

Evaluation of the gasification reactivity of Highveld coals for application in the coal to liquids process

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Declaration

I, Aldré Henning, hereby declare that the dissertation entitled: "Evaluation of the gasification reactivity of Highveld coals for application in the coal to liquids process", submitted in fulfilment of the requirements for the degree Master of Engineering in Chemical Engineering, is my own work, except where acknowledged in the text, and has not been submitted to any other tertiary institution in whole or in part.

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Abstract

Coal is a very heterogeneous substance with widely varying properties from one source to another, requiring continuous analysis to determine the properties and reaction behaviour of coals as new sources become mined. There is furthermore a lack of research and understanding of the gasification behaviour of South African coals under elevated pressure conditions, relevant to the industry. This study was endeavoured to analyse and determine the high pressure gasification behaviour of five South African coals, in order to address knowledge shortfalls.

Five coals from three different seams from the Highveld coalfield of South Africa were characterised by routine analysis techniques. The coals were denoted 2C, 2N, 4C, 4N and 5N, the number referring to the seam of origin. Devolatilisation of the coals was performed to prepare chars. These chars were then subjected to CO₂ gasification (30% CO₂, 70% N₂) at a range of temperatures (825 °C to 925 °C) and operating pressures (1 bar, 10 bar and 20 bar). A new fixed-bed high-pressure reactor was developed to conduct the gasification investigation at elevated pressures, ensuring that commercial operations are better emulated in the laboratory-scale experimentation.

The five coals investigated exhibited widely varying characteristic properties. Notable results include the following for coal samples 2C, 2N, 4C, 4N and 5N respectively:

- Ash yield (dry basis) of 15.5%, 19.5%, 24.8%, 26.5%, and 30.5%.
- Calorific value (MJ/kg) of 25.2, 24.1, 22.6, 21.5, and 20.5.
- Total vitrinite (mineral matter free) of 28.9%, 23.5%, 20.8%, 10.5%, and 60.1%.
- Total inertinite (mineral matter free) of 66.3%, 71.6%, 69.9%, 84.4%, and 28.5%.
- Vitrinite mean reflectance of 0.58, 0.55, 0.60, 0.66, and 0.53.
- Char BET surface area (m²/g) of 136, 134, 111, 92, and 106.

Fixed-beds of 500 µm sized char particles were gasified at isothermal conditions. Activation energies observed from the gasification results were within 244 ± 14 kJ/mol for all five chars, exhibiting low variability. The activation energies were also not observed to vary significantly with increasing operating pressure. An increase in operating pressure was observed to significantly increase the char reaction rates. The observed reaction orders with regards to CO₂ partial pressure were determined to be within 0.35 ± 0.02 for all five chars, again exhibiting low variability. The reaction orders were also not observed to vary with increasing partial pressures, remaining seemingly constant over the partial pressure range investigated. The

observations from the high pressure gasification results suggest that further increases in char reaction rate can be expected at operating pressures greater than 20 bar (corresponding to a CO₂ partial pressure of 6 bar).

Char reaction rate, normalised to instantaneous carbon content, is graphically presented as a function of carbon conversion. These visualisations clearly indicate the behaviour of the chars over the entire conversion range. Visual inspection of these results indicates that the char gasification behaviour was significantly different at low pressure, compared to high pressure. As an example, a comparatively slow reacting char (4C) at 1 bar becomes comparatively fast reacting at 20 bar. Different chars also react differently to an increase in operating pressure, for example char 5N conversion rate increased on average by 266% at 20 bar compared to 1 bar, while for char 2C the increase was only 199%. This suggests that gasification results determined at low (near ambient) pressure may be poor predictors of gasification behaviour at higher pressure, as encountered in commercial equipment. It is therefore suggested that laboratory testing of coal gasification behaviour be conducted under conditions, particularly pressure, representative of the commercial operations in question, in order to ensure relevant results. Such empirical testing may provide the only accurate and sensible indication of performance, until predictors of high pressure gasification behaviour are identified and sufficiently studied.

At 1 bar operating pressure the char reactivity was generally in ascending order: 4C < 4N < 2N < 2C < 5N. At 20 bar operating pressure the char reactivity was generally in ascending order: 4N < 2C < 4C < 2N < 5N. The seam 5 char consistently exhibited the fastest char-CO₂ reaction. The reaction rates of the other chars differ relative to one another at low pressure compared to high pressure. Generally, the seam 4 chars exhibited the lowest reaction rates, followed by the seam 2 chars.

Coal petrographic properties were determined to be good predictors of the char-CO₂ reaction rate at low conversion, after normalising reactivity with regards to operating temperature and CO₂ partial pressure. Particularly, the total vitrinite content, detrovitrinite content, and maceral indices were observed to correlate well to the pre-exponential factors of the five chars. Empirical models were proposed which were able to predict the pre-exponential factors to within 33% of experimental values, utilising only a single variable derived from petrographic characteristics.

Keywords: high pressure; fixed bed; carbon dioxide; gasification; Highveld; coal

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List of Symbols and Abbreviations

List of Symbols:

Symbol:	Description:	Unit:
A	Intrinsic pre-exponential factor	$\text{g/m}^2/\text{s}/\text{bar}^n$
A_{calc}	Calculated (predicted) specific pre-exponential factor	$\text{g/g/s}/\text{bar}^n$
A_s	Specific pre-exponential factor	$\text{g/g/s}/\text{bar}^n$
[CO]	Molar carbon monoxide concentration	ppm
C_f	Total carbon mass reacted during experiment	g
$C^{(t)}$	Carbon mass reacted up to specified reaction time (t)	g
E_a	Activation energy, true	J/mol
$E_{a,\text{app}}$	Activation energy, apparent (observed)	J/mol
f	Time required to reach 100% (final) conversion	s
k	Intrinsic reaction rate constant	$\text{g/m}^2/\text{s}/\text{bar}^n$
k_s	Specific reaction rate constant	$\text{g/g/s}/\text{bar}^n$
$k_{1,2}$	Rate constant for mechanistic reaction rate model	$\text{g/s}/\text{bar}$
k_3	Rate constant for mechanistic reaction rate model	g/s
k_4	Rate constant for mechanistic reaction rate model	$\text{g/s}/\text{bar}^2$
$k_{5,6}$	Rate constant for mechanistic reaction rate model	$1/\text{bar}$
$k_{875^\circ\text{C}}$	Specific reaction rate constant, extrapolated to 875 °C	$\text{g/g/s}/\text{bar}^n$
m_{sample}	Total sample mass	g
$m^{(t)}$	Instantaneous carbon mass in reactor at elapsed time (t)	g
MW_C	Molecular weight of carbon	g/mol
n	Reaction order	-
P_{CO}	Partial pressure of CO	bar
P_{CO_2}	Partial pressure of CO ₂	bar
P_j	Partial pressure of component j	bar
Q_{ideal}	Gas volumetric flow rate at standard conditions	dm^3/min
R	Universal gas constant	J/mol/K
r	Intrinsic reaction rate	$\text{g/m}^2/\text{s}$
r_c	Carbon conversion rate	g/s
r_{calc}	Calculated (predicted) specific reaction rate	g/g/s
r_s	Specific reactivity	g/g/s
r_x	Specific reactivity, extrapolated to 10 bar and 875 °C	g/g/s
R^2	Coefficient of determination (linear regression fit)	-

List of Symbols, continued

R_{50}	Reactivity index at 50% conversion	1/hr
$r_{875^{\circ}\text{C}}$	Specific reactivity, extrapolated to 875 °C	g/g/s
$[S_t]$	Total active reaction site concentration	1/g
$[S_v]$	Vacant active reaction site concentration	1/g
S_0	Sample active surface area	m ² /g
T	Temperature	K
t	Elapsed time up to specified point during reaction	s
t_{50}	Time required to reach 50% conversion	hr
V_{ideal}	Molar volume of ideal gas at standard conditions	dm ³ /mol
X	Fractional conversion of carbon in sample	-

List of Abbreviations and Acronyms:

Abbreviation:	Description:
a.d.	air dried
a.f.	ash free
d.a.f.	dry, ash free
d.b.	dry basis
m.m.f.	mineral matter free
ppm	parts per million
wt	weight
Acronym:	Description:
A	Ash yield, weight % determined by proximate analysis
AC	Activated Carbon
AMI	Adapted Maceral Index
BET	Brunauer–Emmett–Teller
CTL	Coal To Liquids
CV	Calorific Value, reported as MJ/kg on the a.d. basis
DR	Dubinín-Radushkevich
DV	Detrovitrinite, volume % as reported
EPC	Electronic Pressure Controller
EPDM	Ethylene Propylene Diene Monomer
FBDB	Fixed Bed Dry Bottom
FC	Fixed Carbon, weight % determined by proximate analysis
HP	High Pressure

List of Abbreviations and Acronyms, continued

HP-FBR	High-Pressure Fixed-Bed Reactor
HP-TGA	High-Pressure Thermogravimetric Analyser
HVF	Heating Value Factor
I	Inertinite, volume % m.m.f.
IEA	International Energy Agency
L	Liptinite, volume % m.m.f.
LOI	Loss On Ignition
LP	Low Pressure
M	Moisture, weight % determined by proximate analysis
MI	Maceral Index
ND	Not Determined
NDIR	Non-Dispersive Infra-Red
NR	Not Reported
NRI	Non-Reactive Inertinite
PDTF	Pressurised Drop Tube Furnace
RF	Reactivity Factor
RI	Reactive Inertodetrinite, volume % m.m.f.
RMI	Reactive Maceral Index
RS	Reactive Semifusinite, volume % m.m.f.
TGA	Thermal Gravimetric Analysis or Thermogravimetric Analyser
TMFC	Thermal Mass Flow Controller
TV	Total Vitrinite, volume % as reported
V	Vitrinite, volume % m.m.f.
VM	Volatile Matter, weight % determined by proximate analysis
VRR	Vitrinite Rank Reflectance, mean maximum % as reported
WCI	World Coal Institute
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence

CHAPTER 1

Introduction

Chapter 1 presents an overview of the investigation. Background information on the use of coal is provided, followed by motivation regarding the relevance of this study. Further, the objectives are presented and the scope of the investigation outlined.

1.1. Background and motivation

The world is still very much dependent on fossil fuels. In 2012 the world relied on fossil fuels for approximately 81% of its primary energy supply, of which 36% was derived from coal (IEA, 2014). Production of fossil fuels have steadily increased over the past few decades, and is likely to remain high, as the world's energy demands continuously increase (IEA, 2014). From these observations it is clear that fossil fuels will continue to play a crucial role in the decades to come (Wall *et al.*, 2002; Mohr *et al.*, 2015). Particularly important for many nations may be the ability to utilise high-ash coals to ensure energy security in the future (Aranda *et al.*, 2016), which may indeed include South Africa (Hancox & Götz, 2014).

It is well known that fossil fuels are heavily relied upon for the generation of electricity, although in recent times the relative reliance on fossil fuels has slightly decreased in this sector, due to increased use of nuclear and renewable energy (IEA, 2014). One of the fastest growing sectors has been the transportation sector, which is exhibiting a considerable increase in the demand for energy. The predominant source of energy for end-use in the transportation sector is fossil fuels (IEA, 2014), usually consumed in the form of automotive fuels, aviation fuels and other petroleum distillates. As an example of this growth: The number of privately owned automobiles in China in 2004 was 1 per 100 inhabitants, and this number is expected to grow to 15 per 100 inhabitants by 2025 (WCI, 2006).

The reliance on fossil fuels for automotive transportation is likely to remain high. Alternative energy sources such as nuclear, wind, solar and hydropower are viable alternatives to fossil fuels for the supply of energy to fixed grids. Automobiles, however, require portable energy sources such as gasoline, batteries, biofuels or fuel cells. Until portable alternative energy sources are sufficiently developed for convenient, practical and economically viable widespread use, the world will continue to rely on fossil fuels to power its vehicles.

To date, the overwhelming majority of transportation fuel has been produced utilising crude oil as feedstock (IEA, 2014). There are however concerns regarding the sustainability of this practice, which range from supply capabilities to political uncertainties. In response to these concerns, an increased reliance on natural gas has been observed in the transportation sector (IEA, 2014). Coal may also have an increasingly crucial role to play in this sector. Coal is a feedstock capable of producing liquid fuels, electricity and hydrogen. Coal therefore has the potential to reduce the current high demand for oil and gas, and to supplement where oil and gas supply may no longer be sufficient in the future.

There are several reasons why coal is a prime candidate as a fossil fuel feedstock supplying these energy requirements, these include (Higman & van der Burgt, 2003; WCI, 2006):

- There is significantly more coal (in terms of oil equivalence) available on earth, compared to the established reserves of crude oil and natural gas.
- Coal prices have historically remained lower and steadier than oil and gas prices.
- Coal is widely available, compared to the more monopolised sources of oil and gas.

This potential of coal, as well as its current large scale usage, warrants continuous research and improvement regarding its application. Coal, despite its vast reserves, is still a finite resource (Thomas, 2013). If the use of coal is to be considered sustainable for the next century, the efficiency of utilisation and mitigation of the environmental impact thereof has to improve.

In this study, emphasis is placed on production of liquid fuels from coal, known as coal liquefaction. In general there are two branches of this process that are commercially relevant, direct liquefaction and indirect liquefaction. In modern times, with the exception of notable projects in China, the direct liquefaction of coal is not extensively practised at large scale (Liu *et al.*, 2010). Indirect liquefaction, however, remains an important and relevant process technology (WCI, 2006).

The quintessential example, for the past 60 years, of converting coal into liquid fuels on a commercial scale has been the synthetic fuels operations in South Africa. The synthetic fuels plants at Secunda currently possess the capability of producing liquid fuels and other valuable chemicals in excess of 160 000 barrels per day (in terms of oil equivalence). This is achieved by indirect liquefaction of coal, utilising proprietary Coal to Liquids (CTL) process technology.

In short, this CTL process entails:

- Producing synthesis gas by gasification of coal, supplemented by natural gas reforming.
- Converting the synthesis gas into a range of hydrocarbons, utilising Fischer-Tropsch synthesis technology.
- Separation and upgrading of the hydrocarbon products, as necessary.

The focus of this study is on the coal gasification step of the CTL process. The primary goal of gasification is to convert the carbon contained within a material, such as coal, into gas (Higman & van der Burgt, 2003). This gas may be combusted to provide energy or processed to yield chemical products, depending on the goal of the gasification operation. In this context,

desired gases produced would be carbon monoxide (CO), hydrogen (H₂) or methane (CH₄). This is achieved by reacting the coal, represented by carbon (C), with gasification reagents such as steam (H₂O) or carbon dioxide (CO₂) at high temperatures. The main reactions which may occur during carbon gasification to achieve this are the following (Bell *et al.*, 2011):



Equation 1.1 is known as the CO₂ gasification reaction, Equation 1.2 is the steam gasification reaction, Equation 1.3 is the methanation reaction, Equation 1.4 is the water gas shift reaction, and Equation 1.5 is the steam methane reforming reaction. Experimental conditions, as described in Section 4.4, will be controlled such that it can be assumed that only the reaction represented by Equation 1.1 will be observed. Equation 1.1 is in fact an irreversible representation of the reverse Boudouard reaction. Since CO will be produced in dilute concentrations at high temperature, followed by rapid cooling and analysis soon thereafter, it is assumed that the forward Boudouard reaction will not be observable.

Coal is a very heterogeneous substance (Higman & van der Burgt, 2003; Yu *et al.*, 2007). The constitution and properties of coal differ significantly when comparing several factors, such as geographic location and age. Coal produced from the same mine may even exhibit widely differing properties, necessitating frequent laboratory testing (Gräbner, 2015). Laboratory testing is required in order to determine the suitability of a coal for a process, and the expected performance thereof. These laboratory tests range from routine tests, such as determining bulk composition and energy content, to more elaborate and time consuming tests. The latter includes determining conversion behaviour and reactivity (kinetics).

Coal gasification is a coal conversion process, thus the conversion behaviour of coal has to be understood in order to predict its gasification performance. Furthermore, the reactivity of a coal may be significant with regards to the productivity of the plant, thus knowledge of these parameters are required when selecting coals for the process.

1.2. Problem statement

The construction and commissioning of commercial operations for the production of fuels or electricity from coal require large amounts of capital. A smaller plant would likely require less capital and could also incur less operating cost. Therefore, maximising efficiency (i.e. maximising production rates within equipment) could decrease capital requirements and operating costs, as a smaller facility would be required to achieve target production. Similarly, an existing operation would be able to increase its production without much modification, through optimisation and de-bottlenecking. This would result in the endeavour of producing valuable products from coal being much more feasible, economical and attractive. Furthermore, if the life of the plant would exceed the life of the mine, alternative coal feedstock sources would have to be identified and acquired to maintain production at the facility.

Research on clean coal conversion technologies, such as gasification, has received eager attention in the past few decades (Wall *et al.*, 2002; Irfan *et al.*, 2011). Laboratory scale studies on the carbon reactivity of coals have been predominantly performed utilising the principle of thermal gravimetric analysis (Megaritis *et al.*, 1998; Irfan *et al.*, 2011; Mani *et al.*, 2011). In this analysis, a sample is placed in a small pan or basket and heated within a thermogravimetric analyser (TGA) while reaction gases pass over the sample. The TGA continuously monitors the sample weight, thus any change in mass can be observed (Leng, 2013). Carbon combustion or gasification is a gas-solid reaction, yielding gaseous products which are carried out of the system. The progression of the reaction may therefore be inferred from the sample mass-loss data obtained from the TGA as a function of time, as described by e.g. Kaitano (2007).

In order to determine accurate and true chemical reaction kinetic parameters, the influence of mass transfer limitation (internal and external diffusion) has to be restricted to a minimum. Furthermore, to avoid complications pertaining to inhibition, it is also desired to maintain a constant bulk reagent concentration and the absence of product build-up (differential operation). The use of TGA for this purpose has however been scrutinised in the past (Gräbner, 2015). Concern has been expressed regarding the flow of reagent gas generally occurring over the sample basket in a TGA, instead of through the sample bed (Messenböck *et al.*, 1999). Due to factors such as this, it has been argued that mass and heat transfer limitations may exist during gasification experimentation in a TGA (Ollero *et al.*, 2002). This may impact the applicability of the results to scaled-up commercial operations (Malekshahian *et al.*, 2014). A further concern expressed is that chemisorption of oxygen (from the

decomposition of CO₂) may influence mass readings, particularly for samples of high active surface area (Feng & Bhatia, 2002).

Furthermore, the commercial gasification operations relevant to this study are carried out in a configuration better resembling a fixed-bed, and at elevated pressures (van Dyk *et al.*, 2006a). Gasification studies of South African coals at elevated pressures are rare, with few notable examples such as Messenböck *et al.* (2000), Kaitano (2007), and Hattingh (2009). In particular, laboratory-scale studies of the gasification of South African coal in fixed-bed configuration at elevated pressures are not apparent in published literature.

In order to generate results relevant to commercial scale operations, it is desired to conduct gasification experimentation at elevated pressure. It is further desired to conduct the investigation under chemical reaction controlled conditions (Regime I), to determine “true” kinetic parameters. True kinetic parameters are required since it is comparable to results obtained utilising different equipment, and adaptable to different operating conditions (Roberts & Harris, 2006). Operation in a fixed-bed configuration, with negligible mass and heat transfer limitations, is also beneficial. There, however, is a lack of availability of specialised high-pressure laboratory-scale equipment, capable of providing these desired functionalities.

A further concern is that it has been noted that the exploited reserves from seams of some of South Africa’s most important and productive coalfields are steadily becoming depleted (Jeffrey, 2005). This, in addition to logistical constraints, necessitates the consideration of alternative coal sources. These alternative coals have to be studied, in order to determine their suitability towards existing processes. There thus exists a motivation to characterise and determine the kinetic parameters of several different South African coals. This will aid in enabling the development of revised coal-feed strategies for increasing production, or maintaining production when preferred coal sources become depleted or logistically unavailable.

1.3. Aim and objectives

Aim:

- Determine the CO₂ gasification reactivity of several South African coals considered for commercial CTL operations, under laboratory conditions which emulate industrial operations.

Objectives:

- Develop a laboratory-scale reactor system capable of providing the desired functionalities, such as high-pressure operation in fixed-bed configuration with negligible mass and heat transfer limitations.
- Determine the coal characteristics of five South African coals relevant to the CTL industry, utilising established laboratory analysis techniques.
- Determine and compare the char-CO₂ reactivities of the five coals, utilising the developed reactor system.

1.4. Scope

The extent to which the objectives will be pursued are outlined as follows:

- Five coals will be investigated which are relevant to the CTL industry, consisting of coals from several seams in the Highveld coalfields, with varying physical and chemical characteristics. One of these coals will serve as a benchmark, similar to coal currently utilised in commercial CTL operations.
- Coal characterisation techniques will be limited to routine analysis techniques, to enable the industry to easily and affordably analyse and screen future coal feed-stocks. The micropore surface area of the coal-chars will also be determined.
- Devolatilised chars will be prepared from coals prior to gasification, to isolate the effects of pyrolysis conditions and to prevent the formation of condensable matter in the reactor system.

- Gasification will be performed isothermally, to determine accurate and complete conversion profiles of each coal-char.
- Only CO₂ as reagent will be investigated, further development to incorporate steam gasification and reagent mixtures may be endeavoured in future study.
- Gasification conditions will be chosen such as to minimise the effect of mass transfer limitations.
- Gasification experiments will be limited to a single CO₂ concentration, due to the large number of variables already studied. CO₂ concentration is considered to be 30% within the relevant commercial operations (Bunt & Waanders, 2008b).
- Gasification experiments will be conducted at 1 bar(a) to serve as a low pressure benchmark, an intermediate pressure of 10 bar(a), and a maximum pressure of 20 bar(a).
- Four temperatures will be investigated per coal-char per pressure investigated, in order to generate Arrhenius plots to determine the activation energy.

CHAPTER 2

Literature Review

Chapter 2 presents a literature review focusing on theory regarding coal and coal gasification, relevant to the scope of this investigation. Methods and results from similar, previous studies will also be discussed in this chapter.

2.1. Coal

2.1.1. An introduction to coal

2.1.1.1. Nature of coal

Coal is material derived from biomass, converted by processes facilitated by temperature and pressure over a significant period of time (Higman & van der Burgt, 2003). The process facilitating the formation of coal is colloquially referred to as coalification (Thomas, 2013). The extent to which coalification of the biomass has occurred determines the rank of the coal, i.e. the greater the extent of coalification, the higher the rank of the resulting material (Higman & van der Burgt, 2003). The biomass which ultimately became coal originated from vegetation debris, deposited by sedimentary mechanisms (Thomas, 2013). The resulting coal material is comprised of varying proportions of minerals, originating from inorganic matter, and macerals, originating from organic matter (Thomas, 2013). Inorganic matter was introduced either by physical transport prior to coal formation, or precipitated from mineral-rich water during the coalification process (Thomas, 2013). The organic matter originates from several different forms of biomass, such as plant branches and leaves (vitrinite), resins and algae (liptinite) or oxidised plant material (inertinite) such as charcoal (Thomas, 2013).

2.1.1.2. Indirect liquefaction

Several processes exist which aim to derive liquid products from coal-derived mixtures of carbon monoxide and hydrogen (synthesis gas), the most significant of which is Fischer-Tropsch synthesis (Liu *et al.*, 2010). This synthesis technique was developed by Franz Fischer and Hans Tropsch in the 1920's in Germany (Liu *et al.*, 2010). In this process, several hydrocarbons, alcohols and other valuable chemicals can be produced from synthesis gas. These valuable chemicals are produced by converting the synthesis gas, utilising a suitable catalyst. Iron and cobalt catalysts are most frequently utilised commercially for conversion of synthesis gas (Liu *et al.*, 2010). Typical applications include the use of an iron catalyst in a fluidised-bed reactor at high temperature, or a cobalt catalyst in a fixed-bed or slurry-phase reactor at lower temperature (Liu *et al.*, 2010). The capability to produce synthesis gas from coal at high pressure on commercial scale was accomplished by Lurgi in the 1930's (Higman & van der Burgt, 2003). This technology also offered the capability to accept high-ash coals (Gräbner, 2015), as prevalent in South Africa. In practise, the indirect liquefaction of high-ash

coal can therefore be accomplished by gasification, e.g. utilising the Lurgi moving-bed process, followed by Fischer-Tropsch synthesis. Further detail regarding coal gasification is provided in Section 2.3.

2.1.2. Coal characterisation techniques

2.1.2.1. Compositional analysis

2.1.2.1.1. Proximate analysis

The proximate analysis is a rudimentary thermal gravimetric analysis method, which resolves a coal sample into an assay of four bulk constituents, reported as weight percentages. These constituents are traditionally referred to as inherent moisture (M), volatile matter (VM), fixed carbon (FC) and ash (A). The method does not, however, provide any insight as to the composition of these constituents, nor the composition of the material they originate from. An analysis standard dictates the conditions under which the analysis must be performed, such as temperature, hold-time, particle size, gaseous atmosphere etc.

Despite the simplistic appearance of this technique and its results, it could be easily misinterpreted due to the nomenclature utilised: Firstly, the results from this analysis do not imply that a sample of coal is literally comprised of these four constituents in the percentages reported. As an example, if the analysis reports volatile matter as 20%, this does not imply that 20% of the coal sample consists of “volatile matter”, but rather that content which originally represented 20% of the weight of the sample was evolved as volatile matter when subjected to the specific conditions investigated.

Secondly, inherent moisture would generally consist of moisture residing in the pores of the coal structure, but would not include surface moisture. Surface moisture (from an “as received” sample) would be removed by first air drying the sample, thus inherent moisture would be determined from a sample which has been air dried, hence the air dried (a.d.) basis. If the air drying procedure was not executed properly, surface moisture may be erroneously incorporated into the reported inherent moisture determination (Higman & van der Burgt, 2003). Inherent moisture would also not include water generated by chemical decomposition of organic material within the sample, nor water generated from dehydration of minerals within the sample (Speight, 2005). Since a distinction between these different forms of moisture may not be clear, it is usually convenient to report the values of the analysis on the dry basis (d.b.). This entails a normalisation process which removes the inherent moisture from the results, and

by extension, any other forms of moisture which may have been erroneously included in the inherent moisture reported. The determination of the inherent moisture value may also be influenced by factors such as escape of adsorbed gas from the sample (overestimation), or oxidation of the sample if the analysis is performed in air instead of an inert atmosphere (underestimation), this may be particularly true for low rank coals (Speight, 2005).

Thirdly, the ash weight reported does not imply that the sample contains any amount of ash. The ash is merely a residue which remains after combustion of the sample. Ash would predominantly originate from inorganic material, such as mineral matter, within the sample. Furthermore, the ash yield is not necessarily an indication of the weight of the original unaltered material present within the sample (Gräbner, 2015). Since a combustion process has taken place, the weight of the mineral matter is likely altered by oxidation, dehydration of water complexes, and also decomposition and transformation of certain minerals such as carbonates and pyrite, with subsequent volatilisation of certain components such as CO₂ and sulphur (Speight, 2005). The reported ash yield also does not distinguish between inorganic matter originally present *in situ* within the coal structure and extraneous inorganic material contaminating the sample (Van Dyk *et al.*, 2009). Due to the uncertainty regarding ash yield, it is convenient to normalise the results, as was done regarding moisture, to an ash free (a.f.) or dry, ash free (d.a.f.) basis. Since this study is comparative, attempts will not be made to accurately determine the mass of the original unaltered mineral matter *in situ* within the coal.

Finally, the fixed carbon within a sample is merely determined by difference, therefore it is subject to the cumulative uncertainties with regards to the determinations of the other constituents. The result furthermore does not imply that any specific amount of pure carbon was originally present within the coal (Higman & van der Burgt, 2003).

In general, the formula which would be utilised to convert a quantity to the normalised basis is the following, where Z arbitrarily denotes the desired constituent, such as fixed carbon, and Y arbitrarily denotes the constituent to remove, such as inherent moisture:

$$Z_{(Y-free\ basis)} = \frac{Z_{(as\ determined)} \times 100}{100 - Y_{(as\ determined)}} \quad \text{Equation 2.1}$$

2.1.2.1.2. Ultimate analysis

Much like the proximate analysis, the ultimate analysis resolves the coal sample into an assay of constituents, in this case elements such as C, H, N, S and O. There is once again no insight

provided as to the composition of the material which these constituents originate from. Care should be taken when interpreting the results from an ultimate analysis. The reported carbon mass may include carbon contained within minerals such as carbonates. Similarly, the reported hydrogen mass may include hydrogen determined from inherent moisture or water of hydration from minerals (Speight, 2005). In a similar fashion, sulphur may originate from organic material, minerals, or sulphates. The reported oxygen value may also require adjustment for the presence of the various forms of moisture within the sample (Speight, 2005). Depending on the context of the investigation, many of the reported values from the ultimate analysis may thus require adjustment to accurately represent the specific structures within the coal which is being investigated. Since this study is comparative, attempts will not be made to adjust or correct results reported in the ultimate analysis.

2.1.2.1.3. Gross calorific value

The gross calorific value is the amount of energy released, from all constituents of the coal sample, when the sample is combusted with oxygen in a closed and well controlled system. This is analogous to the higher heating value (Speight, 2005). The calorific value is an important consideration when coal is to be utilised as a fuel (Thomas, 2013).

2.1.2.2. Petrographic analysis

A petrographic analysis is a microscopic study of the organic and inorganic constituents of a coal sample (Thomas, 2013). The organic constituents of a bituminous coal can be resolved into different maceral groups, namely vitrinite, liptinite and inertinite, based on a microscopic analysis (Thomas, 2013). The material representing each maceral group has different origins, elemental composition, and behaviour. Each therefore has a different relevance and significance depending on the intended utilisation of the coal (Thomas, 2013).

The usefulness of petrographic properties to predict coal conversion behaviour is illustrated by incorporation in indices such as the maceral index, defined by Su *et al.* (2001), and the reactive maceral index, defined by Helle *et al.* (2003). The properties of vitrinite change in direct relation to the extent of coalification which the material has experienced (Thomas, 2013). A means to quantify the rank of the coal is to observe the proportion of incident light reflected from the vitrinite surface (Thomas, 2013). Vitrinite is therefore a useful indicator of the rank of the coal investigated (Roberts *et al.*, 2015).

2.1.2.3. Mineral analysis

The inorganic matter present in coal may be characterised by determining the elemental constituents it is comprised of, or the mineral phases which it is present as. The technique of X-ray fluorescence (XRF) may be employed to determine the elemental constituents. The sample is combusted to yield ash, and the elemental composition of the ash is subsequently determined by XRF. XRF analysis employs the following principle (Leng, 2013): A sample is irradiated by primary X-rays which excite the elemental constituents. The excited elements subsequently emit secondary X-rays which are detected and analysed. Since the emitted X-rays are characteristic of the elements they originate from, the elements can be identified by comparison to a known standard or calibration. Quantitative results of elemental occurrence can be derived from analysis of the intensities of the detected characteristic X-rays. Since the ash residue of the sample is analysed, the results are not a direct indication of the composition of the actual mineral matter within the unaltered samples, nor the actual weight percentages representing the original mineral phases. Rather, it is an approximation of the relative amounts of inorganic elements which were originally present in the coal samples as different compounds, before combustion.

To determine the presence of the unaltered mineral phases within the sample, the technique of X-ray diffraction (XRD) may be employed. XRD analysis employs the following principle (Leng, 2013): A sample is irradiated by primary X-ray beams which experience diffraction as it passes through the crystal structure of the mineral phases. The diffracted X-rays which have passed through the sample are detected, as a function of the angle which the beams have been diffracted by. This generates a diffraction pattern, which by comparison with known patterns or standards identifies the crystal structures of the minerals within the sample. Quantitative results of mineral phase presence can be derived from the detected intensities of diffracted X-rays associated with the different crystal structures (Loubser & Verryyn, 2008).

2.1.2.4. Structural analysis

Coal and coal-char are porous structures through which reacting gas and produced gas can diffuse inward and outward. It is thus hypothesised that the internal surface area of the pore structures in coal is an important factor pertaining to the gasification reactivity, since an increased surface area would increase the number of active reacting sites simultaneously available (Liu *et al.*, 2000b).

A method for determining the internal surface area of the porous structures is by the application of gas physisorption. During gas physisorption, a gas is allowed to permeate into the porous

structure of the sample, at which point the gas molecules will adsorb onto the internal surface of the pore. By measuring the amount of gas adsorbed within the sample, as a function of the pressure the system is subjected to, an adsorption isotherm is constructed. In order to determine the surface area of the micropores, it is necessary to determine the volume of only the monolayer of gas which has adsorbed directly onto the pore surfaces (Condon, 2006).

The monolayer volume may be estimated from the adsorption isotherm by several means, frequently utilised is the method of Brunauer, Emmett and Teller (BET), and Dubinin and Radushkevich (DR). These methods consist of different mathematical manipulations of the measured isotherm, to yield an approximately linear transformation over a range of the isotherm considered to represent the pore size region investigated. The slope and intercept, extracted from a linear regression performed over this transformation, may be utilised to estimate the monolayer volume (Condon, 2006). The number of molecules of adsorbing gas which the monolayer volume consists of is calculated, from which the surface area may be determined by multiplying the number of molecules by the effective area each molecule occupies. Since the mathematical equations of BET and DR differ, the two methods are likely to yield dissimilar numeric results for the pore surface area determined.

2.2. Commercial gasification

2.2.1. Types of commercial gasifiers

A brief summary of characteristics of the main types of commercial gasifiers will be provided here, detailed descriptions or an exhaustive list of all gasifier designs are beyond the scope of this text. The main types of established gasifier technologies can be grouped into three modes of material behaviour, namely moving-bed, fluidised-bed and entrained-flow (Bell *et al.*, 2011). The characteristics of these three categories can be generalised as follows:

Moving-bed gasifiers are utilised to gasify a bed of relatively large coal particles (approximately 50 mm diameter). The coal particles are not transported within the gasifier by any means other than gravity. Significant heat, gas concentration and material property profiles are expected to exist within the gasifier, due to the lack of relative coal movement. Different designs representing this process may discharge ash in a dry form, or as a molten liquid (slag). These processes are moderately susceptible to unstable operation due to factors such as coal rank, coal fines, or coal caking propensity. If the gasifying reagents are introduced such as to flow counter-current with respect to the coal feed, then the gas outlet temperatures may be

expected to be relatively low. Moderate levels of carbon conversion can be expected. This process is expected to require low amounts of oxidising agent, and large amounts of steam (Higman & van der Burgt, 2003; Bell *et al.*, 2011).

Fluidised-bed gasifiers are utilised to gasify a bed of relatively small coal particles (approximately 10 mm diameter). The coal particles are transported within and out of the gasifier by co-current gas flow of relatively high superficial velocity. Depending on the extent of fluidisation, a coal bed may not be present within the gasifier at all. Due to the movement of gas and coal particles within the gasifier, more uniform distributions of heat, gas concentration, and material property profiles are expected. Due to the uniform distribution of material, unconverted carbon may be discharged with the ash. Due to this, lower overall levels of carbon conversion can be expected. Ash is generally discharged in a dry form. These processes are slightly susceptible to unstable operation due to factors such as coal rank, coal fines, or coal caking propensity. The gas outlet temperatures are expected to be moderate. This process is expected to require moderate amounts of oxidising agent, and moderate amounts of steam (Higman & van der Burgt, 2003; Bell *et al.*, 2011).

Entrained-flow gasifiers introduce a feed of coal powder (approximately 0.1 mm diameter) co-currently with gasification reagent into the gasifier. The small coal particles are continuously entrained within the gaseous stream. The coal particles react rapidly during the co-current flow with the reagents at high temperature. Due to the high temperature, high levels of carbon conversion can be expected. It is thus also expected to discharge the ash in a molten (slag) form. These processes are not expected to be susceptible to unstable operation due to factors such as coal rank, coal fines, or coal caking propensity. The gas outlet temperatures are expected to be relatively high. This process is expected to require large amounts of oxidising agent, and low amounts of steam (Higman & van der Burgt, 2003; Bell *et al.*, 2011).

2.2.2. Commercial gasification in South Africa

Coal is gasified on commercial scale in South Africa, with the intent of producing synthesis gas, utilised for the production of chemicals and liquid fuels utilising Fischer-Tropsch process technology. Bituminous coal is gasified in excess of 30 megatons annually, at a rate capable of producing several million standard cubic metres of synthesis gas per hour (van Dyk *et al.*, 2006a). This is stated as being above the design capacity of the gasifiers, thus illustrating the relevance of continuous optimisation (van Dyk *et al.*, 2006a).

These gasification figures are achieved by the use of fixed-bed dry-bottom (FBDB) gasifiers. Fixed-bed and dry-bottom in this context implies that the coal bed is not agitated or fluidised,

and the ash is not slagging, although from a material point of view it would be considered a moving-bed reactor. Gasification agents, such as oxygen and steam, are injected at the bottom of the gasifier, thus rising through the ash and coal bed, resulting in counter-current flow of the agents with respect to the coal feed (Higman & van der Burgt, 2003).

In the FBDB process the coal is gasified at pressures of approximately 30 bar (van Dyk *et al.*, 2008), while the average CO₂ concentration in the vicinity of carbon gasification is expected to be approximately 30% (Bunt & Waanders, 2008b). The temperature at which the gasification takes place is however not easily determined. It has been established that combustion, gasification and devolatilisation occur within different 'zones' within the gasifier (Bunt & Waanders, 2008a). In a simplified view (Higman & van der Burgt, 2003): Injection of oxygen results in combustion of coal in the bottom zone of the gasifier. The resulting heat and CO₂ produced by this combustion flows upwards, concurrently with the injected steam, to gasify coal in the middle zone of the gasifier. Residual heat passes to the top zone of the gasifier, where it devolatilises the raw feed coal. These zones are distinguishable due to the fact that the gasification reactions are endothermic, thus the temperature in the gasification zone is lower than the combustion zone, while the temperature in the pyrolysis zone has reduced further, such that the rates of the gasification reactions gradually become unobservable.

Work was done by Bunt *et al.* (2008) towards estimating the temperature profile within a commercial FBDB gasifier, by comparing optical reflectance properties of samples taken from the gasifier to those of reference samples prepared at known temperatures. These results suggest that prepared samples from the gasifier, as analysed, have experienced temperatures within the gasification zone of between 828 °C and 1031 °C. Since large coal particles are fed to the commercial FBDB gasifier, it is likely that a temperature gradient develops between the surface of the coal particle (corresponding to samples having observed the higher temperature) and the centre of the coal particle (corresponding to samples having observed the lower temperature). By considering the mean reflectance determined by Bunt *et al.* (2008), it is inferred that the average temperature experienced by material throughout a large coal particle within the gasification zone is approximately 850 °C. This would appear as a meaningful average temperature to consider for lab-scale gasification research, intent on emulating commercial gasifier conditions.

In reality, the gasification reactions occurring in a commercial gasifier are likely observed predominantly on the particle surface (and therefore at the higher surface temperature), due to pore diffusion limitations. Since the intent of this particular study is to observe chemical reaction controlled (Regime I) kinetics, it is opted to rather investigate temperatures representative of the average particle temperature, instead of the surface temperature.

2.3. Gasification kinetics

2.3.1. Gasification reaction rate models

Several mechanisms for the reaction between carbon and CO₂ have been proposed, frequently resulting in a form of a Langmuir-Hinshelwood type reaction rate model. An example of such a model is described by Roberts and Harris (2006) as follows:

Consider the following mechanism for the char-CO₂ reaction (Roberts & Harris, 2006):



$$[S_t] = [S_v] + [C(O)] \quad \text{Equation 2.4}$$

If Equation 2.3 is considered the rate-limiting step, then the following rate law can be derived:

$$r = \frac{[S_t]k_1P_{CO_2}}{S_0(1 + \frac{k_2}{k_3}P_{CO} + \frac{k_1}{k_3}P_{CO_2})} \quad \text{Equation 2.5}$$

With incorporation of additional mechanistic steps, as described by e.g. Liu *et al.* (2000a), more elaborate rate laws can be derived, as example:

$$r = \frac{[S_t](k_1P_{CO_2} + k_4P_{CO_2}^2)}{S_0(1 + k_5P_{CO} + k_6P_{CO_2})} \quad \text{Equation 2.6}$$

As illustrated by Equation 2.5 and Equation 2.6, a significant challenge exists regarding the choice of kinetic model, and the subsequent determination of the values of the many kinetic constants incorporated in the model (Irfan *et al.*, 2011). For these reasons a simplified model incorporating an overall reagent partial pressure dependence, such as the n-th order power rate law, is frequently considered (Roberts & Harris, 2006; Hattingh, 2009). Such a model is represented by Equation 2.7:

$$r = kP_j^n$$

Equation 2.7

The use of the simplified n-th order power rate law has been successfully applied by many researchers (Roberts *et al.*, 2010; Aranda *et al.*, 2016), including investigations at CO₂ partial pressures exceeding 1 bar (Kajitani *et al.*, 2002; Everson *et al.*, 2008; Hattingh, 2009).

2.3.2. Factors affecting gasification reaction rate

2.3.2.1. Reaction conditions

It is unanimously agreed that gasification reaction rate exhibits a strong increasing trend with increasing reaction temperature, particularly within the chemical reaction controlled regime (Harris *et al.*, 2006; Everson *et al.*, 2008; Engelbrecht *et al.*, 2010; Hattingh *et al.*, 2011). Most investigators report an increase in reaction rate when increasing the partial pressure of the gaseous reagent, especially at low reagent partial pressures (Everson *et al.*, 2006; Aranda *et al.*, 2016). Observations made from investigations utilising high CO₂ partial pressures will be discussed in Section 2.3.4.

2.3.2.2. Petrographic properties

Koekemoer (2009) observed an inverse relationship between CO₂ gasification reactivity and inertodetrinite content, after gasification of Highveld seam 4 medium rank C bituminous coals at 1000 °C and higher. Hattingh (2009) observed an increasing relationship between the initial CO₂ reactivity of medium rank C and D Highveld coals, and the maceral index defined by Su *et al.* (2001). These observations suggest a relation between maceral composition and gasification reactivity.

An inverse relationship between vitrinite reflectance of inertinite-rich Highveld parent coals and intrinsic reaction rate, determined from CO₂ gasification of chars in a TGA between 900 °C and 950 °C, was noted by Everson *et al.* (2013). This is in agreement with observations that lower rank coals tend to react faster than higher rank coals (Beamish *et al.*, 1998; Engelbrecht *et al.*, 2010).

Messenböck *et al.* (2000) attempted to correlate the maceral composition of coals to their gasification behaviour. Although it was concluded that the maceral composition is, in itself, a poor predictor of gasification extent, results obtained from maceral enriched samples did suggest clear trends with regards to the gasification behaviour of individual macerals as a

function of pressure. In these experiments the extent of gasification, defined as the weight loss observed after a 10 second hold-time in a wire-mesh reactor at 1000 °C in CO₂ (excluding pyrolysis weight loss), of samples consisting of greater than 90% vitrinite, liptinite, and inertinite, respectively, were compared at different pressures. These results suggest that samples high in vitrinite may exhibit a saturation effect with regards to gasification reactivity at pressures above 10 bar, while samples high in inertinite may exhibit continued increases in gasification reactivity at pressures above 20 bar. This effect is illustrated graphically in Figure 2.1.

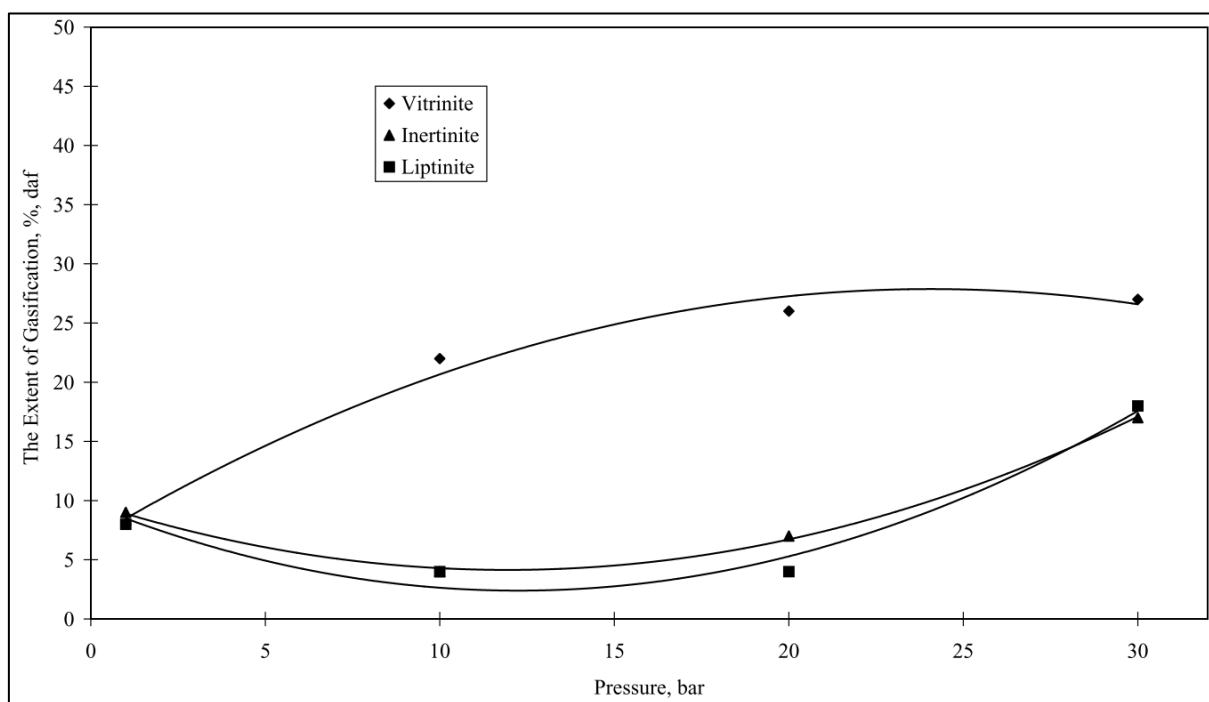


Figure 2.1: Effect of pressure on the extent of gasification of macerals; from Messenböck *et al.* (2000)

With reference to Figure 2.1, consider the behaviour of a coal sample as a superposition of the behaviours of the individual macerals in proportion to their prevalence within the sample. It could then be argued that a high vitrinite coal may experience diminishing increases in reactivity at pressures greater than 10 bar, while a high inertinite coal may experience significant increases in reactivity at pressures greater than 10 bar, and especially 20 bar. This merely suggests a trend, as exact predictions of extent of gasification as a superposition of these results have not been determined to be accurate.

