate more aromatic C=C groups are present in the liquid products and signify the formation of naphthalene during liquefaction. This can be supported by a strong out-of-plane sp^2 C-H bending vibration for ortho disubstituted aromatics at 781 cm^{-1} .³⁵ The band at 741 cm^{-1} indicates that a notable amount of unreacted tetralin is present. The results can be supported by the GC-MS results presented in **Table 3-10**. Evidently, no polar structures containing -C=O and -OH functional groups were produced from the coal samples during the liquefaction process. This can be supported by absent C=O stretching and O-H stretching vibrations in the 1750–1650 cm^{-1} and 3700–3200 cm^{-1} regions. Meanwhile, weak alkoxy C-O stretching vibrations at 1068 cm^{-1} are observed in the liquid products.

From **Figure S4**, presenting the FTIR spectra of the liquid fractions derived from benzene liquefaction conducted at 450°C, aromatic sp^2 C-H stretching bands can be observed in the 3200–3000 cm^{-1} range with no evidence of sp^3 C-H stretching bands in the 2950–2800 cm^{-1} region. This signifies that aromatic structures (like benzenes) are present without any detectable methylene groups (sp^3 C-H). However, from mass balance calculations, a fraction of hydrogen from the feed materials was transferred to the liquid fraction, most likely through hydrogenation reactions. It is possible that the large fraction of unreacted benzene present, supported by the low conversion values from benzene liquefaction, may suppress these methylene bands. The bands observed at 1715 cm^{-1} and 1266 cm^{-1} can be assigned to C=O stretching and acyl C-O stretching bands, respectively. The C=O stretching band is in the region for benzoate esters, i.e., 1730–1715 cm^{-1} . Similar to the liquid yields from

tetralin liquefaction, bands of out-of-plane sp^2 C-H bending vibrations of substituted aromatics are observed at 738 cm^{-1} .

No distinctive differences between the spectra of the VR, VRD, IR, and IRD liquid residues derived from tetralin liquefaction were observed. The same conclusion can be made for the liquid residues derived from benzene liquefaction. Indicating that the liquefaction process produces compounds with similar structural characteristics.

3.3.3.2. Ultimate analysis, calorific values, and GC-MS of liquid yields

Through mass balance calculations, presented in **Table S3-5**, the approximate ultimate analysis values of the liquid yields from tetralin liquefaction at 450°C were determined, as presented in **Table 3-10**. When considering **Table 3-1**, it is evident that the low hydrogen content of the coal samples affected the final hydrogen content of the liquid yields. The lower H/C molar ratio of the liquid yields compared to tetralin supports this statement. **Table S3-5** shows the mass balance results and highlights carbon, hydrogen, and oxygen transfer from the coal samples to the liquid yield during tetralin liquefaction at 450°C . A significant fraction of carbon originating from the feed materials was transferred to the liquid yield, specifically 9.7, 10.0, 5.4, and 7.3g from the feed materials with carbon contents of 12.5, 15.0, 10.4, and 14.9g for VR, VRD, IR, and IRD, respectively. Hydrogen transfer from the IR and IRD coal samples was significantly lower compared to that from the VR and VRD coal samples. It can be assumed that the higher aromatic nature of the inertinite-rich coal results in fewer hydrogen transfer reactions, affecting the overall H/C molar ratios of the liquid yields. Compared to the mass transfer results obtained from benzene liquefaction conducted at 450°C , presented in Table S6, a significantly larger fraction of hydrogen was transferred from the feed material to the liquid yield despite having significantly lower conversion values. Generally, hydrogenation of benzene is a difficult process, however, at high temperatures and pressures, and in the presence of a catalyst, hydrogenation reactions can proceed to produce compounds like 1,3-cyclohexadiene, cyclohexene, and cyclohexane.⁴¹ From these results, it is also evident that a larger fraction of carbon and hydrogen reacted to produce gases during benzene liquefaction experiments conducted on the VR and VRD samples compared to the IR and IRD samples, and may be attributed to the presence of more aliphatic compounds in the VR and VRD samples.

Table 3-10. Approximate ultimate analysis and calorific values of liquid yields from tetralin liquefaction at 450°C .

Sample Identification	Tetralin	VR _{liq}	VRD _{liq}	IR _{liq}	IRD _{liq}
% Carbon Content	90.85	86.9	85.9	87.3	85.7
% Hydrogen Content	9.15	7.9	7.8	8.1	7.7
% Nitrogen Content	n.d.	2.9	3.7	2.8	4.0
% Oxygen Content (calculated)	n.d.	2.2	2.7	1.7	2.5
% Total sulphur	n.d.	0.1	0.0	0.1	0.0
O/C molar ratio	0.00	0.02	0.02	0.01	0.02
H/C molar ratio	1.20	1.08	1.07	1.11	1.07
Calorific values (MJ.kg ⁻¹)	42.4	42.3	42.8	42.1	42.1

Feed materials – VR, VRD, IR, IRD; liq – liquid yield; n.d. – not determined.

The similarities observed during the structural evaluation, discussed in **Section 3.3.1**, can be supported by insignificant differences obtained from calorific value determinations. Calorific values were determined on the liquid products from tetralin liquefaction conducted at 450°C . The results showed that similar values were obtained from the liquids/oils produced from the VR, VRD, IR, and

IRD coals, having calorific values of 42.3, 42.8, 42.1, and 42.1 MJ.kg⁻¹, respectively. The results can, however, be more qualitatively and semi-quantitatively characterized using GC-MS, as presented in **Table 3-11**.

Table 3-11. GC-MS results of the liquid yields produced from liquefaction experiments conducted at 400, 425, and 450°C with tetralin as the solvent.

		Abundance, %						
		Tetralin	Naphthalene	Alkylated benzenes	Bicyclic compounds	PAH's	O-containing HC's	Other
		132.1 g.mol ⁻¹	128.1 g.mol ⁻¹	120.1-142.1 g.mol ⁻¹	118.1-138.1 g.mol ⁻¹	168.1-258.1 g.mol ⁻¹	220.2-258.1 g.mol ⁻¹	254.0-334.0 g.mol ⁻¹
Temp.	Sample							
450	VRt	54.4	32.8	10.6	1.3	0.2	0.3	0.1
	VRDt	51.2	41.7	4.7	0.0	1.4	0.2	0.8
	IRt	62.1	29.9	7.1	0.0	0.5	0.8	0.0
	IRDt	53.9	35.6	7.3	0.4	1.1	1.3	0.3
425	VRt	72.4	25.1	2.0	0.0	0.0	0.5	0.0
	VRDt	68.5	28.5	0.0	0.0	0.5	0.3	0.4
	IRt	79.9	18.6	1.4	0.0	0.0	0.2	0.0
	IRDt	68.9	29.2	1.6	0.0	0.0	0.2	0.1
400	VRt	88.7	11.3	0.0	0.0	0.0	0.0	0.0
	VRDt	83.3	16.7	0.0	0.0	0.0	0.0	0.0
	IRt	93.9	6.1	0.0	0.0	0.0	0.0	0.0
	IRDt	85.6	14.4	0.0	0.0	0.0	0.0	0.0

Feed materials – VR, VRD, IR, IRD; Liquefaction temperatures – 400, 425, 450°C; Solvent used: t – tetralin.

The dehydrogenation of tetralin to form naphthalene shows a linear trend to carbon conversion values at increasing liquefaction temperatures, as presented in **Table 3-3**. The main products from the liquefaction process were naphthalene, with some fractions of alkylated benzenes or tetralin derivatives. The presence hydrocarbons, and the oil samples can be mostly related to the dehydrogenation of tetralin, but can also be a result of the dissolution of organic compounds from the coal samples in tetralin during liquefaction.¹⁷ It can be observed that the breakdown of the coal's macromolecular structure is enhanced at 450°C, where a higher fraction of alkylated benzenes, polyaromatic hydrocarbons, and oxygen containing hydrocarbons are produced, with a lower fraction of naphthalene. The results also indicate that a 1-to-3 coal-to-solvent ratio was sufficient for hydrogenation during the liquefaction experiment.

The formation of naphthalene through dehydrogenation of tetralin provided the necessary hydrogen needed to form compounds such as butylbenzene and indane. Through rearrangement, compounds like 1-methylindane, 1-ethenyl-3-ethylbenzene, 2-methyl-1-propenylbenzene, and 1-phenyl-1-butene could be produced at elevated temperatures. However, the reactions to produce some of these compounds could only proceed when hydrogen atoms are available for initiation.⁴² Other compounds, predominantly butylbenzene, were formed through hydrogenation reactions during tetralin liquefaction experiments conducted at 450°C. Similarly, indane only formed during experiments conducted at 450°C, while 1-methylindane, 1-ethenyl-3-ethylbenzene, 2-methyl-1-propenylbenzene, and 1-phenyl-1-butene production started at 425°C. The total abundance (%) of these four compounds were 8.1, 4.7, 5.1, and 5.5 for VRt, VRDt, IRt, and IRDt at 450°C, respectively. At 425°C, the values were significantly lower with 2.0, 1.9, 1.4, and 2.1 for VRt, VRDt, IRt, and IRDt. The results show that at 400°C the temperature is too low for the production of these compounds.

Blank experiments conducted using only tetralin showed that no reactions occur at these temperatures and pressures. However, at high concentration of tetralin the detector responses might have overlapped, masking the presence of other compounds. It should be noted that the experiments were conducted in an inert environment at elevated pressures. Hooper *et al.* (1979)⁴² found that insignificant amounts of naphthalene by dehydrogenation and 1-methylindane by rearrangement formed during low-temperature pyrolysis, e.g. 350°C. However, from 400 to 450°C the predominant product was 1-methylindane with a maximum yield of 5% (by weight) at 450°C. They also noted the formation of hydrogen and methane at 450°C, which might have formed from, firstly, dehydrogenation reactions, and secondly, demethylation reactions of 1-methylindane to produce indane.

Polar and oxygen-containing compounds were absent or in low concentrations in the oil samples. This can be supported by weak alkoxy C-O bands, and absent C=O and O-H bands in the FTIR spectra of the oil samples. As reported by Isa *et al.* (2018)⁴³, it is favorable to produce residues from liquefaction having low oxygen contents. From this study it is evident that oxygen containing functional groups were removed from the coals during the liquefaction process in the form of carbon dioxide and carbon monoxide. This is evident from the gas analysis results presented in **Figure 3-6**.

3.3.4. Gas analysis – GC-TCD/FID

The data presented in **Table S3-7** includes molar/volume percentage values obtained from the gas analysis, along with the corresponding partial pressures of the generated gases. These results served as essential inputs for calculating the masses of compound gases, applying Dalton's law for partial pressure and the Ideal Gas Law. These results are highlighted in **Figure 3-6**, showing the mass fractions of the gaseous species obtained from liquefaction experiments conducted at 450°C using tetralin.

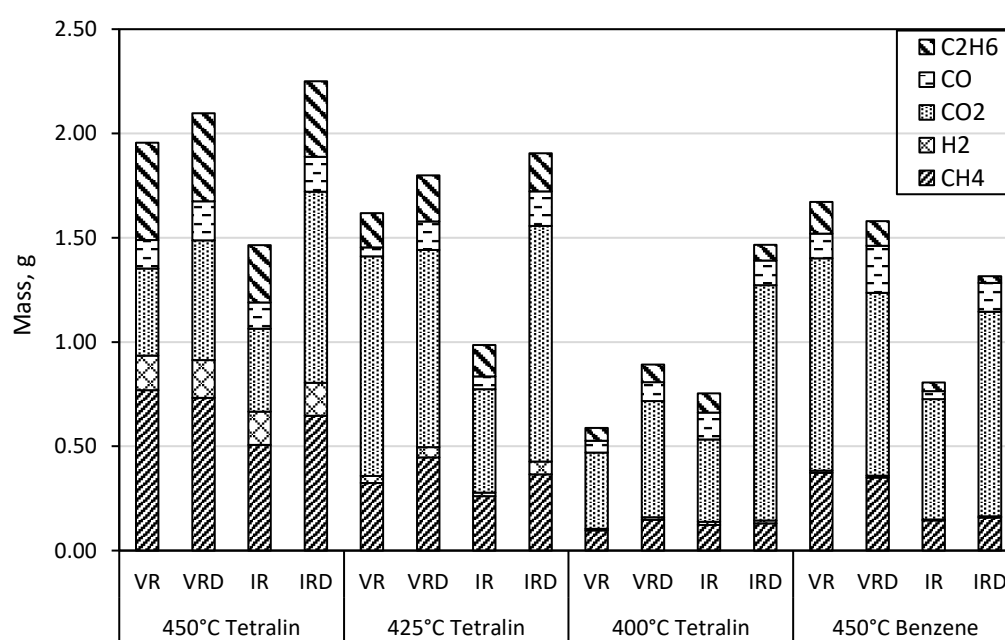


Figure 3-6. Gas chromatography results of the gas fractions produced from liquefaction experiments.

In the liquefaction process, previous research has shown that the primary components of liquefaction gas include hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), and hydrocarbon compounds such as methane, ethane, and propane.³¹ Notably, it has been observed that higher liquefaction temperatures result in an increased production of hydrogen. This phenomenon may be attributed to the thermal breakdown of aliphatic carbon-hydrogen linkages or the cracking of larger molecular compounds at elevated temperatures. Additionally, it is conceivable that the catalyzed dehydrogenation of tetralin is promoted at higher temperatures.

Methane and carbon dioxide start to evolve at relatively low temperatures (200°C). As the temperature continues to rise, there is internal condensation of the macromolecular structure of low-rank coals. This condensation process initiates the evolution of carbon dioxide (CO_2) and water (H_2O) as by-products.³¹ Decarboxylation reactions were favored at 425°C to produce CO_2 during liquefaction experiments conducted on all coal samples. When compared to the gas fractions obtained at 450°C, decarbonylation (and possible dehydration) reactions were favored to produce CO. The reaction of CO_2 and carbon to produce CO may also play a role in the formation of carbon monoxide. The Boudouard reaction demonstrates that at lower temperatures, the equilibrium favors the exothermic production of carbon dioxide, whereas at higher temperatures, the endothermic formation of carbon monoxide becomes the predominant product, as predicted by Le Chatelier's Principle.^{31, 44}

3.4. Conclusions

Liquefaction experiments of an inertinite-rich discard coal and vitrinite-rich coal were performed using tetralin and benzene as the solvents. In addition, the demineralized coal fractions were also considered as feed during liquefaction experiments. It was found that inorganic minerals inhibited the liquefaction carbon conversion reactions in the inertinite-rich coal, while promoting conversion reaction in the vitrinite-rich coal. The results indicated that polar functional groups promoted CO and CO₂ formation in the gaseous products at higher liquefaction temperatures. Low concentrations of oxygen containing functional groups were observed in the liquid and solid residues obtained from the liquefaction experiments. In addition, CO₂ gasification experiments were conducted on the chars of the coals, liquefaction solid residues, and pre-asphaltenes and asphaltenes (PAA). The gasification results indicated that the conversion reactions were enhanced by inorganic minerals in the inertinite-rich coal char, resulting from higher concentrations of alkaline species compared to the vitrinite-rich coal. Significantly low gasification reactivities were observed for the PAA samples. The results indicated that the solid residues from discard coal fines' liquefaction may be utilized during gasification processes, decreasing the amounts of waste generated and adding economic value to the waste. Lastly, the results from this investigation will aid in the understanding of hydrogen-transfer and carbon conversion processes during co-liquefaction of inertinite-rich discard coal with plastics such as polypropylene and polyethylene (low-density) using both tetralin and benzene as a solvent.

Acknowledgments

The information presented in this paper is based on the research financially supported by the National Research Foundation (NRF) and South African Research Chairs Initiatives (SARChI) of the Department of Science and Technology (Coal Research chair Grant No. 86880). Any opinions, conclusions or recommendations expressed are that of the author(s), and no liability is accepted on the NRF's regard.

3.5. Supporting Information

Table S3-1. Approximated proximate analysis from TGA and calculated higher heating value of solid residues produced from tetralin liquefaction at 425 and 400°C, and benzene liquefaction at 450°C.

Sample Identification	VR SR 425t	VRD SR 425t	IR SR 425t	IRD SR 425t	VR SR 400t	VRD SR 400t	IR SR 400t	IRD SR 400t	VR SR 450b	VRD SR 450b	IR SR 450b	IRD SR 450b
% Moisture content	1.5	1.1	0.6	1.1	0.9	0.9	0.7	1.1	1.5	1.3	0.9	1.6
% Ash content	33.0	3.0	43.6	3.1	22.1	3.4	36.7	2.2	14.7	2.3	34.1	1.8
% Volatile Matter	18.0	19.1	16.7	17.2	24.5	25.4	20.4	23.0	15.1	15.4	15.0	15.2
% Fixed Carbon	47.5	76.8	39.2	78.6	52.5	70.3	42.2	73.7	68.8	81.0	50.0	81.4
Fuel Ratio	2.6	4.0	2.3	4.6	2.1	2.8	2.1	3.2	4.6	5.3	3.3	5.4
HHV (MJ.kg ⁻¹)(Eq. 5)	19.6	30.4	16.2	30.8	22.4	29.1	17.9	29.9	27.0	31.4	19.9	31.7
CV (MJ.kg ⁻¹)	21.5	33.1	16.8	33.8	26.1	32.7	19.4	32.8	27.8	32.6	19.5	31.6
% Carbon	83.8	85.6	79.0	87.5	84.9	83.6	78.8	83.8	84.9	84.5	78.7	82.6
% Hydrogen	4.5	4.1	3.9	4.1	5.0	4.6	4.1	4.2	3.3	3.4	3.0	3.0
% Nitrogen	2.9	2.6	2.2	2.2	2.8	2.6	2.2	2.2	2.6	2.5	2.2	2.2
% Oxygen (by diff.)	8.0	7.4	13.4	5.6	6.7	8.7	13.9	9.1	8.4	9.0	14.8	11.3
% Total sulphur	0.8	0.4	1.5	0.7	0.6	0.5	1.1	0.6	0.8	0.6	1.4	0.9
O/C molar ratio	0.07	0.06	0.13	0.05	0.06	0.08	0.13	0.08	0.07	0.08	0.14	0.10
H/C molar ratio	0.64	0.57	0.59	0.56	0.71	0.66	0.61	0.59	0.46	0.47	0.46	0.44

Feed material = VR, VRD, IR, IRD; Solid residue = SR; Liquefaction temperatures = 400, 425, 450°C; Solvent used: t = tetralin, b = benzene.

Table S3-2. CO₂ gasification reactivities at 960°C of solid residues produced from tetralin liquefaction at 425 and 400°C, and benzene liquefaction at 450°C.

Reactivities	VR SR 425t	VRD SR 425t	IR SR 425t	IRD SR 425t	VR SR 400t	VRD SR 400t	IR SR 400t	IRD SR 400t	VR SR 450b	VRD SR 450t	IR SR 450b	IRD SR 450b
$t_{0.5}$, min	11.5	14.0	14.3	10.4	12.9	15.5	11.3	12.1	28.5	26.9	19.4	16.5
$t_{0.9}$, min	29.4	35.9	43.0	19.6	28.1	37.6	29.2	23.9	62.3	57.4	52.7	29.8
$R_{t0.5}$, min ⁻¹ x100	4.36	3.57	3.50	4.80	3.88	3.23	4.44	4.13	1.76	1.86	2.58	3.03
$R_{t0.9}$, min ⁻¹ x100	3.06	2.51	2.09	4.58	3.20	2.39	3.08	3.77	1.45	1.57	1.71	3.02
R_i , min ⁻¹ x100	4.65	3.08	4.41	3.85	2.90	2.62	5.38	2.84	1.29	1.27	2.87	2.17
R_{fo} , min ⁻¹ x100	1.75	1.42	1.06	3.64	2.11	1.45	1.83	2.81	0.93	1.02	0.92	2.52

Table S3-3. RPM and VRM derived time factors (t_f), structural parameters (ψ), quality of fit (QOF), and error sum square (ESS).

		RPM				VRM		
	Sample:	QOF	t_f	ψ	ESS	QOF	t_f	ESS
900°C	VR	99.8	0.00896	4.884	0.0000	91.8	0.01640	0.0688
	VR SR	98.7	0.01653	0.000	0.0019	98.7	0.01653	0.0019
	VR PAA	96.9	0.00137	3.257	0.0089	91.7	0.00220	0.0663
	IR	98.1	0.01812	0.231	0.0029	98.0	0.01951	0.0051
	IR SR	98.9	0.01417	0.000	0.0018	98.9	0.01417	0.0018
	IR PAA	94.6	0.00113	7.044	0.0110	90.4	0.00225	0.1063
930°C	VR	98.9	0.01335	6.981	0.0006	90.3	0.02718	0.0856
	VR SR	98.8	0.03402	0.000	0.0024	98.8	0.03396	0.0024
	VR PAA	97.9	0.00113	5.501	0.0050	90.6	0.00211	0.0877
	IR	99.2	0.02948	0.371	0.0006	98.4	0.03297	0.0049
	IR SR	98.8	0.02219	0.000	0.0021	98.8	0.02219	0.0021
	IR PAA	95.7	0.00128	6.234	0.0076	91.1	0.00252	0.0999
960°C	VR	99.0	0.02251	6.469	0.0006	91.0	0.04489	0.0792
	VR SR	99.3	0.05330	0.000	0.0007	99.3	0.05330	0.0007
	VR PAA	94.4	0.00074	17.393	0.0074	87.8	0.00205	0.1569
	IR	99.7	0.04275	0.773	0.0001	97.3	0.05217	0.0111
	IR SR	98.8	0.03254	0.006	0.0020	98.8	0.03261	0.0020
	IR PAA	95.4	0.00140	7.586	0.0067	91.0	0.00299	0.1084

Table S3-4. Apparent activation energies (E_a , kJ.mol⁻¹) and lumped pre-exponential factors (k_{so} , min⁻¹) calculated using the different reaction reactivity models from CO₂ gasification experiments of VRD and IRD, and their respective solid residue fractions produced from tetralin liquefaction at 450°C.

Sample	Reactivity model	R ²	Slope	Intercept	E_a (kJ.mol ⁻¹)	k_{so} (min ⁻¹)
VRD	R_i	1.000	-21316.3	12.87	177.2	3.9E+05
	$R_{t0.5}$	1.000	-24939.7	16.17	207.4	1.1E+07
	$t_{f(RPM)}$	1.000	-13385.7	5.53	111.3	2.5E+02
	$t_{f(VRM)}$	1.000	-25286	17.02	210.2	2.5E+07
	R_{fo}	1.000	-26809	17.50	222.9	4.0E+07
VRD SR	R_i	0.970	-17925.7	10.94	149.0	5.7E+04
	$R_{t0.5}$	0.986	-20293.7	13.05	168.7	4.6E+05
	$t_{f(RPM)}$	0.968	-20234	13.08	168.2	4.8E+05
	$t_{f(VRM)}$	0.963	-20207.8	13.38	168.0	6.5E+05
	R_{fo}	0.880	-18988.6	10.97	157.9	5.8E+04
IRD	R_i	0.945	-13835.5	7.65	115.0	2.1E+03
	$R_{t0.5}$	0.991	-19505.3	12.46	162.2	2.6E+05
	$t_{f(RPM)}$	0.415	-4188.23	-0.60	34.8	5.5E-01
	$t_{f(VRM)}$	0.997	-22344.6	15.37	185.8	4.7E+06
	R_{fo}	0.995	-30341.7	20.91	252.3	1.2E+09
IRD SR	R_i	0.999	-20731	13.36	172.4	6.4E+05
	$R_{t0.5}$	1.000	-25873.5	17.87	215.1	5.8E+07
	$t_{f(RPM)}$	0.842	-14291.1	7.83	118.8	2.5E+03
	$t_{f(VRM)}$	0.997	-27111.6	19.42	225.4	2.73E+08
	R_{fo}	0.986	-32483.7	22.76	270.1	7.7E+09

The natural logarithm of R_i , $R_{t0.5}$, and R_{fo} were plotted against $1/T$ (K⁻¹) to approximate the values for E_a and k_{so} .

Table S3-5. Mass balance results of the reacting materials and product yields from tetralin liquefaction conducted at 450°C.

Materials	C	H	O	N	S	Molar H/C	Molar O/C
<i>Solvent and feed, g</i>							
Tetralin (60g)	54.5	5.5	0.0	0.00	0.00	1.20	0.00
VR (20g)	12.5	0.9	2.2	2.19	0.11	0.84	0.13
VRD (20g)	15.0	1.0	2.8	2.78	0.12	0.76	0.14
IR (20g)	10.4	0.6	2.0	2.00	0.16	0.70	0.14
IRD (20g)	14.9	0.7	3.0	2.96	0.16	0.58	0.15
<i>Product yields, g</i>							
VR _{SR}	1.7	0.1	0.2	0.02	0.06	0.52	0.10
VRD _{SR}	3.9	0.2	0.3	0.02	0.11	0.52	0.05
IR _{SR}	4.2	0.2	0.5	0.09	0.11	0.54	0.08
IRD _{SR}	6.6	0.3	0.4	0.06	0.15	0.49	0.04
VR _{gas}	1.1	0.5	0.4	n.d.	n.d.	4.81	0.26
VRD _{gas}	1.1	0.5	0.5	n.d.	n.d.	4.77	0.35
IR _{gas}	0.8	0.3	0.4	n.d.	n.d.	5.34	0.36
IRD _{gas}	1.1	0.4	0.8	n.d.	n.d.	4.29	0.52
VR _{liq}	64.2	5.8	1.6	2.2	0.1	1.08	0.02
VRD _{liq}	64.5	5.8	2.0	2.8	0.0	1.07	0.02
IR _{liq}	59.9	5.6	1.2	1.9	0.0	1.11	0.01
IRD _{liq}	61.8	5.6	1.8	2.9	0.0	1.07	0.02
<i>Mass transfer (solid feed to liquid yield), g</i>							
VR to VR _{liq}	9.7	0.4	1.6	2.17	0.06	0.44	0.12
VRD to VRD _{liq}	10.0	0.3	2.0	2.76	0.01	0.40	0.15
IR to IR _{liq}	5.4	0.1	1.2	1.91	0.05	0.18	0.16
IRD to IRD _{liq}	7.3	0.1	1.8	2.90	0.01	0.11	0.19

Feed – VR, VRD, IR, IRD; SR – solid residue; liq – liquid yield; gas – gas yield; n.d. – not determined.

Table S3-6. Mass balance results of the reacting materials and product yields from benzene liquefaction conducted at 450°C.

Materials	C	H	O	N	S	Molar H/C	Molar O/C
<i>Solvent and feed, g</i>							
Benzene (60g)	55.4	4.7	0.0	0.00	0.00	1.00	0.00
VR (20g)	12.5	0.9	2.2	2.19	0.11	0.84	0.13
VRD (20g)	15.0	1.0	2.8	2.78	0.12	0.76	0.14
IR (20g)	10.4	0.6	2.0	2.00	0.16	0.70	0.14
IRD (20g)	14.9	0.7	3.0	2.96	0.16	0.58	0.15
<i>Product yields, g</i>							
VR _{SR}	10.85	0.56	1.24	0.70	0.13	0.61	0.09
VRD _{SR}	12.85	0.52	1.37	0.38	0.09	0.48	0.08
IR _{SR}	8.42	0.32	1.48	0.24	0.15	0.45	0.13
IRD _{SR}	13.82	0.50	1.89	0.37	0.15	0.43	0.10
VR _{gas}	0.73	0.14	0.81	n.d.	n.d.	2.20	0.83
VRD _{gas}	0.69	0.12	0.77	n.d.	n.d.	2.09	0.83
IR _{gas}	0.32	0.05	0.44	n.d.	n.d.	1.86	1.05
IRD _{gas}	0.47	0.05	0.79	n.d.	n.d.	1.29	1.26
VR _{liq}	56.3	4.8	0.1	1.50	-0.02	1.02	0.00
VRD _{liq}	56.8	5.0	0.6	2.40	0.02	1.04	0.01
IR _{liq}	57.0	4.9	0.1	1.77	0.01	1.02	0.00
IRD _{liq}	56.0	4.8	0.3	2.59	0.01	1.03	0.00
<i>Mass transfer (solid feed to liquid yield), g</i>							
VR to VR _{liq}	0.91	0.19	0.14	1.50	-0.02	2.45	0.12
VRD to VRD _{liq}	1.47	0.32	0.65	2.40	0.02	2.56	0.33
IR to IR _{liq}	1.66	0.25	0.08	1.77	0.01	1.76	0.04
IRD to IRD _{liq}	0.65	0.18	0.27	2.59	0.01	3.32	0.32

Feed – VR, VRD, IR, IRD; SR – solid residue; liq – liquid yield; gas – gas yield; n.d. – not determined.

