

The influence of carbon dioxide on the gasification rate of Highveld coal chars at elevated pressures

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DECLARATION

I, Susara Maria (Saartjie) Gouws, hereby declare that the dissertation entitled: "*The influence of carbon dioxide on the gasification rate of Highveld coal chars at elevated pressures*", submitted in fulfilment of the requirements for the degree Master's 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.

Signed at.....on the.....day of.....20....

.....
Saartjie Gouws

CONFERENCE PROCEEDINGS

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ABSTRACT

Gasification is an important process which is applied extensively for coal utilization. In the South African context, coal gasification is the first step in the coal to liquid (CTL) process and is performed in a fixed-bed dry bottom (FBDB) gasifier at high pressure (~ 30 bar). Although the gasification reactivity of Highveld coal chars has received considerable attention in the past, only limited information is available on the high pressure reactivity. It is not known how the coal/char reactivity at elevated pressures is related to the standard reactivity test which is performed at atmospheric pressure.

In this study, the carbon dioxide (CO_2) gasification reactivity of different coal chars was investigated over a wide pressure range (1-30 bar). The samples originated from different seams of the Highveld coalfield. Gasification experiments with char particles in the size range of 425-500 μm were performed in a laboratory-scale high pressure fixed bed reactor within a temperature range of 780-855°C. The CO_2 concentration in the reagent gas was varied between 5-30% with the balance N_2 . These conditions were selected to conduct the experiments in the chemical reaction controlled regime.

It was observed that the reaction rate was solely a function of temperature and CO_2 partial pressure, and the effect of total system pressure was insignificant. The reaction rate increased with increasing CO_2 partial pressure throughout the range of partial pressures investigated (0.05-9.0 bar). The reactivity was well described by both the Langmuir Hinshelwood and the empirical power law kinetic models. Overall activation energies for the Seam 2, 4 and 5 coal chars were 261 ± 20 kJ/mol, 260 ± 26 kJ/mol and 250 ± 30 kJ/mol respectively.

Char structural changes are known to occur during gasification, however up to date the effect of CO_2 partial pressure on the extent of pore development has not been quantified or explained. To investigate the effect of CO_2 partial pressure on pore growth, CO_2 and N_2 adsorption measurements were performed on chars and partially converted chars. The analyses showed that at fixed conversions an increase in CO_2 partial pressure generally resulted in an increase in both the char micro- and mesopore surface areas. These observations suggest that the degree of pore development is a function of CO_2 partial pressure. This is significant and has fundamental implications for the reaction of CO_2 with coal chars. It is required to be incorporated into rate equations for improved kinetic modelling at high pressures.

The structural Random Pore Model (RPM) accurately described the experimental data up to 20% conversion. The structural parameter (ψ) increased with increasing CO_2 partial pressure suggesting an increased char pore growth at higher CO_2 partial pressures which corresponds to the surface analysis results.

Keywords: CO_2 gasification; elevated pressure; Highveld coal char; pore development

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LIST OF SYMBOLS

Symbol	Description	Units
A	Frequency factor	$\text{g g}^{-1} \text{s}^{-1} \text{bar}^n$
C_f	Free carbon active site	-
$C(O)$	Carbon-oxygen surface complex	-
C_t	Total amount of active sites	g^{-1}
D_{eff}	Effective diffusivity coefficient	$\text{m}^2 \text{s}^{-1}$
d_p	Particle diameter	mm
E_a	Observed activation energy	kJ mol^{-1}
E	Activation energy	kJ mol^{-1}
ΔH_0	Enthalpy	kJ mol^{-1}
Δh_{rxn}	Enthalpy of reaction	kJ mol^{-1}
$k_{p,coal}$	Thermal conductivity	$\text{W m}^{-1} \text{K}$
k_s	Reaction rate constant	s^{-1}
$k_1, k_2, k_3,$	Reaction rate constants	s^{-1}
L_0	Total pore length per unit volume	mm^{-3}
$m_{c,cal}$	Calculated carbon converted	g
$m_{c,exp}$	Experimental carbon converted	g
$m_{C,0}$	Carbon in unconverted sample	g
m_{S0}	Sample mass	g
MW	Molecular weight of carbon	g mol^{-1}
n	Reaction order	-
$\dot{n}$	Molar flow rate	mol s^{-1}
p_{CO}	CO partial pressure	bar
p_{CO_2}	CO ₂ partial pressure	bar
R	Gas constant	$\text{J mol}^{-1} \text{K}^{-1}$
r_A	Reaction rate	$\text{mol m}^{-3} \text{s}^{-1}$
r_c	Carbon conversion rate	g s^{-1}
r_s	Specific reaction rate	$\text{g g}^{-1} \text{s}^{-1}$
r_{s0}	Initial reactivity	$\text{g g}^{-1} \text{s}^{-1}$
s	Sample standard deviation	Varies
S_0	Initial surface area	$\text{m}^2 \text{m}^{-3}$
s_P	Error on modelling parameter	Varies
T	Temperature	$^{\circ}\text{C}$ and K
t	Time	s

X	Conversion	-
$\bar{x}$	Sample mean	Varies
x_{ash}	Ash yield fraction	-
$x_c(daf)$	Carbon fraction (dry ash free basis)	-
y_{co}	Fraction of CO	-

Greek Symbols

ε_0	Initial porosity	-
η	Internal effectiveness factor	-
θ	Degree of surface coverage	-
σ_r	Variance on residual	Varies
ψ	Structural parameter	-

LIST OF ABBREVIATIONS AND ACRONYMS

Abbreviation or acronym	Description
a.d.	Air dried basis
BET	Brunauer-Emmet-Teller
BJH	Barrett–Joyner–Halenda
CTL	Coal-to-liquid
d.a.f.	Dry ash free basis
d.b.	Dry basis
DA	Dubinin-Astakhov
DR	Dubinin-Radushkevich
DTF	Drop Tube Furnace
EPC	Electronic pressure controller
FBDB	Fixed-bed dry bottom
FBR	Fixed bed reactor
GM	Grain Model
HK	Horvath-Kawazoe
HM	Homogeneous model
HV	Heating value
HVF	Heating value/30
I	Inertinite
ICL	Indirect coal liquefaction

ISO	International Standards Organization
L	Liptinite
LH	Langmuir-Hinshelwood
m.m.f.	Mineral matter free basis
MFM	Mass flow meter
MI	Maceral Index
NDIR	Non-dispersive infra-red
NDM	Normal Distribution Model
PDTF	Pressurised drop tube furnace
PL	Power law
PTGA	Pressurized thermo-gravimetric analyser
PWHR	Pressurized wire-heating reactor
R	Mean random vitrinite reflectance
RF	Reactivity of the coal
RPM	Random Pore Model
SANS	Small angle X-ray and neutron scattering
SCM	Shrinking Core Model
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
TGA	Thermo-gravimetric analyzer
TPD	Temperature-programmed desorption
V	Vitrinite
VBA	Visual Basic for Applications
vol %	Volume percentage
WM	Wen Model
wt %	Weight percentage
WXRD	Wide angle X-ray diffraction
XRD	X-ray diffraction
XRF	X-ray fluorescence

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CHAPTER 1: INTRODUCTION

1.1 Background and motivation

In a world where the consumption of energy is ever increasing, the efficient use of energy resources has become crucial. Currently coal supplies a third of the world's energy and accounts for 40% of electricity generation (International Energy Agency, 2017).

The South African economy in particular is heavily dependent on coal utilization and reserves. In recent years the mineral has contributed even more to the economy than gold (Statistics South Africa, 2015). The country relies on coal for 77% of primary energy needs (Department of Energy, 2015). Eskom (the national power utility) produces about 90% of its electricity by coal fired power stations and is ranked first in the world as steam coal user (Department of Energy, 2015; Eskom, 2015b). South Africa's coal-to-liquid (CTL) plants account for 30% of the country's petroleum fuels, making it the largest coal to chemicals producer in the world (Eberhard, 2011). Apart from its extensive contribution to the domestic economy, about 28% of South Africa's coal is exported (Department of Energy, 2015).

The country's coal deposits are quite shallow which makes coal mining in South Africa relatively cheap in comparison with other countries (Eskom, 2015a). The country's coal reserves are estimated at 53 billion tonnes and with a current mining rate of 224 million tons of marketable coal a year, the coal supply is estimated to last for almost 200 years (Eskom, 2015a). The efficient use of coal for the generation of electricity as well as the production of chemicals will remain essential for South Africa in the foreseeable future.

The gasification of coal is an important process which is applied extensively for coal utilization (Liu et al., 2000a). In recent years, environmental concerns regarding coal utilization have increased and clean coal technologies have gained renewed interest. Coal gasification has shown to be a clean and effective coal utilization process (Molina and Mondragon, 1998). This process is the first step in coal-to-liquid (CTL) technologies when using an indirect coal liquefaction (ICL) approach (Höök and Aleklett, 2010). Commercially, the process is carried out by feeding a mixture of steam and oxygen into large and complex gasifiers (Bunt and Waanders, 2008). The various reactions occurring in the gasifiers can be divided into coal pyrolysis, combustion, char gasification and gas phase reactions (Kajitani et al., 2006).

Kinetic studies on char gasification play an important role in understanding the gasification process and designing effective gasifiers. These studies are usually performed through laboratory scale experiments using different reagent gas mixtures containing H_2O , O_2 and CO_2 . Although the steam and oxygen reactions are of more practical value, the reaction with CO_2

serves as a reference for fundamental gasification studies (Zhou et al., 2016). Numerous studies have investigated CO₂ gasification kinetics and modelling at low pressures (Lee and Kim, 1995; Ye et al., 1998; Everson et al., 2008; Fermoso et al., 2010; Tanner and Bhattacharya, 2016).

Although low pressure kinetic studies have contributed to gasification modelling, a need exists to study gasification reactivity at industrial reaction conditions. Commercial gasifiers are operated at high temperatures (1000-1600°C) and pressures (20-30 bar) (Garche et al., 2013) but operating lab equipment at these conditions can be challenging. Gasification studies performed at high pressures are more limited specifically for South African coals. Studies at high pressure have been carried out for other coal chars by various authors (Kajitani et al., 2002; Roberts and Harris, 2006; Zhang et al., 2014; Liu et al., 2015). The empirical power law is reported to be valid up to 10 bar CO₂ partial pressure (Roberts and Harris, 2000; Kajitani et al., 2006), however the Langmuir Hinshelwood model is more popular for use at higher CO₂ partial pressures (above 10 bar).

A limitation of some high pressure gasification studies is that the experimental reactivity data is obtained under conditions where pore diffusion processes control the gasification rate (Kajitani et al., 2002). In order to obtain accurate kinetic models which are applicable to different technologies and reaction conditions, the chemical reaction should be the rate-limiting step during experimental runs (Roberts and Harris, 2006).

The gasification rate is not only dependent on the reaction conditions but also on the physical char structure (Liu et al., 2000b). Gasification takes place inside char pores and leads to pore growth as well as the formation of new pores (Liu et al., 2015). Significant physical changes in coal chars have been reported to occur throughout gasification (Coetzee et al., 2015). Parameters of kinetic models such as the Langmuir Hinshelwood equation are determined at a common extent of conversion and therefore pore structural changes are not accounted for. However, it has been suggested that reagent partial pressure affects the internal surface area of the char (Roberts and Harris, 2000).

The uniqueness of the present study lies in the systematic investigation of the effect of CO₂ partial pressure on the gasification rate of South African chars at high pressures as well as the investigation of the effect of CO₂ partial pressure on the char's internal surface area development during CO₂ gasification. Up till date this effect has not been quantified or explained. Changes in internal surface areas have fundamental implications for the reaction of CO₂ with coal chars and are required to be incorporated into rate equations for improved modelling at high pressures.

1.2 Problem statement

Char gasification reactivity requires extensive investigation for accurate kinetic modelling (Tanner and Bhattacharya, 2016). For this reason numerous studies were focused on investigating char gasification reactivity using thermo-gravimetric analysis (TGA) at low pressures. Up till date only limited experimental studies have investigated the high pressure reactivity of Highveld coals and considering that industrial gasifiers are operated at high pressure, it is relevant to determine kinetic parameters for industrial applicability.

The char gasification rate has shown to be dependent on the physical char structure and authors have observed physical changes to occur during gasification at high pressure (Roberts and Harris, 2000; Liu et al., 2015). Extensive investigation is required in order to understand the effect of different process conditions (such as reagent partial pressure) on the char structure development during gasification. In most models these changes are not accounted for and incorporating them will lead to more accurate modelling.

In this study, the CO₂ gasification reactivity of Highveld chars is investigated at high pressures and a model which accurately describes the reactivity of the chars at industrial conditions is developed. Further, the effect of CO₂ partial pressure on the development of internal char surface area is studied.

1.3 Aim and objectives

The aim of this study is to obtain a systematic relationship between CO₂ concentration and gasification reactivity of South African Highveld coal chars over a wide pressure range.

In order to achieve this aim the following objectives are set:

- Determine chemically controlled char gasification kinetics using different concentrations of CO₂ at elevated pressures and different temperatures.
- Develop a kinetic model which can be used to describe gasification rates at elevated pressures as a function of CO₂ partial pressure and temperature.
- Investigate the effect of CO₂ partial pressure on the development of the char's internal surface area.
- Correlate char reactivity with char characteristics.

1.4 Scope of the study

A scope was developed for this study to guide the research process in order to achieve the project objectives. This study will be divided into two sections: CO₂ gasification reactivity and surface area analyses.

CO₂ gasification reactivity

A laboratory scale fixed-bed reactor will be used to perform CO₂ gasification experiments at low and elevated pressures. The samples will include three non-caking Highveld coal chars from different seams (2, 4 and 5). In a previous study by Henning (2017) the gasification reactivity of both caking and non-caking coal chars were studied and no significant difference was observed in the kinetic parameters. Caking coals are generally unsuitable for gasification in a fixed bed dry bottom gasifier and only non-caking coals are used in this study. Pre-experimental tests will be conducted to ensure that the reactivity data is measured under reaction controlled conditions. Gasification experiments will be performed on the different coal chars at different temperatures and CO₂ partial pressures. The reactivity data will then be collected and compared at the different experimental conditions. Kinetic models will be evaluated to obtain a suitable model in order to describe the gasification kinetics of the coal chars at high pressures.

Surface area analyses

Some of the chars and partially converted chars will be analysed using CO₂ and N₂ adsorption techniques. The effect of CO₂ partial pressure on the surface area development of the char will be investigated.

1.5 Study outline

A schematic outline of this study is shown in Figure 1.1. Chapter 1 includes the background and motivation for the study as well as the problem statement, aim and objectives and scope. In Chapter 2 a literature study is provided on CO₂ gasification as well as char pore development. The experimental rig and procedures for the CO₂ gasification reactivity measurements as well as the char surface analyses are discussed in Chapter 3. In Chapter 4 the CO₂ gasification experimental results are presented and different kinetic and structural models are evaluated. The results from the surface analyses are also shown and explained in this chapter. The final conclusions of the study as well as recommendations for future study are discussed in Chapter 5.

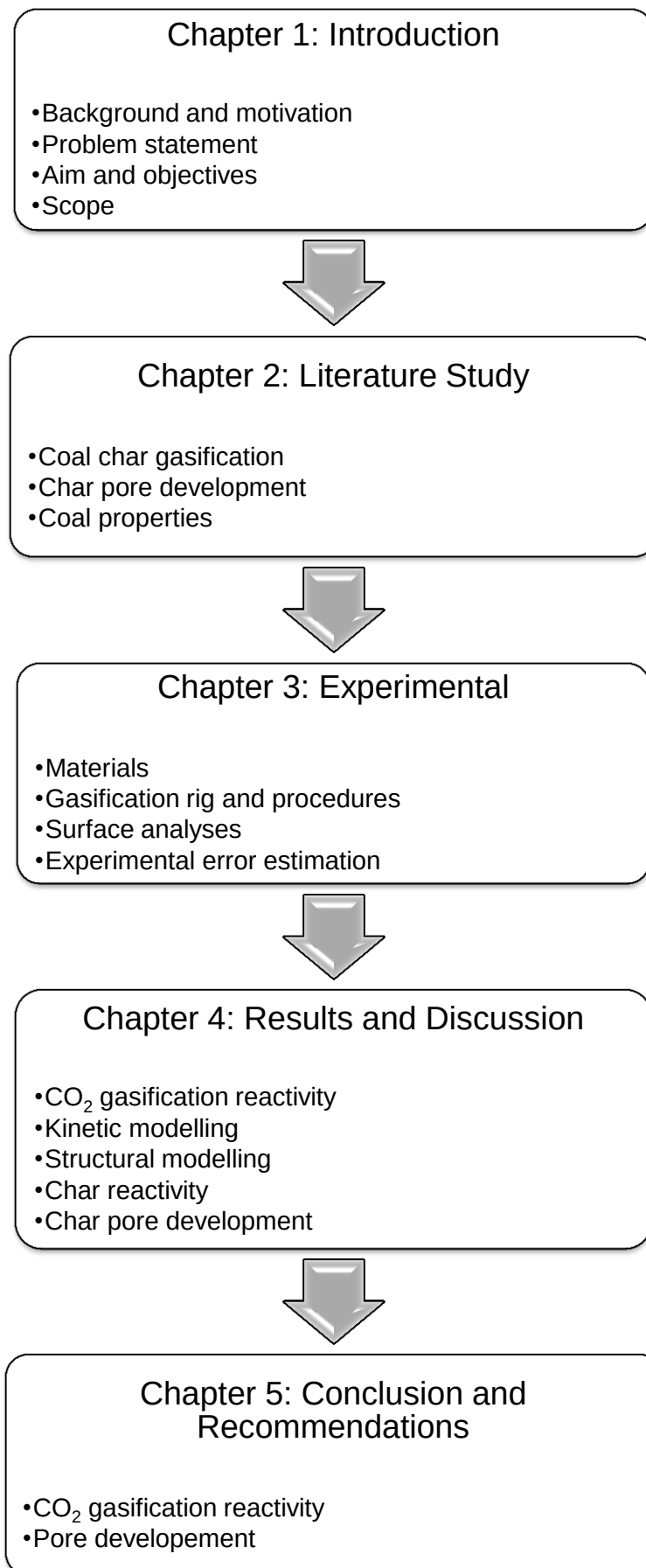


Figure 1.1: Study Outline

CHAPTER 2: LITERATURE STUDY

2.1 Introduction

In this chapter a literature review on coal char gasification as well as char pore development is provided. Background to the area of research is discussed and areas which require further research are identified.

In Section 2.2 coal char gasification with CO₂ is discussed. This includes gasification reactions and the char-CO₂ mechanism (2.2.1). Low pressure CO₂ gasification studies are briefly reviewed in Section 2.2.2 and high pressure studies are discussed in greater detail in Section 2.2.3. Modelling of reactivity data is explained in Section 2.2.4. A summary of the CO₂ gasification studies at both low and high pressures is provided in Section 2.2.5.

In Section 2.3, literature on char structural development during gasification is reviewed. The correlation of different coal properties with char-CO₂ reactivity is discussed in Section 2.4.

2.2 Coal gasification

Coal gasification involves the incomplete combustion of coal. During this process the non-ash fraction of the coal is converted into gases while preserving the heat of combustion of the feedstock. These gases can then either be converted to chemical products or combusted for energy production (Bell et al., 2010). Commercially, the process is carried out in large and complex gasifiers such as the fixed-bed dry bottom (FBDB) gasifier (Bunt and Waanders, 2008). In this gasifier the coal is fed from the top of the gasifier while the reagent gases (H₂O and O₂) are fed counter-currently from the bottom.

2.2.1 Coal char gasification reactions

The first step in a gasifier is pyrolysis or devolatilisation of the coal, followed by gasification of the pyrolysis residue (char) (Bunt and Waanders, 2008). The main reactions taking place during the gasification process are shown in Reactions 2.1-2.5 (Bell et al., 2010):



The reactions shown in Reaction 2.1 and 2.2 are endothermic and are usually regarded as the most important gasification reactions. The energy needed for these reactions is provided by the combustion reaction (Reaction 2.3). The water gas shift reaction (Reaction 2.4) mainly proceeds at high concentrations of steam and the methanation reaction (Reaction 2.5) becomes more important at elevated pressures (Molina and Mondragon, 1998).

Several authors have observed that the char gasification reaction with CO₂ is slower than the reaction with steam (Mühlen et al., 1985; Roberts and Harris, 2000; Kajitani et al., 2002). The reaction of CO₂ with the carbon in the char (Reaction 2.1) (known as the Boudouard reaction) serves as a reference for fundamental gasification studies (Zhou et al., 2016). Different mechanisms have been derived for this reaction however the oxygen-exchange mechanism proposed by Ergun (1956) is most commonly used (Lahijani et al., 2015). Further details of this mechanism are discussed in Section 2.2.4.1.2.

2.2.2 Low pressure CO₂ Gasification

Numerous CO₂ gasification studies have been conducted at atmospheric pressures. The present study deals with high pressure CO₂ gasification of South African coal chars. Only the main findings of low pressure studies using South African coals are discussed in this section. Studies on CO₂ gasification specifically at high pressures are reviewed in more detail in Section 2.2.3.

All the low pressure CO₂ gasification studies reviewed were performed in a TGA apparatus. Both Everson et al. (2008) and Veca and Adrover (2014) observed the reaction rate to be strongly dependant on temperature. Du Toit (2013) attributed this phenomenon to chemical reaction controlled conditions.

The effect of CO₂ partial pressure on the reaction rate was studied by Everson et al. (2008) and du Toit (2013). The CO₂ partial pressure was varied by varying the CO₂ concentration in the reagent gas. The reaction order with respect to CO₂ was determined as 0.50 ± 0.04 by Everson et al. (2008) and 0.56 ± 0.07 by du Toit (2013). Salatino et al. (1998) reported a CO₂ reaction order of 0.74 for a South African coal char.

Other parameters shown to affect the gasification rate (aside from operating conditions) include coal rank, char structure and mineral matter content. Engelbrecht (2008) observed decrease in reactivity with increasing coal rank. Koekemoer (2010) determined activation energies for CO₂ gasification ranging from 163-225 kJ/mol for various coal fractions. The wide range of activation energies was attributed to the large difference in mineral matter content of the coal.

Further details of low pressure studies using South African coal chars are summarised in Table 2.1.

2.2.3 High pressure CO₂ Gasification

Gasification studies at elevated pressures are more limited compared to those at low pressures. In this section the results reported in literature regarding the effects of reaction conditions on the gasification rate at high pressures are reviewed.

2.2.3.1 Temperature

Temperature plays a significant role during gasification. Many authors agree that the rate limiting step in the overall gasification reaction is mainly dependent on temperature (Ahn et al., 2001; Kajitani et al., 2002; Tremel et al., 2012). In Figure 2.1 an Arrhenius plot demonstrates the dependence of the overall reaction rate on temperature. An increase in temperature shifts the reaction rate from chemical reaction controlled to pore diffusion- or external mass transfer controlled.

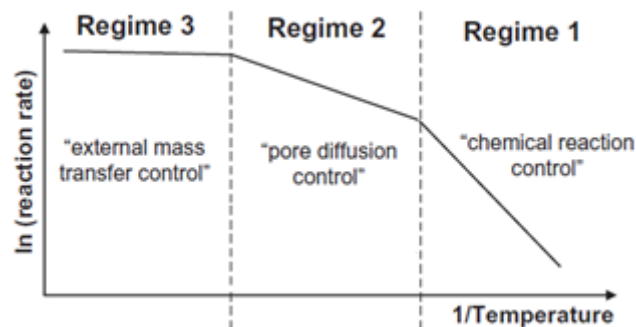


Figure 2.1: Effect of temperature on reaction rate and controlling mechanism (Adapted from Tremel et al., 2012)

According to Tremel et al. (2012) the chemical reaction is the rate determining step at lower temperatures (usually below 1000°C), however the temperature range where this transition occurs will be different for different chars depending on the char properties. Under both chemical reaction controlled and pore diffusion controlled conditions (Regime 1 and 2) the gasification rate increases exponentially with increasing temperature. The increase is more significant under Regime 1 conditions (demonstrated by the steeper gradient in Figure 2.1).

In a high pressure gasification study by Ahn et al. (2001) the influence of temperature on the gasification rate of an Indonesian sub-bituminous coal char was investigated in a pressurized

drop tube furnace (PDTF). The coal was devolatilized in the PDTF under nitrogen at atmospheric pressure prior to gasification. Gasification was performed in the temperature range of 900-1400°C. At higher temperatures (1100-1400°C) the activation energy was determined as 71.5 kJ/mol and at lower temperatures (900-1000°C) it was almost double the amount at 144 kJ/mol. This observed change in activation energy was attributed to pore diffusion controlled conditions at higher temperatures.

Kim et al. (2014) investigated the effect of temperature on the gasification reactivity of a Berau sub-bituminous coal char at elevated pressures. The low temperature runs were performed in a TGA while the high temperature runs were performed in a pressurized wire-heating reactor (PWHR). In order to vary the CO₂ partial pressure the authors varied the system pressure and kept the CO₂ concentration fixed at 100%. The internal and external effectiveness factors were analysed to determine the effects of temperature and CO₂ partial pressure on the reaction regime during gasification. The change in the internal and external effectiveness factors with temperature as a function of CO₂ pressure is shown in Figure 2.2.