2.3.2.3. Mineral matter within coal

Koekemoer (2009) observed an increasing relationship between the activation energy of CO₂ gasification and sample ash yield, suggesting that mineral matter as a whole does not catalyse the carbon reaction *per se* (Beamish *et al.*, 1998). An inverse relationship was however observed between activation energy and calcium content, as well as magnesium and potassium content, after gasification of Highveld seam 4 coals at 1000 °C and higher.

In a similar fashion, Hattingh (2009) observed an increasing relationship between initial reactivity and the CaO content, as well as the MgO content, after CO₂ gasification of Highveld coals in a high pressure TGA at temperatures between 900 °C and 1000 °C. A nearly exponential relationship was also observed between the initial reactivity and the Al₂O₃/SiO₂ ratio, as well as the alkali index.

Lemaignen *et al.* (2002) studied the effects of inorganic salt impregnation, on demineralised Longannet and La Jagua coals, on CO₂ gasification behaviour. Their results indicate that Fe, Ca, K and Na enhance CO₂ reactivity, as determined in a wire-mesh reactor, but the observations were not consistent between different coals and different operating pressures during gasification. It is further stated that the level of dispersion of catalytic species within the coal is an important factor, as it is cautioned that impregnation may not accurately resemble the distribution of original mineral matter. This suggests that correlations between reactivity and the presence of a specific inorganic specie may be anecdotal. Furthermore, that the total amount of a mineral may not be important, but rather the extent of dispersion of that mineral throughout the sample (Beamish *et al.*, 1998). This is supported by findings that total ash yield does not correlate well with gasification reactivity (Irfan *et al.*, 2011).

2.3.2.4. Structural considerations

It is established that the internal structure of a char significantly influences its gasification reaction rate behaviour (Yu *et al.*, 2007). Hattingh (2009) observed an increasing relationship between the CO₂ reactivity of Highveld coals and the initial micropore surface area, as determined by the DR method. This structural property may, however, not be independently significant, as accessibility of micropores during gasification may be limited by the availability of larger pores (Irfan *et al.*, 2011). Furthermore, total surface area does not necessarily represent the amount of reactive sites within the material, this subject matter is discussed by authors such as Feng and Bhatia (2003) and Zoulalian *et al.* (2015). Reaction rate may also be influenced by pore structural changes occurring during gasification conversion. Investigators have reported reaction rates which initially increase with conversion, reaching a

maximum, and then decrease with further conversion (Liu *et al.*, 2000b; Dai *et al.*, 2016). The initial acceleration in reaction rate is theorised to occur due to increases in pore surface area, facilitated by pore growth, while the subsequent deceleration is theorised to occur due to surface area decreases, facilitated by pore coalescence (Liu *et al.*, 2000b). Investigators have reported maximum pore surface areas at sample conversions of 40% (Kajitani *et al.*, 2002), 80% (Liu *et al.*, 2015), and nearly 100% (Feng & Bhatia, 2003). Indeed, it has been observed that pore surface area increases with increasing sample conversion for inertinite-rich South African coal (Coetzee *et al.*, 2015). Maximum reaction rates have been observed at sample conversion levels in the vicinity of 20% (Liu *et al.*, 2000b; Coetzee, 2011) to 40% (Kajitani *et al.*, 2006) for some coals, while many investigators report the initial reactivity as the maximum (Hattingh, 2009; du Toit, 2013), seemingly not correlating well with the aforementioned surface area trends. It is clear from these observations that significant variability exists regarding char structure, structural changes, and the influence thereof during gasification conversion.

2.3.3. Findings from low pressure gasification research

Results from the CO₂ gasification of coals at ambient pressure will be discussed in this section. Since results are naturally expected to vary considerably between coals of varying properties, as discussed above, this section will focus on specific results obtained from South African coals.

du Toit (2013) investigated the CO₂ gasification of char prepared from an inertinite-rich, medium rank C bituminous coal, originating from seam 4 of the Highveld coalfield, over a wide range of CO₂ molar concentrations, at ambient pressure in a TGA. A partial pressure dependence order of 0.56 ± 0.07 was reported, after investigating the influence of CO₂ concentration in a range between 25% and 100%. Activation energy was reported as 243 ± 32 kJ/mol, after investigating the influence of temperature in a range between 775 °C and 900 °C. From the results a strong increasing reactivity trend is apparent with increasing reaction temperature and CO₂ partial pressure.

Koekemoer (2009) investigated the gasification of inertinite-rich, medium rank C bituminous coals, originating from seam 4 of the Highveld coalfield, in a TGA at ambient pressure, utilising pure CO₂. The activation energy was reported to vary between 163 kJ/mol and 225 kJ/mol, after investigating the influence of temperature in a range between 1000 °C and 1070 °C. The wide variation in activation energy was due to a wide variation in sample density (mineral matter content) between different samples.

Engelbrecht (2008) investigated the gasification of an inertinite-rich, medium rank C bituminous coal, originating from the Highveld coalfield, in a TGA at ambient pressure, utilising pure CO₂. An activation energy was reported as 184 ± 20 kJ/mol, after investigating the influence of temperature in a range between 875 °C and 950 °C. Under similar conditions, an activation energy of 252 ± 16 kJ/mol was reported for a coal originating from the Waterberg coalfield, an activation energy of 222 ± 9 kJ/mol was reported for a coal originating from the Witbank coalfield, and an activation energy of 180 ± 14 kJ/mol was reported for a medium rank D bituminous coal originating from the Sasolburg coalfield.

van Wyk (2015) investigated the gasification of char prepared from a vitrinite-rich, medium rank D bituminous coal, originating from seam 5 of the Highveld coalfield, in a TGA at ambient pressure, utilising 25% CO₂. An activation energy was reported as 197 ± 11 kJ/mol for 212 µm powders, and 216 ± 95 kJ/mol for 6 mm particles, after investigating the influence of temperature in a range between 900 °C and 1050 °C. Under similar conditions, activation energies of 174 ± 14 kJ/mol for 212 µm powders, and 211 ± 27 kJ/mol for 6 mm particles were reported for char prepared from an inertinite-rich medium rank C bituminous coal originating from seam 2 of the Witbank coalfield.

Everson *et al.* (2006) investigated the gasification of two chars prepared from inertinite-rich discards of a typical South African coal, in a TGA at ambient pressure utilising CO₂ concentrations ranging from 20% to 100%. Activation energies for the two chars were reported as varying between 93 kJ/mol and 96 kJ/mol for the forward reaction represented by Equation 2.2, and between 109 kJ/mol and 137 kJ/mol for the reaction represented by Equation 2.3, after investigating the influence of temperature in a range between 800 °C and 950 °C. The CO₂ partial pressure dependence, represented by the term $[S_i]k_1$ in Equation 2.5, was reported as varying between $3.96 \times 10^{-9} \text{ s}^{-1}\text{bar}^{-1}$ and $8.96 \times 10^{-9} \text{ s}^{-1}\text{bar}^{-1}$ for the two chars at 900 °C, while the CO₂ partial pressure dependence, represented by the term k_1/k_3 in Equation 2.5, was reported as varying between 1.62 bar^{-1} and 1.98 bar^{-1} for the two chars at 900 °C.

Everson *et al.* (2013) investigated the CO₂ gasification of chars prepared from four inertinite-rich coals originating from the Highveld coalfield, at ambient pressure in a TGA. Partial pressure dependence order was reported to vary between 0.52 and 0.67 for the four chars, after investigating the influence of CO₂ concentration in a range between 25% and 100%. Activation energy was reported to vary between 227 kJ/mol and 236 kJ/mol for three chars prepared from medium rank C bituminous coals, after investigating the influence of temperature in a range between 900 °C and 950 °C. An activation energy of 163 kJ/mol was reported for a char prepared from a medium rank D bituminous coal. From these results it is apparent that kinetic parameters may vary significantly between coals, considering factors

such as coal rank and char structure, despite similarities in geographic location and composition.

2.3.4. Findings from high pressure gasification research

Observations from the CO₂ gasification of coals at elevated operating pressures will be discussed in this section. Since very few studies have been performed on South African coals at elevated pressure, this section will focus on general trends observed from global coal sources, in addition to South African coals.

Everson *et al.* (2008) observed that reaction orders with regards to CO₂ partial pressure were independent of total pressure, after independently varying CO₂ concentration and total pressure in a high-pressure TGA (HP-TGA). These results were determined utilising coal from the Witbank coalfield, gasified at temperatures between 850 °C and 900 °C. The pressure range investigated was however only between ambient and 2 bar(g). The determined reaction orders ranged from 0.48 to 0.50 at elevated pressure, while activation energies were reported to range from 192 kJ/mol to 247 kJ/mol.

Hattingh (2009) investigated the CO₂ gasification reactivity of three Highveld coal powders in a HP-TGA, at operating pressures ranging from 1 bar(a) to 10 bar(a). These results indicated a significant increase in reactivity when CO₂ concentration was increased at high pressure. However, significant increase in reactivity when increasing total pressure, utilising the same CO₂ concentration, was not apparent, despite the higher CO₂ partial pressure. Activation energy was reported to vary between 171 kJ/mol and 202 kJ/mol, after investigating the influence of temperature between 900 °C and 1000 °C. The dependence order on CO₂ partial pressure was reported to vary between 0.49 and 0.77, after varying the CO₂ concentration between 10% and 30%. A dependence order on total system pressure was reported to vary between 0.12 and 0.22, after incorporating a total pressure term in the reaction rate model.

Liu *et al.* (2015) investigated the CO₂ gasification of Kentucky bituminous coal in a HP-TGA, at temperatures ranging from 950 °C to 1150 °C. Qualitative results indicate significant gains in carbon reactivity with increases in total system pressure at constant CO₂ concentration, e.g. an approximate halving of time required to reach 95% conversion at an operating pressure of 20 bar compared to 10 bar, utilising 25% CO₂. A saturation effect with regards to CO₂ partial pressure and carbon reactivity was not apparent, even at very high partial pressures of CO₂. Increases in reactivity were still apparent when increasing CO₂ partial pressure from 10 bar to 20 bar, when comparing the resulting specific reactivity curves beyond 20% conversion.

Hodge (2008) investigated the reaction rates of three Australian chars at various temperatures and pressures. It was observed that the reaction order with regards to CO₂ partial pressure decreased with increasing pressure, although CO₂ partial pressure was not varied independently of total system pressure during these experiments. Previous, related work did however state that total pressure does not have a statistically significant effect on intrinsic char reactivity, thus it is inferred that reaction order only changed as a result of varying CO₂ partial pressure (Roberts *et al.*, 2000). Reaction orders of the Australian chars ranged from 0.32 to 0.46, measured at 900 °C utilising CO₂ partial pressures ranging between 2.5 bar and 7.5 bar. It was further inferred that activation energies observed at high pressure, determined in a HP-TGA, are comparable to activation energies observed at low pressure, determined in a fixed-bed reactor. This was concluded by comparing observed high pressure reaction rates to observed low pressure reaction rates extrapolated to high pressure, utilising the previously determined high pressure CO₂ reaction orders. This agrees with similar findings, stating that pressure does not appear to influence activation energies determined under chemical reaction controlled conditions (Roberts & Harris, 2000). Regime I activation energies of the Australian chars were reported to range from 242 kJ/mol to 282 kJ/mol, inferred from measurements utilising 5 bar CO₂ partial pressure and a temperature range between 800 °C and 900 °C.

Ahn *et al.* (2001) investigated the CO₂ gasification reactivity of an Indonesian sub-bituminous coal-char at high temperature and pressure in a pressurised drop tube furnace (PDTF). An activation energy of 144 kJ/mol was reported after investigating the influence of temperature between 900 °C and 1000 °C, and 71.5 kJ/mol for a temperature range between 1100 °C and 1400 °C, utilising a CO₂ partial pressure of 2 bar. In this study it was reaffirmed that increasing the CO₂ partial pressure, while keeping total system pressure constant, increases the observed char reactivity. The dependence order on CO₂ partial pressure was reported as 0.40, after varying the CO₂ partial pressure between 1 bar and 5 bar at a constant total pressure of 10 bar, utilising a temperature of 1300 °C. It was however determined that increasing total system pressure, while keeping the reagent partial pressure constant, decreased the observed char reaction rate. A dependence order on total system pressure was reported as -0.65, after varying the system pressure between 5 bar and 15 bar at a constant CO₂ partial pressure of 2 bar, by incorporating a total pressure term in the reaction rate model. Since these results were determined at 1300 °C, and were well approximated by the shrinking unreacted core model, it is reasonable to assume that pore diffusion imposed a significant limiting role in the observed reaction rates.

It is stated that diffusion of reagents into the char pores is reduced at increased total pressures (Ahn *et al.*, 2001). This can be confirmed by considering rigorous calculations of effective

diffusivity, e.g. by Liu *et al.* (2000a), wherein an inverse proportionality between molecular diffusion and total pressure is clearly apparent. It is thus concluded that an observation of a suppressed observed reaction rate, to below what is expected at the specific reagent partial pressure, is an indication of pore diffusion resistance (Regime II) significantly affecting the char-CO₂ reaction rate (Liu & Niksa, 2004). A suppression of the expected reaction rate at high pressure may also be due to an exaggerated influence of product inhibition observed at elevated pressures (Wall *et al.*, 2002). The observations of char gasification dependence on total pressure may be significantly influenced by char pore size distributions (Roberts *et al.*, 2010).

Kajitani *et al.* (2002) investigated the gasification of an Australian and a Chinese bituminous coal-char over a range of temperatures and pressures in a PDTF and TGA. A linear increase in initial gasification rate was observed when increasing reagent partial pressure at constant total system pressure. At a constant CO₂ partial pressure of 2 bar, an increase in total system pressure, from 5 bar to 20 bar, had virtually no effect on the observed initial CO₂ gasification rate. A CO₂ partial pressure dependence order of 0.73 was reported for the Australian char after investigating the influence of CO₂ partial pressure in a range between 0.5 bar and 3 bar in the PDTF at 1300 °C. A CO₂ partial pressure dependence order of 0.54 was however reported after an investigation at lower temperatures in the TGA. A CO₂ partial pressure dependence order of 0.49 was reported for the Chinese char. An activation energy of 283 kJ/mol was reported for the Australian char, after investigating the influence of temperature between 850 °C and 1200 °C, and 163 kJ/mol for a temperature range between 1200 °C and 1400 °C. An activation energy of 261 kJ/mol was reported for the Chinese char, after investigating the influence of temperature between 850 °C and 1200 °C.

2.3.5. Summary of gasification kinetics research

2.3.5.1. Summary of ambient pressure gasification kinetics

There is general consensus that increases in reaction temperature and reagent concentration will yield increases in observed gasification reactivity. Coal rank, char structure, and mineral matter content have been observed to significantly influence the gasification reaction rate. For the CO₂ gasification of inertinite-rich, high-ash, bituminous South African coals, it is expected to observe an average activation energy in the vicinity of 200 ± 50 kJ/mol, and an average overall CO₂ partial pressure dependence order in the vicinity of 0.55 ± 0.1 , within the chemical reaction controlled regime. A summary of ambient pressure CO₂ gasification kinetics of South African coals is provided in Table 2.1.

Table 2.1: Ambient pressure gasification kinetics of South African coals

Author	Coal Source	Coal Rank	Temperature (°C)	CO ₂ Concentration (%)	Activation Energy (kJ/mol)	Reaction Order (n)
du Toit (2013)	Highveld seam 4	medium C	775 - 900	25 - 100	243 ± 32	0.56 ± 0.07
Engelbrecht (2008)	Highveld	medium C	875 - 950	100	184 ± 20	NR
	Waterberg	medium C	875 - 950	100	252 ± 16	NR
	Witbank	medium C	875 - 950	100	222 ± 9	NR
	Sasolburg	medium D	875 - 950	100	180 ± 40	NR
Everson <i>et al.</i> (2006)	NR	NR	800 - 950	20 - 100	93 - 96 (reaction) 109 - 137 (desorption)	NR
Everson <i>et al.</i> (2013)	Highveld	medium C	900 - 950	25 - 100	227 - 236	0.52 - 0.67
	Highveld	medium D	900 - 950	25 - 100	163	0.63
Koekemoer (2009)	Highveld seam 4	medium C	1000 - 1070	100	163 - 225	NR
van Wyk (2015)	Highveld seam 5	medium D	900 - 1050	25	197 ± 11	NR
	Witbank seam 2	medium C	900 - 1050	25	174 ± 14	NR

NR – Not Reported

2.3.5.2. Summary of findings from elevated pressure gasification

There is general consensus that increases in reaction temperature will yield increases in observed gasification reactivity. Increases in reagent partial pressure is reported to increase gasification reaction rate, although there is no universal consensus regarding the specifics of the observation. Some authors report a constant reagent partial pressure dependence, while others report a saturation effect, i.e. a decrease in partial pressure dependence order with increasing reagent partial pressure, especially at high reagent partial pressure, inferred to eventually lead to an independence of gasification reactivity from reagent partial pressure. There appears to be no general consensus regarding the independent effect of total pressure on gasification reactivity. Most authors report a negligible effect of total pressure on the observed reaction rates, other authors' reports vary between slight positive relationships to significant inverse relationships. Observations of total pressure dependence may, however, be attributable to other factors interfering with the chemical reaction, or questionable experimental methodologies. A summary of the observations concluded from elevated pressure CO₂ gasification behaviour of several coals is provided in Table 2.2.

Table 2.2: Observed behaviour from coal gasification at elevated pressures

Author	Coal Source	Apparatus	Temperature (°C)	Total Pressure (bar)	CO ₂ Partial Pressure (bar)	CO ₂ Partial Pressure Dependence	Total Pressure Dependence	Activation Energy (kJ/mol)
Ahn <i>et al.</i> (2001)	Indonesia	PDTF	900 - 1400	5 - 15	1 - 5	Increasing, order: 0.4	Decreasing, order: -0.65	71.5 - 144
Everson <i>et al.</i> (2008)	South Africa (Witbank)	HP-TGA	850 - 900	0.9 - 2.9	0.6 - 2.9	Increasing, order: 0.48 - 0.50	Independent	192 - 247
Hattingh (2009)	South Africa (Highveld)	HP-TGA	900 - 1000	1 - 10	0.1 - 3	Increasing, saturation effect, order: 0.49 - 0.77	Increasing, order: 0.12 - 0.22	171 - 202
Hodge (2008)	Australia	HP-TGA	800 - 900	2.5 - 7.5	2.5 - 7.5	Increasing, saturation effect, order: 0.32 - 0.46	Independent (inferred)	242 - 282
Kajitani <i>et al.</i> (2002)	Australia	PDTF	850 - 1400	2 - 20	0.5 - 3	Increasing, order: 0.54 - 0.73	Independent	163 - 283
Kajitani <i>et al.</i> (2002)	China	PDTF	850 - 1200	2 - 20	0.5 - 3	Increasing, order: 0.49	Independent	261
Liu <i>et al.</i> (2015)	Kentucky	HP-TGA	950 - 1150	1 - 20	0.25 - 20	Increasing, no saturation	NR	NR

NR – Not Reported

CHAPTER 3

Coal Characterisation

Chapter 3 presents a description of the coal samples utilised in the investigation, accompanied by the results of several chemical and physical analyses performed on the samples. Further, characterisation results from closely related previous studies utilising similar coals will be compared to the results from this study, where applicable.

3.1. Sample description

3.1.1. Origin and nomenclature

Five coal samples originating from the Highveld coalfields of South Africa were provided by stakeholders of this study. The five samples originate from different seams in the coalfield, namely seam 2, seam 4 and seam 5. The seam 2 and seam 4 samples were provided as drill-cores, while the seam 5 sample was provided as lump coal from an existing mining operation. Furthermore, the samples originating from seam 2 and seam 4 were further distinguished into two categories each, namely samples specifically indicated as exhibiting greater caking propensity than their counterpart from the same seam, and the default sample. Caking propensity was however not confirmed by analysis in this study, only stated as such by the coal supplier. The nomenclature and origin of the samples are summarised in Table 3.1, accompanied by a brief general description of the samples' comparative compositions.

Table 3.1: Description of coal samples investigated

Sample name	Origin	Composition
2C	Seam 2 (caking)	Intermediate vitrinite, high inertinite, low ash
2N	Seam 2	Intermediate vitrinite, high inertinite, low ash
4C	Seam 4 (caking)	Intermediate vitrinite, high inertinite, high ash
4N	Seam 4	Low vitrinite, high inertinite, high ash
5N	Seam 5	High vitrinite, low inertinite, high ash

3.1.2. Preparation methods

3.1.2.1. Coal preparation

The coal samples were received as either lumps or drill cores, an average of 3 kg was provided per coal. The provided coals were subsequently crushed to a particle size of -8 mm utilising a jaw crusher. The -8 mm bulk of each respective coal was then repeatedly mixed and split utilising a riffle splitter into several sub-samples, each sub-sample thus representing the original bulk. Division into smaller sub-samples, as necessary, was performed utilising a rotary splitter. All sub-samples were then packaged into individual zip-seal bags and flushed with high purity nitrogen gas, then stored in a refrigerator until use.

Sub-samples in this state would be provided to external laboratories for any analysis not performed in-house. For analyses performed in-house, further processing will be described in the respective sections that follow, where applicable. In general, a sub-sample would be utilised in its entirety for any further sample processing necessary, instead of simply sieving out a sub-fraction, to maintain bulk representation.

3.1.2.2. Char preparation

Some of the analyses and procedures to be conducted require that the coal samples be devolatilised prior to being utilised. The coals were charred by splitting sub-samples into 150 g batches. Each batch was heated in a Lenton[®] horizontal tube furnace within an inert atmosphere of high purity nitrogen gas. The furnace was programmed to heat at a rate of 10 °C/min up to 950 °C, thereafter to hold isothermal. This heating process was allowed a total of two hours per batch, after which the furnace was allowed to naturally cool down to room temperature. The isothermal temperature was appropriate since further devolatilisation would be avoided in the gasification experiments, which would be conducted up to a temperature of 925 °C. A flow of high purity nitrogen gas at 1 dm³_n/min was maintained through the sample bed during the entire process. After all batches of a particular coal had been charred, the batches were mixed together to form a uniform bulk, to eliminate variation between batches. The bulk was then split into sub-samples utilising a riffle splitter and rotary splitter, then individually stored in zip-seal bags until use.

3.2. Characterisation analyses

3.2.1. Characterisation procedures

3.2.1.1. Preface

Since the majority of the coal samples were provided as drill cores or blends of several drill cores, the samples utilised may not necessarily be representative of any particular seam as a whole, nor the product produced by any existing mining operation. The sample analysis results will be interpreted comparatively with one another. Comparisons to the characterisation results from other studies will be done with this in mind, since results of equivalent coals are likely not available. It is however endeavoured to study a sample which is comparable to Highveld seam 4 coal currently utilised in commercial gasification operations. The sample most resembling

such coal is sample 4N, and therefore 4N represents a benchmark against which the other samples will be evaluated.

3.2.1.2. Compositional analysis

Sub-samples of both coal and char consisting of -8 mm particles were provided to an external laboratory, Bureau Veritas Testing and Inspections South Africa, to perform a proximate analysis, ultimate analysis and to determine the gross calorific value of each sample. The standards utilised during the proximate analysis are based on ISO 11722:1999 for determining moisture, ISO 1171:2010 for ash and ISO 562:2010 for volatile matter. The remaining constituent, fixed carbon, is calculated by difference. The standards utilised during the ultimate analysis are based on ISO 29541:2010, while total oxygen is determined by subtraction of C, H, N, total sulphur, inherent moisture and ash yield (all a.d. basis) from 100. The determination of total sulphur is based on ISO 19579:2006. The standard utilised to determine the gross calorific value is based on ISO 1928:2009.

3.2.1.3. Petrographic analysis

Sub-samples of -8 mm coal particles were provided to Sasol Technology Research and Development, to be analysed by an accredited petrographer, to determine the maceral composition and vitrinite reflectance. Total reactivities, derived from the maceral composition, is calculated as the sum of total vitrinite, total liptinite, reactive semifusinite and reactive inertodetrinite. Based on the vitrinite reflectance results, the coal ranks can be determined according to the ISO 11760:2005 classification system.

3.2.1.4. Mineral analysis

Sub-samples of -8 mm coal particles were provided to an external laboratory, Sci-Ba Laboratories and Scientific Consultants, to perform X-ray Fluorescence (XRF) analyses. The equipment utilised was a PANalytical® Epsilon™ spectrometer. These results provide the composition of the ash, after combustion of the sample.

Sub-samples of -8 mm coal particles were provided to an external laboratory, XRD Analytical and Consulting, to perform X-ray Diffraction (XRD) analyses. Fe filtered Co-K α radiation was utilised, and mineral phase weight percentages were estimated utilising the Rietveld method. The equipment utilised was a PANalytical® Empyrean™ diffractometer with a PIXcel™ detector, and the results were processed utilising X'Pert Highscore Plus™ software. The procedures utilised were similar to practises as described in e.g. Loubser and Verryn (2008).

3.2.1.5. Structural analysis

The pore surface area of the char was determined by CO₂ adsorption analysis, performed in-house. The char samples were prepared by crushing a sub-sample of -8 mm char to -212 µm. These samples were dried in an oven overnight at 80 °C to remove adsorbed moisture, prior to analysis. A Micromeritics® ASAP 2010™ analyser was utilised to perform the analysis. Char samples of 0.25 g were degassed at 380 °C for 24 hours under vacuum of approximately 5 µmHg. CO₂ adsorption was subsequently performed on the degassed samples at a temperature of 0 °C, as controlled by an ice bath. The procedures utilised were similar to practises as described in e.g. Okolo *et al.* (2015). Software, utilising the short coal method, controlled the analysis and computed the surface area results from the measurements. For each char type the analysis was performed twice. The average surface area of the two runs per char will be reported, as determined by both the BET and DR method.

3.2.2. Characterisation results and discussion

3.2.2.1. Compositional analysis

The results of the proximate analysis, for both the raw coal and char samples, are presented in Table 3.2, on both the air dried basis and the dry basis.

Table 3.2: Proximate analysis results

	Coal					Char				
	2C	2N	4C	4N	5N	2C	2N	4C	4N	5N
Air dried (a.d.) wt %										
Inherent moisture	4.0	4.3	3.7	3.8	5.2	0.9	0.9	0.7	0.6	1.0
Ash yield	14.9	18.7	23.9	25.5	28.9	20.4	26.8	31.0	33.9	39.8
Volatile matter	28.1	23.6	24.5	21.1	27.6	1.4	1.2	1.2	1.2	1.0
Fixed carbon	53.0	53.4	47.9	49.6	38.3	77.3	71.1	67.1	64.3	58.2
Dry basis (d.b.) wt %										
Ash yield	15.5	19.5	24.8	26.5	30.5	20.6	27.0	31.2	34.1	40.2
Volatile matter	29.3	24.7	25.4	21.9	29.1	1.4	1.2	1.2	1.2	1.0
Fixed carbon	55.2	55.8	49.7	51.6	40.4	78.0	71.7	67.6	64.7	58.8

In general, the proximate analysis results indicate clear trends with regards to the differences in composition of the samples from different seams. The ash yield of the samples compare with one another in the order: seam 2 < seam 4 < seam 5, while for the fixed carbon content

the order is the opposite. The volatile matter released from the samples compare with one another in the following manner: coal 4N < coal 2N $\approx$ coal 4C < coal 5N $\approx$ coal 2C. There is thus a significant distribution of properties among the samples, some clearly distinguished between different seams, while some are in agreement across different seams.

Koekemoer (2009) presented results of the proximate analysis of several seam 4 Highveld coals, of which one was a blend representative of a commercial gasification feedstock. The proximate analysis results for coal 4N are very similar to this blend (reported as 5.3%, 24.1%, 21.1%, and 49.5% for M, A, VM, and FC, respectively), confirming 4N as a suitable benchmark. The proximate analysis results of coal 4N are also within the range of typical properties reported by Van Dyk *et al.* (2009) for base case test results of South African coals utilised for gasification, reported as 2.7 - 5.5%, 22.2 - 31.6%, 17.0 - 28.6%, and 39.3 - 51.6% for M, A, VM, and FC, respectively.

The results of the gross calorific value (CV) determination of the coal and char samples are presented in Table 3.3, on an air dried basis.

Table 3.3: Gross calorific values

CV (a.d.)	Coal					Char				
	2C	2N	4C	4N	5N	2C	2N	4C	4N	5N
MJ/kg	25.2	24.1	22.6	21.5	20.5	25.8	22.1	21.6	19.9	17.2

There is once again a clear trend observed for the samples from different seams, the calorific value being in the order: seam 5 < seam 4 < seam 2, correlating to fixed carbon content. The calorific value obtained for coal 4N is very similar to that of the blend investigated by Koekemoer (2009), reported as 21.1 MJ/kg, and a seam 4 Highveld coal investigated by du Toit (2013), reported as 21.7 MJ/kg.

The results of the ultimate analysis, for both the raw coal and char samples, are presented in Table 3.4 on the dry, ash free basis.

Table 3.4: Ultimate analysis results

	Coal					Char				
	2C	2N	4C	4N	5N	2C	2N	4C	4N	5N
Carbon (d.a.f. %)	79.7	78.8	77.3	77.6	76.7	96.5	95.9	96.0	96.5	95.2
Hydrogen (d.a.f. %)	4.7	4.3	4.4	3.9	5.6	0.0	0.3	0.1	0.1	0.3
Nitrogen (d.a.f. %)	2.0	2.0	2.1	2.1	2.1	2.2	2.0	2.1	2.1	2.0
Oxygen (d.a.f. %)	12.4	13.8	14.1	15.1	14.2	0.4	0.0	0.0	0.0	1.0
Sulphur (d.a.f. %)	1.3	1.1	2.1	1.4	1.4	0.9	1.8	1.9	1.3	1.5

There are no significant differences observed between the ultimate analysis results of the different seam samples. The ultimate analysis results of the seam 4 samples are in very good agreement with the seam 4 sample investigated by du Toit (2013), reported as 78.4%, 4.0%, 2.0%, 14.7%, and 0.9% for C, H, N, O, and S, respectively. The results of coal 4N are also in good agreement with the results (reported as 80.7%, 4.9%, 2.1%, 11.1%, and 1.1% for C, H, N, O, and S, respectively) observed for the blend investigated by Koekemoer (2009), although coal 4N exhibits a slightly lower carbon and hydrogen content.

The general comparison between char composition and coal composition is similar to what has been reported in other studies of South African coals charred at 950 °C (du Toit, 2013; van Wyk, 2015).

3.2.2.2. Petrographic analysis

The results of the petrographic analysis of the coal samples are presented in Table 3.5, providing the maceral volume percentages “as reported” (including visible mineral matter). Alternatively, maceral volume percentages on the mineral matter free basis are presented in Table 3.10.

Table 3.5: Petrographic analysis results

Composition (volume % as reported)	2C	2N	4C	4N	5N
Total Vitrinite	26.6	21.1	17.6	8.8	50.5
of which:					
Telovitrinite	15.9	13.8	14.7	6.4	27.5
Detrovitrinite	8.0	6.6	2.5	2.5	23.0
Pseudovitrinite	2.7	0.6	0.4	0.0	0.0
Total Liptinite	4.5	4.4	8.0	4.3	9.6
Total Inertinite	61.1	64.1	59.3	71.3	24.0
of which:					
Reactive semifusinite	37.0	43.3	43.1	54.7	11.0
Semifusinite	5.3	4.9	4.9	5.3	0.4
Fusinite + Sclerotinite	10.6	7.2	4.5	2.8	5.4
Micrinite	4.3	5.3	6.1	6.0	5.8
Reactive inertodetrinite	2.2	2.5	0.2	1.6	0.4
Inert inertodetrinite	1.8	1.0	0.6	0.9	1.0
Total Visible Minerals	7.8	10.5	15.1	15.5	15.9
of which:					
Clay	7.1	10.1	14.5	15.2	14.3
Pyrite	0.8	0.4	0.6	0.4	1.6
Total Reactives*	70.2	71.2	68.8	69.4	71.5

*Total Reactives = Total Vitrinite + Total Liptinite + Reactive semifusinite + Reactive inertodetrinite

The difference in vitrinite content is very apparent between the different seam samples, with a definite trend of seam 4 < seam 2 < seam 5. Compared to the blend investigated by Koekemoer (2009), coal 4N has a lower vitrinite content, higher inertinite content and much higher total reactives, mostly attributed to a higher reactive semifusinite and a lower inert inertodetrinite fraction. Compared to the coal investigated by du Toit (2013), coal 4N has a lower vitrinite content, higher inertinite content and a much higher total reactives content, mostly attributed to the higher reactive semifusinite fraction. Coal 4N also has a lower vitrinite

content and higher inertinite content than the range reported by Van Dyk *et al.* (2009), although coal 4C is well within this range.

The results of the vitrinite reflectance analysis of the coal samples are presented in Table 3.6.

Table 3.6: Vitrinite reflectance results

	2C	2N	4C	4N	5N
Vitrinite rank reflectance (%)	0.58	0.55	0.60	0.66	0.53
Standard deviation	0.068	0.052	0.072	0.087	0.042
Rank (medium rank bituminous)	D	D	C	C	D

Trends are once again observed between the different seams, the seam 5 sample being the lowest rank and the seam 4 samples being the highest rank. Based on these results, the coals are classified as medium rank bituminous coals. Specifically, the seam 5 coal and seam 2 coals are classified as bituminous rank D, while the seam 4 coals are classified as bituminous rank C. The vitrinite reflectance results for coal 4C and coal 4N are similar to the results determined for seam 4 coals by Koekemoer (2009) and du Toit (2013), and is also within the range reported by Van Dyk *et al.* (2009).

3.2.2.3. Mineral analysis

The results of the XRD analysis are presented in Table 3.7. The prevalence of the phases identified within the samples are indicated on two bases. Firstly, as the “as reported” absolute weight percentages including graphite, indicated in parentheses. Secondly, as the relative weight percentages of the mineral matter, normalised to the graphite free (minerals only) basis, indicated in square brackets.

Table 3.7: XRD analysis results

Mineral	2C		2N		4C		4N		5N	
	(wt % as reported) [wt % graphite free]									
Alunite	(0.0)	[0.0]	(0.0)	[0.0]	(1.6)	[4.5]	(1.3)	[3.6]	(0.0)	[0.0]
Calcite	(0.9)	[3.4]	(1.5)	[5.6]	(1.8)	[5.1]	(1.3)	[3.7]	(0.0)	[0.0]
Dolomite	(3.6)	[13.8]	(0.7)	[2.6]	(2.7)	[7.7]	(2.8)	[8.1]	(0.0)	[0.0]
Kaolinite	(16.8)	[65.0]	(21.2)	[78.9]	(19.1)	[54.7]	(18.4)	[53.3]	(18.0)	[57.7]
Pyrite	(0.4)	[1.5]	(0.4)	[1.3]	(2.3)	[6.4]	(1.1)	[3.2]	(1.6)	[5.1]
Quartz	(2.0)	[7.6]	(3.1)	[11.6]	(7.5)	[21.6]	(9.7)	[28.1]	(11.6)	[37.2]
Siderite	(2.3)	[8.8]	(0.0)	[0.0]	(0.0)	[0.0]	(0.0)	[0.0]	(0.0)	[0.0]
Graphite	(74.1)		(73.2)		(65.1)		(65.5)		(68.8)	

When comparing the XRD results for coal 4N to the results of the blend investigated by Koekemoer (2009), the results exhibit moderate agreement, but significantly more pyrite is observed in coal 4N. The quartz content correlates well to the sample ash yield, with a clearly increasing trend of seam 2 < seam 4 < seam 5. Kaolinite is observed as the predominant mineral present in all samples, as is frequently reported for South African coals (van Dyk *et al.*, 2006b; Hattingh *et al.*, 2011; Everson *et al.*, 2014).

The results of the XRF analysis are presented in Table 3.8. The prevalence of the constituents within the ash are indicated on two bases. Firstly, as the “as reported” absolute weight percentages including the loss on ignition (LOI) at 1000 °C, indicated in parentheses. Secondly, as the relative weight percentages of the ash constituents, normalised to the LOI-free (non-volatile only) basis, indicated in square brackets.

Table 3.8: XRF analysis results

Component	2C		2N		4C		4N		5N	
	(wt % as reported) [wt % LOI-free]									
SiO ₂	(6.4)	[38.3]	(10.6)	[47.8]	(12.5)	[49.4]	(15.5)	[53.6]	(19.8)	[58.5]
TiO ₂	(0.3)	[1.6]	(0.5)	[2.1]	(0.5)	[1.9]	(0.5)	[1.8]	(0.4)	[1.2]
Al ₂ O ₃	(5.0)	[29.9]	(7.6)	[34.5]	(7.2)	[28.5]	(8.4)	[29.0]	(8.5)	[25.1]
Fe ₂ O ₃	(2.1)	[12.5]	(1.1)	[4.8]	(1.8)	[6.9]	(1.4)	[4.7]	(2.7)	[7.9]
MnO	(0.0)	[0.2]	(0.0)	[0.1]	(0.0)	[0.1]	(0.0)	[0.1]	(0.0)	[0.0]
MgO	(0.6)	[3.4]	(0.4)	[1.7]	(0.6)	[2.3]	(0.5)	[1.6]	(0.6)	[1.8]
CaO	(1.8)	[10.9]	(1.3)	[6.1]	(1.7)	[6.8]	(1.6)	[5.7]	(0.8)	[2.4]
Na ₂ O	(0.1)	[0.6]	(0.3)	[1.4]	(0.2)	[0.9]	(0.2)	[0.8]	(0.1)	[0.4]
K ₂ O	(0.0)	[0.2]	(0.1)	[0.5]	(0.2)	[0.9]	(0.2)	[0.8]	(0.7)	[2.1]
P ₂ O ₅	(0.1)	[0.5]	(0.0)	[0.1]	(0.1)	[0.4]	(0.0)	[0.1]	(0.0)	[0.1]
SO ₃	(0.4)	[2.1]	(0.2)	[0.9]	(0.5)	[1.9]	(0.6)	[1.9]	(0.1)	[0.4]
LOI	(83.2)		(77.9)		(74.7)		(71.1)		(66.2)	

The SiO₂ yield correlates well to the sample ash yield, with an increasing trend of seam 2 < seam 4 < seam 5, the relationship to quartz content is clearly evident. No striking trends are otherwise observed for the mineral analyses between the different seam samples. Very good agreement is observed between coal 4N and the blend investigated by Koekemoer (2009), except coal 4N exhibits more Fe₂O₃, corresponding to the higher pyrite content observed. The results of coal 4N fall mostly within the range reported by Van Dyk *et al.* (2009), although better agreement is once again noted for coal 4C.

3.2.2.4. Structural analysis

The results of the CO₂ physisorption analysis, processed utilising both the BET and DR method, are presented in Table 3.9.

Table 3.9: Pore surface areas of chars

Micropore surface area (m ² /g)	2C	2N	4C	4N	5N
BET	136	135	111	92	106
DR	215	215	176	144	167

It is clear that the seam 2 chars have greater micropore surface area than the other chars. The results of char 2C and 2N are virtually the same, although a large difference is observed between char 4C and 4N, char 4N having the lowest micropore surface area of all chars.

du Toit (2013) determined a micropore surface area of a seam 4 char of 182 m²/g utilising the DR method, after similar char preparation as was performed in this study, which agrees well with the result for char 4C, but char 4N exhibits a lower micropore surface area. Char 5N exhibits the second lowest micropore surface area, despite the high vitrinite content of coal 5N.

3.2.3. Summary of characterisation results

For convenience, a summary of the results from the coal and char characterisation analyses is presented in Table 3.10.

Table 3.10: Summary of characterisation results

Property	Coal					Char				
	2C	2N	4C	4N	5N	2C	2N	4C	4N	5N
Proximate Analysis (wt % d.b.)										
Ash yield	15.5	19.5	24.8	26.5	30.5	20.6	27.0	31.2	34.1	40.2
Volatile matter	29.3	24.7	25.4	21.9	29.1	1.4	1.2	1.2	1.2	1.0
Fixed carbon	55.2	55.8	49.7	51.6	40.4	78.0	71.7	67.6	64.7	58.8
Gross Calorific Value (MJ/kg a.d.)										
CV	25.2	24.1	22.6	21.5	20.5	25.8	22.1	21.6	19.9	17.2
Ultimate Analysis (wt % d.a.f.)										
Carbon	79.7	78.8	77.3	77.6	76.7	96.5	95.9	96.0	96.5	95.2
Hydrogen	4.7	4.3	4.4	3.9	5.6	0.0	0.3	0.1	0.1	0.3
Nitrogen	2.0	2.0	2.1	2.1	2.1	2.2	2.0	2.1	2.1	2.0
Oxygen	12.4	13.8	14.1	15.1	14.2	0.4	0.0	0.0	0.0	1.0
Sulphur	1.3	1.1	2.1	1.4	1.4	0.9	1.8	1.9	1.3	1.5
Maceral Composition (volume % m.m.f.)										
Total Vitrinite	28.9	23.5	20.8	10.5	60.1	ND	ND	ND	ND	ND
Total Liptinite	4.9	4.9	9.4	5.1	11.5	ND	ND	ND	ND	ND
Total Inertinite	66.3	71.6	69.9	84.4	28.5	ND	ND	ND	ND	ND
Total Reactives	76.2	79.5	81.1	82.2	85.0	ND	ND	ND	ND	ND
Vitrinite Reflectance										
Reflectance (%)	0.58	0.55	0.60	0.66	0.53	ND	ND	ND	ND	ND
Rank (bituminous)	D	D	C	C	D	ND	ND	ND	ND	ND
Micropore Surface Area (m²/g)										
BET	ND	ND	ND	ND	ND	136	135	111	92	106
DR	ND	ND	ND	ND	ND	215	215	176	144	167
XRD Mineral Phase (wt % as reported)										
Alunite	0.0	0.0	1.6	1.3	0.0	ND	ND	ND	ND	ND
Calcite	0.9	1.5	1.8	1.3	0.0	ND	ND	ND	ND	ND
Dolomite	3.6	0.7	2.7	2.8	0.0	ND	ND	ND	ND	ND
Graphite	74.1	73.2	65.1	65.5	68.8	ND	ND	ND	ND	ND
Kaolinite	16.8	21.2	19.1	18.4	18.0	ND	ND	ND	ND	ND
Pyrite	0.4	0.4	2.3	1.1	1.6	ND	ND	ND	ND	ND
Quartz	2.0	3.1	7.5	9.7	11.6	ND	ND	ND	ND	ND
Siderite	2.3	0.0	0.0	0.0	0.0	ND	ND	ND	ND	ND

ND – Not Determined

CHAPTER 4

Experimental Procedures

Chapter 4 presents the experimental procedures utilised to generate gasification results. This section will provide detail regarding the reagents utilised, experimental equipment, a summary of the procedures and methods employed during the experimental work, a summary regarding experimental validation, and the experimental conditions chosen under which the gasification runs will be conducted. The summary regarding experimental validation is provided in support of the choice of experimental conditions, and since the equipment and procedures developed for this study have not been detailed previously. Finally, the procedures and mathematics employed to process the data to yield results will be discussed.

4.1. Reagent overview

The chars utilised for the gasification experiments were prepared by crushing a -8 mm sub-sample of char down to -500 μm , and sieving out the -425 μm undersize, yielding a -500 μm +425 μm fraction. This particle size range was chosen as a compromise between several conflicting physical factors, as discussed in Appendix E.1.

Activated carbon powder of ~ 75 μm particles, consisting of minimum 87% fixed carbon (d.b.), was utilised to test the gasification repeatability. The powder was procured from Merck®.

N_2 gas utilised as dilutant or inert during the gasification experiments is nominally minimum 99.999% pure. CO_2 gas utilised as gaseous reagent is nominally minimum 99.9% pure. CO gas utilised for analyser calibration is certified as containing 3200 ppm CO with balance N_2 , and a second CO gas utilised for calibration is certified as containing 4500 ppm CO with balance N_2 . The gases were procured from Afrox®.

4.2. Equipment overview

As part of this study, a new laboratory-scale high-pressure fixed-bed reactor (HP-FBR) system has been designed and constructed in-house to provide the capabilities necessary for the experimental gasification work. This system has the capability of performing gasification runs up to a total system pressure of 20 bar(a). The reaction is monitored and logged from the detection of product carbon monoxide (CO) concentration, utilising a non-dispersive infra-red (NDIR) analyser. The analyser is an MGA3000™ model from ADC Gas Analysis®. Heat is provided by a vertical split-tube furnace manufactured by Carbolite®. The reaction vessel is a tube constructed of quartz, with a porous quartz disc serving as support for the sample bed. The sample is loaded as a fixed-bed into the reactor, with reagent gas-flow through the sample bed from top to bottom. The reagent gas amount and concentration is controlled by thermal mass flow controllers (TMFC), supplied by Bronkhorst High-Tech®. Pressure is controlled by an electronic pressure controller (EPC), supplied by Bronkhorst High-Tech®. A schematic of the equipment is provided in Figure 4.1. Further detail regarding the HP-FBR system is available in Appendix B.