Table S3-7. Gas chromatography results of the gas fractions produced from liquefaction experiments.

	Sample	Molar/Volume, %					$\Delta P_{r.t.}$ (bar)	Mass, g					
		CH ₄	H ₂	CO ₂	CO	C ₂ H ₆		CH ₄	H ₂	CO ₂	CO	C ₂ H ₆	Total
450°C Tetralin	VR	29.9	51.5	5.9	3.0	9.7	8.1	0.77	0.17	0.42	0.14	0.47	1.96
	VRD	26.9	53.1	7.7	3.9	8.3	8.5	0.73	0.18	0.57	0.19	0.42	2.10
	IR	23.7	59.3	6.8	3.4	6.8	6.9	0.51	0.16	0.40	0.13	0.27	1.46
	IRD	25.5	50.0	13.2	3.8	7.6	8.0	0.65	0.16	0.92	0.17	0.36	2.25
425°C Tetralin	VR	29.8	24.6	35.3	2.3	8.0	4.0	0.32	0.03	1.05	0.04	0.16	1.62
	VRD	32.5	28.3	25.0	5.7	8.5	4.8	0.45	0.05	0.95	0.14	0.22	1.80
	IR	38.0	19.1	26.2	5.0	11.6	2.9	0.26	0.02	0.50	0.06	0.15	0.98
	IRD	25.2	33.1	28.4	6.5	6.7	5.0	0.37	0.06	1.13	0.17	0.18	1.91
400°C Tetralin	VR	26.6	18.8	36.7	9.0	8.9	2.0	0.10	0.01	0.36	0.06	0.06	0.59
	VRD	27.2	17.6	37.3	9.6	8.3	2.5	0.15	0.01	0.56	0.09	0.08	0.89
	IR	24.3	23.1	28.3	14.6	9.7	2.4	0.12	0.01	0.39	0.13	0.09	0.75
	IRD	17.1	14.6	54.0	8.9	5.3	3.1	0.13	0.01	1.13	0.12	0.08	1.47
450°C Benzene	VR	38.1	8.8	37.9	6.9	8.3	3.7	0.37	0.01	1.02	0.12	0.15	1.67
	VRD	37.1	8.6	33.9	13.7	6.8	3.6	0.35	0.01	0.88	0.23	0.12	1.58
	IR	33.2	8.2	48.4	4.9	5.3	2.2	0.14	0.00	0.58	0.04	0.04	0.81
	IRD	24.4	6.0	54.8	12.2	2.6	2.8	0.16	0.00	0.98	0.14	0.03	1.32

Feed materials – VR, VRD, IR, IRD; Liquefaction temperatures – 400, 425, 450°C. $\Delta P_{r.t.}$ = Partial pressure of gases at 25°C.

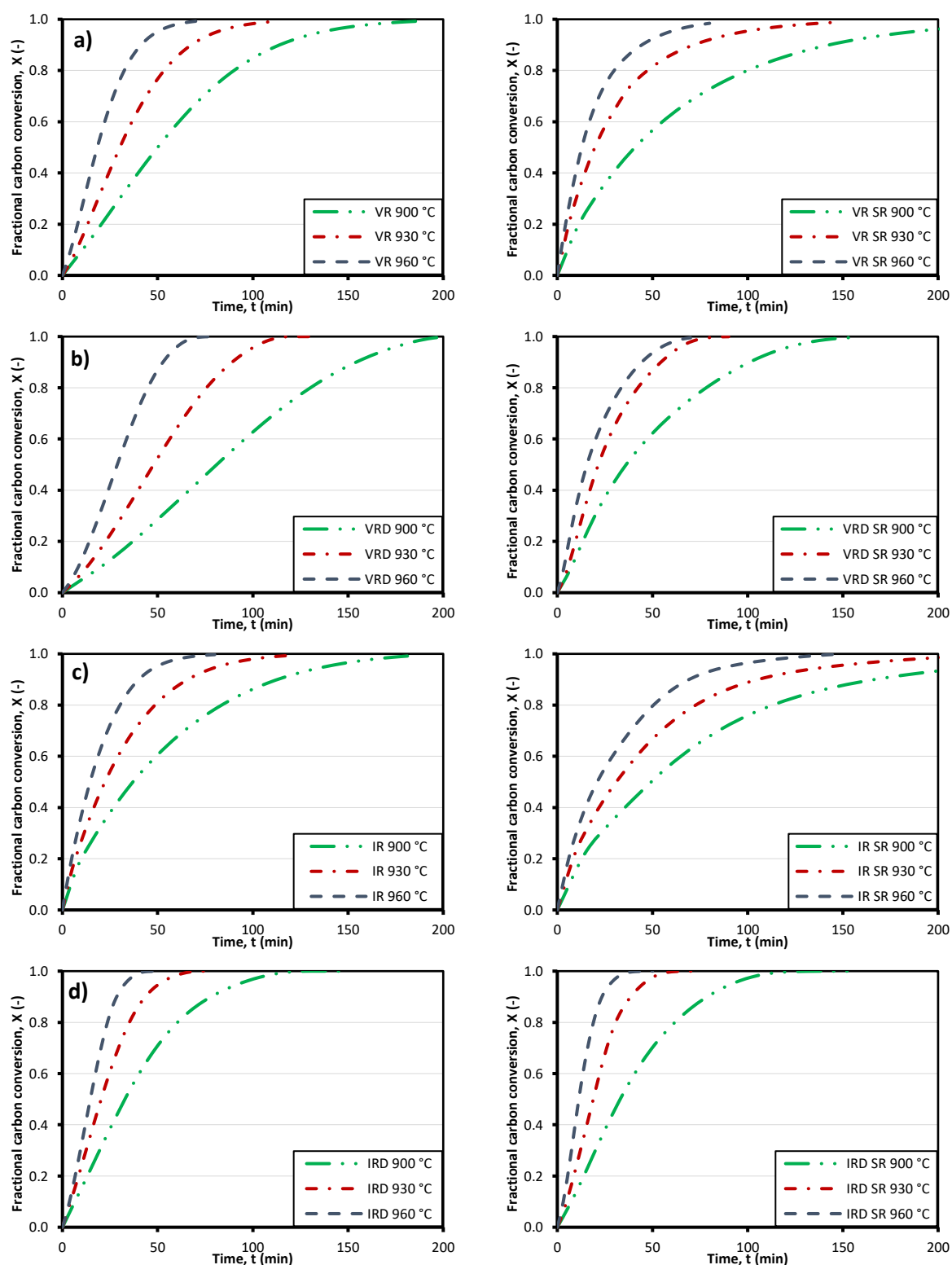


Figure S3-1. Effect of CO₂ gasification temperature on the fractional conversion of the chars from a) VR, b) VRD, c) IR, and d) IRD. The results obtained from the 450°C tetralin liquefaction solid residue char fractions are adjacent to the coal chars.

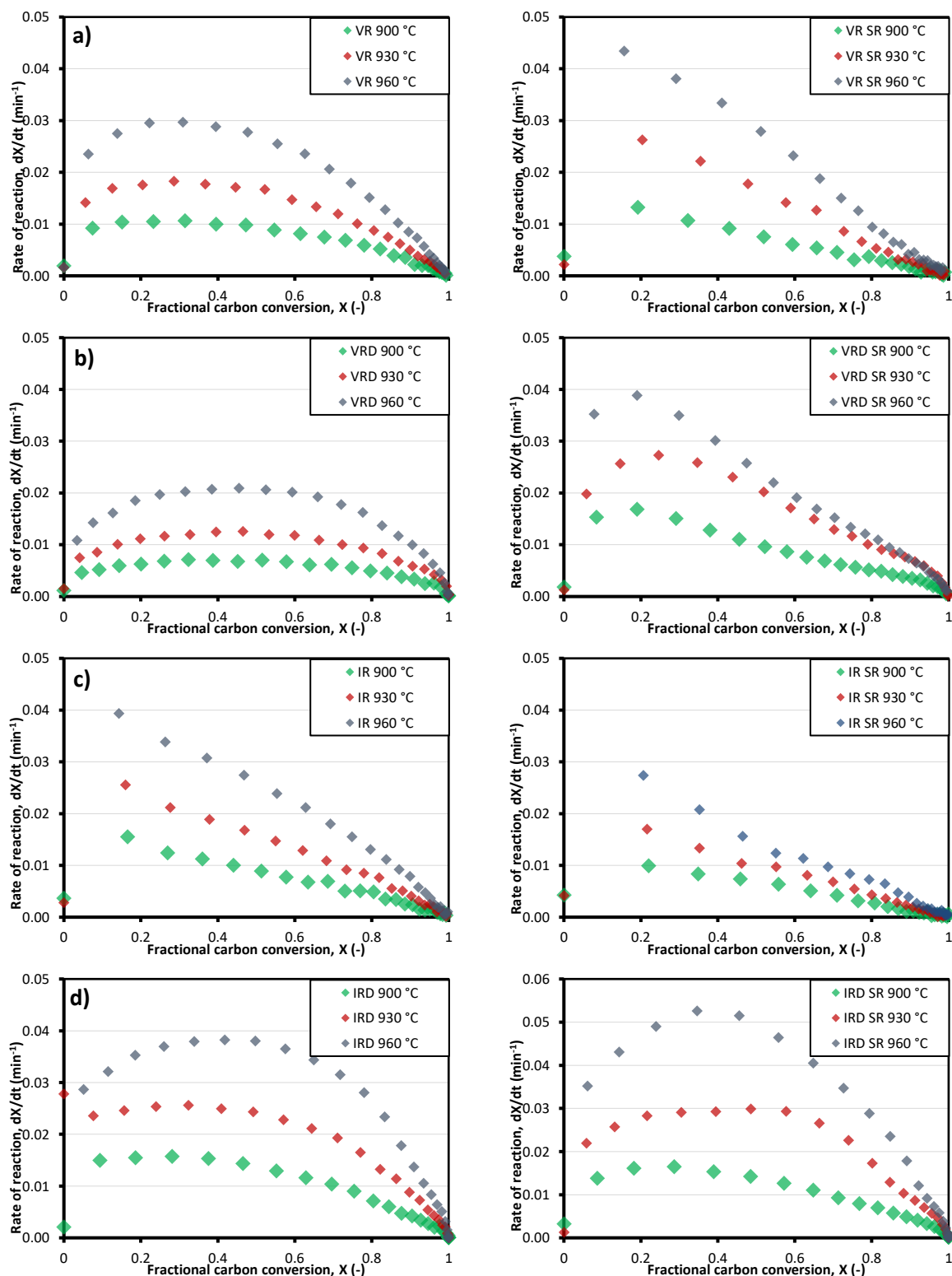


Figure S3-2. Effect of CO_2 gasification temperature on the rate of the reaction as a function of conversion from a) VR, b) VRD, c) IR, and d) IRD. The results obtained from the 450 °C tetralin liquefaction solid residue char fractions are adjacent to the coal chars.

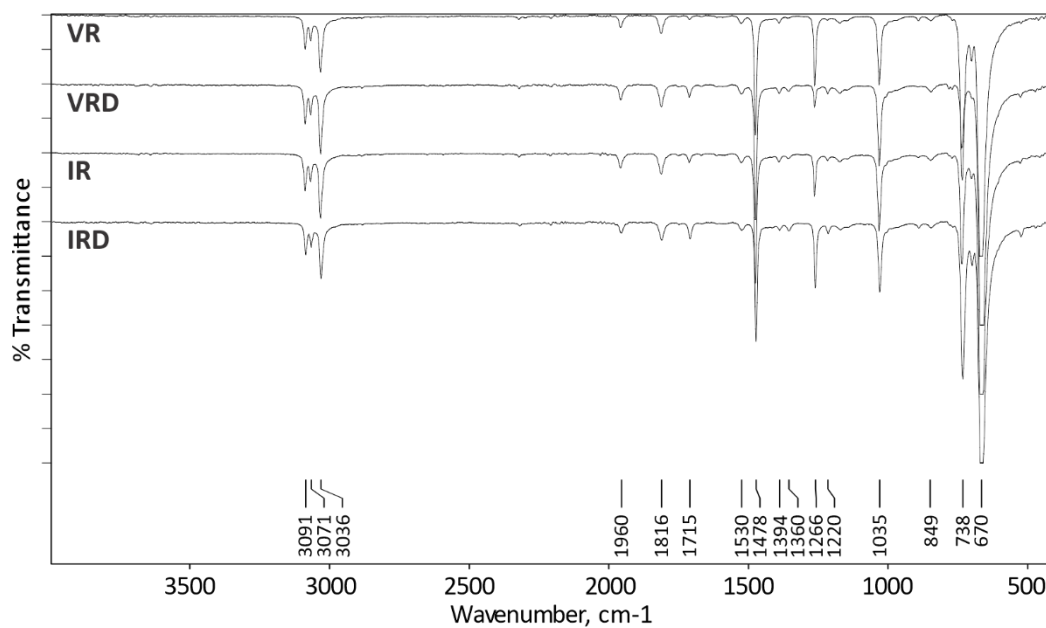


Figure S3-3. FTIR spectra of liquid/oil residues obtained from benzene liquefaction conducted at 450°C on the VR, VRD, IR, and IRD coals.

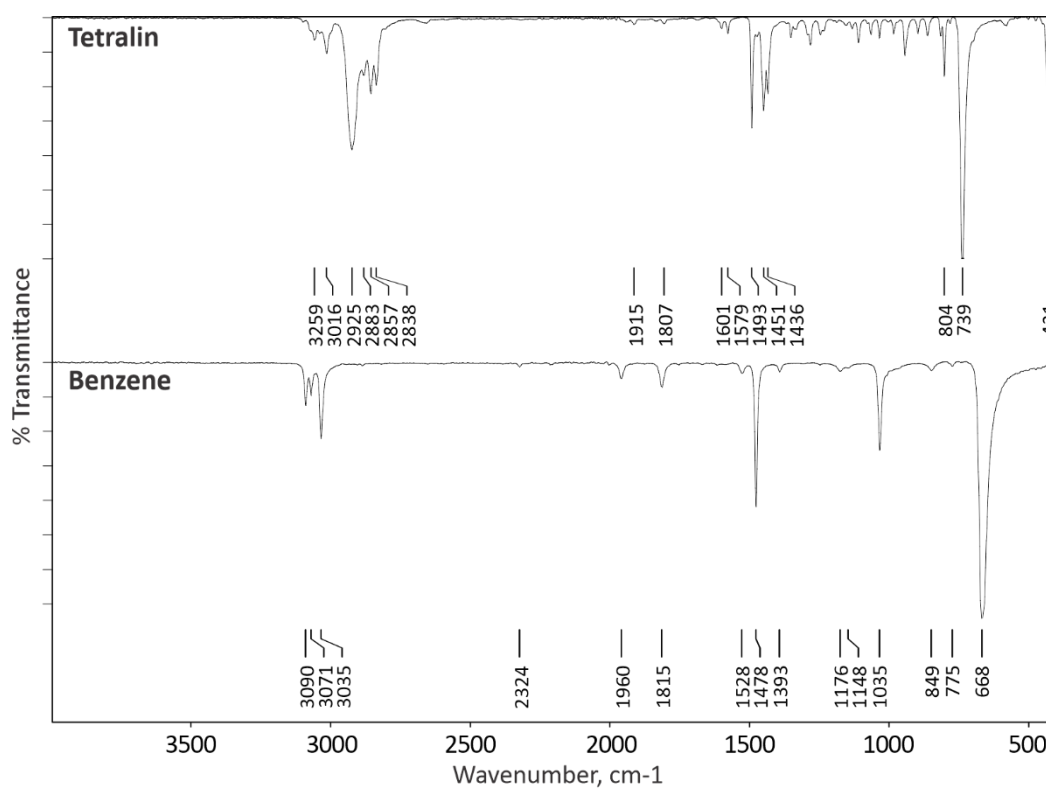


Figure S3-4. FTIR spectra obtained from tetralin and benzene.

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CHAPTER 4 DIRECT LIQUEFACTION OF POLYPROPYLENE AND LOW-DENSITY POLYETHYLENE

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Abstract

In this investigation, polypropylene (PP) and low-density polyethylene (LDPE) were used in liquefaction experiments using tetralin and benzene as solvents. The temperature of the reaction vessel was increased to 450°C at 10 °C/min, with an isothermal reaction time of 60 minutes. This study investigated the influence of feed material and choice of solvent on conversion values and liquid yield composition during liquefaction experiments. Results showed that differences in the molecular structure of polypropylene and low-density polyethylene significantly affected conversion. Tetralin liquefaction yielded conversion values of 97.0% for PP and 23.8% for LDPE, while benzene liquefaction yielded conversion values of 98.5% for PP and 97.5% for LDPE at 450°C. Benzene liquefaction of PP and LDPE produced liquid fractions comprising alkanes and alkenes. Furthermore, it was found that benzene acted as a hydrogen-donor solvent, which was supported by the presence of biphenyl in the liquid fraction derived from benzene liquefaction. Overall, PP and LDPE demonstrated potential for high conversion to liquid products in liquefaction experiments conducted at 425–450°C.

Keywords: Direct plastic liquefaction; polypropylene; low-density polyethylene; H-donor solvent; tetralin; benzene.

4.1. Introduction

The increase in plastic production and consumption over the past decades is driven by the numerous advantages of plastics, including their lightweight nature, strength, durability, affordability, corrosion resistance, and low production costs.^{1, 2} It is estimated that the annual plastic consumption in South Africa ranges from 30–50 kg per capita, resulting in a total consumption of around 1.8 to 3 million tons.³ Over the past decade, it was estimated that more than 6.3 million tons of waste plastics have been mismanaged in the country.^{4, 5} Waste plastics are predominantly disposed of as municipal solid waste (MSW) with minimal formal recycling, estimated to be around 10%.¹ Moreover, there is limited energy recovery from waste plastics through methods such as incineration, leading to the accumulation of waste plastics in dumpsites and waterways.^{1, 6} Previous studies have identified the most commonly used and discarded plastics to be high-density polyethylene (HDPE), low-density polyethylene (LDPE), polyvinyl chloride (PVC), polystyrene (PS), polypropylene (PP), and polyethylene terephthalate (PET).^{2, 7, 8}

Thermochemical conversion methods such as pyrolysis, gasification, and hydrothermal processing or liquefaction provide an innovative route for addressing the challenges arising from plastic waste.^{7, 9-12} Thermal liquefaction, or direct plastic liquefaction, involves the cleavage of polymer chains through reactions with a solvent. The solvent acts to break down the polymer into smaller chains and forms hydrogen ends, a process facilitated by a sufficient amount of solvent allowing intermolecular hydrogen transfer during the reactions.¹³ In a study by Jie *et al.* (2006)¹⁴, the reaction of ethanol with polycarbonate suggested reactions at random positions along the polycarbonate main chain, resulting in two smaller fragments of the polymer chains. Conversely, thermal processing with a lower amount of solvent followed a free radical mechanism similar to thermal pyrolysis.¹⁵ Serrano *et al.* (2007)¹⁶ also suggested a radical approach in the degradation of high-density polyethylene (HDPE) using different types of solvents. The liquefaction of plastic typically involves introducing the feedstock and solvent into the reactor. This is followed by purging the reactor with an appropriate gas to create an inert or reactive atmosphere.¹⁷

The use of solvents during plastic waste liquefaction has garnered attention due to their ability to lower reaction temperatures. Solvents enhance mass and heat transfer during the reaction, reduce the viscosity of the liquid product, and result in a higher quality oil yield.¹⁶ Researchers like Serrano *et al.* (2007)¹⁶ have suggested selecting solvents based on their ability to donate hydrogen during the reaction. Solvents are classified based on the amount of weak C–H bonds compared to other types. Solvents with low hydrogen-donating capability, i.e., 1-methylnaphthalene, contribute up to approximately 40% of hydrocarbons within the C₅–C₂₀ range during HDPE liquefaction. Poor hydrogen-donating solvents progress by slow hydrogen transfer, allowing the degradation of plastics into smaller hydrocarbons. In contrast, good hydrogen-donating solvents facilitate faster hydrogen transfer, preventing the formation of lower molecular weight hydrocarbons.¹⁶

In this investigation, recycled polypropylene and low-density polyethylene was used in liquefaction experiments with tetralin and benzene as the solvents at 400, 425, and 450°C. The quantities and qualities of the different liquefaction products were determined and examined. Tetralin, a hydrogen donor solvent, and benzene, a hydrogen-poor solvent was used as solvents in this study. This allowed for the evaluation of liquefaction effectiveness and the quantity and quality of products derived using two aromatic solvents possessing different hydrogen-donor capabilities.

4.2. Experimental

4.2.1. Materials

Recycled polypropylene (PP) and low-density polyethylene (LDPE), procured from Potch Plastics in Potchefstroom (South Africa), were used as the feed material in this study. The plastic samples were characterized using the methods summarized in **Table 4-1**. The data presents the results and methods used for proximate and ultimate analyses, calorific value, and O/C and H/C molar ratios.

Table 4-1. Characterization of polypropylene (PP) and low-density polyethylene (LDPE).

Properties	Method of analysis	PP	LDPE
<i>Proximate analysis (wt.%, a.d.)</i>			
% Inherent moisture content	ISO 11722:1999	0.3	0.3
% Ash yield	ISO 1171:2010	1.2	1.6
% Volatile Matter	ISO 562:2010	98.5	97.7
% Fixed carbon	by difference	0.0	0.3
Fuel Ratio	FC/VM	0.0	0.0
Gross Calorific Value (MJ.kg ⁻¹)	ISO 1928:2009	46.7	46.2
<i>Ultimate analysis (wt.%, d.a.f.)</i>			
% Carbon Content	ISO 12902 – CHN	84.0	83.4
% Hydrogen Content	ISO 12902 – CHN	14.8	14.6
% Nitrogen Content	ISO 12902 – CHN	0.0	0.1
% Oxygen Content	by difference	1.2	1.2
% Total sulphur	ISO 19579:2006	0.1	0.7
O/C molar ratio		0.01	0.01
H/C molar ratio		2.09	2.09

a.d. = Air-dried; d.a.f. = dry ash free.

4.2.2. Liquefaction experiments

The liquefaction experiments were carried out using a 600 mL stainless steel autoclave reactor (Parr Instruments, US), controlled using a 4848 controller from Parr. The feed materials were mixed with tetralin (1,2,3,4-Tetrahydronaphthalene for synthesis; ≥98%), a hydrogen-donor organic solvent, and benzene (ReagentPlus; purity ≥99%), a hydrogen-poor organic solvent, to a 1-to-3 weight ratio. An initial pressure of 0.2 MPa (2 bar) (absolute pressure), measured using a pressure display module integrated in the reactor controller, was applied by introducing an inert argon (AFROX, 99.999%) atmosphere. The temperature of the reaction vessel was increased to 450°C at 10 °C/min with an isothermal reaction time of 60 minutes. To ensure thorough mixing of the reacting materials and solvent during the experiment, the stirrer speed was set to 250 rpm. After the reaction period, the reaction vessel was cooled to room temperature using an internal cooling coil controlled by a solenoid valve module. Once the temperature attained room temperature, the gas fraction was collected in a 5 L Tedlar gas bag and set aside for analysis. The liquid and solid products were removed from the reactor vessel and separated using dichloromethane as the solvent and vacuum filtration to obtain the solid residue fraction. The dichloromethane was removed from the liquid product using rotary evaporation. Three replicates of the liquefaction experiments were performed, and the standard deviations of the yields obtained were determined to be less than 2%.

The weight percentages of the solid residues, liquid/oil residues, and gas yields were determined using the methods described in **Chapter 3**.¹⁸ All yields were presented on a dry and ash-free basis.

The carbon conversions, C_{daf} , of the feed materials during solvent extraction were calculated on a dry, ash-free basis using the following equation and is presented as a percentage:

$$C_{daf} = \left[\frac{m_{feed} - m_{SR}}{m_{feed}} \right] \times 100\% \quad (1)$$

Carbon conversion values were calculated to determine the percentage of feed material that reacted to produce the liquid and gaseous products during the liquefaction processes.

4.2.3. Characterization of liquid products

FTIR spectroscopic analysis, Gas Chromatography–Mass Spectrometry (GC-MS) and simulated distillation (SimDis) were conducted to characterize the liquid products obtained from the plastic liquefaction experiments using the methods mentioned in **Section 3.2.4.3** and **Section 3.2.5.1**.¹⁸ A Bruker Avance III Ultrashield Plus 600 MHz NMR spectrometer was utilized for the analyses, operating at frequencies of 600 MHz for ^1H nuclei and 150 MHz for ^{13}C nuclei. Samples were prepared by dissolving 30–40 mg of the sample in 0.6 mL CDCl_3 .

As a result of the volatility of the oil fraction, elemental analysis and calorific value determinations were unreliable and were therefore not included. In addition, the results from H-balance calculations (derived from elemental analysis) were also excluded.

4.2.4. Gas composition using gas chromatography (GC-TCD/FID)

Gas chromatography was used to analyze the gas fraction, similar to the method used in **Section 3.2.6**. For the gas analysis, a PerkinElmer Clarus 500 Gas Chromatograph was used, with two columns (Agilent J&W HP-PLOT/Q 30 m x 0.535 mm and PerkinElmer Elite GC GS MSIEVE 30 m x 0.53 mm) interconnected to the injector and detectors via a VICI 10-port gas sampling valve from Valco Instruments. The thermal conductivity detector (TCD) was set to 100°C and the flame ionization detector (FID) was set to 200°C. Argon, supplied by AFROX with a purity of 99.999%, served as the carrier gas at an initial flow rate of 2 mL/min, increasing to 8 mL/min after 16 minutes. The oven temperature was set to 40°C, and the GC system was calibrated for CO_2 , CO , H_2 , CH_4 , C_2H_6 , C_2H_4 , C_3H_8 , C_4H_{10} , O_2 , and N_2 analysis.

The change in total pressure is attributed to the increase in partial pressures of the gases produced. By monitoring the change in pressure and knowing the initial pressure and the properties of the gases involved, the amount of gas produced may be quantified. Dalton's law was used to determine the partial pressures of the individual gas components together with the volume or molar percentages obtained from gas chromatography. Dalton's Law states that the total pressure exerted by a mixture of non-reacting gases is the sum of the partial pressures of each individual gas: $P_{\text{total}} = P_1 + P_2 + \dots + P_n$, where P_{total} = Total pressure of the gas mixture, and $P_1, P_2, \dots, P_n$ = Partial pressures of individual gases in the mixture. Lastly, the ideal gas law ($PV = nRT$) was used to calculate the number of moles of each gas species in the mixture at a specific temperature (25°C) and pressure. From the number of moles of each gas component, the mass could be determined.