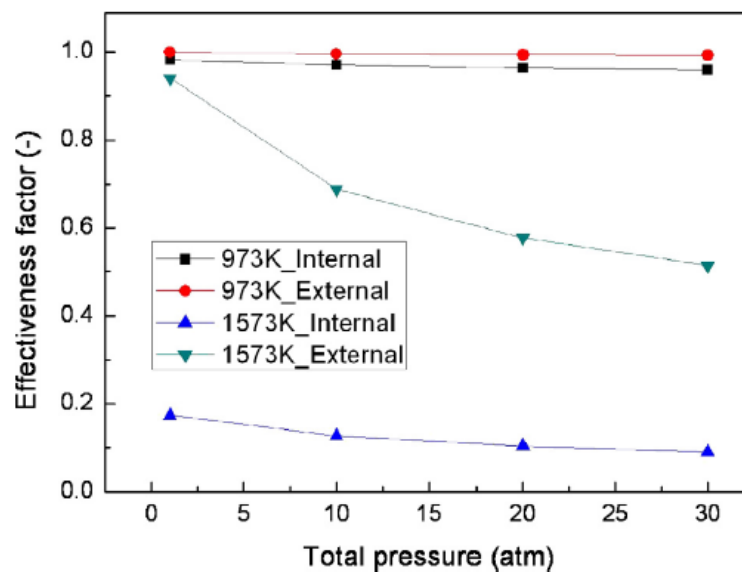


Figure 2.2: Effect of temperature and CO₂ partial pressure on effectiveness factors (Taken from Kim et al., 2014)

At 973K (700°C) both effectiveness factors (internal and external) remain close to 1 over the entire pressure range which indicates reaction controlled conditions. At the higher temperature of 1573K (1300°C), the external effectiveness factor and the internal effectiveness factor decrease with increasing CO₂ partial pressure. This demonstrates that reactions occurring at

high temperatures (which are not reaction controlled) become even more limited by internal and external diffusion limitations at high CO₂ partial pressures.

2.2.3.2 CO₂ partial pressure

Various authors have investigated the effect of CO₂ partial pressure on gasification reactivity by either changing the concentration of the CO₂ gas at a constant system pressure (Ahn et al., 2001; Kajitani et al., 2002; Park and Ahn, 2007) or by changing the system pressure at a constant CO₂ concentration (Roberts and Harris, 2006; Kim et al., 2014). Globally the CO₂ gasification reaction follows a reaction order on the CO₂ partial pressure which is usually lower than 1 (Lee et al., 2014). A summary of the reaction orders determined for different high pressure studies is shown in Table 2.2.

The experimental results obtained by Park and Ahn (2007) in a pressurized TGA for five different coals (Alaska, Cyprus, Drayton, CNCIEC and Denisovsky) ranging from sub-bituminous (Alaska) to bituminous (Denisovsky) are shown in Figure 2.3. The effect of CO₂ partial pressure was studied at a constant temperature of 900°C and 10 bar total pressure. The partial pressure was varied from 1.8 to 4.95 bar. A reaction order of 0.4-0.7 was observed for the five different chars.

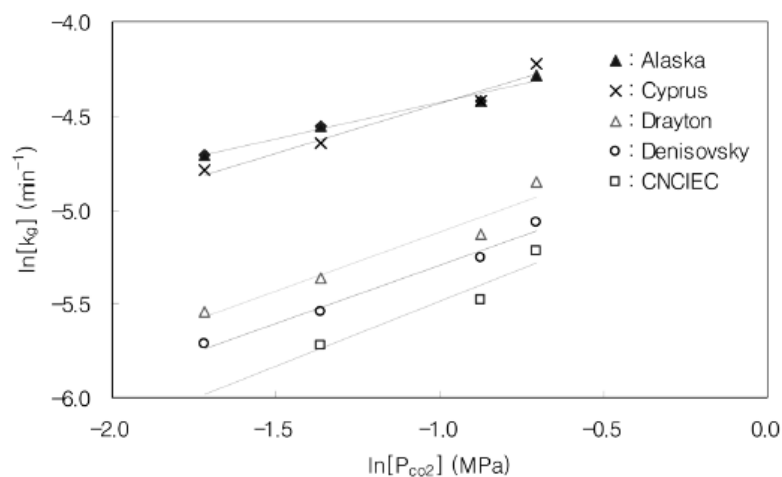


Figure 2.3: Effect of CO₂ partial pressure on the gasification rate (Taken from Park and Ahn (2007))

Ahn et al. (2001) also investigated the effect of CO₂ partial pressure on the gasification rate at a temperature of 1300°C and a total system pressure of 10 bar. The CO₂ partial pressure was varied in the range of 1-5 bar. The apparent reaction rate was proportional to the CO₂ partial pressure with an order of 0.4.

Mühlen et al. (1985) performed gasification experiments in a pressure range of 1-70 bar and observed similar results as Ahn et al. (2001) and Park and Ahn (2007) however they observed the reaction rate to level off at high partial pressures. Roberts and Harris (2000) also observed this phenomenon for Australian bituminous and semi-anthracite chars in a PTGA. At low CO₂ partial pressures (1-10 atm) the reaction rate showed an order similar to the order measured for the chars at 1 atm (0.5-0.7). When the partial pressure was increased further the effect of partial pressure was less and the apparent reaction order was found to be close to zero at partial pressures of 20-30 atm. Further investigation by Roberts and Harris (2006) showed that the reason for the drop in reaction order observed at higher CO₂ partial pressures was due to the saturation of the active sites on the char surface area. The authors performed temperature-programmed desorption (TPD) experimental work in order to determine the concentration of the intermediate surface complex C(O) (the complex of the CO₂ molecule adsorbed on an active site). The concentration of CO that desorbs is indicative of the concentration of the intermediate surface complex C(O) present at the time the reaction was stopped. The desorption peak obtained from the TPD analysis following gasification at 20 bar was similar in size to the peak obtained after gasification at 30 bar. This confirmed the suggestion that the reason for the decrease in reaction order at high reagent pressures was due to the saturation of the surface active sites.

In general, it can be concluded that there is no consensus in literature regarding the reaction order with respect to CO₂ at high pressures. As shown in Table 2.2 most authors observe it to be in the range of 0.2-0.8. The order has also been observed to change at higher pressure (Mühlen et al., 1985; Roberts and Harris, 2006).

2.2.3.3 Total system pressure

Most authors agree on the effect of temperature and reactant partial pressure on the gasification rate of chars, however there is some disagreement regarding the effect of total system pressure. Park and Ahn (2007) studied the influence of total pressure on the CO₂ gasification rate of 3 different coal chars by varying the pressure between 5 and 20 bar at a constant temperature and CO₂ partial pressure of 900°C and 2.87 bar respectively. The total system pressure was not observed to have a significant influence on the reaction rate as shown in Figure 2.4.

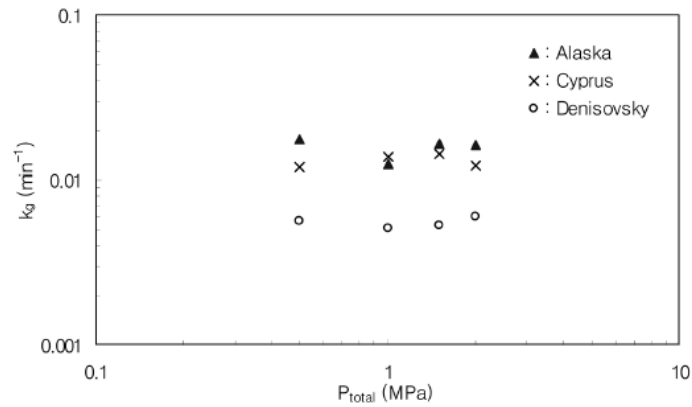


Figure 2.4: Effect of total system pressure on the reaction rate constant (Taken from Park and Ahn (2007))

In a different study by Ahn et al. (2001) the gasification rate was found to be dependent on the total system pressure at a constant CO_2 partial pressure of 2 bar and a temperature of $1300^\circ C$. The apparent reaction rate constant (k) decreased exponentially with increasing total pressure as shown in Figure 2.5. Due to the pressure dependency of the reaction rate constant, the authors proposed to include a term for total system pressure in the reaction rate equation.

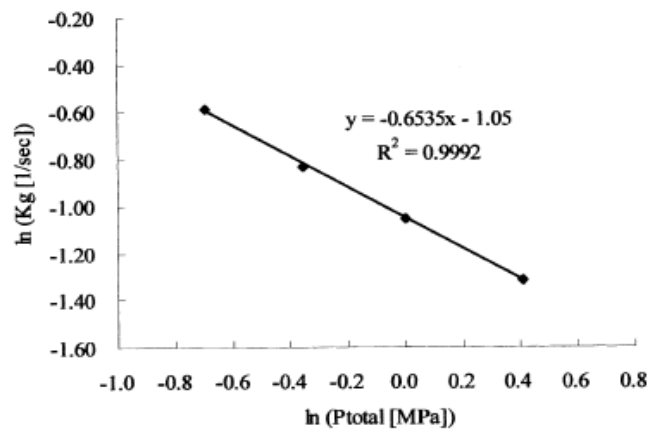


Figure 2.5: Effect of total system pressure on the reaction rate constant (Taken from Ahn et al. (2001))

Kajitani et al. (2002) investigated gasification with CO_2 in a Pressurized Drop Tube Furnace (PDF). The coals used included an Australian bituminous coal with a high fuel ratio and a Chinese bituminous coal with a low fuel ratio. The coals were devolatilized by rapid pyrolysis in a Drop Tube Furnace (DTF) using nitrogen. This was performed at atmospheric pressure and a temperature of $1400^\circ C$. To investigate the effect of total pressure, the CO_2 partial pressure and temperature was fixed at 2 bar and $1300^\circ C$ respectively and the total system pressure was varied. The results are shown in Figure 2.6. The reaction rates at 2 and 20 bar differ by no more

than $\pm 20\%$ from the reaction rate at 5 bar and the authors concluded that the total system pressure did not have a significant influence on the reaction rate. In contrast to the study by Ahn et al. (2001), the authors did not include a term for the total system pressure in the reaction rate equation.

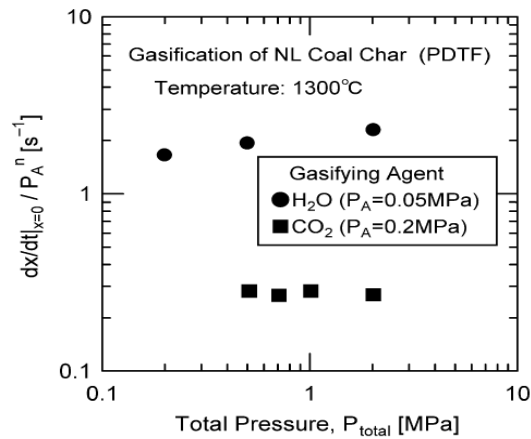


Figure 2.6: Reaction rate at constant partial pressure and different total pressures (Taken from Kajitani et al. (2002))

Clearly there is a lack of agreement between authors regarding the effect of total system pressure on the gasification rate. Roberts and Harris (2000) and Roberts and Harris (2006) attempted to clarify the matter by investigating CO_2 gasification at high temperatures and high partial pressures. Roberts and Harris (2000) determined the intrinsic reaction rates ($g/m^2/s$) of two different Australian coal chars. The coals were charred under ambient pressure at $1100^\circ C$ for 3 hours in a nitrogen environment. The authors ensured that the experiments were carried out in the chemical reaction controlled regime by determining the internal effectiveness factor (η) for each experiment using the method of Wheeler (1951) and ensuring that it was close to one. An intrinsic reaction rate free from the physical influence of surface area was calculated by normalizing the apparent reaction rate with the initial surface area of the char. The intrinsic rate was less sensitive to partial pressure compared to the apparent rate. The authors concluded that the variations in apparent reaction rates observed at high pressures should be attributed to a physical change brought on by char properties (such as surface area) rather than a fundamental change in the reaction mechanism.

From the various studies it is concluded that under chemical controlled conditions the intrinsic gasification rate is independent of total system pressure. When internal pore diffusion is the rate controlling step, total pressure has a more significant effect on the intrinsic reaction rate since the effective diffusivity coefficient (D_{eff}) is inversely proportional to pressure (Liu et al., 2000a). This means the resistance of the CO_2 gas diffusion into the pore structure of the char increases

with increasing pressure. When the reaction rate is controlled by processes other than the surface chemical reaction the effect of total pressure can be significant.

2.2.4 Modelling

The typical commercialization of a petrochemical reaction involves running laboratory scale experiments to determine a reaction rate equation which can then be used in the design of the reactor (Bell et al., 2010). Although the lack of a global reaction rate equation for the gasification process complicates the reactor design, researchers have made progress in describing gasification reactivity. The different structural and kinetic models used to describe the reaction with CO₂ are reviewed in this section. A summary of the models used by different authors is provided in Table 2.1 and Table 2.2.

2.2.4.1 Kinetic models

2.2.4.1.1 Power law

The empirical power law is the most popular kinetic model used in literature to model the intrinsic reaction rate of char gasification. The rate equation is shown in Equation 2.1.

$$r_s = k_s p_{CO_2}^n \quad (2.1)$$

The rate constant (k_s) is conventionally assumed to follow an Arrhenius temperature dependency as shown in Equation 2.2.

$$k_s = A \exp\left(\frac{-E}{RT}\right) \quad (2.2)$$

This equation is popular for gasification studies at atmospheric pressures but the applicability over a wide pressure range has been questioned due to the change in reaction order observed at higher CO₂ partial pressures (Roberts and Harris, 2006). Roberts and Harris (2000) observed the reaction order at partial pressures of 1-10 atm to be similar to the order at 1 atm, however at partial pressures of 20-30 atm the order was almost zero. Kajitani et al. (2006) observed that above 10 bar partial pressure the reaction rate of a Chinese bituminous coal char did not increase further with increasing pressure. This phenomenon is attributed to the saturation of the active surface area of the char (Roberts and Harris, 2006). Mühlen et al. (1985) observed the reaction rate to increase with partial pressure up to 15-20 atm and further increases to have little effect.

It is concluded that the empirical power law is generally applicable at low CO₂ partial pressures (<10 bar).

2.2.4.1.2 Langmuir-Hinshelwood model

Many authors have observed the power law to be unsuitable in describing the gasification reaction rate at high CO₂ partial pressure (as discussed previously). The Langmuir-Hinshelwood (LH) reaction rate model is a more fundamental model derived from the char-CO₂ mechanism. For this reason the LH model is preferred by some authors for use at high partial pressures (Kajitani et al., 2006; Roberts and Harris, 2006).

The steps of the generally accepted mechanism proposed by Ergun (1956) are shown in Equation 2.3 and Equation 2.4:



k_1 and k_2 are the rate constants for the forward and reverse reaction respectively. k_3 is the rate constant for the second step. All three rate constants follow an Arrhenius dependency. C_f is a free active site and $\text{C}(\text{O})$ is an adsorbed carbon-oxygen surface complex.

In the first step of this reaction (Equation 2.3) a CO₂ molecule is dissociated at a carbon active site (C_f) forming a CO molecule (in the gas phase) as well as a carbon-oxygen surface complex ($\text{C}(\text{O})$). This describes the oxygen exchange phenomenon. The second step (Equation 2.4) is regarded as the rate limiting step in the reaction when the carbon-oxygen surface complex desorbs and the carbon is transferred from solid to gas phase leading to the mass loss of the char (Ergun, 1956). This step is usually regarded as irreversible, however some authors such as Gadsby et al. (1948) consider it reversible.

The inhibition of the char-CO₂ reaction by CO was recognized in early work by Gadsby et al. (1948). Later studies by Moilanen and Mühlen (1996) showed that CO and H₂ strongly inhibit the reaction specifically at high pressures. The inhibition by CO is usually accounted for in the char-CO₂ mechanism by one of the following two assumptions i.e. Step 2 is reversible meaning the carbon monoxide molecules are adsorbed onto the char surface and equally compete with oxygen for active sites, or Step 1 is reversible meaning the breakdown of CO₂ is prevented (Blackwood and Ingeme, 1960). Regardless of the chosen assumption the form of the reaction rate derived remains the same.

If Step 1 is considered reversible the overall rate of reaction is given by Equation 2.5.

$$r_s = k_3 [C(O)] \quad (2.5)$$

After substituting for the $[C(O)]$ term and performing a site balance the rate equation becomes:

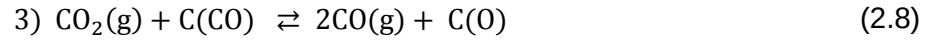
$$r_s = \frac{[C_t]k_1p_{CO_2}}{1 + \frac{k_2}{k_3}p_{CO} + \frac{k_1}{k_3}p_{CO_2}} \quad (2.6)$$

The $[C_t]$ term is usually incorporated into the value of k_1 (Roberts and Harris, 2006). This approach is satisfactory if $[C_t]$ remains constant under all experimental conditions, however it has been suggested by Roberts and Harris (2011) that this assumption may be invalid. The authors measured the reaction rates of 3 Australian bituminous coal chars gasified at high CO and CO₂ partial pressures (0.4-20 bar) and used the standard LH equation by Ergun (1956) to analyse their results. They observed that the equation was unable to describe the experimental data. After measuring the char surface area, the authors suggested that there was a significant impact of the CO and CO₂ partial pressure on the development of the char surface area during gasification and thus most likely on the term which describes the amount of active sites in the LH equation, the $[C_t]$ term. Due to the difficulties of quantifying the $[C_t]$ term the CO-inhibited reaction was normalized to the uninhibited reaction in order to eliminate the $[C_t]$ term. The mathematical framework derived after normalization was shown to well describe the data.

The rate equation of the uninhibited reaction is shown in Equation 2.7

$$r_{CO_2} = \frac{[C_t]k_1p_{CO_2}}{1 + \frac{k_1}{k_3}p_{CO_2}} \quad (2.7)$$

Other authors have also observed a deviation from expected reactivity behaviour at high partial pressures and attributed this change in behaviour compared to the behaviour at atmospheric pressure to the LH equation's inability to accurately describe the reactivity at high pressures (Blackwood and Ingeme, 1960; Nozaki et al., 1992). To improve the model, Blackwood and Ingeme (1960) suggested that the following extra steps should be added to the reaction mechanism:



When these steps are included in the mechanism the rate equation derived is shown in Equation 2.10.

$$r_{\text{CO}_2} = \frac{k_1 p_{\text{CO}_2} + k_5 p_{\text{CO}_2}^2}{1 + k_2 p_{\text{CO}} + k_3 p_{\text{CO}_2}} \quad (2.10)$$

Mühlen et al. (1985) observed that the model derived by Blackwood and Ingeme (1960) fitted their kinetic data better compared to the model proposed by Ergun (1956) and Gadsby et al. (1948). Kajitani et al. (2006) also evaluated the LH model (in the form of Equation 2.10) as well as the power law and observed both models to be applicable up to 20 bar partial pressure, however they recommended that the LH rate equation be used at high partial pressure (above 10 bar) since the power law gave an over prediction of the reaction rate at these conditions. They also observed that the inhibition of the reaction by carbon monoxide could only be described by the LH model.

Although some authors have found the LH model proposed by Ergun (1956) to be invalid others have shown it to be valid for both atmospheric and high pressure CO_2 gasification. Everson et al. (2006) found that the intrinsic reaction rate of an inertinite rich South African coal char at atmospheric pressure (87.5 kPa) was adequately described by the LH-type rate equation. Du Toit (2013) also observed the LH rate equation to be valid when predicting the CO_2 gasification reactivity of a typical Highveld seam 4 coal char at 87.5 kPa and temperatures of 775-900°C. Zhang et al. (2014) obtained good fits when using the LH model for a Bituminous coal char gasified at CO_2 partial pressures of 2-5 bar. Roberts and Harris (2006) concluded that the general LH rate equation was suitable for pressure up to 30 bar.

The LH rate equation would thus seem superior in its ability to predict gasification reactivity when compared to the empirical power law. In the LH equation the intrinsic reaction rate is a non-linear function of CO_2 partial pressure and does not contain an empirical pressure order like the power law model. The LH model also accounts for CO inhibition (Irfan et al., 2011). Although this model has shown to be valid by several authors, other authors have observed it to be invalid at high pressures.

2.2.4.2 Structural models

Structural changes are known to occur in char particles during gasification and are discussed in Section 2.3. It is important to consider structural changes when modelling the reaction as a function of conversion (Zou et al., 2007). Different models which incorporate structural effects have been evaluated in literature.

The shrinking core model (SCM) was developed by Yagi and Kunii (1961) and assumes that the reaction takes place on the surface of the unreacted core. An ash layer is formed around the unreacted core as the gasification reaction proceeds. The model contains a structural factor which is only dependent on the initial surface area and porosity of the char (Irfan et al., 2011). Various authors have observed that the SCM is able to well describe CO₂ gasification reactivity of coal chars at both low and high pressures (Everson et al., 2006; Zhang et al., 2006).

The grain model (GM) was developed by Szekely and Evans (1971) and is based on the assumption that the char particle is a combination of smaller spherical grains which follow the unreacted shrinking core model. The model has successfully been applied at low pressures by Engelbrecht (2008) and at high pressures by Chmielniak et al. (2014).

Another structural model which has been widely used is the random pore model (RPM) developed by Bhatia and Perlmutter (1980). This model takes into account char pore structure and the development of pores throughout gasification. The reaction surface is assumed to consist of overlapping cylindrical pores which grow up to a certain conversion and then start to coalesce and collapse. The reaction rate is described as a function of conversion in Equation 2.11.

$$\frac{dX}{dt} = \frac{k_s(1-X)S_0\sqrt{1-\psi\ln(1-X)}}{(1-\varepsilon_0)} \quad (2.11)$$

ψ is a structural parameter determined from the initial char properties and defined as:

$$\psi = \frac{4\pi L_0(1-\varepsilon_0)}{S_0^2} \quad (2.12)$$

The structural parameter (ψ) is usually determined from regression with experimental data and gives an indication of the amount of pore growth that will take place during the reaction (Bhatia and Perlmutter, 1980). Higher values of ψ correspond to a higher amount of pore growth (Kajitani et al., 2006).

Equation 2.11 can be written in terms of the specific reaction rate as shown in Equation 2.13.

$$r_s = \frac{\frac{dX}{dt}}{1-X} = r_{s0} \sqrt{1 - \psi \ln(1-X)} \quad (2.13)$$

Where r_{s0} (the initial reactivity) is defined by Equation 2.14.

$$r_{s0} = \frac{k_s S_0}{1 - \varepsilon_0} \quad (2.14)$$

Kajitani et al. (2002) observed that the RPM was superior to the GM when predicting the CO₂ gasification rate and surface areas of chars. The RPM was however unable to simultaneously describe the experimental data of both the reaction rate and the surface areas. It was suggested that some major structural changes are not accounted for if ψ is assumed to remain constant throughout the reaction. This demonstrated the need for improving the RPM developed by Bhatia and Perlmutter (1980).

2.2.5 Summary of gasification studies

The results of several low and high pressure CO₂ gasification studies have been discussed in this section and the focus has mainly been on high pressure studies. A summary of the studies at low pressure are shown in Table 2.1 and at high pressure in Table 2.2.

The gasification reactivity models used by authors at low pressure have included structural models such as the Shrinking Core Model (SCM), Random Pore Model (RPM), Grain Model (GM), Homogeneous model (HM) and the Wen Model (WM). The power law (PL) is most popular for use as kinetic model, however the Langmuir Hinshelwood model (LH) has also been applied successfully.

For the high pressure studies the majority of the studies were performed using a pressurized TGA. The temperature and pressure ranged between 700-1500°C and 1-70 bar respectively. Char particle sizes ranged between 0.04-3 mm. The reaction orders observed for CO₂ gasification usually vary between 0.3-0.7. The reactivity models used by authors have included structural models such as the Shrinking Core Model (SCM), Random Pore Model (RPM), Normal Distribution Model (NDM) and the Grain Model (GM). The power law (PL) is most popular for use as kinetic model up to CO₂ partial pressures of 10 bar, but the Langmuir Hinshelwood model (LH) is mostly recommended for use at high partial pressures.

Table 2.1: Summary of low pressure CO₂ gasification studies

Reference	Analysis Technique	Coal Rank	Particle size (mm)	Temperature (°C)	Pressure (bar)	Model	E (kJ/mol)	Reaction order
(Salatino et al., 1998)	TGA	NR	0.075-0.125	750-900	0.1-1	PL	213	0.74
(Everson et al., 2006)	TGA	NR	1	800-950	1.013	SCM, LH	204,212	NR
(Engelbrecht, 2008)	TGA	B	0.85-1.2	875-950	0.875	GM	184	NR
(Everson et al., 2008)	TGA	NR	1	850-900	1-3	RPM, PL	192-247	0.46-0.54
(Koekemoer, 2009)	TGA	B	1	1000-1070	0.875	RPM	163-225	NR
(du Toit et al., 2013)	TGA	B	1	775-900	0.875	WM, LH	243	0.56
(Veca & Adrover, 2014)	TGA	SB	0.125-1.4	800-1100	1.013	HM, SCM	NR	NR

TGA – Thermo-gravimetric analyzer, NR – Not reported, PL – Power law, SCM – Shrinking core model, LH – Langmuir Hinshelwood, B – Bituminous, GM – Grain model, RPM – Random pore model, WM – Wen model, SB – Sub-bituminous, HM – Homogeneous model

Table 2.2: Summary of high pressure CO₂ gasification studies

Reference	Analysis Technique	Coal Rank	Particle size (mm)	Temperature (°C)	Pressure (bar)	Model	E (kJ/mol)	Reaction order
(Mühlen et al., 1985)	FBR	B	NR	800-1000	1-70	LH	153.1	NR
(Shufen & Ruizheng, 1994)	FBR	L	0.25-0.42	800-950	19.6	SCM, PL	149.1	0.34
(Messenböck et al., 1999)	PWMR	B	0.106-0.150	1000	1-30	NR	NR	NR
(Roberts & Harris, 2000)	PTGA	B, SA	0.6-1	900-940	1-30	PL	209-250	0.5-0.7
(Ahn et al., 2001)	PDTF	SB	0.045-0.064	900-1400	5-15	SCM, PL	72-144	0.4
(Kajitani et al., 2002)	PDTF	B	0.01-0.1	1100-1500	2-20	RPM, PL	163-283	0.73
(Sun et al., 2004)	PTGA	NR	<0.074	850-900	1,30	PL	50-250	NR
(Kajitani et al., 2006)	PDTF,PTGA	B	0.04	1000-1400	1-10	RPM, LH, PL	240-280	0.43-0.56
(Roberts & Harris, 2006)	PTGA	B, SA	0.6-1	900-940	1-30	LH	NR	NR
(Zhang et al., 2006)	PTGA	A	< 0.1	920-1050	2-10	SCM, PL	146-202	0.4-0.7
(Park & Ahn, 2007)	PTGA	SB, B	0.045-0.063	850-1000	5-20	SCM, PL	149-223	0.4-0.7
(Hattigh et al., 2009)	PTGA	B	0.2-2.6	900-1000	1-10	RPM, PL	171-202	0.47-0.77
(Roberts and Harris, 2011)	PTGA	B	0.6-1	900-950	0.4-20	LH	NR	NR
(Tremel et al., 2012)	PTGA	L, B, A	0.08-0.16	600-850	1-50	NR	NR	NR
(Chmielniak et al., 2014)	FBR	L, B	1-3.15	950	1-20	GM, PL	NR	0.012-0.180
(Kim et al., 2014)	PWHR	SB	0.075-0.8	700-1450	1-30	RPM, PL	149-152	0.85-0.98
(Zhang et al., 2014)	PTGA	B	0.08	875-925	2-5	LH	280	NR
(Huo et al., 2015)	PTGA	B	0.1	900-1050	1-30	NDM, RPM	150-185	NR
(Liu et al., 2015)	PTGA	B	0.2	950-1150	1-20	NR	NR	NR

FBR – Fixed bed reactor, L – Lignite, PWHR – Pressurized wire-heating reactor, PTGA – Pressurized thermo-gravimetric analyser, SA – Semi-anthracite, PDTF – Pressurized drop tube furnace, SB – Sub-bituminous, A – Anthracite, PWMR – Pressurized wire-mesh reactor, NDM – Normal distribution model.