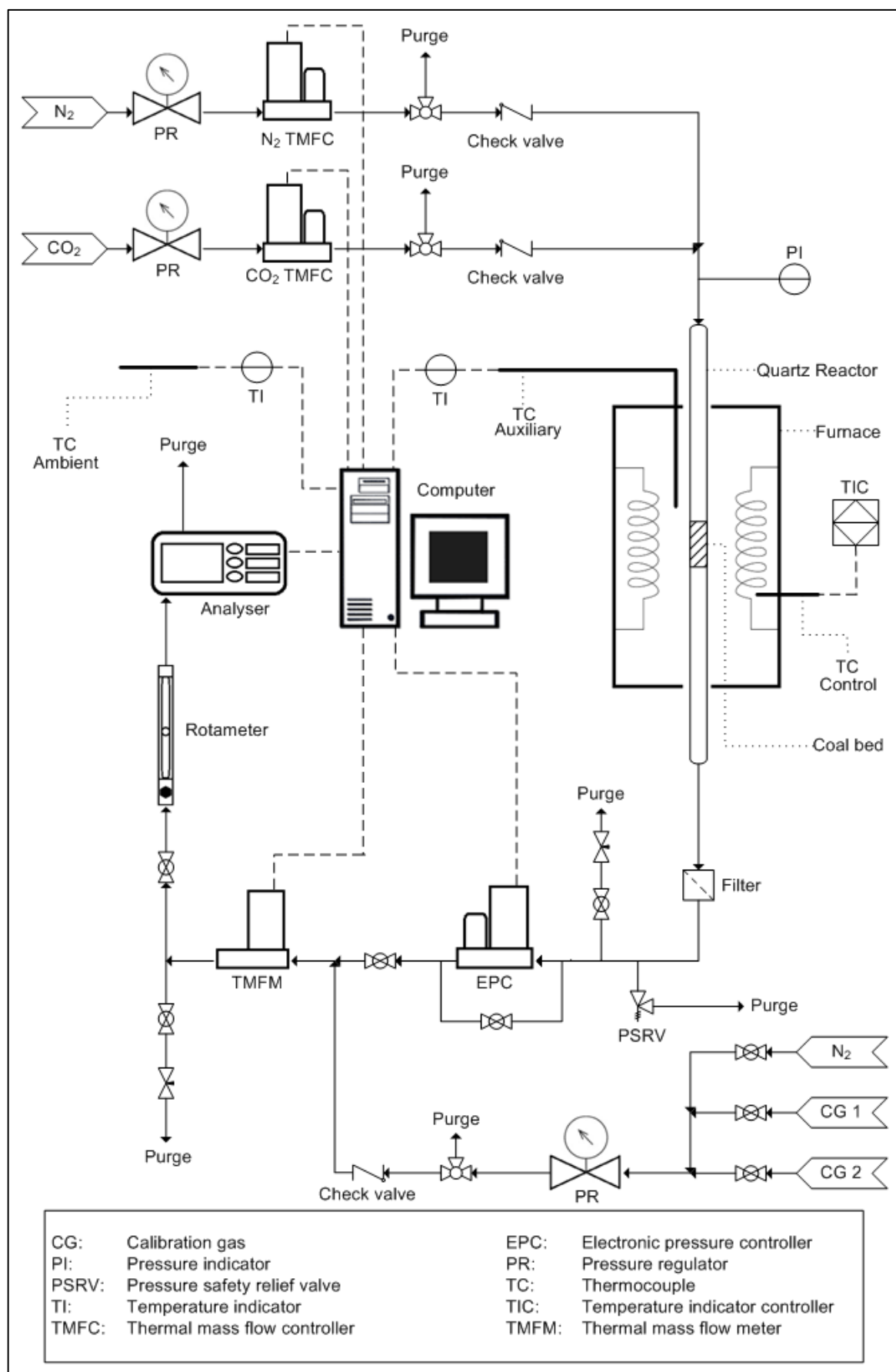


Figure 4.1: Process and instrumentation diagram of the HP-FBR system

4.3. Experimental validation

The experimental conditions during gasification have a significant impact on the rate at which the reactions occur. Factors which have a significant influence on the gasification rate include the temperature and the gaseous reagent partial pressure. Other factors which may observably influence the reaction rate, due to heat and mass transfer effects, include the solid reagent particle size, gaseous reagent flow velocity, sample mass, and the solid reagent fixed-bed height. Furthermore, the range and accuracy of the detection equipment utilised also have to be taken into consideration. Due to these factors, the conditions under which the gasification experiments are to be conducted require careful consideration and testing. It is desired to, as far as possible, remain within the chemical reaction controlled regime during gasification. It is also desired to ensure differential operation. This implies maintaining a significant stoichiometric excess of gaseous reagent without an appreciable concentration gradient through the sample bed, and preventing product accumulation within the sample vicinity.

Due to these factors, it was necessary to test the influence of several operating conditions to determine a suitable range for obtaining dependable results. Since the equipment and the corresponding experimental procedures utilised are new, the accuracy and repeatability of the system was determined as part of the validation.

The repeatability of the experimental system was tested by repeatedly gasifying homogenous samples of activated carbon and comparing the results. Based on the observations made during these tests, it was concluded that the experimental repeatability of the system is excellent. This is inferred from the nearly identical conversion profiles of repeat runs, as presented in Figure D1. For the runs conducted at low pressure, the span between the three repeats is approximately 3% of their average. For the runs conducted at high pressure, the span between the three repeats is approximately 2% of their average. The results of these tests, accompanied by further detail, is available in Appendix D.1.

The accuracy of the experimental system, with regards to reconciling a carbon mass balance, was determined by comparing the theoretical sample carbon content with the total detected CO after gasification. The theoretical carbon content was estimated by the fixed carbon percentage, determined from a proximate analysis, multiplied by total sample mass. The average discrepancy between the theoretical and experimental values was determined as $\pm 8\%$, relative to the theoretical carbon content. This error margin includes uncertainty with regards to reported fixed carbon representing the actual amount of carbon in the sample undergoing gasification. Due to this uncertainty, an alternative method was also employed to

estimate an indication of experimental error. The reaction rate results of all experimental runs were extrapolated to a single temperature and pressure, enabling direct comparison. The average of the extrapolated reaction rates of each char was determined, as well as the standard deviation. The standard deviation, as a percentage relative to the average, was determined to be below 5%. This is considered as an indication of the extent of data scatter, incorporating all factors which may contribute to inconsistencies during the experimental work. As the standard deviation is determined from extrapolations, and not true observations, calculation of a confidence interval is not relevant, since the concept of a population average is not applicable. Instead, the standard deviation is considered as an indication of experimental uncertainty, *in lieu* of an experimental error or confidence interval. Further detail regarding the investigation of the carbon mass balance is available in Appendix D.2. Further detail regarding the procedures and results of determining the experimental uncertainty is available in Appendix D.3.

A total gas flow rate of 1 dm³_n/min is optimal for performance of the gas analysis equipment. In an effort to determine whether gas flow in this range has an independent effect on the observed gasification results, experimental results generated at 1 dm³_n/min gas flow were compared to experimental results generated at 0.5 dm³_n/min gas flow. Based on the observations made during these tests, it was concluded that results are not influenced by gas flow rates within this range. The results of these tests are presented in Figure E1, and discussed in further detail in Appendix E.1.

The amount of char sample loaded into the reactor is varied, according to the rate at which the reaction takes place. This is done to better maintain the CO product concentration within a consistent range within the detection equipment, as well as to better maintain a consistent stoichiometric ratio between the sample carbon consumption rate and CO₂ admitted to the reactor. Thus, under faster reacting conditions the total amount of carbon loaded in the system is decreased, and *vice versa*. Testing was conducted in order to determine which char loading amounts are appropriate under different reaction conditions, as to ensure that heat and mass transfer effects relating to sample bed height are not significantly apparent. Based on the observations made during these tests, it was concluded that a char loading of 0.2 g is appropriate during high pressure experimental runs at 900 °C (fast reaction rate), and a char loading of 0.5 g is appropriate during experimental runs at 850 °C (slow reaction rate). The results of these tests are presented in Figure E3, and discussed in further detail in Appendix E.1.

During preliminary testing, it was observed that a reduction in char particle size has a significant influence on the observed gasification rate. In an effort to compromise between the

practical benefits of utilising larger particles, and the reduced possibility of encountering pore diffusion resistance when utilising smaller particles, a particle size range between 500 μm and 425 μm was chosen for the gasification investigation. An indication of the effect of particle size on the observed gasification reaction rate is presented in Figure E2, and discussed in further detail in Appendix E.1.

In order to insure that the reactor temperature is known and stable, trial runs were conducted with a thermocouple mounted in the reactor, probing within the sample bed. Data gathered from these runs were utilised to determine the furnace temperature profile, and a relationship between the actual sample bed temperature and the temperatures reported by the furnace control thermocouple and the auxiliary thermocouple. During experimental runs the thermocouple within the reactor is removed to avoid interference with gas flow and CO production. The bed temperature is therefore inferred from the auxiliary thermocouple and the relationship previously established. Further elaboration regarding this matter is provided in Appendix E.2.

4.4. Experimental conditions

The influence of varying gasification pressure and gasification temperature, on the reaction behaviour of the five char samples, is investigated. The values of fixed conditions have been chosen based on the results of preliminary testing, as summarised in Section 4.3, and detailed in Appendix E.1. Gasification temperature will be varied in 25 $^{\circ}\text{C}$ increments. Gasification pressures of 1 bar(a), 10 bar(a) and 20 bar(a) will be investigated. A summary of the gasification conditions to be utilised is provided in Table 4.1.

Table 4.1: Gasification conditions investigated

Condition	Value Utilised
Temperature	825 $^{\circ}\text{C}$ to 925 $^{\circ}\text{C}$
CO ₂ concentration	30% (Balance N ₂)
Char particle size	-500 μm +425 μm
Total gas flow rate	1 dm ³ /min
Char mass	0.2 g to 0.5 g
Operating pressure	1 bar(a), 10 bar(a) and 20 bar(a)

With reference to Table 4.1, 925 $^{\circ}\text{C}$ will only be utilised for 1 bar runs, since the reaction is too fast at this temperature and higher pressures. Similarly, 825 $^{\circ}\text{C}$ will only be utilised for the

faster 10 bar and 20 bar runs, since the reaction at this temperature at 1 bar is too slow to produce CO within an accurate range of the gas detection equipment. Thus, runs at low pressure (1 bar) will be performed at 850 °C, 875 °C, 900 °C and 925 °C. Runs at high pressure (10 bar and 20 bar) will be performed at 825 °C, 850 °C, 875 °C and 900 °C. For each pressure investigated there will therefore be four temperature points available for the construction of Arrhenius curves, of which three temperature points are overlapping for direct comparisons between low pressure and high pressure results.

Experimental runs at 825 °C and 850 °C will be loaded with 0.5 g char, runs at 875 °C will be loaded with 0.35 g char, and runs at 900 °C and 925 °C will be loaded with 0.2 g char.

The conditions selected for the gasification experiments ensure that there is at least a 150-fold stoichiometric excess between the amount of CO₂ fed to the reactor per second, and the amount of carbon reacting per second. Furthermore, the CO₂ partial pressure is therefore at least 75 times greater than the maximum observed CO partial pressure in the reactor and product stream. The superficial gas velocity in the reactor, approximated by the ideal gas law, is expected to be between 0.04 m/s and 0.95 m/s, depending on the pressure and temperature utilised.

A summary of the experimental runs conducted is presented in Table 4.2, a total of 60 runs are performed as part of the main investigation.

Table 4.2: Summary of gasification experimental runs

Total pressure	Temperature	Char samples	Sample mass
1 bar(a)	850 °C	2C, 2N, 4C, 4N and 5N	0.50 g
	875 °C	2C, 2N, 4C, 4N and 5N	0.35 g
	900 °C	2C, 2N, 4C, 4N and 5N	0.20 g
	925 °C	2C, 2N, 4C, 4N and 5N	0.20 g
10 bar(a)	825 °C	2C, 2N, 4C, 4N and 5N	0.50 g
	850 °C	2C, 2N, 4C, 4N and 5N	0.50 g
	875 °C	2C, 2N, 4C, 4N and 5N	0.35 g
	900 °C	2C, 2N, 4C, 4N and 5N	0.20 g
20 bar(a)	825 °C	2C, 2N, 4C, 4N and 5N	0.50 g
	850 °C	2C, 2N, 4C, 4N and 5N	0.50 g
	875 °C	2C, 2N, 4C, 4N and 5N	0.35 g
	900 °C	2C, 2N, 4C, 4N and 5N	0.20 g

4.5. Experimental methodology

An experimental run is started by loading a weighed char sample into the reactor to form a uniform bed. Refer to Figure 4.2, indicating such a char bed resting on the porous support within the quartz reactor tube.



Figure 4.2: Char bed loaded into quartz reactor tube

The reactor, containing the char sample, is flushed with nitrogen before being placed into the heated furnace. Time is allowed for the furnace and sample to become isothermal, and the system is pressurised. Data logging is started and CO₂ flow is introduced into the reactor. As the gasification progresses, data regarding the CO concentration, system pressure, furnace temperature, total gas flow rate and ambient temperature is logged every two seconds. This data is utilised to conduct further processing and to verify that desired conditions were maintained throughout the entire duration of the experiment. The experiment is stopped when the sample has achieved complete carbon conversion, inferred from an asymptotic stabilisation of the CO concentration curve. Further detail regarding the experimental methodology, as well as instrument calibration, is available in Appendix E.2. Exact procedures conducted to perform an experimental run are listed in Appendix E.3.

4.6. Data interpretation

4.6.1. Determination of reaction rate

By the end of a gasification experimental run, a raw CO concentration curve has been captured from the logging of the NDIR analyser output. This raw data is transformed into true CO concentration through the use of a three-point calibration curve, obtained from analysis of certified calibration gases. This procedure is further elaborated in Appendix C. The result is a range of data indicating the CO concentration in the gas outlet stream, throughout the duration of the gasification experiment, at any point in time. An example of a graphical plot of such a data range is presented in Figure 4.3. The CO concentration is indicated in ppm, and is displayed as a function of elapsed reaction time in minutes.

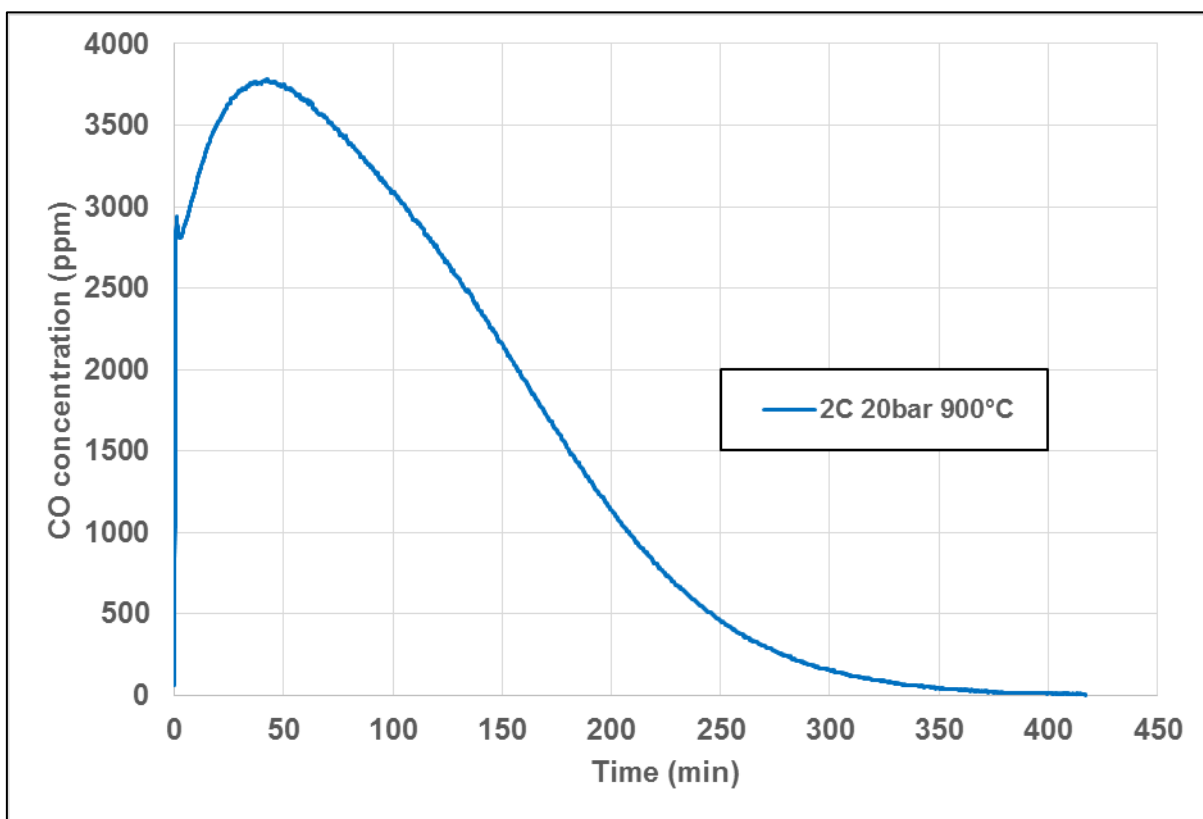


Figure 4.3: Example of CO concentration as function of time

Figure 4.3 depicts how the CO production changes throughout the course of a gasification experimental run. The CO production rate reaches a maximum at 45 minutes after the start of the gasification reaction, resulting in a CO concentration of 3800 ppm in the product gas stream. CO production then steadily decreases up to a point where no further decrease or

changes are observed, in this example at 420 minutes. This particular gasification run thus achieved 100% conversion after seven hours, as evident from the graph.

In order to derive meaningful results, the CO concentration data is transformed into a more absolute representation of the reaction rate, by converting the CO production rate into a carbon consumption rate. This is achieved by incorporating the reaction stoichiometry, as indicated in Equation 1.1, and the total volumetric flow rate of the gas stream from which the CO concentration is measured. Equation 4.1 is utilised for this purpose:

$$r_c = \frac{[CO]}{2} \times \frac{Q_{ideal}}{60} \times \frac{MW_c}{V_{ideal}} \quad \text{Equation 4.1}$$

Equation 4.1 is applied to calculate the number of grams per second of carbon within the reactor which is reacting with CO₂ at that instant in time. This is termed the carbon conversion rate, denoted by r_c .

Integration of Equation 4.1 from the start of the gasification, up to a specified time (t), will yield the cumulative amount of carbon which has been converted up to that elapsed reaction time. This is denoted by $C^{(t)}$, which is a range of values dependent on time, calculated by Equation 4.2:

$$C^{(t)} = \int_0^t r_c dt \quad \text{Equation 4.2}$$

Similarly, integration of Equation 4.1 from the start of the gasification, up to the final reaction time (f) when the carbon reaction is no longer observable, will yield the total amount of carbon which has been converted throughout the entire experiment. This is denoted by C_f which is a single constant value, since f is a constant specific to each gasification experimental run, calculated by Equation 4.3:

$$C_f = \int_0^f r_c dt \quad \text{Equation 4.3}$$

It is generally assumed that the total amount of carbon detected in the form of CO, incorporating the stoichiometry as indicated in Equation 1.1, represents the total carbon content of the sample available for reaction.

With the results from Equation 4.2 and Equation 4.3 available, the fractional conversion (X) of the char can be calculated by Equation 4.4:

$$X = \frac{C^{(t)}}{C_f} \quad \text{Equation 4.4}$$

Equation 4.4 is applied to determine the sample fractional conversion value at any point during the reaction. A graph of this range as a function of time yields a conversion curve (X versus t graph on the d.a.f. basis), frequently presented in coal conversion studies, an example is provided in Figure 4.4.

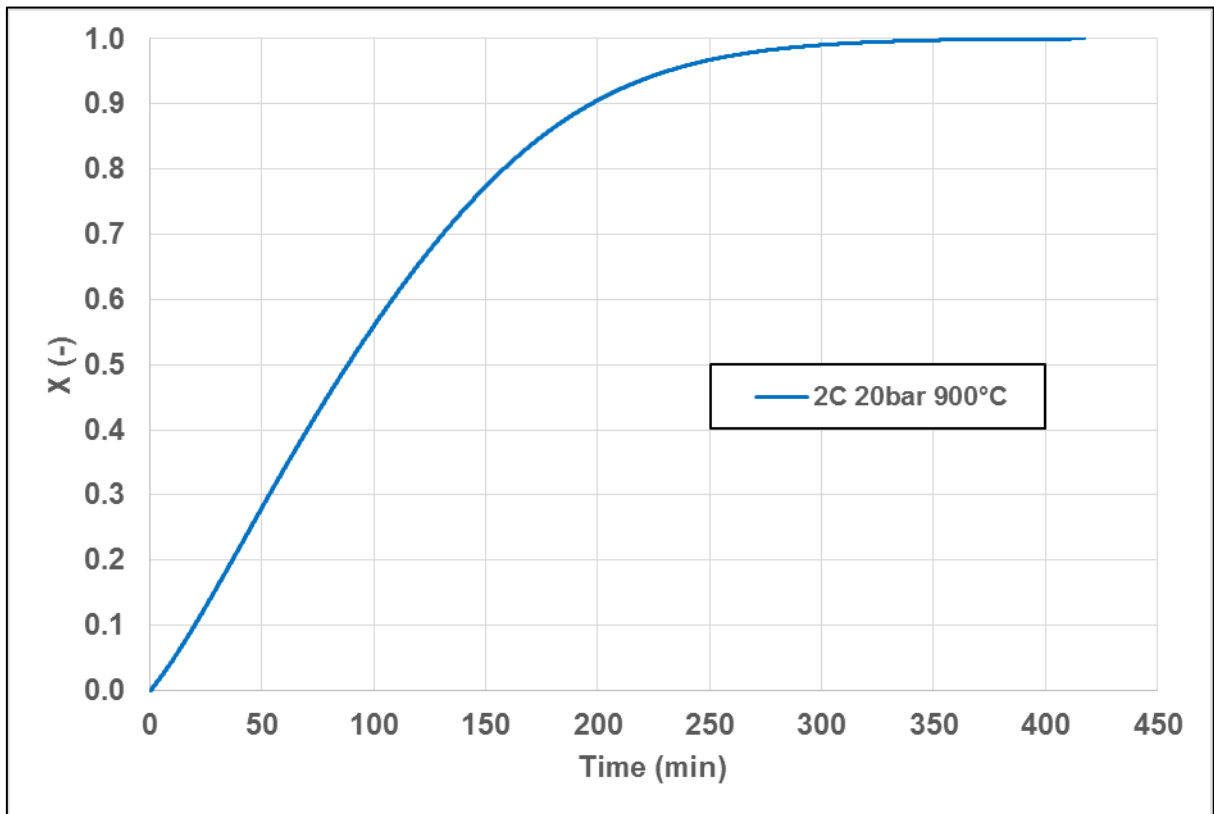


Figure 4.4: Example of fractional conversion as function of time

Figure 4.4 depicts the fractional carbon conversion of the sample as the experiment progresses. This example has been constructed from the data presented in Figure 4.3, the relationship is apparent when comparing the slope observed in Figure 4.4 with the magnitude observed in Figure 4.3 at the same point in time.

The general trend observable from Figure 4.3 is that the CO production rate increases to a maximum and then steadily decreases. Since a batch process has taken place, the overall

conversion rate inherently decreases as the carbon in the sample becomes consumed. Furthermore, the magnitude of r_c is dependent on the amount of carbon loaded into the reactor. For these reasons, a normalised representation of the carbon reactivity is derived, enabling direct comparison of results regardless of factors such as sample loading or char fixed carbon content. This is achieved by normalising the carbon reaction rate at a specific point in time, r_c , with respect to the actual amount of carbon available to react at that same point in time, $m^{(t)}$. The amount of carbon available at any point in time can be calculated by subtracting the cumulative amount of carbon reacted up to the time in question (Equation 4.2), from the total amount of carbon reacted during the entire experiment (Equation 4.3). This normalisation procedure results in a quantity termed the specific reactivity, denoted by r_s , which is represented by Equation 4.5.

$$r_s = \frac{r_c}{m^{(t)}} = \frac{r_c}{C_f - C^{(t)}} \quad \text{Equation 4.5}$$

The specific reactivity represents the amount of carbon reacting, per amount of carbon available to react in the system, per unit time. This is comparable to the method employed by many authors, e.g. Roberts *et al.* (2000), to present results obtained from a TGA as a mass-loss derivative normalised to instantaneous carbon mass. This is a valuable quantity for directly comparing the carbon reactivity of different carbon samples with one another, irrespective of total carbon content. When graphed as a function of conversion, r_s provides a useful means of observing the change in carbon reactivity as the reaction progresses. An example of a graph of r_s as a function of X is presented in Figure 4.5.

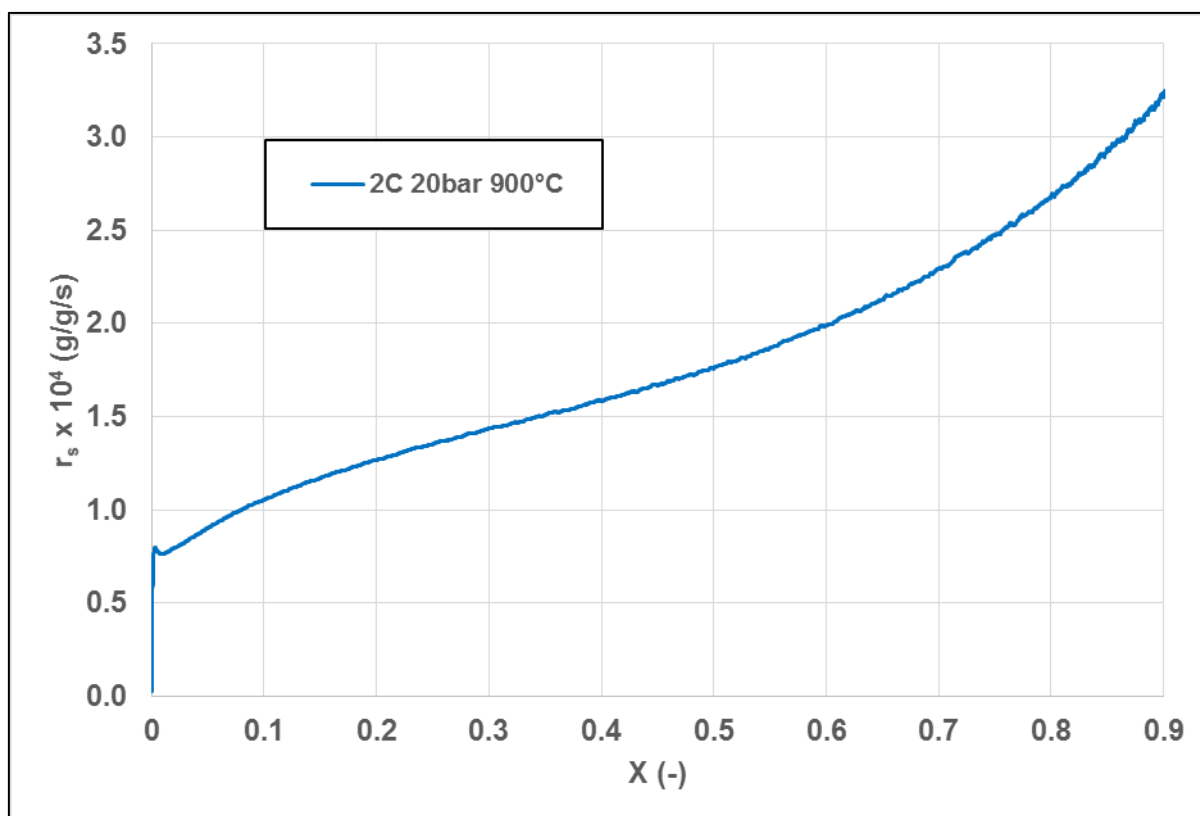


Figure 4.5: Example of specific reactivity as function of conversion

Figure 4.5 depicts the specific reactivity (normalised carbon conversion rate) of a char sample as a function of the char conversion. It is observed that as soon as the gasification reaction starts, the carbon reactivity reaches a value of 7.5×10^{-5} g/g/s. This value then steadily increases as the sample undergoes further conversion. Even though the total amount of carbon reacting decreases throughout the course of the reaction (due to depletion), the rate at which individual carbon units are reacting appear to be increasing during the reaction, as evident from Figure 4.5. This increase in reactivity may be attributed to factors such as pore development, as described by e.g. Liu *et al.* (2000b) and Coetzee *et al.* (2015), or other transformations occurring within the char particles during the reaction, such as concentration of catalytic mineral matter (Gräbner, 2015).

Graphs of r_s will only be constructed up to a carbon conversion of 90%. As is evident from Equation 4.5, r_s will inherently tend to approach infinity as the cumulative amount of carbon converted approaches the total sample carbon content. The value of r_s therefore becomes less meaningful at conversions approaching 100%.

The use of Equation 4.4 and Equation 4.5 require that a dependable value for the total sample carbon content is available. The use of a proximate analysis for this purpose is not the most

dependable option, as the conditions under which a proximate analysis is conducted differs from the gasification conditions. Instead, Equation 4.3 is utilized to calculate C_f from the gasification data itself, requiring that every gasification run be allowed to reach 100% conversion, with the resulting CO detected accordingly. Every attempt has been made in an effort to ensure that these requirements were met during the gasification study. Further elaboration, regarding the data capturing and processing procedure, is available in Appendix C.

4.6.2. Determination of activation energy

As indicated in Table 4.2, each char type was gasified at each pressure at four different isothermal temperatures. Data from these four runs can be utilised to construct Arrhenius curves for each sample at each pressure, consisting of four data points each. Arrhenius curves can be constructed by graphical representation of the Arrhenius equation, represented by Equation 4.6.

$$k = Ae^{-\frac{E_a}{RT}} \quad \text{Equation 4.6}$$

This is best accomplished by linearization of Equation 4.6 into the form of Equation 4.7.

$$\ln(k) = \frac{1}{T} \left(\frac{-E_a}{R} \right) + \ln(A) \quad \text{Equation 4.7}$$

Preliminary testing, as detailed in Appendix E.1, has indicated that char particle size may have an influence on the observed reaction rate under conditions investigated, suggesting that pore diffusion resistance could possibly be encountered. Due to this, as a conservative judgement, true activation energy (E_a) will not be reported. Instead, the reaction rate “as observed” will be utilised to determine the apparent activation energy ($E_{a,app}$). Furthermore, since the molar concentration of reagent (CO_2) has not been varied, the apparent activation energy will be directly determined from the specific reactivity (r_s), instead of having to determine the reaction rate constant (k). The intrinsic reaction rate constant is mathematically equivalent to the specific reactivity when incorporating the sample active surface area and a partial pressure dependence model, such as represented by Equation 2.7. Modifying the linearized Arrhenius equation to reflect these considerations, results in the form represented by Equation 4.8.

$$\ln(r_s) = \frac{1}{T} \left(\frac{-E_{a,app}}{R} \right) + \ln(A_s P_{CO_2}^n) \quad \text{Equation 4.8}$$

The value of $E_{a,app}$ determined from Equation 4.8 will be the same as if it were determined from Equation 4.7. The substitution does not influence the slope of the Arrhenius plot due to the constant relationship between k and r_s . The use of Equation 4.8 is, however, more convenient and accurate in the context of this investigation. Utilising Equation 4.8 for a set of specific reactivity values at four different temperatures yields a straight line, from which $E_{a,app}$ can be calculated from the slope of the line. This process is then repeated for each set of results from different char samples and different system pressures.

The specific reactivity at a sample conversion of 10% will be utilised in Equation 4.8, instead of initial reactivity. The initial reactivity is not a dependable indication of the true initial carbon reaction rate, since CO production is exaggerated at start-of-run, possibly due to interaction between CO_2 and mineral matter within the sample. The subject of reduction of CO_2 to CO by iron-containing minerals has been discussed by many authors (Furimsky *et al.*, 1988; Ohme & Suzuki, 1996; Huang *et al.*, 2015; Zhang *et al.*, 2015), and summarised in the review by Irfan *et al.* (2011). At 10% conversion the sample structural transformation is minimal, such that the reaction rate is still indicative of the true initial carbon reaction rate, whilst ensuring that sufficient reaction time was allowed for stabilisation, and the exaggeration phenomenon to cease for all experimental runs.

CHAPTER 5

Results and Discussion

Chapter 5 presents the experimental results after performing the gasification procedures, accompanied by discussion regarding the interpretation of the results and the apparent observations. Further, results from this study will be compared to those of closely related previous studies utilising similar coals, where applicable.

5.1. Effect of temperature on char reaction rate

The gasification experiments, as outlined in Table 4.1 and Table 4.2, have been performed and the data has been processed to yield a range of specific reactivity values for each experiment. These values will be presented as graphs of specific reactivity as a function of carbon conversion. All these results will however also be presented as conversion curves in Appendix A.

The effect of increasing temperature on the rate of the char gasification chemical reactions is generally well understood. The rate can be easily extrapolated to different temperatures utilising the activation energy, provided that the reactions remain within the chemical reaction controlled regime. An example of the influence of temperature on the specific reactivity of char 5N during gasification is provided in Figure 5.1.

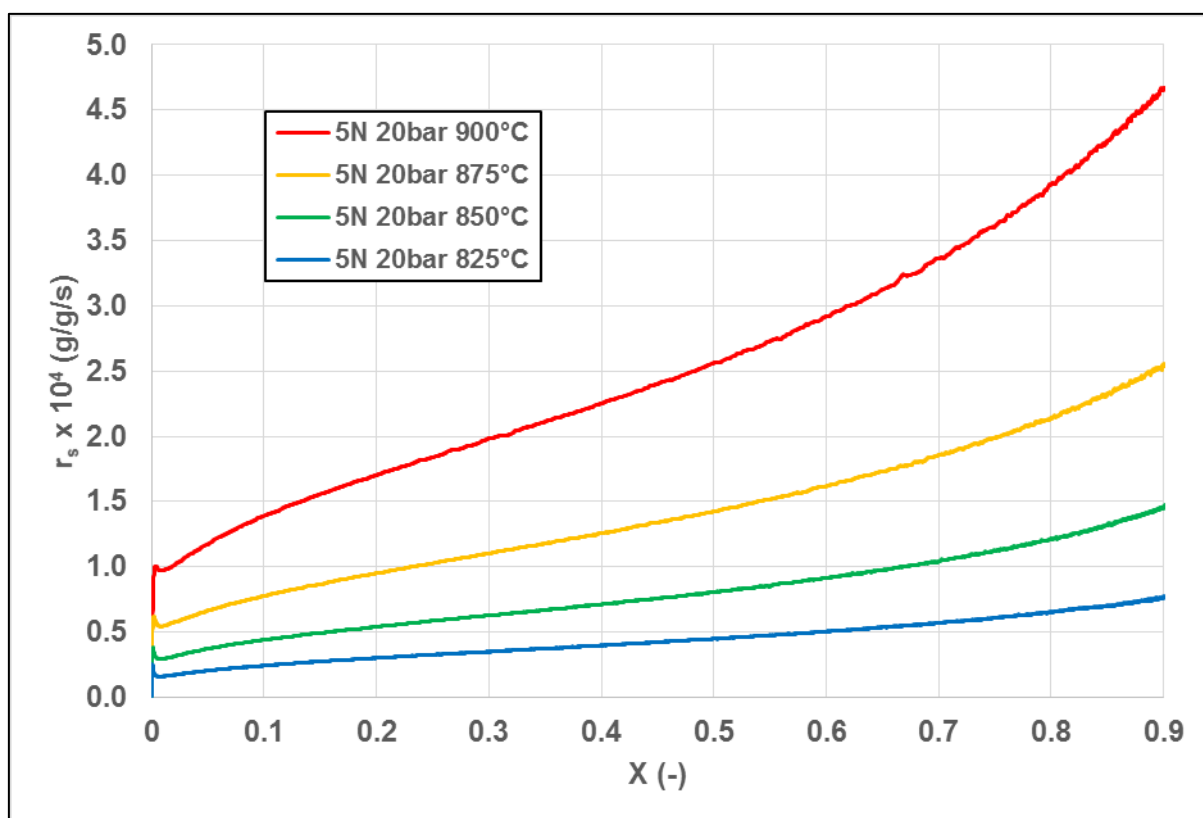


Figure 5.1: Effect of temperature on the specific reactivity of char 5N at 20 bar

In Figure 5.1 the reaction rate of char 5N at 20 bar is presented, indicating the increase in rate observed as the temperature at which the gasification occurs is increased. It is clear to observe, due to the higher order relationship between temperature and reaction rate in the

chemical reaction controlled regime, that the relative differences in reaction rate broaden as the temperature is incrementally increased by the same amount. Graphs illustrating the effect of temperature on char reactivity, for all chars at all pressures investigated, are available as specific reactivity curves in Appendix A.3, and conversion curves in Appendix A.4.

For each of the curves indicated in Figure 5.1, the value of r_s at the point of 10% sample conversion was utilised in Equation 4.8, in order to generate an Arrhenius plot. The same method was employed for the results obtained for all other chars and pressures investigated, to generate their respective Arrhenius plots. As an example, the constructed Arrhenius plots for char 5N will be presented in this section, followed by a table summarising the numeric values determined for $E_{a,app}$ of all char samples. Since $E_{a,app}$ is determined on an “as observed” basis, $E_{a,app}$ values will be separately determined and presented for the different pressures investigated.

The Arrhenius plots generated for char 5N are presented in Figure 5.2. The Arrhenius plots generated for the other char samples are available in Appendix A.5.

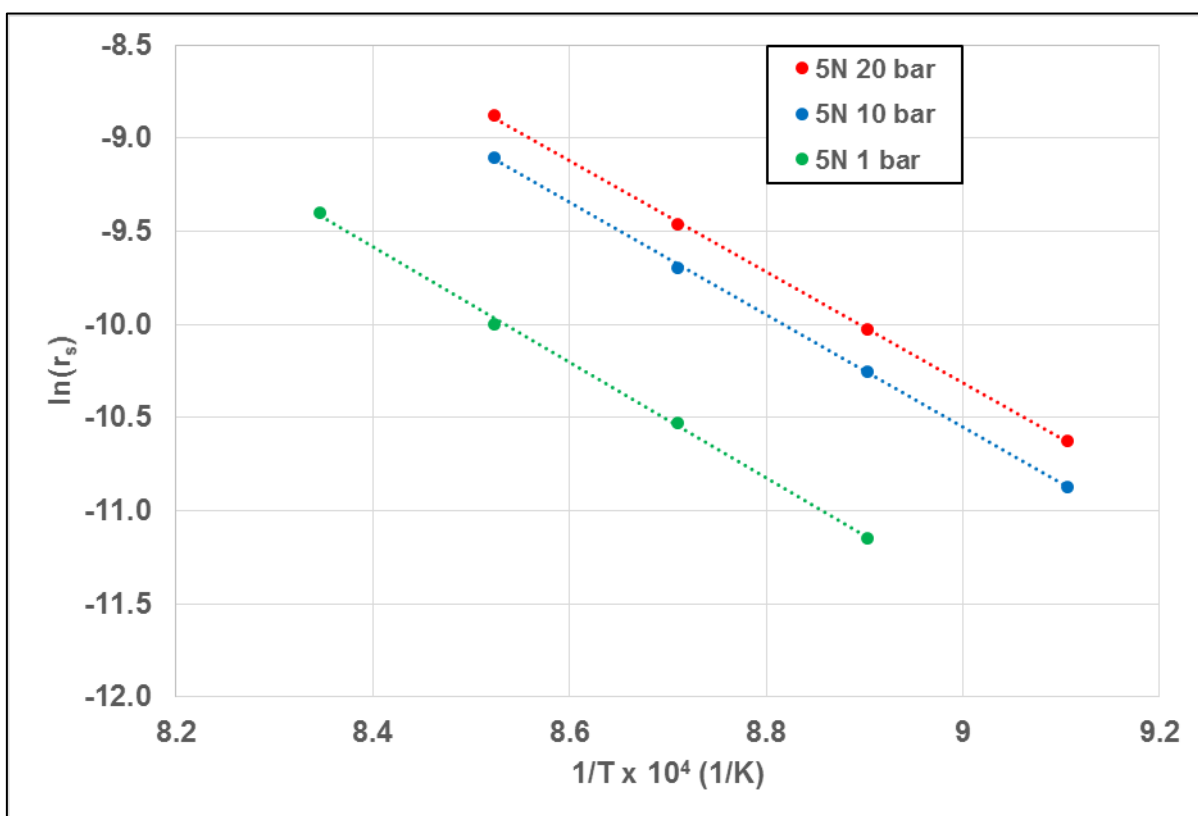


Figure 5.2: Arrhenius plots of char 5N

Figure 5.2 presents the Arrhenius plots obtained from the specific reactivity of char 5N at 20 bar, 10 bar and 1 bar, respectively. For each set of data, a linear trend line is fit by the

method of least squares. The coefficient of determination (R^2) for the fit between the trend line and the four data points is greater than 0.992 for all chars at all pressures investigated, consistently indicating very good linear fits. The value of $E_{a,app}$ is extracted from the slope of the trend line. For the other chars, the values are determined in the same manner from the Arrhenius plots as was done in this example, the results are presented in Table 5.1.

Table 5.1: Apparent activation energy of char-CO₂ gasification

Sample	Apparent Activation Energy (kJ/mol)		
	1 bar	10 bar	20 bar
Char 2C	246	237	241
Char 2N	239	236	242
Char 4C	236	233	232
Char 4N	243	231	233
Char 5N	258	251	248

From Table 5.1 it is observed that, for any char, the span of $E_{a,app}$ between the different pressures is never greater than 12 kJ/mol. This may indicate that influence of mass transfer limitations was not appreciably increased by altering the operating pressure, since the temperature dependence of the observed reaction rate is similar at 20 bar compared to 1 bar. Other investigators, e.g. Roberts and Harris (2000), have also observed activation energy to be independent of pressure within the chemical reaction controlled regime. This supports the notion that operation was predominantly within the chemical reaction controlled regime.

For a blend of seam 4 coal utilised for commercial gasification, Koekemoer (2009) determined activation energies ranging from 169 kJ/mol to 225 kJ/mol, following ambient pressure CO₂ gasification in a TGA at 1000 °C and above. The activation energies for char 4C and 4N are slightly larger, likely due to the use of a fixed-bed reactor and lower temperatures. du Toit (2013) determined an activation energy for a seam 4 char of 243 kJ/mol, following ambient pressure CO₂ gasification in a TGA at 900 °C and lower, agreeing very well with the results of char 4C and 4N at 1 bar.

5.2. Effect of pressure on char reaction rate

In this section, the results will be presented in such a manner as to illustrate the effect of increasing pressure on the CO₂ gasification reactivity of a char. Only results obtained at 900 °C will be presented here. The effect of pressure at other investigated temperatures is

similar to the observations at 900 °C. Additional graphs illustrating the effect of pressure are available as specific reactivity curves in Appendix A.1 for the remaining temperatures investigated, and as conversion curves in Appendix A.2 for all temperatures investigated.

5.2.1. Effect of pressure on char 5N

A comparison of the specific reactivity of char 5N at 900 °C, at total system pressures of 20 bar(a), 10 bar(a) and 1 bar(a), is presented in Figure 5.3. Since CO₂ is utilised at 30% molar concentration, the CO₂ partial pressures during these experiments are 6 bar, 3 bar and 0.3 bar, respectively.