4.3. Results and discussion

4.3.1. Liquefaction product distribution and conversion

Polypropylene (PP) and low-density polyethylene (LDPE) were subjected to liquefaction experiments conducted at 400, 425, and 450°C using both tetralin, a hydrogen donor solvent, and benzene, a hydrogen-poor solvent. This allowed for the evaluation of liquefaction effectiveness and the quantity and quality of products produced with two aromatic solvents possessing different hydrogen-donor capabilities. **Table 4-2** presents the initial and final pressures recorded at the reaction temperatures, along with the partial pressures obtained from the plastic liquefaction experiments carried out at 450°C, 425°C, and 400°C. In the tetralin liquefaction experiments of polypropylene (PP) and low-density polyethylene (LDPE), the initial pressures at the reaction temperatures were 19.5 and 19.1 bar, 24.0 and 23.6 bar, and 27.7 and 26.8 bar for temperatures of 400°C, 425°C, and 450°C, respectively. The final pressures determined after the reaction period at these temperatures were 20.0 and 19.0 bar, 29.4 and 23.4 bar, and 50.2 and 29.0 bar, respectively. Experiments conducted using benzene resulted in significantly higher pressures, along with higher overall conversion values.

Table 4-2. Initial and final pressures at the reaction temperature, and partial pressures measured from plastic liquefaction experiments conducted at 450, 425, and 400°C.

Phase Transition Experiments Conducted at 100, 125, and 150 °C					
	Material	Temp. (°C)	Pressure, bar		
			Initial	Final	$\Delta P_{r.t.}$
Tetralin	PP	450	27.7	50.2	5.6
		425	24.0	29.4	2.2
		400	19.5	20.0	1.3
	LDPE	450	26.8	29.0	2.9
		425	23.6	23.4	1.7
		400	19.1	19.0	1.0
Benzene	PP	450	64.4	76.6	5.2
		425	56.2	65.2	2.8
		400	50.2	55.7	1.8
	LDPE	450	61.4	78.2	4.8
		425	51.7	58.7	2.0
		400	50.4	50.2	1.2

Solvents used: tetralin and benzene. Feed materials: polypropylene (PP) and low-density polyethylene (LDPE).

Liquefaction temperatures: 450, 425, 400°C; Atmosphere: argon at 1.0 bar (initial pressure at 25°C).

$\Delta P_{r.t.}$ = Partial pressure of gases at 25°C.

Polypropylene exhibited higher initial and final pressures at the reaction temperatures, as well as higher partial pressures measured at 25°C compared to low-density polyethylene. The partial pressures are directly proportional to the mass of the gases produced from the process. The reaction pressures obtained from liquefaction experiments conducted in benzene fell within the typical range of pressures used in DCL processes (between 69 and 155 bar)¹⁹. Tetralin liquefaction pressures were significantly lower than these pressures. Higher reaction pressures can be achieved by increasing the amount of solvent used, thereby increasing the total volume occupation, or by increasing the initial argon pressure.

Table 4-3 displays the carbon conversion values and product yields (wt.%) obtained from the liquefaction experiments conducted with tetralin and benzene at 400, 425, and 450°C.

Table 4-3. Liquefaction product yields and conversion of feed material at 400, 425, and 450°C using tetralin and benzene as the solvent.

	Material	Temp. (°C)	Yield, weight % (d.a.f.) *			Carbon conversion, % (d.a.f.) *
			Solid residue	Liquid	Gas	
Tetralin	PP	450	3.0	86.7	10.3	97.0
		425	17.5	79.8	2.7	82.6
		400	71.5	27.9	0.6	28.5
	LDPE	450	75.9	21.5	2.6	23.8
		425	93.6	5.4	1.1	6.2
		400	99.0	0.9	0.1	1.0
Benzene	PP	450	1.6	87.0	11.4	98.5
		425	1.9	92.7	5.3	98.1
		400	12.1	85.1	2.8	87.9
	LDPE	450	2.5	87.6	9.9	97.5
		425	13.9	83.3	2.8	86.1
		400	77.6	21.5	0.9	22.4

*Product yields and conversion values were determined on a dry, ash-free basis (d.a.f.).

The results from the experiments conducted at 400°C show low conversion values (1.0–28.5% conversion), with the exception of benzene liquefaction conducted on PP that exhibited good conversion at 400°C. Tetralin liquefaction conducted at 450°C yielded carbon conversion values of 97.0 and 23.8% for PP and LDPE, respectively. The overall conversion of PP is higher than that of LDPE. Liquefaction experiments conducted on PP and LDPE using benzene showed promising results at all reaction temperatures (excluding LDPE at 400°C).

The main difference between the conversion values obtained for PP and LDPE can be ascribed to differences in the molecular structure. In addition, at these reaction temperatures, the results indicate that the conversion is predominantly influenced by the nature of the feed materials, choice of solvent, and pressure. It is expected that different reaction mechanisms occur during tetralin and benzene liquefaction, affecting the oil quality and composition (discussed in **Section 4.3.3**).

4.3.2. Characterization of liquid yields from liquefaction experiments

4.3.2.1. FTIR

The FTIR spectra of the liquid yields derived from the tetralin liquefaction of PP and LDPE are presented in **Figure S4-3** and **Figure S4-4**, respectively. Additionally, the FTIR spectra of the liquid yields from the benzene liquefaction of PP and LDPE are presented in **Figure S4-5** and **Figure S4-6**, respectively. The FTIR spectra of the two solvents used, namely tetralin and benzene, are presented in **Figure S4-2**. The liquid yields also show similarities when compared to the original feed materials, i.e. PP and LDPE (**Figure S4-1**).

Relevant FTIR wavenumbers of the liquid yields from tetralin liquefaction (cm⁻¹): 3058 and 3017 (sp² C-H stretching, aromatic); 2925, 2858 and 2839 (sp³ C-H stretching, methylene/CH₂); 1494, 1452 and 1436 (C=C stretching, aromatic); 783 and 741-739 (out-of-plane sp² C-H bending, ortho disubstituted aromatics); 618 (sp² C-H bend, methylene/CH₂); 476 (out-of-plane ring bending).

Aromatic sp² C-H bands in the 3200–3000 cm⁻¹ region indicate that the molecular structures of the liquid residues are similar to that of tetralin (**Figure S4-2**), signifying aromatic structures with connected methylene groups (methylene C-H stretch, 2925 and 2858 cm⁻¹). No bands were observed at 1596 cm⁻¹ indicating that the fraction of aromatic structure was unaffected and that the formation of naphthalene during tetralin liquefaction is absent. The formation of substituted aromatics can be

supported by a strong out-of-plane sp^2 C-H bending vibration for ortho disubstituted aromatics at 781 cm^{-1} .²⁰ This is evident in the liquid fraction obtained during PP liquefaction at 450°C compared to lower intensity bands of the liquids produced from lower liquefaction temperatures. The band at 741 cm^{-1} indicates that a notable amount of unreacted tetralin is present. This is supported by similar overall spectrums obtained from all liquefaction experiments conducted using tetralin as a solvent. The results can also be supported by the GC-MS results presented in **Table 4-4**. Evidently, no polar structures containing -C=O and -OH functional groups were produced from the plastic samples during the liquefaction process. This can be supported by absent alkoxy C-O stretching vibrations, C=O stretching, and O-H stretching vibrations in the 1068 cm^{-1} , $1750\text{--}1650\text{ cm}^{-1}$ and $3700\text{--}3200\text{ cm}^{-1}$ regions, respectively.

Relevant FTIR wavenumbers of liquid yields from benzene liquefaction (cm^{-1}): 3091, 3072 and 3036 (sp^2 C-H stretching, aromatic); 2954, 2924, 2870 (PP), and (LDPE) 2839 (sp^3 C-H stretching, methylene/ CH_2); 2000–1650 (weak combination and overtone bands); 1478–1466, 1458, 1377 and 1266 (C=C stretching, aromatic); 1266 and 1035 (in-plane bending vibrations of sp^2 aromatic C-H); 1035 ; 783 and 741-739 (out-of-plane sp^2 C-H bend, ortho disubstituted aromatics); 618 (sp^2 C-H bending, methylene/ CH_2); 476 (out-of-plane ring bending).

Figure S4-5 and **Figure S4-6** presents the FTIR spectra of the liquid fractions derived from benzene liquefaction conducted on PP and LDPE. Aromatic sp^2 C-H stretching bands can be observed in the $3100\text{--}3000\text{ cm}^{-1}$ range accompanied by sp^3 C-H stretching bands in the $2955\text{--}2800\text{ cm}^{-1}$ region. This signifies that aromatic structures (such as benzenes) are present with detectable methylene groups (sp^3 C-H) from aliphatic chains derived from PP and LDPE. It can be observed that a larger fraction of aliphatic components is present in the liquid yields produced at lower reaction temperatures. This is supported by lower band intensities at higher temperatures. Higher reaction temperatures may dehydrogenate previously hydrogenated structures producing hydrogen gas, or by dealkylation reactions producing hydrocarbon gases. Gas chromatography results show increasing hydrogen, methane, ethane, ethylene, propane, and butane production with elevated temperatures. These reactions can effectively produce more unsaturated structures in the liquid fractions.

From **Figure S4-1**, a broad peak at 1032 cm^{-1} was observed for the raw LDPE sample. This indicates C-O stretching vibrations and the presence of alcohol, carboxylic acid, ester, and ether groups. With weak O-H stretching vibration bands in the $3500\text{--}3200\text{ cm}^{-1}$ region.²¹ This is usually only observed in LDPE samples that have undergone degradation reactions and subsequent oxidation reactions.²¹ However, these bands were not evident in any liquid fractions derived from LDPE liquefaction. It should be noted that the bands observed at 1035 cm^{-1} in benzene and the liquid fractions produced from PP and LDPE liquefaction can be assigned to in-plane bending vibration of sp^2 aromatic C-H bonds. Similar to the tetralin liquefaction results, no polar structures containing -C=O and -OH functional groups were produced from the plastic samples during the liquefaction process. This can be supported by absent alkoxy C-O stretching vibrations, C=O stretching, and O-H stretching vibrations in the 1068 cm^{-1} , $1750\text{--}1650\text{ cm}^{-1}$ and $3700\text{--}3200\text{ cm}^{-1}$ regions, respectively. For both tetralin and benzene liquefaction derived liquids, weak combination and overtone bands were observed between $2000\text{--}1650\text{ cm}^{-1}$. The patterns of overtone bands are generally unreliable to describe the substitution of a ring. They are usually weak and are readily observed in thick aromatic compounds.²⁰

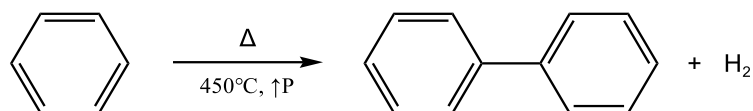
Similar to the liquid yields obtained from tetralin liquefaction, bands of out-of-plane sp^2 C-H bending vibrations of substituted aromatics are observed at $738\text{--}740\text{ cm}^{-1}$. These peaks have increasing intensities for liquid fraction produced at higher liquefaction temperatures signifying increasing concentrations of substituted aromatics.

4.3.2.2. GC-MS and simulated distillation

The GC-MS results, as presented in **Table 4-4**, show a qualitative and semi-quantitative overview of the range of compounds produced from liquefaction experiments at 450°C and their respective relative abundance in percentage.

During experiments conducted using tetralin, a large fraction of unreacted tetralin with a smaller fraction of naphthalene can be seen in the liquid yield. It may be assumed that only a small amount of hydrogen is needed for the hydrogenation reaction in plastic liquefaction compared to coal liquefaction (**Table 3-11**). The excess hydrogen, predominantly derived from tetralin, not taken up during liquefaction is present in the gas fraction. This is supported by high H_2 contents in the gas fraction (**Figure 4-1** and **Table S4-3**). The liquefaction of LDPE using tetralin showed low conversion values at 450°C (28.5% from **Table 4-2**) and can explain the smaller and lower fraction of alkanes present in the oil. During PP liquefaction (using both tetralin and benzene), it is also evident that PP will mainly react with benzene to form alkylated or substituted aromatics.

The results from LDPE liquefaction using benzene showed promising results. Higher conversion values (97.5%) obtained for LDPE were accompanied by a large fraction of oils consisting of $\text{C}_{10}\text{--}\text{C}_{29}$ alkanes and $\text{C}_{10}\text{--}\text{C}_{19}$ alkenes that accounts for around 49.6 and 19.0% % of the product composition, respectively. It is also interesting to note that a significant fraction of biphenyl formed during benzene liquefaction with PP and LDPE, accounting for around 45.9 and 15.7% of the liquid fraction. The presence of biphenyl can support the occurrence of dehydrogenation reactions of benzene to produce hydrogen. The following reaction equation can be assumed:



The hydrogen produced from this reaction can saturate alkenes or protonate radical chains that formed through chain scission or fragmentation reactions. The conclusion from these results highlights that benzene, known to be a H-poor aromatic solvent, may be considered as a hydrogen donor solvent during direct liquefaction of PP and LDPE. Lastly, polar and/or oxygen-containing compounds were absent or in low concentrations in the liquid fraction produced from this study. This is supported by weak alkoxy C-O bands, and absent C=O and O-H bands in the FTIR spectra of the liquid fraction. As reported by Isa *et al.* (2018)²², it is favorable to produce residues from liquefaction having low oxygen contents.

Table 4-4. Molecular abundance (%) results determined from GC-MS analysis conducted on the liquid fractions produced from tetralin and benzene liquefaction experiments of PP and LDPE at 450°C.

Tetralin						Benzene					
PP			LDPE			PP			LDPE		
Compound	g.mol ⁻¹	A _{abs} , %	Compound	g.mol ⁻¹	A _{abs} , %	Compound	g.mol ⁻¹	A _{abs} , %	Compound	g.mol ⁻¹	A _{abs} , %
Naphthalene	128.1	9.9	Naphthalene	128.1	4.9	Benzene, 1-ethyl-3-methyl-	120.1	5.3	Benzene, 1-ethyl-2-methyl-	120.1	0.8
Benzene, (2-methyl-1-propenyl)-	132.1	6.2	Naphthalene, 1,2,3,4-tetrahydro-	132.1	82.8	Benzene, 1,2,3-trimethyl-	120.1	39.8	Benzene, (2-methyl-1-propenyl)-	132.1	1.9
Naphthalene, 1,2,3,4-tetrahydro-	132.1	81.8	Benzene, butyl-	134.1	0.5	Benzene, (1-methylenepropyl)-	132.1	2.2	Benzene, 1-methyl-3-propyl-	134.1	0.5
Benzocycloheptatriene	142.1	1.0	Naphthalene, decahydro-	138.1	0.5	Benzene, (1,2-dimethyl-1-propenyl)-	146.1	6.8	1-Decene	140.2	2.6
Naphthalene, 1,2,3,4-tetrahydro-1-methyl-	146.1	0.7	Naphthalene, 1-methyl-	142.1	0.7	Biphenyl	154.1	45.9	Naphthalene, 1-methyl-	142.1	0.8
			Benzene, (2-methyl-1-butenyl)-	146.1	1.5				Decane	142.2	4.0
			Octadecane	254.3	0.5				Benzene, (1-methyl-2-butenyl)-	144.1	1.8
			Naphthalene, 1,2,3,4-tetrahydro-1-nonyl-	258.2	1.1				2,2-Dimethylindene,	146.1	0.7
			Tetracosane	338.4	0.7				2,3-dihydro-		
									Biphenyl	154.1	15.7
									1-Undecene	154.2	1.3
									Undecane	156.2	3.7
									(1-Methylpenta-1,3-dienyl)benzene	158.1	1.0
									4-Dodecene, (Z)-	168.2	1.3
									Dodecane	170.2	3.2
									1-Tridecene	182.2	1.6
									Tridecane	184.2	3.1
									1-Tetradecene	196.2	1.6
									Tetradecane	198.2	3.1
									1-Pentadecene	210.2	1.8
									Pentadecane	212.3	3.0
									Cetene	224.3	4.8
									Hexadecane	226.3	3.2
									Heptadecane	240.3	2.8
									E-15-Heptadecenal	252.2	2.8
									Octadecane	254.3	2.5
									1-Nonadecene	266.3	3.1
									Nonadecane	268.3	2.0
									Eicosane	282.3	6.1
									Hexadecanoic acid, 2-hydroxy-, methyl ester	286.3	0.5
									Heneicosane	296.3	2.1
									Docosane	310.4	1.5
									Tricosane	324.4	1.7
									Cyclotetracosane	336.4	1.0
									Tetracosane	338.4	1.8
									Hexadecane, 1-iodo-	352.2	1.2
									Heptacosane	380.4	1.2
									Octacosane	394.5	1.5
									Nonacosane	408.5	0.8
									Heptacosyl acetate	438.4	0.8
									Triacetyl acetate	480.5	0.7
Alkanes (N/A)		0.0	Alkanes (C ₁₈ –C ₂₄)		1.2	Alkanes (N/A)		0.0	Alkanes (C ₁₀ –C ₂₉)		49.6
Alkenes (N/A)		0.0	Alkenes (N/A)		0.0	Alkenes (N/A)		0.0	Alkenes (C ₁₀ –C ₁₉)		19.0

A_{abs}, % = Absolute Area in percentage.

Table 4-5 reports the simulated distillation results obtained from the liquid yields derived from liquefaction experiments conducted on PP and LDPE using tetralin and benzene at 450°C. Boiling ranges were separated into kerosene (166–249°C), diesel (249–343°C), and vacuum gas oil (343–538°C).²³ The kerosene fraction in the liquid yields from tetralin liquefaction are significantly

higher compared to the results obtained from benzene liquefaction. This can be assigned to high concentration of naphthalene and residual tetralin in the formerly mentioned experiments. The results from simulated distillation confirm the range of compounds determined using GC-MS.

Table 4-5. Summarized simulated distillation results of the liquid fractions from liquefaction experiments conducted on PP and LDPE using tetralin and benzene at 450°C.

		Cumulative peak area, %		
		Kerosene	Diesel	Vacuum gas oil
Tetralin	PP _{liq}	97.5	1.4	0.4
	LDPE _{liq}	86.4	3.5	8.6
Benzene	PP _{liq}	52.0	16.3	8.0
	LDPE _{liq}	33.6	33.3	26.7

Kerosene: BP = 166–249°C (C₁₀–C₁₄); diesel = 249–343°C (C₁₄–C₂₀); and vacuum gas oil = 343–538°C (C₂₀–C₄₀).

The NMR data, as reported in **Table 4-6**, provides empirical support for the significant differences in the aliphatic fractions compared to the aromatic fractions between LDPE_{liq} and PP_{liq}. These differences indicate that LDPE, characterized by a scarcity of methine functional groups and abundance of methylene functional groups, is more prone to side chain cleavage, facilitating the formation of a range of aliphatic compounds. Conversely, PP, with its abundance of methyl branches, demonstrates a higher propensity for cleavage that results in the formation of smaller molecules or radicals. These molecules or radicals interact with the solvent, generating various benzene derivatives, highlighting a distinct reaction pathway.

Table 4-6. Summarized relative proton integrated values of liquid fractions from liquefaction experiments conducted on PP and LDPE using tetralin and benzene at 450°C

		Relative proton integrated values, %		
		Aliphatic	Aromatic	Vinyllic
Tetralin	PP _{liq}	61.9	32.1	3.7
	LDPE _{liq}	69.7	25.8	4.1
Benzene	PP _{liq}	25.8	69.4	1.3
	LDPE _{liq}	49.3	47.0	3.7

Absolute integrals obtained via ¹H-NMR (600MHz, CDCl₃)

4.3.3. Gas composition using gas chromatography

The data presented in **Table S4-3** includes molar/volume percentage values obtained from the gas analysis, along with the corresponding partial pressures of the generated gases. These results served as essential inputs for calculating the mass of compound gases, applying Dalton's law for partial pressure and the Ideal Gas Law. These results are summarized in **Figure 4-1**, showing the mass fractions of the gaseous species obtained from the liquefaction experiments conducted on PP LDPE at 400, 425, and 450°C using tetralin and benzene as the solvents.

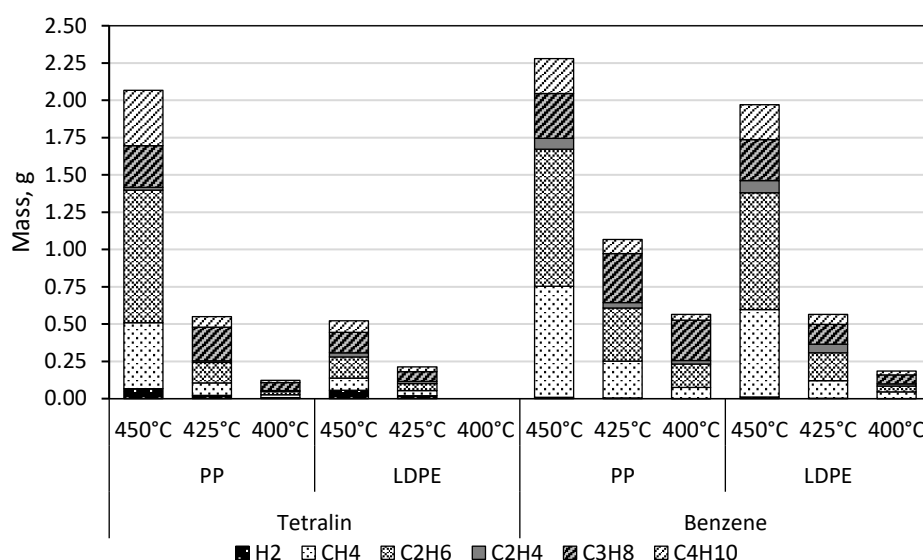


Figure 4-1. Gas chromatography results of the gas fractions produced from liquefaction experiments.

Previous liquefaction experiments has shown that the primary components of liquefaction gas include hydrogen, carbon monoxide, carbon dioxide, and hydrocarbon compounds such as methane, ethane, and propane.^{18, 24} Notably, it has been observed that higher liquefaction temperatures result in an increased production of hydrogen. This phenomenon may be attributed to the thermal breakdown of aliphatic carbon-hydrogen linkages in the polymeric chains at elevated temperatures. Additionally, it is conceivable that the dehydrogenation of tetralin is promoted at higher temperatures. This was not evident in the gas fractions obtained from the liquefaction experiments involving benzene as the solvent. Supported by significantly low concentration of oxygen in the plastic materials (**Table 4-1**) and the nature of the reacting environment, the presence of oxygen containing compounds such as carbon dioxide and carbon monoxide in the gas fraction were not detected.

The results presented in **Figure 4-1** and **Table S4-3** shows clear correlations between the liquefaction temperature, feed material type, and solvent with the total mass and composition of the gas fractions obtained. The liquefaction of PP using tetralin and benzene at 450°C had the highest gas yields. Whereas LDPE only produced a considerable amount of gas during the experiments conducted using benzene as the solvent. The significantly lower gas yield obtained from the experiments conducted using tetralin can be explained by a low conversion value of 28.5% (**Table 4-2**). Methane, ethane, propane, and butane production increased as a function of increasing liquefaction temperatures. Ethylene production was mostly observed in gaseous products derived from benzene liquefaction.

4.4. Conclusions

The following conclusions can be made from the results discussed in this chapter:

- The main difference between the conversion values can predominantly be ascribed to differences in the molecular structure of the feed materials. In addition, the results indicate that the conversion is influenced by the nature of the feed materials and choice of solvent.
- Tetralin liquefaction conducted at 450°C presented carbon conversion values of 97.0 and 23.8% for PP and LDPE, respectively. The overall conversion of PP was higher than that of LDPE during the liquefaction experiments.
- LDPE readily converts to produce liquids that consist of aliphatic compounds.
- The liquid fractions derived from the benzene liquefaction experiments of LDPE consisted of C₁₀–C₂₉ alkanes and C₁₀–C₁₉ alkenes amounting to 49.6 and 19.0%, respectively.
- Benzene, known to be a H-poor aromatic solvent, may be considered as a hydrogen-donor solvent during plastic liquefaction experiments – supported by the presence of biphenyl in high concentrations in the liquid yield.

The results from this chapter indicate that PP and LDPE can readily convert to produce liquid products during liquefaction experiments conducted at 425–450°C.

Acknowledgments

The information presented in this paper is based on the research financially supported by the National Research Foundation (NRF) and South African Research Chairs Initiatives (SARChI) of the Department of Science and Technology (Coal Research chair Grant No. 86880). Any opinions, conclusions or recommendations expressed are that of the author(s), and no liability is accepted on the NRF's regard.

4.5. Supporting Information

Table S4-1. Molecular abundance (%) results determined from GC-MS analysis conducted on the liquid fractions produced from tetralin and benzene liquefaction experiments of PP and LDPE at 425°C.

Tetralin			Benzene						
PP			LDPE	PP			LDPE		
Compound	g.mol ⁻¹	A _{abs} , %	N/A	Compound	g.mol ⁻¹	A _{abs} , %	Compound	g.mol ⁻¹	A _{abs} , %
Naphthalene	128.1	4.4	Liquid yield too low	2-Hexene, (Z)-	84.1	4.2	2-n-Butylacrolein	112.1	2.34
Benzene, 1-butyryl-	130.1	0.1		3-Methylpenta-1,4-diene-3-ol	98.1	1.2	Cyclopentane, 1-methyl-3-(2-methylpropyl)-Biphenyl	140.2	2.64
Benzene, (2-methyl-1-propenyl)-	132.1	4.1		Cyclopentane, 1,1-dimethyl-	98.1	2.0		154.1	2.38
Naphthalene, 1,2,3,4-tetrahydro-	132.1	86.0		2-Heptenal, (Z)-	112.1	9.5	Undecane	156.2	2.84
Benzene, butyl-	134.1	0.3		Cyclopentane, 1-ethyl-1-methyl-	112.1	4.0	Octane, 2,4,6-trimethyl-	156.2	5.83
Tricyclo[4.4.0.0(2,8)]decane	136.1	0.1		Benzene, 1,2,3-trimethyl-	120.1	13.0	Dodecane	170.2	2.97
Naphthalene, decahydro	138.1	0.5		2-Butyl-1,2-azaborolidine	125.1	8.7	Pentadecane	212.3	3.64
Naphthalene, 2-methyl-	142.1	0.7		2-Methyl-5-octyn-4-ol	140.1	6.8	Tridecane, 4,8-dimethyl-	212.3	4.13
Naphthalene, 1,2-dihydro-3-methyl-	144.1	0.1		Cyclohexane, 1,1,3,5-tetramethyl-, trans-Biphenyl	140.2	1.6	Pentadecane, 2-methyl-	226.3	4.57
Benzene, (1-ethyl-1-propenyl)-	146.1	0.1			154.1	19.2	Hexadecane	226.3	3.72
1H-Indene, 2,3-dihydro-1,6-dimethyl-	146.1	0.3		(E)-2-Hexenyl tiglate	182.1	3.2	Heptadecane	240.3	4.79
Benzene, (2-methyl-1-butenyl)-	146.1	0.7		Cyclopentane, 1,2-dibutyl-	182.2	4.1	1-Hexadecanol	242.3	1.90
Benzene, 1,3-hexadienyl-	158.1	0.1		Cyclopentane, 1-pentyl-2-propyl-	182.2	1.5	Tetradecanoic acid, 2-oxo-, methyl ester	256.2	4.63
Naphthalene, 1-ethyl-1,2,3,4-tetrahydro-	160.1	0.1		4-Octanol, 7-methyl-, acetate	186.2	3.9	1-Dodecanesulfonyl chloride	268.1	2.57
3-Chlorotricyclo	166.1	0.1		Silane, [(10-chlorodecyl)oxy]trimethyl-	264.2	3.4	Tridecane, 7-hexyl-	268.3	4.69
[5.2.1.0(4,8)]deca-2,5-diene	174.1	0.4		Chloroacetic acid, 2-tridecyl ester	276.2	1.8	Sulfurous acid, hexyl octyl ester	278.2	4.68
1-Phenyl-1-hexyn-3-ol				1,19-Eicosadiene	278.3	2.8	Nonadecane, 2-methyl-	282.3	3.24
Dodecane, 4,6-dimethyl-	198.2	0.1		Acetic acid, trifluoro-, dodecyl ester	282.2	1.6	Sulfurous acid, butyl undecyl ester	292.2	2.86
Heptadecane	240.3	0.0		Sulfurous acid, dodecyl 2-propyl ester	292.2	2.9	Heneicosane	296.3	2.99
1H-Indene, 2,3-dihydro-1-methyl-3-octyl-	244.2	0.1		n-Propyl 9-octadecenoate	324.3	1.2	Eicosane, 10-methyl-	296.3	4.74
Naphthalene, 1,2,3,4-tetrahydro-1-octyl-	244.2	0.4		4-Trifluoroacetoxy hexadecane	338.2	1.8	3-Trifluoroacetoxy pentadecane	324.2	2.62
Octadecane	254.3	0.4		4-Heptafluorobutyryloxy hexadecane	438.2	1.8	3-Chloropropionic acid, hexadecyl ester	332.2	2.02
Hexadecane, 2,6,10,14-tetramethyl-	282.3	0.1					Tetracosane	338.4	3.38
Eicosane	282.3	0.1					Sulfurous acid, butyl hexadecyl ester	362.3	2.59
Heneicosane	296.3	0.0					Docosane, 7-butyl-	366.4	6.33
Docosane	310.4	0.2					Heptacosane	380.4	3.58
Hexadecane, 1-iodo-	352.2	0.1					4-Heptafluorobutyryloxy hexadecane	438.2	2.57
Hentriacontane	436.5	0.2					Silane, trichlorodocosyl-Hexatriacontane	442.2	2.75
								506.6	1.98
Alkanes	C ₁₀ -C ₂₆	1.0		Alkanes	C ₁₀ -C ₂₆	7.1	Alkanes	C ₁₀ -C ₂₆	63.4
Alkenes	N/A	0.0		Alkenes	C ₂₀	2.8	Alkenes	N/A	0.0

Table S4-2. Summarized simulated distillation results of the liquid fractions from liquefaction experiments conducted on PP and LDPE using tetralin and benzene at 425°C.