2.3 Char structural development during gasification

Due to the adsorption/desorption mechanism of the CO₂ gasification reaction it is often proposed that the physical properties of the char (such as the internal surface area and pore structure) have a significant effect on the CO₂ gasification kinetics at elevated pressures. Many studies have shown that the gasification rate is not only dependent on the reaction conditions but also on the physical char structure (Liu et al., 2000b; Roberts and Harris, 2000; Kajitani et al., 2002).

Coal is characterized by dual porosity and contains micro-, meso- and macropore systems (Harpalani and Chen, 1995). Pores with widths not exceeding 2 nm are classified as micropores, widths between 2 nm and 50 nm as mesopores, and widths exceeding 50 nm as macropores (Sing, 1985). Rodrigues and De Sousa (2002) observed that pore sizes tend to decrease with increasing coal rank, where lignite's porosity is mainly in the form of macropores. Gan et al. (1972) observed that for intermediate-ranked bituminous coal (elemental carbon *daf* ranging between 76-84%) about 80% of the coal's porosity is contributed by micro- and mesopores.

Various techniques have been used to investigate the pore structure of chars including wide angle X-ray diffraction (WXR), small angle X-ray and neutron scattering (SANS), scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

Coetzee et al. (2015) used small angle X-ray Scattering (SAXS) to investigate the pore development of an inertinite rich Witbank Seam 4 coal char during gasification in a TGA at 1000°C and atmospheric conditions. The authors observed that 98% of the char's pore surface area was contributed by micropores. An increase in surface area from the onset of CO₂ gasification was observed for all pore sizes, however the different pore sizes grew at different rates. The authors concluded that the reagent gas had access to most pore sizes and that the difference in individual sized pore development could not solely be explained by gas accessibility.

The SAXS technique used by Coetzee et al. (2015) is a useful method when studying pore structures however gas adsorption methods using CO₂ or N₂ are more common since these methods are less expensive and easier compared to other advanced methods (Okolo et al., 2015). Gas adsorption measurements can only probe pores in a specific size range depending on the gas used for adsorption (Okolo et al., 2015). Low pressure adsorption measurements with CO₂ probes pores in the lower micropore size range ($3 \text{ \AA} \leq d_p \leq 5 \text{ \AA}$) (Okolo et al., 2015), while analyses with N₂ are claimed to cover the higher micropore and entire mesopore range ($17 \text{ \AA} \leq d_p \leq 3000 \text{ \AA}$) (Mastalerz et al., 2008). To calculate the micropore surface area from CO₂

adsorption the Dubinin-Radushkevich (DR) method is often used (Şenel et al., 2001). For the mesopore surface area the Brunauer-Emmet-Teller (BET) method is popular (Clarkson et al., 2012).

Liu et al. (2015) investigated the physical changes occurring in a Kentucky bituminous coal char during gasification at high pressures. Devolatilization followed by gasification with pure CO₂ was performed in a PTGA in a pressure range of 1-20 bar and at temperatures of 950-1150°C. In order to investigate the change in structural properties of the char during gasification, different samples were prepared under the same operating conditions (100% CO₂, 20 bar, 1050°C) but at different conversions. BET specific surface areas as well as pore volume measurements are shown in Figure 2.7.

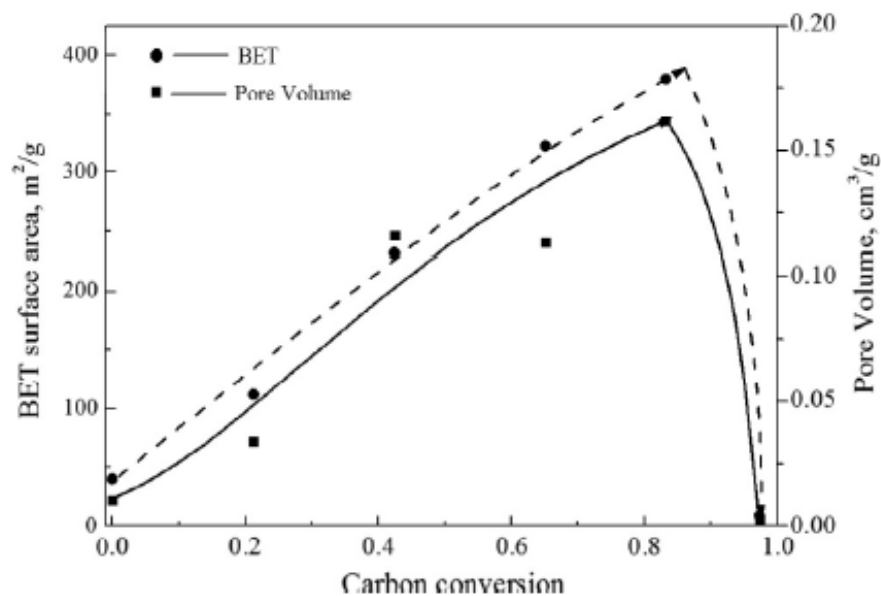


Figure 2.7: The change in pore volume and surface area during gasification (Taken from Liu et al. (2015))

The surface area and pore volume increases significantly below 90% conversion suggesting that gasification takes place inside the pores and leads to pore growth. After 90% conversion the pores start to coalesce and collapse.

Kajitani et al. (2002) investigated the change in specific surface area of an Australian NL bituminous char by analysis of N₂ isotherms at 77 K using the BET method as well as CO₂ isotherms at 273 K using the Dubinin-Astakhov (DA) method. Both these analyses showed an initial increase in specific surface area upon gasification. The surface area peaked at 40% conversion and then decreased with further conversion. The surface area obtained from the

CO₂ adsorption analysis was almost 10 times larger than the surface area from the N₂ adsorption analysis. This demonstrates that the char was dominated by micropores. The authors inferred that these micropores widened into mesopores throughout gasification.

Although the development of internal surface area during gasification has been studied extensively, the effect of reagent partial pressure on char structural development has been studied to a lesser extent. Roberts and Harris (2011) investigated the effect of increasing CO₂ and CO partial pressures on the measured CO₂ DR surface area after 10% conversion. They observed that an increase in partial pressure generally resulted in an increase in internal surface area. The Langmuir Hinshelwood kinetic model (discussed in Section 2.2.4.1.2), which is usually used to describe the reaction rate at atmospheric pressures, takes the initial surface area of the char into account via the $[C_i]$ term (the total amount of active sites) (Roberts and Harris, 2011). In the LH model this term is assumed to remain constant, however the surface area data reported in Roberts and Harris (2011) showed that this assumption was not valid for a wider range of CO₂ partial pressures since there was a significant change in the surface area (and thus the $[C_i]$ term) with changing CO₂ and CO partial pressures.

From the studies discussed it is clear that significant variations in internal char surface area occur during gasification and that these structural changes have an effect on the gasification kinetics. In order to improve the overall understanding of CO₂ gasification at high pressures, more research is required to investigate the effect of different parameters such as partial pressure and temperature on the changes in internal structure of chars during gasification.

2.4 Coal properties and reactivity with CO₂

The reactivity of a coal char is affected by various factors such as sample preparation, reaction conditions and physical char structure (Sun et al., 2004). In addition to these factors the different coal properties of the parent coal have also been observed to affect the reaction rate (Molina and Mondragon, 1998).

Coal rank is an important coal characteristic property however its suitability for predicting gasification reactivity has been questioned (Sun et al., 2004). The reactivity is usually observed to decrease with increasing coal rank but there is no general trend (Ye et al., 1998). Miura et al. (1989) observed gasification reactivity to decrease with increasing coal rank, however the reactivity data was more scattered for low rank coal (%C < 80%). Beamish et al. (1998) reported the reactivity of New Zealand bituminous coal chars to be 20-30 times lower than most sub-bituminous coal-chars. Engelbrecht (2008) also observed a decrease in reactivity with increasing coal rank for different South African coals.

The mineral matter content of the coal is also known to affect the gasification reactivity due to the presence of catalytically active components (Sun et al., 2004). Koekemoer (2010) observed that Ca, Mg and K act as catalysts during CO₂ gasification of Highveld coals. The alkali index defined by Sakawa et al. (1982) has frequently been used to describe the overall influence of catalytically active components. Hattingh (2010) observed that the coal char reactivity of 3 different South African coal chars increased with an increase in the alkali index. A similar trend was also observed by Zhang et al. (2006) for CO₂ gasification of Chinese anthracite chars.

A petrographic property which has shown to significantly affect gasification reactivity is the maceral composition. Sun et al. (2004) investigated the CO₂ gasification reactivity of maceral chars at 1 and 30 bar. The authors observed that the vitrinite char always showed a higher reactivity than the inertinite char, even when the macerals were demineralized. The vitrinite char also had a lower activation energy compared to the inertinite char.

Megaritis et al. (1999) investigated the gasification behaviour of maceral concentrates in a fixed-bed wire-mesh reactor and observed that during short hold-time gasification experiments (10s) liptinites gave the highest conversion followed by vitrinites and inertinites.

In order to combine the effects of different macerals into one descriptive index Su et al. (2001) proposed a maceral index to predict combustion performance in coal-fired boilers. This index has also show to be applicable in predicting the gasification behaviour of coal chars (Hattingh, 2010). The index is given by Equation 2.15.

$$MI = (HVF)^{2.5}(RF) \quad (2.15)$$

With $HVF = HV/30 \quad (2.16)$

and $RF = (L + V/R^2)/I^{1.25} \quad (2.17)$

HV refers to the heating value of the coal in MJ/kg defined on an air dried basis (a.d.). RF represents the reactivity of the coal which includes the liptinite (L), vitrinite (V) and inertinite (I) content by volume as well as the mean random vitrinite reflectance (R). All these terms are defined on a mineral matter free basis (m.m.f.).

Although authors agree that maceral composition affects coal char reactivity, using a maceral analysis to predict gasification reactivity has also been reported to give unreliable predictions (Messenböck et al., 2000).

To characterize the reactivity of different coal chars, a standard CO₂ reactivity test is often used for comparative reasons. Different methods are used to perform these tests including isothermal and non-isothermal thermo-gravimetric methods (Dutta et al., 1977; Fan et al., 2013). During isothermal tests the sample is first heated to the reaction temperature before introducing a reagent gas. The weight loss of the char sample against time is then recorded. A popular way of quantifying gasification reactivity is by a reactivity index R_s shown in Equation 2.18 (Ye et al., 1998):

$$R_s = \frac{0.5}{\tau_{0.5}} \quad (2.18)$$

With $\tau_{0.5}$ the time required to reach 50% carbon conversion.

This definition is commonly used to describe the reactivity of a coal char, however the value of R_s is strongly dependent on the experimental conditions and the analysis method used (Ye et al., 1998). The reactivity index provides an indication of the expected gasification rate and is often determined for the sole purpose of comparing the reactivity of different coals (Bunt and Waanders, 2008).

CHAPTER 3: EXPERIMENTAL

3.1 Introduction

In this chapter the experimental setup and the procedures used during experimentation are discussed. The materials used are described in Section 3.2. This includes a summary of the sample origins, sample preparation and characterization of the coals and chars.

The experimental work was divided into two different sections: CO₂ gasification experiments (Section 3.3) and char internal surface area analyses (Section 3.4). The gasification rig is described in Section 3.3.1 followed by the experimental procedure in Section 3.3.2 and the data processing method in Section 3.3.3. Rig evaluation and regime identification procedures are provided in Section 3.3.4. A summary of the gasification experiments and operating conditions is shown in Section 3.3.5.

The surface area analysis equipment and procedures are discussed in Section 3.4.1 followed by the surface analyses experimental program in Section 3.4.2. The experimental error estimation for both the CO₂ gasification runs and the surface area analyses is discussed in Section 3.5.

3.2 Materials

3.2.1 Sample origins and description

Three different coal samples were used. All three coals were South African Highveld coals used in a previous gasification study by Henning (2017). The samples were collected from different coal seams (seam 2, 4 and 5).

A summary of the sample origin and composition of the samples is shown in Table 3.1.

Table 3.1: Sample origin and composition

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

3.2.2 Sample preparation

The preparation of the coal samples was performed previously by Henning (2017). The coals were crushed in a jaw crusher to a particle size of -8 mm. The -8 mm bulk of each coal was split

into smaller samples representative of the bulk by using a riffle splitter. Charring was conducted in 150 g batches using a Lenton® horizontal tube furnace. The coal was heated to 950°C at 10°C/min for 2 hours under atmospheric pressure with a 1 Nl/min flow of nitrogen. After charring, the batches were mixed and split into smaller samples which were stored in zip-seal bags. The chars were then crushed further and sieved to a particle size range of -500 µm +425 µm. In this particle size range the particles were small enough to ensure that the system operated under reaction controlled conditions without causing a too high pressure drop in the reactor. The samples were stored in airtight containers.

3.2.3 Sample analyses results

A summary of the characterisation results obtained by Henning (2017) is shown in Table 3.2.

3.2.4 Gases used

The reagent gases used in this study included CO₂ and N₂. Both these gases were instrument grade with 99.9% purity. Different gas mixtures containing CO and N₂ were used as calibration gases (see Appendix A-1). All the gases were supplied by Afrox South Africa.

Table 3.2: Summary of coal and char characteristics (adapted from Henning (2017))

	Coal			Char		
	2N	4N	5N	2N	4N	5N
Proximate Analysis (wt % d.b.) (Bureau Veritas Testing and Inspectors South Africa)						
Ash Yield (ISO 1171:2010)	19.5	26.5	30.5	27.0	34.1	40.2
Volatile matter (ISO 562:2010)	24.7	21.9	29.1	1.2	1.2	1.0
Fixed carbon (by difference)	55.8	51.6	40.4	71.7	64.7	58.8
Gross Calorific Value (MJ/kg a.d.) (Bureau Veritas Testing and Inspectors South Africa)						
CV (ISO 1928:2009)	24.1	21.5	20.5	22.1	19.9	17.2
Ultimate Analysis (Bureau Veritas Testing and Inspectors South Africa, (wt % d.a.f.)						
Carbon (ISO 29541:2010)	78.8	77.6	76.7	95.9	96.5	95.2
Hydrogen (ISO 29541:2010)	4.3	3.9	5.6	0.3	0.1	0.3
Nitrogen (ISO 29541:2010)	2.0	2.1	2.1	2.0	2.1	2.0
Oxygen (by difference)	13.8	15.1	14.2	0.0	0.0	0.0
Sulphur (ISO 19579:2006)	1.1	1.4	1.4	1.8	1.3	1.5
Maceral Composition (volume % m.m.f.) (Sasol Technology Research and Development)						
Total Vitrinite	23.5	10.5	60.1	ND	ND	ND
Total Liptinite	4.9	5.1	11.5	ND	ND	ND
Total Inertinite	71.6	84.4	28.5	ND	ND	ND
Total Reactives	79.5	82.2	85.0	ND	ND	ND
Vitrinite Reflectance (Sasol Technology Research and Development)						
Reflectance (%)	0.55	0.66	0.53	ND	ND	ND
Rank (bituminous) ISO 11760:2005	D	C	D	ND	ND	ND

XRD Mineral Phase (wt % as reported) (XRD Analytical and Consulting)						
Alunite	0.0	1.3	0.0	ND	ND	ND
Calcite	1.5	1.3	0.0	ND	ND	ND
Dolomite	0.7	2.8	0.0	ND	ND	ND
Graphite	73.2	65.5	68.8	ND	ND	ND
Kaolinite	21.2	18.4	18.0	ND	ND	ND
Pyrite	0.4	1.1	1.6	ND	ND	ND
Quartz	3.1	9.7	11.6	ND	ND	ND
Siderite	0.0	0.0	0.0	ND	ND	ND

ND – Not determined

3.3 Gasification rig and procedures

3.3.1 Rig

An in-house high pressure fixed bed reactor was used to perform gasification experiments. The reactor system was designed to operate up to a maximum pressure of 20 bar. For the purpose of this study the system was modified to perform gasification experiments up to 70 bar. The experimental setup is shown schematically in Figure 3.1.

The reagent gases (CO_2 and N_2) were stored separately in high pressure gas cylinders. Pressure regulators were used to ensure that the outlet pressure of the gas cylinders remained constant throughout the experimental runs. The reagent gas flow was controlled by the two mass flow controllers (type EL-FLOW from Bronkhorst High Tech®) which were calibrated separately with a flow meter as discussed in Appendix A-2. Both mass flow controllers were connected to a computer via RS-232. The composition of the reagent gas mixture was varied for different experiments by changing the set points of the controllers. Flow View software provided by Bronkhorts High Tech® was used for this purpose.

After obtaining the desired reagent gas composition, the gas mixture was fed to the top of the reactor tube which consisted of a 93 cm $\frac{3}{4}$ " schedule 40 alloy C276 pipe (OD 1.050" (2.7 cm), ID 0.824" (2.1 cm)) supplied by Multi Alloys (Pty) Ltd. Alloy C276 is a nickel-molybdenum-chromium-iron-tungsten alloy used for its corrosion resistance and ability to remain inert at high temperatures and pressures (Special Metals Corporation, 2004). The alloy pipe was tested to be inert at the experimental conditions (Appendix B-1). A porous quartz filter disc with a nominal pore size of 150 μm manufactured by LSP Quartz B.V. was mounted in the middle of the tube to support the sample bed.

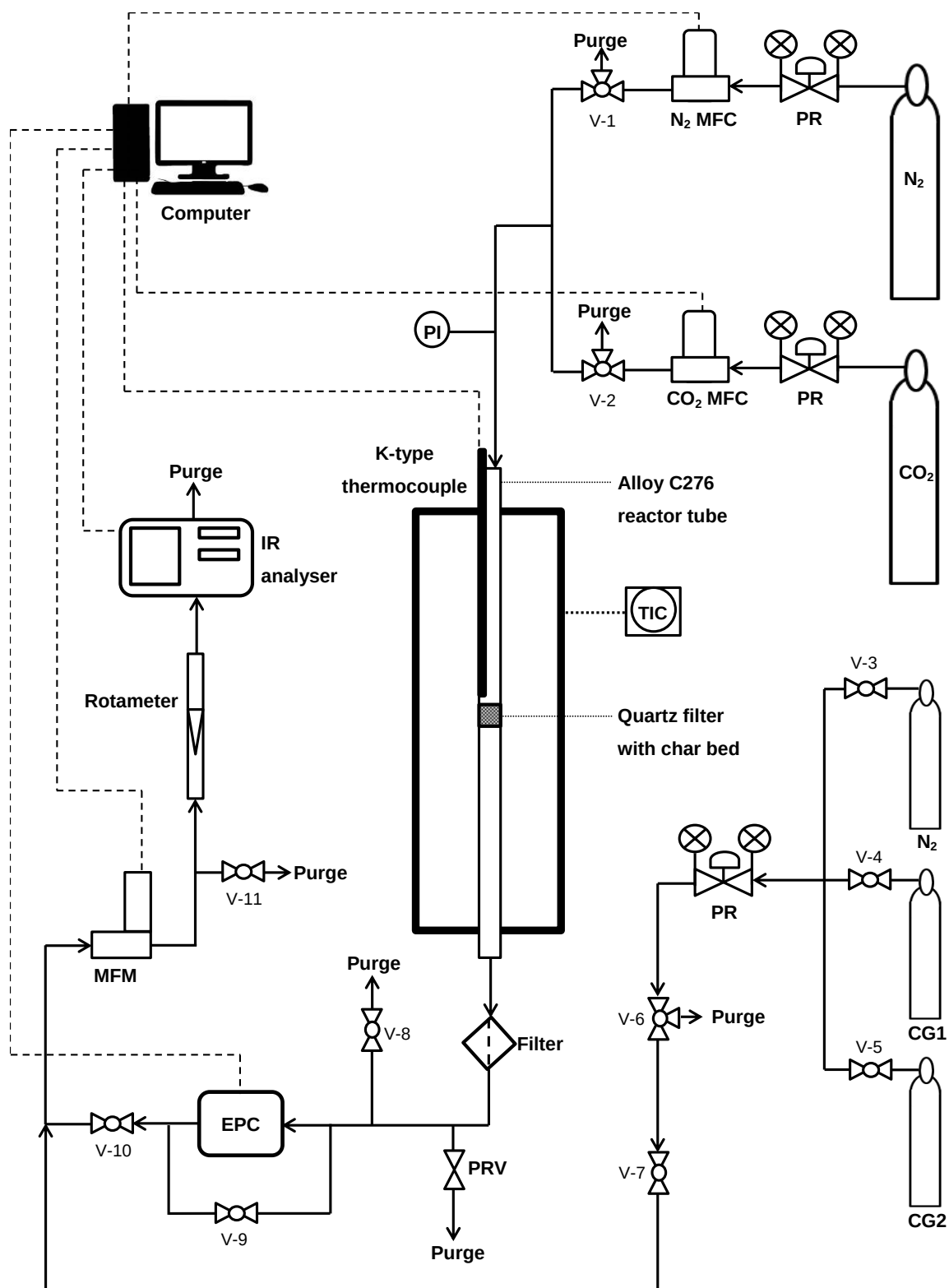
A vertical split-tube furnace (Carbolite®) was used as a heat source. The furnace included a model 201 PID temperature controller made for Carbolite® by Eurotherm Pty (Ltd). A 3 mm K-type thermocouple was placed ± 5 mm above the sample bed in the thermal stable region of the reactor which was determined prior to experimentation as explained in Appendix B-2. The thermocouple was shown to be inert under the experimental conditions (Appendix B-3). Furthermore, the sample bed was tested and found to be under isothermal conditions using the technique described in Appendix B-4. The thermocouple reading was logged on the computer during experimental runs.

The product gas from the reactor tube was sent through a filter screen with an aperture of 15 μm in order to protect the downstream equipment from particulate matter which may have been carried through the quartz filter.

In order to perform the gasification experiments at high pressures, an electronic pressure controller (EPC) (type EL-PRESS from Bronkhorst High Tech®) was installed downstream of the reactor. The inlet pressure to the reactor was also measured using a UniTrans® pressure transmitter. The system was depressurized after each experimental run by opening valve V-8 upstream of the EPC.

A mass flow meter (MFM) (type EL-FLOW from Bronkhorst High Tech®) was installed downstream of the reactor. The measurements of both the EPC and MFM were logged during experimentation for monitoring purposes. Both these instruments were connected to a computer and electronic communication was accomplished by the RS-232 data interface. The measurements were saved in .csv file format by using the Flow Plot software designed for the Bronkhorst High Tech® instruments.

After leaving the MFM, the product gas was split into a purge stream and a stream used for analysis. The latter flowed through a rotameter which monitored the flow rate to the non-dispersive infra-red (NDIR) analyser (MGA3000™ model from ADC Gas Analysis®) which operates optimally at a flow range of ~ 1 NL/min. The carbon monoxide (CO) concentration (ppm) in the product gas was detected by the analyser and the measurement logged every 2 seconds. The logged measurements were saved in Excel by making use of an Excel VBA programming code. The analyser reading was calibrated by using the different CO calibration gases (Appendix A-1).



EPC: Electronic pressure controller	PR: Pressure regulator	— Pipe line
MFC: Mass flow controller	PRV: Pressure relief valve	- - - Cable
MFM: Mass flow meter	TIC: Temperature indicator controller	
PI: Pressure indicator	CG: Calibration gas	

Figure 3.1: Experimental rig

3.3.2 Procedures

At the start of an experimental run the char sample was weighed and inserted on top of the quartz filter disc in the reactor tube. The sample size was varied between 0.2-0.5 g depending on the reactivity of the char. After the sample had been loaded the N₂ gas was introduced into the system.

The furnace was set to the desired reaction temperature prior to each run. Once the furnace had reached the reaction temperature it was closed over the reactor tube and the system was allowed some time to reach isothermal conditions. The reading from the thermocouple inside the reactor tube was monitored to ensure that the sample bed was at the required reaction temperature. After the temperature reading on the thermocouple had remained constant for 3 minutes, the system was pressurized to the desired pressure. After the system had reached isothermal and isobaric conditions, the data logging software was started. Thereafter the gasification reagent gas (CO₂) was introduced into the system.