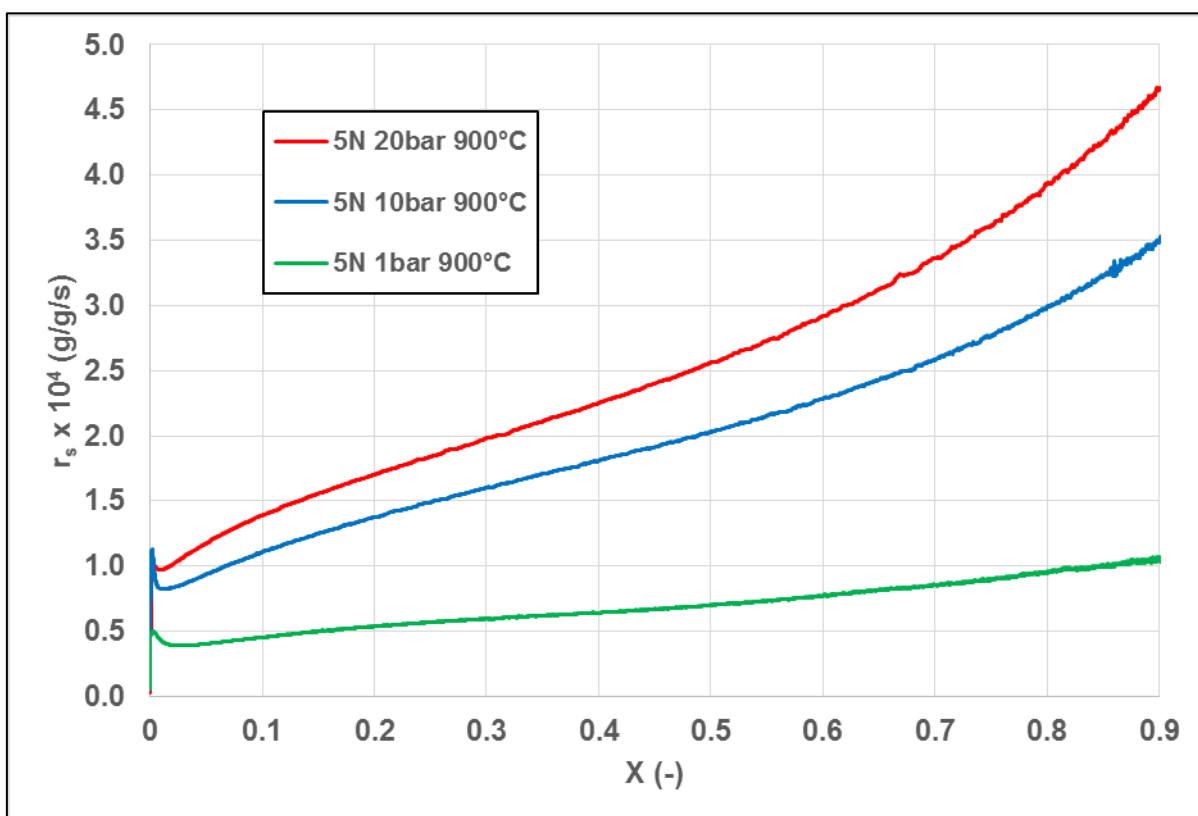


Figure 5.3: Effect of pressure on the specific reactivity of char 5N at 900 °C

With reference to Figure 5.3, when comparing the specific reactivity of char 5N at 900 °C and 1 bar (green line) to that at 10 bar (blue line), it is observed that the reactivity more than doubles at 10 bar compared to 1 bar. The increase in reactivity becomes even more pronounced as conversion progresses. When comparing the reactivity at 20 bar (red line) to that at 10 bar, it is observed that a significant increase in reactivity is still observed over the 10 bar results. When considering the results at a conversion of 50%, it is observed that the reactivity of char 5N at 10 bar had increased by 190% compared to the reactivity at 1 bar, while the reactivity at

20 bar had increased by 26% compared to the reactivity at 10 bar. In total the reactivity increased by 266% by increasing the pressure from 1 bar to 20 bar.

5.2.2. Effect of pressure on char 2C

A similar comparison, as was done for char 5N, will also be performed for char 2C, presented in Figure 5.4.

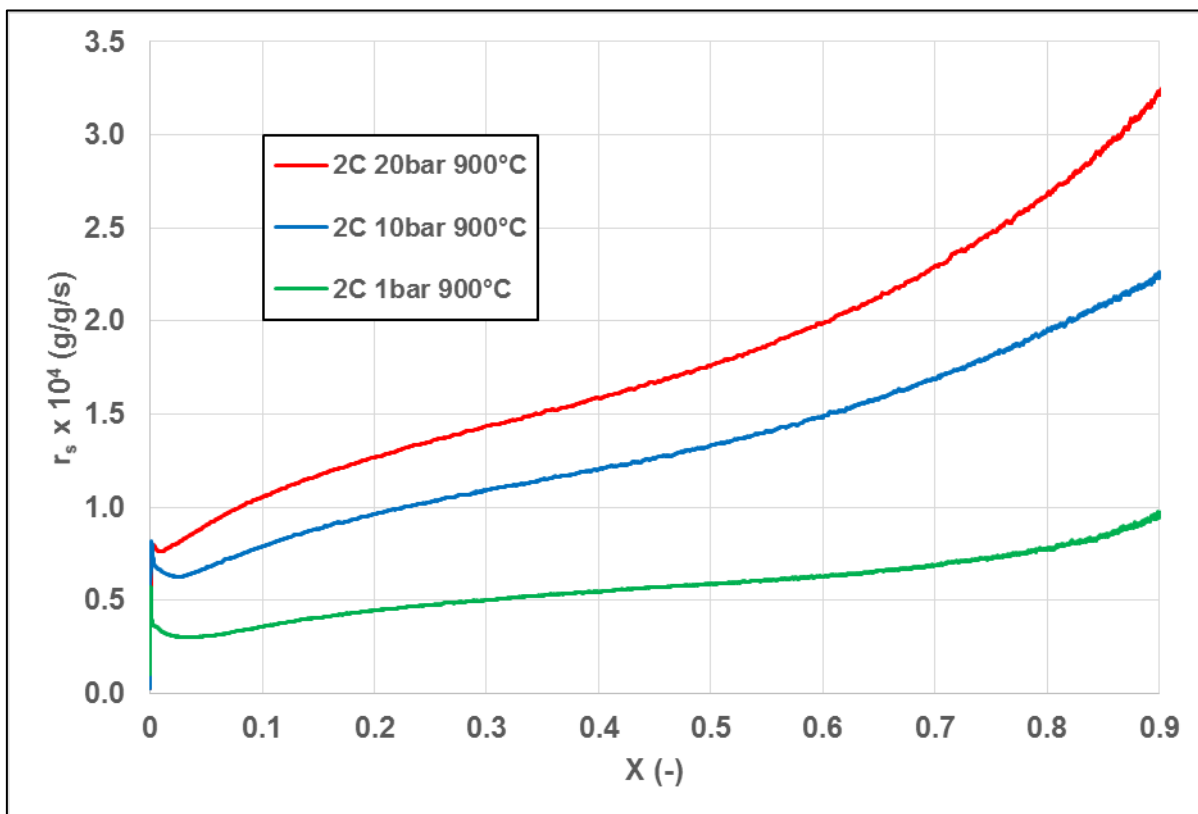


Figure 5.4: Effect of pressure on the specific reactivity of char 2C at 900 °C

In the case of char 2C, a similar trend is observed as was observed for char 5N. The reactivity at 10 bar is also approximately double the reactivity at 1 bar, although the increase is not as pronounced as in the case of char 5N. Char 2C did however indicate a greater relative increase in reactivity at 20 bar compared to 10 bar than the results of char 5N. When considering the results at a conversion of 50%, it is observed that the reactivity of char 2C at 10 bar had increased by 127% compared to the reactivity at 1 bar, while the reactivity at 20 bar had increased by 32% compared to the reactivity at 10 bar. In total the reactivity increased by 199% by increasing the pressure from 1 bar to 20 bar.

5.2.3. Effect of pressure on char 2N

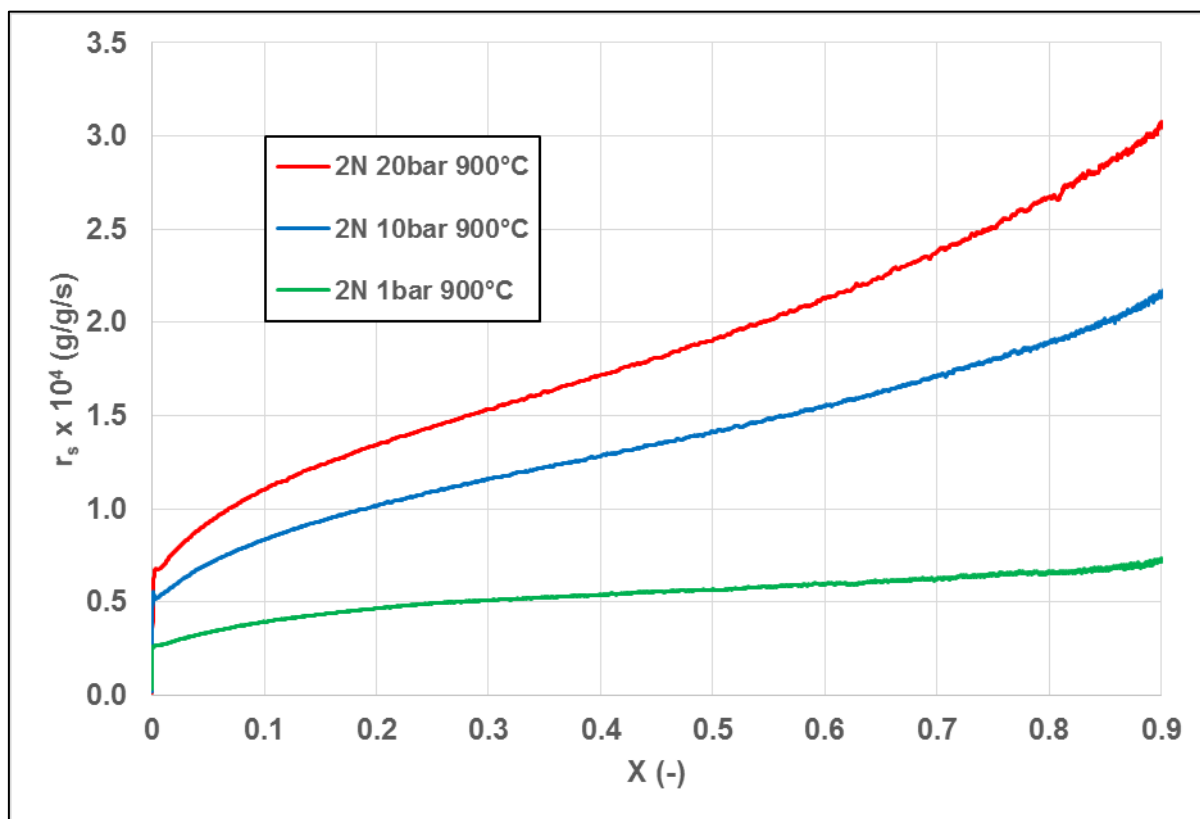


Figure 5.5: Effect of pressure on the specific reactivity of char 2N at 900 °C

By observing the results of char 2N, significant increases in reactivity are also noted as pressure is increased. When considering the results at a conversion of 50%, it is observed that the reactivity of char 2N at 10 bar had increased by 149% compared to the reactivity at 1 bar, while the reactivity at 20 bar had increased by 34% compared to the reactivity at 10 bar. In total the reactivity increased by 235% by increasing the pressure from 1 bar to 20 bar. It is thus clear that, despite having very similar specific reactivity at 1 bar as its 2C counterpart, the increase in reactivity due to pressure for 2N is more pronounced than 2C. 2C does however exhibit a greater upward inflection in specific reactivity at conversions higher than 70% than 2N. This indicates that coal samples, although appearing very similar in many regards, may display dissimilar gasification behaviour when subjected to high pressure.

5.2.4. Effect of pressure on char 4C

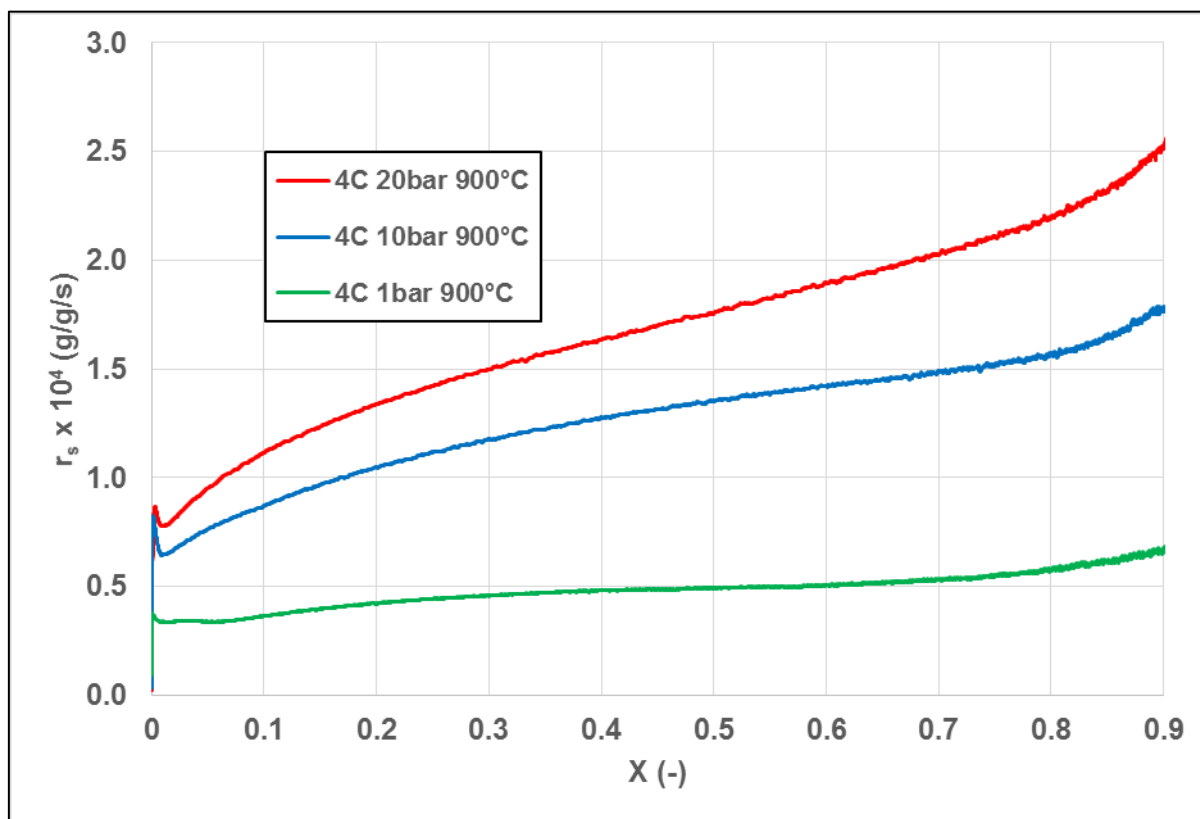


Figure 5.6: Effect of pressure on the specific reactivity of char 4C at 900 °C

In the case of char 4C, the overall trend is similar to what was observed for char 2C. When considering the results at a conversion of 50%, it is observed that the reactivity of char 4C at 10 bar had increased by 175% compared to the reactivity at 1 bar, while the reactivity at 20 bar had increased by 30% compared to the reactivity at 10 bar. In total the reactivity increased by 257% by increasing the pressure from 1 bar to 20 bar. Compared to char 2C and char 2N, char 4C exhibits a much greater increase in reactivity at 10 bar compared to 1 bar. The total increase in reactivity when comparing the 1 bar results with the 20 bar results is nearly as much as was observed for char 5N.

5.2.5. Effect of pressure on char 4N

Char 4N is generally the slowest reacting of the five samples investigated. 4N also represents an important benchmark, since coal with a similar origin and properties as 4N is currently the most utilised coal in commercial gasification operations in South Africa.

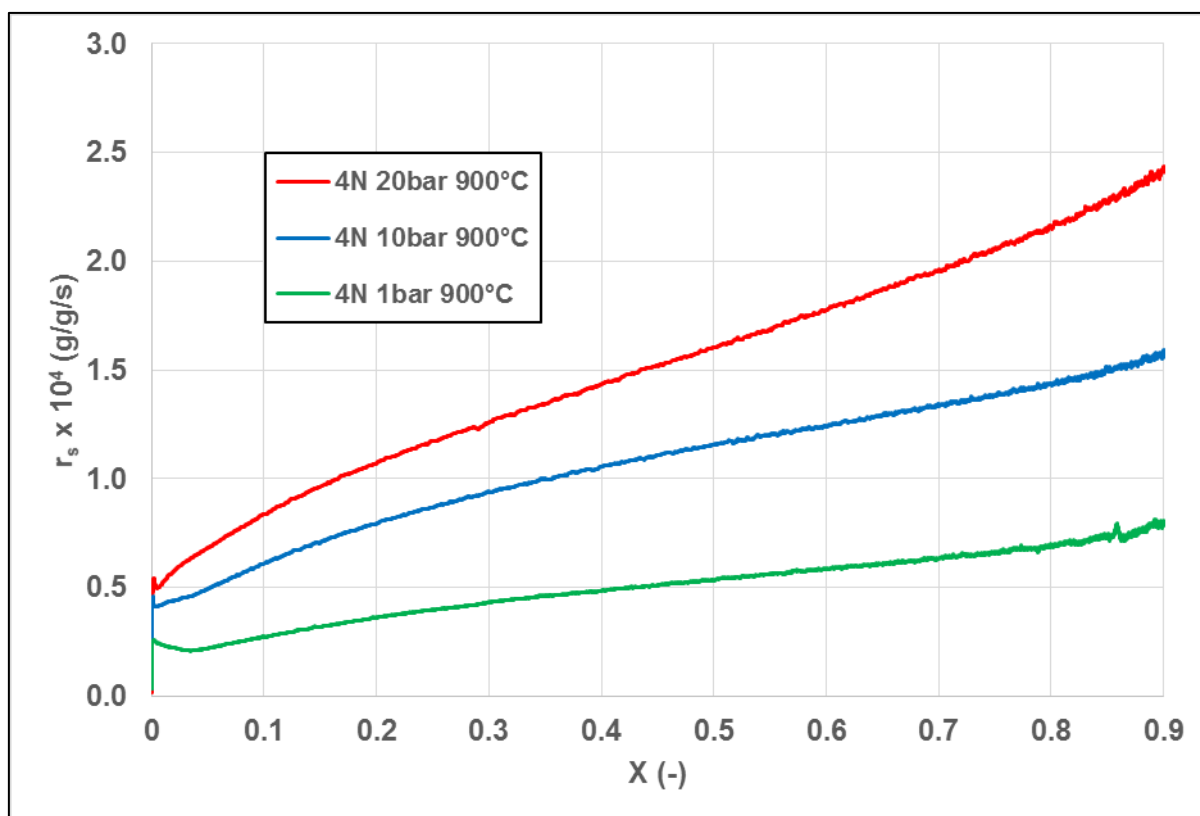


Figure 5.7: Effect of pressure on the specific reactivity of char 4N at 900 °C

Char 4N exhibits very linear specific reactivity trends, the pronounced upward inflection in reactivity at high conversion which was observed for the other samples is absent in char 4N. This indicates that the char reaction rate at high conversion remains relatively low. In practise this implies that char 4N requires significantly more time for the final remaining carbon in the sample to react completely. The possible implication thereof is that commercial gasification operations utilising 4N coal would either have to allow a higher residence time in the gasifier, or discharge ash containing more fixed carbon, compared to utilising one of the other coals investigated. When considering the results at a conversion of 50%, it is observed that the reactivity of char 4N at 10 bar had increased by 117% compared to the reactivity at 1 bar, while the reactivity at 20 bar had increased by 39% compared to the reactivity at 10 bar. In total the reactivity increased by 201% by increasing the pressure from 1 bar to 20 bar.

5.3. Comparative results

5.3.1. Comparison of the reactivity index of different chars

A simple and convenient means of comparing the reaction rate obtained from one experiment to that of another, is to make use of the reactivity indexes of those experiments. The reactivity index is a representation of the average rate of reaction observed of an experimental run by a single numeric value. This value is based on the time required to reach a specified sample fractional conversion. The specified fractional conversion usually considered is arbitrarily chosen as 50% conversion (Ye *et al.*, 1998). The reactivity index at 50% conversion is calculated by Equation 5.1.

$$R_{50} = \frac{0.5}{t_{50}} \quad \text{Equation 5.1}$$

From Equation 5.1 it is noted that a larger value for R_{50} corresponds to less time required to reach 50% conversion, and therefore interpreted to represent a faster reaction. The reactivity index values calculated for all char samples at all investigated temperatures and pressures are presented in Table 5.2.

Table 5.2: Reactivity index values for all gasification experiments

	Reactivity Index (hr^{-1})				
	Char 2C	Char 2N	Char 4C	Char 4N	Char 5N
825 °C					
1 bar	ND	ND	ND	ND	ND
10 bar	0.048	0.052	0.054	0.041	0.063
20 bar	0.063	0.067	0.068	0.054	0.081
850 °C					
1 bar	0.039	0.044	0.040	0.032	0.048
10 bar	0.086	0.093	0.089	0.072	0.117
20 bar	0.109	0.120	0.119	0.097	0.146
875 °C					
1 bar	0.077	0.070	0.072	0.064	0.087
10 bar	0.148	0.163	0.157	0.124	0.206
20 bar	0.189	0.205	0.198	0.162	0.259
900 °C					
1 bar	0.119	0.121	0.112	0.097	0.145
10 bar	0.259	0.270	0.278	0.211	0.373
20 bar	0.339	0.356	0.353	0.285	0.461
925 °C					
1 bar	0.204	0.205	0.191	0.155	0.264
10 bar	ND	ND	ND	ND	ND
20 bar	ND	ND	ND	ND	ND

ND – Not Determined

The results presented in Table 5.2 provide a means of quick and simple comparison of the representative reaction rates between the different chars and different gasification conditions. The reactivity indexes of char 4N at 1 bar are in good agreement to those determined by du Toit (2013) for a seam 4 char at ambient pressure, reported as 0.035 and 0.091 at 850 °C and 900 °C, respectively.

The reactivity index is not intended to be a precise measure of char reactivity, since only one value is considered per experiment. Furthermore, this value is based on an averaged observation, namely time to 50% conversion. For a more detailed and precise comparison of the reactivity of the different chars over a broad conversion range, it may be considered to directly compare the specific reactivity curves of the different chars with one another.

5.3.2. Comparison of the specific reactivity curves of different chars

In this section, the specific reactivity curves of different chars will be directly compared to one another. This presents a comparison of the reactivity of the different chars when gasified under the same conditions, and how the reactivity changes as the samples undergo conversion. The results will be presented separately for each pressure investigated, and only the results obtained at 900 °C will be presented here. Additional graphs providing a direct comparison of char reactivities are available as specific reactivity curves in Appendix A.6 for the remaining temperatures investigated, and as conversion curves in Appendix A.7 for all temperatures investigated.

5.3.2.1. Char reactivity at 20 bar gasification pressure

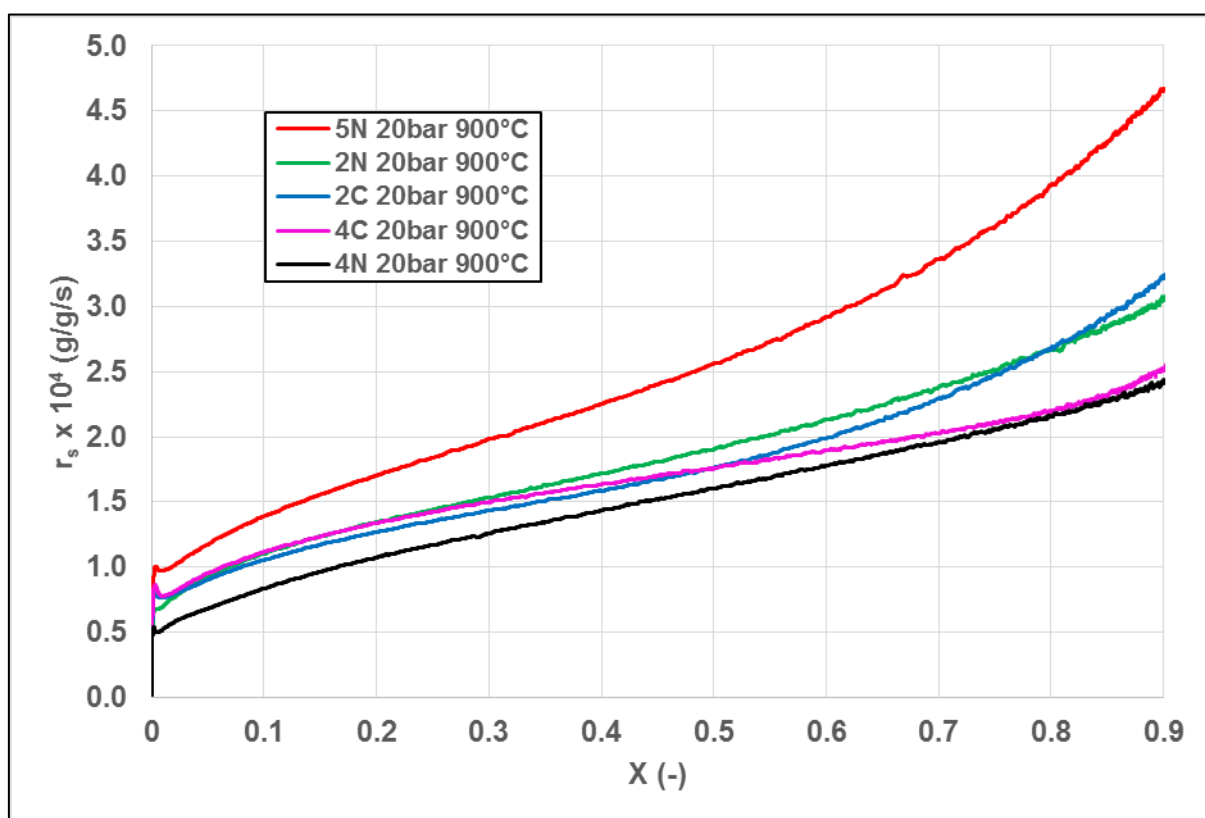


Figure 5.8: Comparison of char specific reactivity at 20 bar and 900 °C

Figure 5.8 presents the specific reactivity curves of all five chars gasified at 900 °C and 20 bar operating pressure. From this representation, the reaction rate and the behaviour of all chars can be directly compared to one another. In Figure 5.8 it is observed that char 5N (red line) initially exhibits higher reactivity than the other chars, and remains the fastest reacting as the samples undergo conversion. Char 2N (green line), char 2C (blue line) and char 4C (magenta

line) have similar initial reactivities. Char 2C exhibits an accelerated reactivity at high conversion, while char 4C exhibits a declined reactivity at high conversion. Char 4N (black line) is initially the slowest reacting char, and remains the slowest reacting of all the chars as the samples undergo conversion.

5.3.2.2. Char reactivity at 10 bar gasification pressure

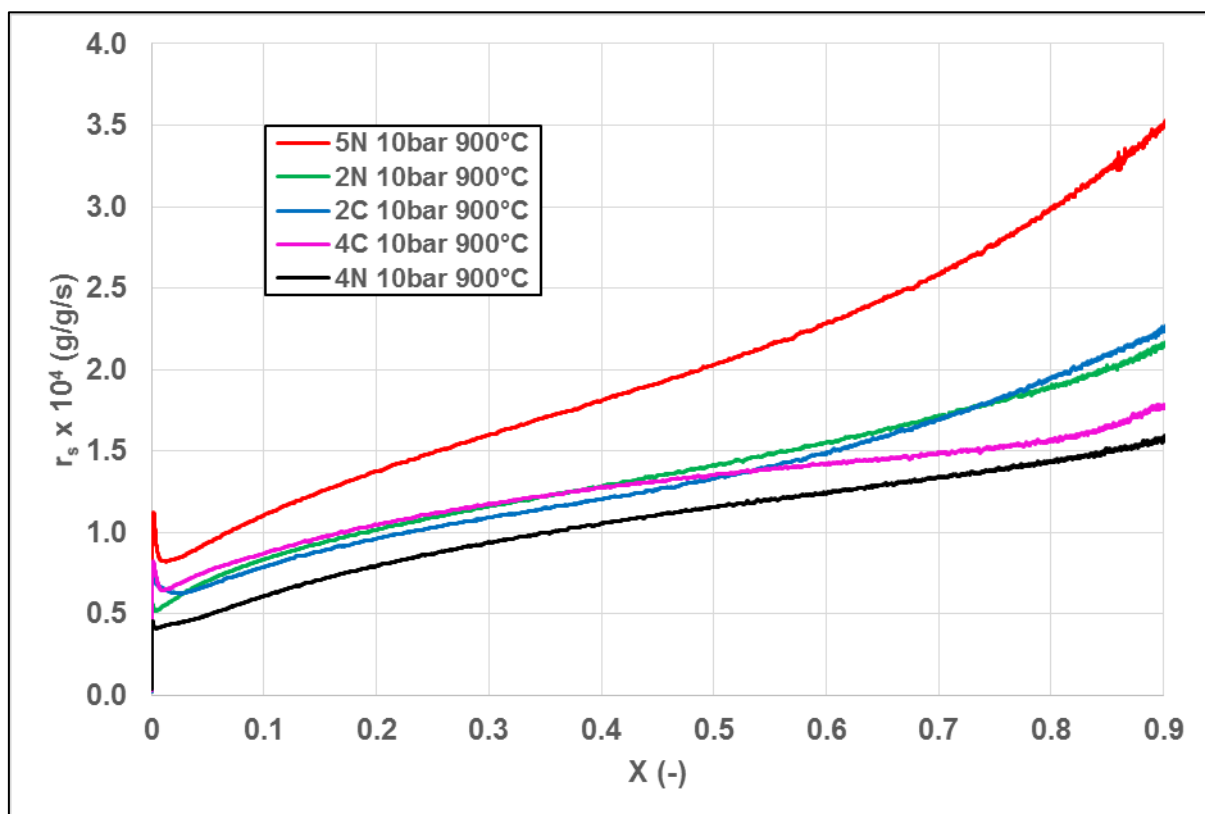


Figure 5.9: Comparison of char specific reactivity at 10 bar and 900 °C

Figure 5.9 presents the specific reactivity curves of all five chars gasified at 900 °C and 10 bar operating pressure. It is observed that all chars have appreciably lower specific reactivity at 10 bar compared to 20 bar. The results at 10 bar indicate that the behaviour of the chars, i.e. the manner in which the specific reactivity changes as the samples undergo conversion, is nearly identical to what was observed at 20 bar. The discussion of Figure 5.8 is thus also applicable to Figure 5.9. The similarity of the reaction profiles of the chars at 20 bar compared to 10 bar supports the notion of consistency, with regards to the ability of the experimental system to dependably determine the manner in which the chars behave when subjected to high pressure gasification. It further suggests that the gasification behaviour of a particular char type is very specific and unique.

5.3.2.3. Char reactivity at 1 bar gasification pressure

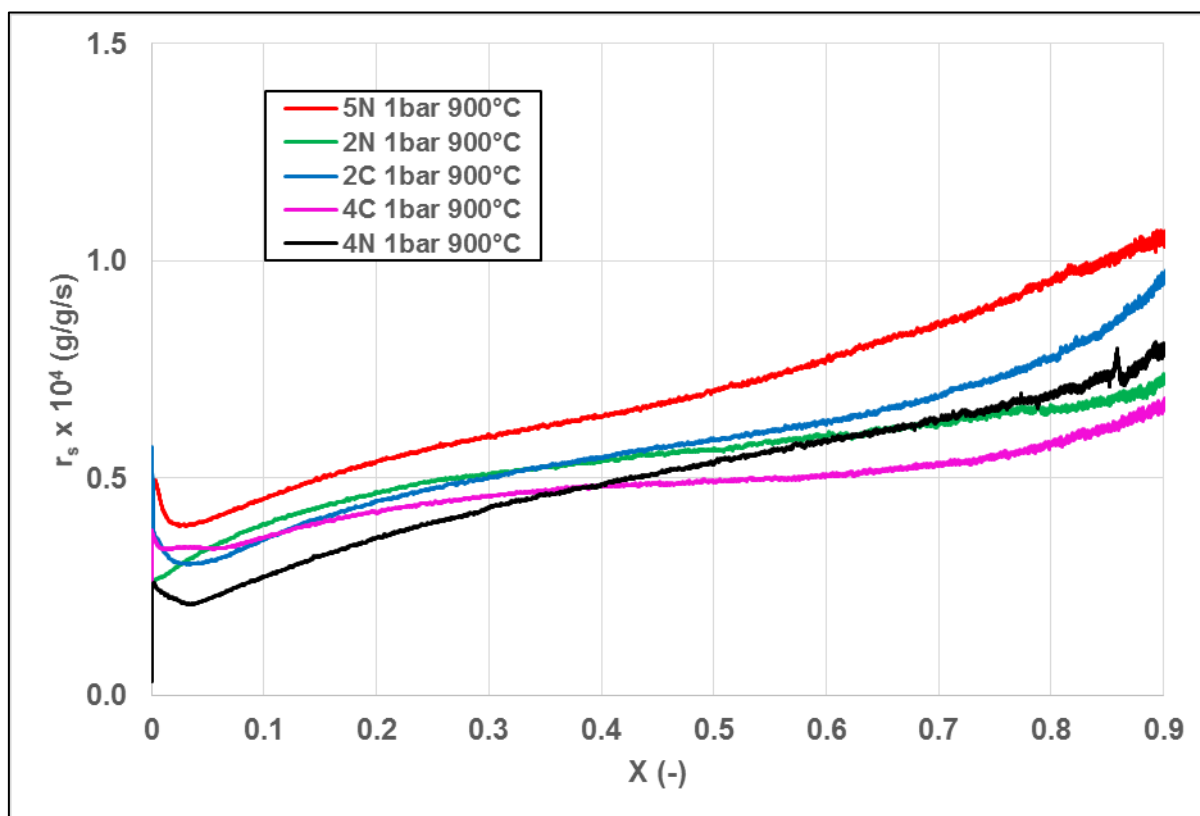


Figure 5.10: Comparison of char specific reactivity at 1 bar and 900 °C

Figure 5.10 presents the specific reactivity curves of all five chars gasified at 900 °C and 1 bar operating pressure. It is observed that all chars have significantly lower specific reactivity at 1 bar compared to 10 bar. In this case, the reaction profiles of the chars are not similar to the other results, indicating that the behaviour of the chars when gasified vary greatly at low pressure compared to high pressure. In Figure 5.10 it is once again observed that char 5N reacts the fastest, however its specific reactivity does not increase as sharply with conversion compared to the high pressure gasification results. The other chars rank similarly during the initial reaction stage, compared to the observations at high pressure. Their behaviour as the samples undergo further conversion is, however, much different to the observations made at high pressure. The reactivity of char 2N drops below the reactivity of char 2C much sooner, and continues to drop to even below the reactivity of char 4N at high conversion. Char 4C, having been consistently faster reacting than char 4N at high pressure, now becomes slower reacting than char 4N beyond 40% conversion. The discrepancies in relative behaviour at low pressure compared to high pressure do not appreciably manifest below 10% conversion. This suggests that kinetic constants determined at low conversion levels may be misleading, if

considered in isolation without a suitable structural model to account for the erratic behaviour at progressing conversion.

5.3.2.4. Char reactivity normalised to 4N benchmark reactivity

Coal 4N is the most similar to coal utilised for commercial gasification in South Africa of the samples studied, thus representing a benchmark against which the other samples' reactivity can be compared. By normalising the specific reactivity of all samples to that of 4N, over the entire conversion range, a sharp visualisation is obtained for the comparison of the char gasification behaviour relative to the benchmark. This procedure has been performed on the results at 1 bar and 20 bar, to provide a comparison between low pressure and high pressure, at 900 °C. The normalised results are presented in Figure 5.11, indicating the 1 bar results in the graph on the left, and the 20 bar results in the graph on the right. The reactivity of char 4N is represented by the flat horizontal black line at a magnitude of unity.

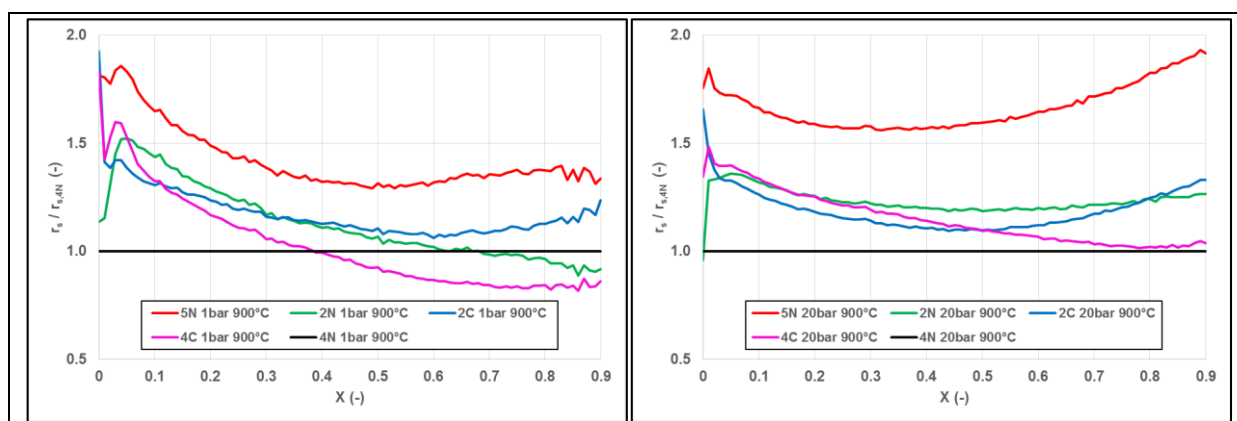


Figure 5.11: Char specific reactivity normalised to the reactivity of 4N

The normalised results presented in Figure 5.11 confirm that, not only do the chars' reactivities rank differently relative to char 4N at low pressure compared to high pressure, but they also rank differently relative to one another at low pressure compared to high pressure. The data presented in Figure 5.11 clearly suggests that experimental results generated at low pressure may not be accurate for inference of high pressure char gasification performance. Specific discussion of the normalised results at 1 bar and at 20 bar are as provided for the results presented in Figure 5.10 and Figure 5.8, respectively.

5.4. Summary of char gasification results

Increasing temperature exhibited an expected increasing influence on char reactivity for all runs. Apparent activation energies for CO₂ gasification of the chars at 20 bar total pressure were: 241 kJ/mol for char 2C, 242 kJ/mol for char 2N, 232 kJ/mol for char 4C, 233 kJ/mol for char 4N, and 248 kJ/mol for char 5N. These results do not differ by more than 12 kJ/mol than those obtained at other investigated pressures. These and other observations obtained empirically suggest that pore diffusion limitations were not appreciably present during the experimental investigation. Kinetic results are however still reported “as observed” instead of “true”, since an indisputable absence of mass transfer limitation has not been determined.

Increasing the gasification pressure, thereby increasing the reagent partial pressure, was observed to significantly increase the reaction rate of all chars at all investigated temperatures. This is in agreement with the research as reported in Sections 2.3.3 and 2.3.4, and summarised in Table 2.2. The extent of this influence is however dissimilar between different chars over the conversion range. Considering the specific reactivity at 50% conversion and 1 bar, the samples were in ascending order with regards to reaction rate: 4C < 4N < 2N < 2C < 5N, while at 20 bar the order changed to: 4N < 4C < 2C < 2N < 5N.

The results indicate that a saturation effect with regards to the reactivity with increasing reagent partial pressure is not yet apparent at 10 bar total pressure (3 bar CO₂ partial pressure). This conflicts with observations made by Hattingh (2009) of saturation behaviour already strongly apparent at 3 bar CO₂ partial pressure. The results also suggest that further gains in reactivity may be expected at CO₂ partial pressures greater than 6 bar. The anticipated gains in reactivity beyond 6 bar CO₂ partial pressure are expected to be dissimilar between different chars.

Of all the samples, char 4N exhibited the lowest relative increase in reactivity at 10 bar compared to 1 bar, but the greatest relative increase in reactivity at 20 bar compared to 10 bar. Conversely, Char 5N exhibited the greatest relative increase in reactivity at 10 bar compared to 1 bar, but the lowest relative increase in reactivity at 20 bar compared to 10 bar. With reference to the petrographic results presented in Table 3.5, it is observed that coal 4N has the highest inertinite content and the lowest vitrinite content, while coal 5N has the lowest inertinite content and the highest vitrinite content. Considering observations made by Messenböck *et al.* (2000), presented in Figure 2.1, high vitrinite coals might be expected to exhibit diminished gains in reactivity at pressures higher than 20 bar, while high inertinite coals might be expected to exhibit more significant gains in reactivity at pressures higher than 20 bar. This appears to concur with the observations made regarding the comparison between the

20 bar and 10 bar results of char 4N and char 5N, suggesting that petrographic composition may be an indicator of the extent of reactivity gains at increasing pressures.

Over the CO₂ partial pressure range of 0.3 bar to 6 bar, the reaction order was observed to be in the range of 0.35 ± 0.02 for all chars (determined in Appendix D.3). The natural logarithm of r_s at 10% conversion is observed to be linear with respect to the natural logarithm of CO₂ partial pressure, for all chars at all temperatures investigated. This suggests that the reaction order is independent of partial pressure, which conflicts with observations of Hodge (2008). This conclusion is however reached after considering only three data-points (pressures) per observation, and that this is only considered at the instant of 10% conversion. It is therefore deemed more valuable to consider a visual comparison of reactivity over an extended conversion range, to elucidate pressure dependence, as presented in Sections 5.2 and 5.3.2. This conflict may also be due to the inherent variability of different coal sources and experimental methods. It remains to be concluded whether total pressure has an influence on these chars, independent of reagent partial pressure, and investigation wherein reagent concentration is varied independently of total pressure is proposed to clarify. Based on the research reported in Section 2.3.4 and summarised in Table 2.2, total pressure is not expected to have an independent influence.

The effect of increasing pressure on the rate of char gasification has not been observed to be easily predictable over the conversion ranges. There is generally a discrepancy between how a char behaves at low (near ambient) pressure, compared to high (10 bar or greater) pressure. The chars do behave very similarly at 10 bar compared to 20 bar, but there appears to be no clear pattern as to predict the behaviour at 10 bar or 20 bar from the results at 1 bar alone. Char 2N, having a very similar origin and properties as char 2C, did not experience the same increase in reactivity as char 2C did. Similarly, char 4N, having a very similar origin and properties as char 4C, also did not experience the same increase in reactivity as char 4C did. 5N was the fastest reacting char at 1 bar, and experienced the greatest overall increase in reactivity at 20 bar compared to 1 bar. 2C was, on average, the second fastest reacting char at 1 bar, but experienced the lowest overall increase in reactivity at 20 bar compared to 1 bar.

The greatest variations in reaction rates between different chars typically manifest at conversions higher than what is usually considered for the determination of kinetic constants. This suggests that the usefulness of kinetic constants for predictive purposes may be diminished, and perhaps even misleading, if not considered over a wider conversion range. As an example, referring to Figure 5.11, it may appear simple to extrapolate the initial reaction rate of char 4C at 1 bar to 20 bar utilising the reaction order, but predicting that 4C would consistently react faster than 4N does not seem trivial (considering the similar reaction orders,

activation energies, and initial reactivity ratio between char 4C and 4N). If kinetic constants determined at only one instant at low conversion is considered for predictive purposes, it is necessary to utilise a suitable structural model combined with the kinetic model to account for the erratic behaviour at higher conversions. As is evident from Figure 4.3, the gasification rate exhibits a pronounced maximum at a point which is appreciably distant from the start of the reaction. The structural model is therefore proposed to incorporate at least two shaping parameters, in order to fit the experimental data exhibiting maximum reaction rates of differing magnitudes at differing levels of conversion between samples. Structural models with more than one parameter have been proposed in the past, such as a modification to the random pore model (Bhatia & Vartak, 1996).

5.5. Correlations with characterisation results

The observed specific reaction rate of all chars at 10% conversion was reduced to the pre-exponential factor, in order to eliminate the influence of operating conditions on char reactivity. The pre-exponential factor, A_s , was subsequently compared to all coal and char characterisation results, in order to determine whether a correlation exists between the inherent char reactivity and the characterised properties. It was apparent that coal petrographic properties exhibited the strongest relation to the pre-exponential factor. Specifically, the most useful coal properties to predict A_s was observed to be the total vitrinite content (TV), and in particular the detrovitrinite content (DV). Two further indices derived from the coal petrography were also observed to be useful, namely the maceral index (MI) defined by Su *et al.* (2001), and an adapted maceral index (AMI) defined in Appendix F. The char micropore surface area was not observed to correlate well with char reactivity, despite the apparent dependence on vitrinite content. Furthermore, no strong correlation was observed between char reactivity and total mineral matter content, or individual mineral presences.

Utilising any of the four indices mentioned above, namely TV, DV, MI or AMI, a value for the pre-exponential factor can be estimated, without the requirement of empirical reactivity testing (other than verification). The four respective correlations to calculate an estimated pre-exponential factor value, A_{calc} , are represented by the following equations:

$$A_{calc} = 267(TV^{2.7}) + 1307 \times 10^3 \quad \text{Equation 5.2}$$

$$A_{calc} = 7761 \times 10^3(MI^{1.2}) + 1116 \times 10^3 \quad \text{Equation 5.3}$$

$$A_{calc} = 3805 \times 10^3(AMI^{3.2}) + 1343 \times 10^3 \quad \text{Equation 5.4}$$

$$A_{calc} = 71220(DV^{1.6}) + 1186 \times 10^3 \quad \text{Equation 5.5}$$

In general, for the samples investigated, the accuracy of the indices to estimate A_s increase in the order $TV < MI < AMI < DV$. Thus, depending on the detail of petrographic information available, the index to utilise, with its respective correlation, would rank in this order. A practical application for the use of these correlations would be to calculate the expected specific reactivity, r_{calc} , of a sample, based on its petrographic characteristics. This may be achieved by the use of a reaction rate model, an example of such represented by Equation 5.6.

$$r_{calc} = P_{CO_2}^n A_{calc} e^{-\frac{E_{a,app}}{RT}} \quad \text{Equation 5.6}$$

As an example, Equation 5.6 was applied with Equation 5.5 substituted for A_{calc} , to predict the reactivity of the five chars at operating conditions of 875 °C and 10 bar. The values for the parameters n and $E_{a,app}$ in Equation 5.6 were utilised as reported in Table F1. The predicted values, r_{calc} , were within 5% of the experimentally determined values, r_s . The results of this example are reported in further detail in Table F4. There thus exists great potential to utilise these correlations and a reaction rate model, in combination with a suitable structural model, to model gasification rate behaviour.

Further detail regarding the determination, testing, and application of these correlations is available in Appendix F.

CHAPTER 6

Conclusions and Recommendations

Chapter 6 presents the conclusions and recommendations arising from the investigation and results of this study. Conclusions will be provided regarding the experimental results and the significance thereof. Recommendations will be provided regarding valuable considerations for future studies on the subject of this investigation.