		Cumulative peak area, %		
		Kerosene	Diesel	Vacuum gas oil
Tetralin	PP _{liq}	85.9	4.3	7.1
	LDPE _{liq}	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>
Benzene	PP _{liq}	40.2	29.2	19.8
	LDPE _{liq}	17.3	25.6	47.8

Kerosene: BP = 166–249°C (C₁₀–C₁₄); diesel = 249–343°C (C₁₄–C₂₀); and vacuum gas oil = 343–538°C (C₂₀–C₄₀).

Table S4-3. Gas chromatography results of the gas fractions produced from plastic liquefaction experiments conducted at 400, 425, and 450°C.

Sample	Temp. (°C)	Molar/Volume, %						$\Delta P_{r.t.}$ (bar)	Mass, g							
		H ₂	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₄ H ₁₀		H ₂	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₄ H ₁₀	Total	
Tetralin	PP	450	32.2	26.5	28.4	0.7	6.1	6.1	4.6	0.07	0.44	0.89	0.02	0.28	0.37	2.07
		425	39.1	19.2	16.9	1.4	19.0	4.5	1.2	0.02	0.08	0.14	0.01	0.23	0.07	0.55
		400	46.0	18.6	10.3	3.9	17.6	3.7	0.3	0.01	0.02	0.02	0.01	0.05	0.01	0.12
	LDPE	450	64.4	12.0	10.9	2.2	7.3	3.1	1.9	0.06	0.08	0.14	0.03	0.14	0.08	0.52
		425	60.5	13.4	10.1	3.3	9.3	3.4	0.7	0.02	0.03	0.05	0.01	0.06	0.03	0.21
		400	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Benzene	PP	450	4.7	48.9	32.2	2.7	7.2	4.3	4.2	0.01	0.74	0.92	0.07	0.30	0.23	2.28
		425	4.7	39.2	29.9	3.3	18.8	4.1	1.8	0.00	0.25	0.36	0.04	0.33	0.09	1.07
		400	3.3	25.5	28.9	4.7	34.0	3.6	0.8	0.00	0.07	0.16	0.02	0.27	0.04	0.56
	LDPE	450	6.8	45.0	32.0	3.6	7.6	5.0	3.6	0.01	0.59	0.78	0.08	0.27	0.23	1.97
		425	8.2	33.7	29.0	9.6	14.0	5.4	1.0	0.00	0.12	0.19	0.06	0.13	0.07	0.57
		400	5.5	40.9	18.7	8.6	20.1	6.2	0.3	0.00	0.04	0.04	0.02	0.06	0.02	0.18

Feed materials – VR, VRD, IR, IRD; Liquefaction temperatures – 400, 425, 450°C. $\Delta P_{r.t.}$ = Partial pressure of gases at 25°C.

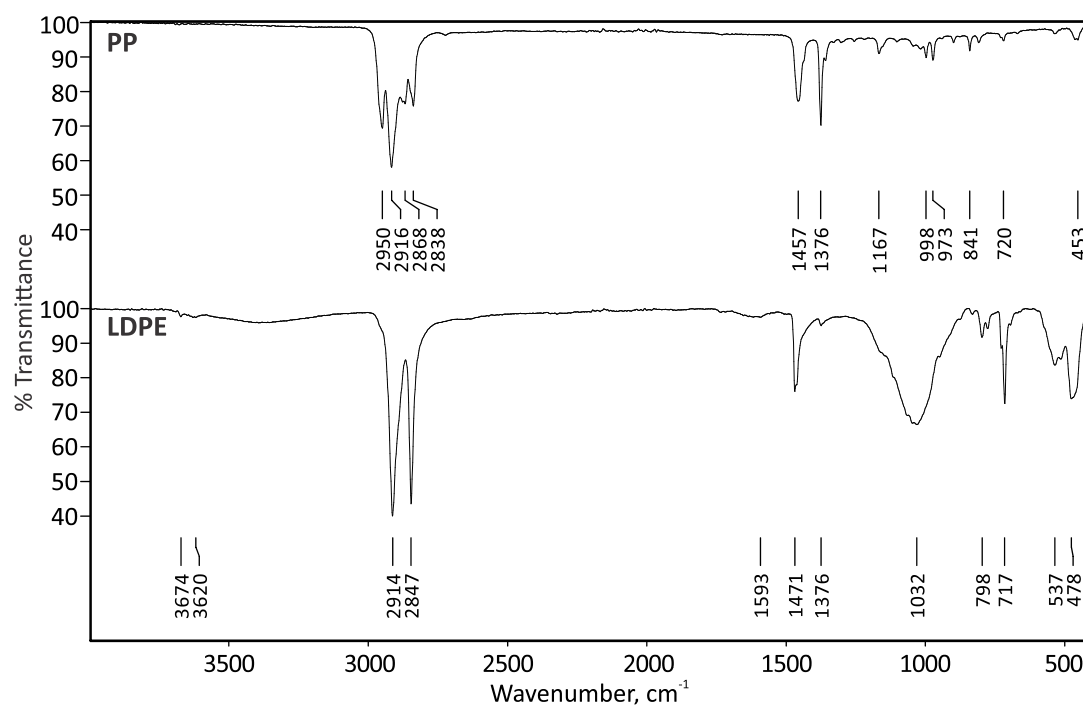


Figure S4-1. FTIR spectra of polypropylene and low-density polyethylene.

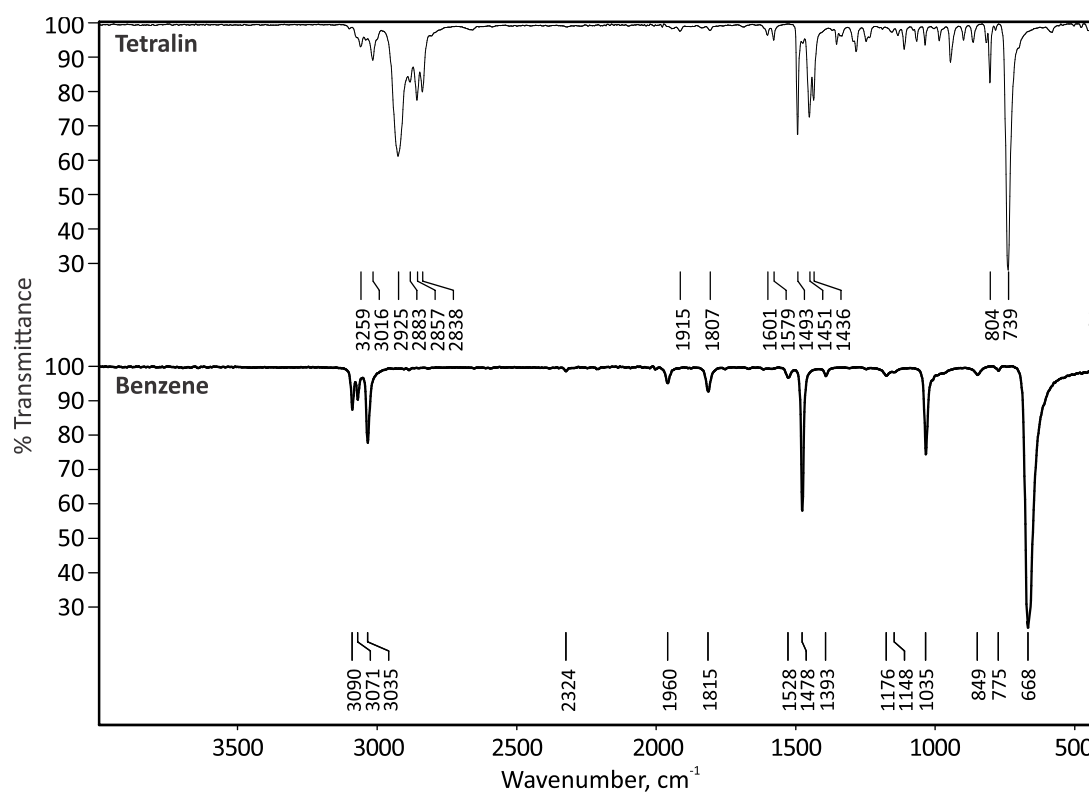


Figure S4-2. FTIR spectra of tetralin and benzene.

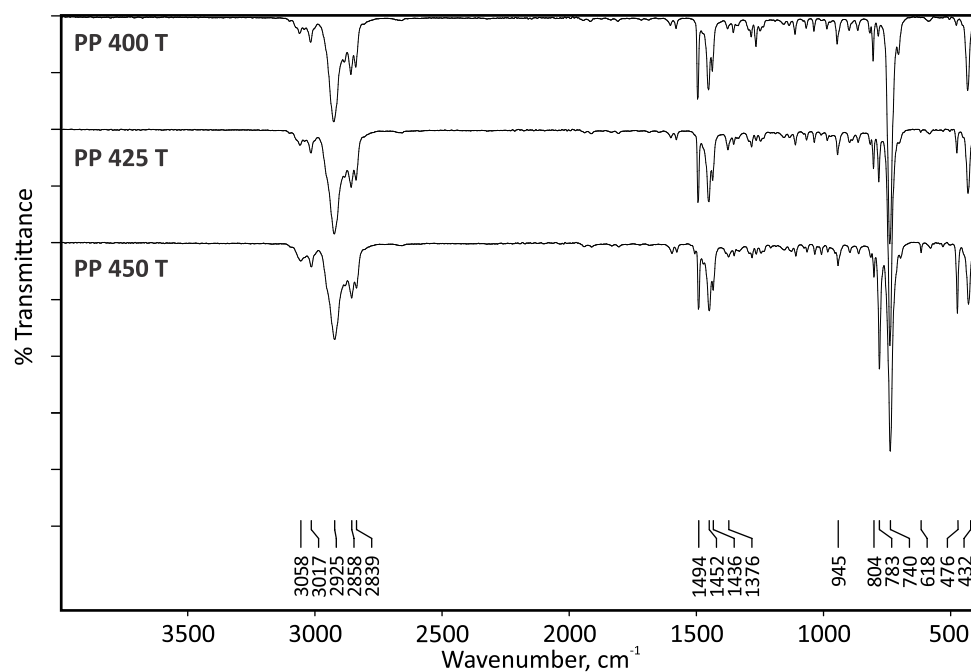


Figure S4-3. FTIR spectra of the liquid yield produced from polypropylene liquefaction in tetralin.

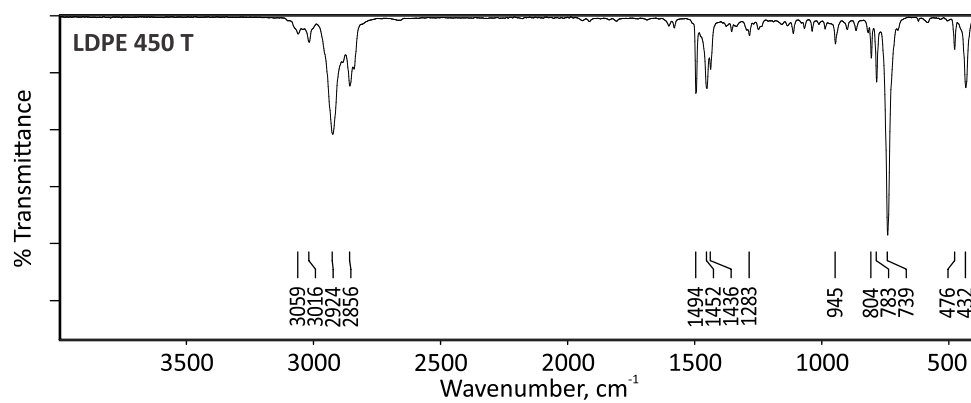


Figure S4-4. FTIR spectra of the liquid yield produced from low-density polyethylene liquefaction in tetralin.

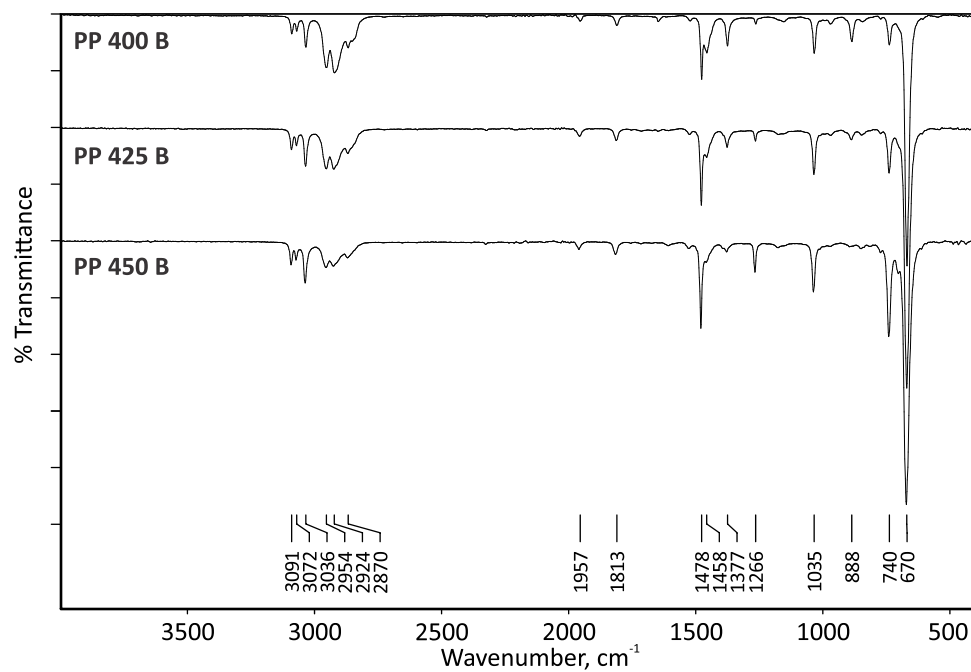


Figure S4-5. FTIR spectra of the liquid yield produced from polypropylene liquefaction in benzene.

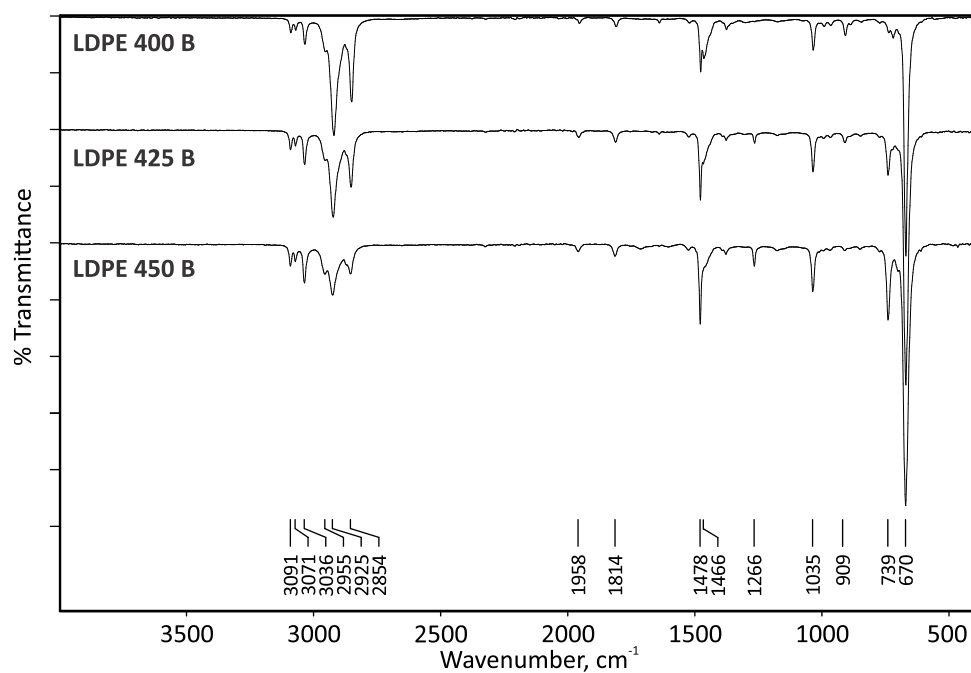


Figure S4-6. FTIR spectra of the liquid yield produced from low-density polyethylene liquefaction in benzene.

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CHAPTER 5 DIRECT CO-LIQUEFACTION OF SOUTH AFRICAN VITRINITE AND INERTINITE-RICH COAL FINES WITH POLYPROPYLENE AND LOW-DENSITY POLYETHYLENE

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Abstract

In this investigation, a vitrinite-rich coal and inertinite-rich discard coal was used in co-liquefaction experiments together with polypropylene and low-density polyethylene. The temperature of the reaction vessel was increased to 450°C at 10 °C/min, with an isothermal reaction time of 60 minutes. It was observed that differences in molecular structure of feed materials significantly impacted conversion values, with aliphatic components predominantly present in the liquid yields derived from blends containing polypropylene and low-density polyethylene. These plastics readily convert to liquids and gases, while the solid residues exhibit aromatic characteristics. Liquid fractions derived from the co-liquefaction experiments when using benzene as solvent mainly consisted of alkanes and alkenes. It was found that benzene served as a hydrogen-donor solvent during co-liquefaction experiments. Furthermore, polypropylene and low-density polyethylene are shown to facilitate hydrogen transfer in the co-liquefaction process, effectively converting inertinite-rich discard coal into liquid products when co-processed. Additionally, the solid residue chars derived from blends containing the inertinite-rich coal demonstrated higher gasification reactivities compared to those containing the vitrinite-rich coal. These findings underscore the potential of utilizing plastics in co-liquefaction processes for enhanced liquid product yields.

Keywords: Direct co-liquefaction; coal fines; discard coal; vitrinite-rich; inertinite-rich; polypropylene; low-density polyethylene; H-donor solvent; tetralin; benzene.

5.1. Introduction

Growing concerns about environmental sustainability have prompted increased exploration into novel approaches to waste management and resource utilization. Co-liquefaction, a method involving the simultaneous liquefaction of diverse materials, has emerged as a promising solution to address challenges related to both fossil fuel consumption and waste management. In recent years, co-liquefaction research has received considerable attention, particularly focusing on the co-processing of coal and waste materials such as plastics.¹⁻⁴ This approach aims to address environmental challenges associated with both fossil fuel utilization and plastic pollution.² Studies have explored various combinations of coal and plastic waste, employing different solvents and processing conditions to optimize the co-liquefaction process. These investigations have revealed promising outcomes including heightened oil yields, enhanced energy recovery, and reduced residue generation.

Wang and Chen (2004)⁵ conducted direct liquefaction experiments involving different plastics such as polyethylene (PE), polypropylene (PP), and polystyrene (PS); and Chinese coal (Xianfeng lignite) in tetralin as the solvent at elevated temperatures and pressures. They observed substantial conversions and oil yields, particularly noting the effectiveness of LDPE, PP, and PS plastics in achieving high conversion rates. Specifically, HDPE was found to be the most challenging plastic to convert even at relatively high temperatures (430°C), while LDPE, PP, and PS showed 100% conversions with oil yields ranging from 69.4% to 79.9%. Moreover, the inclusion of plastic in the co-liquefaction process exhibited synergistic effects, resulting in notably high conversion rates (approximately 98%) and oil yields (over 70%). Additionally, the lower hydrogen consumption observed during co-liquefaction compared to coal liquefaction alone indicated improved process efficiency. The utilization of a molybdenum-based catalyst (FAMo) further bolstered total conversion and oil yield during co-liquefaction, enhancing them by approximately 10%. Similarly, Feng *et al.* (1996)³ investigated the co-liquefaction of medium and high-density polyethylene (MDPE and HDPE) and a waste plastic with subbituminous coal (Black Thunder). Their research highlighted the significant impact of catalysts and process parameters on liquefaction outcomes. Notably, solid acid catalysts like HZSM-5 or $\text{Al}_2\text{O}_3\text{-SiO}_2$ significantly improved oil yields and total conversions during plastic liquefaction. Co-liquefaction experiments using coal-plastic mixtures demonstrated synergistic effects, resulting in enhanced oil yields. Specifically, PP-coal mixtures showed substantially higher oil yields (approximately 70%) and total conversion rates (>95%) compared to PE-coal mixtures (with around 40% oil yields and 70% total conversion). Taghiei *et al.* (1994)⁶ also reported similar findings, emphasizing the effectiveness of solid acid catalysts in plastics liquefaction and the synergistic effects observed in coal-plastic co-liquefaction. Their study found that solid acid catalysts yielded oil yields ranging from 80% to 95% and total conversions between 90% and 100% during the liquefaction of HDPE, MDPE, PP, and PET. Co-liquefaction experiments using coal-plastic mixtures exhibited enhanced oil yields exceeding 80% during PE and lignite coal liquefaction at 450°C, with total conversions exceeding 90%. Furthermore, the choice of solvents significantly influenced liquefaction yields, with waste oil proving to be more effective than tetralin for plastics. Additionally, the activity of catalysts varied with temperature, with solid acid catalysts like HZSM-5 showing higher effectiveness at moderate temperatures compared to iron-based catalysts.⁶ In a related study, Pinto *et al.* (2019)⁷ investigated the co-liquefaction of coal with a range of carbonaceous wastes, including plastics (such as PE, PP, and PS), used tires, and biomass. Their

experimentation, conducted under controlled conditions, showcased the enhancement of the liquefaction process through the inclusion of waste materials, leading to improved liquid yields and oil quality. Notably, coal blended with PS waste yielded the highest liquid yield and total conversion.

Researchers highlighted the significance of tailored conditions for optimizing the co-liquefaction process. Moreover, synergistic effects were observed during co-liquefaction, resulting in increased oil yields and reduced hydrogen consumption. These studies highlight the intricate dynamics of co-liquefaction processes, emphasizing the importance of feed, solvent, and catalyst selection for optimizing liquefaction yields and overall process efficiency. Understanding the interactions between the different characteristics of feed materials during thermochemical conversion is crucial.

The main innovation of the work presented in this investigation is the use of various wastes such as coal fines and plastics, and a solvent that has limited use in liquefaction processes, i.e. benzene. For this study, a vitrinite-rich medium rank C bituminous coal that is typically utilized in coal-to-liquid processes and an inertinite-rich medium rank C bituminous coal discard fraction was used during co-liquefaction experiments with polypropylene and low-density polyethylene at 450°C. Tetralin, a H-donor solvent, and benzene, a H-poor solvent, was utilized during these experiments. The quantities and quality of the various solid, liquid, and gaseous fractions were determined to evaluate the effectiveness of co-processing.

5.2. Experimental

5.2.1. Materials

Highveld inertinite-rich fine coal filter cake (IR) and a seam 4 vitrinite-rich (VR) coal from the Witbank coalfields (a typical coal used in coal to liquid processes in South Africa) were used as the coal fractions of feed material in this study. The pulverized ($\sim 300 \mu\text{m}$) samples were dried at 100°C for 24 hours to reduce the inherent moisture content in the samples. Both coals were classified as bituminous medium rank C coals. Additionally, recycled polypropylene (PP) and low-density polyethylene (LDPE), procured from Potch Plastics in Potchefstroom (South Africa), were used as the plastics in this study. The materials were characterized using the methods summarized in **Table 5-1**. **Table 5-1** presents the characterization results from proximate- and ultimate analysis, calorific values, and O/C and H/C molar ratios.

Table 5-1. Characterization of the coals (VR and IR) and plastics (PP and LDPE).

Properties	Method of analysis	VR	IR	PP	LDPE
<i>Proximate analysis (wt.%, a.d.)</i>					
% Inherent moisture content	ISO 11722:1999	7.6	4.5	0.3	0.3
% Ash yield	ISO 1171:2010	12.4	28.3	1.2	1.6
% Volatile Matter	ISO 562:2010	31.8	23.8	98.5	97.7
% Fixed carbon	by difference	48.2	43.4	0.0	0.3
Fuel Ratio	FC/VM	1.52	1.82	0.0	0.0
Gross Calorific Value (MJ.kg^{-1})	ISO 1928:2009	25.4	20.3	46.7	46.2
<i>Ultimate analysis (wt.%, d.a.f.)</i>					
% Carbon Content	ISO 12902 – CHN	77.9	77.3	84.0	83.4
% Hydrogen Content	ISO 12902 – CHN	5.5	4.6	14.8	14.6
% Nitrogen Content	ISO 12902 – CHN	2.1	2.0	0.0	0.1
% Oxygen Content	by difference	13.7	14.9	1.2	1.2
% Total sulphur	ISO 19579:2006	0.7	1.2	0.1	0.7
O/C molar ratio		0.132	0.145	0.01	0.01
H/C molar ratio		0.842	0.706	2.09	2.09
Decomposition temp. ($^\circ\text{C}$)	From TGA				

a.d. = Air-dried; d.a.f. = dry ash free.