The experimental runs were stopped after a conversion of approximately 20% was reached. The kinetic data at a conversion of 10% was used for modelling purposes. At this stage the reaction rate is still indicative of the initial char properties however sufficient time has passed to allow for stabilization (Roberts and Harris, 2000). Once the reaction had reached the desired conversion, the data logging software was stopped. The CO₂ reagent gas flow to the reactor was terminated and the system was flushed with N₂ for 2 minutes. Thereafter the system was depressurized. The reactor tube was then removed from the furnace and allowed time to cool down before removing and weighing the char content left in the tube.

3.3.3 Data processing

3.3.3.1 CO concentration

After processing the raw data measurements, a plot of the CO concentration in the product gas was obtained. Due to the short time interval between the CO concentration readings, the experimental results appear as a continuous line although they are individual measurements. All the gasification reactivity experimental results presented in this study therefore appear to be lines. To demonstrate the data processing procedure, a high temperature run was performed on the 2N char and allowed to run to complete conversion. The correctness of the measurement was verified through a mass balance (Appendix B-6). The results of the gasification of 2N char at 875°C, 20 bar and 30% CO₂ are shown in Figure 3.2.

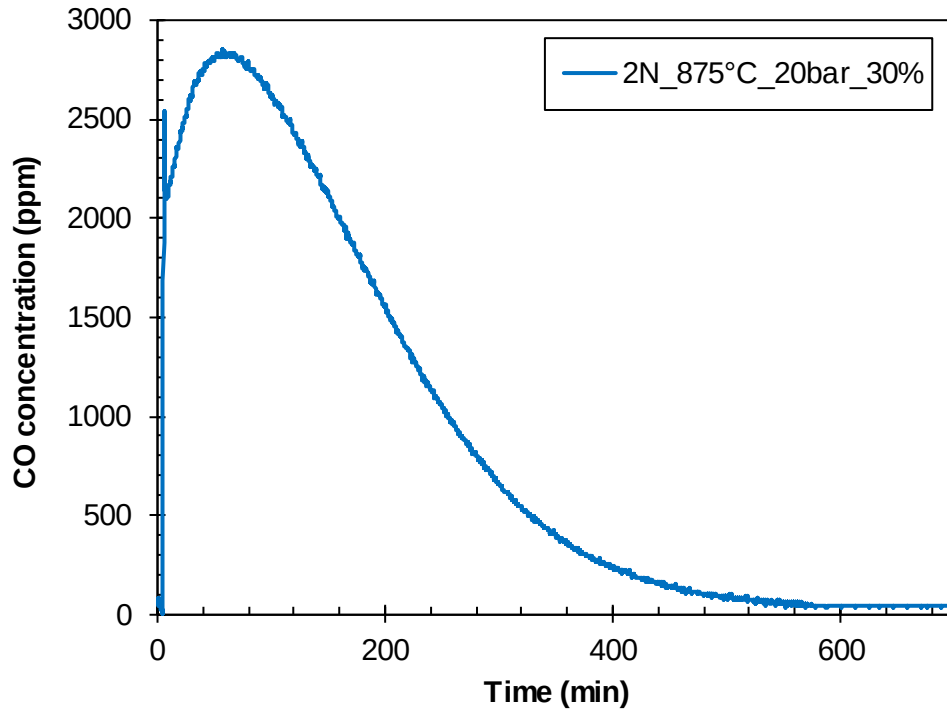


Figure 3.2: CO concentration curve for 2N at 875°C 20 bar 30% CO₂

At the start of the run the CO concentration increases and reaches a maximum of 2800 ppm after about 60 minutes. Thereafter the concentration decreases and at 600 minutes no further concentration changes are observed. At this point the reaction is assumed to have reached completion. The initial peak observed at the start of the run is attributed to dynamic disruptions in the system after introducing the CO₂ gas flow.

3.3.3.2 Conversion

After obtaining the CO concentration curve of the product gas, the carbon conversion rate (amount of carbon (g) reacting with CO₂ per second) was determined through knowledge of the reaction stoichiometry and flow rate of the product gas stream. Equation 3.1 was used to determine the carbon conversion rate (r_c) at each time interval.

$$r_c = \frac{y_{CO}}{2} \times \dot{n} \times MW_C \text{ [g/s]} \quad (3.1)$$

Where y_{CO} is the fraction of CO (-), $\dot{n}$ is the molar flow rate (mol/s) and MW_C the molecular weight of carbon (g/mol).

Next, the amount of carbon remaining in the sample at each time interval was calculated by Equation 3.2.

$$m_c(t) = m_{c,0} - \int_0^t r_c dt \quad [\text{g}] \quad (3.2)$$

$m_{c,0}$ is the total amount of carbon in the unconverted sample, calculated using Equation 3.3.

$$m_{c,0} = m_{s0}(1 - x_{ash}) \times x_c(daf) \quad [\text{g}] \quad (3.3)$$

m_{s0} is the sample mass (g), x_{ash} the ash yield fraction and $x_c(daf)$ the carbon fraction on a dry ash free basis. The values for the ash yield wt% and the carbon fraction amount were obtained from the proximate and ultimate analysis respectively. Finally, the conversion (on a dry ash free basis) was calculated with Equation 3.4.

$$X(t) = \frac{m_{c,0} - m_c(t)}{m_{c,0}} \quad [-] \quad (3.4)$$

The correspondent plot of conversion versus time for the gasification of 2N at 875°C, 20 bar and 30% CO₂ is shown in Figure 3.3.

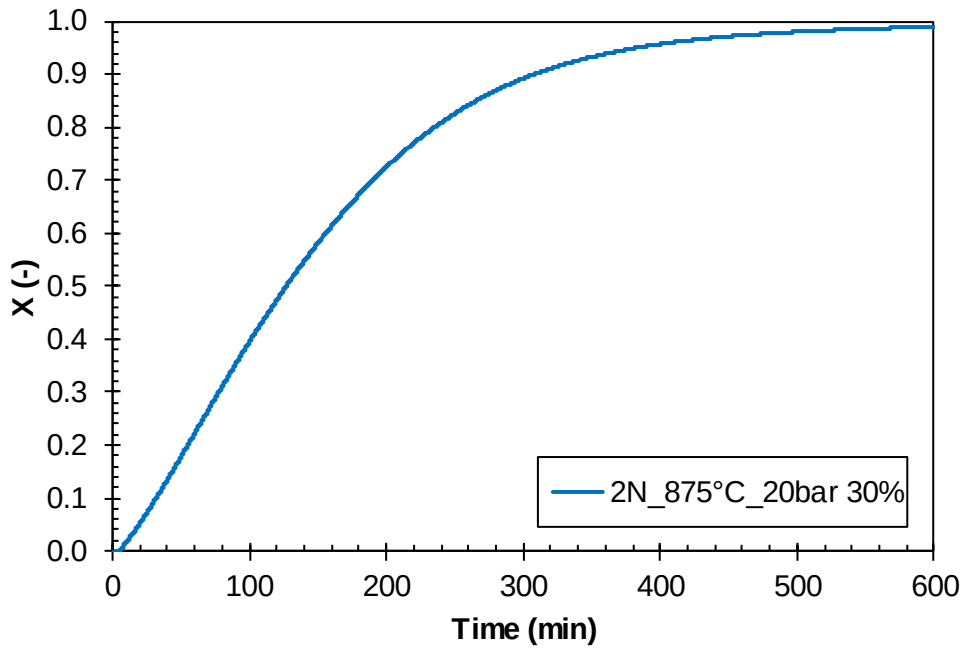


Figure 3.3: Conversion plot of 2N at 875°C 20 bar 30% CO₂

3.3.3.3 Reaction rate

The carbon conversion rate (r_c) in g/s was determined at each time interval using Equation 3.1. The value of r_c was normalized with the amount of carbon remaining in the char sample at the reaction time and termed the specific reaction rate (r_s). Various authors used the same normalization technique when determining the specific reaction rate for TGA experiments (Roberts and Harris, 2000; du Toit, 2013). The specific reaction rate is described as a function of time in Equation 3.5.

$$r_s(t) = \frac{r_c(t)}{m_0 - m(t)} \text{ [g/g/s]}^1 \quad (3.5)$$

The specific reaction rate was plotted as a function of conversion. The r_s curve for the gasification of 2N char at 875°C, 20 bar and 30% CO₂ is shown in Figure 3.4.

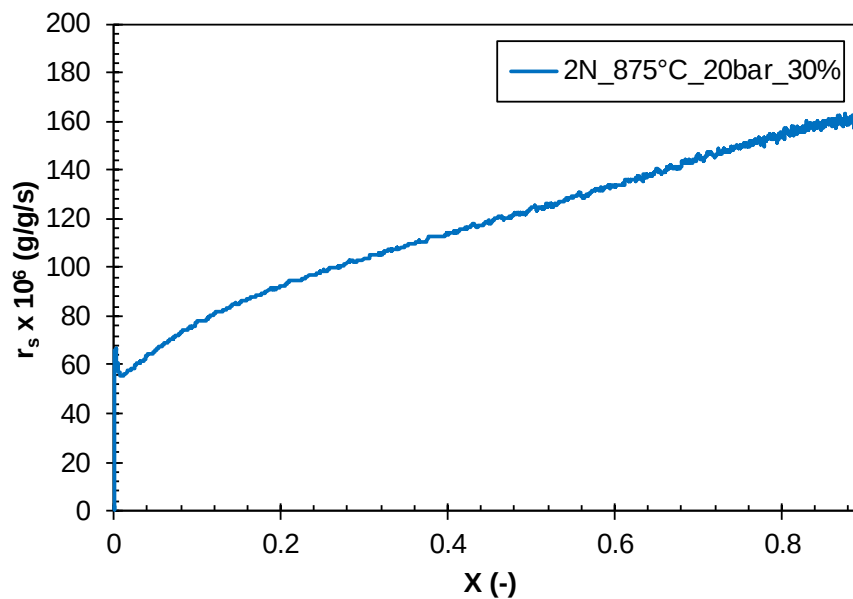


Figure 3.4: Specific reaction rate versus conversion of 2N at 875°C 20 bar 30% CO₂

3.3.4 Rig evaluation and regime identification

Pre-experimental tests were performed on the rig in order to identify Regime I operating conditions and are discussed in Section 3.3.4.1. Further, the use of a carbon mass balance to verify the accuracy of the experimental results is discussed in Section 3.3.4.2.

¹ g/g/s refers to the amount of carbon (g) reacted per amount of char (g) per second

3.3.4.1 Operating conditions

The operating conditions were chosen to represent typical conditions in an industrial gasifier (high pressure) while still working in the chemical reaction controlled regime (low temperatures). The experimental variables included temperature, pressure, CO₂ concentration and the three different char samples. In order to establish experimental conditions and ranges where the surface reaction alone controls the reaction rate (Regime I conditions), multiple tests were conducted which are discussed in Sections 3.3.4.1.1 to 3.3.4.1.5.

In Section 3.3.4.1.1 the gasification reactivity of the chars over a wide temperature range was investigated and an upper temperature bound for which Regime I conditions apply was established separately for each char. In Section 3.3.4.1.2 the absence of internal diffusion limitations at the highest gasification temperature for each char was tested by varying the sample particle size. To further test for diffusion limitations, the effect of total system pressure on the reaction rate at a constant CO₂ partial pressure was investigated in Section 3.3.4.1.3. The presence of external mass transfer effects was investigated in Section 3.3.4.1.4 by varying the reagent flow rate. In Section 3.3.4.1.5 the presence of heat and mass transfer effects was tested by investigating the influence of sample mass on the reaction rate.

3.3.4.1.1 Temperature range

A gasification temperature range where the reaction is chemically controlled was established separately for each char. An Arrhenius figure was used to investigate the dependence of the reaction rate on temperature. The results at 10% conversion for the different chars gasified at 20 bar and 30% CO₂ and different temperatures are shown in Figure 3.5.

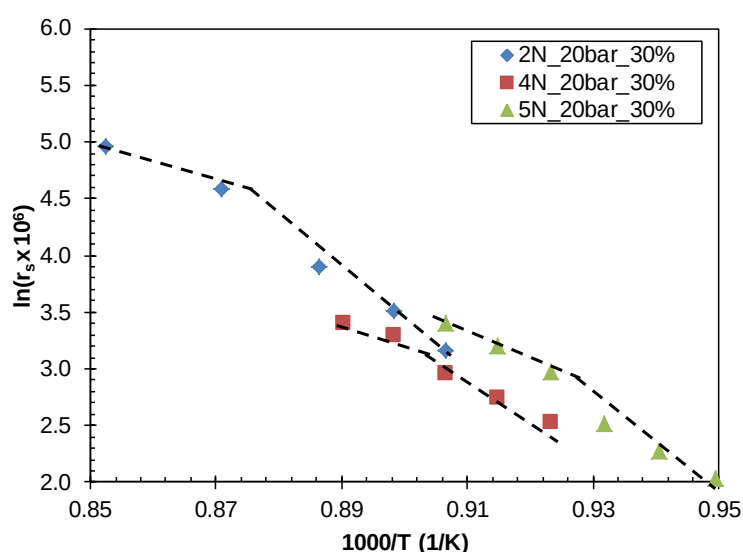


Figure 3.5: Arrhenius plots for different chars over a wide temperature range

A change in the slope of the 2N data above 855°C was observed. The observed activation energy was determined for the lower temperature range (855-830°C) as 268 kJ/mol and 167 kJ/mol for the higher temperature range (875-925°C). From this observation it was concluded that a change in reaction regime takes place above 855°C and the reaction shifts from Regime I to Regime II. The gasification experiments for 2N char needed to be performed below 855°C to ensure that the reaction takes place under reaction controlled conditions.

For the 4N data a slope change takes place above 830°C, and a temperature range of 810-830°C was chosen for 4N. The observed activation energy for the higher temperature range (840-850°C) was 109 kJ/mol compared to 218 kJ/mol for the lower temperature range (810-830°C) which again demonstrates the regime shift above 830°C.

The change in slope for 5N was less pronounced than for 2N and 4N, however there was a slight change in slope above 800°C. The observed activation energy for the higher temperature range (850-810°C) was 194 kJ/mol compared to 211 kJ/mol for the lower temperature range (800-780°C). A temperature range of 780-800°C was chosen for 5N.

3.3.4.1.2 Influence of sample particle size

The presence of internal mass transfer limitations was further tested by varying the sample particle size and observing the change in reactivity. A char particle in the size range of -500+425 µm was compared to a particle in size range of -1180+850 µm. The tests were conducted at the highest temperature where reaction controlled conditions apply as well as at a slightly higher temperature. The results for 5N char at 810 and 800°C are shown in Figure 3.6a and Figure 3.6b respectively.

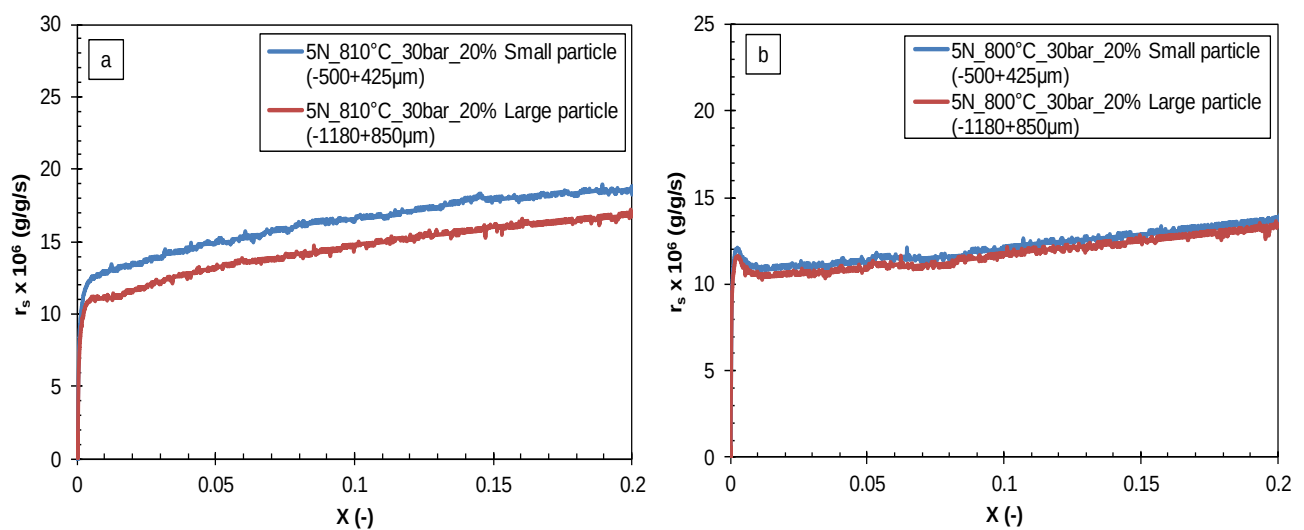


Figure 3.6: Specific reactivity of small and large char particles of 5N at 30 bar 20% for a) 810° and b) 800°C

From Figure 3.6a it is observed that the reaction is limited by internal diffusion at a temperature of 810°C and the reaction rate is lower in the larger char particles. When the temperature is decreased to 800°C (Figure 3.6b) the reaction rate is no longer affected by particle size and is assumed to be reaction controlled for temperatures at and below 800°C. For 2N and 4N Regime I conditions apply at and below 855 and 830°C respectively. The results for 4N and 2N are shown in Appendix B-5.

3.3.4.1.3 Influence of total system pressure

To further test for the presence of diffusion limitations, the effect of total system pressure on the reaction rate at constant CO₂ partial pressures was investigated. The reactivity at a constant partial pressure of 2.0 bar was studied at system pressures of 10, 20 and 30 bar. The results at the highest temperature used for each char are shown in Figures 3.7 a-c.

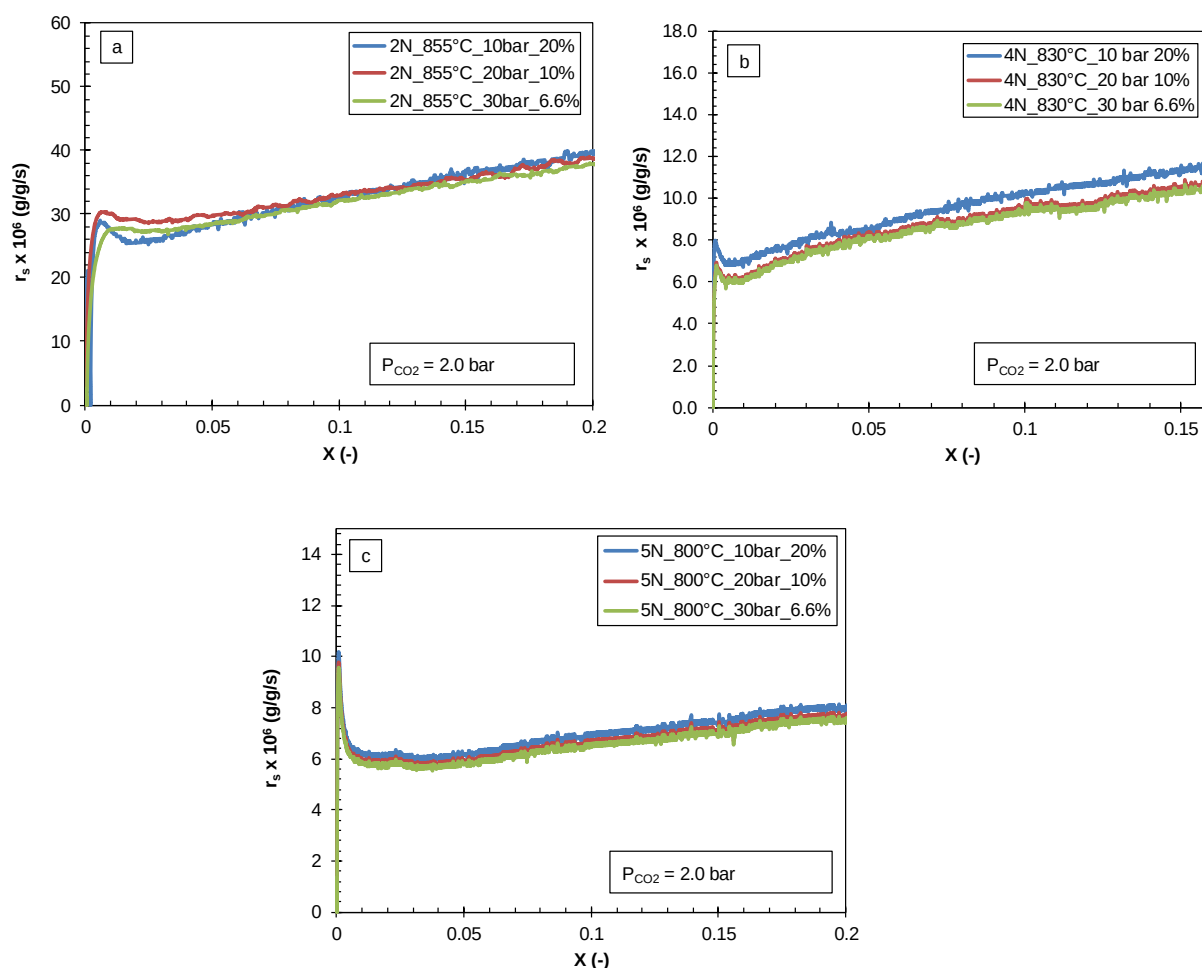


Figure 3.7: Effect of total pressure at constant CO₂ partial pressure (2 bar) on specific reactivity of a) 2N at 855°C, b) 4N at 830°C and c) 5N at 800°C

The total system pressure did not significantly affect the reaction rate at a constant CO₂ partial pressure (deviation between the curves is $\leq 5\%$). These results further demonstrate the

absence of diffusion effects at the highest gasification temperatures (855°C for 2N, 830°C for 4N and 800°C for 5N). For lower temperatures diffusion effects will also be absent. Subsequently these results show that the product gas CO does not inhibit the reaction.

3.3.4.1.4 Influence of flow rate

In order to test for the presence of external mass transfer effects, the total flow rate was varied. The reactivity of 2N char at 830°C, 30 bar and 30% CO₂ using different reagent gas flow rates is shown in Figure 3.8.

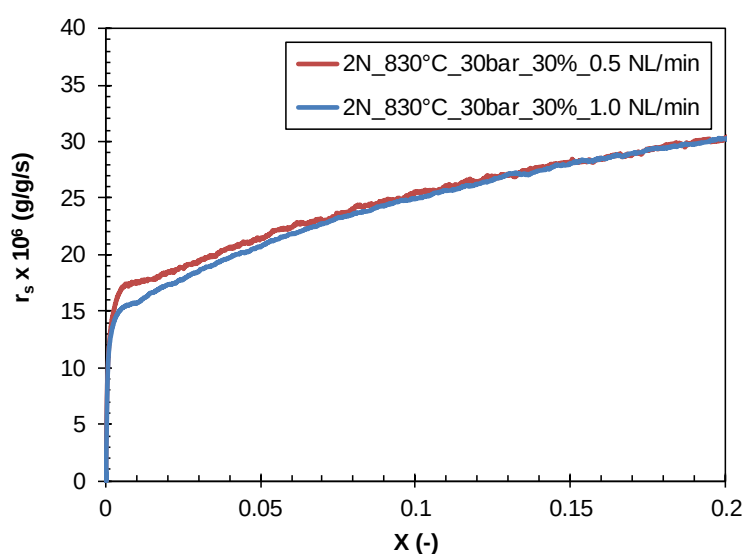


Figure 3.8: Effect of flow rate on specific reactivity of 2N at 830°C 30 bar 30%

The reactivity was not significantly affected by the change in flow rate and the curves differ by no more than 3%. From this observation it is concluded that external mass transfer effects do not limit the reaction. The gas analysing equipment requires an optimum flow rate of 1 NL/min and thus this flow rate was selected for the gasification experiments.

3.3.4.1.5 Influence of sample mass

Different sample masses were used for experimental runs at different operating conditions. This was done in order to maintain the CO concentration within a detectable level consistent with the analysis equipment. Tests were performed at the highest operating temperature to determine whether the sample mass would influence the reactivity which could indicate the presence of heat and mass transfer effects in the sample bed. An experimental run was repeated and the sample mass varied. The results for 4N char using different sample masses is shown in Figure 3.9. The samples were gasified at 830°C, 20 bar and 10% CO₂.

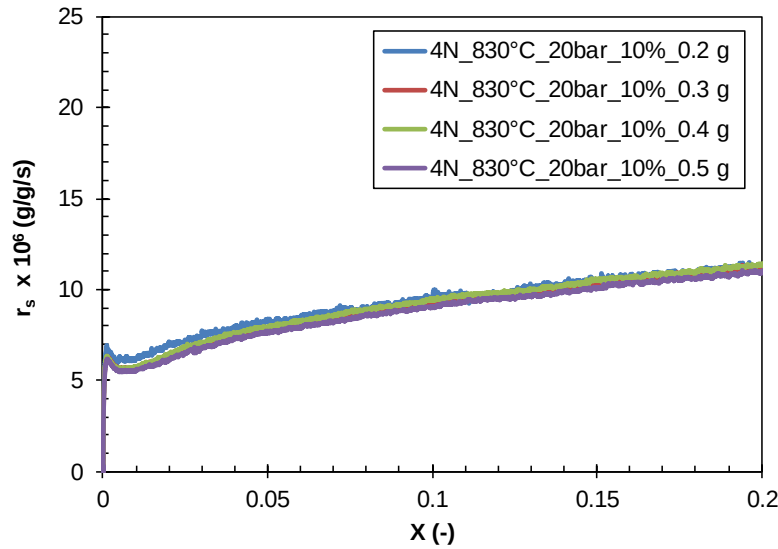


Figure 3.9: Effect of different sample mass on specific reaction rate of 4N at 830°C 20 bar 10%

From Figure 3.9 it is clear that increasing the sample mass does not have a significant influence on the reaction rate. The specific reaction rate at 10% conversion differs by no more than 5% over the range of sample masses used. This also shows that the concentration of the product CO which is formed is sufficiently low and does not have an inhibiting effect on the reaction.