6.1. Conclusions

6.1.1. Development of high-pressure reactor system

A high-pressure fixed-bed reactor (HP-FBR) system was successfully designed, constructed and commissioned, in order to provide the necessary experimental functionality to determine char-CO₂ gasification reactivity at elevated pressures. The system currently possesses the capability of operating at up to 1000 °C and 20 bar(a). Accurate monitoring and control of reaction conditions is possible, with the ability to easily confirm that desired conditions were maintained adequately stable over extended experiment durations. The experimental repeatability of the system was determined to be excellent. The effect of operating variables, such as gas flow rates and sample mass, on observed reaction rates was well characterised. Reaction conditions and operating variables were subsequently chosen such that there are no significant adverse interferences or influence on the observed reaction rates. The choice of char particle size, in conjunction with reaction temperature, remains as a very important and sensitive factor with regards to determining reaction rates within the desired reaction regime.

6.1.2. Coal characterisation

Five coals from three different seams of the Highveld coalfield of South Africa were characterised by routine laboratory techniques. The different coals and chars had widely varying properties with regards to composition, pore surface area and mineral matter content. It was observed that gasification reaction rate correlated well with coal petrographic composition and indices, particularly detrovitrinite content. Empirical models, based on petrographic characteristics, were proposed as predictors of the chemical reaction rate. Strong correlations were however not apparent between gasification reaction rate and factors such as mineral matter content or micropore surface area, usually reported as being strongly correlated with gasification reaction rate. The seam 4 coals investigated, particularly 4N, have characteristics agreeing very well with coals generally utilised for commercial gasification in South Africa, therefore serving as a suitable benchmark.

6.1.3. Gasification conditions

It is consistently observed that an increase in gasification temperature has a substantial increasing effect on the gasification reactivity. It is also consistently observed that an increase

in operating pressure, resulting in an increase in reagent partial pressure, significantly increases the observed reaction rate. The results indicate that the gasification reaction rate between 10 bar and 20 bar operating pressure (3 bar and 6 bar CO₂ partial pressure) is not yet saturated. The results suggest that further gains in reactivity are expected at greater partial pressures. The activation energies observed for the CO₂ gasification of the chars were on average 241 kJ/mol for char 2C, 239 kJ/mol for char 2N, 234 kJ/mol for char 4C, 237 kJ/mol for char 4N, and 252 kJ/mol for char 5N. The activation energies were not observed to vary appreciably with increasing operating pressure. The observed activation energies of the different chars are very similar, despite the differences in coal properties and gasification reactivity between the different chars.

6.1.4. Gasification behaviour at elevated pressure

The reaction orders with regards to CO₂ partial pressure are 0.342 for char 2C, 0.333 for char 2N, 0.357 for char 4C, 0.370 for char 4N, and 0.369 for char 5N. The observed reaction orders of the different chars are very similar, despite the differences in coal properties and gasification reactivity between the different chars, to such an extent that the reaction order may be considered to be 0.35 ± 0.02 for all chars. The reaction orders were not observed to vary with increasing partial pressures, but were seemingly constant over the partial pressure range investigated. Kinetic constants are only resolved at a specific instant throughout the course of the reaction, in this study at 10% carbon conversion. The consistency with regards to reaction order and activation energy is therefore not necessarily an indication that the gasification behaviour at elevated pressure is easily predictable over the entire conversion range.

The gasification reactivity is conveniently illustrated graphically as carbon reactivity normalised to instantaneous carbon content (specific reactivity), as a function of sample conversion. In this visualisation it is clear to observe in which manner the chars behave over the entire conversion range with regards to gasification reaction rate. When observing these results, it is clear that there is a significant difference between the gasification behaviour of the chars at low pressure, compared to the gasification behaviour at high pressure. This suggests that empirical results obtained at low (near ambient) pressure, may be poor predictors of gasification behaviour at higher pressure, as encountered in commercial equipment. At 1 bar operating pressure, the char reactivity is generally in ascending order: $4C < 4N < 2N < 2C < 5N$. At 20 bar operating pressure, the char reactivity is generally in ascending order: $4N < 2C < 4C < 2N < 5N$. This ranking is however not constant over the entire conversion range, as the reaction rates of the chars continuously change relative to one another and may overlap.

Since the comparative char behaviour is not consistent between low and high pressure, the behaviour cannot be attributed to the operating conditions alone, and therefore cannot be predicted solely by models accounting for the influence of operating conditions. It appears that in order to enable modelling and predictions of high pressure performance, particularly at conversions greater than 10%, a suitable structural model has to be incorporated to account for the conversion behaviour. Until this is accomplished, dependable indications of gasification behaviour at high pressure can perhaps only be determined empirically. The availability of high pressure kinetic results should, however, aid in making modelling and performance prediction for commercial operations more dependable, as the requirement of uncertain extrapolation is reduced.

6.2. Recommendations

Based on the knowledge and experience gained from this study, the following recommendations are made with regards to future studies to supplement the results obtained in this investigation:

It is proposed to study the effects of reagent partial pressure independently of total pressure, i.e. varying both reagent concentration and operating pressure. This may resolve the uncertainty regarding total pressure dependence of gasification reactivity.

It is proposed to conduct a study, similar in scope to this investigation, utilising steam as the gasification reagent. The steam gasification reaction is very important in commercial operations, thus the influence of high steam partial pressure on the gasification reactivity of South African coals may be very valuable.

More elaborate studies may be considered wherein the high pressure gasification of South African coal is conducted with both steam and CO₂ as reagents simultaneously. Similarly as with the influence of total pressure on the gasification reactivity, the influence of CO₂ on the rate of steam gasification is still disputed. Some authors report that a competitive model represents experimental mixed reagent gasification data, while others report an additive model to better represent the data (Irfan *et al.*, 2011; Li *et al.*, 2014). Conducting such research in the equipment developed for this study, which has demonstrated excellent dependability and repeatability, may provide valuable insight into this issue.

More elaborate studies may be considered wherein known concentrations of gasification reaction products are fed concurrently with the reagent into the system. This will be valuable for the study of product inhibition on the gasification kinetics. This may be very useful to the

industry, since inhibition is likely to occur in commercial equipment where differential operation is not present. More elaborate models incorporating inhibition, such as Langmuir-Hinshelwood reaction rate models, may be more accurate with regards to describing the experimental observations, especially with gas composition conditions better emulating commercial operations.

More elaborate studies may be considered wherein operation in the mass transfer limited regime (pore diffusion resistance) is undertaken. This, in conjunction with results obtained in the chemical reaction controlled regime, may be valuable in quantifying the extent of pore diffusion resistance, the temperature and other conditions at which it becomes significant, and the models applicable to accurately describe it.

It may be insightful to consider further studies at higher pressures than investigated here. It is apparent from the experimental results that further increases in reaction rate, beyond 20 bar total pressure and 6 bar CO₂ partial pressure, is expected. Studies at higher reagent partial pressures may reveal further changes in gasification behaviour than what was already observed. The point at which possible reaction rate saturation becomes apparent may also be determined from higher pressure studies.

The proposition of accurately predicting coal gasification behaviour, solely from routine analysis results of coal characteristics, remains elusive. Further studies in this regard may resolve useful correlations which could possibly decrease the reliance on empirical testing in the future, with regards to determining gasification behaviour of different coals. In particular, a suitable structural model, proposed to incorporate at least two shaping parameters, is required to supplement a reaction rate model in order to provide the capability of modelling the erratic gasification behaviour observed at elevated pressure, especially at high conversion.

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Appendix A

Expanded Experimental Results

In this section, graphical representations of the processed data of the experimental gasification runs are presented. The gasification reactivity results are presented in several different combinations, each combination highlighting the effect of a single variable on the results. Depending on the subject of interest, different combinations will provide the best visualisation of the dependency between the results and the varied parameters. The combinations available are the effect of pressure (on a particular char at the same temperature), the effect of temperature (on a particular char at the same pressure) and a direct comparison of the different chars (comparing reactivity at the same temperature and pressure). Furthermore, these results are available as both specific reactivity curves and conversion curves, in order to suit any preference for the result representation. Arrhenius plots derived from the results are also presented here. Interpretation of the results presented in these graphs can be done analogous to the examples discussed in the respective sections of the main text (Chapter 5).

A.1: Specific reactivity curves illustrating the effect of pressure on char reactivity

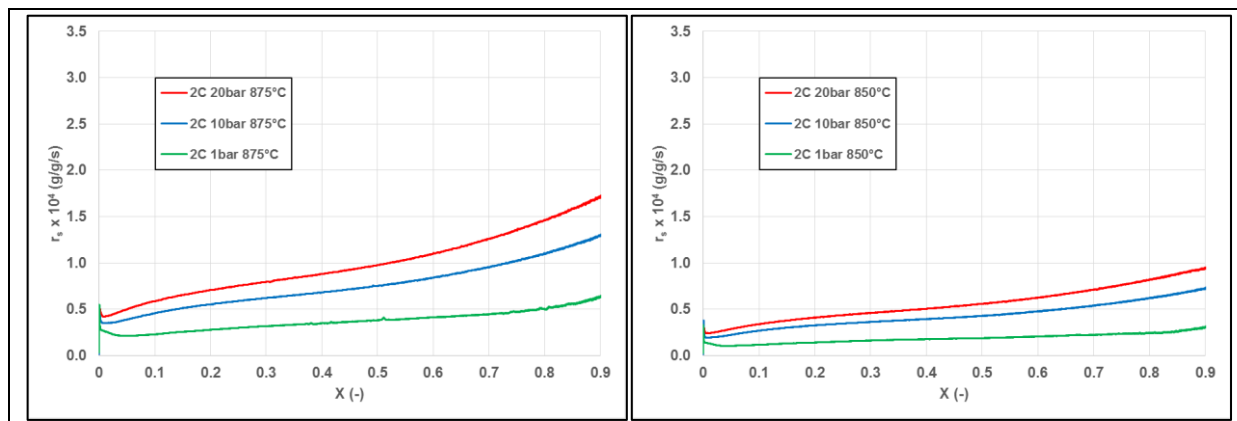


Figure A1: Effect of pressure on the specific reactivity of char 2C at 875 °C and 850 °C

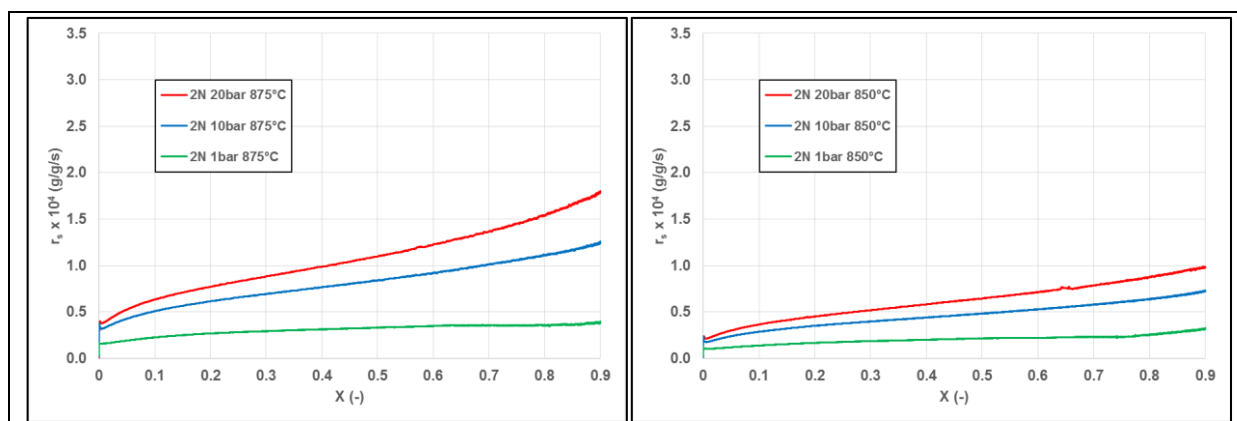


Figure A2: Effect of pressure on the specific reactivity of char 2N at 875 °C and 850 °C

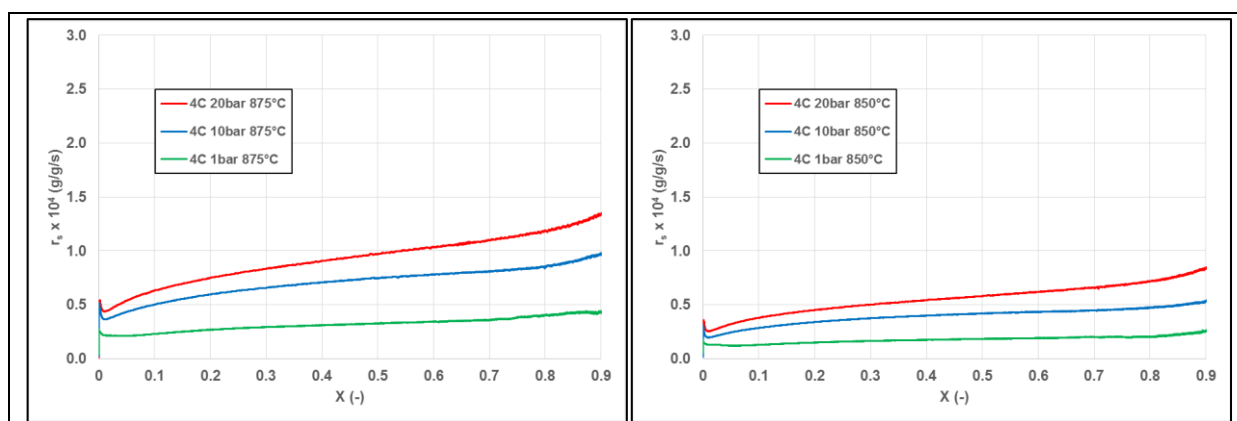


Figure A3: Effect of pressure on the specific reactivity of char 4C at 875 °C and 850 °C

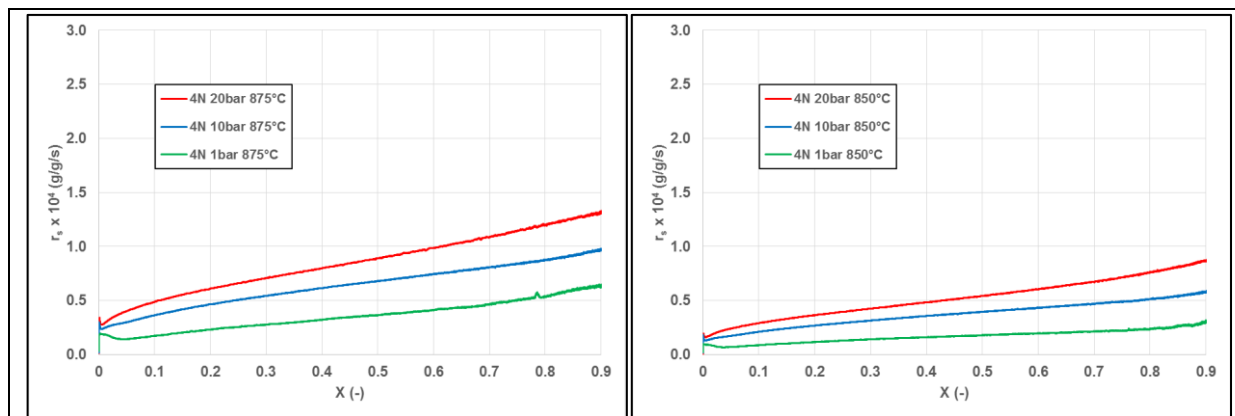


Figure A4: Effect of pressure on the specific reactivity of char 4N at 875 °C and 850 °C

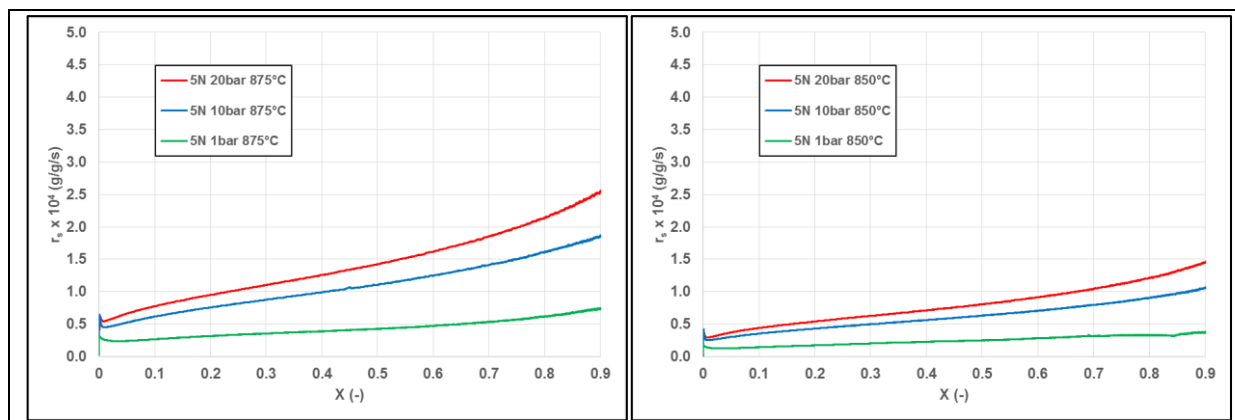


Figure A5: Effect of pressure on the specific reactivity of char 5N at 875 °C and 850 °C

A.2: Conversion curves illustrating the effect of pressure on char conversion

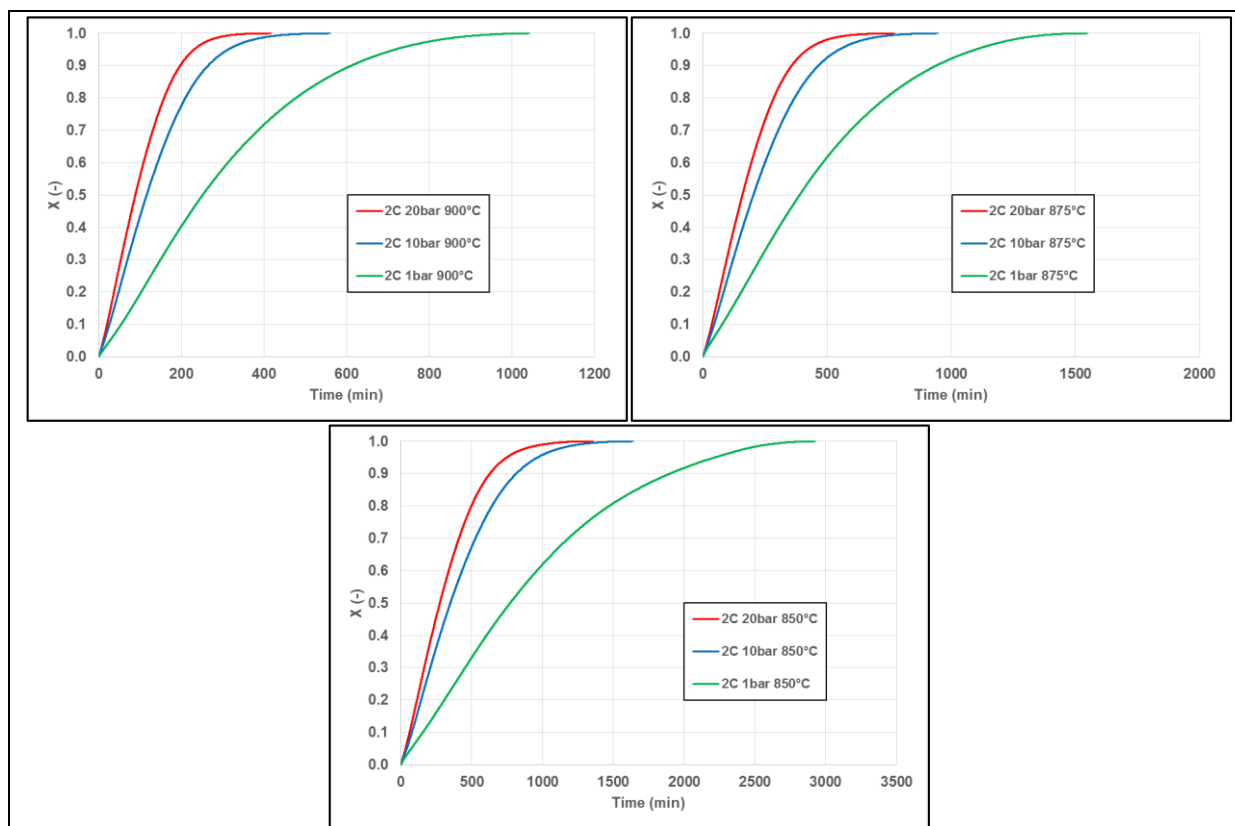


Figure A6: Effect of pressure on the conversion profiles of char 2C

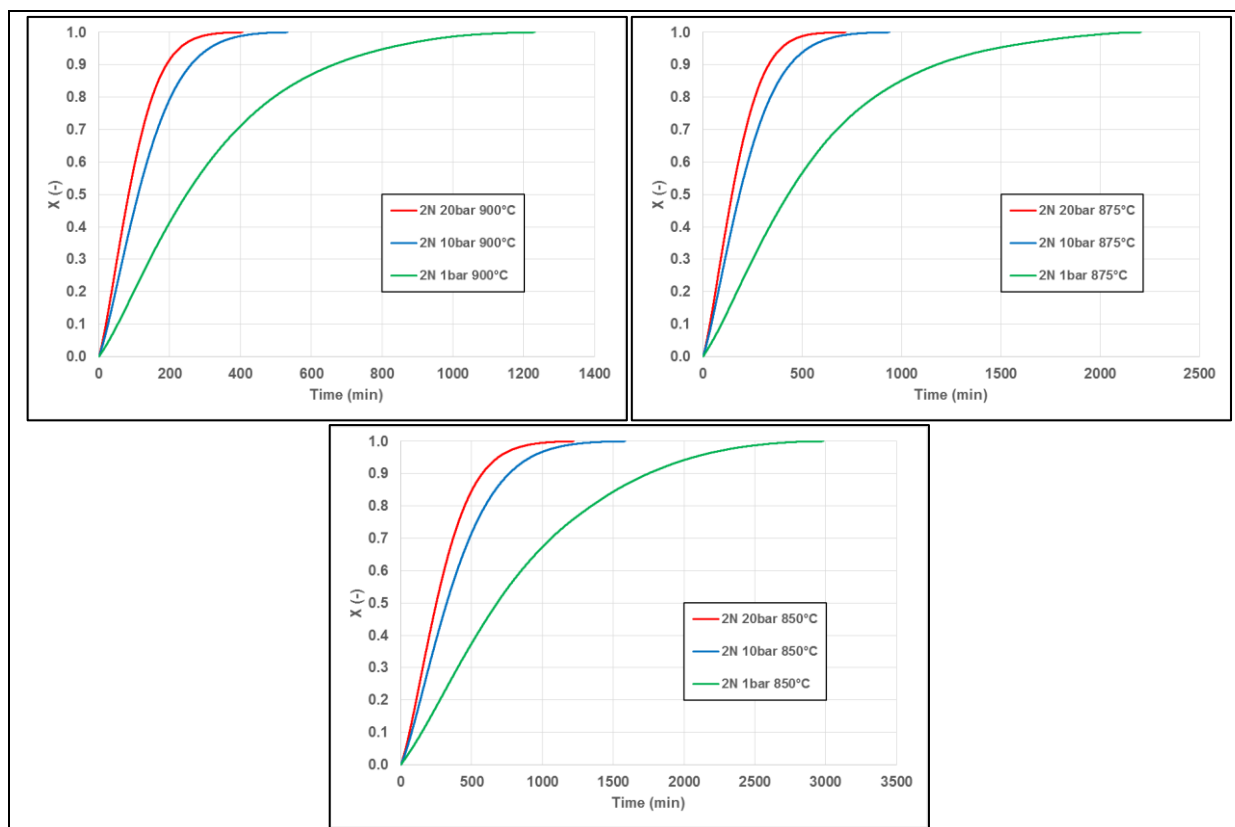


Figure A7: Effect of pressure on the conversion profiles of char 2N

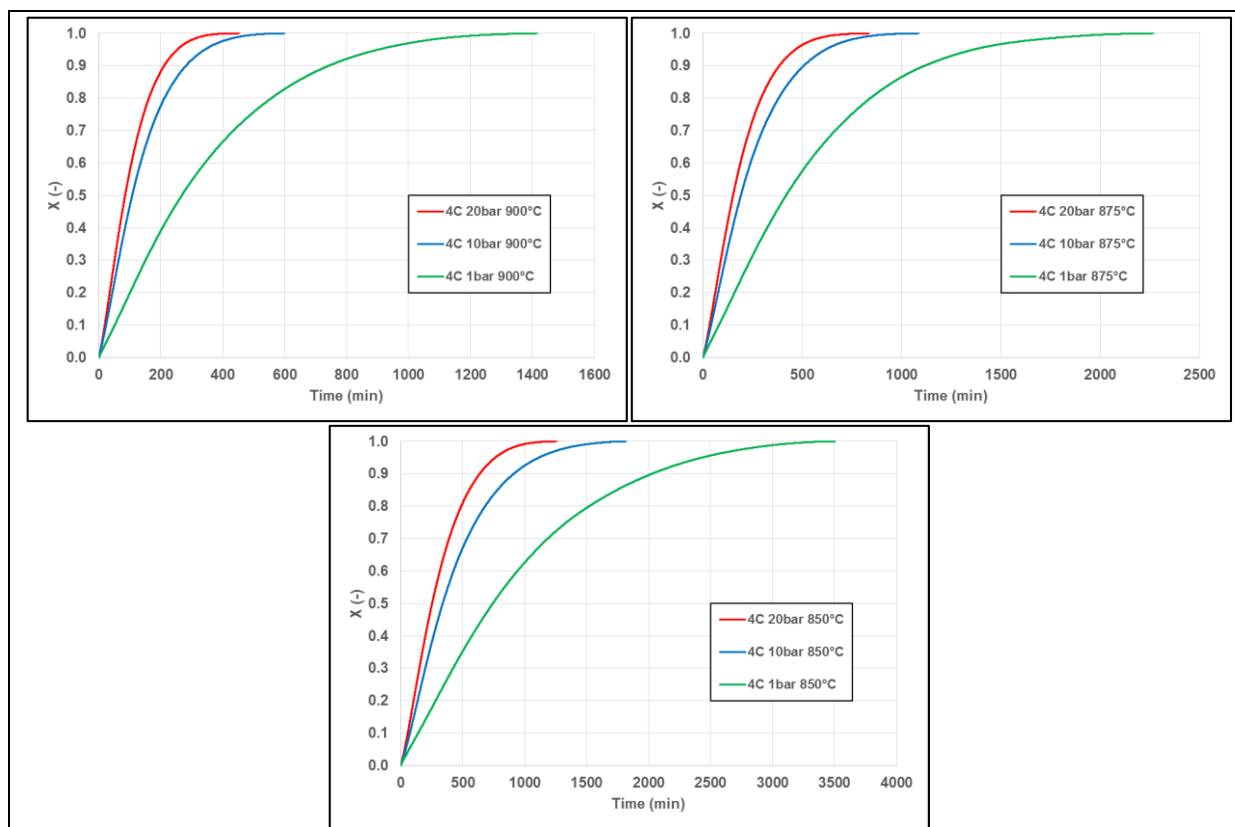


Figure A8: Effect of pressure on the conversion profiles of char 4C

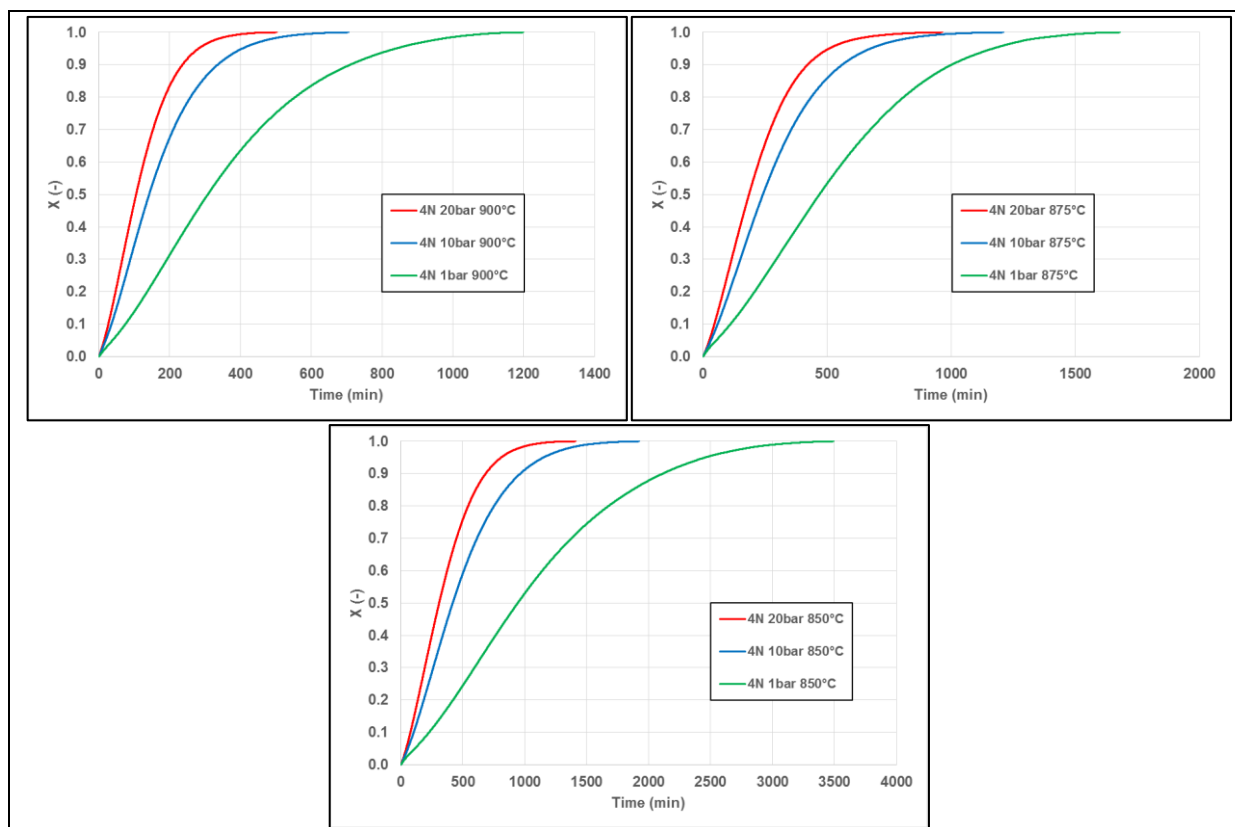


Figure A9: Effect of pressure on the conversion profiles of char 4N

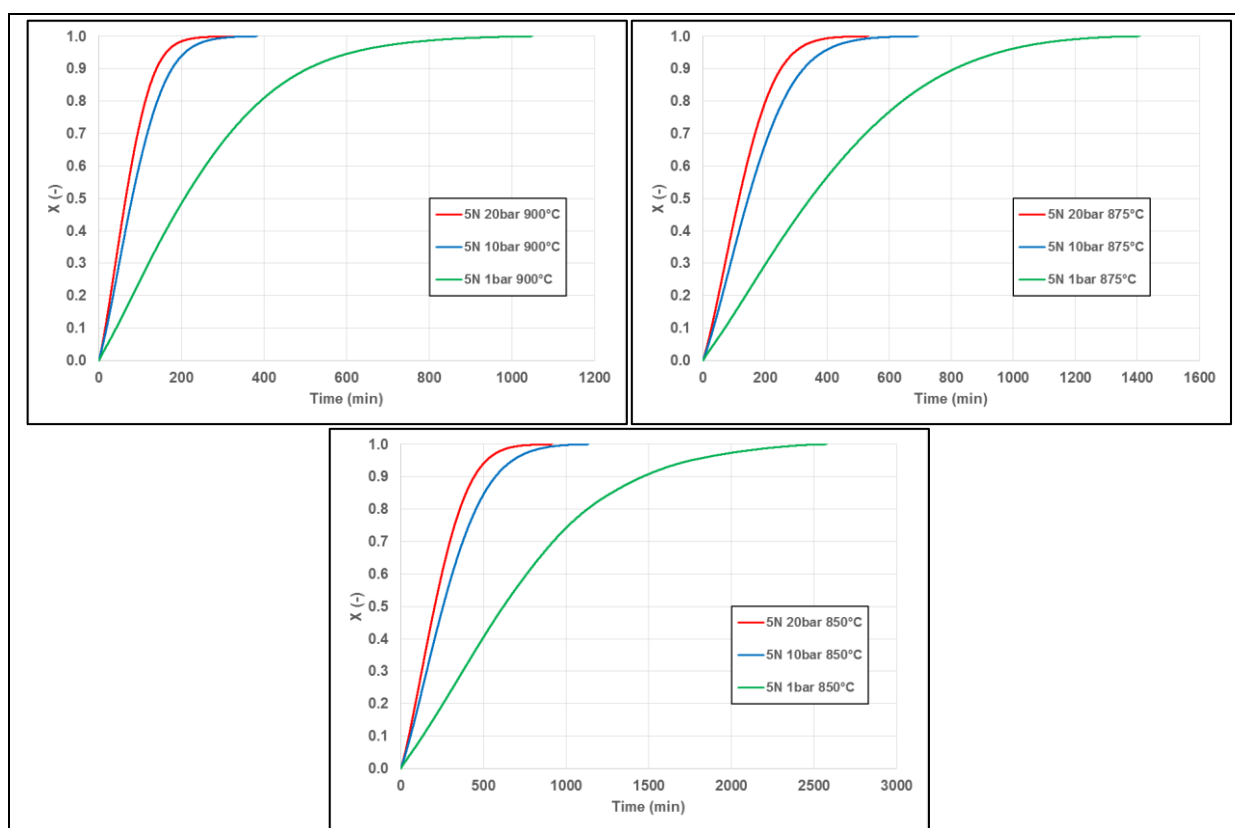


Figure A10: Effect of pressure on the conversion profiles of char 5N

A.3: Specific reactivity curves illustrating the effect of temperature on char reactivity