5.2.2. Liquefaction experiments

Blends consisting of a 1:1 coal-to-plastic ratio were used as the feed during the co-liquefaction experiments. The liquefaction experiments were carried out using a 600 mL stainless steel autoclave reactor (Parr Instruments, US), controlled using a 4848 controller from Parr. The feed materials were mixed with tetralin (1,2,3,4-Tetrahydronaphthalene for synthesis; $\geq 98\%$), a hydrogen-donor organic solvent, and benzene (ReagentPlus; $\geq 99\%$), a hydrogen-poor organic solvent, to a 1-to-3 weight ratio. An initial pressure of 0.2 MPa (2 bar) (absolute pressure), measured using a pressure display module integrated in the reactor controller, was applied by introducing an inert argon (AFROX, 99.999%) atmosphere. The temperature of the reaction vessel was increased to 450°C at 10°C/min with an isothermal reaction time of 60 minutes. To ensure thorough mixing of the reacting materials and solvent during the experiment, the stirrer speed was set to 250 rpm. After the reaction period, the reaction vessel was cooled to room temperature using an internal cooling coil controlled by a solenoid valve module. Once the temperature attained room temperature, the gas fraction was collected in a 5 L Tedlar gas bag and set aside for analysis. The liquid and solid products were removed from the reactor vessel and separated using dichloromethane as the solvent and vacuum

filtration to obtain the solid residue fraction. The dichloromethane was removed from the liquid fraction using rotary evaporation. Three replicates of the liquefaction experiments were performed, and the standard deviations of the yields obtained were determined to be less than 2%.

The methods used to calculate the solid residue yield, liquid/oil yield, gas yield, and carbon conversion values are described in **Section 3.2.3**. The carbon conversions, C_{daf} , of the feed materials obtained during solvent separation were calculated on a dry, ash-free basis and presented as a percentage as showed in **Eq. 1**.

$$C_{daf} = \left[\frac{m_{feed} - m_{SR}}{m_{feed}} \right] \times 100\% \quad (1)$$

These values were used to determine the percentage of feed material that reacted to produce the liquid and gaseous products during the liquefaction process.

5.2.3. Characterization of feed materials and solid residues

5.2.3.1. Proximate analysis, ultimate analysis, calorific values, and FTIR

The coals, plastics, and solid residues were subject to proximate analysis, ultimate analysis, and calorific value determinations using the methods highlighted in **Table 5-1**. The results from the approximated proximate analysis were used to determine the approximate higher heating values (HHV) of the solid residues from the liquefaction experiments using **Eq. 2**:⁸

$$HHV (MJ \cdot kg^{-1}) = 0.3536FC + 0.1559VM - 0.0078ASH \quad (2)$$

Where the fixed carbon content, volatile matter content, and ash yield are represented by FC , VM , and ASH , respectively.

Fourier-transform infrared spectroscopy, FTIR, was employed for the characterization of solid materials and residues. A BRUKER ALPHA-P attenuated total reflection Fourier-transform infrared spectrometer (ATR-FTIR) was utilized for solid-state analyses. OPUS version 6.0 (BRUKER software) was used for spectrum acquisition and processing. The FTIR spectra were captured with a wavelength range of 4000–400 cm^{-1} .

5.2.3.2. Pyrolysis of solid fractions

Pyrolysis experiments of the coal, demineralized coal, and residues were conducted using an SDT Q600 TGA instrument from TA Instruments. The results show the relationship between mass loss and temperature as a result of decomposition and dehydration reactions on a mass loss (%) versus temperature ($^{\circ}C$) plot and its derivative ($\%/^{\circ}C$) as a function of temperature in a differential thermal gravimetric analysis (DTG) plot. Approximately 15 mg (± 1 mg) of the sample was loaded in a 90 μL alumina crucible and subject to thermogravimetric analysis. An inert environment was created using nitrogen (AFROX, 99.999%) with a constant flow rate of 100 mL/min. The samples were heated from 25–960 $^{\circ}C$ with a linear heating rate of 20 $^{\circ}C/min$.^{9, 10}

Additionally, moisture content ($MC_{approx.}$), ash yield ($ASH_{approx.}$), volatile matter content ($VM_{approx.}$), and fixed carbon content ($FC_{approx.}$) were approximated from the pyrolysis and gasification results (**Section 5.2.3.3**). The approximate proximate analysis was calculated using **Eqs. 3–6**:¹¹

$$MC_{approx.} = \frac{m_i - m_{180^\circ C}}{m_i} \times 100\% \quad (3)$$

$$ASH_{approx.} = \frac{m_{ash}}{m_i} \times 100\% \quad (4)$$

$$VM_{approx.} = \frac{m_{180^\circ C} - m_{char}}{m_i} \times 100\% \quad (5)$$

$$FC_{approx.} = \frac{m_{char} - m_{ash}}{m_i} \times 100\% \quad (6)$$

Where m_i , $m_{180^\circ C}$, m_{ash} , and m_{char} denotes the initial sample mass at 25°C, mass at 180°C, mass of the ash after full conversion, and the mass of the char prior to CO₂ gasification at 960°C, respectively. The approximate HVV's (in MJ.kg⁻¹) were calculated from these results using Eq. 2.

5.2.3.3. Char-CO₂ gasification and kinetics

CO₂ gasification experiments were conducted on the chars derived from the liquefaction solid residues using an SDT Q600 thermogravimetric analyzer from TA instruments. The samples were heated to the desired isothermal reaction temperature (960°C) at 20 °C/min in an inert atmosphere to remove the residual volatile contents before the gasification experiments. When the desired isothermal temperatures were reached, the atmosphere was switched to CO₂ with a 30 mL/min flow rate until the reaction was completed and full conversion was reached. The reactivities at 50 and 90% ($R_{0.5}$ and $R_{0.9}$) conversion were calculated using Eqs. 7 and 8, where t is the time at conversion in minutes. The fractional carbon conversions (X), initial reactivities (R_i), and average final reactivities (R_{fa}) were evaluated using Eqs. 9–11.¹⁰⁻¹²

$$R_{0.5} = \frac{0.5}{t_{0.5}} \quad (7)$$

$$R_{0.9} = \frac{0.9}{t_{0.9}} \quad (8)$$

$$X = \frac{m_0 - m_t}{m_0 - m_{ash}} \quad (9)$$

$$R_i = \left. \frac{dX}{dt} \right|_{X=0.1} \quad (10)$$

$$R_{fa} = \frac{\sum_{X=0.9}^{X=0.7} \frac{dX}{dt}}{N} \quad (11)$$

Where X is the fractional carbon conversion, m_0 is the initial mass of the char before gasification, m_t is the mass of the char at reaction time (t), m_{ash} is the mass of the residual ash remaining after gasification occurred, and N in the number of data points.

5.2.4. Characterization of liquid yields

Gas Chromatography-Mass Spectrometry (GC-MS) analysis was conducted to characterize the liquid products obtained from the coal liquefaction experiments. An Agilent 6890N gas chromatograph (GC) coupled with an Agilent 5975 mass detector was utilized for this purpose. The GC instrument was equipped with an Agilent 19091S column, having a length of 30 m, a diameter of 0.25 mm, and a film thickness of 0.25 μm. The column temperature was programmed to increase at a rate of 5 °C/min until reaching 290°C. Once the desired temperature was reached, it was maintained isothermally for 30 minutes to ensure complete evolution of all sample components. For peak

identification, the National Institute of Standards and Technology (NIST) database was employed. This database served as a reference for identifying the peaks obtained during the GC-MS analysis, aiding in the characterization of the samples.

In addition, FTIR spectroscopic analysis was conducted using the method previously mentioned (**Section 5.2.3.1**). A Bruker Avance III Ultrashield Plus 600 MHz NMR spectrometer was utilized for the analyses, operating at frequencies of 600 MHz for ^1H nuclei and 150 MHz for ^{13}C nuclei. Samples were prepared by dissolving 30–40 mg of the sample in 0.6 mL CDCl_3 .

5.2.5. Gas composition using gas chromatography

Gas chromatography was used to analyze the gas fraction similar to the method used in **Section 3.2.6**. For the gas analysis, a PerkinElmer Clarus 500 Gas Chromatograph was used, with two columns (Agilent J&W HP-PLOT/Q 30 m x 0.535 mm and PerkinElmer Elite GC GS MSIEVE 30 m x 0.53 mm) interconnected to the injector and detectors via a VICI 10-port gas sampling valve from Valco Instruments. The thermal conductivity detector (TCD) was set to 100°C and the flame ionization detector (FID) was set to 200°C. Argon, supplied by AFROX with a purity of 99.999%, served as the carrier gas at an initial flow rate of 2 mL/min, increasing to 8 mL/min after 16 minutes. The oven temperature was set to 40°C, and the GC system was calibrated for CO_2 , CO, H_2 , CH_4 , C_2H_6 , C_2H_4 , C_3H_8 , C_4H_{10} , O_2 , and N_2 analysis.

The change in total pressure is attributed to the increase in partial pressures of the gases produced. By monitoring the change in pressure and knowing the initial pressure and the properties of the gases involved, the amount of gas produced may be quantified. Dalton's law was used to determine the partial pressures of the individual gas components together with the volume or molar percentage from gas chromatography. Dalton's Law states that the total pressure exerted by a mixture of non-reacting gases is the sum of the partial pressures of each individual gas: $P_{\text{total}} = P_1 + P_2 + \dots + P_n$, where P_{total} = Total pressure of the gas mixture, and $P_1, P_2, \dots, P_n$ = Partial pressures of individual gases in the mixture. Lastly, the ideal gas law ($PV = nRT$) was used to calculate the number of moles of each gas species in the mixture at a specific temperature (25°C) and pressure. From the number of moles of each gas, the mass could be determined.

5.3. Results and discussion

5.3.1. Co-liquefaction product distribution and conversion

Co-liquefaction experiments were conducted on vitrinite-rich (VR) and inertinite-rich coals with polypropylene (PP) and low-density polyethylene (LDPE) at 450°C using both tetralin, a hydrogen donor solvent, and benzene, a hydrogen-poor solvent. This allowed for the evaluation of liquefaction effectiveness and product quality and quantity of the products produced using two aromatic solvents possessing different hydrogen-transfer capabilities. The results from **Chapter 4** highlighted the probability of benzene acting as a hydrogen donor during plastic liquefaction experiments. **Table 5-2** presents the initial and final pressures recorded at 450°C, along with the partial pressures (at 25°C) obtained from co-liquefaction experiments. In the tetralin co-liquefaction experiments involving LDPE, higher partial pressures were obtained when compared to experiments involving PP. This is supported by the higher gas yield presented in **Table 5-3**. Co-liquefaction experiments using benzene were also conducted on a feed material comprising of a 1:3 coal-to-plastic ratio and resulted in lower recorded pressures after the reaction period at 450°C when compared to the results obtained from the use of blends in a 1:1 ratio. From the results, it is evident that benzene liquefaction experiments resulted in higher operating pressures along with lower overall conversion values.

Table 5-2. Initial and final pressures at the reaction temperature, and partial pressures measured from the co-liquefaction experiments conducted at 450°C.

	Coal	Plastic	C:P ratio	Pressure, bar		$\Delta P_{r.t.}$
				Initial at 450°C	Final at 450°C	
Tetralin	VR	PP	1:1	32.9	44.6	4.5
		LDPE	1:1	32.5	43.8	6.0
	IR	PP	1:1	29.0	43.5	4.2
		LDPE	1:1	31.1	41.4	5.7
Benzene	VR	PP	1:1	55.3	64.2	3.3
		LDPE	1:1	56.8	67.3	3.5
	IR	PP	1:1	55.0	63.5	2.9
		LDPE	1:1	53.4	61.2	2.8
Benzene	VR	PP	1:3	58.2	63.9	3.0
		LDPE	1:3	56.2	60.8	2.4
	IR	PP	1:3	52.4	57.2	2.2
		LDPE	1:3	52.0	57.0	1.7

Solvents used: tetralin and benzene. Feed materials: vitrinite-rich coal (VR), inertinite-rich coal (IR), polypropylene (PP), and low-density polyethylene (LDPE). Liquefaction temperatures: 450, 425, 400°C; Atmosphere: argon at 1.0 bar (initial pressure at 25°C). $\Delta P_{r.t.}$ = Partial pressure of gases at 25°C.

The partial pressures are directly proportional to the mass of the gases produced from the process. The reaction pressures obtained from the liquefaction experiments conducted in benzene were slightly lower than the typical range of pressures used in DCL processes (69–155 bar)¹³. Tetralin liquefaction pressures were significantly lower than these pressures. Higher reaction pressures can be achieved by increasing the amount of solvent used, thereby increasing the total volume occupation, or by increasing the initial argon pressure. An increase in reaction pressure may promote liquid yields and reduce char formation by suppressing retrogressive recombination reactions.^{14, 15}

Table 5-3 displays the carbon conversion values and product yields (wt.%) obtained from the co-liquefaction experiments conducted using tetralin and benzene at 450°C. In addition, product yields

obtained for the co-liquefaction experiment conducted on a feed material consisting of a 1:3 coal-to-plastic in benzene at 450°C, where included.

Table 5-3. Co-liquefaction product distribution and conversion at 450°C.

Solvent	Coal	Plastic	C:P ratio	Yield, weight % (d.a.f.)			Carbon conversion, % (d.a.f.)	Predicted conversion*, % (d.a.f.)
				Solid residue	Liquid residue	Gas fraction		
Tetralin	VR	PP	1:1	16.7	77.0	6.3	83.3	89.0
		LDPE	1:1	19.2	72.6	8.2	80.8	52.4
	IR	PP	1:1	23.6	70.3	6.1	76.4	74.0
		LDPE	1:1	27.5	65.6	7.0	72.5	37.4
Benzene	VR	PP	1:1	40.1	52.8	7.1	59.9	58.5
		LDPE	1:1	37.2	55.2	7.6	62.8	58.0
	IR	PP	1:1	39.0	54.6	6.4	61.0	58.1
		LDPE	1:1	38.7	55.1	6.2	61.3	57.6
Benzene	VR	PP	1:3	68.0	25.3	6.7	32.0	38.5
		LDPE	1:3	68.8	26.3	4.9	31.2	38.2
	IR	PP	1:3	66.5	29.0	4.5	33.5	37.9
		LDPE	1:3	63.9	33.2	2.9	36.1	37.6

Feed materials: Coal = VR and IR, Plastic = PP and LDPE; Coal-to-plastic ratio = 1:1 and 1:3; feed-to-solvent = 1:3.

* Predicted conversion calculated from the conversion values of the respective coals and plastics at 450°C.

It can be observed that tetralin co-liquefaction experiments involving the VR coal showed the highest carbon conversion values of 83.3 and 80.8% for PP and LDPE, respectively. The overall conversion during tetralin liquefaction involving the IR coal is lower than that of the VR coal. The difference between these conversion values may be ascribed to the different maceral compositions of the two coals. The fractions of reactive macerals, namely vitrinite and exinite, are significantly higher in the VR coal compared to the IR.¹¹ The results from the co-liquefaction of the IR coal with PP and LDPE had conversion values of 76.4 and 72.5%, respectively. During tetralin liquefaction experiments involving LDPE, significantly higher conversion of the feed material was found when compared to the calculated predicted conversion values. Co-liquefaction of VR/LDPE resulted in 80.8% conversion with a predicted conversion value of 52.4%. Similarly, IR/LDPE resulted in 72.5% conversion with a predicted conversion value of 37.4%. Gas yields from co-liquefaction experiments involving LDPE showed higher yields when compared to results from **Table 4-3**, excluding the results from the liquefaction of the 1:3 blends. The results indicate that synergistic effects between the coal and plastic materials are present, thereby affecting the product yield and overall conversion values. Alkali indices for both coals are relatively high (**Section 3.2.1**), and it has been shown that Al₂O₃ and catalysts like Al₂O₃-SiO₂ catalyse the conversion of plastics during liquefaction and co-liquefaction experiments with coal.³

The main difference between the conversion values can predominantly be ascribed to differences in the molecular structure. In addition, the results indicate that the conversion is influenced by the nature of the feed materials, coal-to-plastic blend ratio, and choice of solvent. It is expected that different reaction mechanisms occur during tetralin and benzene liquefaction, affecting the oil quality and composition (discussed in **Section 5.3.3**). The discussions in the following section will mostly focus on the results obtained from the co-liquefaction experiments conducted on the 1:1 coal-to-plastic blends following the low conversion values obtained from the 1:3 coal-to-plastic blends, as presented in **Table 5-3**.

5.3.2. Characterization of solid residue fractions from liquefaction experiments

5.3.2.1. Physicochemical characterization and FTIR spectroscopy

Table 5-4 shows the approximated proximate analysis and calorific values of solid residues produced from co-liquefaction experiments using tetralin and benzene at 450°C. The volatile matter contents of the solid residues derived from the co-liquefaction of the feed containing LDPE is significantly higher than PP. This shows that a larger fraction of unreacted LDPE is present in the solid residue fraction or that radicals derived from LDPE may take part in recombination reactions to form volatile matter constituents. The solid residues derived from experiments conducted in benzene show higher fixed carbon contents when compared to experiments conducted using tetralin. These results suggest that the conversion of the feed favor char or coke formation through retrogressive recombination reactions which results in lower liquid yields with reciprocal higher solid residue yields when compared to co-liquefaction experiments conducted using tetralin.

Table 5-4. Characterization of the solid residues produced from co-liquefaction experiments conducted at 450°C.

	Tetralin				Benzene			
	VR/PP _{SR}	VR/LDPE _{SR}	IR/PP _{SR}	IR/LDPE _{SR}	VR/PP _{SR}	VR/LDPE _{SR}	IR/PP _{SR}	IR/LDPE _{SR}
<i>Proximate analysis (wt.%, a.d.) *</i>								
% Moisture content	1.03	0.75	0.94	0.44	0.80	1.14	0.99	0.71
% Ash yield	30.44	27.08	44.51	39.64	16.43	15.66	30.98	31.31
% Volatile Matter	13.49	27.85	14.61	29.53	14.89	14.85	14.71	14.48
% Fixed carbon	55.04	44.32	39.94	30.38	67.88	68.35	53.32	53.50
Fuel Ratio	4.08	1.59	2.73	1.03	4.56	4.60	3.63	3.70
HHV (MJ.kg ⁻¹) **	21.33	19.80	16.05	15.04	26.20	26.36	20.91	20.93
<i>Ultimate analysis (wt.%, d.a.f.)</i>								
% Carbon Content	85.1	82.1	80.9	78.4	86.6	84.6	80.6	81.8
% Hydrogen Content	3.7	6.0	3.5	6.5	3.5	3.5	3.5	3.3
% Nitrogen Content	2.6	1.9	2.0	1.4	2.4	2.4	2.0	2.0
% Oxygen Content (calculated)	8.6	9.9	13.7	13.8	7.5	9.5	13.9	12.8
% Total sulphur	-	-	-	-	-	-	-	-
O/C molar ratio	0.08	0.09	0.13	0.13	0.06	0.08	0.13	0.12
H/C molar ratio	0.52	0.88	0.51	0.99	0.48	0.49	0.52	0.49

SR = solid residues; * Approximated from thermogravimetric analysis; ** Calculated using Eq. 2.

The H/C molar ratios of the solid residues derived from the co-liquefaction involving LDPE in tetralin was significantly higher compared to the experiments with PP. This could have resulted from a higher fraction of volatile matter contents comprising predominantly of aliphatic components. The H/C molar ratios of the benzene liquefaction derived residues are lower compared to those of the feed coal samples, also significantly lower than those of the plastic feed materials. These values are similar to the values obtained from the solid residues derived from tetralin and benzene liquefaction at 450°C (**Table 3-4** and **Table S3-1**).

The FTIR spectra of the solid residues derived from tetralin and benzene co-liquefaction of VR and IR with PP and LDPE are presented in **Figure S5-3** and **Figure S5-4**. The FTIR spectra of the two solvents used, namely tetralin and benzene, are presented in **Figure S5-2**. **Figure S5-1** presents the spectra obtained from the feed materials, i.e. VR, IR, PP, and LDPE.

Relevant FTIR wavenumbers of solid residues from tetralin and benzene co-liquefaction (cm^{-1}): 3700–3600 (O-H stretching); 2955, 2915 and 2847 (sp^3 C-H stretching, methylene/ CH_2); 1594 (C=O stretching, aromatic carbonyl); 1478–1431 (C=C stretching, aromatic); 1035–1000 (in-plane sp^2 aromatic C-H bending vibrations); 790–740 (out-of-plane sp^2 C-H bending, disubstituted aromatics).

It can be assumed that aliphatic components (predominantly evident in the plastic materials) readily convert to produce liquids and gases, and that the solid residues are more aromatic in nature. Weak aromatic sp^2 C-H bands in the 3200–3000 cm^{-1} region indicate that macromolecular structures of the coals and solid residues are mostly made up of quaternary aromatic carbons. In the region of 2955 and 2847 cm^{-1} , strong sp^3 C-H stretching bands were observed in the solid residues derived from tetralin co-liquefaction experiments involving LDPE (**Figure S5-3**). This suggests that a significant amount of unreacted LDPE is present in the solid residue fraction. The peak intensities of acyl and alkoxy C-O stretching bands at 1200–1000 cm^{-1} of the VR derived residues are weaker than residues derived from IR but have stronger aromatic C=O stretching bands near 1594 cm^{-1} . The results show that the residues exhibit similar structural characteristics to the feed coals.

5.3.2.2. CO_2 gasification reactivity using thermogravimetric analysis (TGA)

Table 5-5 presents reactivity results obtained from the CO_2 gasification of the VR and IR solid residue chars derived from tetralin liquefaction (**Table 3-8**), tetralin co-liquefaction derived solid residue chars, and tetralin co-liquefaction derived solid residue chars produced at 960°C. Various parameters, such as $t_{0.5}$ (time for 50% conversion), $R_{0.5}$ (reactivity at 50% conversion), $t_{0.9}$ (time for 90% conversion), $R_{0.9}$ (reactivity at 90% conversion), R_i (initial reactivity), and R_{fa} (average final reactivity) from the CO_2 gasification experiments, have been determined using **Eq. 3-7**. In addition, **Figure S5-6** and **Figure S5-7** provide fractional conversion and rate of reactivity curves.

Table 5-5. CO_2 gasification reactivities of the chars from co-liquefaction derived solid residues produced at 450°C.

Reactivities	Coal chars		Tetralin ¹¹		Tetralin				Benzene			
	VR	IR	VR _{SRC}	IR _{SRC}	VR/PP _{SRC}	VR/LDPE _{SRC}	IR/PP _{SRC}	IR/LDPE _{SRC}	VR/PP _{SRC}	VR/LDPE _{SRC}	IR/PP _{SRC}	IR/LDPE _{SRC}
$t_{0.5}$, min	18.3	14.5	12.9	20.9	23.4	19.1	21.8	14.7	26.4	26.7	19.9	19.4
$t_{0.9}$, min	41.3	40.1	44.4	69.2	72.9	60.8	77.7	54.1	59.5	60.6	55.3	54.1
$R_{0.5}$, $\text{min}^{-1} \times 10^2$	2.73	3.44	3.88	2.39	2.13	2.62	2.30	3.40	1.89	1.87	2.51	2.58
$R_{0.9}$, $\text{min}^{-1} \times 10^2$	2.18	2.24	2.03	1.30	1.24	1.48	1.16	1.67	1.51	1.49	1.63	1.66
R_i , $\text{min}^{-1} \times 10^2$	2.29	4.38	4.92	3.77	2.08	3.21	3.68	5.45	1.51	1.60	2.73	2.78
R_{fa} , $\text{min}^{-1} \times 10^2$	1.37	1.22	0.89	0.65	0.60	0.72	0.54	0.75	0.96	0.94	0.88	0.87

Feed materials = Vitrinite-rich coal (VR), inertinite-rich coal fines (IR), polypropylene (PP), and low-density polyethylene (LDPE); coal-to-plastic blend ratio = 1:1.

SR = solid residues from tetralin or benzene liquefaction; SRC = solid residue chars produced at 960°C.

From tetralin and benzene liquefaction, the IR/LDPE SR (solid residue) chars exhibited higher reactivities at 50% conversion ($R_{0.5}$) compared to the IR SR char. This indicates that the co-liquefaction experiments with the addition of LDPE produced SR chars with enhanced gasification reactivities. This trend did not hold for the SR chars from the co-liquefaction with VR coal. The IR/LDPE (tetralin), and IR/PP and IR/LDPE (benzene) chars exhibited higher $R_{0.9}$ values compared to VR SR char, but lower than the VR char. Co-liquefaction residue chars produced from IR coal generally had higher reactivities than VR derived SR chars. This was most prominent in the initial reactivities (R_i). A higher R_i value indicates a higher initial reactivity, meaning that the char is more reactive at the onset of the reaction than at 50% and 90% conversion. In this context, the presence of inorganic minerals and a higher alkali index in the IR coal appears to have a catalytic effect on the

initial and overall carbon conversion reactions.¹⁶ Yao *et al.* (2022)¹⁷ found that CO₂ gasification rates were higher in coals with higher inertinite contents but also expressed that higher inertinite contents were generally accompanied by high alkali indices.

It can be assumed that the catalytic effect of inorganic minerals in the IR coal appears to outweigh the inherently lower reactivity of inertinite-rich macerals, leading to a higher R_i in the IR coal char and solid residues derived from blends containing the IR coal. The data also indicates that, despite the inherently higher reactivity of vitrinite-rich macerals in VR coal, the higher ash yield and the catalytic effect of inorganic minerals in the IR coal result in a more pronounced increase in initial reactivity (R_i). The results suggest that the catalytic effect of inorganic minerals can be particularly influential in enhancing the initial stages of carbon conversion reactions during gasification.¹⁷

5.3.3. Characterization of liquid yields derived from co-liquefaction experiments

5.3.3.1. FTIR

The FTIR spectra obtained from the liquid yields derived from the co-liquefaction of VR and IR with PP and LDPE using tetralin at 450°C are presented in **Figure S5-8**. Additionally, the FTIR spectra obtained from the liquid yields derived from the co-liquefaction of VR and IR with PP and LDPE using benzene at 450°C are presented in **Figure S5-9**. The FTIR spectra of the two solvents used (i.e. tetralin and benzene) and feed materials (i.e. VR, IR, PP, and LDPE) are presented in **Figure S5-2** and **Figure S5-1**, respectively.

Relevant FTIR wavenumbers of the liquid yields derived from co-liquefaction with tetralin (cm⁻¹): 3053 and 3017 (sp² C-H stretch, aromatic); 2925, 2857, 2839 (sp³ C-H stretch, methylene/CH₂); 1715 (weak combination and overtone bands); 1597, 1494, 1451, 1436 (C=C stretching, aromatic); 782 and 740 (out-of-plane sp² C-H bending, ortho disubstituted aromatics); 677 (sp² C-H bending, substituted benzenes); 618 (sp² C-H bend, methylene/CH₂); 475 (out-of-plane ring bending).

Aromatic sp² C-H bands in the 3200–3000 cm⁻¹ region and methylene C-H stretching bands at 2925, 2857, and 2839 cm⁻¹ indicate that the molecular structures of the liquid yields are similar to that of tetralin (**Figure S5-2**), signifying aromatic structures with connected methylene groups. The vibrational band at 1715 cm⁻¹, strongly observed in the VR/LDPE sample, is usually associated with C=O stretching bands but can also be assigned to weak combination and overtone band that are between 2000–1650 cm⁻¹. Evidently, no polar structures containing -C=O and -OH functional groups are present in the VR/PP, IR/PP, and IR/LDPE liquid fractions. This is supported by absent alkoxy C-O stretching, C=O stretching, and O-H stretching vibrations in the 1068 cm⁻¹, 1750–1650 cm⁻¹ and 3700–3200 cm⁻¹ regions, respectively. Weak bands were observed at 1596 cm⁻¹ indicating the presence of naphthalene, a common derivative of tetralin through dehydrogenation reactions.¹¹ The formation of substituted aromatics is supported by a strong out-of-plane sp² C-H bending vibration for ortho disubstituted aromatics at 782 and 740 cm⁻¹.¹⁸ The band at 741 cm⁻¹, commonly associated with tetralin, indicates that a notable amount of unreacted tetralin is present. This is supported by similar overall spectrums obtained from all the co-liquefaction experiments conducted using tetralin as a solvent. The vibrations observed at 677 cm⁻¹ indicate the presence of substituted benzenes. The results are also supported by the GC-MS results presented in **Table 5-6**.