To further test for the presence of heat transfer effects the char sample was mixed (in equal quantities) with inert sand particles with a particle size distribution comparable to the sample. No significant change in the reaction rate was observed leading to the conclusion that heat transfer effects do not limit the reaction. This test is discussed in more detail in Appendix B-4.

3.3.4.2 Carbon mass balance

In order to test the accuracy of the system, a carbon mass balance was performed on a high temperature run (2N 875°20 bar 30%) as well as other randomly selected runs using another independent method. This method involved weighing the char sample before and after gasification. The initial carbon content in the sample ($m_{c,0}$) and the carbon remaining after partial gasification ($m_{c,1}$) was calculated using Equation 3.6 and Equation 3.7 respectively.

$$m_{c,0} = m_{s0}(1 - x_{ash}) \times x_c(daf) \quad [g] \quad (3.6)$$

$$m_{c,1} = m_{s1}(1 - x_{ash}) \times x_c(daf) \quad [g] \quad (3.7)$$

m_{s0} is the initial sample mass and m_{s1} is the sample mass after partial gasification, x_{ash} is the ash yield wt% and $x_c(daf)$ is the carbon fraction amount on a dry ash free basis.

The calculated carbon converted during gasification ($m_{c,cal}$) was determined by Equation 3.8

$$m_{c,cal} = m_{c,0} - m_{c,1} \quad [g] \quad (3.8)$$

The amount of carbon converted using the method above was compared to the amount calculated from the CO concentration curve obtained by the analysis equipment as discussed in Section 3.3.3.2.

The results for different experimental runs are shown in Appendix B-6. The maximum error was found to be < 10%. This shows that the amount of carbon converted calculated from the CO concentration curve obtained during experimentation agrees well with the amount calculated using values from the proximate and ultimate analyses. By verifying the experimental results through an independent method the accuracy of the data was demonstrated.

3.3.5 Summary

After conducting the different tests it was concluded that the highest gasification temperature where Regime I conditions apply was different for each char. For this reason different gasification temperature ranges were selected for the different chars i.e. 2N: 830-855°C, 4N: 810-830°C, 5N: 780-800°C. The absence of internal and external diffusion limitations as well as heat transfer effects at these temperatures was confirmed through various tests. From these tests it was concluded that under Regime I conditions the reaction rate is independent of particle size, total system pressure at a constant CO₂ partial pressure, reagent flow rate and sample mass.

In order to investigate the effect of CO₂ partial pressure on the reaction rate the system pressure was varied between 1-30 bar and the CO₂ concentration in the reagent gas between 5-30%. This is equivalent to varying the CO₂ partial pressure between 0.05-9.0 bar.

The char particles in the size range of 425-500 µm (prepared by (Henning, 2017)) were used since the absence of internal diffusion limitations in these particles were confirmed. A reagent flow rate of 1 Nl/min was used in order to optimize the performance of the gas analyser.

Different sample masses were used for different runs after it was confirmed that the reaction rate was not significantly affected by the sample mass. At lower reactivity conditions (low temperature and CO₂ partial pressure) a sample mass of 0.5 g was used while at high reactivity conditions (high temperature and CO₂ partial pressure) the sample mass was adjusted to 0.2 g. This was done in order to maintain the CO concentration within a detectable level consistent with the gas analyser.

The experimental variables and operating conditions are summarized in Table 3.3.

Table 3.3: Experimental variables and operating conditions

Variable	Specification
Char samples	2N, 4N and 5N
Temperature	830-855°C (2N), 810-830°C (4N), 780-800°C (5N)
Pressure	1-30 bar
CO ₂ concentration	5-30%
CO ₂ partial pressure	0.05-9 bar
Char particle size	0.5 mm (-500/+425 µm)
Total gas flow	1 NI/min
Sample mass	0.2-0.5 g

3.4 Surface analyses

Surface area analyses were performed in order to investigate the effect of CO₂ partial pressure on the development of micro- and mesopore surface areas. For this purpose different char samples were gasified up to 10 and 20% conversion. The CO₂ partial pressure in the reagent gas was varied for these runs and the temperature was kept constant.

3.4.1 Equipment and procedures

Once the chars were partially gasified, the CO₂ and N₂ surface areas were determined on a Micromeritics ASAP 2020 surface area and porosity analyser. The micropore surface areas were determined at both 10 and 20% conversion and the mesopore surface areas at 10% conversion. The samples (0.2 g) were degassed under vacuum (10 µm Hg) at 380°C for 24 hours on the degassing port of the equipment prior to the analysis. The CO₂ and N₂ adsorption measurements were conducted at 0°C in an ice bath for CO₂ and at -196°C (77K) in liquid nitrogen for N₂. The adsorption data was obtained from the ASAP 2020 v4.0 software for the relative pressure ranges of $0 < P/P_0 \leq 0.032$ for CO₂ and $0 < P/P_0 \leq 0.3$ for N₂ analysis respectively. The micropore surface areas of the partially converted chars were determined from the CO₂ adsorption data by using the Dubinin-Radushkevich (D-R) method (Şenel et al., 2001). The mesopore surface areas were determined from the N₂ adsorption data using the Brunauer-Emmet-Teller (BET) method (Clarkson et al., 2012).

3.4.2 Experimental program

The experimental conditions for the different gasification runs are summarized in Table 3.4.

Table 3.4: Gasification conditions of chars used for surface analyses

Char	Temperature (°C)	CO ₂ partial pressure (bar)	Conversion (%)
2N	830	0.1, 1.5, 9.0	10, 20
4N	810	0.1, 1.5, 9.0	10, 20
5N	800	0.1, 1.5, 9.0	10, 20

3.5 Experimental error estimation

The uncertainty on the experimental data of the CO₂ gasification reactivity as well as on the surface area analyses data is discussed in this section. The uncertainty estimation on the CO₂ gasification reactivity data and the kinetic modelling parameters is discussed in Section 3.5.1 followed by the uncertainty estimation on the surface area results in Section 3.5.2.

3.5.1 CO₂ gasification reactivity and kinetic modelling

The total uncertainty on the kinetic modelling parameters was estimated to be a combination of the deviation on an experimental run (termed the “repeatability uncertainty”) and the uncertainty on the modelling of the experimental data (the “modelling uncertainty”). The estimation of the repeatability- and modelling uncertainty is discussed in Section 3.5.1.1 and Section 3.5.1.2 respectively.

3.5.1.1 Repeat runs

The experimental repeatability for 4N char at 830°C and 30 bar total system using 5 and 30% CO₂ is shown in Figure 3.10a and Figure 3.10b respectively. The average deviation (repeatability uncertainty) was determined to be 6% on a 95% confidence interval. Detailed calculations are shown in Appendix C-1.

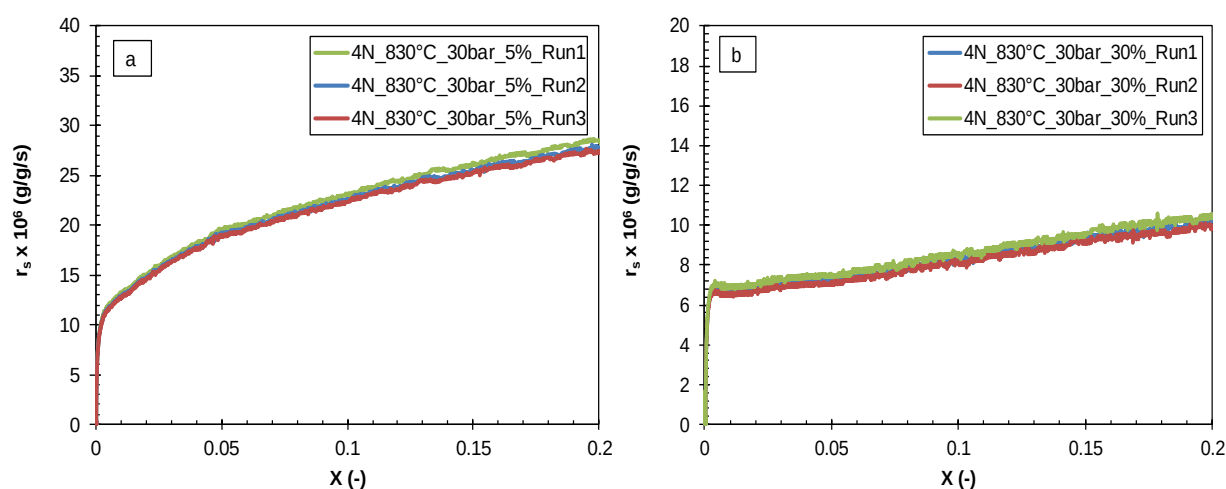


Figure 3.10: Specific reactivity of different runs of 4N at a) 830°C 30 bar 5% and b) 30 bar 30%

3.5.1.2 Model parameters

The parameters n (reaction order) and E (activation energy) were estimated by using an iterative sum of least squares method. The *lsqcurvefit* function in MATLAB was used for this purpose. The modelling uncertainty for a 95% confidence level was determined by using the nonlinear parameter confidence interval (*nlparci*) function in MATLAB. This function returns the 95% confidence intervals for the nonlinear least squares parameter estimates calculated by the least squares curve fit (*lsqcurvefit*) function. The algorithm used by the *nlparci* MATLAB function as well as the reported confidence intervals is shown in Appendix C-2. The modelling uncertainty on the activation energy (E) and reaction order (n) was 10% and 6% respectively. The repeatability uncertainty (determined in Section 3.5.1.1 as 6%) was added to the modelling uncertainty to give an estimated total uncertainty on the parameters E and n of <15% and <10% respectively.

3.5.2 Surface analyses

To determine the experimental error on the surface analyses results some of the adsorption analyses were repeated. The deviation percentage was calculated using the different values obtained for the runs by Equation 3.9.

$$Deviation \% = \left| \frac{r_1 - r_2}{(r_1 + r_2)/2} \right| \times 100 \quad (3.9)$$

Table 3.5 contains a summary of the repeated runs.

Table 3.5: Summary of repeated surface area analyses

Sample	Run1	Run2	Deviation (%)
5N_unconverted	167	170	1.8
4N_9 bar p_{CO_2} $X=0.2$	308	306	0.7
4N_unconverted	144	139	3.5

It was concluded that the maximum error on the surface analysis was < 5%.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Introduction

The results of the study are presented and discussed in this chapter. The CO₂ gasification experimental data is provided in Section 4.2 followed by the kinetic modelling of the data in Section 4.3. In Section 4.4 the use of a structural model (the RPM) for modelling of the data is discussed. The char reactivity comparison and correlation with char characteristics is presented in Section 4.5. The results from the surface area analyses are reported and discussed in Section 4.6.

4.2 CO₂ gasification reactivity

4.2.1 Effect of temperature

The effect of temperature on the specific reaction rate of 2N, 4N and 5N at 30 bar and 30% CO₂ is shown in Figure 4.1 a-c respectively.

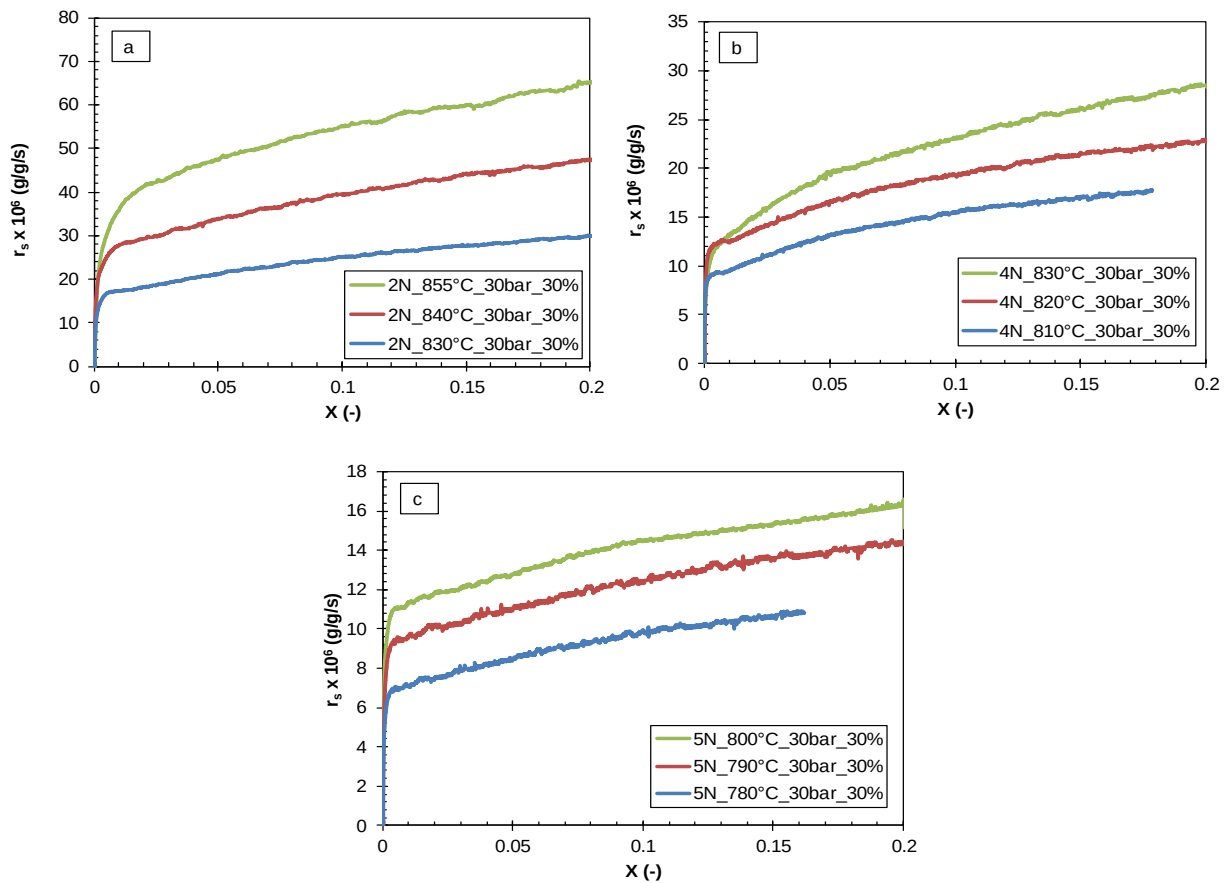


Figure 4.1: Effect of temperature on specific reactivity of a) 2N, b) 4N and c) 5N at 30 bar 30%

The CO₂ gasification reactivity increased significantly with increasing temperature for all three chars. In general, a 10°C increase in the reaction temperature resulted in almost a 50% increase in the specific reaction rate of the chars. The strong temperature dependence corresponds to observations by various authors when performing experiments under surface reaction controlled conditions (Ye et al., 1998; Everson et al., 2008; Tremel et al., 2012). Kajitani et al. (2002) also observed the strong effect of temperature on the CO₂ gasification rate of an Australian bituminous char at temperatures below 1200°C but the effect was less significant at higher temperatures due to pore diffusion limitations.

4.2.2 Effect of CO₂ partial pressure

The effect of CO₂ partial pressure on the specific reaction rate of 2N at 855°C, 4N at 830°C and 5N at 800°C is shown in Figure 4.2 a-c respectively. For these runs the total system pressure was kept constant at 30 bar and the partial pressure changed by varying the CO₂ concentration in the reagent gas (5, 10, 20 and 30%). This corresponds to partial pressures of 1.5, 3.0, 6.0 and 9.0 bar respectively.

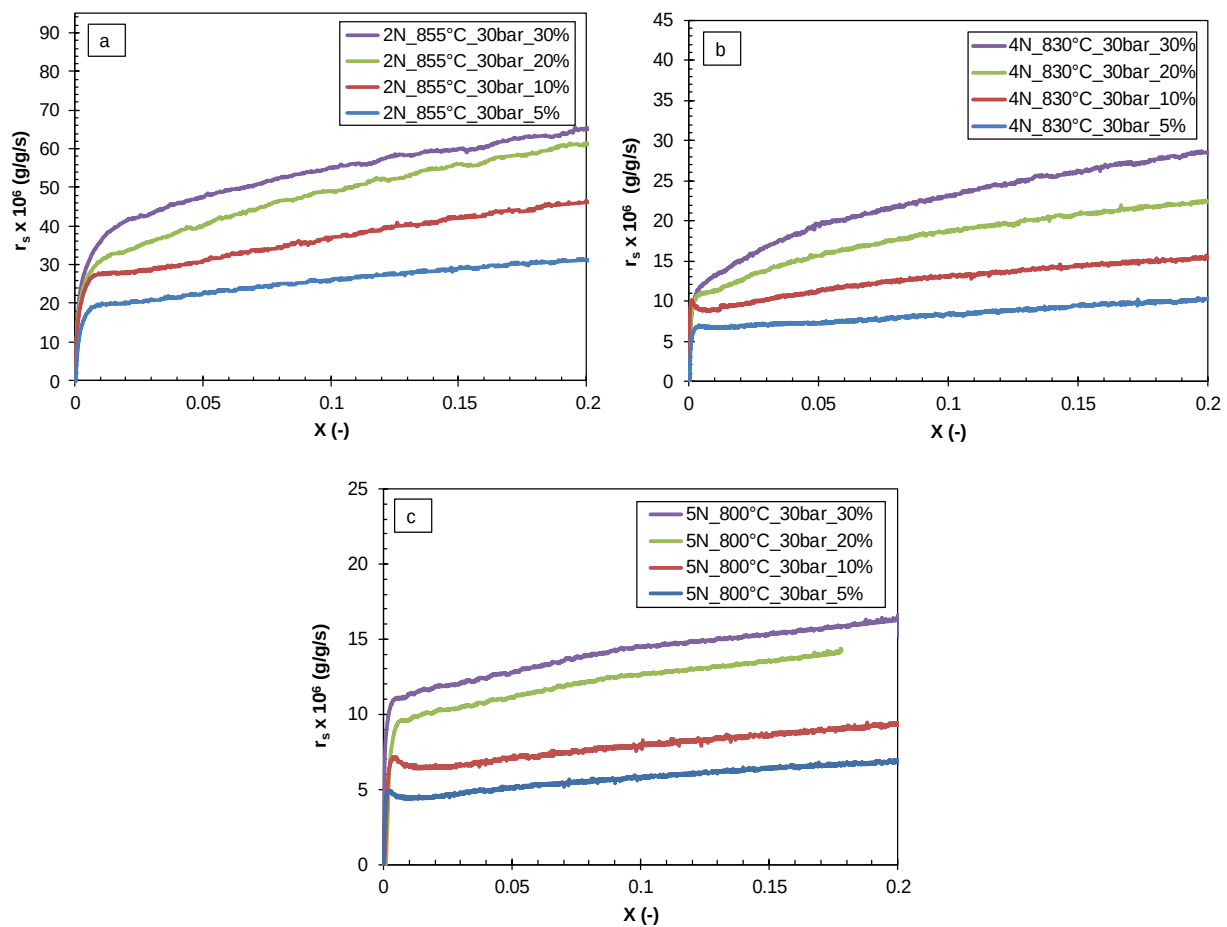


Figure 4.2: Effect of CO₂ partial pressure on specific reactivity of a) 2N at 855°C, b) 4N at 830°C and c) 5N at 800°C

The specific reaction rate increased significantly with increasing CO₂ partial pressure. In general, the specific reaction rate almost doubled with a 20% increase in CO₂ concentration at 30 bar. This can be attributed to the increased amount of CO₂ molecules present in the reagent gas at higher concentrations. Ahn et al. (2001) observed that the CO₂ gasification reactivity of a sub-bituminous coal char was dependant on the CO₂ partial pressure (1-5 bar) in the reagent gas with an order of 0.4. An order of 0.5-0.7 was observed by Roberts and Harris (2000) for CO₂ partial pressures of 1-10 bar and Park and Ahn (2007) reported an order of 0.4-0.7 for CO₂ partial pressures of 1.8-4.95 bar.

To determine the observed reaction order on CO₂ partial pressure, the natural logarithm of the specific reaction rate at 10% conversion was plotted against the natural logarithm of the CO₂ partial pressure. The experimental data given in Table 4.1 was used to produce the results for the chars shown in Figure 4.3 a-c.

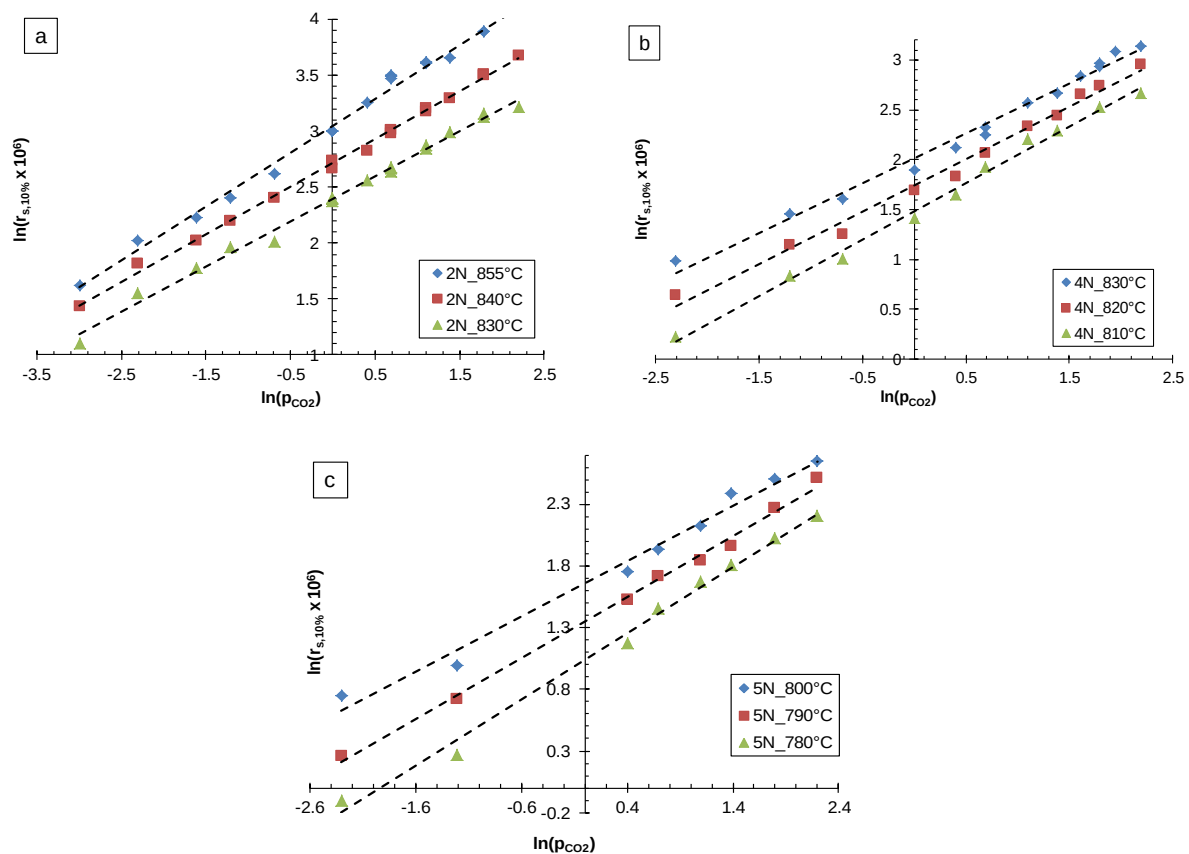


Figure 4.3: Reaction order on CO₂ partial pressure at different temperatures for a) 2N, b) 4N and c) 5N

The experimental data shows a power law trend and the reaction orders of the chars do not differ significantly throughout the partial pressure range. The observed reaction orders of the 2N char increased from 0.41 to 0.48 when the temperature increased from 830 to 855°C. For the 4N char the observed reaction order decreased from 0.56 to 0.50 when the temperature

increased from 810 to 830°C. The observed reaction order for the 5N char decreased from 0.53 to 0.45 when the temperature increased from 780°C to 800°C. The deviation in reaction order for all three chars was <15%.

From these results it was concluded that the temperature does not significantly affect the observed reaction order when the experiments are performed under Regime I conditions. Kajitani et al. (2002) reported a CO₂ reaction order of 0.54 for an Australian bituminous char and 0.49 for a Chinese bituminous char gasified under Regime I conditions (low temperatures). At high temperatures (Regime II conditions) the reaction order of the Australian bituminous char increased significantly to 0.73. Roberts and Harris (2000) reported a CO₂ reaction order of 0.5 for an Australian bituminous char gasified at 1-10 atm and 900°C. Everson et al. (2008) observed the CO₂ reaction order of an inertinite rich char to vary between 0.46-0.54 at atmospheric pressure.

4.2.3 Combined effect of temperature and CO₂ partial pressure

The combined effects of temperature and CO₂ partial pressure on the gasification rate of the different chars at 10% conversion are shown in Figure 4.4 a-c.