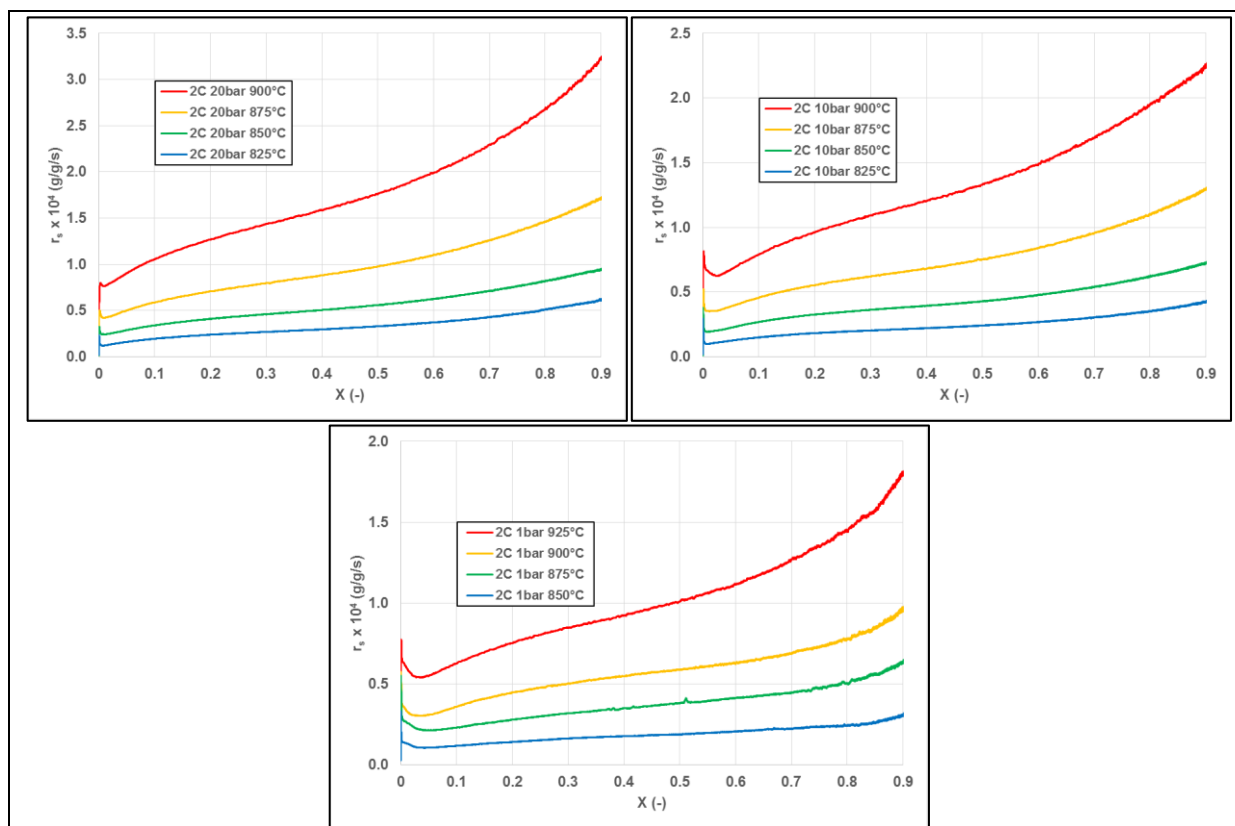


Figure A11: Effect of temperature on the specific reactivity of char 2C

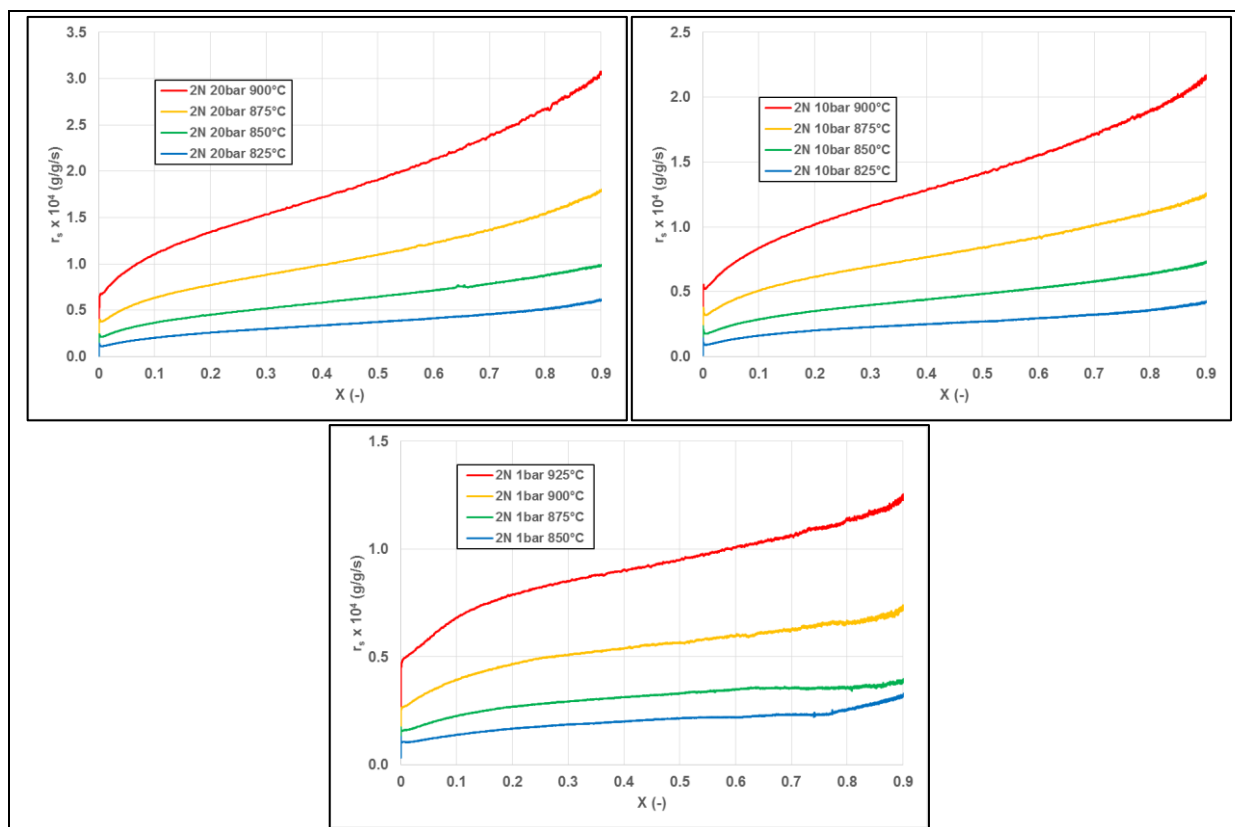


Figure A12: Effect of temperature on the specific reactivity of char 2N

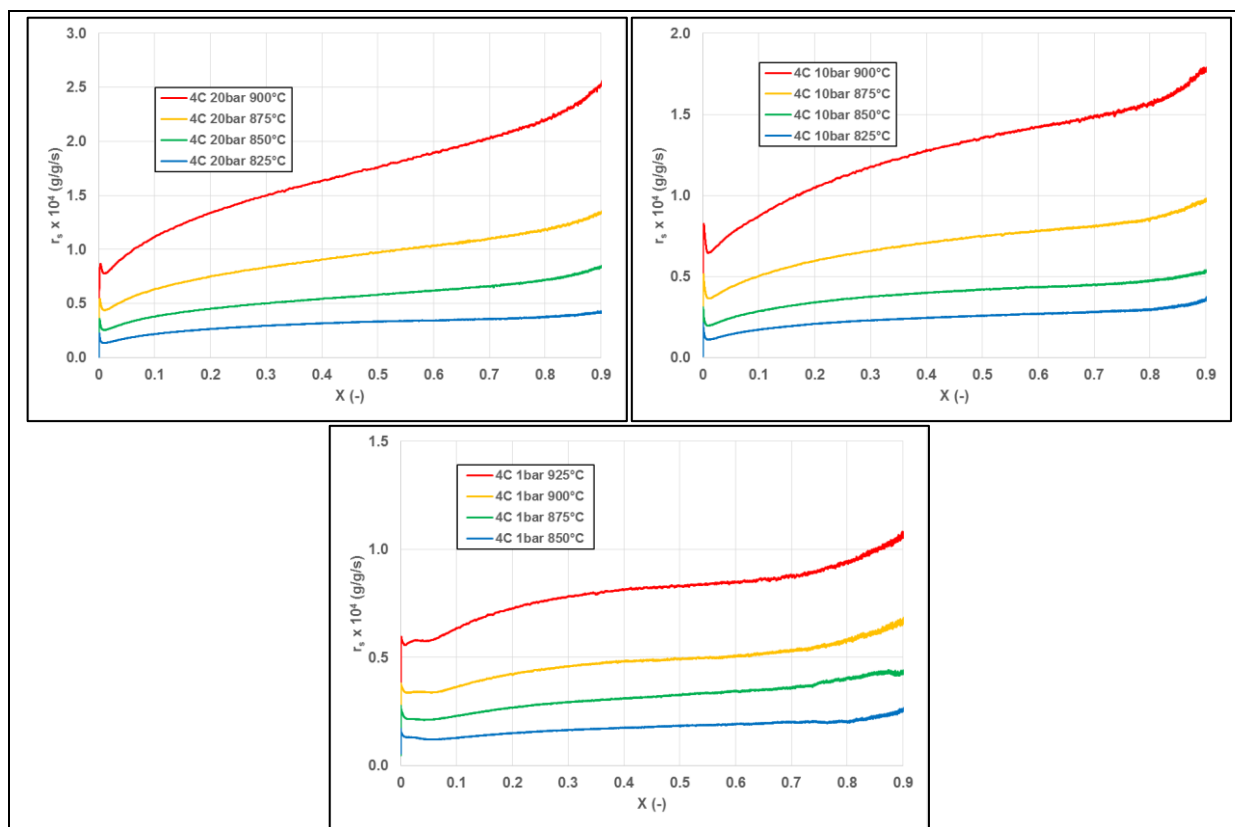


Figure A13: Effect of temperature on the specific reactivity of char 4C

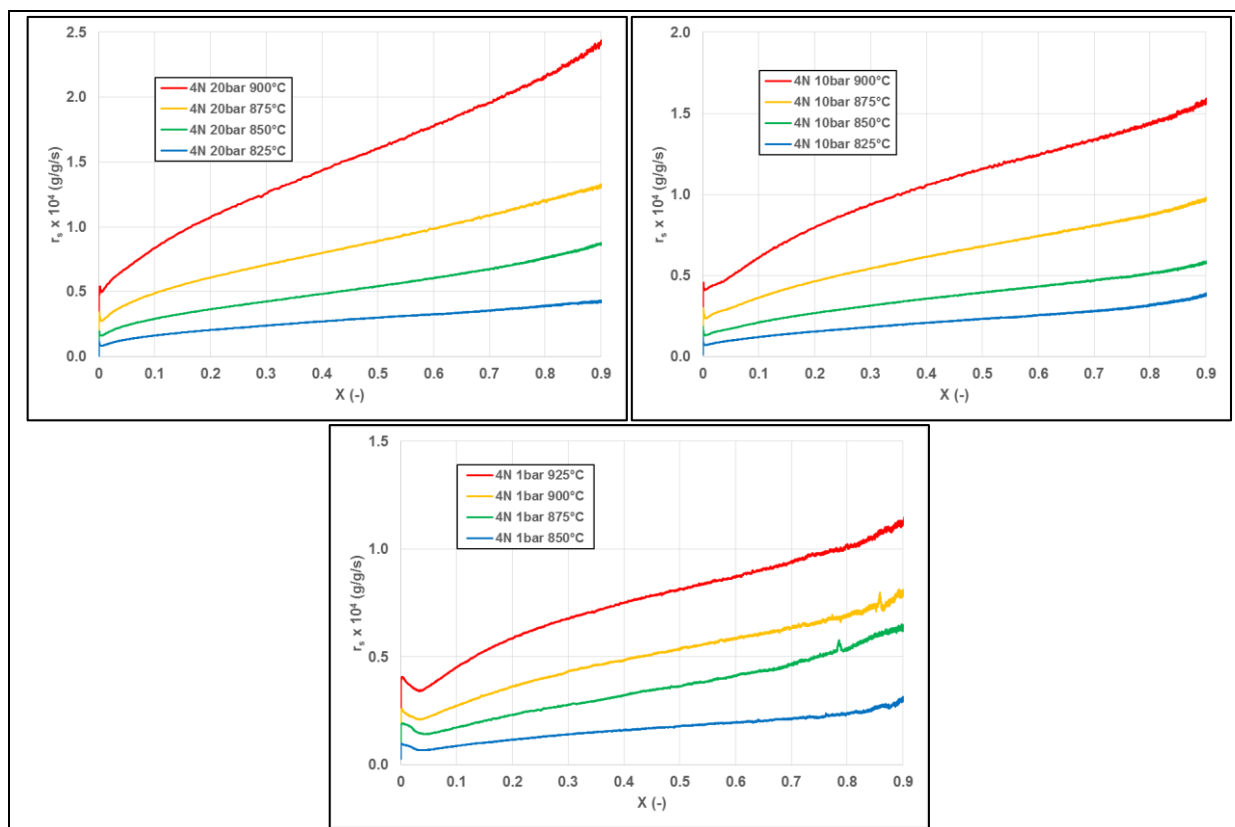


Figure A14: Effect of temperature on the specific reactivity of char 4N

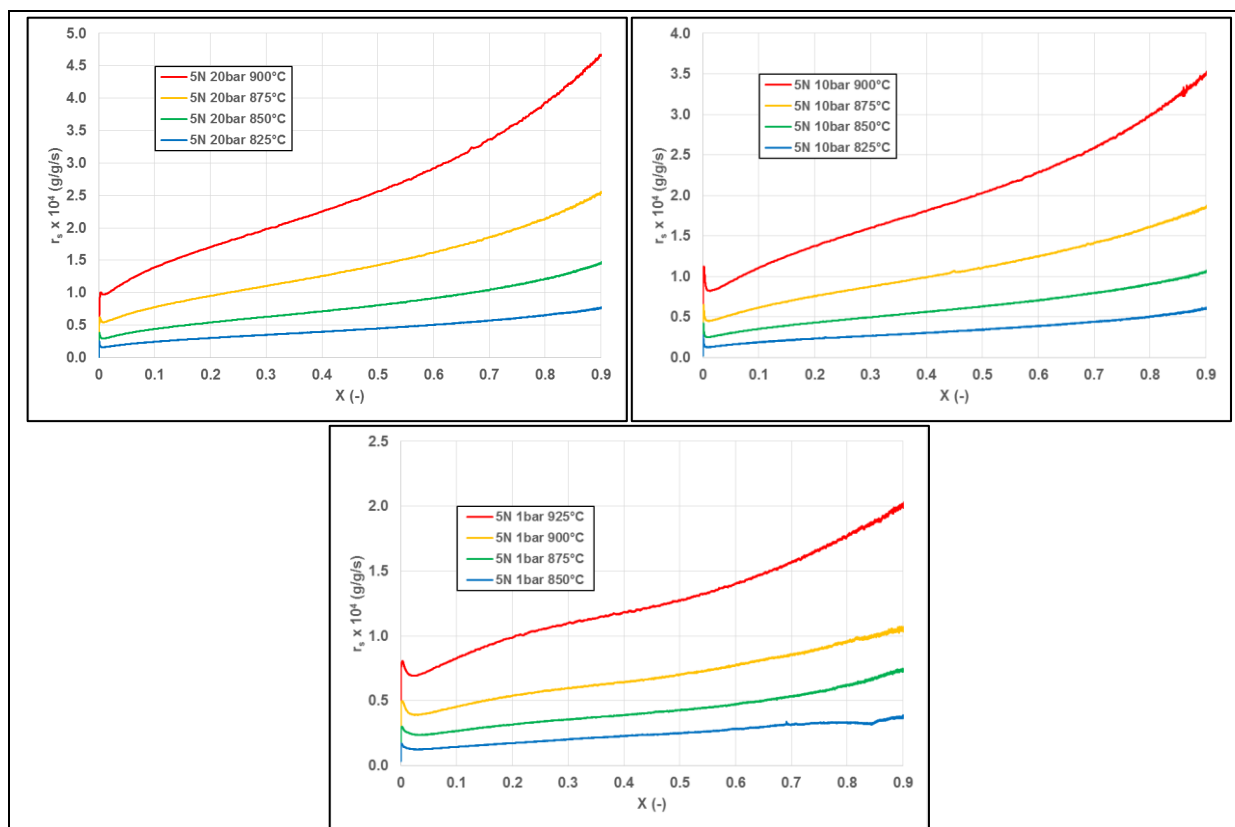


Figure A15: Effect of temperature on the specific reactivity of char 5N

A.4: Conversion curves illustrating the effect of temperature on char conversion

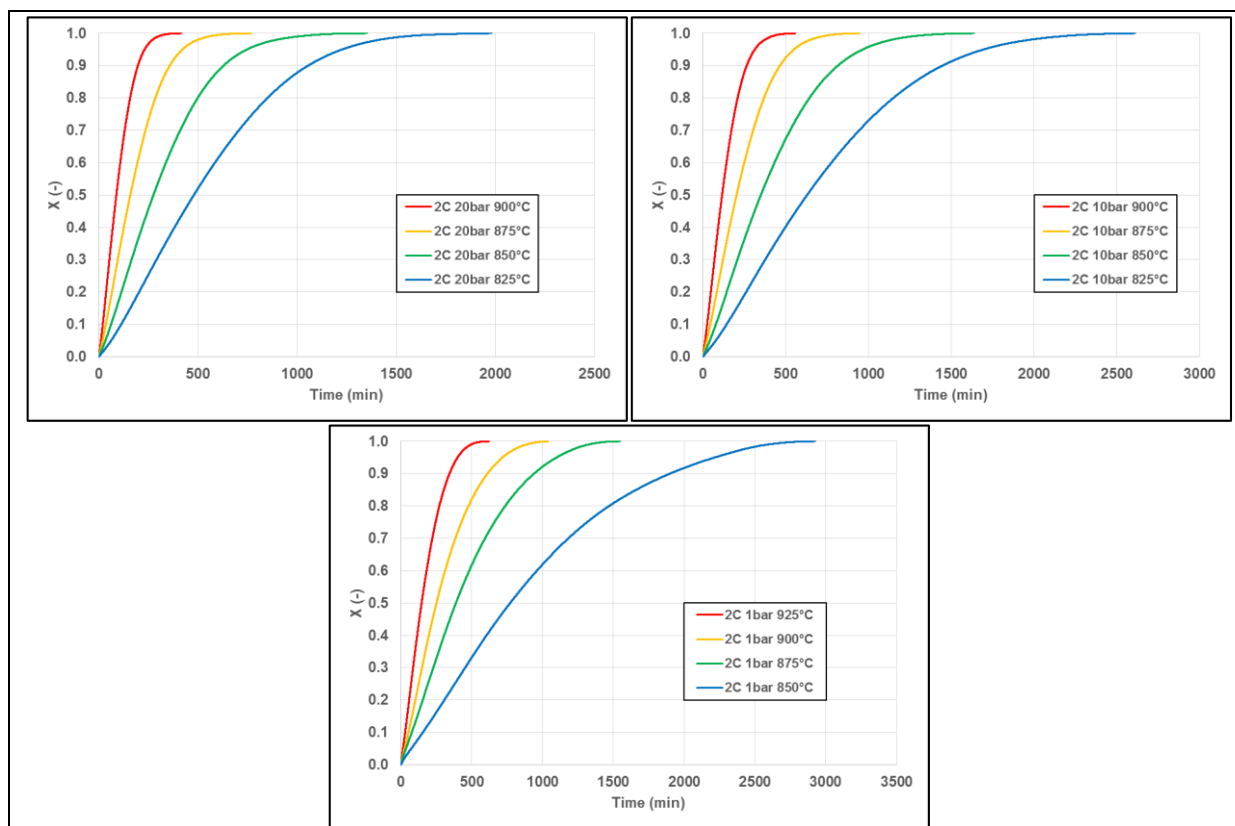


Figure A16: Effect of temperature on the conversion profiles of char 2C

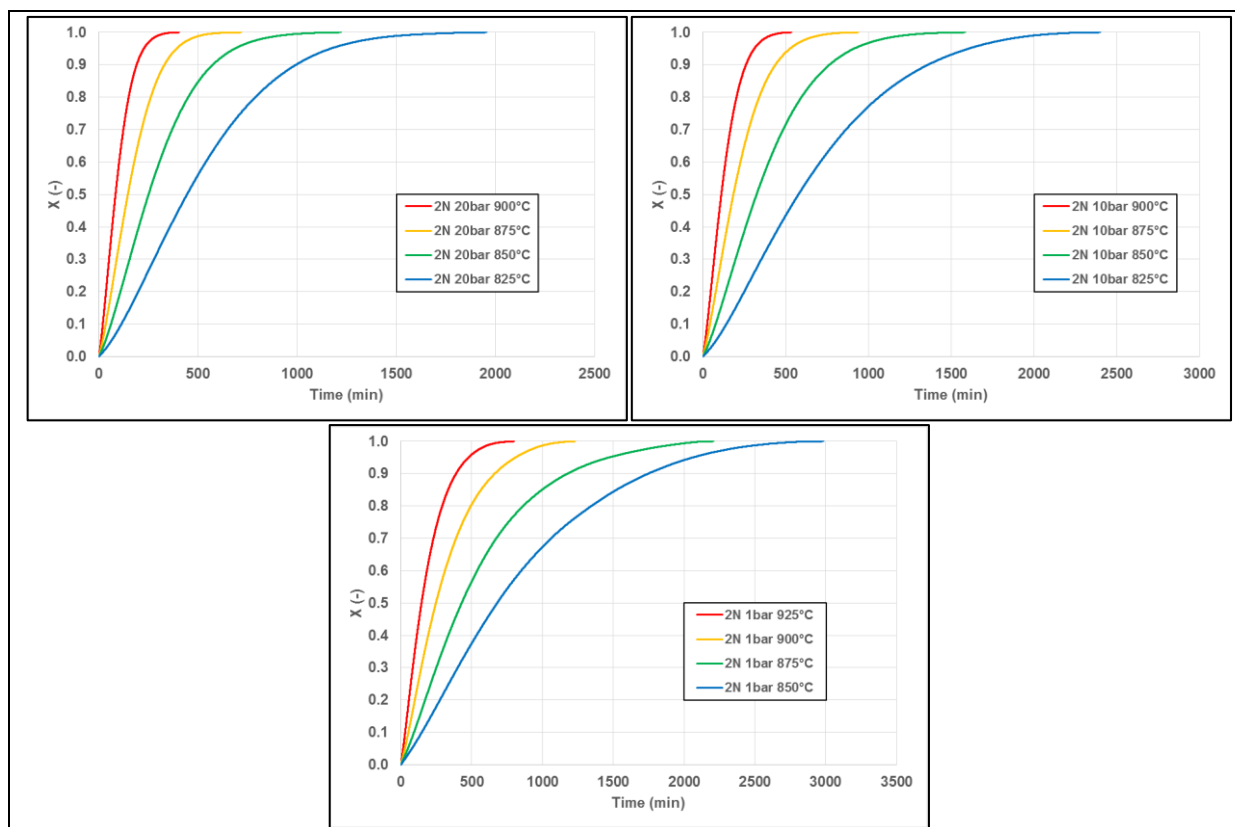


Figure A17: Effect of temperature on the conversion profiles of char 2N

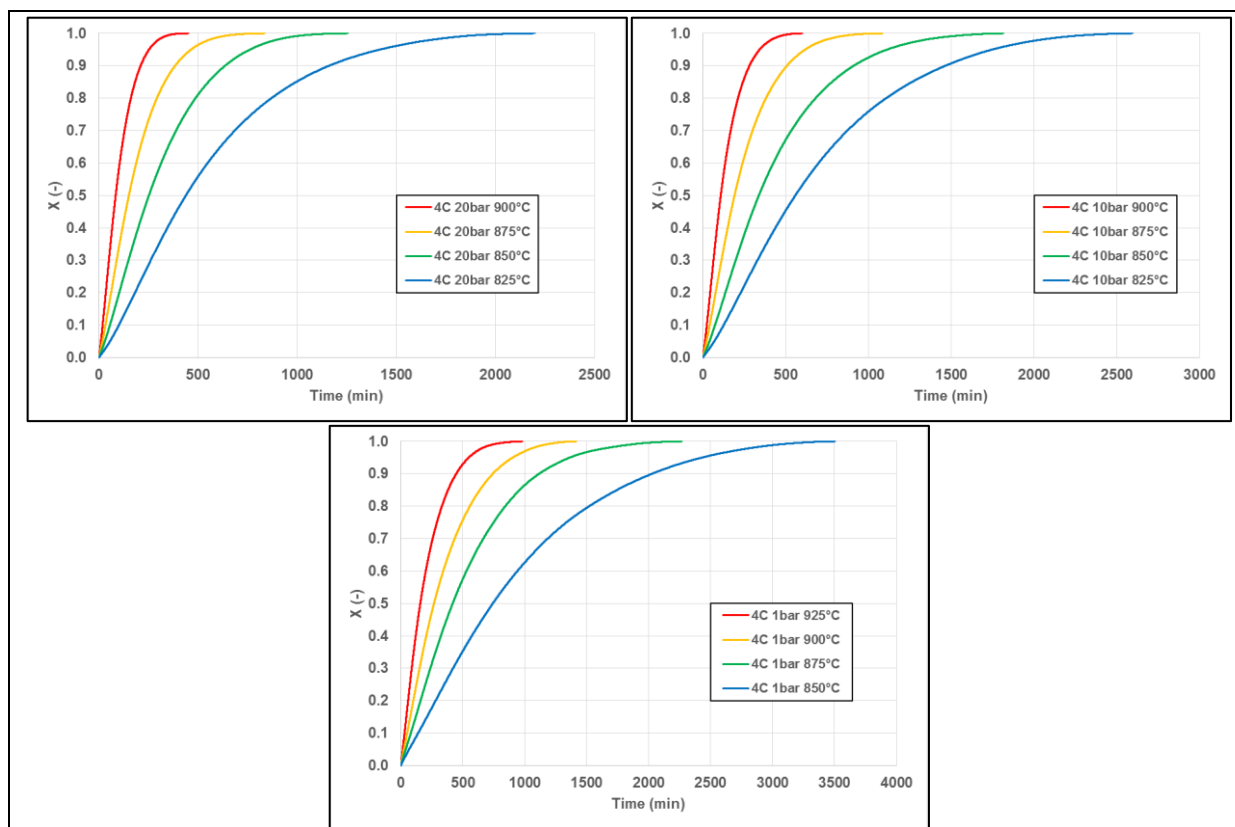


Figure A18: Effect of temperature on the conversion profiles of char 4C

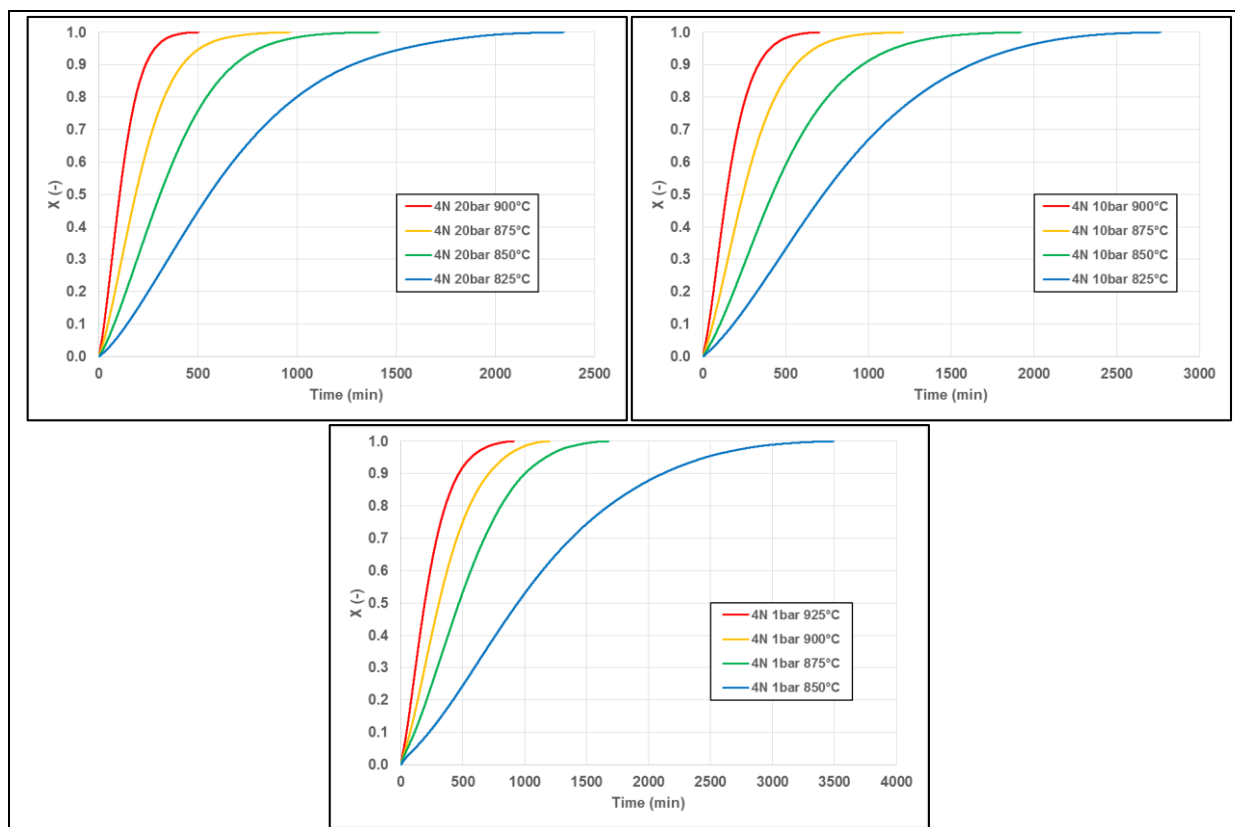


Figure A19: Effect of temperature on the conversion profiles of char 4N

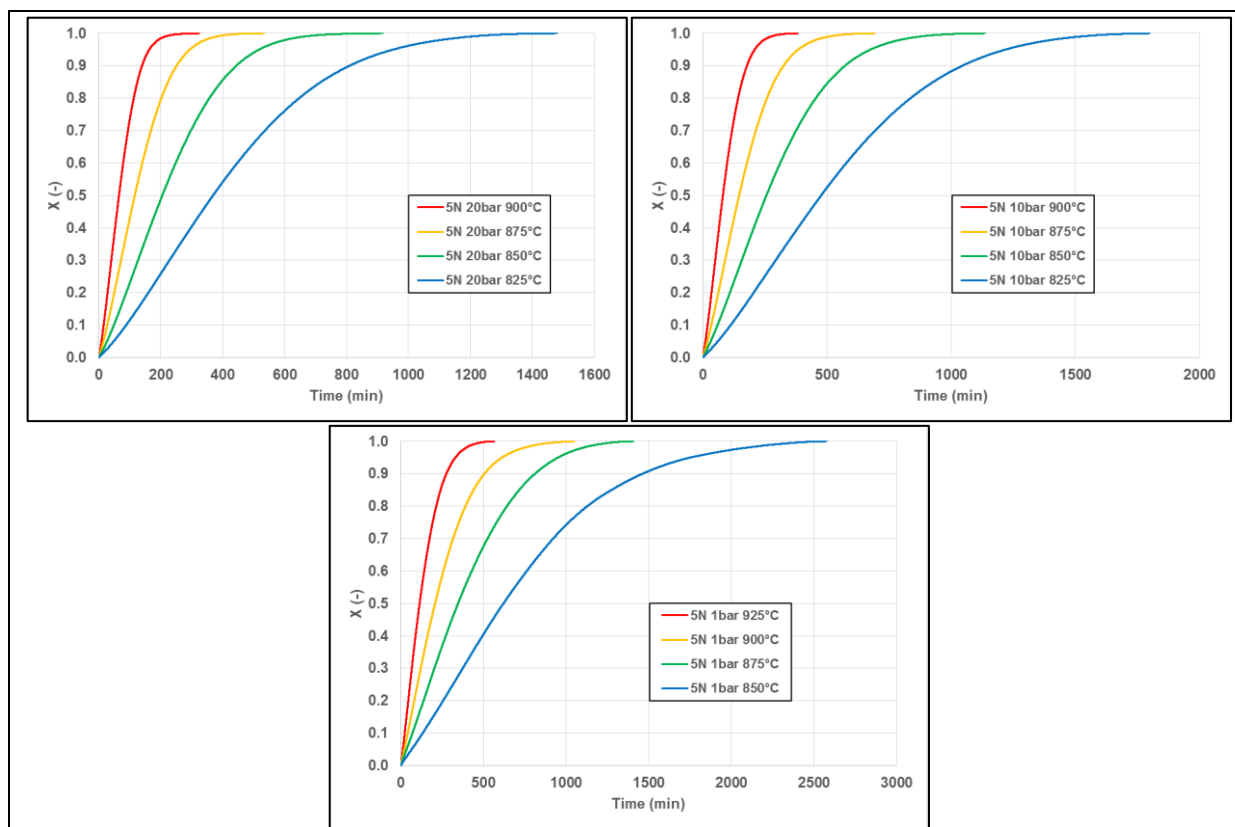


Figure A20: Effect of temperature on the conversion profiles of char 5N

A.5: Arrhenius plots generated from char gasification results

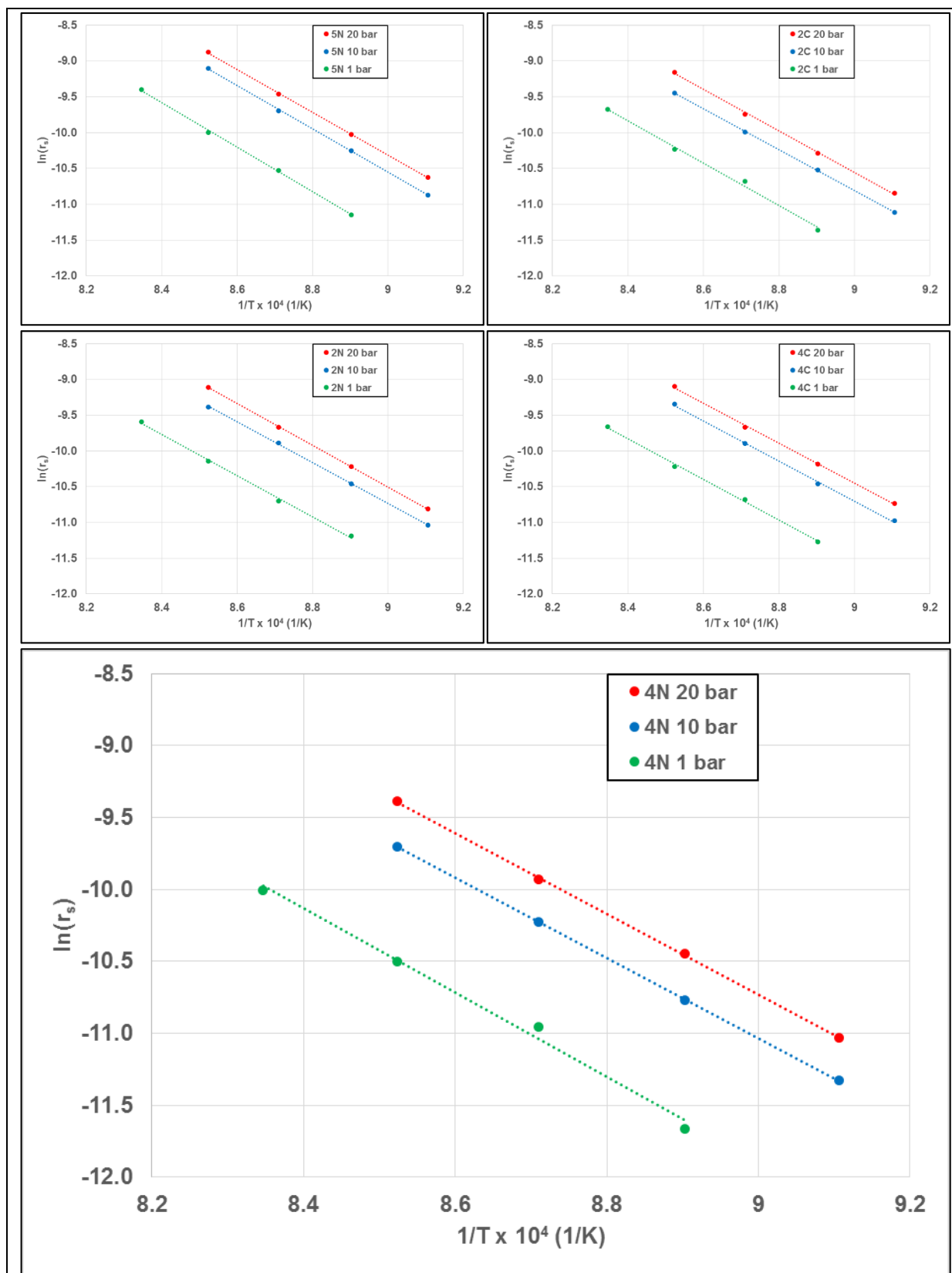


Figure A21: Arrhenius plots of char 5N, 2C, 2N, 4C and 4N

A.6: Comparison of specific reactivity curves of different chars at specified conditions

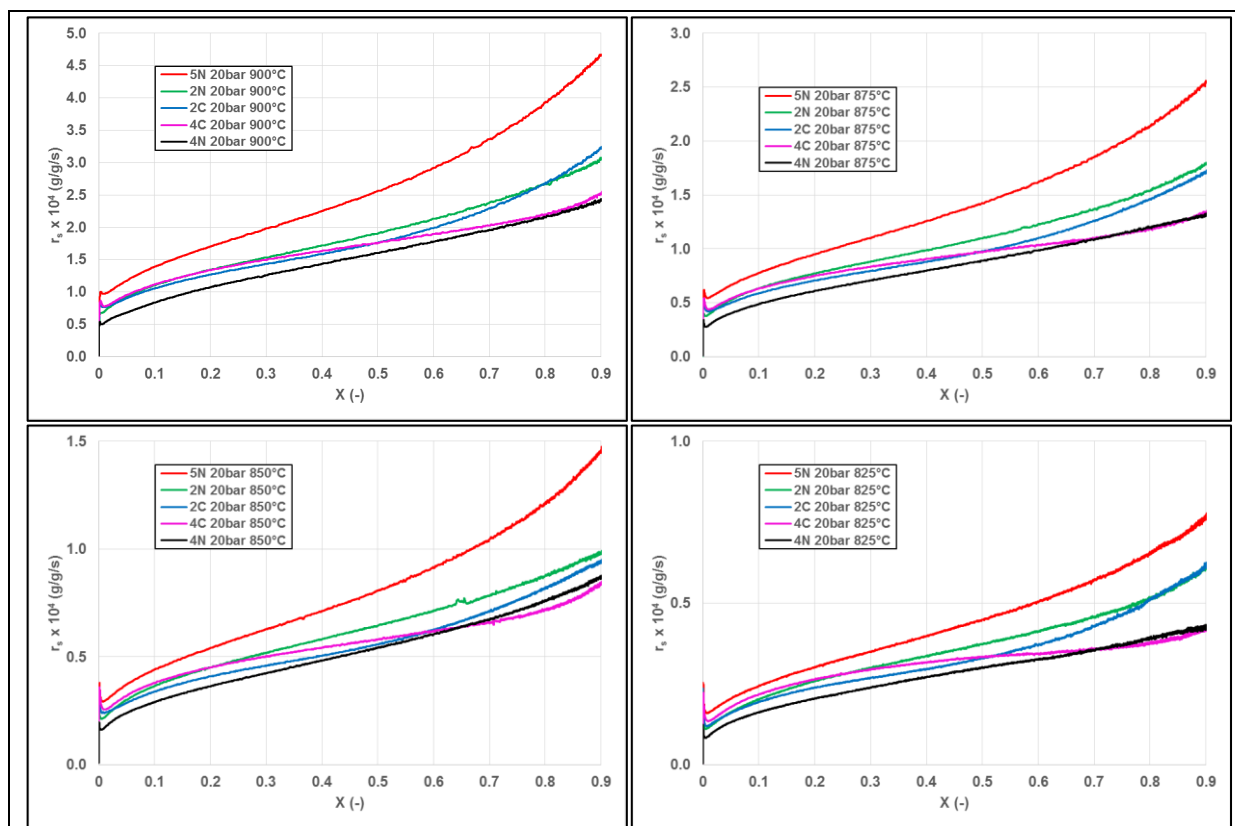


Figure A22: Comparison of char specific reactivity at 20 bar

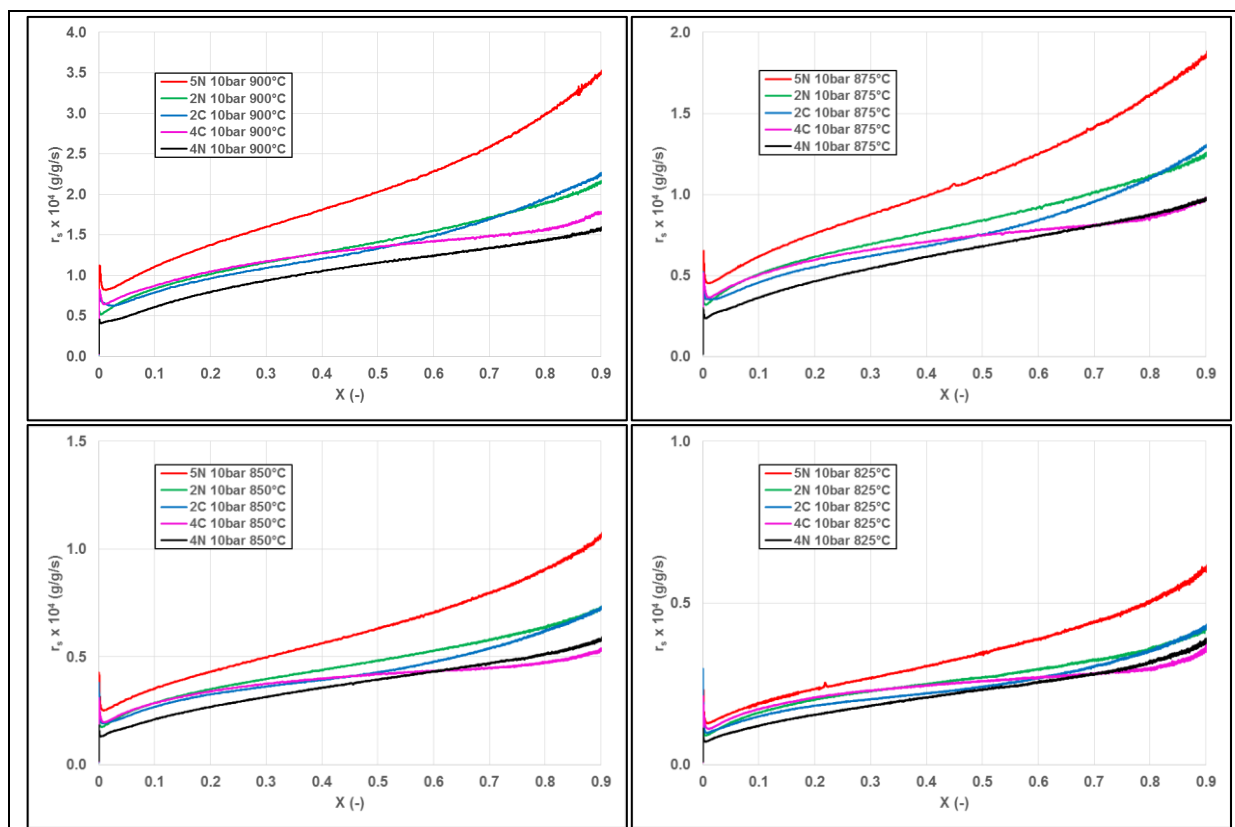


Figure A23: Comparison of char specific reactivity at 10 bar

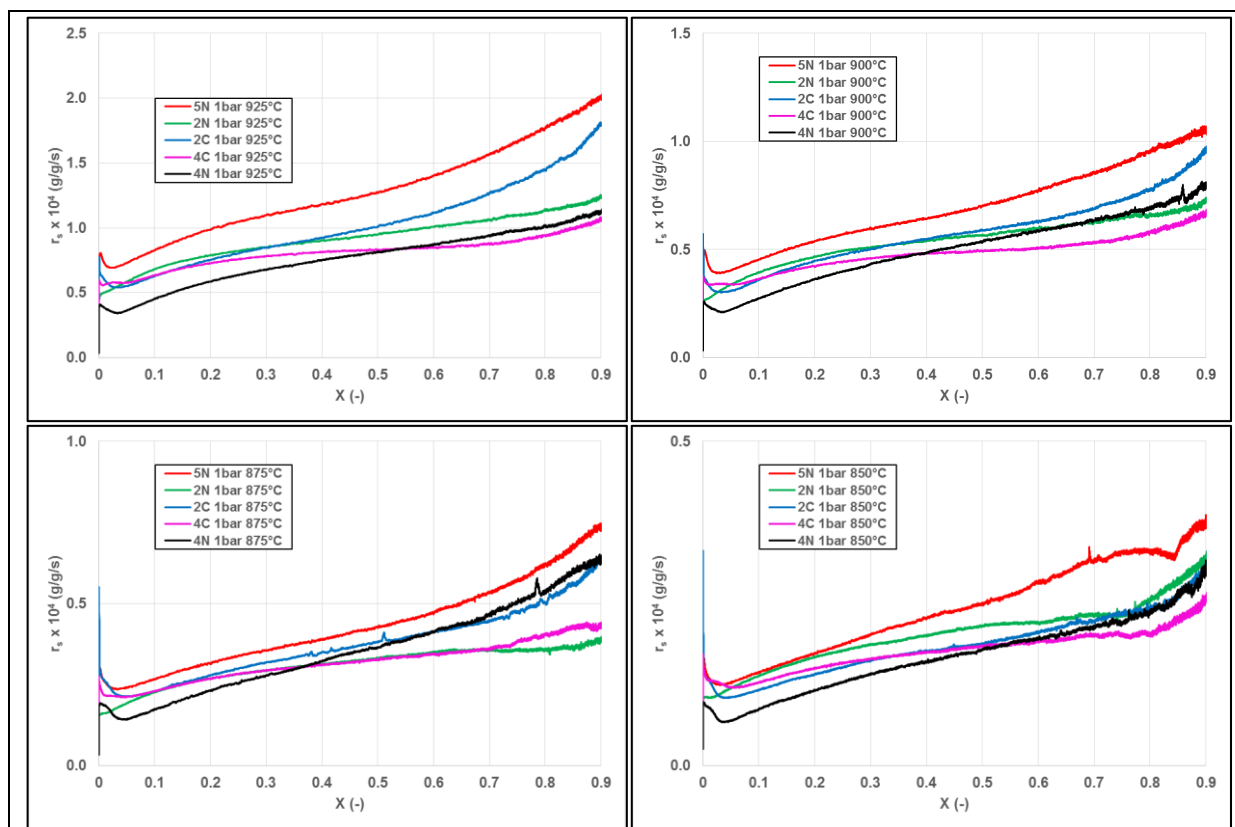


Figure A24: Comparison of char specific reactivity at 1 bar

A.7: Comparison of conversion curves of different chars at specified conditions

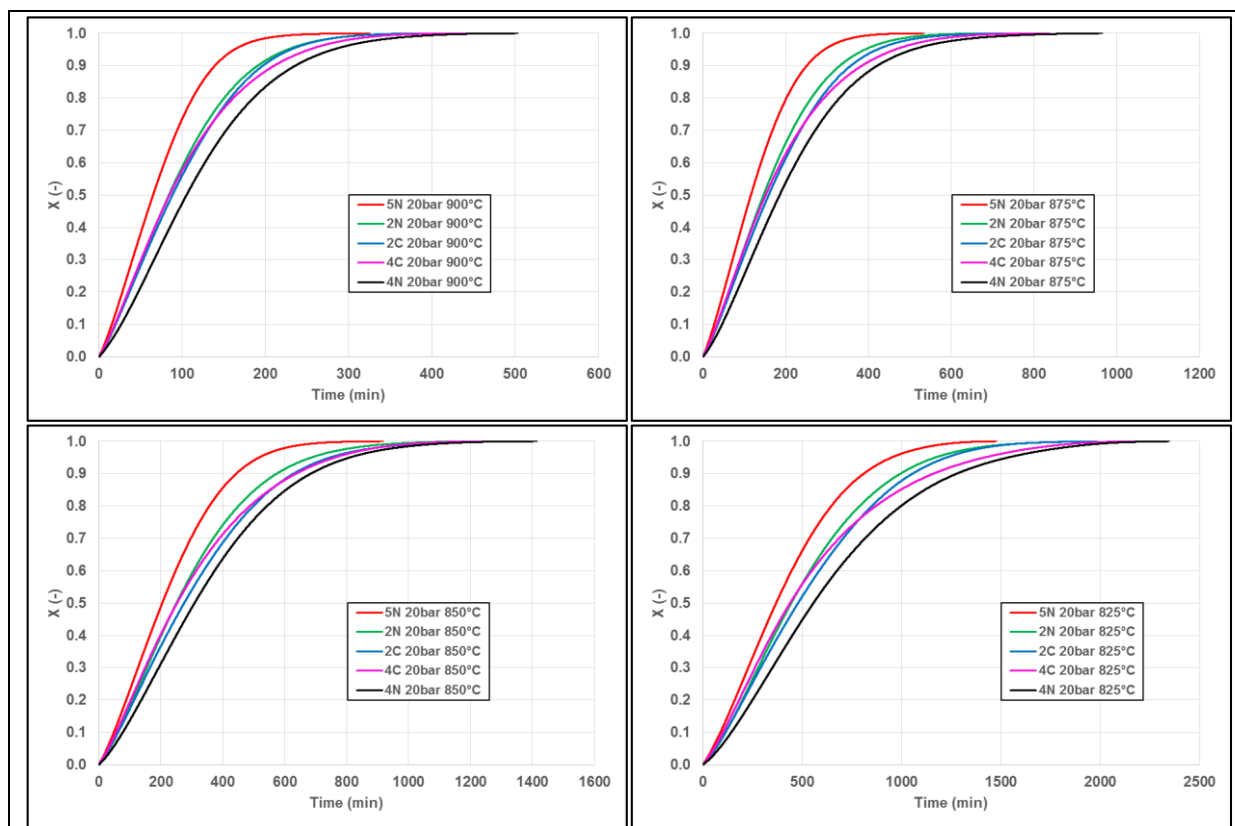


Figure A25: Comparison of char conversion profiles at 20 bar

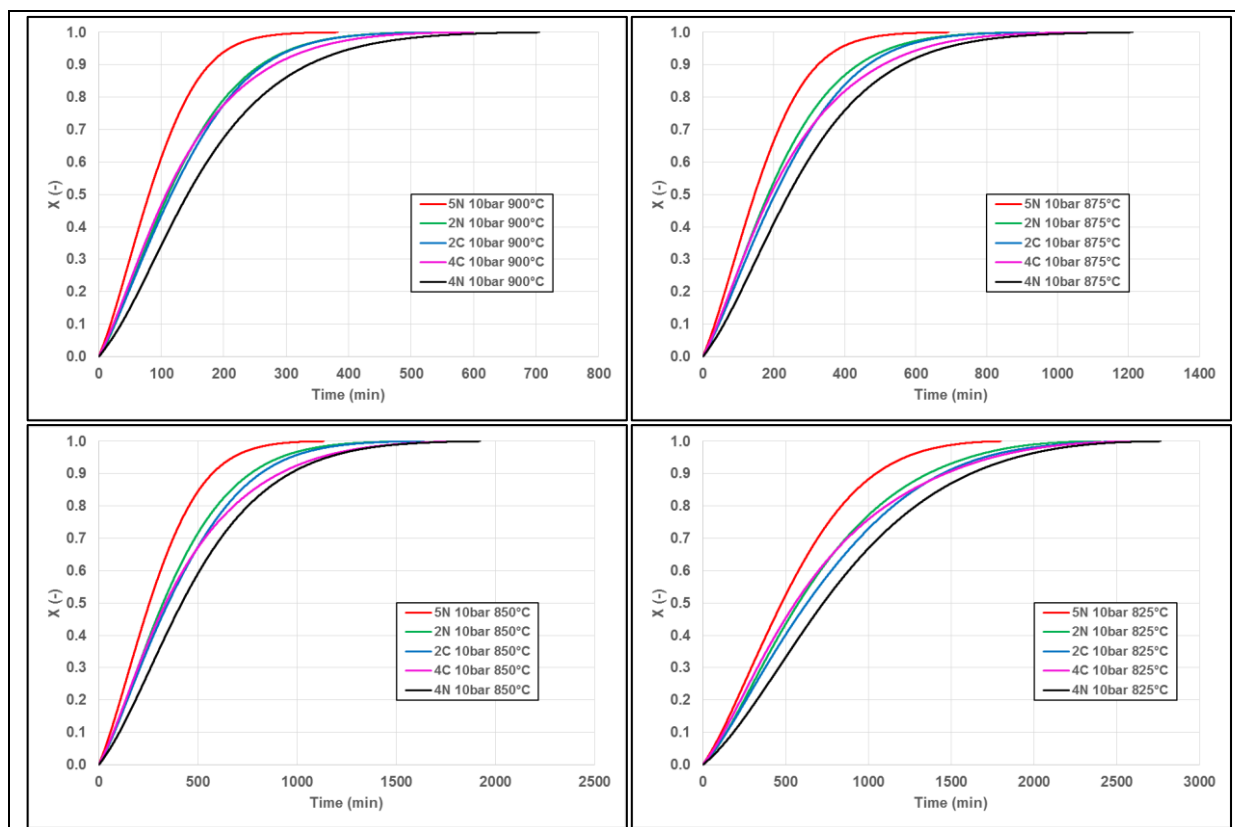


Figure A26: Comparison of char conversion profiles at 10 bar

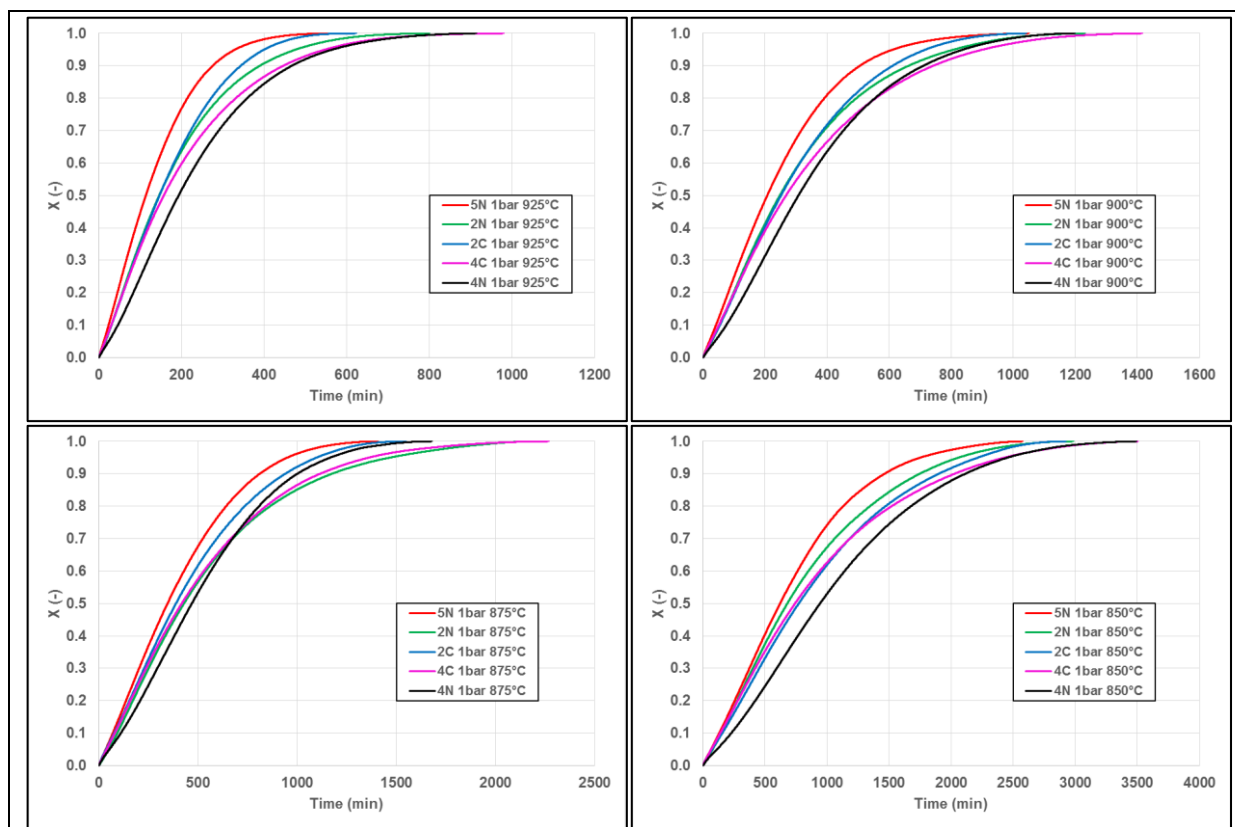


Figure A27: Comparison of char conversion profiles at 1 bar

Appendix B

Design of HP-FBR System

The equipment required to perform the necessary experimental work has been designed and constructed in-house for the purpose of executing this study. Since the equipment is new and has therefore not been described elsewhere, this section will be dedicated to providing detail regarding the design and features of this system, the HP-FBR.