Relevant FTIR wavenumbers of the liquid yields derived from co-liquefaction with benzene (cm^{-1}): 3091, 3072 and 3036 (sp^2 C-H stretching, aromatic); 2954, 2924, 2870, and 2855 (sp^3 C-H stretching, methylene/ CH_2); 2000–1650 (weak combination and overtone bands); 1478 (overlapping bands from C-H bending vibrations from ethylene groups and C=C stretching vibrations from aromatics); 1377 (C-H bending, propylene); 1266 and 1035 (in-plane sp^2 C-H bending vibrations, aromatics); 738 (out-of-plane sp^2 C-H bending, ortho disubstituted aromatics); 670 (sp^2 C-H bending, substituted benzenes).

Similar to the spectra obtained from the liquid fractions produced using tetralin as a solvent (**Figure S5-8**), aromatic sp^2 C-H stretching vibrations in the 3200–3000 cm^{-1} region and sp^3 C-H stretching vibrations at 2954, 2924, 2857, and 2839 cm^{-1} are observed, indicating that aromatic structures such as benzenes and aliphatic structures such as methylene and ethylene groups are present. The bands at 1266 and 1035 cm^{-1} represent in-plane sp^2 C-H bending vibrations mainly associated with aromatics. Strong sp^2 C-H bending vibrations at 670 cm^{-1} are observed in all the liquid fractions derived from co-liquefaction experiments using benzene as the solvent. These vibrations are indicative of benzene and substituted aromatics – supported by out-of-plane sp^2 C-H bending vibrations for monosubstituted and ortho disubstituted aromatics (738 cm^{-1}). The presence of aromatic compounds can occasionally be supported by C=C stretching vibrations at 1478 cm^{-1} , however, overlapping bands from C-H bending vibrations from alkanes which are generally present in this region.¹⁸ The higher intensity of sp^3 C-H stretching vibrations (between 3000–2800 cm^{-1}) from the liquid fractions derived from LDPE, i.e. VR/LDPE and IR/LDPE, are indicative of chained alkanes. Moreover, the intensities of the bands from IR/LDPE are higher than VR/LDPE, indicating a higher fraction of aliphatic components. These claims are supported by the GC-MS results presented in **Table 5-7**, showcasing a higher abundance of alkanes, and lower abundance of alkenes, in the IR/LDPE liquid fraction. The band observed at 1715 cm^{-1} can be assigned to carbonyl C=O stretching vibrations such as saturated ketones. However, there is no evidence of other oxygen containing functional groups. This is supported by absent alkoxy C-O stretching vibrations and O-H stretching vibrations around 1068 cm^{-1} and 3700–3200 cm^{-1} , respectively.

5.3.3.2. GC-MS and Simulated Distillation

The GC-MS results, as presented in **Table 5-6** and **Table 5-7**, show a qualitative and semi-quantitative overview of the range of compounds produced from the co-liquefaction experiments conducted using tetralin and benzene at 450°C. The relative abundance of the compounds is reported in percentage.

Table 5-6. Molecular abundance (%) results determined from GC-MS analysis conducted on the liquid fractions produced from tetralin co-liquefaction experiments of VR and IR coal with PP and LDPE (1:1 coal-to-plastic ratio) at 450°C.

VR (tetralin)						IR (tetralin)					
PP			LDPE			PP			LDPE		
Compound	g.mol ⁻¹	A _{abs} , %	Compound	g.mol ⁻¹	A _{abs} , %	Compound	g.mol ⁻¹	A _{abs} , %	Compound	g.mol ⁻¹	A _{abs} , %
Naphthalene	128.1	26.3	Naphthalene	128.1	22.9	Naphthalene	128.1	21.9	Naphthalene	128.1	19.1
Benzene, (2-methyl-1-propenyl)-	132.1	6.2	Benzene, 1-ethenyl-3-ethyl-	132.1	7.2	Benzene, (2-methyl-1-propenyl)-	132.1	5.8	Benzene, (2-methyl-1-propenyl)-	132.1	6.9
Naphthalene, 1,2,3,4-tetrahydro-	132.1	62.1	Naphthalene, 1,2,3,4-tetrahydro-	132.1	57.4	Naphthalene, 1,2,3,4-tetrahydro-	132.1	67.9	Naphthalene, 1,2,3,4-tetrahydro-	132.1	63.0
Benzene, butyl-	134.1	0.9	Benzene, butyl-	134.1	1.1	Benzene, butyl-	134.1	0.8	Benzene, butyl-	134.1	1.0
Naphthalene, 1-methyl-	142.1	0.7	Benzene, (2-methyl-1-butenyl)-	146.1	0.6	Benzene, (2-methyl-1-butenyl)-	146.1	0.5	Benzene, (2-methyl-1-butenyl)-	146.1	0.6
			Eicosane	282.3	1.1				Heptadecane	240.3	0.7
			Heneicosane	296.3	0.5				Tetracosane	338.4	0.6
			Tetracosane	338.4	0.5				Heptacosane	380.4	0.5
			Heptacosane	380.4	0.6				Octacosane	394.5	0.5
			Octacosane	394.5	0.5						
Alkanes (N/A)		0.0	Alkanes (C ₂₀ –C ₂₈)		3.2	Alkanes (N/A)		0.0	Alkanes (C ₁₇ –C ₂₈)		2.3
Alkenes (N/A)		0.0	Alkenes (N/A)		0.0	Alkenes (N/A)		0.0	Alkenes (N/A)		0.0

A_{abs}, % = Absolute Area in percentage. Naphthalene, 1,2,3,4-tetrahydro- = tetralin

During the co-liquefaction experiments conducted using tetralin, a large fraction of unreacted tetralin with a smaller fraction of naphthalene can be observed in the liquid yield. The formation of naphthalene can be associated with the dehydrogenation of tetralin to produce hydrogen accompanied by compounds such as butylbenzene and indane. Through rearrangement tetralin, compounds, such as 1-ethenyl-3-ethylbenzene and 2-methyl-1-propenylbenzene, were also produced. The availability of hydrogen can promote reactions with radicals or unsaturated compounds. The results show that LDPE derived liquids have lower concentrations of naphthalene and tetralin than the liquid yields derived from the co-liquefaction experiments involving PP. It can be seen that excess hydrogen is produced, predominantly derived from tetralin, that are not taken up during liquefaction and is present in the gas fraction. This can be supported by high H₂ contents present in the gas fraction (**Figure 5-1** and **Table S5-3**). When evaluating the liquid yields and conversion values presented in **Table 5-3**, VR/LDPE and IR/LDPE have lower values compared to VR/PP and IR/PP. It should be noted that the predicted conversion values of VR/LDPE and IR/LDPE are significantly lower than the experimental values, indicating synergistic effects between both the VR and IR coal with LDPE. The inorganic components in the coals can also promote catalytic effects for the decomposition of LDPE. The formation of chained alkanes from co-liquefaction experiments with LDPE (i.e. VR/LDPE and IR/LDPE) were also evident in the liquid yields.

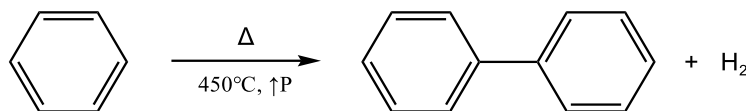
Table 5-7. Molecular abundance (%) results determined from GC-MS analysis conducted on the liquid fractions produced from benzene co-liquefaction experiments of VR and IR coal with PP and LDPE (1:1 coal-to-plastic ratio) at 450°C.

VR (benzene)						IR (benzene)					
PP			LDPE			PP			LDPE		
Compound	g.mol ⁻¹	A _{abs} , %	Compound	g.mol ⁻¹	A _{abs} , %	Compound	g.mol ⁻¹	A _{abs} , %	Compound	g.mol ⁻¹	A _{abs} , %
Benzene, 1,2,3-trimethyl-	120.1	30.3	Naphthalene	128.1	1.0	Benzene, 1-ethyl-2-methyl-	120.1	2.9	Naphthalene, 1,2,3,4-tetrahydro-	132.1	1.9
Benzene, 1,2,4-trimethyl-	120.1	7.8	Naphthalene, 1,2,3,4-tetrahydro-	132.1	3.4	Benzene, 1,2,3-trimethyl-	120.1	21.1	Bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene	142.1	2.1
Naphthalene, 1,2,3,4-tetrahydro-	132.1	4.8	Decane	142.2	4.0	Naphthalene, 1,2,3,4-tetrahydro-	132.1	4.7	Decane	142.2	4.1
Biphenyl	154.1	48.2	Biphenyl	154.1	26.6	Biphenyl	154.1	62.4	Biphenyl	154.1	31.3
(1-Methylpenta-1,3-dienyl)benzene	158.1	3.0	Undecane	156.2	3.2	1,2,3-Trimethylindene	158.1	5.9	Undecane	156.2	3.0
1,4-Benzenedithiol, S,S'-dimethyl-	170.0	0.7	Dodecane	170.2	4.1	Naphthalene, 2,3,6-trimethyl-	170.1	0.5	Decane, 3,8-dimethyl-	170.2	1.5
cis-Stilbene	180.1	1.6	1-Tridecene	182.2	2.4	Phenol, 2,2'-methylenebis[6-(1,1-dimethylethyl)-4-methyl-	340.2	0.8	Cyclotetradecane	196.2	2.7
4-Stilbene	208.1	1.6	Tridecane	184.2	3.0	Octasiloxane, 1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-hexadecamethyl-	578.2	1.3	Tetradecane	198.2	10.1
Phenol, 2,2'-methylenebis[6-(1,1-dimethylethyl)-4-methyl-	340.2	1.0	Cyclotetradecane	196.2	1.5				1-Pentadecene	210.2	2.3
			Tetradecane	198.2	2.5				Pentadecane	212.3	3.8
			1-Pentadecene	210.2	4.9				Cetene	224.3	2.5
			Hexadecane	226.3	7.9				Hexadecane	226.3	4.9
			1-Heptadecene	238.3	3.7				Octadecane	254.3	5.4
			Heptadecane	240.3	5.5				1-Nonadecene	266.3	1.0
			E-15-Heptadecenal	252.2	2.5				Nonadecane	268.3	3.6
			Octadecane	254.3	6.1				Cycloeicosane	280.3	1.2
			Eicosane	282.3	3.4				Eicosane	282.3	5.8
			Heneicosane	296.3	7.0				Heneicosane	296.3	4.0
			Nonadecane, 1-chloro-	302.3	2.1				Docosane	310.4	2.4
			Tetracosane	338.4	3.1				Tricosane	324.4	0.5
			1,4-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester	390.3	0.5				Tetracosane	338.4	4.0
			Octacosane	394.5	0.6				Heptacosane, 1-chloro-	414.4	0.6
			Tetracosane, 1-bromo-	416.3	0.9						
Alkanes (N/A)		0.0	Alkanes (C ₁₀ –C ₂₈)		54.9	Alkanes (N/A)		0.0	Alkanes (C ₁₀ –C ₂₄)		57.2
Alkenes (N/A)		0.0	Alkenes (C ₁₃ –C ₁₇)		11.1	Alkenes (N/A)		0.0	Alkenes (C ₁₅ –C ₁₉)		5.8

A_{abs}, % = Absolute Area in percentage. Naphthalene, 1,2,3,4-tetrahydro- = tetralin

During co-liquefaction experiments conducted using benzene (**Table 5-7**), VR/LDPE and IR/LDPE showed promising results. A large fraction of the oils consists of C₁₀–C₂₈ alkanes and C₁₃–C₁₉ alkenes that account for around 54.9 and 11.1% of the VR/LDPE liquid yield, around 57.2 and 5.8% of the IR/LDPE liquid yield, respectively. Experiments conducted using PP in the feed, i.e. VR/PP and IR/PP, produced high concentrations of substituted aromatics with no detectable aliphatic components, similar to tetralin liquefaction experiments conducted with PP. High concentrations of alkanes are usually not expected when using a hydrogen-poor solvent. Similar to the results reported in **Chapter 4**, a significant fraction of biphenyl formed during co-liquefaction experiments using benzene, accounting for around 48.2, 26.6, 62.4, and 31.3% of the derived liquid fractions from VR/PP, VR/LDPE, IR/PP, and IR/LDPE, respectively. The presence of biphenyl can support the

occurrence of dehydrogenation reactions of benzene to produce hydrogen. The following reaction equation can be assumed:



The hydrogen produced from this reaction can saturate alkenes or protonate radical chains that formed through chain scission or fragmentation reactions. The low H_2 yields obtained from benzene co-liquefaction presented in **Figure 5-1** (**Table S5-3**) indicate that most of the hydrogen reacted to form alkanes. The conclusion from these results highlights that benzene, known to be a H-poor aromatic solvent, may be considered as a hydrogen-donor solvent under the specific conditions of this study. Lastly, oxygen-containing compounds were absent or in very low concentrations in the liquid fractions produced from this study. This can be supported by weak alkoxy C-O bands, and absent C=O and O-H bands in the FTIR spectra of the liquid fraction. The gas yields, however, consist of considerable amounts of CO_2 and CO (discussed in **Section 5.3.3.3**). Isa *et al.* (2018)¹⁹ reported that it is favorable to produce liquid residues having low oxygen contents during liquefaction.

Table 5-8 report the simulated distillation results from the liquid yields from co-liquefaction experiments. Boiling ranges were separated into kerosene (166–249°C), diesel (249–343°C), and vacuum gas oil (343–538°C).²⁰ The kerosene fraction in the liquid yields derived from tetralin co-liquefaction are significantly higher compared to the results obtained from benzene co-liquefaction. This can be assigned to a high concentration of naphthalene and residual tetralin present in the formerly mentioned experiments. The results from simulated distillation confirm the range of compounds determined using GC-MS.

Table 5-8. Summarized simulated distillation results of the liquid fractions from co-liquefaction experiments conducted at 450°C.

		Cumulative peak area, %		
		Kerosene	Diesel	Vacuum gas oil
Tetralin	VR/PP _{liq}	94.5	1.9	2.8
	VR/LDPE _{liq}	87.2	3.4	7.8
	IR/PP _{liq}	95.6	1.8	2.1
	IR/LDPE _{liq}	89.5	2.9	6.6
Benzene	VR/PP _{liq}	41.4	22.2	12.5
	VR/LDPE _{liq}	44.3	25.9	22.6
	IR/PP _{liq}	45.8	25.6	13.9
	IR/LDPE _{liq}	31.0	31.8	23.1

Kerosene: BP = 166–249°C (C_{10} – C_{14}); diesel = 249–343°C (C_{14} – C_{20}); and vacuum gas oil = 343–538°C (C_{20} – C_{40}).

Analyzing the NMR data depicted in **Table 5-9** reveals an abundant presence of tetralin and its derivatives post-co-liquefaction. This analysis highlights a higher aliphatic-to-aromatic proton ratio in LDPE compared to PP, indicating a tendency for aliphatic hydrocarbon formation in LDPE. Similarities between the results obtained from the co-liquefaction of blends containing VR and IR coal suggest that the strong proton peaks from tetralin and its derivatives may mask other NMR peaks, preventing differentiation. In experiments using benzene, a solvent lacking aliphatic protons, a marked presence of aliphatic protons was observed in the liquid fraction, particularly in LDPE, reinforcing the notion that LDPE is predominantly converted into aliphatic hydrocarbons, and the solvent is not necessarily substituted.

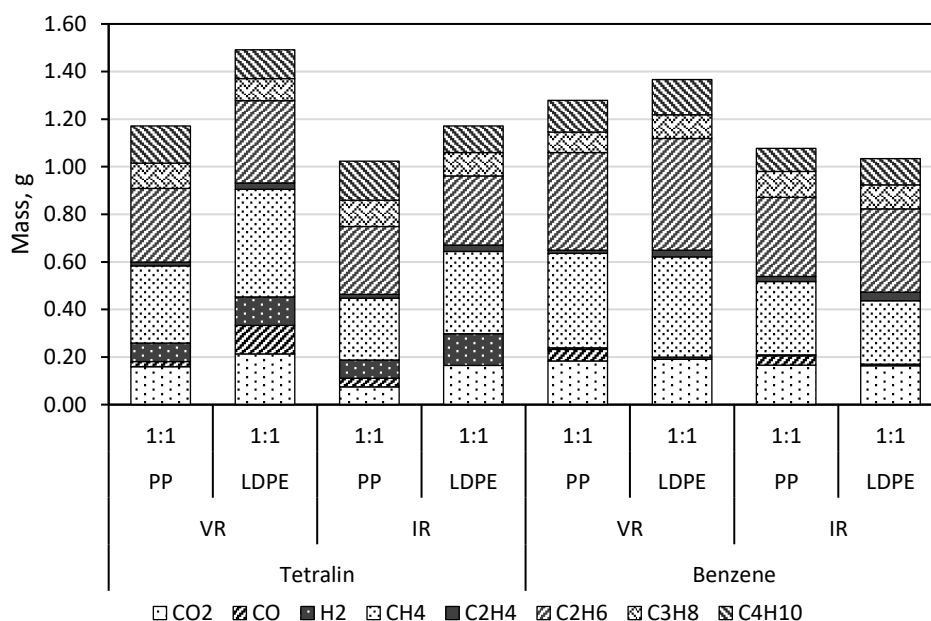
Table 5-9. Summarized relative proton integrated values of liquid fractions from co-liquefaction experiments conducted on VR and IR with PP and LDPE using tetralin and benzene at 450°C.

		Relative proton integrated values, %		
		Aliphatic	Aromatic	Vinylic
Tetralin	VR/PP _{liq}	57.2	38.4	4.5
	VR/LDPE _{liq}	58.9	36.8	4.1
	IR/PP _{liq}	59.8	37.0	3.2
	IR/LDPE _{liq}	61.8	35.2	3.0
Benzene	VR/PP _{liq}	17.9	74.9	7.2
	VR/LDPE _{liq}	20.0	70.1	9.9
	IR/PP _{liq}	15.6	73.6	10.8
	IR/LDPE _{liq}	21.1	69.0	9.9
Solvent	Tetralin	66.7	33.3	-
	Benzene	0.0	100.0	-

Absolute integrals obtained via ¹H-NMR (600MHz, CDCl₃)

5.3.4. Gas composition using gas chromatography (GC-TCD/FID)

The data presented in **Table S5-3** shows the molar/volume percentage values obtained from the gas fractions, and total gas yields with corresponding partial pressures from the co-liquefaction experiments of VR and IR with PP and LDPE using tetralin and benzene. The total gas yields, molar ratios, and partial pressures were used to calculate the masses of the compound gases, applying Dalton's law for partial pressure and the Ideal Gas Law. These results are presented in **Figure 5-1**.

**Figure 5-1. Gas chromatography results of the gas fractions produced from co-liquefaction experiments.**

During liquefaction processes, previous research has shown that the primary components in gas fractions include carbon monoxide, carbon dioxide, hydrogen, and hydrocarbon compounds such as methane, ethane, ethylene, propane, and butane.^{11, 21} Methane and carbon dioxide start to evolve at relatively low temperatures (200°C). As the temperature continues to rise, there is internal condensation of the macromolecular structure of low-rank coals. This condensation process initiates the evolution of carbon dioxide (CO₂) and water (H₂O) as by-products.²² Decarboxylation reactions

were evident during all the co-liquefaction experiments in this, producing CO₂. The gas fractions obtained from VR/LDPE indicate that decarbonylation reactions were favored to produce CO.

The production of hydrogen was predominantly observed in the gas fractions produced from the tetralin liquefaction experiments, favoring experiments conducted on the blends containing LDPE. This may be attributed to the thermal breakdown of aliphatic carbon-hydrogen linkages in the polymeric chains and the dehydrogenation of tetralin. This was not evident in the gas fractions obtained from the liquefaction experiments involving benzene as the solvent. The proposed production of hydrogen radicals through dehydrogenation of benzene and tetralin may react with unsaturated gas species such as ethylene (if present during the liquefaction process) to produce ethane. This can be the reason for the significantly low ethylene concentrations in all samples. The gas fraction produced from the co-liquefaction experiments were predominantly comprised of carbon dioxide, methane, ethane, propane, and butane. The results show that the composition of the gas fractions is mostly affected by the type of feed materials and solvent selection.

5.3.5. Mass balance calculations

The carbon, hydrogen, and oxygen contents of the feed materials and products (in grams) are presented in **Table 5-9** (co-liquefaction with tetralin) and **Table 5-10** (co-liquefaction with benzene). Through mass balance calculations, the elemental mass transfer from the feed materials to the liquid fraction could be determined.

Table 5-10. Mass balance results from co-liquefaction with tetralin conducted at 450°C.

Materials	Elemental mass, g (d.a.f.)					Molar ratios	
	C	H	O	N	S	H/C	O/C
<i>Solvent and feed, g</i>							
Tetralin (60.0g)	54.51	5.50	0.00	-	-	1.20	0.00
VR (10.0g)	6.24	0.44	1.10	0.17	0.06	0.84	0.13
IR (10.0g)	5.20	0.31	1.00	0.13	0.08	0.70	0.14
PP (10.0g)	8.27	1.45	0.11	0.00	0.01	2.09	0.01
LDPE (10.0g)	8.18	1.43	0.12	0.01	0.07	2.08	0.01
<i>Product yields, g</i>							
VR/PP _{SR}	2.64	0.11	0.08	0.27	<i>n.d.</i>	0.52	0.02
VR/LDPE _{SR}	2.86	0.21	0.07	0.35	<i>n.d.</i>	0.87	0.02
IR/PP _{SR}	3.19	0.14	0.08	0.54	<i>n.d.</i>	0.51	0.02
IR/LDPE _{SR}	3.62	0.30	0.06	0.63	<i>n.d.</i>	0.99	0.01
VR/PP _{gas}	0.77	0.27	0.13	<i>n.d.</i>	<i>n.d.</i>	4.16	0.12
VR/LDPE _{gas}	0.92	0.34	0.22	<i>n.d.</i>	<i>n.d.</i>	4.43	0.18
IR/PP _{gas}	0.70	0.25	0.08	<i>n.d.</i>	<i>n.d.</i>	4.25	0.08
IR/LDPE _{gas}	0.73	0.32	0.12	<i>n.d.</i>	<i>n.d.</i>	5.20	0.12
VR/PP _{liq}	65.60	7.01	1.00	<i>n.d.</i>	<i>n.d.</i>	1.27	0.01
VR/LDPE _{liq}	65.14	6.82	0.93	<i>n.d.</i>	<i>n.d.</i>	1.24	0.01
IR/PP _{liq}	64.09	6.88	0.96	<i>n.d.</i>	<i>n.d.</i>	1.28	0.01
IR/LDPE _{liq}	63.54	6.62	0.94	<i>n.d.</i>	<i>n.d.</i>	1.24	0.01
<i>Mass transfer (solid feed to liquid yield), g</i>							
VR/PP to VR/PP _{liq}	11.09	1.51	1.00	<i>N/A</i>	<i>N/A</i>	1.62	0.07
VR/LDPE to VR/LDPE _{liq}	10.63	1.32	0.93	<i>N/A</i>	<i>N/A</i>	1.48	0.07
IR/PP to IR/PP _{liq}	9.58	1.37	0.96	<i>N/A</i>	<i>N/A</i>	1.71	0.08
IR/LDPE to IR/LDPE _{liq}	9.03	1.12	0.94	<i>N/A</i>	<i>N/A</i>	1.47	0.08

Feed = VR, IR, PP, LDPE with Coal-to-plastic = 1:1; SR = solid residue; liq = liquid yield; gas = gas yield; *n.d.* = not determined.

Considering the low hydrogen contents of the coals, the liquid yields presented H/C molar ratios higher than tetralin (1.20) and indicate that hydrogen transfer from PP and LDPE to their respective liquid fractions occurred. This can be supported by the results from tetralin and benzene liquefaction of the VR and IR coals (**Chapter 4**) producing liquid fractions of lower H/C molar ratios – 1.08 and 1.11, respectively. A significant fraction of carbon originating from the feed materials was transferred to the liquid yield, specifically 11.1, 10.6, 9.6, and 9.0 g for VR/PP, VR/LDPE, IR/PP, and IR/LDPE, respectively. This trend is directly related to the conversion values as presented in **Table 5-3**. Hydrogen transfer from the IR containing blends were slightly lower compared to that from the VR containing blends. It can be assumed that the higher aromatic nature of the inertinite-rich coal resulted in fewer hydrogen transfer reactions but produced liquid yields with similar H/C molar ratios.

When compared to the mass transfer results obtained from the co-liquefaction using benzene (**Table 5-10**), lower fractions of hydrogen were transferred from the feed material to the liquid yield. This difference can be associated with lower conversion values. The liquid yields produced from the co-liquefaction using benzene had higher H/C molar ratios than the liquid yields from the co-liquefaction involving the VR and IR coals using benzene. The difference can be associated with the depolymerization of PP and LDPE to produce a higher fraction of aliphatic components that increases the overall H/C molar ratios. The GC-MS results from **Table 5-6** and **Table 5-7** support these statements. Moreover, plastics may also supply some hydrogen to the reaction medium, due to thermal break-down reactions.

Table 5-11. Mass balance results from co-liquefaction with benzene conducted at 450°C.

Materials	Elemental mass, g (d.a.f.)					Molar ratios	
	C	H	O	N	S	H/C	O/C
<i>Solvent and feed, g</i>							
Benzene (60.0g)	55.35	4.65	0.00	-	-	1.00	0.00
VR (10.0g)	6.24	0.44	1.10	0.17	0.06	0.84	0.13
IR (10.0g)	5.20	0.31	1.00	0.13	0.08	0.70	0.14
PP (10.0g)	8.27	1.45	0.11	0.00	0.01	2.09	0.01
LDPE (10.0g)	8.18	1.43	0.12	0.01	0.07	2.08	0.01
<i>Product yields, g</i>							
VR/PP _{SR}	6.25	0.25	0.17	0.54	<i>n.d.</i>	0.48	0.02
VR/LDPE _{SR}	5.66	0.23	0.16	0.64	<i>n.d.</i>	0.49	0.02
IR/PP _{SR}	5.27	0.23	0.13	0.91	<i>n.d.</i>	0.52	0.02
IR/LDPE _{SR}	5.32	0.22	0.13	0.83	<i>n.d.</i>	0.48	0.02
VR/PP _{gas}	0.89	0.23	0.16	<i>n.d.</i>	<i>n.d.</i>	3.07	0.14
VR/LDPE _{gas}	0.97	0.26	0.14	<i>n.d.</i>	<i>n.d.</i>	3.15	0.11
IR/PP _{gas}	0.75	0.19	0.14	<i>n.d.</i>	<i>n.d.</i>	3.02	0.14
IR/LDPE _{gas}	0.73	0.19	0.12	<i>n.d.</i>	<i>n.d.</i>	3.05	0.12
VR/PP _{liq}	62.73	6.07	0.87	<i>n.d.</i>	<i>n.d.</i>	1.15	0.01
VR/LDPE _{liq}	63.14	6.04	0.92	<i>n.d.</i>	<i>n.d.</i>	1.14	0.01
IR/PP _{liq}	62.81	6.00	0.84	<i>n.d.</i>	<i>n.d.</i>	1.14	0.01
IR/LDPE _{liq}	62.68	5.99	0.87	<i>n.d.</i>	<i>n.d.</i>	1.14	0.01
<i>Mass transfer (solid feed to liquid yield), g</i>							
VR/PP to VR/PP _{liq}	7.37	1.41	0.87	<i>N/A</i>	<i>N/A</i>	2.28	0.09
VR/LDPE to VR/LDPE _{liq}	7.79	1.38	0.92	<i>N/A</i>	<i>N/A</i>	2.11	0.09
IR/PP to IR/PP _{liq}	7.46	1.34	0.84	<i>N/A</i>	<i>N/A</i>	2.14	0.08
IR/LDPE to IR/LDPE _{liq}	7.33	1.34	0.87	<i>N/A</i>	<i>N/A</i>	2.17	0.09

Feed = VR, IR, PP, LDPE with Coal-to-plastic = 1:1; SR = solid residue; liq = liquid yield; gas = gas yield; *n.d.* = not determined.