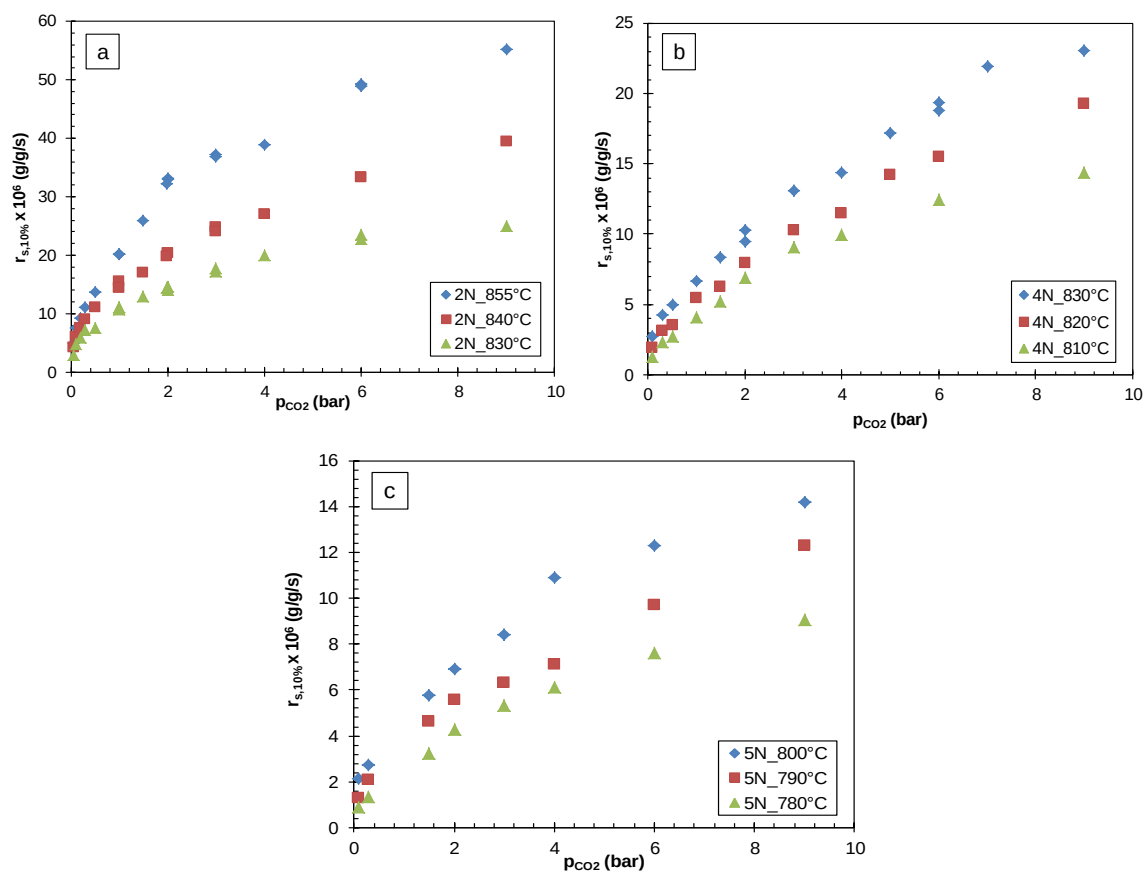


Figure 4.4: Effects of temperature and CO₂ partial pressure on reactivity at 10% conversion for a) 2N, b) 4N and c) 5N

The specific reaction rate increased with increasing temperature as well as increasing CO₂ partial pressure (as discussed in Section 4.2.1 and Section 4.2.2 respectively). The low reaction rates are characteristic of the slow Boudouard reaction (Everson et al., 2008). A summary of the reactivity data obtained at 10% conversion for 2N, 4N and 5N char is shown in Table 4.1.

Table 4.1: Summary of gasification reactivity data at 10% conversion for 2N, 4N and 5N chars

			$r_{s,10\%} \times 10^6 \text{ (g/g/s)}$								
			2N			4N			5N		
P (bar)	[CO ₂] (%)	p _{CO2} (bar)	830°C	840°C	855°C	810°C	820°C	830°C	780°C	790°C	800°C
1	5	0.05	3.0	4.2	5.1	ND	ND	ND	ND	ND	ND
1	10	0.1	4.7	6.2	7.6	1.2	1.9	2.7	0.9	1.3	2.1
1	20	0.2	5.9	7.6	9.3	ND	ND	ND	ND	ND	ND
1	30	0.3	7.1	9.1	11.1	2.3	3.2	4.3	1.3	2.1	2.7
10	5	0.5	7.5	11.1	13.7	2.7	3.5	5.0	ND	ND	ND
10	10	1.0	11.1	15.5	20.2	4.1	5.4	6.7	ND	ND	ND
10	20	2.0	14.6	20.3	33.1	6.9	7.9	10.3	4.3	5.6	6.9
10	30	3.0	17.8	24.8	37.3	9.1	10.3	13.1	5.3	6.3	8.3
20	5	1.0	11.0	14.5	20.1	4.1	5.4	6.6	ND	ND	ND
20	10	2.0	14.0	20.3	32.9	6.8	7.9	9.5	4.3	5.5	6.9
20	20	4.0	20.0	27.1	38.9	9.9	11.5	14.4	6.1	7.1	10.9
20	25	5.0	ND	ND	ND	12.1	14.2	17.1	ND	ND	ND
20	30	6.0	23.5	33.4	49.4	12.5	15.5	18.7	7.6	9.7	12.3
30	5	1.5	12.9	17.0	26.0	5.2	6.2	8.3	3.2	4.6	5.8
30	10	3.0	17.1	24.0	36.9	9.1	10.3	13.2	5.3	6.3	8.4
30	20	6.0	22.9	33.3	49.0	12.2	15.5	18.8	7.6	9.8	12.3
30	30	9.0	25.0	39.5	55.1	14.4	19.3	23.0	9.1	12.3	14.2

ND – Not determined

4.3 Kinetic modelling

The empirical power law as well as the Langmuir Hinshelwood kinetic model was used to describe the specific reactivity of the chars at 10% conversion. The power law is discussed in Section 4.3.1 followed by the Langmuir Hinshelwood model in Section 4.3.2.

4.3.1 Power law

The empirical power law equation was discussed in Section 2.2.4.1.1. The temperature dependence of the rate constant (k_s) was described with the Arrhenius equation. A summary of

the parameters for the chars is shown in Table 4.2 and comparisons of the experimental data and the model are shown in the parity plots provided in Figure 4.5 a-c.

Table 4.2: Power law kinetic parameters for 2N, 4N and 5N chars

Parameter	2N	4N	5N	Units
A	2.7×10^7	1.5×10^7	7.6×10^6	$\text{g g}^{-1} \text{s}^{-1} \text{bar}^n$
E	261 ± 20	260 ± 26	250 ± 30	kJ/mol
n	0.45 ± 0.02	0.56 ± 0.03	0.51 ± 0.04	-

Uncertainties based on a 95% confidence level

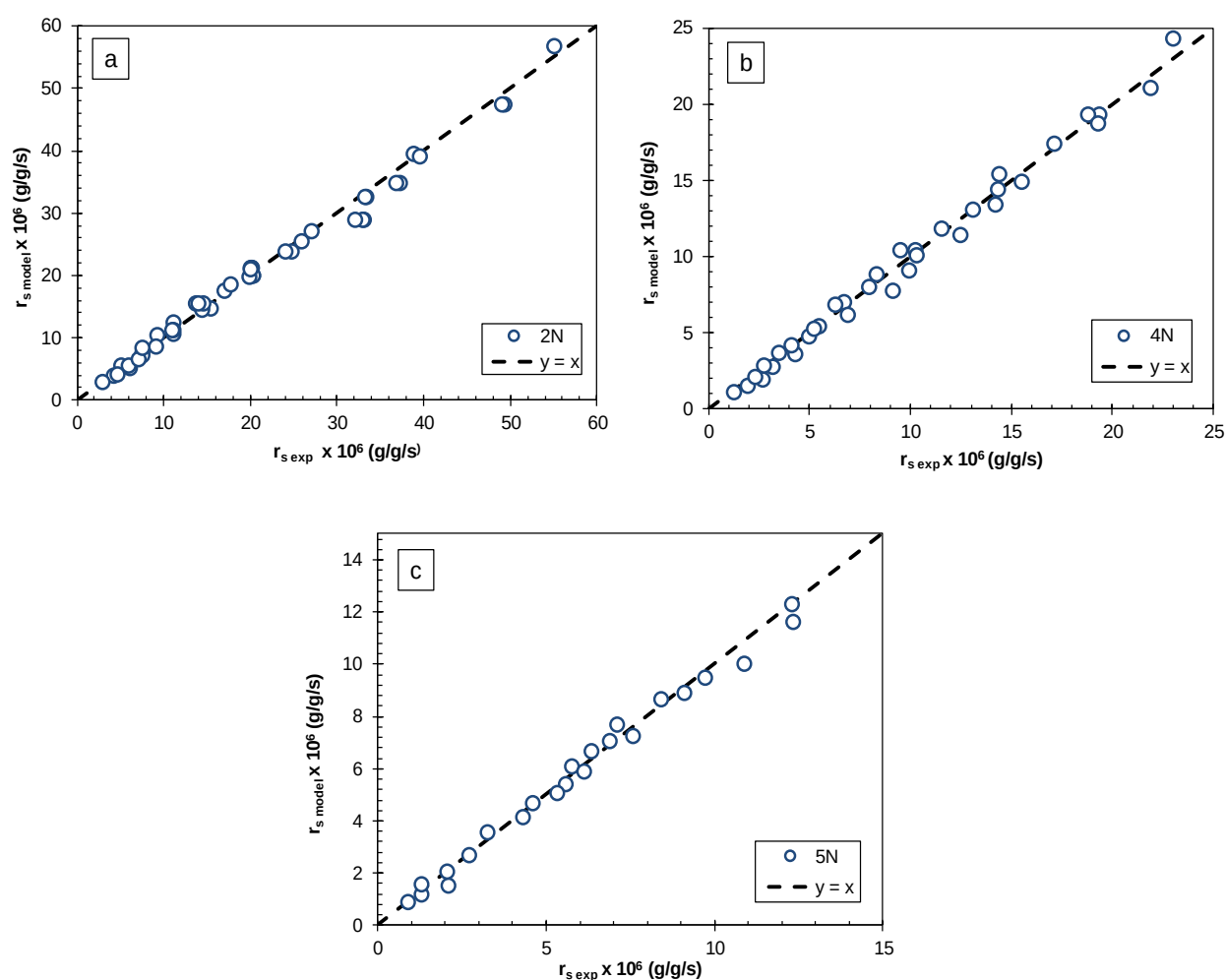


Figure 4.5: Specific reaction rate predicted by power law versus experimental specific reaction rate at 10% conversion for a) 2N, b) 4N and c) 5N

From the parity plots it is observed that the experimental data of all three chars is well described by the power law. The coefficients of multiple determination (R^2) for the models of 2N, 4N and

5N char are 0.98, 0.99 and 0.99 respectively. The power law was shown to be applicable when predicting CO₂ gasification reactivity at CO₂ partial pressures below 9.0 bar.

The observed activation energies agree with literature reported for similar coal chars at both low and high pressures. Everson et al. (2008) obtained an average activation energy of 235 ± 37 kJ/mol for an inertinite rich coal char gasified at 287.5 kPa with the CO₂ concentration ranging from 20-100%. Roberts and Harris (2000) reported observed activation energies of 209 and 211 kJ/mol for an Australian bituminous char gasified with pure CO₂ at 1 and 10 atm respectively. They concluded that there was no significant effect of pressure on the activation energy which corresponds to the results from this study. Kajitani et al. (2002) reported an activation energy of 283 kJ/mol for CO₂ gasification of an Australian bituminous char at 10 bar under Regime I conditions (low temperatures). At higher temperatures (Regime II conditions) the activation energy decreased to 163 kJ/mol.

Although the activation energies of the chars differed by no more than 11 kJ/mol, the activation energies of the inertinite rich chars (2N and 4N) were slightly higher than that of the vitrinite rich char (5N). This corresponds to observations by Sun et al. (2004) who found that inertinite rich chars have higher activation energies compared to vitrinite rich chars.

It was also observed that an increase in carbon content of the char resulted in an increase in activation energy which agrees with findings by Kwon et al. (1988) and Hattingh (2010). The frequency factors (A) increased with increasing activation energy due to a compensation effect between the frequency factor and the activation energy (Sun et al., 2004).

4.3.2 Langmuir Hinshelwood

The derivation of the Langmuir Hinshelwood rate equation was discussed in Section 2.2.4.1.2. In this study the equation derived by Ergun (1956) was used. Experimental tests showed that the total system pressure had no significant influence on the specific reaction rate at a constant CO₂ partial pressure and it was concluded that inhibition by the product gas (CO) was negligible. Equation 2.6 was thus simplified to Equation 4.1.

$$r_s = \frac{[C_t]k_1p_{CO_2}}{1 + \frac{k_1}{k_3}p_{CO_2}} \quad (4.1)$$

C_t is the total amount of active sites available for reaction, k_1 is the rate constant for the oxygen exchange step (step 1) and k_3 is the rate constant for the desorption of the oxygen surface complex (step 2).

The rate constants were determined at different temperatures by linearizing Equation 4.1 and plotting the inverse of the experimental reaction rate against the inverse of the CO₂ partial pressure. The value of $[C_t]k_1$ was determined from the inverse of the gradient and k_1/k_3 through dividing the intercept by the gradient. The rate constants determined at different temperatures for 2N, 4N and 5N are shown in Table 4.3, Table 4.4 and Table 4.5 respectively.

Table 4.3: LH rate constants for 2N

2N	830°C	840°C	855°C
$[C_t]k_1$ (bar s) ⁻¹	2.0×10^{-5}	2.9×10^{-5}	3.3×10^{-5}
k_1/k_3 (bar ⁻¹)	0.70	0.66	0.54
$[C_t]k_3$ (s ⁻¹)	2.9×10^{-5}	4.3×10^{-5}	6.2×10^{-5}

Table 4.4: LH rate constants for 4N

4N	810°C	820°C	830°C
$[C_t]k_1$ (bar s) ⁻¹	5.0×10^{-6}	6.5×10^{-6}	8.1×10^{-6}
k_1/k_3 (bar ⁻¹)	0.23	0.24	0.25
$[C_t]k_3$ (s ⁻¹)	2.1×10^{-5}	2.7×10^{-5}	3.3×10^{-5}

Table 4.5: LH rate constants for 5N

5N	780°C	790°C	800°C
$[C_t]k_1$ (bar s) ⁻¹	2.9×10^{-6}	4.4×10^{-6}	5.3×10^{-6}
k_1/k_3 (bar ⁻¹)	0.24	0.26	0.27
$[C_t]k_3$ (s ⁻¹)	1.2×10^{-5}	1.7×10^{-5}	2.0×10^{-5}

The activation energies (E_1 and E_3) were determined from the rate constants and are shown in Table 4.6 for the different chars.

Table 4.6: LH activation energies for 2N, 4N and 5N chars

Parameter	2N	4N	5N	Units
E_1	202 ± 20	239 ± 26	281 ± 30	kJ/mol
E_3	311 ± 20	231 ± 26	227 ± 30	kJ/mol

Uncertainties based on a 95% confidence level

The activation energies correspond well to values reported in literature for similar coal chars. Du Toit (2013) used the Langmuir Hinshelwood (LH) equation to describe the reactivity of a Highveld Seam 4 char gasified with CO₂ under atmospheric pressure. They used Arrhenius plots to determine the activation energy and Van't Hoff plots to determine the adsorption enthalpy. An activation energy of 243 ± 32 kJ/mol and an adsorption enthalpy of -16 ± 5 kJ/mol was reported. Activation energies ranging between 222-251 kJ/mol were determined by Kajitani et al. (2006) for a bituminous coal char gasified at CO₂ partial pressures up to 7 bar when using the LH model in the form of Equation 2.10. Zhang et al. (2014) also used the LH model in this form to describe the high pressure (2-5 bar) CO₂ gasification reactivity of a bituminous coal char and reported activation energies ranging from 131-280 kJ/mol.

A comparison between the experimental data of this study and the reactivity predicted by the LH rate equation at 10% conversion is shown in Figure 4.6 a-c for the different chars.

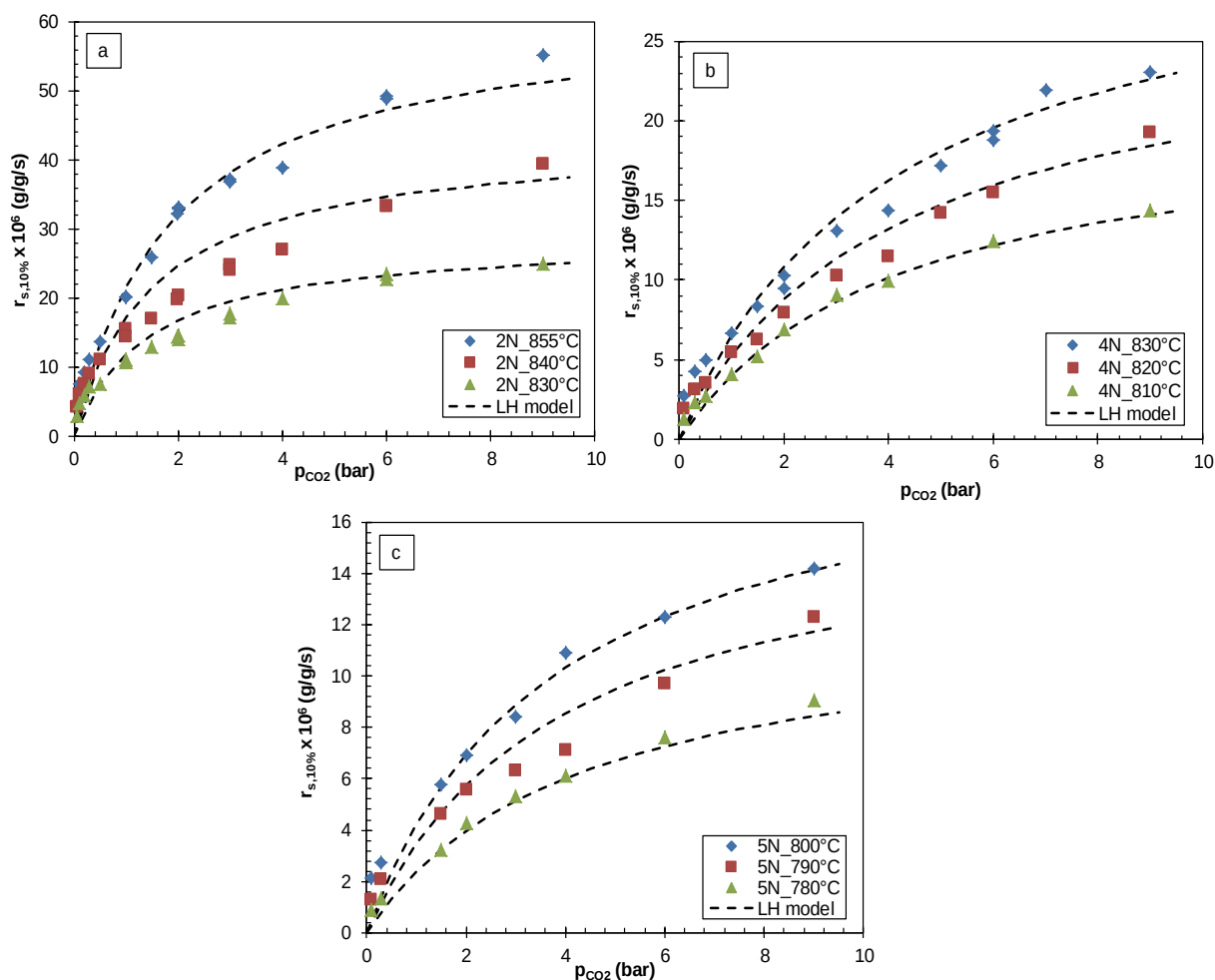


Figure 4.6: Comparison of specific reactivity experimental data at 10% conversion and LH model for a) 2N, b) 4N and c) 5N

The model is observed to well describe the experimental data for the different chars which corresponds well with observations by other authors when modelling high pressure gasification reactivity. Zhang et al. (2014) observed that experimental data for a bituminous coal char gasified at CO₂ partial pressures of 2-5 bar was accurately predicted by the LH model. Kajitani et al. (2006) investigated the CO₂ gasification reactivity of an Australian and a Chinese bituminous coal char at low temperatures (Regime I conditions). They reported that for the entire CO₂ partial pressures range of 0.1-10 bar, the LH equation gave better predictions compared to the empirical power law. Roberts and Harris (2006) concluded that the LH model in the form of Equation 2.7 is suitable for describing the Char-CO₂ reaction kinetics up to CO₂ partial pressures of 30 bar.

At CO₂ partial pressures below 10 bar (used in this study) both the LH model and the empirical power law is able to accurately describe the experimental data. This is consistent with general reports which suggest that the LH rate equation can be reduced to a power rate law at lower CO₂ partial pressures (Irfan et al., 2011).

4.4 Structural modelling

Although the main modelling focus of this study is kinetic modelling, the structural Random Pore Model (RPM) was used to describe the experimental data up to 20% conversion in order to obtain some insight into the structural development of the char with conversion. The results are discussed in Section 4.4.1.

4.4.1 Random Pore Model

The RPM in the form of Equation 2.13 was used. The model was fitted to the specific reaction rate at different CO₂ partial pressures (0.1, 1.5, 9.0 bar). These partial pressures were selected in order to compare the modelling results with surface area analyses discussed in Section 4.6. The structural parameter (ψ) and initial reactivity (r_{s0}) determined at different CO₂ partial pressures is reported in Table 4.7 and a comparison of the experimental data and the specific reaction rate predicted by the RPM is shown in Figure 4.7 a-c for the different chars.

Table 4.7: Parameters of the RPM

	2N (830°C)		4N (810°C)		5N (800°C)	
PCO ₂ (bar)	ψ	r_{s0} (g/g/s)	ψ	r_{s0} (g/g/s)	ψ	r_{s0} (g/g/s)
0.1	6.8	2.1×10^{-6}	5.0	1.1×10^{-6}	6.9	1.4×10^{-6}
1.5	7.5	6.1×10^{-6}	6.1	4.1×10^{-6}	7.6	4.2×10^{-6}
9.0	15.5	1.5×10^{-5}	8.6	9.1×10^{-6}	8.2	1.1×10^{-5}

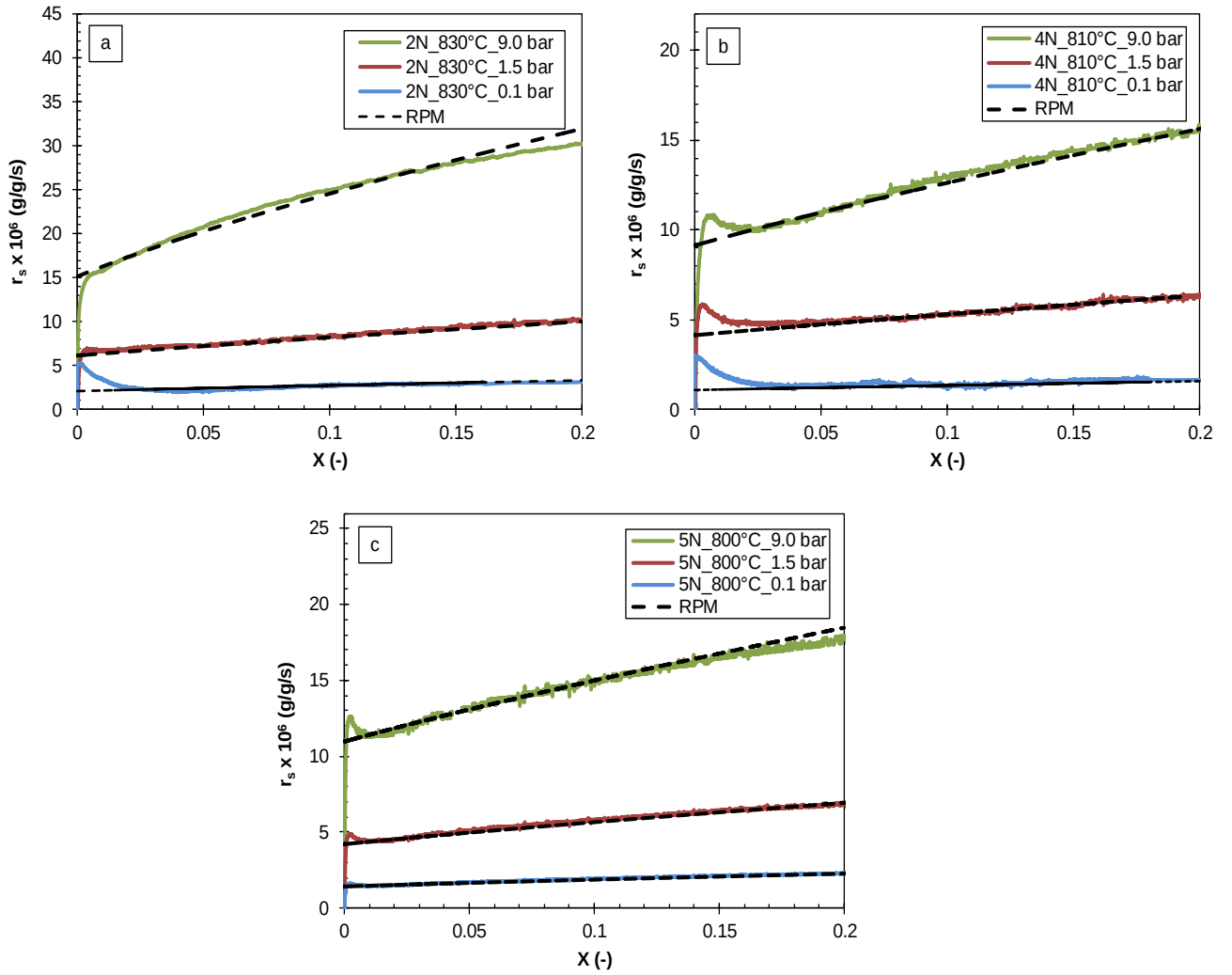


Figure 4.7: Comparison of experimental specific reactivity data and RPM model for a) 2N at 830°C, b) 4N at 810°C and c) 5N at 800°C

The RPM is shown to be valid for describing the experimental data of the three chars at different CO_2 partial pressures which is consistent with previous work. Kajitani et al. (2006) reported that the RPM well described the CO_2 gasification reactivity of four different bituminous coal chars at CO_2 partial pressures of 1-2 bar. Everson et al. (2008) also observed the RPM to be valid for describing the gasification reactivity of an inertinite-rich coal char at atmospheric pressure.