B.1: Background and requirements

Commercial coal conversion operations relevant to this study are carried out at pressures above ambient. Since the gasification behaviour of South African coals at elevated pressure has not been extensively researched, uncertainty exists regarding the applicability of experimental data generated at low pressure, for the understanding of high pressure applications.

Due to this, a desire exists for determining the gasification behaviour of South African coals at elevated pressure. High pressure gasification results are considered to be more relevant to the commercial industry, or would at least provide insight into the matter of extrapolating ambient pressure results to predict high pressure behaviour. For the sake of determining results that are free of intervening factors such as mass transfer limitations, heat transfer limitations or non-ideal fluid dynamics, bench-scale testing is required since it is more feasible to control the operating conditions as to achieve ideal results in bench-scale equipment. Ideal results are desired as it is more universally applicable, that is, mathematical models accounting for non-ideality may be applied to the extent as necessary to model a true process, while data generated under non-ideal conditions are only valid and applicable to those particular conditions.

Bench-scale equipment which have been utilised to conduct high pressure gasification of coal range from commonly utilised high pressure TGA's, to more novel equipment such as wire mesh reactors. As noted earlier in this text, certain limitations may exist in these equipment which may diminish the applicability of the results with regards to the commercial operations in question. It was therefore opted to design and construct a new laboratory-scale system which will enable gasification of coal in such a manner that the uncertainties regarding the applicability of the results are greatly reduced. In order to generate results which are representative of ideal conditions, at temperatures and pressures better representative of commercial CTL operations, the following capabilities are required:

- A high stoichiometric excess of gaseous reagent must be deliverable, to avoid depletion of reagent, while ensuring constant reagent partial pressure.
- Accurate control of reagent concentration, while ensuring reagent concentration at the particle surface is the same as the known bulk reagent concentration.

- A high superficial gas velocity is required, to ensure that external mass transfer (film diffusion) limitation is not encountered, and ensuring that reaction products are promptly removed from the system to avoid competitive inhibition.
- A fixed-bed configuration is desired, to ensure there is continuous forced flow of reagent through the sample bed, removing uncertainty regarding bed permeability and concentration gradients.
- Idealised fluid dynamics, to minimise dead volumes and to reduce the lag time between product formation and the analysis thereof.
- Accurate monitoring of reaction progression.
- Operation at temperatures of up to 1000 °C.
- Isothermal conditions are required to avoid heat transfer limitations.
- The system must be able to accommodate particles sizes larger than powders, and sample amounts greater than milligram ranges, in order to emulate more realistic feedstock conditions.
- Operation at pressures of up to 20 bar(a).

The new high-pressure fixed-bed reactor (HP-FBR) has been designed to address and meet these considerations. A simplified process diagram of the system is provided in Figure B1, with specific descriptions of the different parts of the system and its features to follow in the next section.

B.2: Design and features of the system

The system consists of a gas control panel, a furnace with the reactor, and a computer system. In general the following details apply throughout the system: Piping, valves, and other parts in contact with gases are constructed of stainless steel, unless otherwise stated. Piping is $\frac{1}{4}$ " nominal diameter, unless otherwise stated. All parts through which gas flow occurs, other than the reactor itself, are at ambient temperature at all times. Piping utilised for purging gas to ambient pressure is $\frac{1}{4}$ " diameter polyethylene tubing, rated for up to 10 bar pressure. The relatively small diameter piping and low system volume ensures that gas flow is nearly in plug-flow, as determined by monitoring analyser readings after performing step changes at gas inlets. Switching of flow destination and on or off switching of flow is accomplished by ball valves. Manual control of flow rates, where applicable, is accomplished by needle valves. Sufficient flow control measures are incorporated in the system to ensure that any configuration of necessary flow direction, mixing, splitting or routing is possible, without the requirement of rearranging piping to provide capabilities. Electronic communication between instruments and the computer system is accomplished by the RS232 protocol. With reference to Figure B1, individual parts of the system will be explained in further detail, starting at the point of reagent gas inlet at the top left of Figure B1, and following the flow direction according to Figure B1, until the flow finally reaches the gas analyser.

Gas is supplied from gas cylinders to the inlets of the control panel via 0.125" nominal diameter stainless steel piping. N_2 and CO_2 are piped separately to the control panel. The inlets are connected to respective two-stage stainless steel pressure regulators utilising alloy X-750 diaphragms. The minimum rated operating pressure of components in this section is 248 bar at ambient temperature.

The pressure regulators can be set to outlet pressures of up to 34 bar. Two-stage regulators are utilised to ensure constant outlet pressure is maintained throughout the course of long experimental runs, without requiring periodical adjustments. Gas cylinder pressures may fluctuate significantly due to gradual cylinder depletion or changes in ambient temperature in the vicinity of the cylinder storage area. The outlet of the regulators are connected to the inlets of separate thermal mass flow controllers. These controllers control the gas flow automatically according to desired set-points received from the computer. The N_2 controller is sealed by Viton™ material while the CO_2 controller is sealed by EPDM material.

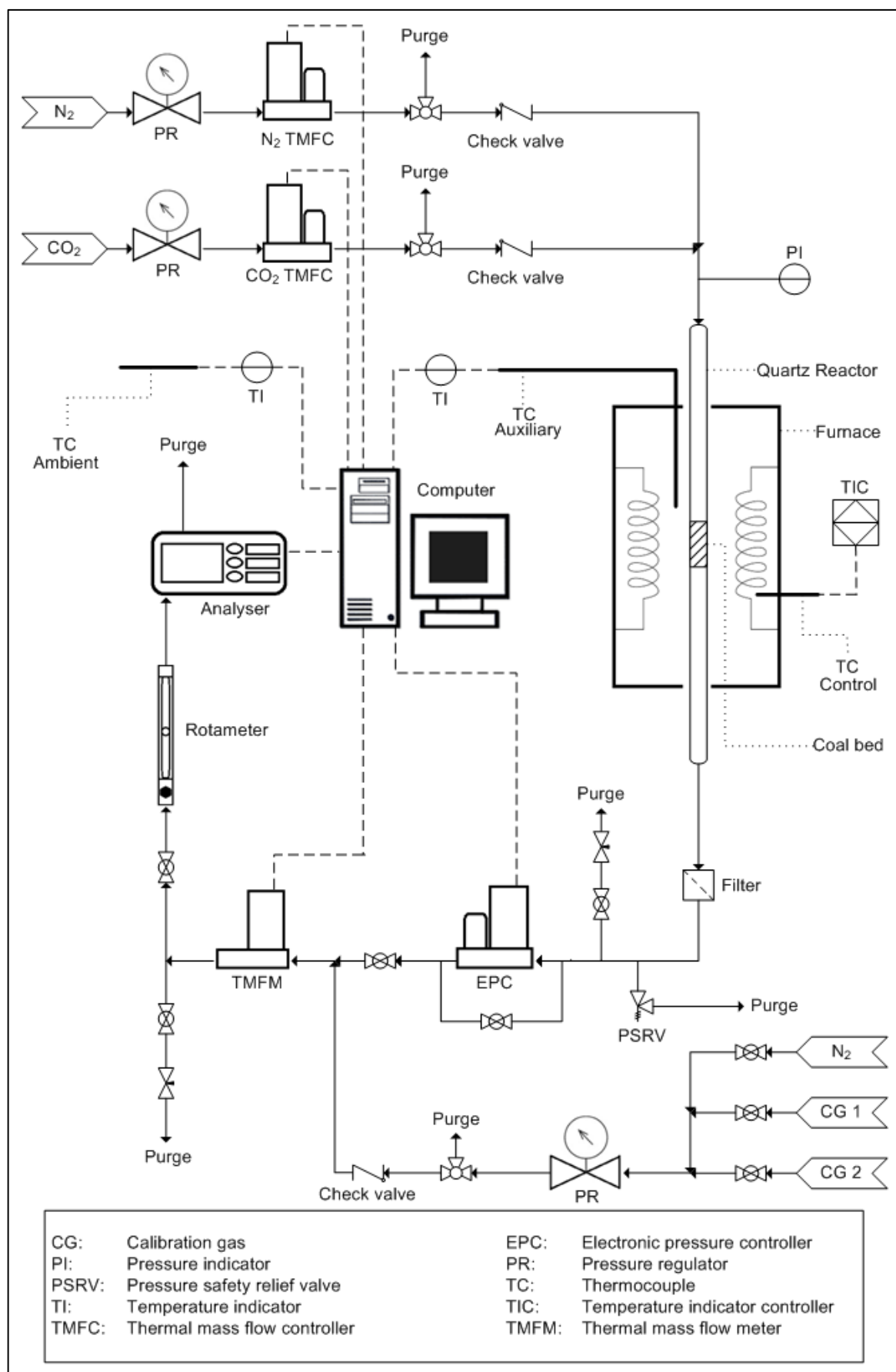


Figure B1: Process and instrumentation diagram of the HP-FBR system

The pressure regulators are set such that optimal inlet pressure is available to the flow controllers to operate properly, depending on the system pressure utilised. The outlets of the flow controllers are connected to three-way valves which may be set to route the flow either to the reactor, or to purge the flow. This capability is provided such that, for example, the CO₂ flow may be set to the required value, but initially purged to prevent the gasification reaction from taking place. When ready, the correct CO₂ flow may then be instantly routed to the reactor to minimise flow or concentration fluctuations. The routing capability is also provided to divert the controller outlet flow for the purpose of conducting controller flow rate calibrations. If routed to the reactor, the flow passes through non-return check valves to prevent back-flow, after which the flow is mixed. A pressure reading is taken of the mixed gas stream prior to the reactor inlet. The minimum rated operating pressure of components in this section is 100 bar at ambient temperature.

The reagent gas is delivered to aluminium flanges which attach to and seal the reactor. The final length of piping to the flanges is reduced to a diameter of 0.125", to ensure slight flexibility of the piping. The reactor is constructed of 15 mm outer diameter (10 mm inner diameter) electrically-fused quartz tubing. A quartz sintered disc containing pores of approximately 150 µm diameter is mounted in the centre of the tube, serving as the sample support bed. The reactor is 1 m in length, providing sufficient protrusion from the top and bottom of the furnace such that natural convective cooling of the aluminium flanges is sufficient. Additional forced cooling to protect the material and sealing O-rings is therefore not necessary. This section has been subjected to operation at pressures of up to 20 bar while at temperatures of up to 950 °C without failure. The heat for the reactions to take place is provided by an electrically powered vertical split-tube furnace. Coiled vertical metal heating elements, radially arranged, are utilised in the furnace to generate heat. The reactor is clamped in place and the furnace is closed over the reactor to commence heating of the sample. The furnace set-point is controlled locally. A separate thermocouple is also utilised to monitor the temperature within the furnace as additional verification of consistent temperature. The temperature reading from the separate "auxiliary" thermocouple is logged on the computer.

The outlet of the reactor is returned to the control panel, where it is connected to a filter. The filter contains a screen with aperture of approximately 15 µm, incorporated to trap any dust or particles which may be carried from the sample, to protect downstream equipment. The filter may be periodically back-flushed to remove particulates. A pressure relief valve is incorporated at this point to protect the system from over-pressurisation. The relief valve is set to open at a pressure of 25 bar. A purge facility, controllable by a needle valve, is also incorporated in this section to provide the capability of de-pressurising the system in a

controlled manner. An electronic back-pressure controller, sealed by EPDM material, controls the reactor pressure from a set-point received from the computer. The measured system pressure, determined by the pressure controller, is also transmitted to the computer and logged. The pressure controller is ranged to control up to 20 bar(a). The section of the system upstream of the pressure controller is thus a high pressure section, while the downstream section is low pressure since flow is released to ambient conditions. The pressure controller is usually bypassed, to enable low pressure work to be conducted. The bypass is only closed if and when pressurisation is desired. An additional valve directly downstream of the pressure controller is available to isolate and protect the downstream low pressure section if necessary, and to prevent back-flow into the upstream section when it is not utilised and the pressure controller is bypassed. The minimum rated operating pressure of components, excluding the reactor, in this section is 100 bar at ambient temperature. For all intents and purposes, the operating limit of the reactor can be considered as 20 bar(a) at 950 °C at this time.

The high pressure section of the system ends at the isolation valve at the pressure controller outlet. The remaining section of the system is intended for operation only at low (near ambient) pressure. At this point a new gas stream is merged with the stream from the reactor outlet, utilised when necessary. This gas stream is fed from several sources, similar in description to the reagent gas inlet section. The system currently accommodates three addition gases, which may be fed to the low pressure section of the system. Currently, two of these gases are carbon monoxide in certified concentrations, with balance N₂, utilised as calibration gases for the analyser. A third gas, in this case N₂, may be incorporated to dilute the reactor outlet stream, be utilised as a sweep gas, be utilised to purge the low pressure section, or be utilised to back-flush the filter. Selection of which gas to admit into the system is accomplished by a manifold of ball valves. More than one gas may not be utilised simultaneously, as a precaution to prevent back-flow which may contaminate the calibration gas. The selected gas, at high pressure, is directed to a pressure regulator before being admitted to the low pressure section. The pressure regulator is a two-stage stainless steel regulator, with only low pressure outlet capability. Up to the point of the pressure regulator, the minimum rated operating pressure of the components is 206 bar at ambient temperature. A purge facility is provided, followed by a check valve to prevent back-flow of gas from the low pressure section into this section when it is not being utilised. It is particularly important to prevent back-flow or dead volumes at this point to ensure accurate flow measurement and analysis, hence the use of check valves and isolation valves. From the point of the regulator outlet up to the point of the check valve, the minimum rated operating pressure of the components is 172 bar at ambient temperature.

The final merged gas stream flows through a thermal mass flow meter. The mass flow meter measures and transmits the total gas flow rate to the computer, where it is logged. The mass flow meter is rated for operating pressure of up to 8 bar. After the mass flow meter, the stream is split into a purge stream and a stream directed to the gas analyser for analysis. The entire stream may be purged when it is not desired to analyse the gas concentration. When gas analysis is desired, the gas stream is admitted to the gas analysis section where it first flows through a rotameter. The rotameter is utilised to monitor the flow rate to the gas analyser, which operates optimally within a certain flow range. The amount of gas admitted for analysis is controlled by manipulating the proportion of gas purged, by adjustment of the needle valve in the purge stream and a needle valve integrated into the rotameter. The gas admitted for analysis is then analysed to determine carbon monoxide concentration. The gas analysis is achieved by the non-dispersive infra-red principle within the analyser. ¼" diameter polyethylene tubing transports the gas from the rotameter outlet to the analyser inlet. The gas analyser may not be pressurised to any extent, but since no flow control measures exist downstream of the analyser to ambient conditions, pressurisation is unlikely. An additional thermocouple is utilised to measure the ambient temperature in the vicinity of the gas analyser, which is transmitted to the computer for logging. An air conditioning system is utilised in the laboratory to aid in control of the ambient temperature.

Appendix C

Description of Data Processing Methods

In this section, further detailed elaboration will be provided regarding the endeavour of processing raw experimental data, as logged by the relevant instrumentation, into useful gasification results. Since the experimental equipment, and the corresponding data processing methodology, is new and not previously discussed, detailed discussion is provided here. This section serves as an expansion of the information provided in Section 4.6.1.

A total of five operating variables are continuously logged throughout the course of a gasification experimental run. These variables are:

- Ambient temperature
- Furnace temperature
- System pressure
- Total gas flow rate
- Carbon monoxide concentration

With reference to Figure B1, these variables are measured by the following instruments for the following purposes: Ambient temperature is measured by the ambient thermocouple in the vicinity of the gas analyser. This is logged to provide an ambient temperature profile during the experimental run which is considered in conjunction with the gas analyser readings, since the analyser reading is influenced by temperature. Furnace temperature is measured by the auxiliary thermocouple which is located in the furnace in the vicinity of the quartz reactor. The furnace temperature is logged to ensure that the temperature inside the furnace remains constant throughout the course of an experimental run. The system pressure is logged from the reading of the electronic pressure controller. The pressure is logged to confirm that the system pressure remains constant throughout the course of an experimental run. Total gas flow rate is logged from the reading of the thermal mass flow controller. The total flow is logged to confirm that the gas flow rate remains within an expected range throughout the course of an experimental run. The carbon monoxide concentration raw data is logged from the NDIR analyser reading. The concentration is required in order to calculate the carbon conversion rate, as determined by Equation 4.1. The measurements from these instruments were logged every two seconds.

To perform the data processing of a gasification experimental run, the following procedures are conducted:

The raw data logged from the outputs of the five instruments described above are copied into suitable software, such as a spreadsheet, for further processing. Readings which are not directly in a meaningful form, for example as percentage of analyser span, are transformed by a simple mathematical function, where applicable. Most of the data is only considered for the purpose of confirming that no adverse events occurred throughout the course of the experiment, which may cause operating condition deviations or instability, thus confirming that the remaining experimental data is dependable and a repetition of the experiment is not necessary.

Ambient temperature, furnace temperature, system pressure and total gas flow rate are only considered to confirm stable operation. Examples of these parameters logged during a gasification run are graphically presented in Figure C1. These examples are from the same experiment which was considered as an example in Section 4.6.1, namely the gasification of char 2C at 20 bar and 900 °C.

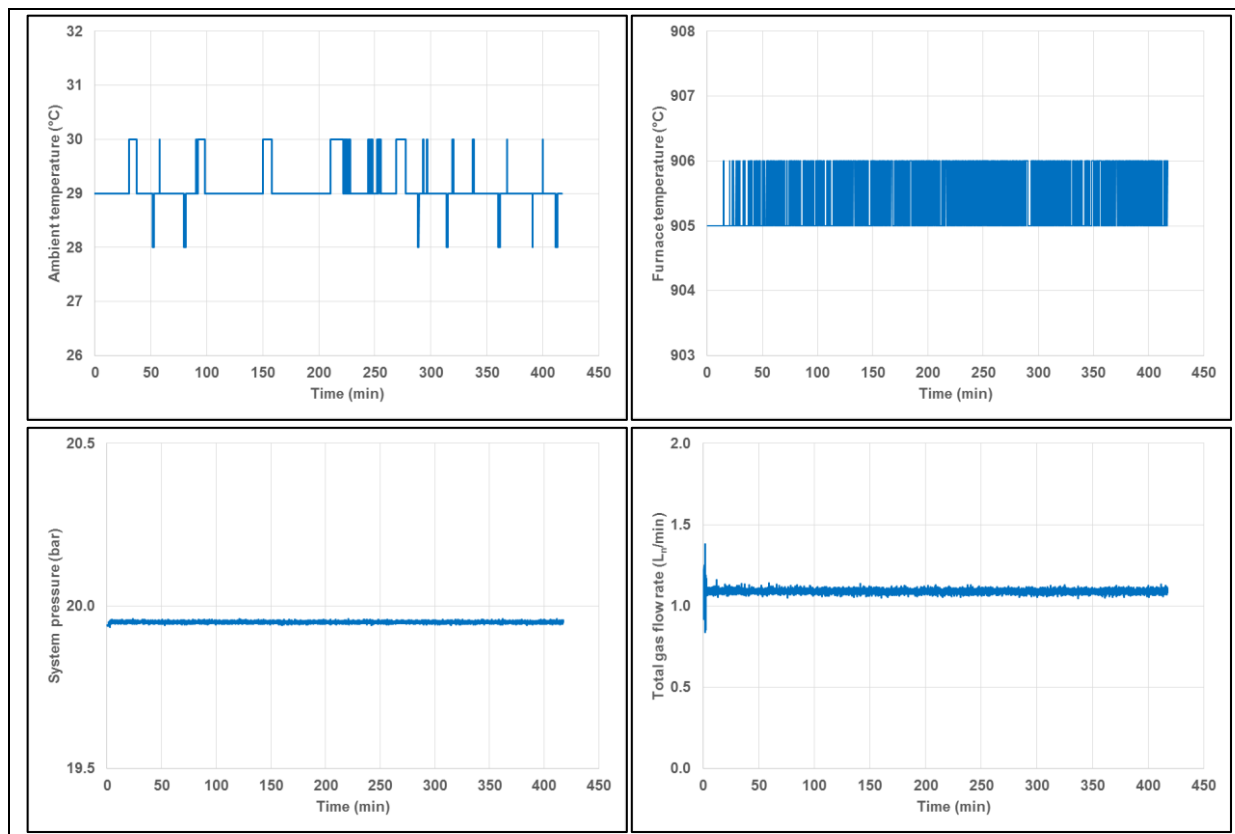


Figure C1: Operating parameters logged during experiment

From Figure C1, the first graph (top left) is an indication of the ambient temperature as a function of time. In this example it is observed that the average ambient temperature was $29\text{ °C} \pm 1\text{ °C}$, the ambient temperature was thus very stable. It is thus assumed that the gas analysis readings of this experiment have not been influenced by temperature fluctuations. The second graph (top right) is an indication of the internal furnace temperature as a function of time. In this example it is observed that the average furnace temperature was 905 °C, with momentary readings of 906 °C, the furnace temperature was thus very stable. This reading does not imply that the temperature within the sample bed was 905 °C, this is just a verification that the furnace temperature was stable. In general, a furnace temperature reading of 905 °C was determined to correspond to a sample bed temperature of 900 °C, due to heat transfer effects. The third graph (bottom left) is an indication of system pressure as a function of time.

In this example it is observed that system pressure was dependably maintained on set-point throughout the entire experiment, thus no complications occurred in this regard. The pressure set-point in this example was set slightly lower than 20 bar, to compensate for pressure drop over the sample support disc, resulting in a pressure of 20 bar within the sample bed. The fourth graph (bottom right) is an indication of total gas flow rate (in $\text{dm}^3_{\text{n}}/\text{min}$) as a function of time. In this example it is observed that the gas flow maintained a constant average value throughout the entire experiment, indicating that leaks or an interruption of feed gas did not occur. At the very beginning of the graph, it is observed that greater flow rate fluctuations occurred. This is due to an operating methodology whereby the pressure controller is initially set to respond fast at the start of the experimental run, to prevent controller oscillations from developing when CO_2 flow is introduced. When the system is stable, the pressure controller is set to a slower response to smooth out the flow pattern. This initial moment of greater flow rate fluctuation does not influence the gas analysis readings, since the average gas flow rate is not affected. The measured flow rate is indicated slightly higher than $1 \text{ dm}^3_{\text{n}}/\text{min}$, this is only due to the measurement of a gas mixture which has different average properties than the fluid utilised for factory calibration of the meter. It is known that $1 \text{ dm}^3_{\text{n}}/\text{min}$ of gas is fed to the system, due to independent control by the mass flow controllers at the inlet. These considerations provide reasonable certainty that the experiment was carried out under stable, favourable conditions.

A similar check to verify correct and stable operating conditions is conducted for all experimental runs. Upon confirmation that the experimental conditions are satisfactory, the gas analysis data may be dependably utilised for further processing. The raw data from the carbon monoxide (CO) analysis is considered next. It is first required to judge when, and thus at which reading, the gasification reaction completed, due to carbon depletion. It is not possible to simply consider a specific reading for all experimental runs to interpret as the end of the reaction, nor the same reading as what was observed before the reaction started, since the gas analysis reading is unfortunately susceptible to zero-drift, span-drift and temperature interference. The end of the reaction is rather judged by observing a flattening-out of the raw CO concentration curve. Refer to Figure C2 to illustrate this approach. This is an example of the raw data from the CO analysis of the run presented in all examples thus far, namely the gasification of char 2C at 20 bar and 900°C .

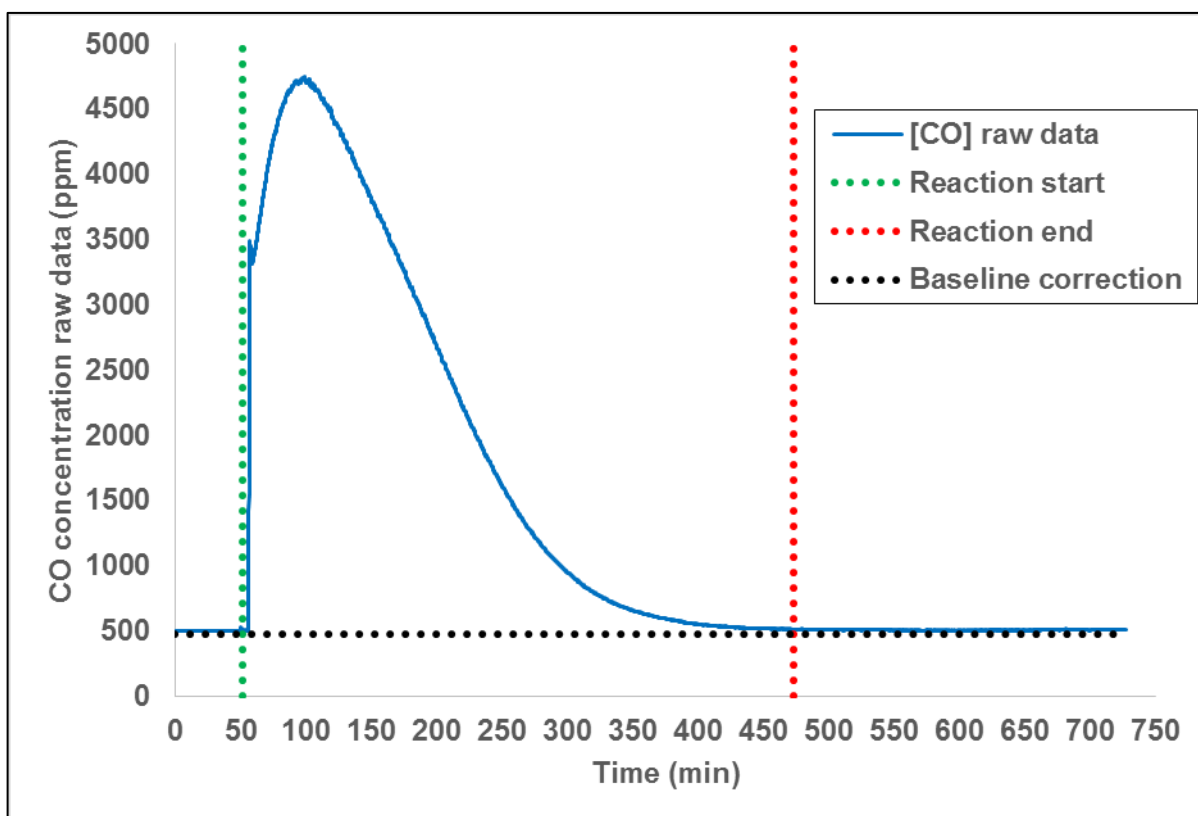


Figure C2: Gasification raw data interpretation example

With reference to Figure C2, the blue line represents the reading logged from the gas analyser during the entire period from when the data logging was first started, to when the entire experiment was terminated, approximately twelve hours later. The carbon in the sample is inferred to be depleted when no further CO production is detected, observed as an asymptotic flattening of the curve. Due to complications from analyser reading drift and temperature interference, it is best to omit data which is not considered to form part of the reaction period. It is, somewhat subjectively, judged when the reaction has started and stopped. In this example, the point at which the reaction is considered to have stopped is indicated by the vertical dotted red line. The minimum reading in the vicinity of the red line is considered to be the end of the reaction. When fluctuations in ambient temperature occur during the same period as when the reaction is believed to stop, judgement of where to mark the end of the reaction is more challenging. A gradual increase in ambient temperature will result in a gradual decrease of the analyser reading, appearing as a slow continuation of the reaction. Due to this, the ambient temperature is logged and considered in conjunction with the gas analyser readings, to determine the reaction end point.

As soon as CO₂ is introduced into the reactor, CO is rapidly produced and is manifested as a sharp increase in the analyser reading. Judgement of when the reaction has started is thus

very simple, indicated by the vertical dotted green line. All data after the minimum reading in the vicinity of the dotted red line is deleted. Similarly, all data before the first increased reading in the vicinity of the dotted green line is deleted. Since all data not associated with the gasification reaction has been removed, the result of Equation 4.3 cannot be influenced by anything other than the gasification reaction itself. At this point it is now known when the reaction has started and ended, and interference from ambient temperature fluctuation has been taken into consideration.

The next matter to consider is that of analyser reading span-drift. This is done by correcting the remaining raw data from the analyser reading, by applying a mathematical calibration curve. The calibration curve is a second order function, derived from a three-point calibration procedure. The calibration procedure is accomplished by feeding a gas with a known CO concentration to the gas analyser, and noting the reading generated. Uncertainty and errors with regards to the accuracy of the analyser reading due to span-drift is thereby addressed. This calibration procedure is elaborated in further detail in Appendix E.2. The final consideration with regards to correcting the raw data from the analyser is the matter of zero-drift. This is simply accomplished by performing a baseline correction procedure, i.e. correcting a constant bias between the minimum observed reading and absolute zero. An illustration of such a bias is indicated by the horizontal dotted black line in Figure C2, although the actual bias encountered after performing all preceding corrections is usually much closer to zero. Subtracting the bias from the calibrated CO concentration readings shifts the curve to zero, thereby addressing the uncertainty and errors due to analyser reading zero-drift.

After performing all the corrections as detailed above, the raw data from the gas analyser has been transformed into an accurate and dependable “true” representation of the CO produced by the gasification reactions, as presented in Figure 4.3. All further procedures, as described in Section 4.6.1, can now be performed utilising the corrected CO concentration data.

In order to utilise Equation 4.1, the value of the total volumetric flow rate of the CO-containing stream at standard conditions (Q_{ideal}) is required. This can be determined from the thermal mass flow meter readings, provided that an accurate calibration is available to adapt the readings to the properties of the actual measured mixed-gas stream. Under certain circumstances, a simpler and more accurate method may apply: In this study, the CO concentration in the reactor outlet stream never exceeded 0.4%. Due to this, the product stream did not require dilution to be analysed. Thus, with reference to Figure B1, additional gas was not introduced into the product stream directly before the thermal mass flow meter. It was thus also not necessary to purge any gas directly after the thermal mass flow meter, since reagent is fed at a flow rate which is also optimal for the gas analyser. Since the produced CO

concentration was below 0.4%, it was assumed that volume changes due to conversion of carbon and CO₂ to CO was negligible. The product gas stream standard volume is therefore considered to be the same as the reagent inlet standard volume. The flow rate control of the reagent inlet, controlled by the thermal mass flow controllers, was observed to be very stable and dependable. It is therefore considered more accurate and convenient to infer the product stream volumetric flow from the sum of the reagent inlet volumetric flows, if the conditions above are satisfied. Q_{ideal} is therefore taken as a constant value in this study, equal to the sum of the N₂ inlet and CO₂ inlet flows. These inlet values are known and stable, since desired flows are stipulated by set-points, and confirmed by flow rate calibrations. The value of V_{ideal} in Equation 4.1 is taken as 22.4 dm³/mol, since the product stream consists of majority N₂, a very ideal behaving gas.

Integration of the data obtained from Equation 4.1, as represented by Equation 4.2 and Equation 4.3, will enable the calculation of all further quantities utilised in this study for representation of reaction rate. This integration procedure was accomplished by numerical integration of the data generated by Equation 4.1. The trapezoidal rule was applied to calculate the integral of every two second interval. Since this is done at the same resolution as the data logging, i.e. a first order function exists between every data point which is two seconds apart, no loss in accuracy occurred through the use of the trapezoidal rule. The cumulative integral was calculated by summation of the individual integrals of every two second interval up to the time in question, for Equation 4.2, and up to the final reaction time, for Equation 4.3. All information required for the application of Equation 4.4 and Equation 4.5 is now available.

Appendix D

Accuracy and Repeatability

In this section, tests and validations will be discussed regarding several factors related to the quality and dependability of data generated utilising the experimental system developed for this study. Since the experimental system is new and not previously proven or validated, empirical testing has been conducted to test factors related to repeatability and accuracy. This section will focus on the experimental repeatability of the system, the accuracy of total carbon detection, and the experimental uncertainty.

D.1: Experimental repeatability

The repeatability of the entire experimental system, that is, the combined repeatability of the HP-FBR system, the experimental methodology and the data interpretation methodology, was empirically tested. This was done by repeatedly gasifying homogenous samples of activated carbon, and comparing the processed results. Fine powder of activated carbon (AC) was utilised in order to exclude any variability due to sample inconsistency. Three repeat runs were conducted at both low pressure (LP) and high pressure (HP). The LP runs were conducted at 900 °C and 1.5 bar(a), while the HP runs were conducted at 875 °C and 10 bar(a). Other experimental conditions were similar to those of the main coal-char study. The conversion profiles and specific reactivity curves of these runs are presented in Figure D1, the LP and HP runs are indicated separately.

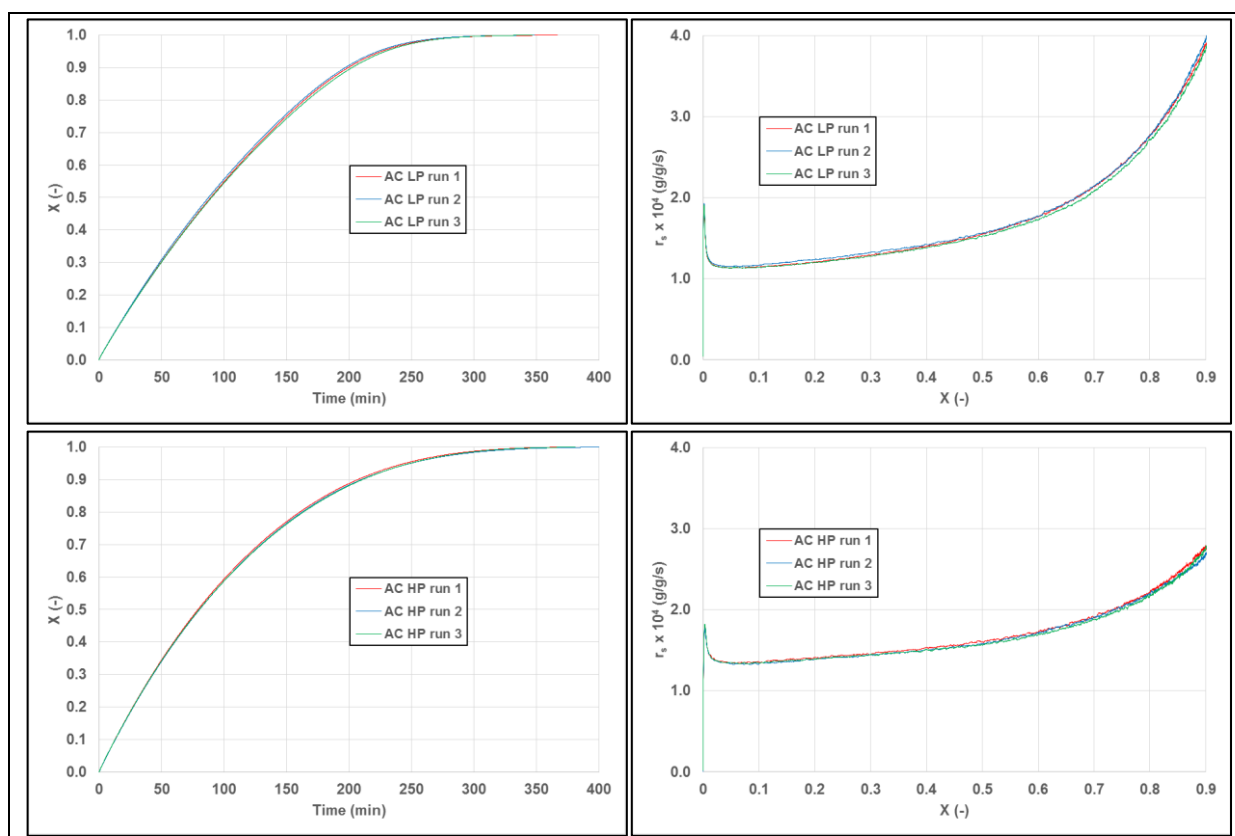


Figure D1: Experimental repeatability demonstrated by activated carbon gasification

Figure D1 presents the conversion profiles (left) and the specific reactivity curves (right) of the three repeat runs of the activated carbon gasification results at low pressure (top), and three

repeat runs at high pressure (bottom). At both low pressure and high pressure, the conversion curves as well as the specific reactivity curves of the three repeat runs are virtually indistinguishable. This indicates that near exact results are achieved when performing the same task repeatedly. Due to the nearly identical results of three different runs over the entire conversion range, the repeatability of the experimental system is considered to be excellent.

D.2: Carbon mass balance

As a test of the accuracy of the experimental system, a comparison was made between the carbon content of a char sample inferred from the processed gasification results, and the expected carbon content according to another independent method.

The carbon content of the char sample inferred from the processed gasification results was determined as follows: The raw data from the char gasification run was processed to determine true CO concentration produced, as described in Appendix C. The processed CO concentration data was utilised in Equation 4.1 to calculate the carbon conversion rate. Equation 4.3 was applied to the data obtained from Equation 4.1. The value of C_f determined from Equation 4.3 is considered to be the total carbon content of the sample subjected to gasification. This will be referred to as the experimental carbon content.

The expected carbon content according to another independent method was determined as follows: Samples from the char sub-samples utilised for gasification were analysed by a proximate analysis in-house (results not presented in this text). The inherent moisture content of the samples was also confirmed independently by an infra-red heating and weighing analysis. These results were utilised to calculate the fixed carbon content of the bulk gasification samples on the air dried basis. Prior to each gasification run, the char sample was weighed before being loaded into the gasification reactor. Thus for each gasification run conducted, the expected carbon content of the loaded sample can be calculated by multiplying the sample mass with the determined fixed carbon percentage. This will be referred to as the proximate carbon content.

The experimental carbon content, of each gasification run conducted as part of the main investigation, was compared to its theoretically expected (proximate) carbon content. These results are presented in Table D1.

Table D1: Carbon mass balance results of gasification experiments

Gasification run	Proximate carbon content (g)	Experimental carbon content (g)	Error %
2C 850 °C 1 bar	0.3943	0.3777	-4.21
2C 875 °C 1 bar	0.2742	0.2390	-12.84
2C 900 °C 1 bar	0.1573	0.1554	-1.19
2C 925 °C 1 bar	0.1587	0.1441	-9.20
2C 825 °C 10 bar	0.3914	0.4271	9.13
2C 850 °C 10 bar	0.3887	0.4225	8.69
2C 875 °C 10 bar	0.2750	0.2930	6.55
2C 900 °C 10 bar	0.1615	0.1711	5.96
2C 825 °C 20 bar	0.3936	0.4350	10.52
2C 850 °C 20 bar	0.3900	0.4328	10.96
2C 875 °C 20 bar	0.2759	0.2967	7.54
2C 900 °C 20 bar	0.1564	0.1654	5.75
2N 850 °C 1 bar	0.3452	0.3231	-6.38
2N 875 °C 1 bar	0.2418	0.2603	7.64
2N 900 °C 1 bar	0.1407	0.1463	3.94
2N 925 °C 1 bar	0.1390	0.1458	4.92
2N 825 °C 10 bar	0.3453	0.3932	13.87
2N 850 °C 10 bar	0.3480	0.3759	8.00
2N 875 °C 10 bar	0.2448	0.2636	7.68
2N 900 °C 10 bar	0.1401	0.1528	9.10
2N 825 °C 20 bar	0.3465	0.3895	12.43
2N 850 °C 20 bar	0.3474	0.3753	8.03
2N 875 °C 20 bar	0.2441	0.2537	3.95
2N 900 °C 20 bar	0.1400	0.1477	5.49
4C 850 °C 1 bar	0.3344	0.3231	-3.38
4C 875 °C 1 bar	0.2349	0.2311	-1.64
4C 900 °C 1 bar	0.1366	0.1446	5.87
4C 925 °C 1 bar	0.1372	0.1482	8.03
4C 825 °C 10 bar	0.3345	0.3542	5.90
4C 850 °C 10 bar	0.3364	0.3856	14.63
4C 875 °C 10 bar	0.2352	0.2555	8.64
4C 900 °C 10 bar	0.1343	0.1451	8.05
4C 825 °C 20 bar	0.3348	0.3964	18.39
4C 850 °C 20 bar	0.3374	0.3739	10.80

Table D1, continued

4C 875 °C 20 bar	0.2373	0.2613	10.13
4C 900 °C 20 bar	0.1374	0.1460	6.27
4N 850 °C 1 bar	0.3184	0.2850	-10.51
4N 875 °C 1 bar	0.2198	0.1736	-21.05
4N 900 °C 1 bar	0.1271	0.1186	-6.67
4N 925 °C 1 bar	0.1275	0.1304	2.30
4N 825 °C 10 bar	0.3129	0.3335	6.58
4N 850 °C 10 bar	0.3146	0.3546	12.73
4N 875 °C 10 bar	0.2213	0.2473	11.74
4N 900 °C 10 bar	0.1262	0.1415	12.10
4N 825 °C 20 bar	0.3166	0.3804	20.16
4N 850 °C 20 bar	0.3147	0.3621	15.04
4N 875 °C 20 bar	0.2217	0.2529	14.11
4N 900 °C 20 bar	0.1273	0.1409	10.68
5N 850 °C 1 bar	0.2771	0.2820	1.76
5N 875 °C 1 bar	0.1941	0.1986	2.34
5N 900 °C 1 bar	0.1107	0.1188	7.33
5N 925 °C 1 bar	0.1107	0.1123	1.49
5N 825 °C 10 bar	0.2770	0.2977	7.51
5N 850 °C 10 bar	0.2784	0.2925	5.08
5N 875 °C 10 bar	0.1936	0.1977	2.12
5N 900 °C 10 bar	0.1112	0.1120	0.76
5N 825 °C 20 bar	0.2764	0.3253	17.69
5N 850 °C 20 bar	0.2789	0.3067	9.97
5N 875 °C 20 bar	0.1935	0.2029	4.84
5N 900 °C 20 bar	0.1120	0.1170	4.45
Absolute Average			8.25

In Table D1 the experimentally calculated carbon content, from the detected CO, is presented alongside the expected carbon content based on a proximate analysis. The difference between these two values is indicated as an error percentage, relative to the proximate carbon content result. The absolute average value, reported at the bottom of Table D1, is calculated as the average of the absolute values of the error percentages. The experimental carbon content thus differs from the proximate carbon content by an average of $\pm 8.25\%$, relative to the proximate carbon content.

There are several possible reasons why the experimental carbon content differs from the expected carbon content, these include:

- Systematic error, such as an inaccurate CO concentration calibration curve or expected gas flow rate.
- Random error, such as fluctuations in CO reading due to changes in ambient conditions during the course of an experimental run, or analyser drift.
- Sample inconsistency, coal is a very heterogeneous substance, thus variations may occur from sample to sample.
- Interference, such as CO produced by interaction between CO₂ and mineral matter.
- Proximate analysis inaccuracy, the fixed carbon content as determined is perhaps not a precise quantification of the amount of material which will react with CO₂.

It has not been determined which one, or several, of these factors may be responsible for the deviations in the carbon mass balance. It is a possibility that there might be miniscule errors with regards to the experimental system, with the majority of the error attributable to the method of determining the reference carbon content, or inherent sample variability.

The experimental repeatability has been determined to be excellent, as observable in Figure D1. It is therefore accepted that the value of the experiments, in the context of determining comparative results, is not diminished by a lack of perfect accuracy regarding the carbon mass balance. Due to the complexity of the system, there may be negligible error in the carbon content determined from CO detection, or errors in this regard may be irrelevant with regards to considerations such as the conversion profile or observed kinetic parameters.

D.3: Overall experimental uncertainty

Char gasification runs were not repeated in this study. It has been inferred from the repeatability of activated carbon gasification runs that the experimental system has excellent repeatability. Furthermore, the confirmation procedures as detailed in Appendix C were considered sufficient to verify that a char gasification run was completed without adverse interferences corrupting the results. As a further verification of data consistency, a quantitative indication of such is still desired. In order to derive such a result, it was endeavoured to extrapolate all experimental results of a particular char to comparable conditions. The

extrapolated results can then be directly compared to one another, *in lieu* of actual repeated experimental runs. Since twelve runs were conducted per char, the extrapolated results will provide twelve points for comparison. Perfect accuracy and repeatability would result in the twelve extrapolated points to be exactly similar in value. The inevitable variation in the extrapolated values will therefore be an indication of the experimental uncertainty. All factors contributing to inconsistencies, from the start of the gasification run up to the final mathematical manipulation of the results, would have been taken into consideration in this procedure. These factors include: Inherent variability in sample properties, variability in experimental conditions, inherent accuracy and repeatability of the experimental system, inconsistencies in data processing, and the error associated with determining the kinetic constants utilised for extrapolation.