5.4. Conclusions

The following conclusions can be made from the results discussed in this chapter:

- The main difference between the conversion values obtained can be ascribed to differences in the molecular structure of the feed materials. In addition, the results indicate that the conversion is influenced by the nature of the feed materials, coal-to-plastic blend ratio, and choice of solvent.
- Aliphatic components (predominantly evident in plastic materials) readily convert to produce liquids and gases, while the solid residues are more aromatic in nature.
- Co-liquefaction solid residue chars produced from blends containing IR coal generally had higher reactivities than chars derived from blends containing VR coal.
- The liquid fractions derived from the co-liquefaction experiments conducted using benzene consisted of C₁₀–C₂₈ alkanes and C₁₃–C₁₉ alkenes amounting to 54.9 and 11.1% of the VR/LDPE liquid yield, and 57.2 and 5.8% of the IR/LDPE liquid yield, respectively.
- Benzene, known to be a H-poor aromatic solvent, may be considered as a hydrogen-donor solvent during co-liquefaction processes.

The results from this chapter indicate that PP and LDPE can assist and promote hydrogen transfer during co-liquefaction processes, and that the co-liquefaction of an inertinite-rich discard coal can be effectively converted into liquid product with the addition of plastics such as polypropylene and low-density polyethylene.

Acknowledgments

The information presented in this paper is based on the research financially supported by the National Research Foundation (NRF) and South African Research Chairs Initiatives (SARChI) of the Department of Science and Technology (Coal Research chair Grant No. 86880). Any opinions, conclusions or recommendations expressed are that of the author(s), and no liability is accepted on the NRF's regard.

5.5. Supporting Information

Table S5-1. Characterization of the solid residues produced from the liquefaction of 1:3 coal-to-plastic blends at 450°C in benzene.

Sample Identification	VR PP 1:3 B	VR LDPE 1:3 B	IR PP 1:3 B	IR LDPE 1:3 B
<i>Proximate analysis (wt.%, a.d.) *</i>				
% Moisture content	1.2	1.4	1.1	0.9
% Ash yield	13.8	13.1	29.2	30.2
% Volatile Matter	15.7	15.8	14.6	15.3
% Fixed carbon	69.3	69.7	55.1	53.7
Fuel Ratio	4.4	4.4	3.8	3.5
HHV (MJ.kg ⁻¹) **	26.8	27.0	21.5	21.1
<i>Ultimate analysis (wt.%, d.a.f.)</i>				
% Carbon Content	82.4	81.2	80.2	79.0
% Hydrogen Content	3.3	3.1	3.1	3.2
% Nitrogen Content	2.4	2.3	2.1	2.0
% Oxygen Content (calculated)	11.9	13.4	14.7	15.7
% Total sulphur	-	-	-	-
O/C molar ratio	0.11	0.12	0.14	0.15
H/C molar ratio	0.47	0.46	0.46	0.48

* Approximated from thermogravimetric analysis. SR = liquefaction solid residue; PAA = pre-asphaltenes and asphaltenes.

** Calculated using Eq. 8

Table S5-2. CO₂ gasification reactivities at 960°C of the liquefaction derived solid residues from the coal-plastic blends (1:3 coal-to-plastic ratio) produced at 450°C.

Reactivities		Benzene			
		VR PP (1:3)	VR LDPE (1:3)	IR PP (1:3)	IR LDPE (1:3)
t _{0.5} , min		27.7	29.5	20.0	20.6
t _{0.9} , min		61.8	65.2	55.6	56.6
R _{0.5} , min ⁻¹	x10 ²	1.81	1.70	2.50	2.43
R _{0.9} , min ⁻¹	x10 ²	1.46	1.38	1.62	1.59
R _i , min ⁻¹	x10 ²	1.38	1.31	2.62	2.63
R _{fa} , min ⁻¹	x10 ²	0.93	0.89	0.85	0.85

Feed materials: Vitrinite-rich coal (VR), inertinite-rich coal fines (IR), polypropylene (PP), and low-density polyethylene (LDPE). Blend ratio = 1:3 coal-to-plastic.

Table S5-3. Gas chromatography results of the gas fractions produced from co-liquefaction experiments conducted at 450°C.

			Molar/Volume, %									$\Delta P_{r.t.}$ (bar)	Mass, g								
Coal	Plastic	C:P	H ₂	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₄ H ₁₀	CO ₂	CO	H ₂		CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₄ H ₁₀	CO ₂	CO	Total	
Tetralin	VR	PP	1:1	48.7	25.6	13.0	0.7	3.1	3.4	4.6	1.0	3.5	0.078	0.324	0.309	0.016	0.107	0.156	0.160	0.022	1.17
		LDPE	1:1	52.2	25.0	10.2	0.9	1.9	1.8	4.3	3.8	5.0	0.119	0.452	0.345	0.027	0.093	0.121	0.213	0.120	1.49
	IR	PP	1:1	52.1	22.4	13.1	0.8	3.5	3.9	2.3	1.8	3.2	0.076	0.260	0.286	0.015	0.111	0.164	0.074	0.037	1.02
		LDPE	1:1	62.3	20.3	9.1	0.9	2.1	1.8	3.5	0.0	4.7	0.133	0.346	0.290	0.027	0.098	0.112	0.165	0.000	1.17
Benzene	VR	PP	1:1	5.6	47.7	26.3	0.9	3.7	4.4	8.0	3.4	2.3	0.006	0.397	0.410	0.014	0.086	0.133	0.183	0.049	1.28
		LDPE	1:1	7.8	46.6	27.6	1.7	4.0	4.5	7.7	0.0	2.5	0.009	0.422	0.469	0.027	0.101	0.147	0.190	0.000	1.37
	IR	PP	1:1	6.2	44.7	25.7	1.8	5.8	3.9	8.8	3.2	1.9	0.005	0.307	0.332	0.022	0.109	0.098	0.167	0.038	1.08
		LDPE	1:1	7.8	41.0	28.6	3.1	5.6	4.7	9.1	0.0	1.8	0.006	0.267	0.350	0.035	0.101	0.111	0.164	0.000	1.03
Benzene	VR	PP	1:3	7.2	44.1	18.9	1.1	2.9	3.3	16.6	6.0	2.0	0.007	0.320	0.256	0.014	0.058	0.086	0.329	0.076	1.15
		LDPE	1:3	4.7	43.4	20.8	1.5	2.5	3.1	19.0	4.9	1.4	0.003	0.220	0.197	0.014	0.035	0.056	0.265	0.044	0.83
	IR	PP	1:3	7.5	43.5	20.6	1.2	4.0	3.6	12.1	7.3	1.2	0.004	0.189	0.168	0.009	0.048	0.057	0.145	0.055	0.68
		LDPE	1:3	8.5	33.7	20.2	2.5	4.3	3.4	22.6	4.8	0.7	0.003	0.085	0.096	0.011	0.030	0.031	0.157	0.021	0.44

Feed materials – VR, VRD, IR, IRD; Liquefaction temperatures – 400, 425, 450°C. $\Delta P_{r.t.}$ = Partial pressure of gases at 25°C.

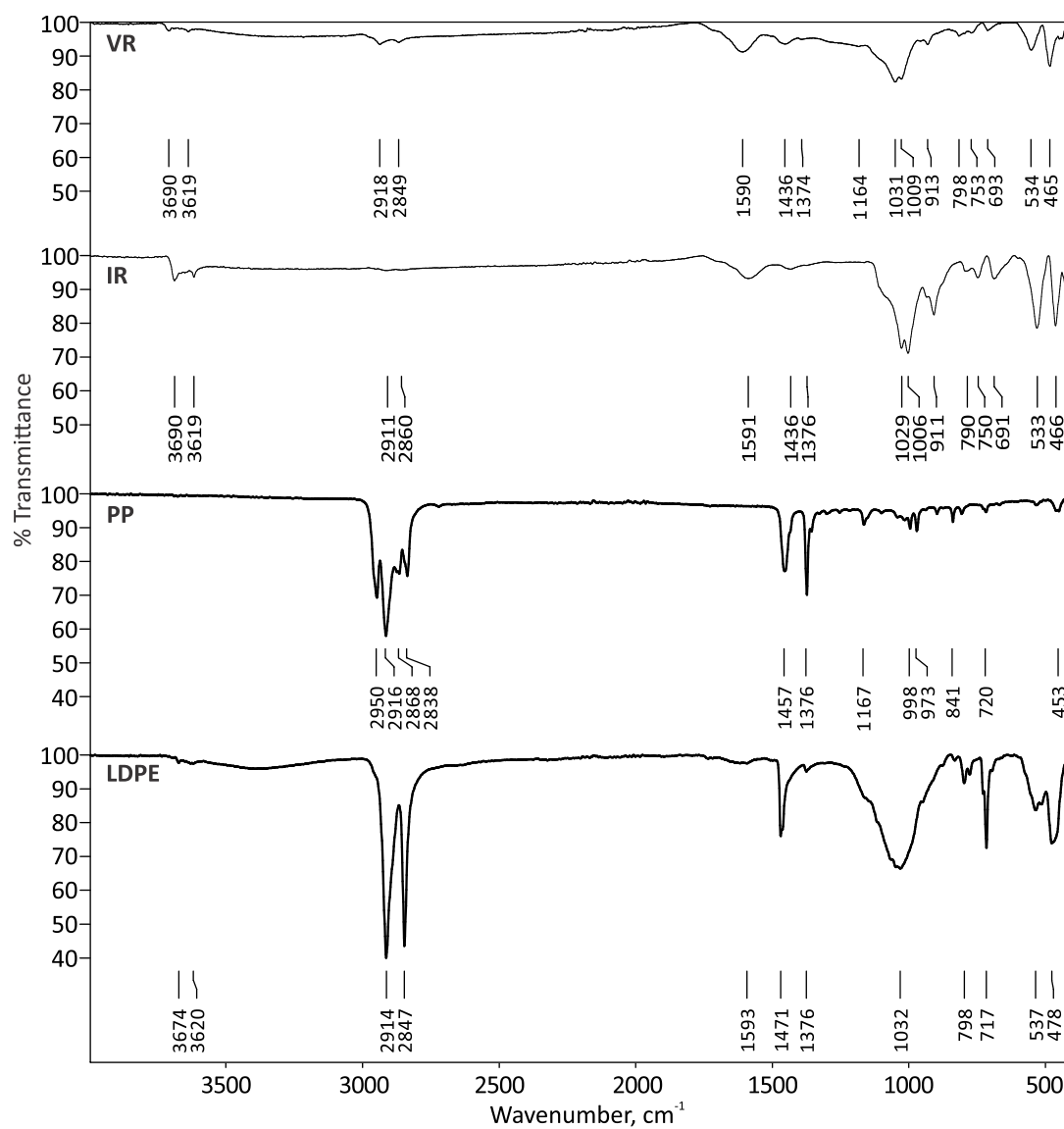


Figure S5-1. FTIR spectra of vitrinite- and inertinite-rich coal, polypropylene and low-density polyethylene.

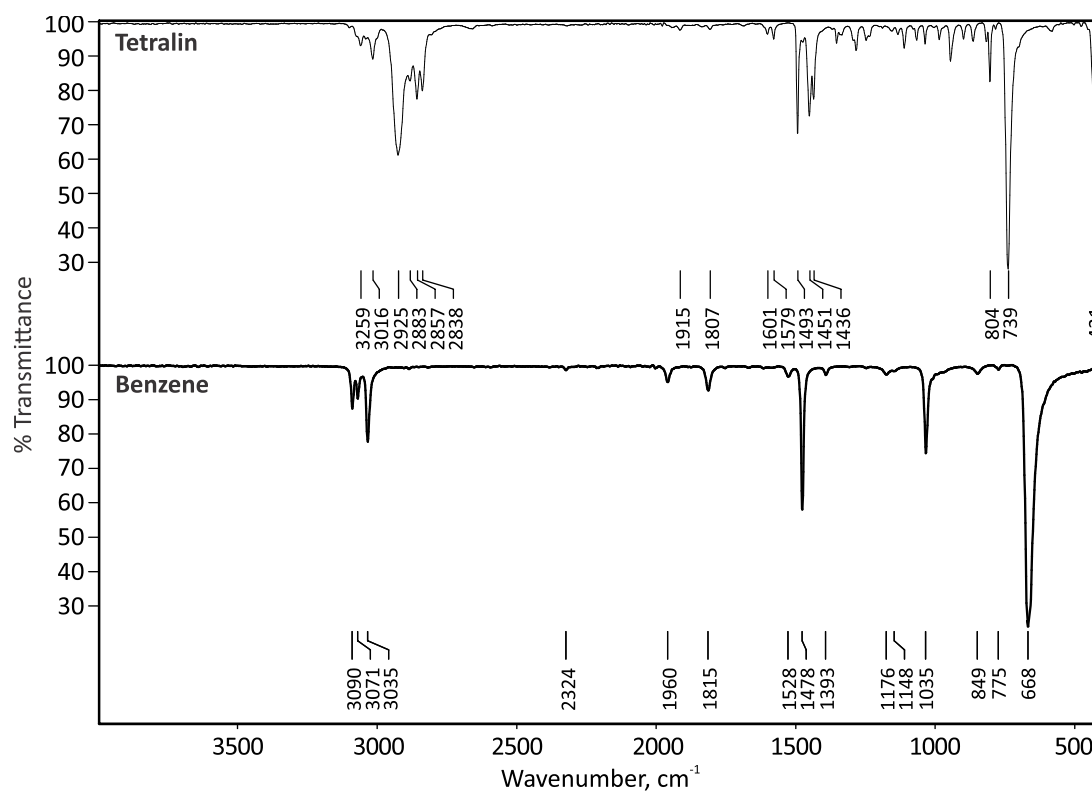


Figure S5-2. FTIR spectra of tetralin and benzene.

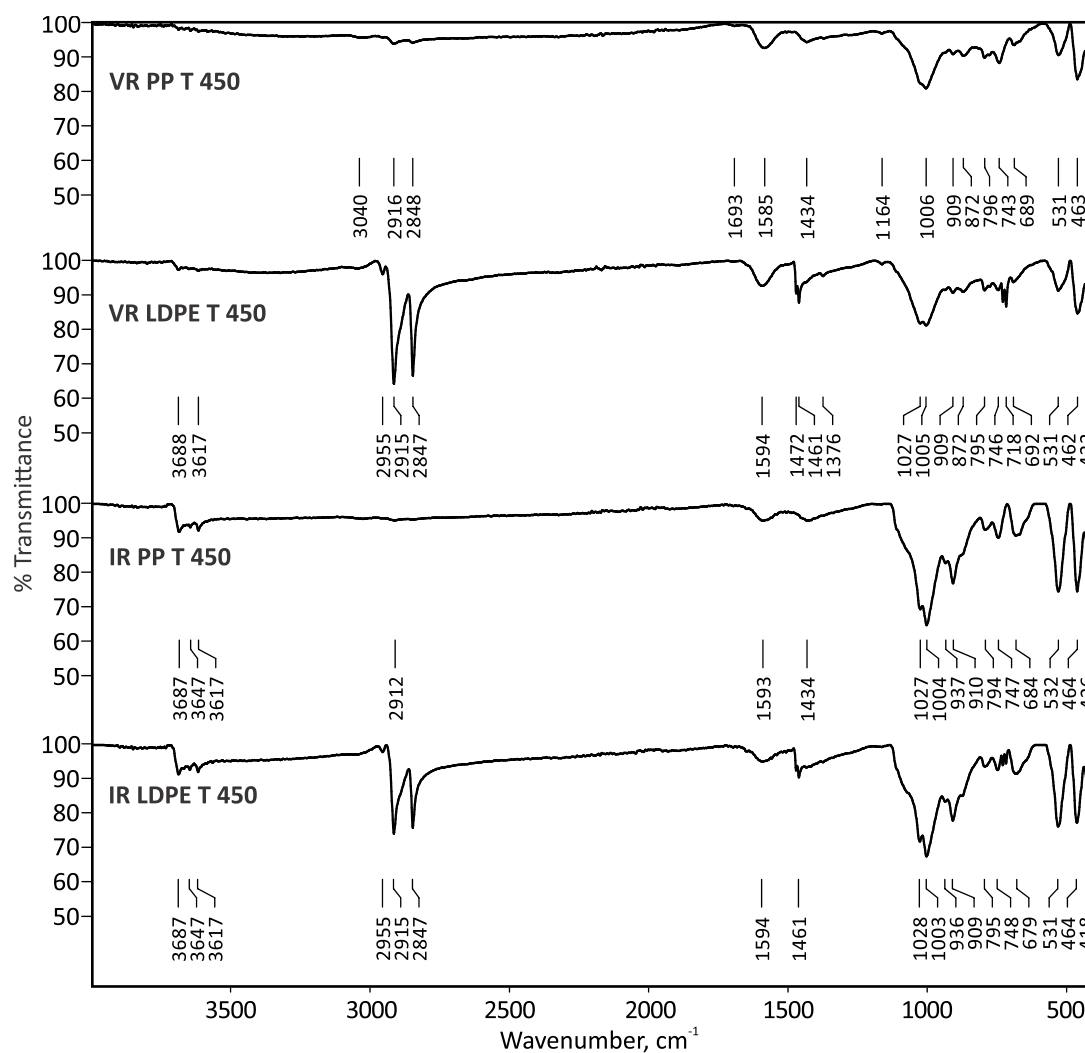


Figure S5-3. FTIR spectra of the solid residue fraction produced from the co-liquefaction of coal and plastic (1:1 coal-to-plastic ratio) in tetralin at 450°C.

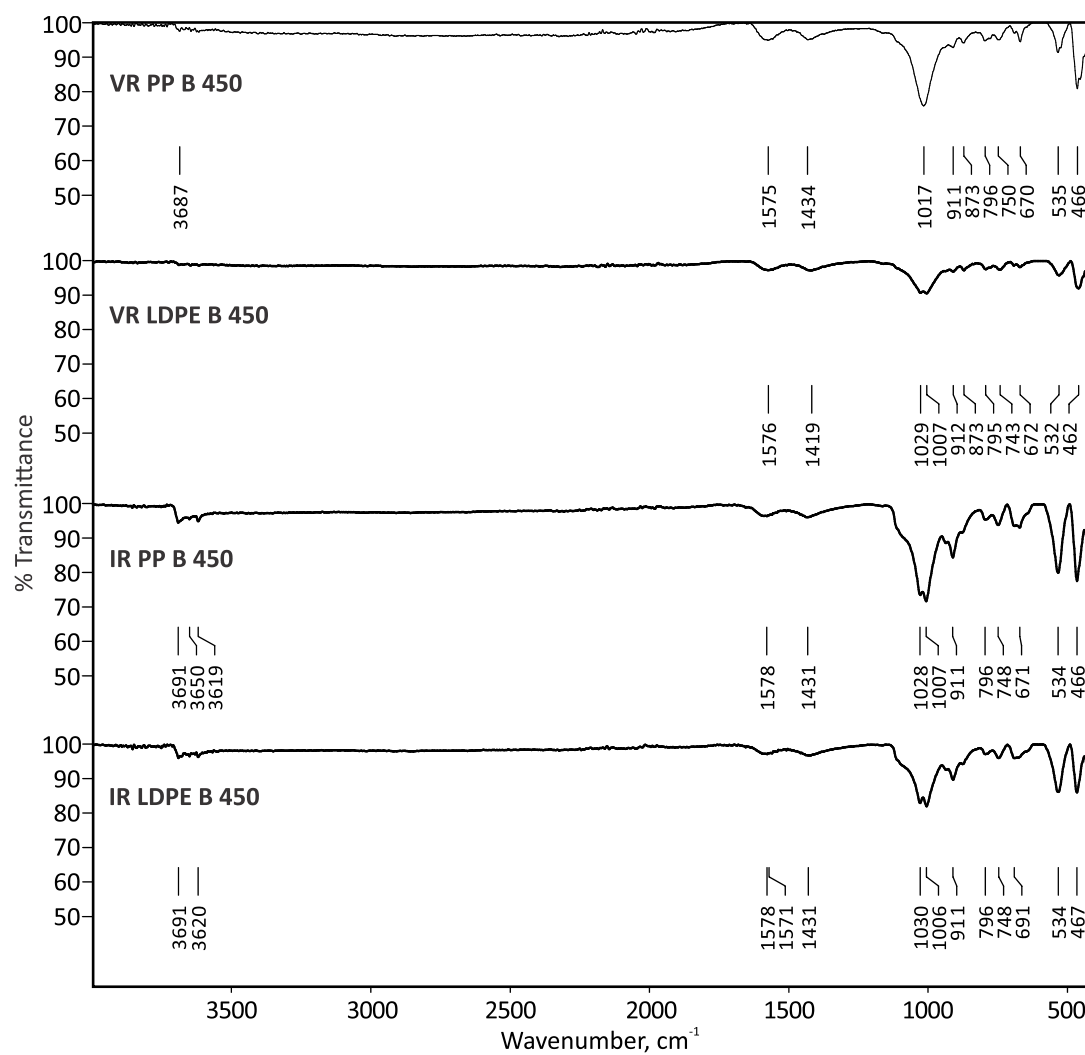


Figure S5-4. FTIR spectra of the solid residue fraction produced from the co-liquefaction of coal and plastic (1:1 coal-to-plastic ratio) in benzene at 450°C.

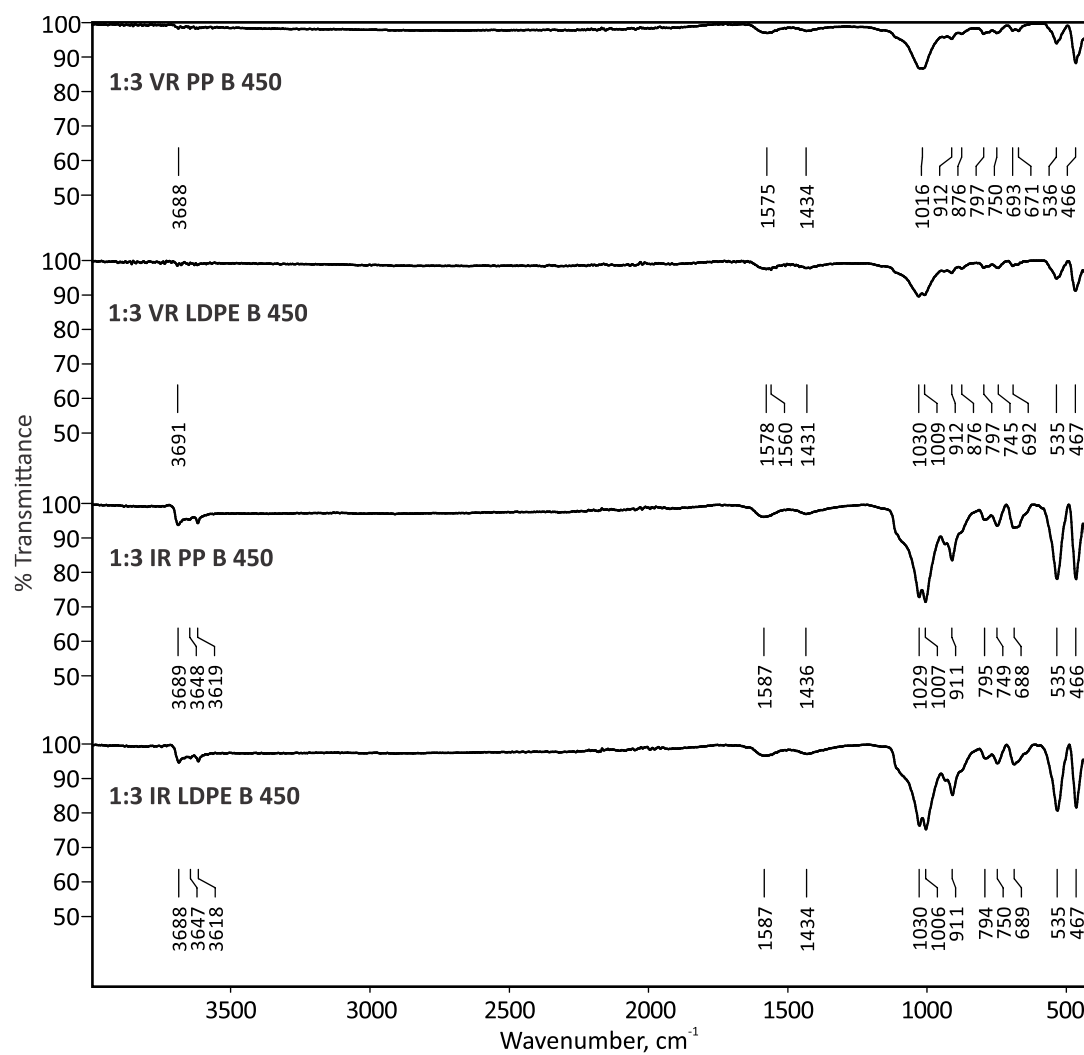


Figure S5-5. FTIR spectra of the solid residue fraction produced from the co-liquefaction of coal and plastic (1:3 coal-to-plastic ratio) in tetralin at 450°C.

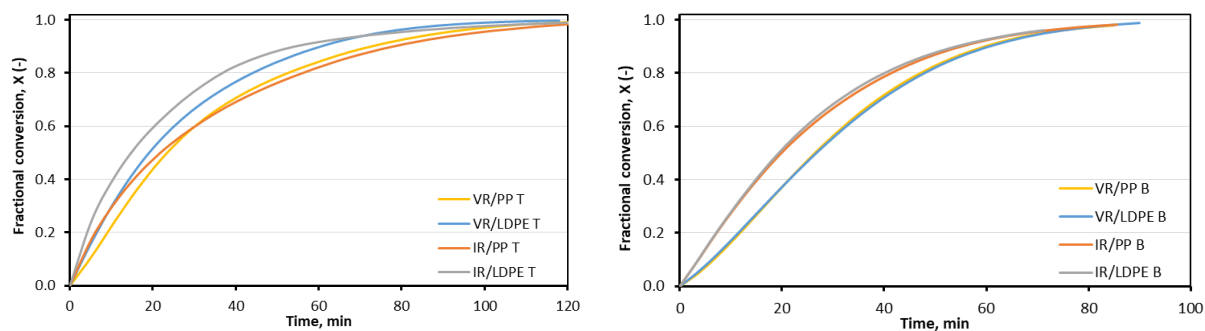


Figure S5-6. Fractional conversion in CO_2 of the chars from co-liquefaction derived solid residues using: A) Tetralin and B) Benzene.