The structural parameter (ψ) gives an indication of the amount of pore development which will take place throughout gasification (Kajitani et al., 2006). The values reported in Table 4.7 correspond well to values reported in literature. Kajitani et al. (2006) observed values for ψ ranging from 1-26 for different bituminous chars. Kim et al. (2014) determined the value of ψ for a sub-bituminous char with particle sizes of 75 μm and 800 μm to be 4 and 14 respectively. The

apparent reaction rate of the 800 μm particle was observed to increase more rapidly compared to the 75 μm particle which further indicated more significant pore growth in the larger particle.

From the results presented in Table 4.7, the structural parameter was observed to increase with increasing CO_2 partial pressure suggesting that the amount of pore growth increases with increasing reagent partial pressure. The reaction at a higher CO_2 partial pressure will reach a maximum surface area at lower conversion compared to the reaction at low partial pressure.

Although the random pore model accounts for pore development taking place with conversion, it does not account for changes in pore structure due to reagent partial pressure. The structural parameter ψ is assumed to remain constant at different operating conditions. From the results discussed, the structural parameter is observed to be function of CO_2 partial pressure. Kajitani et al. (2002) also questioned the use of a constant value for ψ in the RPM. They investigated the CO_2 gasification rate and surface area development of a bituminous coal char at CO_2 partial pressures of 0.5-3 bar and observed that the RPM was unable to simultaneously describe the experimental reactivity and the surface area data. From their results they concluded that some major structural changes are not accounted for if ψ is assumed to remain constant.

Although ψ is merely a fitting parameter in the RPM (and can thus not be used as physical evidence for an increase in the degree of pore growth with increasing CO_2 partial pressure) its value does to some extent give an indication of structural changes occurring in the char during gasification. Experimental evidence demonstrating the effect of CO_2 partial pressure on pore development is discussed further in Section 4.6.

4.5 Char reactivity

In this section the CO_2 gasification reactivity of the different chars are discussed. The reactivities of the three chars are compared in Section 4.5.1. In Section 4.5.2 kinetic data reported in literature for various chars are compared to the kinetic data of the chars used in this study. The reactivity of the chars is related to their characteristics in Section 4.5.3.

4.5.1 Comparison of different chars

In order to remain within Regime I conditions different upper temperature bounds were established for each char (see Section 3.3.4.1.1). The chars used in this study were therefore not all gasified at the same temperature. The 2N and 4N chars were both gasified at 830°C. In order to compare the reactivity, the data for the 5N char was extrapolated to 830°C using the power law with the kinetic parameters obtained in Section 4.3.1. The results at 10% conversion are shown in Figure 4.8.

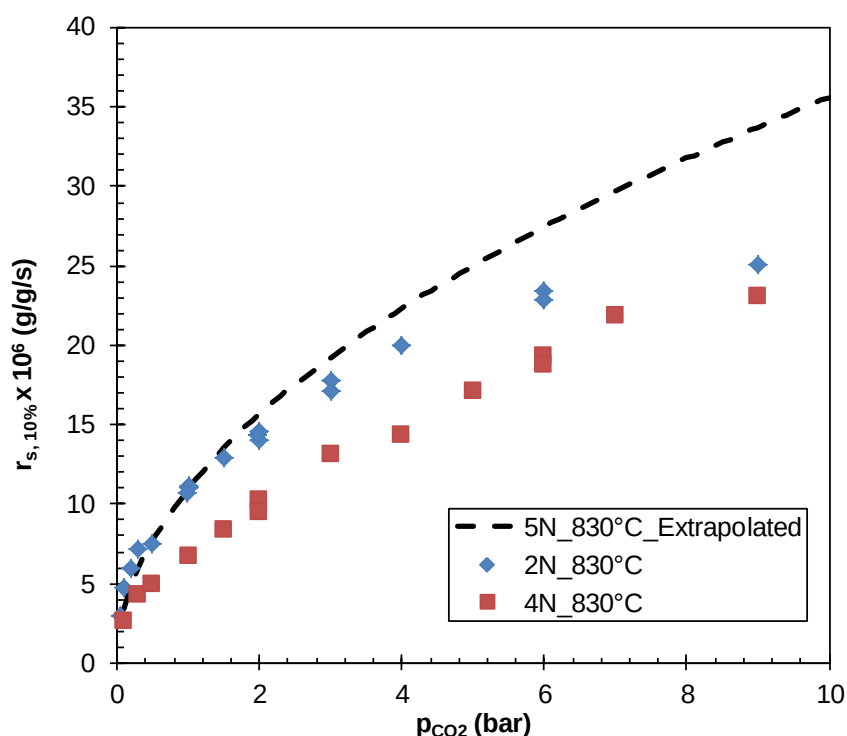


Figure 4.8: Comparison of specific reaction rate of 2N, 4N and 5N at 10% conversion and 830°C

The 5N char was observed to have the highest reactivity and 4N char the lowest. These results agree with the observations of Henning (2017) for the same chars. The char reactivity is related to the char characteristics in Section 4.5.3.

4.5.2 Comparison with literature

The reaction rates of the chars used in this study were compared to the CO₂ gasification reactivity results of similar coal chars reported in literature. A summary of these chars are shown in Table 4.8. All the authors claimed to have performed their experiments under Regime I conditions.

Table 4.8: Summary of chars reported in literature

Char name	Reference	Coal	Charring temperature (°C)	Kinetic model
Char D	Roberts and Harris (2000)	High-volatile bituminous	1100	PL
NL Char	Kajitani et al. (2002)	Bituminous, high fuel ratio	1400	PL
Char BA	Kajitani et al. (2006)	Bituminous, high fuel ratio	1400	LH
Seam 4 Char	Du Toit (2013)	Bituminous, Highveld seam 4	950	LH

In order to compare the reactivity of the different chars at the same temperature and CO₂ partial pressures, the model parameters reported by the various authors was used to extrapolate their

data to the required gasification reaction conditions used in this study. To account for changes in reactivity due to the different micropore surface area of the chars, the specific reaction rates (g/g/s) were normalized with the initial surface areas of the chars. The intrinsic rates were reported in g/m²/s. A comparison of the intrinsic reactivity of the different chars is shown in Figure 4.9.

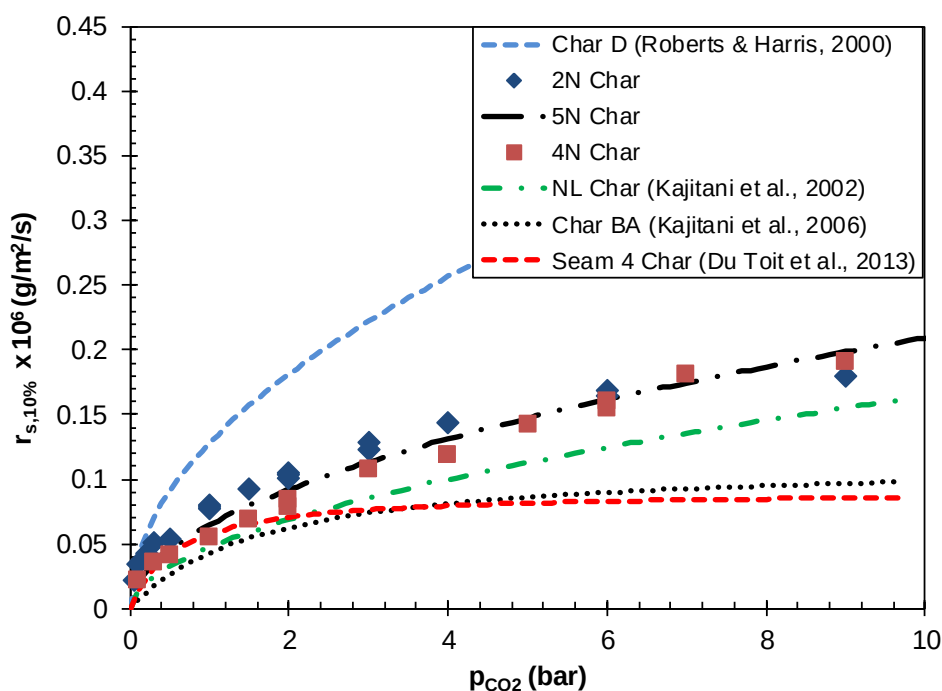


Figure 4.9: Comparison of experimental data and kinetic models from literature

The intrinsic reactivity of Char D (Roberts and Harris, 2000) (extrapolated using the power law) was the highest of all and this was attributed to the high volatile content of the char. The intrinsic reactivity of both NL Char (Kajitani et al., 2002) (extrapolated using the power law) and Char BA (Kajitani et al., 2006) (extrapolated using the LH model) was comparable to the reactivity of the chars used in this study. This may be due to the similarity in the characteristics of the coals and resulting chars. The NL char had a relative high mineral matter (21% d.b.) and high inertinite (58% m.m.f) content similar to the 2N and 4N chars used in this study. The coal used to prepare Char BA had a low mineral matter content (9% d.b.), however the high fuel ratio (2.1) was comparable to the fuel ratios of the coal used in this study (2N: 2.3, 4N: 2.4 and 5N: 1.4).

The intrinsic reactivity of the seam 4 Highveld char used by du Toit (2013) at low pressures is almost identical to the reactivity of the 4N char used in this study at CO₂ partial pressures below 2 bar. This is expected when considering that both these chars were prepared from seam 4 Highveld coals and devolatilized at the same temperature (950°C). At higher partial pressure (above 2 bar), the extrapolated reactivity of the char used by du Toit (2013) is lower than the

reactivity of 4N. It is suggested that the model parameters obtained for the LH model by du Toit (2013) at low CO₂ partial pressures (21.9-87.5 kPa) cannot be used to extrapolate the reactivity data to higher partial pressures. This might be due to changes in the $[C_i]$ term (the total amount of active sites) at higher partial pressures which was discussed in Section 2.2.4.1.2. In the current study the char surface area measurements (discussed in Section 4.6) indicated that there was a significant effect of CO₂ partial pressure on char surface area development. It is suggested that a significant change in surface area is accompanied by a significant change in the total amount of active sites $[C_i]$. An effect of CO₂ partial pressure on the $[C_i]$ term will likely cause a significant deviation from the standard LH behaviour over a wide pressure range which explains why the extrapolated reactivity data from du Toit (2013) deviates from the reactivity data of the 4N char used in this study.

4.5.3 Char reactivity related to char characteristics

In this section the different char characteristics are correlated with the char reactivity. The initial specific reactivity of the 3 chars was plotted against the respective char characteristics. This was done at 830°C and various CO₂ partial pressures.

4.5.3.1 Influence of macerals

The maceral content of the 3 chars differed significantly. The 5N char had a high vitrinite and low inertinite content, while the 4N char had high inertinite and low vitrinite. The 2N char had an intermediate vitrinite and a high inertinite content. All three chars had a low liptinite content which is generally accepted for bituminous chars (du Toit, 2013). A clear correlation was observed between the vitrinite and inertinite content and the initial reactivity. These correlations are shown in Figure 4.10 a-b.

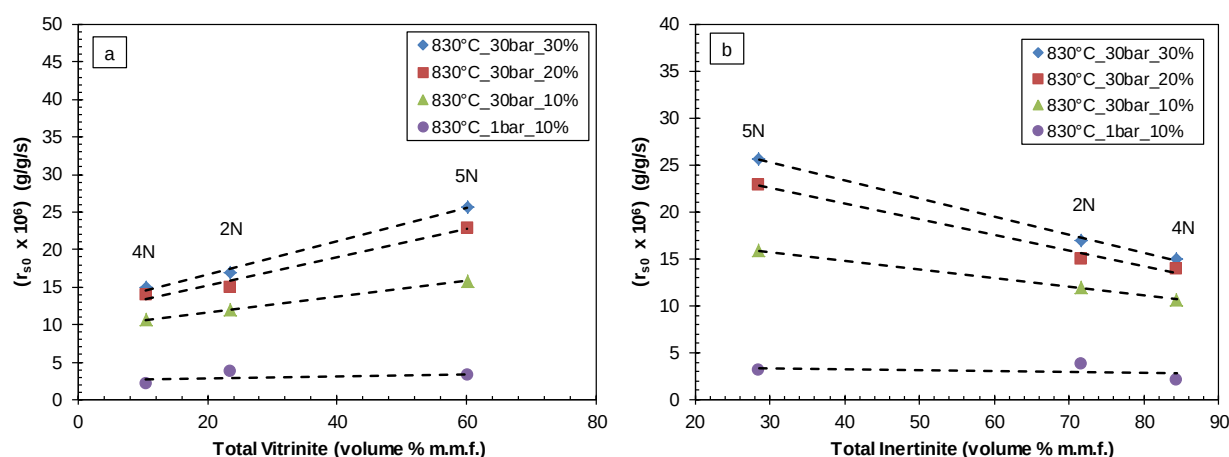


Figure 4.10: Correlation of initial reactivity of chars and a) vitrinite content, b) inertinite content

From Figure 4.10 it is clear that a higher vitrinite content corresponds to a higher initial reactivity whereas a higher inertinite content corresponds to a lower initial reactivity. Similar trends have been observed by Sun et al. (2004) for the gasification of different maceral chars in a PTGA. Megaritis et al. (1999) also observed vitrinite concentrates to have a higher CO₂ gasification reactivity compared to inertinites.

In order to investigate the combined effects of maceral content the maceral index proposed by Su et al. (2001) (discussed in Section 2.4) was correlated with the initial reactivity of the 3 chars. The results are shown in Figure 4.11.

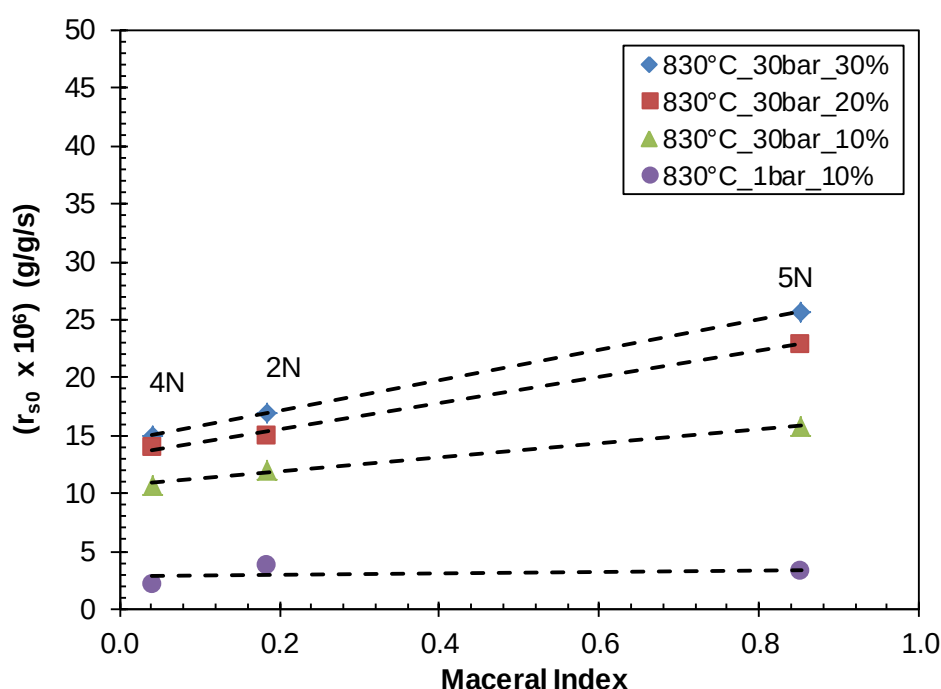


Figure 4.11: Correlation of initial reactivity and maceral index

The maceral content of the coals has a significant influence on the initial char reactivity. The initial reactivity is observed to increase with increasing MI. This is to be expected when considering the effect of vitrinite and inertinite content on the reactivity (discussed previously). The HVF does not differ significantly for the 3 chars (0.74 for 2N, 0.66 for 4N and 0.57 for 5N) due to the small difference in their heating values. The increase in MI with increasing reactivity can thus be attributed to the RF value which differs significantly for the different chars (0.40 for 2N, 0.11 for 4N and 3.42 for 5N).

4.5.3.2 Influence of micropore surface area

The micropore surface areas of the unconverted chars are shown in Table 4.9. Due to the relative high mineral matter content of the char samples used in this study, the initial micropore

surface area is also reported on a mineral matter free (m.m.f) basis. Further details on the char microporosity are reported in Section 4.6.1.

Table 4.9: Initial micropore surface area of different chars

Char	Micropore surface area (m²/g)	Micropore surface area m.m.f. (m²/g)
2N	189	259
4N	139	211
5N	170	284

Surface area and porosity measurements provide an indication of the number of pores and the pore sizes in the char (Liu et al., 2000b). The high surface area and low porosity observed from the CO₂ adsorption data suggests that the micropores are of high number but small size. The internal surface area of the chars is dominated by micropores which corresponds to observations by others for similar coal chars. Coetzee et al. (2015) determined a micropore surface area of 161 m²/g for a Witbank seam 4 coal char using small angle X-ray scattering (SAXS). The parent coal was charred at 1000°C. Kajitani et al. (2006) determined the micropore surface areas (using CO₂ adsorption) of four different bituminous coals after rapid pyrolysis at 1400°C and reported values ranging from 170-250 m²/g. Du Toit (2013) reported the micropore surface area of a Highveld seam 4 char containing a high amount of mineral matter (26 wt. % d.b.) as 182 m²/g.

It was observed that the micropore surface area of the vitrinite rich 5N char was larger compared to the inertinite rich 4N char. This corresponds to observations by Gan et al. (1972) and Lamberson and Bustin (1993) that vitrinite rich coal pore structures are more dominated by micropores compared to inertinite rich coals.

The 2N char shows the highest surface area of all despite having a lower vitrinite content than the 5N char. This can be attributed to the lower mineral matter content of this char compared to the other chars. Lamberson and Bustin (1993) have also observed that micropore surface area (measured through CO₂ adsorption) increases with decreasing mineral matter content. To obtain a more direct correlation between micropore surface area and reactivity, the micropore surface area of the chars was normalized to a mineral matter free basis. The micropore surface area m.m.f. of the chars increased in the order of 4N < 2N < 5N corresponding to the vitrinite content in the chars. A correlation between the initial micropore surface area m.m.f. of the chars and their initial reactivity is shown in Figure 4.12.

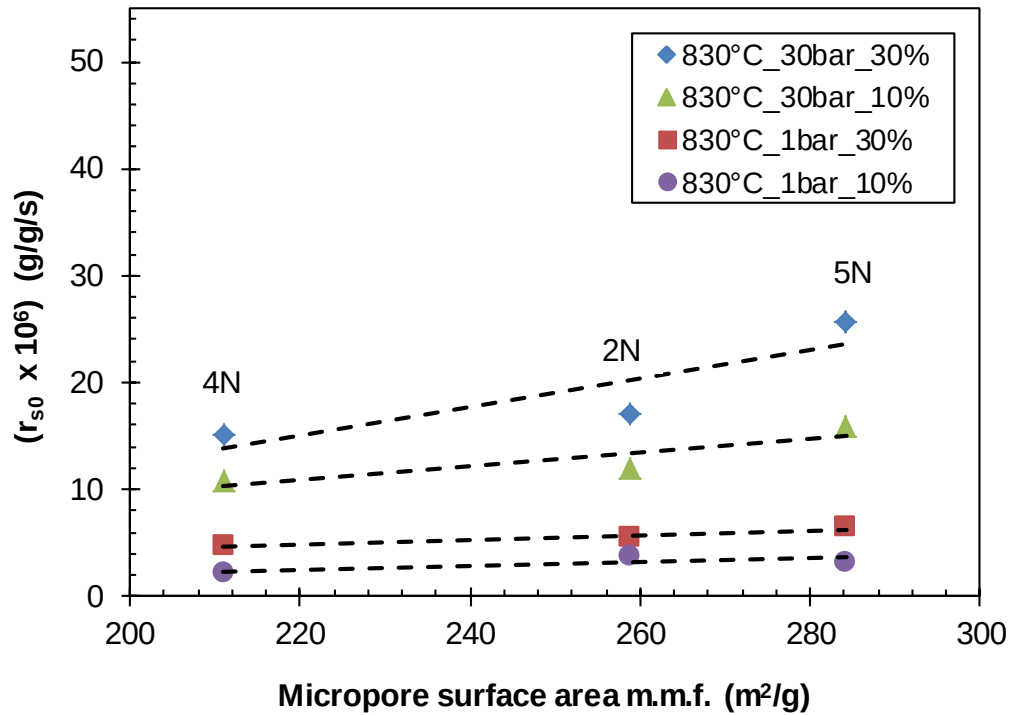


Figure 4.12: Correlation of initial reactivity and initial micropore surface area m.m.f.

The initial reactivity increased with an increase in micropore surface area (m.m.f.). This is due to the larger surface area available for the char-CO₂ reaction. Çakal et al. (2007) reported that an increase in internal surface area enhances the CO₂ gasification reactivity of coals. Hattingh (2010) also observed that a coal with a higher initial micropore surface area showed a higher initial CO₂ gasification reactivity but noted that the micropore surface area will change throughout pyrolysis and gasification. The changes in micropore surface area due to pore development during CO₂ gasification of the chars used in this study are presented and discussed in Section 4.6.

4.6 Char pore development

The surface analyses results are presented and discussed in this section. The results for the micropore development is discussed in Section 4.6.1 followed by the mesopore development in Section 4.6.2. Explanations for the results observed are discussed in Section 4.6.3.

4.6.1 Micropore development

The effect of CO₂ partial pressure (0.1, 1.5 and 9.0 bar) and conversion on the micropore surface area development of 2N char at 830°C, 4N char at 810°C, 5N char at 800°C is shown in Figure 4.13 a-c respectively. The tabulated values are shown in Appendix D-1.

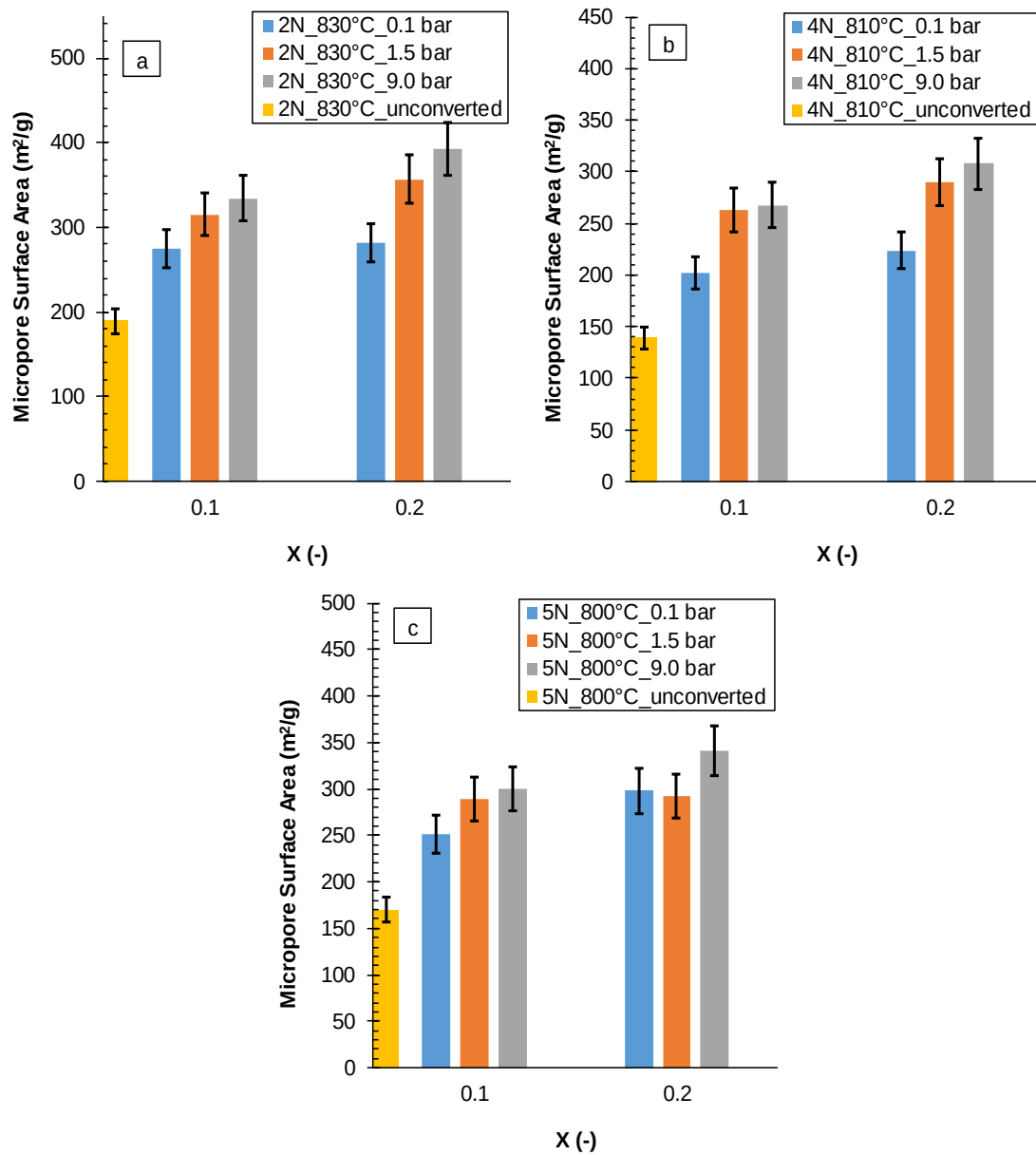


Figure 4.13: Effect of CO₂ partial pressure on micropore surface area at 10% and 20% conversion of a) 2N at 830°C, b) 4N at 810°C and c) 5N at 800°C

At fixed CO₂ partial pressures, the micropore surface area of all three chars increased significantly from the onset of gasification and continued to increase up to 20% conversion. The increase in surface area with conversion was more significant at the higher CO₂ partial pressures compared to the lower CO₂ partial pressures. For both the 4N and 5N chars (gasified at 30 bar 30% CO₂) the initial micropore surface area doubled after reaching 20% conversion. The significant increase in char micropore surface area throughout CO₂ gasification corresponds to results reported in literature. Liu et al. (2015) observed that the micropore surface area of a bituminous coal char changed significantly during CO₂ gasification at 20 bar

and 1050°C. The surface area increased from 40 to 380 m²/g over a conversion range of 0 to 0.9 and the porosity development showed that more micropores were generated. Coetzee et al. (2015) observed that the micropore surface area (m.m.f. basis) of a Witbank seam 4 char increased from 161 to 435 m²/g during conversion up to 50%.