This procedure was conducted in the following manner: For direct comparison, the gasification conditions of 875 °C and 10 bar were chosen, since these conditions represent the midpoint of the temperature and pressure ranges investigated. The specific reactivity at the moment of 10% conversion will be considered. All experimental r_s results will therefore be extrapolated to 875 °C and 10 bar, corresponding to a CO₂ partial pressure of 3 bar. In order to achieve this, mathematical models accounting for the influence of temperature and pressure will be required, in conjunction with the associated parameter constants. It is assumed that the n-th order power rate law and the Arrhenius equation are sufficient to model the results. The following equations were utilised to achieve this:

$$r_s = k_s P_{CO_2}^n \quad \text{Equation D1}$$

$$\ln(k_s) = \frac{1}{T} \left(\frac{-E_{a,app}}{R} \right) + \text{constant 1} \quad \text{Equation D2}$$

$$\ln(r_{875^\circ C}) = \ln(r_s) + \left(\frac{-E_{a,app}}{R} \right) \left(\frac{1}{T} - \frac{1}{1148.15} \right) \quad \text{Equation D3}$$

$$\ln(r_{875^\circ C}) = (n) \ln(P_{CO_2}) + \text{constant 2} \quad \text{Equation D4}$$

$$\ln(k_{875^\circ C}) = \ln(k_s) + \left(\frac{-E_{a,app}}{R} \right) \left(\frac{1}{T} - \frac{1}{1148.15} \right) \quad \text{Equation D5}$$

$$r_X = k_{875^\circ C} (3)^n \quad \text{Equation D6}$$

These equations were utilised in the following manner:

1. A guessed value for n was assumed.
2. k_s is calculated for each experiment, utilising Equation D1.
3. $E_{a,app}$ is determined from the slope of Equation D2.
4. r_s of each experiment is extrapolated to 875 °C, utilising Equation D3.
5. n is determined from the slope of Equation D4, replacing the guessed value for n .
6. Steps 2 through 5 are repeated until a final value for n has converged.
7. k_s of each experiment is extrapolated to 875 °C, utilising Equation D5.
8. r_s extrapolated to 10 bar and 875 °C, r_x , is calculated utilising Equation D6.

The results from this procedure are summarised in Table D2, presenting the kinetic constants, the averaged results of the extrapolations, and the standard deviation of the results.

Table D2: Kinetic parameters and overall experimental uncertainty

Parameter	Char 2C	Char 2N	Char 4C	Char 4N	Char 5N
n	0.342	0.333	0.357	0.370	0.369
R^2 for determining n	0.995	0.998	0.998	0.993	0.998
$E_{a,app}$ (kJ/mol)	241	239	234	237	252
R^2 for determining $E_{a,app}$	0.998	0.999	0.999	0.996	0.999
Average r_x (g/g/s)	4.72×10^{-5}	5.04×10^{-5}	5.09×10^{-5}	3.76×10^{-5}	6.21×10^{-5}
Standard deviation of r_x (g/g/s)	1.49×10^{-6}	1.00×10^{-6}	1.20×10^{-6}	1.55×10^{-6}	1.28×10^{-6}
Standard deviation as percentage of average	3.2	2.0	2.4	4.2	2.1

With reference to Table D2: The reaction orders of the CO₂ gasification of each char are presented. It is clear that, despite the significant differences in char properties, the reaction orders are very similar, all being within 0.35 ± 0.02 . The coefficient of determination (R^2) between the natural logarithms of $r_{875^\circ\text{C}}$ and P_{CO_2} , utilised to determine n (Equation D4), is very high for all chars, indicating very strong linear relations. This further suggests that the reaction orders remain constant throughout the partial pressure range investigated.

The apparent activation energies determined by this method are all within the ranges as reported in Table 5.1. It is again observed that, despite the significant differences in char properties, the activation energies are very similar, all being within 241 ± 11 kJ/mol. The coefficient of determination between the natural logarithm of k_s and the inverse of temperature,

utilised to determine $E_{a,app}$ (Equation D2), is very high for all chars, indicating very strong linear relations.

As the specific reactivity of all experimental runs per char were extrapolated to a single condition, twelve extrapolated observations (r_x) are available per char. The average of these twelve extrapolated results is presented in Table D2, for each char. The values of these extrapolations and their averages are of no significance, but is only illustrated with the intent of quantifying data scatter. The standard deviation of the extrapolated values from their mean is indicated for each char. If the repeatability of the entire experimental system were perfect, the standard deviation would theoretically have been zero, i.e. there would have been no variability. The standard deviation is therefore interpreted as the extent to which variability exists, quantifying the departure from the perfect situation. The standard deviation for each char is also reported as percentage of the average. Considering char 2C as an example, the standard deviation of the individual r_x values is 3.2% of the average of r_x . Therefore it can be considered that the compounded effect of all factors causing inconsistencies throughout the experimental system results in an expected overall experimental uncertainty of $\pm 3.2\%$ around the average. The standard deviation is broader than a 95% confidence interval in the case of these results, thus representing the worst case scenario of the two. The largest standard deviation observed is for that of char 4N, of 4.2% of the average. This corresponds to char 4N being the slowest reacting char, thus being susceptible to more variations in ambient conditions throughout the experiment, as well as greater relative errors in the gas analysis due to the lower readings. The experimental uncertainty, inferred from the standard deviation, is considered to be relatively low.

Appendix E

Supplementary to Experimental Procedures

In this section, further detailed elaboration will be provided regarding the experimental procedures and methodology utilised throughout the process leading up to, and during the execution of, a gasification run and generating raw data. Since the experimental equipment, and the corresponding experimental methodology, is new and not previously discussed, detailed discussion is provided here. Elaboration will also be provided regarding the choice and influence of experimental conditions, as well as comments regarding operation in the chemical reaction controlled regime. This section serves as an expansion of the information provided in Chapter 4.

E.1: Determination and testing of experimental conditions

Testing was performed to determine the coal gasification behaviour in the new experimental system under different conditions. The operating conditions have to be carefully selected in order to ensure that the experimental results are valid and useful. Factors such as operating temperature and char particle size may influence the extent to which pore diffusion resistance impacts the observed results. Similarly, the gas flow velocity may influence factors such as film diffusion and concentration gradients of reactants and products. The sample loading amount, affecting the carbon content and sample bed height, may influence factors pertaining to concentration gradients and temperature gradients through the sample bed. Testing was therefore done, prior to the main gasification study, to aid in determining optimal operating conditions for the study.

The first test was a variation of total reagent flow rate. In this test $\pm 500\ \mu\text{m}$ char particles were gasified in a 30% CO_2 atmosphere. The total sample amount loaded into the reactor was 0.1 g. Char 5N was utilised for these tests to simulate a fast reaction scenario. A total gas flow rate of $1\ \text{dm}^3_{\text{n}}/\text{min}$ was compared to a flow of $0.5\ \text{dm}^3_{\text{n}}/\text{min}$. This comparison was performed at both a low pressure and a high pressure. The high pressure runs were conducted at $900\ ^\circ\text{C}$ and 10 bar(a), while the low pressure runs were conducted at $925\ ^\circ\text{C}$ and 1 bar(a). Since a variation in gas flow rate slightly influences the sample bed temperature and pressure drop, furnace temperature and pressure control set-point adjustments were made accordingly in an effort to compensate. These results are presented in Figure E1.

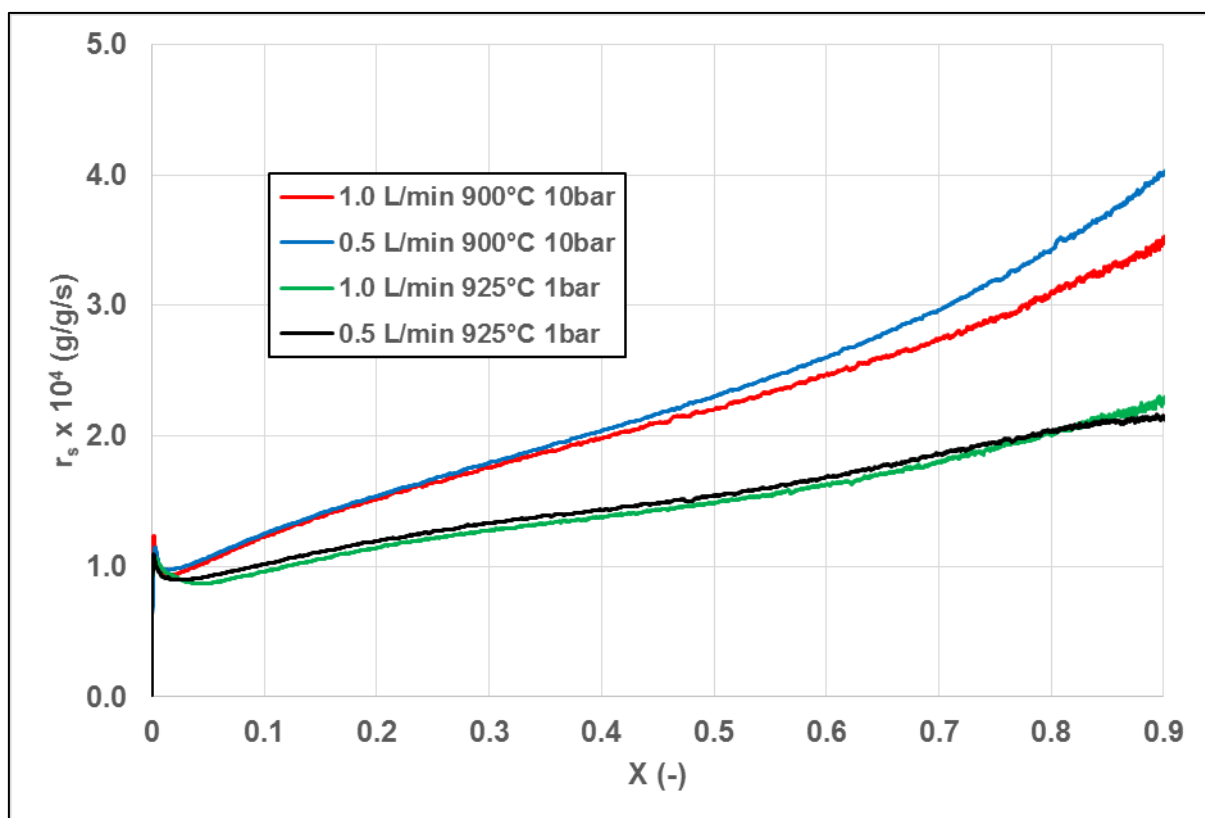


Figure E1: Effect of gas flow rate on char gasification reactivity

In Figure E1 the results are presented for the high pressure tests (red line at 1 dm³_n/min gas flow and blue line at 0.5 dm³_n/min gas flow), and the low pressure tests (green line at 1 dm³_n/min gas flow and black line at 0.5 dm³_n/min gas flow). At low pressure it is observed that the total gas flow rate has nearly no influence on the reaction rate. At high pressure there is initially no difference in reaction rate between the different flow rates, but a difference becomes apparent at higher conversion. Since the reaction rate at 10% conversion is utilised in this study for the determination of kinetic values, either flow rate may be considered as there is no appreciable dependence on flow rate at 10% conversion. For the main study, a total gas flow rate of 1 dm³_n/min was chosen, since this flow rate is also optimal for the gas analysis equipment without requiring dilution.

The next test was a variation of char particle size. In this test char particles were gasified in a 30% CO₂ atmosphere and 1 dm³_n/min total gas flow rate. The total sample amount loaded into the reactor was 0.1 g. Char 5N was utilised for these tests to simulate a fast reaction scenario. A char particle size of ± 500 µm was compared to a particle size of ± 75 µm. This comparison was done at both a low pressure and a high pressure. The high pressure runs were conducted at 900 °C and 10 bar(a), while the low pressure runs were conducted at 925 °C and 2.5 bar(a). A pressure of 2.5 bar(a) was utilised for the low pressure runs since the pressure drop over

the powdered sample bed is significant, thus operation at 1 bar(a) is not feasible. Since a decrease in particle size in the fixed-bed influences pressure drop, pressure control set-point adjustments were made accordingly in an effort to compensate. These results are presented in Figure E2.

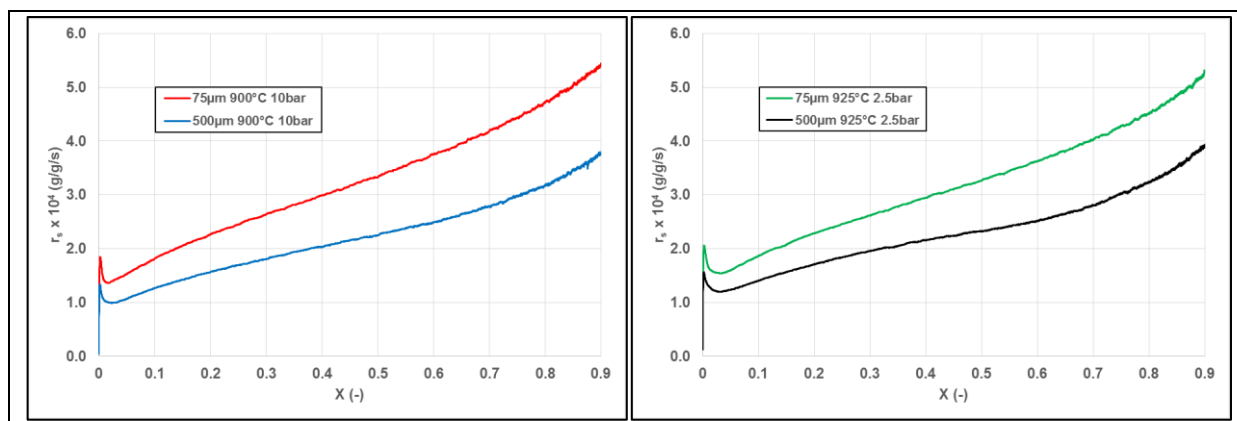


Figure E2: Effect of particle size on char gasification reactivity

In Figure E2 the graph on the left presents the results for the high pressure tests (red line for 75 μm particles and blue line for 500 μm particles), while the graph on the right presents the results for the low pressure tests (green line for 75 μm particles and black line for 500 μm particles). At high pressure it is observed that the powdered sample, consisting of 75 μm particles, reacts significantly faster than the sample consisting of 500 μm particles. It thus appears that the reaction rate is influenced by a change in particle size at these conditions. At low pressure it is also observed that the powdered sample reacts significantly faster than the sample consisting of 500 μm particles. It should be noted that the reaction rates observed here are higher than what would be observed in the main study, due to the operation at 925 °C and 2.5 bar(a). None the less, it appears that the reaction rate is also influenced by a change in particle size at these conditions. The existence of pore diffusion resistance is therefore a possibility at both high pressure operation and lower pressure operation.

It should be noted that the sample bed properties, including the bed pressure drop, tend to change over the course of the reaction for the powdered sample experiments. If bed pressure drop decreases over the course of an experimental run, operating pressure within the sample bed will increase, due to the use of a back-pressure control scheme. This is not the case with the larger particle sizes, since the sample bed properties remain more consistent when utilising larger particles. The results of small particle experiments and larger particle experiments in fixed-bed configuration are therefore not directly comparable, and caution should be exercised in the interpretation of the results. It is also a possibility that mineral matter distribution is

different between the larger particles and the powdered samples, which could be responsible for different observations in reaction rate. These results thus neither explicitly confirm nor deny the existence of pore diffusion limitation, since the change in reaction rate could be due to other factors. As a conservative judgement, it is however inferred from the results that pore diffusion resistance may be influencing the observed reaction rates. For this reason kinetic parameters in the main study are reported as “observed” or “apparent” instead of “true”, since the possibility exists that operation may not entirely be in the chemical reaction controlled regime.

In order to limit the possible influence of pore diffusion resistance, operation with particle sizes larger than 500 μm is ruled out. Due to practical concerns, particle sizes significantly lower than 500 μm will not be utilised. Smaller particles introduce complications such as significant pressure drop, variations in sample bed properties throughout the course of an experimental run, infeasibility of operating near ambient pressure, and difficulty loading sample into a fixed-bed due to static charge development and interaction with the reactor tube walls. A particle size range of $-500 \mu\text{m} +425 \mu\text{m}$ is therefore utilised for the main study.

The final test was a variation of char sample loading amount. In this test char particles of $\pm 500 \mu\text{m}$ were gasified in a 30% CO_2 atmosphere and 1 dm^3/min total gas flow rate. Char 5N was utilised for these tests to simulate a fast reaction scenario. Char sample mass was compared at 0.05 g, 0.1 g, 0.2 g, and 0.3 g loading at high temperature. A comparison was also performed between 0.1 g and 0.5 g sample loading at low temperature. The high temperature runs were conducted at 900 $^\circ\text{C}$ and 10 bar(a), while the low temperature runs were conducted at 850 $^\circ\text{C}$ and 10 bar(a). These results are presented in Figure E3.

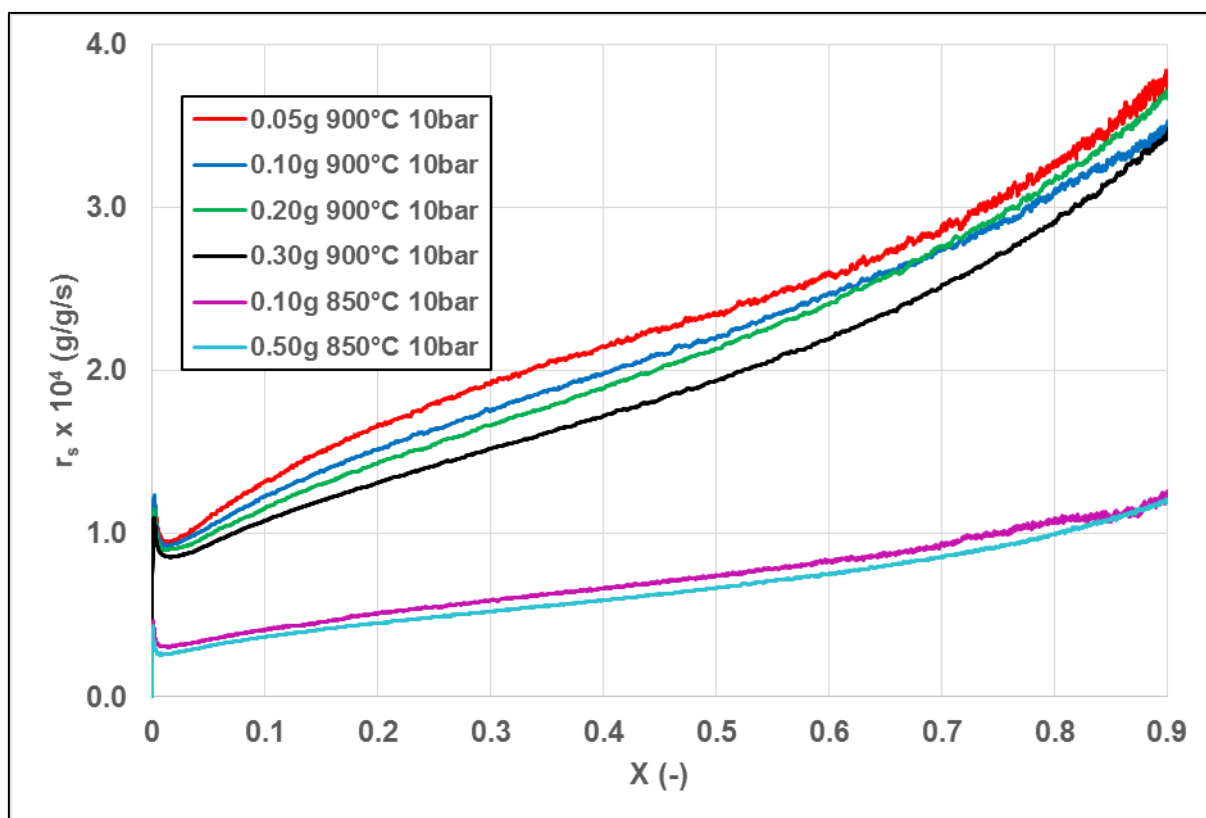


Figure E3: Effect of sample loading mass on char gasification reactivity

In Figure E3 the high temperature results are visible at the top of the graph (red line for 0.05 g, blue line for 0.1 g, green line for 0.2 g and black line for 0.3 g), while the low temperature results are visible at the bottom of the graph (magenta line for 0.1 g and cyan line for 0.5 g). When considering the high temperature results it is clear that an increase in sample loading appreciably decreases the observed reaction rate. Factors such as concentration gradients and temperature gradients may therefore become apparent at high sample loading and high bed heights. An optimisation is necessary between minimising these influences, suggesting a low sample loading, and increasing product detection accuracy, suggesting a high sample loading. Product detection is more accurate at high sample loading, since the CO concentration produced is higher, resulting in utilising a broader span of the analyser detection range and minimising relative errors. To best satisfy these two conflicting considerations, a sample loading of 0.2 g was chosen to be utilised in the main study for the high temperature runs.

When considering the low temperature results in Figure E3, it is clear that a five-fold increase in sample loading has a nearly negligible effect on the observed reaction rate. At low temperature a higher sample loading may therefore be considered, to increase product detection accuracy, as explained above. A sample loading of 0.5 g was therefore chosen to

be utilised in the main study for the low temperature runs. Intermediate temperature runs were arbitrarily chosen to be loaded with an intermediate sample amount of 0.35 g.

The temperatures utilised for the investigations of the main study were chosen as an optimisation between the considerations of higher temperature, which ensures gasification reactions are observable, and lower temperature, which ensures operation in the chemical reaction controlled regime. Temperatures above 925 °C were thus not considered, to minimise the influence of pore diffusion resistance on the observed reaction rates. Temperatures below 825 °C were not considered, since experimental runs at this temperature require as many as 60 hours for completion, thus lower temperatures were not feasible.

The CO₂ concentration utilised was chosen to represent the expected CO₂ concentration encountered in a commercial FBDB gasifier, thus to optimally emulate the commercial operations with the laboratory scale research.

The operating pressures considered were chosen based on the following considerations: An operating pressure of 1 bar(a) was desired in order to generate results near ambient pressure, since most gasification studies of South African coals were conducted at ambient pressure. Near ambient pressure results are desired in order to compare the gasification behaviour of chars at low pressure to that at high pressure. High pressure results are desired to better emulate the commercial FBDB gasification operations with the laboratory-scale research study. The commercial process is stated to operate at a pressure of approximately 30 bar. The pressure in this study was however limited to 20 bar(a), due to equipment limitation and safety considerations. An intermediate pressure to investigate was arbitrarily chosen as 10 bar(a).

E.2: Procedures and methodology prior to gasification

In order to ensure that the conditions under which the gasifications occur are accurate, dependable and stable, several tests and determinations were necessary prior to gasification. These serve to provide confidence and assurance that important factors which may significantly influence the results were sufficiently taken into consideration and understood. These factors include the accuracy of the thermal mass flow controllers, the accuracy of the gas analysis, and the profile and accuracy of the furnace temperature.

Accuracy regarding the performance of the thermal mass flow controllers were determined by performing a flow rate calibration. A flow meter for this purpose was designed and constructed in-house. This meter operates on the principle of observing displacement of a water level due to admitted gas flow, while timing the observed displacement. This is done in such a manner that changes in hydrostatic pressure do not influence the results. The outlet of the mass flow controller is connected to a closed graduated cylinder filled with water. A specific set-point on the controller is set, and the time required to displace a certain volume of water is measured. The observed volumetric flow is converted to flow at standard conditions, incorporating ambient temperature and ambient pressure readings. The observed flow at standard conditions is compared to the set-point of the mass flow controller utilised to achieve this flow. This procedure is then repeated several times and for several different controller set-points. Graphically representing the controller set-points as a function of measured standard flow results in a straight line (not presented in this text). A first order regression of the straight line provides a calibration curve. This calibration can be utilised to determine the exact set-point the controller must be set on, for a desired molar flow. This operation is done separately for the N₂ controller utilising N₂ gas and water saturated with N₂, and the CO₂ controller utilising CO₂ gas and water saturated with CO₂. After performing this procedure and utilising the results, there is confidence in the reagent flow rate and concentration fed to the reactor during gasification. A typical calibration curve for the N₂ controller is, for example: Set-point = 1.0641 x Desired_flow – 0.0263 with an R² of 0.997. A typical calibration curve for the CO₂ controller is, for example: Set-point = 0.9135 x Desired_flow – 0.0247 with an R² of 0.996.

The gas analyser readings are transformed from the raw values with the use of a three-point calibration curve. This calibration is obtained by feeding gas with known CO concentrations to the analyser, and noting the readings. When this procedure is undertaken, careful consideration is committed to the analyser internal temperature and the flow rate of calibration gas admitted to the analyser. The conditions are maintained as comparable to the conditions encountered during gasification as possible. The first calibration gas utilised is certified as containing 3200 ppm CO with balance N₂. The second calibration gas utilised is certified as containing 4500 ppm CO with balance N₂. The third gas utilised is a zeroing gas, containing no CO. The zeroing gas utilised has the same composition as the reagent fed to the reactor during gasification, namely 30% CO₂ and 70% N₂. Even though CO₂ generally has a very small influence on the readings of the CO analyser, the influence may be significant relative to the low readings reported for the zero-point. Thus the gasification reagent mixture is fed as the zeroing gas instead of pure N₂. Performing the calibration, usually with six data points per calibration gas, results in a near-linear relationship between the known concentration and the

analyser reading (not presented in this text). Regressing the relationship with a second order function provides a calibration curve which is utilised to transform the raw analyser readings to true CO readings. Any discrepancy which may still exist due to analyser zero-drift is corrected by the performance of a baseline-correction procedure, as detailed in Appendix C. After performing this procedure and utilising the results, there is confidence in the reported CO concentration produced in the reactor during gasification. A typical calibration curve for the CO analyser readings is, for example: $\text{True_CO} = -7.5736 \times 10^{-5} \times \text{Reading}^2 + 1.2911 \times \text{Reading} - 601.2734$ with an R^2 of 0.999.

To determine the temperature profile within the furnace, utilised for providing the heat of the reaction, temperature measurements were taken under conditions emulating a gasification experimental run. This was accomplished by mounting a thermocouple in the quartz reactor and placing the reactor in the furnace. The same gas flow as utilised during a gasification run was also fed to the reactor during these temperature measurements, since the gas flow has a slight cooling effect on the reactor temperature. The height of the reactor was varied in the furnace in order to determine an axial temperature profile. This procedure was repeated at several furnace control set-points. The result is a series of temperature profiles determined for different furnace temperature set-points (not presented in this text). Evaluating this data, it can be determined at which height the reactor must be secured in the furnace, to ensure that the sample bed resides within an axially stable temperature zone within the furnace. This data is also utilised to determine a relationship between the necessary furnace set-point, as to achieve a desired temperature within the reactor, since the reactor temperature is influenced by reagent gas flow and air convection over the outer surface. Tests were also conducted during char gasification to confirm whether the endothermic gasification reactions influence the bed temperature. It was determined that the gasification reaction does not decrease the observed temperature within the sample bed. After the necessary temperature information has been determined, the thermocouple is removed from the quartz reactor. Gasification experimental runs are conducted without a thermocouple in the reactor or sample bed. This is done due to the fact that the thermocouple material interacts with the gaseous reagent to produce interfering CO detections at high temperature. Consistent reactor temperature is instead inferred by ensuring that a constant relationship always exists between the local furnace control temperature and the temperature logged from within the furnace, near the outside of the reactor, by an independent thermocouple. It is considered unlikely that both temperature readings would drift by the same amount in the same direction simultaneously. Thus a consistent agreement in temperatures, considered with the temperature profile data gathered from within the reactor, is considered as sufficient reassurance that the reaction temperatures are known and consistent.

E.3: Procedures and methodology during gasification

The exact procedures conducted to start a gasification experimental run will now be outlined, in chronological order in which it is conducted.

- The furnace is pre-heated to 925 °C, all char samples are introduced at this temperature to ensure any further sample transformation or residual pyrolysis occurs equivalently for all samples, regardless of gasification temperature.
- A char sample is weighed on a laboratory balance and charged into the quartz reactor.
- The sample bed is inspected to ensure uniform distribution of char particles.
- The reactor is closed with aluminium flanges and mounted into position outside the furnace, gas piping is connected to the reactor.
- The reactor is wiped down with distilled water to remove contaminants from the outside.
- The CO₂ mass flow controller is set to its desired set-point, the flow is set to purge.
- The N₂ mass flow controller is set to its desired set-point, and routed to the reactor.
- The N₂ flow flushes the sample and the reactor with N₂. This is done for 10 minutes, equating to roughly 100 reactor volumes of inert gas flushing the system.
- The thermal mass flow meter reading is checked to ensure the nitrogen flow is diverted correctly and within an expected range.
- After flushing with N₂ is complete, the furnace is closed over the reactor.
- Time is allowed for the furnace temperature to stabilise, after having been opened.
- After stabilisation the furnace set-point is decreased to the desired gasification temperature, if a gasification run is to be conducted below 925 °C.
- Time is allowed for the furnace temperature to stabilise at the new set-point.
- An additional 10 minutes is allowed after this time, to allow the system and sample bed to become isothermal.
- The reactor is pressurised during this time, by setting the electronic pressure controller to a fast response time and closing its bypass valve.
- Once the desired system pressure is achieved, the gas fittings on the reactor flanges are leak tested with a soap solution to insure there are no gas leaks.
- The data logging of all relevant instruments is started.
- The auxiliary thermocouple reading is checked, in conjunction with the furnace control temperature reading, to infer that the reactor is at the correct temperature.
- The CO₂ flow is switched from purge to flow to the reactor.
- The gasification reaction starts.

- Once CO is detected by the gas analyser, a final check is performed to ensure that the pressure and temperature readings are correct.
- The thermal mass flow meter reading is checked again to ensure the total flow is within an expected range.
- The electronic pressure controller is set to a slower response time, to smooth flow fluctuations.
- The gasification reaction is allowed time to reach completion.
- The detected CO concentration curve is inspected to ensure the gasification run has ended.
- Data logging is stopped.
- The system is depressurised by opening a depressurisation valve.
- Once the system is fully depressurised, the electronic pressure controller bypass valve is opened, to permit flow to continue to the gas analyser.
- The furnace is opened and removed from the reactor.
- As the reactor rapidly cools, the analyser readings are noted to ensure that the readings do not decrease with a drop in reactor temperature, signifying that CO producing reactions have indeed ceased prior to removing the reaction heat source.
- Once the reactor is cooled, the CO₂ flow is switched from the reactor to purge.
- Once the reactor is flushed with N₂, it is removed from its mountings and opened.
- The ash is removed from the reactor, and the reactor is blown through with compressed air to remove residual ash and to expel ash particles from the porous support disc.
- The furnace is set to heat to 925 °C, in preparation for the next run.

Appendix F

Statistical Correlations

In this section, detail is provided regarding the endeavour of relating coal and char analysis results to observed gasification reaction rates. Successful correlations are subsequently applied to derive empirical models with which to predict a key kinetic parameter. An empirical model is then tested in order to compare the predicted values to the experimentally determined results.

In order to enable modelling of char gasification progression, a means to estimate gasification reaction rate, without the requirement of time consuming empirical testing, would be greatly beneficial. If the char reactivity could be predicted at an arbitrary point during reaction progression (in this study, reactivity at 10% conversion is considered for determination of kinetic parameters), this reactivity could be combined with a suitable structural model in an attempt to model gasification rate behaviour. Adapting Equation 2.7 and Equation 4.6, by substituting the intrinsic parameters with observed specific parameters, yield the kinetic relationships represented by Equation F1 and Equation F2, respectively.

$$r_s = k_s P_{CO_2}^n \quad \text{Equation F1}$$

$$k_s = A_s e^{-\frac{E_{a,app}}{RT}} \quad \text{Equation F2}$$

The parameters k_s and n are determined from Equation F1 at 10% conversion, while the parameters A_s and $E_{a,app}$ are subsequently determined from Equation F2. The values of these parameters, determined as averages for each char, are presented in Table F1.

Table F1: Kinetic parameters for modelling

Char	$E_{a,app}$ (J/mol)	n (-)	A_s (g/g/s/bar ⁿ)
2C	241×10^3	0.342	314×10^4
2N	239×10^3	0.333	271×10^4
4C	234×10^3	0.357	151×10^4
4N	237×10^3	0.370	147×10^4
5N	252×10^3	0.369	119×10^5

The parameter $E_{a,app}$ represents the reaction rate dependence on temperature, while the parameter n represents the reaction rate dependence on reagent partial pressure. The parameter A_s is then considered to represent the inherent reactivity of the char sample, to the exclusion of operating conditions. The values for $E_{a,app}$ determined here are in good agreement with the values reported in Table 5.1, determined from Arrhenius plots. The values for $E_{a,app}$ and n are fairly consistent between different chars, despite the significant differences in char properties in many cases, implying that neither $E_{a,app}$ nor n are strongly correlated to inherent reactivity or char properties, and that they may henceforth perhaps be considered constant and universally applicable for a coal of similar origin. The remaining parameter is A_s , which would have to be determined for each individual sample, due to the significant differences in

magnitude thereof between the chars. Therefore, it is endeavoured to correlate A_s with coal and char properties in an attempt to derive a model to predict A_s .

The values of A_s , as reported in Table F1, were compared to all coal and char characterisation analysis results. The analysis results were considered in the forms of the values raised to a certain power, square roots of the values, natural logarithms of the values, natural exponential functions of the values, and the values as is. A useful correlation was inferred from a strongly linear relationship between the values of A_s of all five chars, and their respective characterisation values in any of the forms mentioned above.

By correlating the values of A_s to all the coal and char properties in this manner, petrographic results appeared as the best predictors of A_s . Specifically, the following indices, as reported or derived, are the most useful to predict A_s :

- Total vitrinite % (TV), as reported.
- The maceral index (MI), as defined by Su *et al.* (2001).
- An adapted maceral index (AMI), based on the MI, and reactive maceral index (RMI) defined by Helle *et al.* (2003).
- Detrovitrinite % (DV), as reported.

The following equations are utilised to calculate the indices mentioned above:

$$MI = HVF^{2.5} RF \quad \text{Equation F3}$$

$$HVF = \frac{CV}{30} \quad \text{Equation F4}$$

$$RF = \frac{L + \frac{V}{VRR^2}}{I^{1.25}} \quad \text{Equation F5}$$

$$AMI = HVF^{4.5} RMI \quad \text{Equation F6}$$

$$RMI = \frac{L + \frac{V}{VRR^2}}{NRI^{1.25}} \quad \text{Equation F7}$$

$$NRI = I - RS - RI \quad \text{Equation F8}$$

Depending on the detail of the petrographic results available, the indices may be considered in the order: TV → MI → AMI → DV. The values of these indices of each char are provided in Table F2.

Table F2: Petrographic index values for correlations

Char	TV	MI	AMI	DV
2C	26.6	0.315	0.801	8.0
2N	21.1	0.226	0.699	6.6
4C	17.6	0.164	0.478	2.5
4N	8.8	0.050	0.179	2.5
5N	50.5	1.316	1.376	23.0

The following equations represent the best fit correlations between A_s and these four indices, respectively:

$$A_s \cong 267(TV^{2.7}) + 1307 \times 10^3 \quad \text{Equation F9}$$

$$A_s \cong 7761 \times 10^3(MI^{1.2}) + 1116 \times 10^3 \quad \text{Equation F10}$$

$$A_s \cong 3805 \times 10^3(AMI^{3.2}) + 1343 \times 10^3 \quad \text{Equation F11}$$

$$A_s \cong 71220(DV^{1.6}) + 1186 \times 10^3 \quad \text{Equation F12}$$

Graphically, these correlations are presented in Figure F1, visualising Equation F9 (red graph), Equation F10 (blue graph), Equation F11 (green graph), and Equation F12 (black graph).

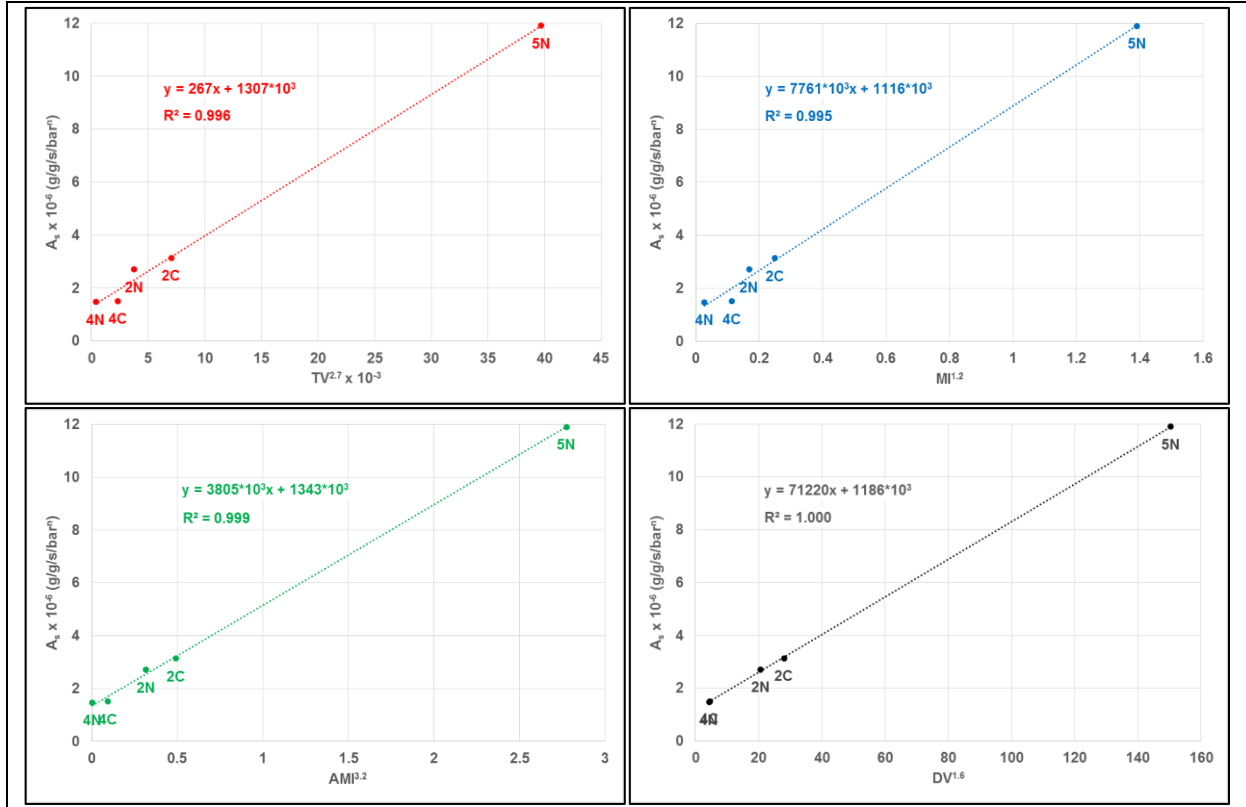


Figure F1: Correlations between coal properties and the pre-exponential factor

Utilising the correlations represented by Equation F9 through Equation F12, predicted values of the pre-exponential factor, A_{calc} , were determined. These values are presented in Table F3, accompanied by the respective error percentages of the deviation of A_{calc} relative to the experimentally determined values of A_s .

Table F3: Predicted pre-exponential factor values

	Char 2C	Char 2N	Char 4C	Char 4N	Char 5N
A_{calc} (g/g/s/barⁿ)					
Equation F9 (TV)	3187745	2305708	1923921	1403205	11908683
Equation F10 (MI)	3059998	2419854	2005024	1328414	11910814
Equation F11 (AMI)	3214674	2551157	1701297	1358511	11898840
Equation F12 (DV)	3179346	2654184	1503276	1490179	11900654
Error (%)					
Equation F9 (TV)	1.6	-14.9	27.5	-4.6	0.1
Equation F10 (MI)	-2.4	-10.6	32.9	-9.7	0.1
Equation F11 (AMI)	2.5	-5.8	12.7	-7.7	0.0
Equation F12 (DV)	1.4	-2.0	-0.4	1.3	0.0

Graphically, the accuracies of the correlation predictions are presented in Figure F2 as parity plots between the experimentally determined values, A_s , and the calculated values, A_{calc} , utilising the coal properties TV (red graph), MI (blue graph), AMI (green graph), and DV (black graph).

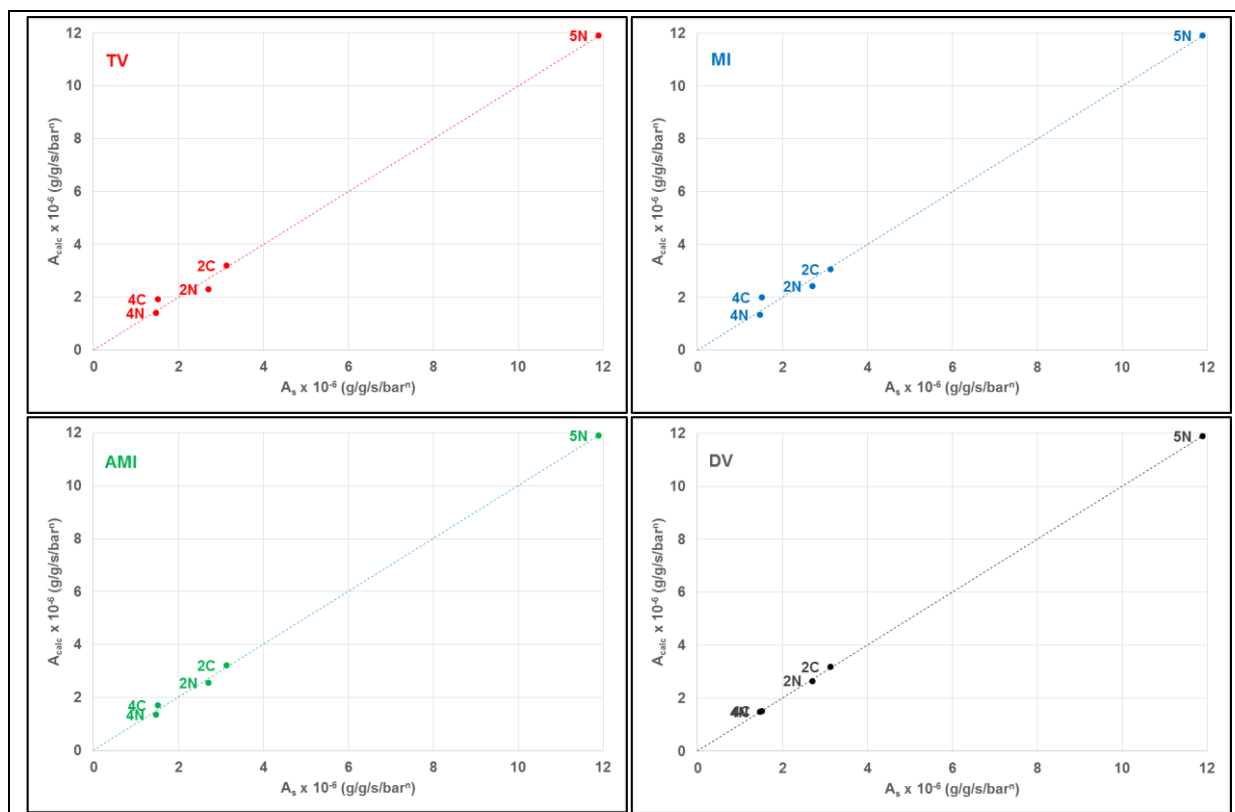


Figure F2: Parity plots of predicted pre-exponential factor values

In general, the greater the petrographic detail considered, the more accurate the model predictions appear to be. If the content of only the main groups of macerals are known, then the property TV must be utilised. If the vitrinite rank reflectance is known in addition, then the property MI can be calculated and utilised. If inertinite can be distinguished and quantified between reactive and non-reactive, then the property AMI can be calculated and utilised. If the forms of vitrinite are distinguished and quantified, then the property DV can be utilised. Utilising DV as a predictor of A_s appears to be the most accurate for the coal types studied.

In practise, these correlations can be incorporated into a reaction rate model, in order to predict sample reactivity utilising only coal properties and operating conditions. An example of such a model is obtained by combining Equation F1 and Equation F2, and substituting the experimental parameters with calculated parameters, resulting in Equation F13.

$$r_{calc} = P_{CO_2}^n A_{calc} e^{-\frac{E_{a,app}}{RT}} \quad \text{Equation F13}$$

The parameter A_{calc} in Equation F13 may be substituted by any function which approximates A_s , such as Equation F9 through Equation F12. The accuracy of r_{calc} will be influenced by the compounded errors of the approximation of A_s , and the determination of the parameters n and $E_{a,app}$. None the less, r_{calc} may still be relatively accurate and useful, considering that the use of the model does not require further empirical testing (other than for verification). As a demonstration, Equation F13 will be combined with Equation F12 to predict the char specific reactivity. A temperature of 875 °C ($T = 1148.15$ K) will be considered at an operating pressure of 10 bar ($P_{CO_2} = 3$ bar), representing the average of the experimental conditions investigated. The values of the parameters n and $E_{a,app}$ will be set to those as reported in Table F1 for the respective chars. The results of the model at these conditions, r_{calc} , are compared to the actual experimental values, r_s , in Table F4, accompanied by the respective error percentages of the deviation of r_{calc} relative to r_s .

Table F4: Predicted specific reactivity compared to experimental values

Char	$r_s \times 10^5$ (g/g/s)	$r_{calc} \times 10^5$ (g/g/s)	Error (%)
2C	4.57	4.78	4.7
2N	5.07	4.94	-2.6
4C	5.02	5.07	0.9
4N	3.63	3.81	4.9
5N	6.17	6.20	0.6

The predicted values of specific reactivity are within 5% of the actual experimental values, in this example. The significance hereof is that the proposed kinetic model may be successfully integrated with a suitable structural model, to model the gasification progression. This endeavour may be pursued in future study. In this example the specific reactivity would be modelled, however, other representations of reaction rate could also be modelled in a similar manner, by converting the specific reactivity to other quantities according to the relationships provided by Equation F14 and Equation F15.

$$r_c|_{X=0.1} = 0.9 r_s C_f \cong 0.9 r_s (m_{sample} \times FC) \quad \text{Equation F14}$$

$$\left. \frac{dX}{dt} \right|_{X=0.1} = 0.9 r_s \quad \text{Equation F15}$$