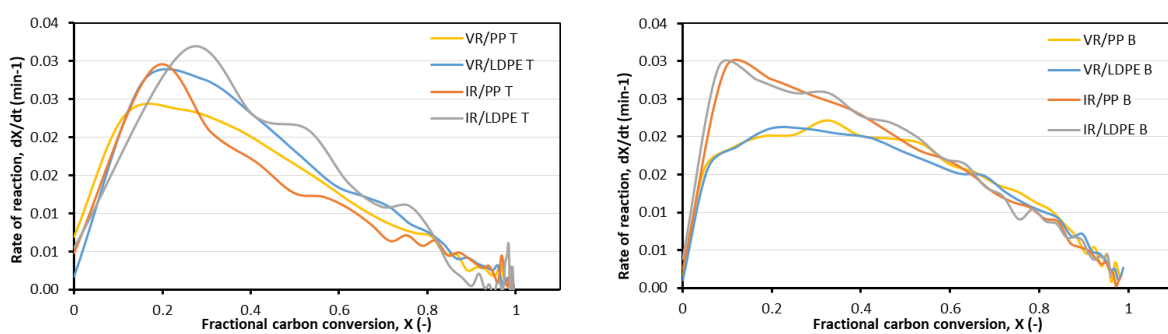


Figure S5-7. Rate of reaction in CO_2 of the chars from co-liquefaction derived solid residues using: A) Tetralin and B) Benzene.

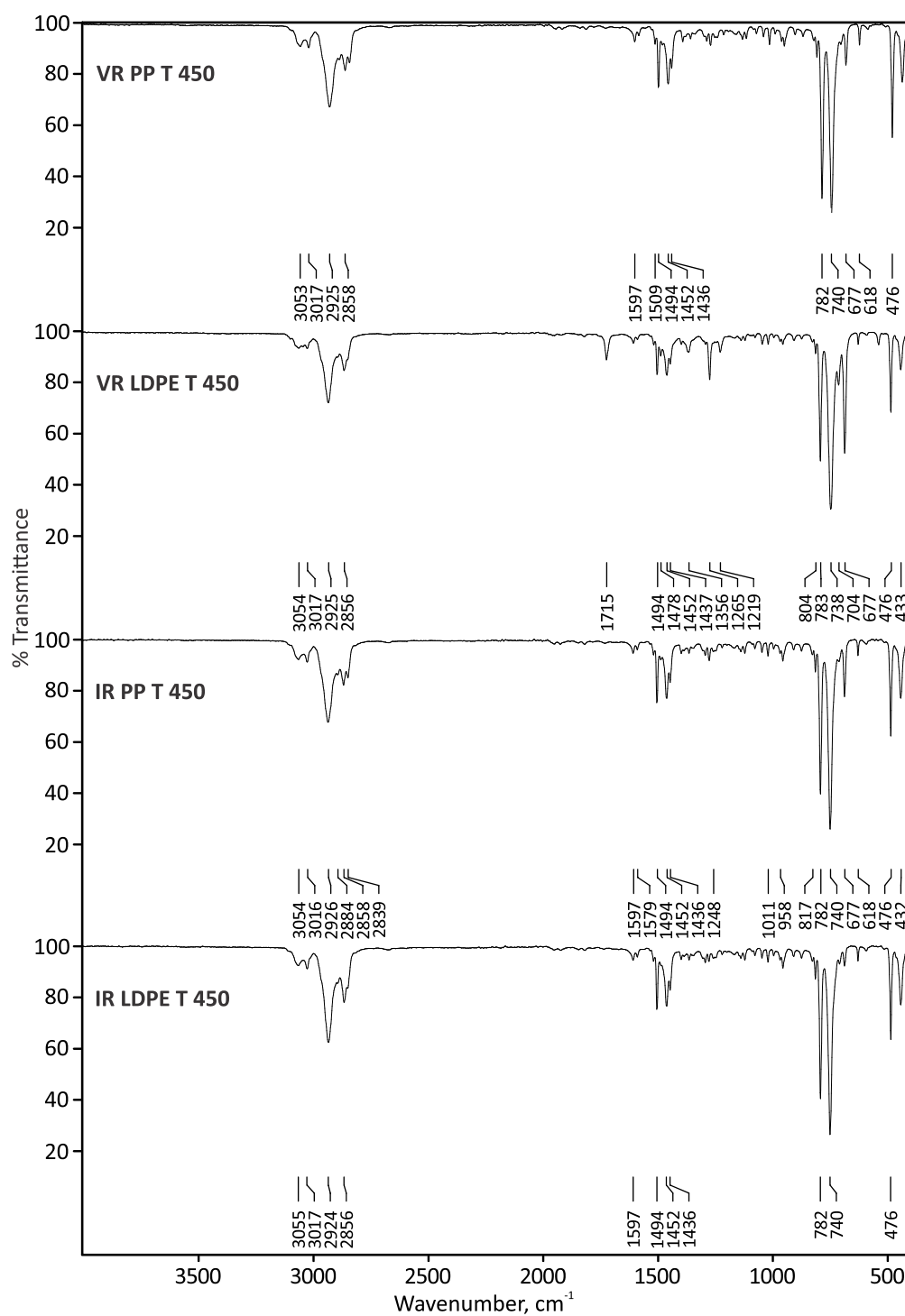


Figure S5-8. FTIR spectra of the liquid fraction produced from the co-liquefaction of coal and plastic (1:1 coal-to-plastic ratio) in tetralin at 450°C.

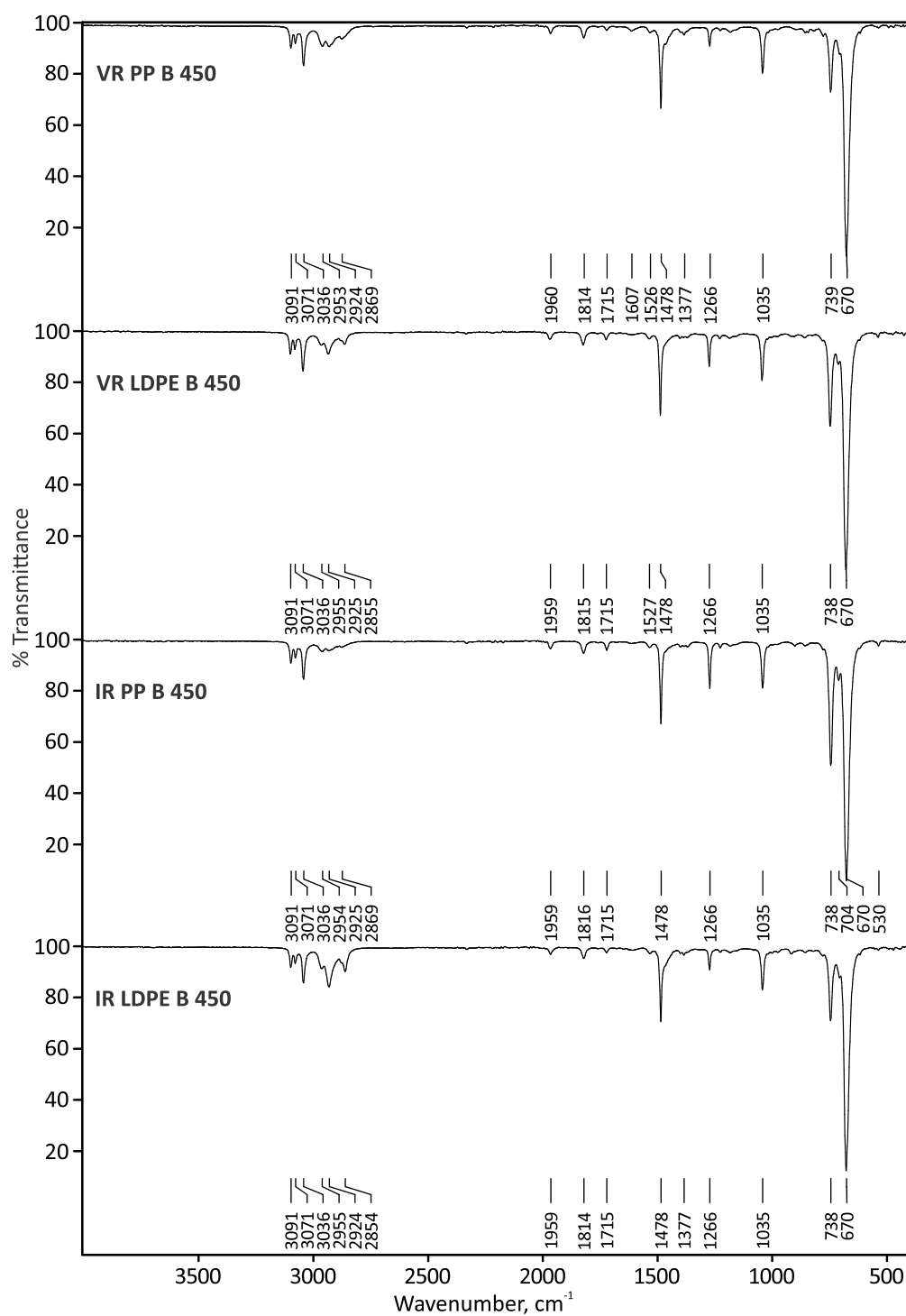


Figure S5-9. FTIR spectra of the liquid fraction produced from the co-liquefaction of coal and plastic (1:1 coal-to-plastic ratio) in benzene at 450°C.

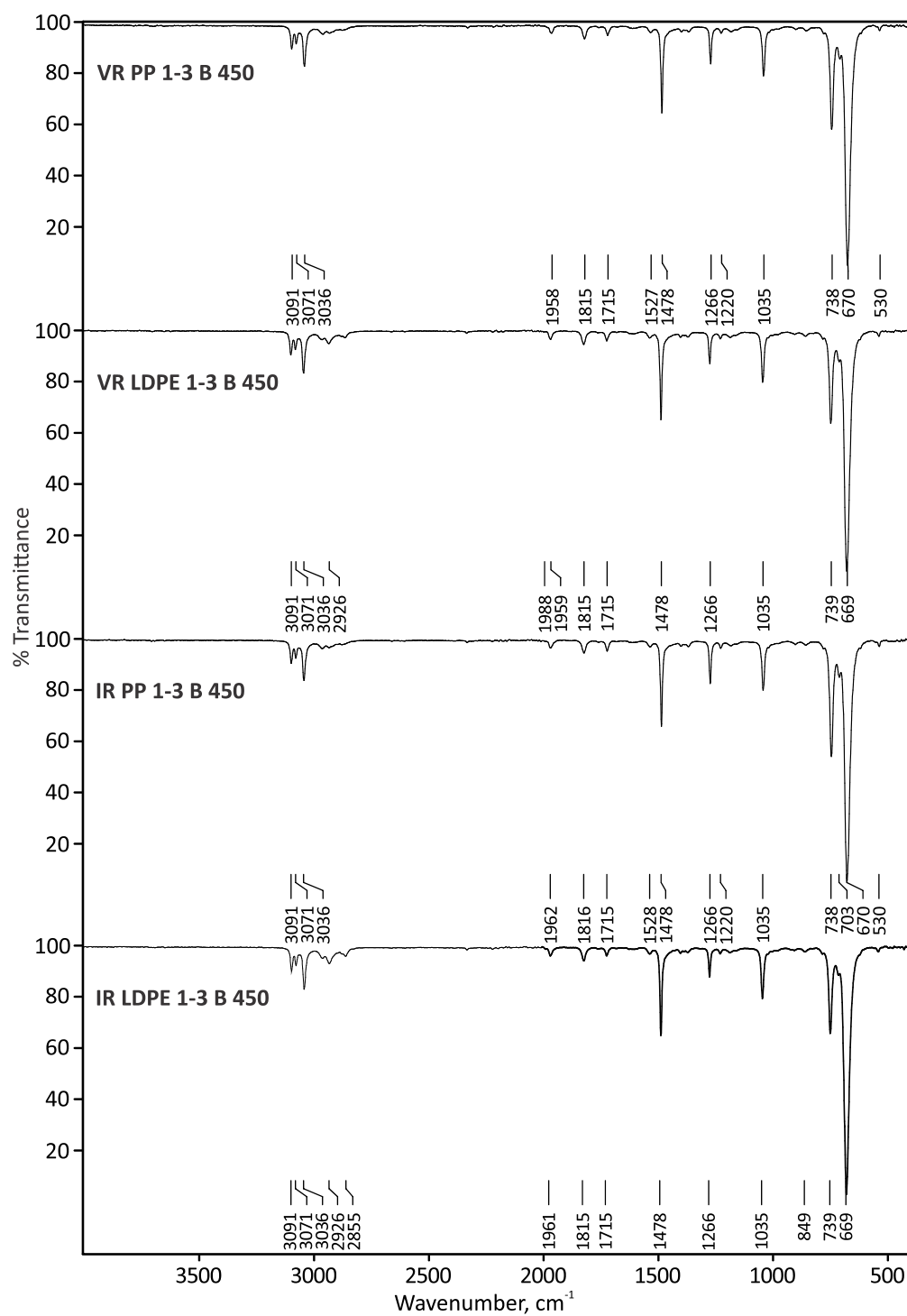


Figure S5-10. FTIR spectra of the liquid fraction produced from the co-liquefaction of coal and plastic (1:3 coal-to-plastic ratio) in benzene at 450°C.

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CHAPTER 6 CONCLUSIONS AND RECOMMENDATIONS

The aim of this study was to investigate the yields and composition of products derived during liquefaction and co-liquefaction experiments of inertinite-rich coal fines and vitrinite-rich coal (typically used in direct coal liquefaction processes in South Africa) with polypropylene and polyethylene at temperatures selected from the initial direct liquefaction experiments. Additionally, the observation that plastic and benzene acted as a hydrogen source to facilitate hydrogen transfer during co-liquefaction was evaluated. In alignment with the objectives as expressed in **Section 1.2**, the following conclusions have been established:

6.1. Phases of this study and conclusions based on the outlined objectives

6.1.1. Phase 1: Direct coal liquefaction

Determine the conversion, product yield, and composition of the products derived from direct coal liquefaction of vitrinite-rich coal compared to inertinite-rich coal fines at different reaction temperatures.

During tetralin liquefaction at 450°C, carbon conversion values of 81.0, 77.0, 50.9, and 61.7% were obtained from the VR, VRD, IR, and IRD coals, respectively. The difference between these conversion values can predominantly be ascribed to the different maceral compositions of the two coals. The fractions of reactive macerals, namely vitrinite and exinite, are significantly higher in the VR coal (72.2 and 5.3%) compared to the IR coal (37.0 and 0.7%). The exinite contents for the VR and IR coal were 3.9 and 0.7%, while reactive semifusinite contents were 5.3 and 24.9%, respectively. The results from experiments conducted at 400 and 425°C reported low conversion values (5–10%) and were excluded from further analysis and co-liquefaction experiments. On the other hand, liquefaction experiments performed at 450°C using benzene, a H-poor aromatic solvent, exhibited inefficacy during direct liquefaction experiments, resulting in lower conversion values (<22%) in contrast to the 450°C tetralin liquefaction experiments (50.9–81.0% conversion).

Evaluate hydrogen transfer and donation reaction during conversion using tetralin and benzene as solvents.

The findings from the conversion values obtained underscore the necessity of a hydrogen-donating solvent in coal liquefaction, which is independent of the coal's molecular composition. The resulting fragments and radicals from thermal decompositions reaction undergo hydrogenation through active hydrogen interactions, leading to the creation of oil or hydrocarbon gases. This process is contingent with the availability of sufficient active hydrogen or hydrogen radicals, typically sourced from a hydrogen donor solvent such as tetralin.

Assess the catalytic and inhibitory effects of inorganic species during the liquefaction process by employing a demineralization treatment on the coals.

While the alkali indices for the IR coal are high and catalytic effects may be anticipated, the results show that the high ash yield in the IR coal inhibits liquefaction conversion reactions when compared to its demineralized counterpart, IRD. However, the VR coal resulted in higher conversion values than its demineralized counterpart, VRD, indicating that catalytic effects may be caused by its

inorganic constituents. Certain minerals are known for their definite catalytic effects during gasification, while others are noted for their catalytic effects in liquefaction.

Evaluate the potential of liquefaction residue chars for gasification purposes by conducting CO₂ gasification experiments and applying kinetic models to calculate apparent gasification activation energies.

VR SR, VRD SR, and IRD SR (excluding IR SR) chars exhibit higher gasification reactivities at 50% conversion compared to their parent coal derived chars, i.e. VR, VRD, and IRD. This indicates that the liquefaction process produces char residues with enhanced gasification reactivities. The presence of inorganic minerals appeared to have a catalytic effect on the initial carbon conversion reactions, and the removal of these inorganic minerals through demineralization inhibited gasification reactions. Furthermore, the catalytic effect of inorganic minerals in the IR coal appeared to outweigh the inherently lower reactivity of inertinite-rich macerals, leading to higher initial reactivities in the IR coal. The data indicates that, despite the inherently higher reactivity of vitrinite-rich macerals present in VR coal, the higher ash yield and the catalytic effect of inorganic minerals in the IR coal resulted in a more pronounced increase in initial reactivity in the IR coal char. This suggests that the catalytic effect of inorganic minerals can be particularly influential in enhancing the initial stages of carbon conversion reactions during gasification.

6.1.2. Phase 2: Liquefaction of polypropylene and polyethylene

Determine the conversion, product yields, and composition of the products derived from the liquefaction of polypropylene and polyethylene using tetralin and benzene as the solvent at different reaction temperatures.

The results from the experiments conducted at 400°C have shown low carbon conversion values (1.0–28.5%), except for benzene liquefaction conducted on PP that exhibited good conversion at 400°C (87.9%). Tetralin liquefaction conducted at 450°C yielded carbon conversion values of 97.0 and 23.8% for PP and LDPE, respectively. The overall conversion of the PP is higher than that of the LDPE. Liquefaction experiments conducted on PP and LDPE using benzene showed promising results at all reaction temperatures (excluding LDPE at 400°C).

During experiments conducted using tetralin, a large fraction of untreated tetralin with a smaller fraction of naphthalene can be seen in the liquid yield. It may be assumed that only a small amount of hydrogen is needed for the hydrogenation reaction during plastic liquefaction compared to coal liquefaction. Hydrogen, predominantly derived from tetralin, not taken up during liquefaction is present in the gas fraction. This is supported by high H₂ contents in the gas fractions derived from tetralin liquefaction experiments. The liquefaction of LDPE using tetralin showed low conversion values at 450°C (28.5%) and can explain the small and lower fraction of alkanes in the oil yield. During PP liquefaction (using both tetralin and benzene), it was also evident that PP mainly reacted with benzene to form alkylated or substituted aromatics. The results from LDPE liquefaction using benzene showed promising results. This was supported by higher conversion values (97.5%) of the feed accompanied by a large fraction of the oils consisting of C₁₀–C₂₉ alkanes and C₁₀–C₁₉ alkenes that accounts for around 49.6 and 19.0% of the liquid product composition, respectively. It was noted that a significant fraction of biphenyl formed during benzene liquefaction with PP and LDPE, accounting for around 45.9 and 15.7% of the liquid fraction, respectively. The presence of biphenyl supported the occurrence of dehydrogenation reactions of benzene to produce hydrogen.

Evaluate the liquid products from fragmentation and chain scission reactions, and subsequent hydrogenation during liquefaction experiments.

PP and LDPE readily converted to produce liquids consisting of aliphatic components. Fragmentation of polymer chains led to the formation of saturated and unsaturated (to a lesser extent) aliphatic structures consisting of C₁₀–C₂₉ alkanes and C₁₀–C₁₉ alkenes. The hydrogen produced from the dehydrogenation of benzene was used to saturate alkenes or protonate radical chains that formed through chain scission or fragmentation reactions. The conclusion from these results highlight that benzene, known to be a H-poor aromatic solvent, may be considered as a H-donor solvent under the experimental conditions and with the material used in this study.

6.1.3. Phase 3: Co-liquefaction of plastic materials with coals

Determine the conversion, product yields, and composition of the products derived from the co-liquefaction of vitrinite-rich and inertinite-rich discard coal with polypropylene and polyethylene using tetralin and benzene.

Tetralin co-liquefaction experiments involving the VR coal showed the highest carbon conversion values of 83.3 and 80.8% for PP and LDPE, respectively. The overall conversion during tetralin liquefaction involving the IR coal was lower than that of the VR coal. The results obtained from the co-liquefaction of the IR coal with PP and LDPE achieved conversion values of 76.4 and 72.5%, respectively. During tetralin liquefaction experiments involving LDPE, significantly higher conversion of the feed material was found when compared to the calculated predicted conversion values. Co-liquefaction of VR/LDPE resulted in 80.8% conversion with a predicted conversion value of 52.4%. Similarly, IR/LDPE resulted in 72.5% conversion with a predicted conversion value of 37.4%. The results indicate that synergistic effects between the coal and plastic materials are evident, thereby affecting the product yield and overall conversion values.

Assess possible synergistic and catalytic effects during co-liquefaction based on the conversion and composition of the products derived from co-liquefaction using tetralin and benzene as the solvent.

During the co-liquefaction experiments conducted using tetralin, a large fraction of unreacted tetralin with a smaller fraction of naphthalene was observed in the liquid yields. The formation of naphthalene can be associated with the dehydrogenation of tetralin. The availability of hydrogen can promote reactions with radicals or unsaturated compounds. The results showed that the LDPE derived liquids have lower concentrations of naphthalene and tetralin than the liquid yields derived from the co-liquefaction experiments involving PP. It was observed that excess hydrogen was produced, predominantly derived from tetralin that was not taken up during liquefaction and was present in the gas fraction.

When evaluating the liquid yields and conversion values obtained from co-liquefaction experiments using tetralin, VR/LDPE and IR/LDPE had lower values compared to VR/PP and IR/PP. It was noted that the predicted conversion values of VR/LDPE and IR/LDPE are significantly lower than the experimental values, indicating synergistic effects between both the VR and IR coal with LDPE during co-liquefaction experiments. The inorganic components in the coals were assumed to promote catalytic effects during the decomposition of LDPE. The formation of chained alkanes from co-liquefaction experiments with LDPE (i.e. VR/LDPE and IR/LDPE) were also evident in the liquid yields.

During co-liquefaction experiments conducted using benzene, VR/LDPE and IR/LDPE showed promising results. A large fraction of the liquid products consisting of C₁₀–C₂₈ alkanes and C₁₃–C₁₉ alkenes were detected, accounting for around 54.9 and 11.1% of the VR/LDPE liquid yield, and around 57.2 and 5.8% of the IR/LDPE liquid yield, respectively. Experiments conducted on the blends containing PP, i.e. VR/PP and IR/PP, produced high concentrations of substituted aromatics with no detectable aliphatic components, similar to tetralin liquefaction experiments conducted with PP. Similar to the results obtained from the liquefaction of the plastic materials, a significant fraction of biphenyl formed during co-liquefaction experiments using benzene, accounting for around 48.2, 26.6, 62.4, and 31.3% of the liquid fractions derived from VR/PP, VR/LDPE, IR/PP, and IR/LDPE, respectively. The presence of biphenyl supports the occurrence of dehydrogenation reactions of benzene to produce hydrogen available for the hydrogenation radicals on unsaturated components.

Evaluate the potential of liquefaction residue chars for gasification purposes by conducting CO₂ gasification experiments.

From tetralin and benzene liquefaction, the IR/LDPE SR (solid residue) chars exhibited higher reactivities at 50% conversion compared to the IR SR char. This indicates that the co-liquefaction experiments with the addition of LDPE produced SR chars with enhanced gasification reactivities. Co-liquefaction residue chars produced from IR coal generally had higher reactivities than VR derived SR chars. This was most prominent in the initial reactivities. It can be assumed that the catalytic effect of inorganic minerals in the IR coal appears to outweigh the inherently lower reactivity of inertinite-rich macerals, leading to a higher initial reactivity in the IR coal char and solid residues derived from blends containing IR coal. The data also indicates that, despite the inherently higher reactivity of vitrinite-rich macerals in VR coal, the higher ash yield and the catalytic effect of inorganic minerals present in the IR coal resulted in a more pronounced increase in initial reactivity. The results suggest that the catalytic effect of inorganic minerals can be particularly influential in enhancing the initial stages of carbon conversion reactions during gasification processes.

Identify the predominant factors influencing the yield and composition of the products during liquefaction processes.

The results indicated that the conversion and product yield and composition was influenced by the nature of the feed materials, coal-to-plastic blend ratio, and choice of solvent. Molecular structure disparities in the feed materials notably impacted conversion outcomes. GC-MS analysis of the liquid fractions derived from the co-liquefaction experiments of LDPE using benzene as the solvent revealed high yields of alkanes and alkenes, indicative of benzene's hydrogen-donor properties. ¹H NMR analysis of the liquid yields derived from the co-liquefaction using benzene revealed an abundant presence of tetralin and its derivatives, with LDPE derived liquids exhibiting higher aliphatic-to-aromatic proton ratios compared to PP. Remarkably, experiments conducted using benzene demonstrated a high presence of aliphatic protons in the liquid fraction. Alongside the formation of biphenyl, as determined using GC-MS, the results indicate that dehydrogenation of benzene occurred to produce hydrogen. Moreover, polypropylene and low-density polyethylene were found to facilitate hydrogen transfer in the co-liquefaction process, effectively converting inertinite-rich discard coal into liquid products when co-processed. Additionally, solid residue chars derived from inertinite-rich coal blends exhibited higher gasification reactivities compared to those containing vitrinite-rich coal. The results from this study indicate the potential of utilizing inertinite-rich coal fines and plastics such as PP and LDPE in co-liquefaction processes.

6.2. Challenges and Future Outlook

The adoption of CTL technologies faces several challenges, including economic viability, environmental concerns, and the availability of alternative energy sources. Some of the main challenges and considerations for the future of coal liquefaction include environmental impacts, energy efficiency, alternative energy sources, and product quality.

Coal-based CTL processes can result in significant greenhouse gas emissions, including carbon dioxide. As countries prioritize reducing emissions and addressing climate change, the environmental impact of coal liquefaction remains a concern. Carbon capture and storage (CCS) technologies may play a crucial role in mitigating these emissions. Additionally, CTL processes are energy-intensive, especially direct liquefaction. High temperatures and pressures, along with the need for hydrogen, contribute to the energy requirements. Improving energy efficiency and reducing operational costs are essential for the economic viability of these processes. Furthermore, ensuring the quality and consistency of the final liquid products is essential for market acceptance. The choice of catalysts, solvents, and process conditions plays a critical role in achieving high-quality products.

Despite these challenges, coal liquefaction technologies, particularly indirect methods like Fischer–Tropsch synthesis, continue to find applications in regions with abundant coal resources and where the need for liquid fuels and chemicals is high. Innovations in catalyst development, process optimization, carbon capture, and co-processing technologies such as co-liquefaction can contribute to the future sustainability and competitiveness of CTL processes.

Future research in direct co-liquefaction should focus on refining and optimizing the process for enhanced economic and environmental performance. Exploring novel catalysts and solvents, as well as their interactions, which may uncover synergies that further improve liquid yields and overall efficiency. Research efforts should extend to investigating the potential of co-liquefaction for other waste materials beyond plastics and tires, broadening the applicability of this approach. The integration of co-liquefaction into a circular economy framework, where waste materials are continuously recycled and repurposed, holds significant promise. Collaboration between industry, academia, and governmental bodies is essential to drive innovation, address challenges, and facilitate the transition from laboratory-scale studies to large-scale implementation.

In conclusion, direct co-liquefaction represents a promising avenue for converting coal and plastic waste into valuable liquid fuels. The reviewed literature provides a comprehensive understanding of the fundamentals, recent advancements, and challenges associated with co-liquefaction. The economic feasibility, environmental impact, and scalability of co-liquefaction processes should be carefully assessed to ensure the successful integration of this approach into waste management strategies. With continued research and development, co-liquefaction has the potential to contribute significantly to a sustainable and circular approach to waste utilization and energy production.