The increase in micropore surface area with conversion can be attributed to the broadening of pores due to the surface reaction (Liu et al., 2015). During gasification the CO₂ molecules diffuse into the pores and form carbon-oxygen surface complexes on the surface of the pores. Desorption of these complexes during the second step of the reaction mechanism leads to the gradual erosion of pores and thus pore growth (Kajitani et al., 2002). Structural gasification models such as the random pore model (RPM) (discussed in Section 4.4.1) account for pore growth with conversion.

At fixed conversions of 10% and 20%, the micropore surface areas of the chars increased significantly with an increase in CO₂ partial pressure. At 10% conversion the initial micropore surface area of both the 4N and 5N chars increased by 20% when the CO₂ partial pressure increased from 0.1-9.0 bar. A 30% increase was observed for the 2N char. At 20% conversion the effect was more significant and the micropore surface area of both the 2N and the 4N chars increased by almost 40% when the CO₂ partial pressure increased from 0.1-9.0 bar. A 20% increase was observed for the 5N char.

The effect of CO₂ partial pressure on the micropore surface area is thus more pronounced at higher conversion which suggests that it may be related to pore development. Roberts and Harris (2011) also observed that a higher CO partial pressure resulted in an increase in the internal surface area of Australian bituminous chars at 10% conversion. They concluded that more experimental investigation was required in order to explain this effect.

The pore size distributions (PSD) in the size range of $3 \text{ \AA} \leq d_p \leq 5 \text{ \AA}$ for the 2N, 4N and 5N chars gasified up to 20% conversion are shown in Figure 4.14 a-c respectively. All three chars show a mono-modal PSD in the size range of $3 \text{ \AA} \leq d_p \leq 5 \text{ \AA}$ which is comparable to PSD's reported in literature for Highveld coals using CO₂ adsorption measurements (Okolo et al., 2015). At a given level of conversion, the chars gasified at higher CO₂ partial pressures exhibit a higher volume of micropores compared to chars gasified at lower partial pressures which is consistent with the increased micropore surface area reported at higher CO₂ partial pressures. These results suggest that the degree of micropore development which occurs during gasification is not only affected by the extent of conversion but also by the reagent partial pressure. Possible explanations for the effect of CO₂ partial pressure on the degree of pore development are discussed in Section 4.6.3.

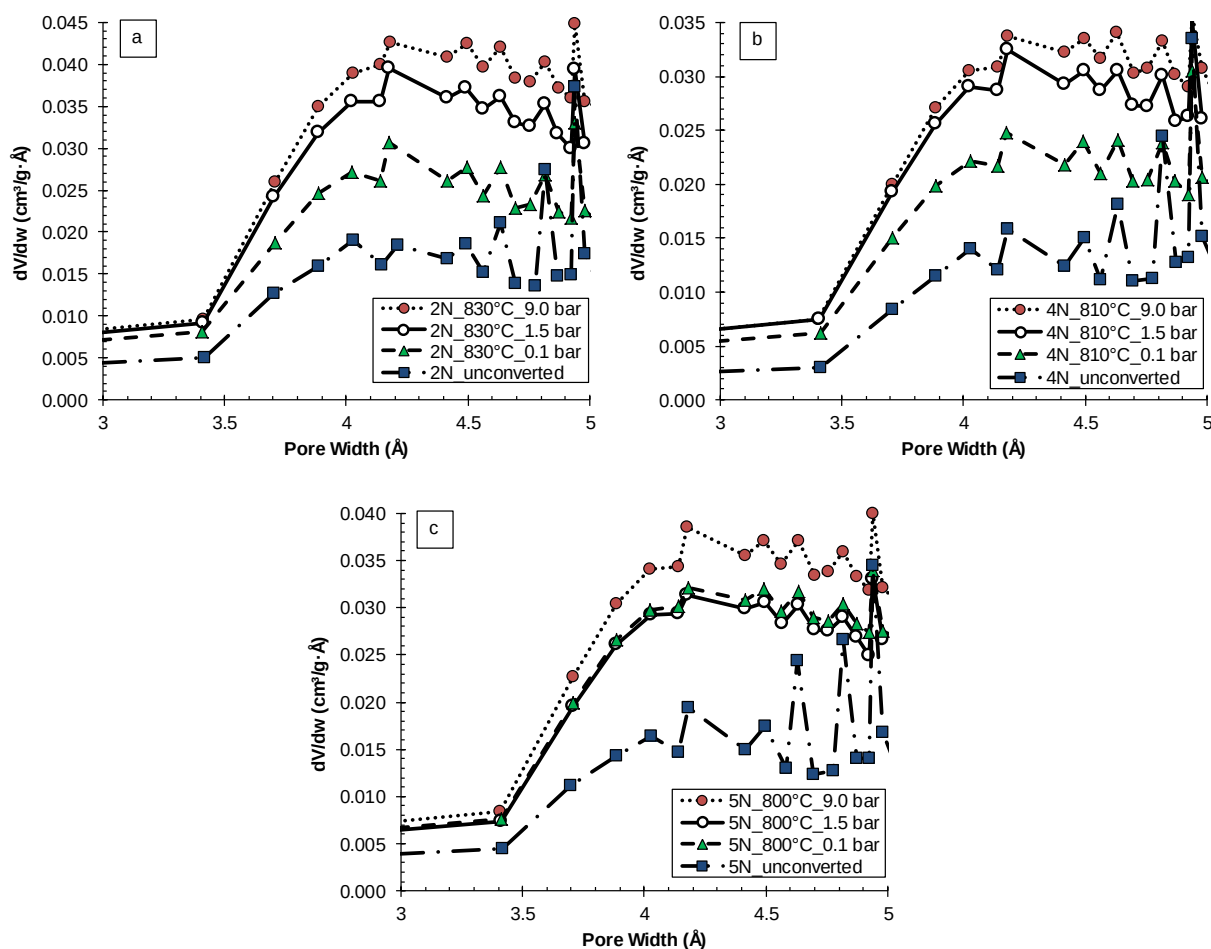


Figure 4.14: Micropore size distribution at 20% conversion of a) 2N at 830°C, b) 4N at 810°C and c) 5N at 800°C

4.6.2 Mesopore development

To further investigate the effect of CO₂ partial pressure on the degree of pore development, the mesopore surface area and pore volume of the chars gasified at different CO₂ partial pressure up to 10% conversion was investigated. The results are reported in Table 4.10. The PSD determined from the BJH desorption curve showed that the pores probed by the N₂ adsorption analysis were in the size range of $20 \text{ Å} \leq d_p \leq 150 \text{ Å}$ (lower mesopore range). Some differences were observed between the results determined from the N₂ adsorption and desorption isotherm data and this was attributed to equilibrium not being established during the time period allowed for adsorption (Okolo et al., 2015).

Table 4.10: Mesopore surface area and volume at 10% conversion and different CO₂ partial pressures

p_{CO2} (bar)	Mesopore surface area (m²/g)			Mesopore volume (cm³/g) x 10²		
	2N	4N	5N	2N	4N	5N
0.1	7.9 ± 0.4	6.8 ± 0.3	11.0 ± 0.6	4.2 ± 0.2	3.7 ± 0.2	6.1 ± 0.3
1.5	18.4 ± 0.9	10.7 ± 0.5	16.5 ± 0.8	9.6 ± 0.5	5.7 ± 0.3	8.5 ± 0.4
9.0	17.3 ± 0.9	14.4 ± 0.7	18.2 ± 0.9	9.2 ± 0.5	7.6 ± 0.4	9.3 ± 0.5

Uncertainties based on maximum surface area deviation (See Section 3.5.2)

In general the mesopore surface areas of the chars (determined from N₂ adsorption) were much lower compared to the micropore surface areas (determined from CO₂ adsorption). This result is consistent to what is generally reported in literature for bituminous coals. Kajitani et al. (2002) reported that the surface area of bituminous coal chars obtained from CO₂ adsorption analysis was almost 10 times larger than the surface area from the N₂ adsorption analysis. The large differences have been attributed to kinetic restriction of N₂ molecules at -196°C (Şenel et al., 2001). Hatting (2010) reported BET surface areas of 3.8-6.8 m²/g for three different South African coals. Şenel et al. (2001) reported that the BET surface areas for various bituminous coals were < 7.4 m²/g. Okolo et al. (2015) determined BET surface areas ranging from 2.9-5.7 m²/g for Highveld coals.

Similar to the micropore surface area, the mesopore surface area also increased significantly with increasing CO₂ partial pressure at 10% conversion. The mesopore surface area and corresponding pore volume of both the 2N and 4N chars gasified at 9.0 bar partial pressure was more than double the surface area and volume of the chars gasified at 0.1 bar partial pressure. For the micropores at 10% conversion a maximum increase in surface area of 30% was observed when the CO₂ partial pressure increased from 0.1-9.0 bar. This demonstrates that the effect of CO₂ partial pressure on pore development at a fixed conversion seems to be more significant in the mesopores compared to the micropores. Coetzee et al. (2015) also observed the highest rate of pore generation during gasification with CO₂ for pores in the size range of 12 Å ≤ d_p ≤ 380 Å (upper micropore and lower mesopore range). Pores < 10 Å (micropores) were much less affected by pore development. The increase in mesopore surface area at higher CO₂ partial pressure could however also be a direct result of the increased micropore development. An increased micropore development will mean that more micropores evolve into mesopores which are then also probed by N₂ adsorption leading to a higher mesopore surface area.

4.6.3 Explanations of pore development

From the results of the micro- and mesopore development it is clear that the extent of pore development is not only a function of conversion but also of reagent partial pressure. At fixed

conversions, pores in both the micro- and mesopore size ranges showed increased growth at higher reagent partial pressure. Possible explanations for the pore structural changes caused solely by reagent partial pressure are the following:

- **Surface coverage**

The degree of surface coverage (θ) is a measure of the occupancy of active sites by C(O) complexes and can be expressed as a function of CO₂ partial pressure using Equation 4.2 (Roberts and Harris, 2006).

$$\theta = \frac{\frac{k_1}{k_3} p_{CO_2}}{1 + \frac{k_1}{k_3} p_{CO_2}} \quad (4.2)$$

The values of k_1 and k_3 were obtained from the parameters reported for the LH model given in Table 4.3 to Table 4.5. Plots of θ versus CO₂ partial pressure are shown in Figure 4.15 for the different chars used in the surface analyses.

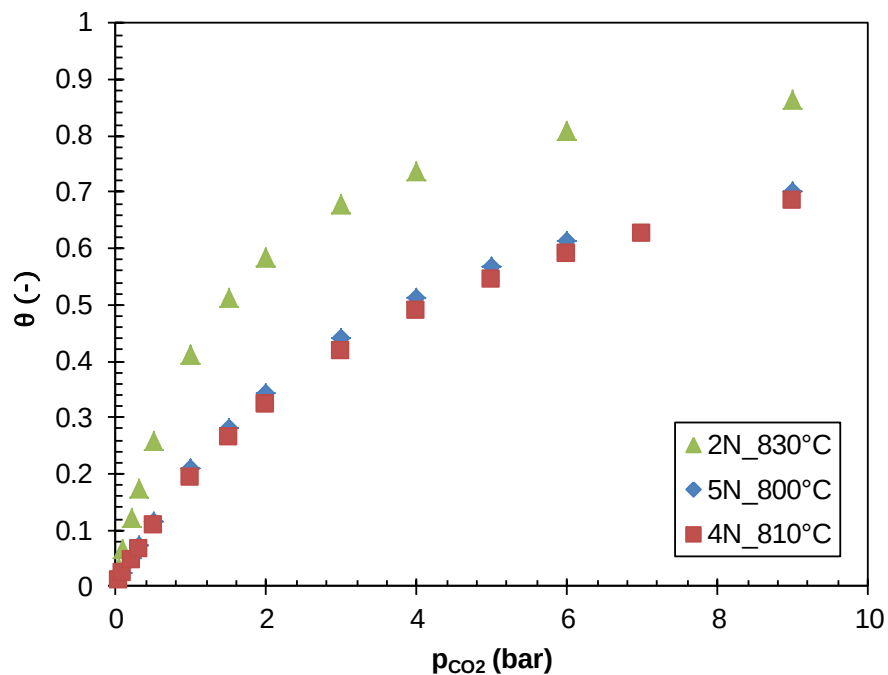


Figure 4.15: Effect of CO₂ partial pressure on the degree of surface coverage for 2N at 830°C, 4N at 810°C and 5N at 800°C

At a given level of conversion, the degree of surface coverage is observed to increase with increasing CO₂ partial pressure for all 3 chars which is consistent with previous work and the

reaction mechanism (Roberts and Harris, 2006). The increased surface coverage at high CO_2 partial pressure results in an increased development of micropores. The small micropores grow into larger micropores and the larger micropores grow into mesopores. This explains why an increase in CO_2 partial pressure results in an increase in both the micro- and mesopore surface area of the char. A visual representation of the effect is shown in Figure 4.16a for low CO_2 partial pressure and in Figure 4.16b for high CO_2 partial pressure.

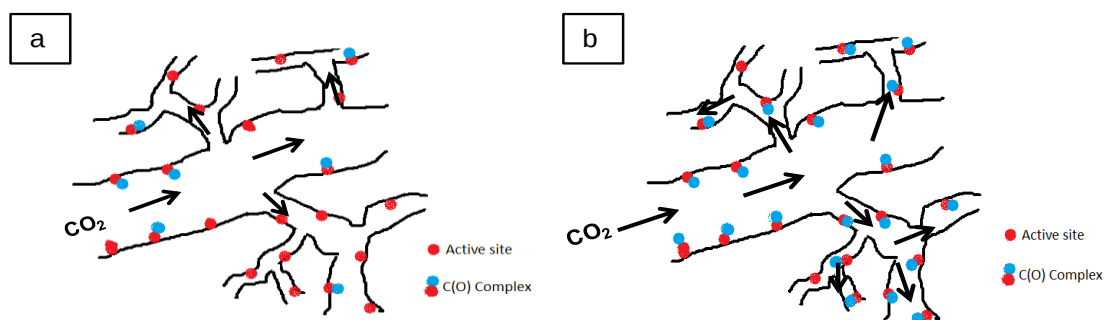


Figure 4.16: Visual representation of the effect of CO_2 partial pressure on surface coverage and micropore development of chars at a) low CO_2 partial pressure and b) high CO_2 partial pressure

- **Gas diffusion inside the pores**

An alternative explanation for higher internal surface areas may be that the diffusion of the CO_2 molecules inside the pores is affected by pressure. An increase in CO_2 partial pressure may force the reacting CO_2 molecules into pores that are inaccessible within the available reaction times at lower pressures. This results in a higher amount of pore development in the smaller pores at higher CO_2 partial pressure leading to an increase in the char internal surface area. A visual representation of the effect is shown in Figure 4.17a for low CO_2 partial pressure and in Figure 4.17b for high CO_2 partial pressure.

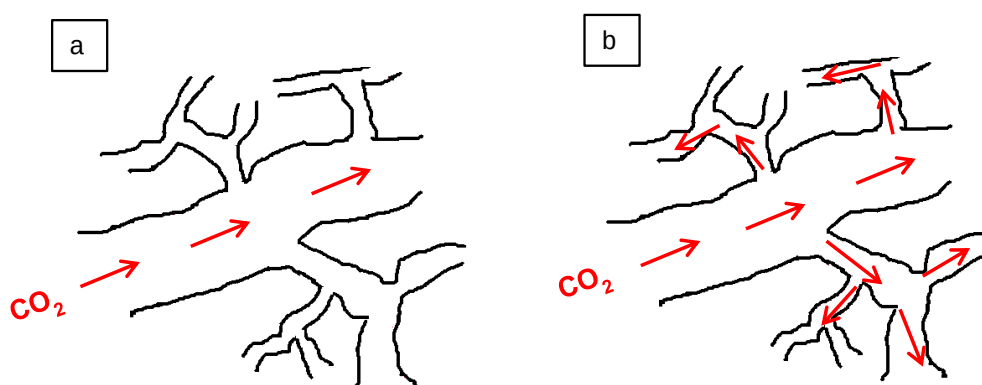


Figure 4.17: Visual representation of the effect of CO_2 partial pressure on pore development due to gas diffusion at a) low CO_2 partial pressure and b) high CO_2 partial pressure

CHAPTER 5: CONCLUSION AND RECOMMENDATIONS

5.1 Introduction

In this study, the CO₂ gasification reactivity and subsequent pore development of three different non-caking South African Highveld coal chars was investigated. The samples consisted of three non-caking Highveld coal chars from Seam 2, 4 and 5. All three were bituminous chars with a relative high ash content (>19 wt.% d.b.). The chars differed most significantly in their maceral compositions where 4N had a high inertinite and 5N a high vitrinite content. The 2N char had a more intermediate maceral content. The main conclusions drawn from the results of the CO₂ gasification, char reactivity correlations and char pore development are discussed in Section 5.2. Contributions to the knowledge of coal science and technology are reported in Section 5.3. Finally, recommendations for future work are discussed in Section 5.4.

5.2 Conclusions

5.2.1 CO₂ gasification and modelling

The CO₂ gasification reactivity was performed under conditions where the surface reaction alone controls the overall reaction rate. Under these conditions the reaction rate was solely a function of temperature and CO₂ partial pressure. The reaction rate increased with an increase in temperature as well as an increase in CO₂ partial pressure corresponding to general results reported in literature.

At 10% conversion both the empirical power law (PL) kinetic model and the more fundamental Langmuir Hinshelwood (LH) model were shown to accurately describe the experimental data up to a CO₂ partial pressure of 9.0 bar. The power law was used to determine the overall activation energies of the chars and the kinetic parameters obtained from the LH model allowed some insight into the adsorption of the CO₂ molecules on the active sites.

Reaction orders for the 2N, 4N and 5N chars were 0.45, 0.56 and 0.51 respectively. The observed activation energies ranged from 261 ± 20 kJ/mol for 2N, 260 ± 26 kJ/mol for 4N and 250 ± 30 kJ/mol for 5N. Although the activation energies of the chars differed by no more than 11 kJ/mol, the activation energies of the inertinite rich chars (2N and 4N) were slightly higher than the that of the vitrinite rich char (5N).

The structural Random Pore Model (RPM) was shown to well describe the experimental data up to 20% conversion. The structural parameter (ψ) was observed to increase with increasing CO₂ partial pressure suggesting that the amount of pore growth taking place in a char sample is a function of the reagent partial pressure.

5.2.2 Char reactivity

5N char showed the highest CO₂ gasification reactivity followed by 2N and 4N. The char's initial reactivity correlated well with the maceral content and corresponding maceral index (MI). The reactivity increased with an increase in vitrinite and decreased with an increase in inertinite. The initial reactivity also correlated with the char's initial micropore internal surface area (m.m.f.) where an increase in micropore surface area resulted in an increased reaction surface area and thus a higher reactivity.

5.2.3 Char pore development

The effect of conversion and CO₂ partial pressure on the development of the micro- and mesopore surface areas of the chars during gasification was investigated. At fixed CO₂ partial pressures the micropore surface area and volume increased with conversion which demonstrated pore growth occurring during CO₂ gasification up to 20% conversion.

At fixed conversions the micro- and mesopore surface area and corresponding pore volumes increased with increasing CO₂ partial pressure. For the micropores the effect was more pronounced at higher conversions suggesting that it is related to pore development. This result corresponded to the increase in the structural parameter of the Random Pore Model (RPM) with increasing CO₂ partial pressure and demonstrated that pore growth was not only affected by conversion but also by the reagent partial pressure.

The effect of CO₂ partial pressure on pore development was explained by considering the effect of partial pressure on the degree of surface coverage. At a given conversion, an increase in CO₂ partial pressure results in a higher degree of surface coverage which means that more micropores are developed corresponding to a higher internal surface area. An alternative explanation was based on the assumption that gas diffusion inside the pores is affected by pressure. An increase in pressure increases gas diffusion and thus the amount of smaller pores accessed by the reagent gas. This results in a larger internal surface area.

5.3 Contributions to the knowledge of coal science and technology

The following are regarded as contributions to the field of coal science:

- Systematic investigation of the effect of CO₂ on the gasification rate of different Highveld coal chars at elevated pressures.
- Quantification and explanation of the effect of CO₂ partial pressure on the pore development of chars during gasification.

- The results of this investigation can be incorporated into coal gasifier models to simulate the gasification of the selected Highveld chars at elevated pressures.

5.4 Recommendations

After reviewing the results and discussion of this study as well as the conclusions drawn from the results, the following is recommended for future work in char gasification reactivity:

- The CO₂ gasification reactivity should be investigated at higher CO₂ partial pressures (above 9.0 bar) to explore if a saturation effect is observed and to test whether the current LH model is able to accurately predict the reactivity at these conditions.
- The inhibition effect of CO partial pressure on the gasification reaction at both low and high CO₂ partial pressures should be investigated and incorporated into the current LH model.
- The reaction kinetics and modelling of the char-steam reaction at high pressures should be investigated.
- The reaction kinetics of a combined CO₂ and steam gasification system should be investigated in order to determine if a competitive or additive model is most suited for describing the reactivity under these conditions.

To further investigate pore development during gasification the following future work is recommended:

- Investigate the effect of CO₂ partial pressure on the char pore development over a wider range of CO₂ partial pressures and conversions.
- The effect of temperature on char pore development should be investigated at fixed conversions.
- Investigate the effect of H₂O partial pressure on pore development and compare with the effects of CO₂ partial pressure.
- After obtaining sufficient experimental data a model should be developed to incorporate the changes in internal surface area (due to reagent partial pressure) in the current kinetic models.

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APPENDIX A: EXPERIMENTAL CALIBRATIONS

A-1 CO analyser calibration

The CO reading by the non-dispersive infra-red (NDIR) analyser was calibrated by using calibration gases with a standard concentration of CO and recording the reading on the analyser. The calibration curve obtained is shown in Figure A1.1.

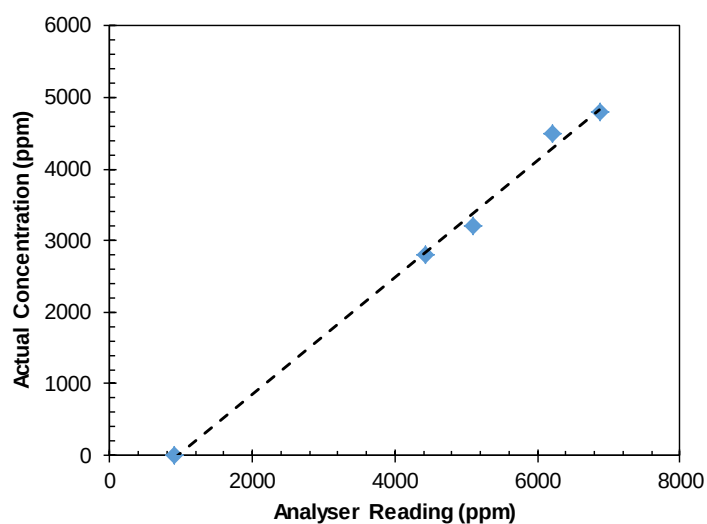


Figure A1.1: Analyser calibration curve

A-2 Mass flow controller calibrations

The calibration curves for the CO₂ and N₂ mass flow controllers are shown in Figure A2.1 a-b respectively.

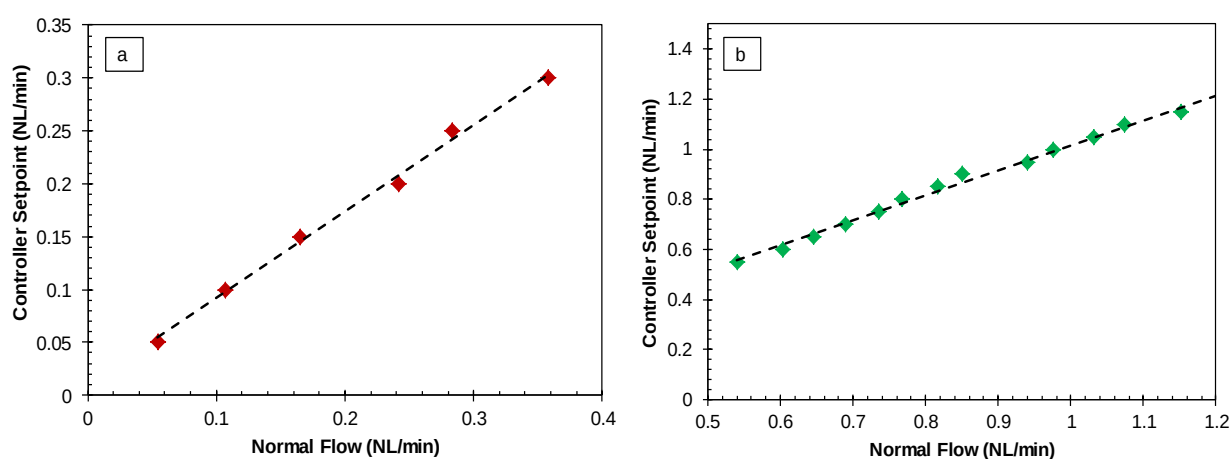


Figure A2.1: Mass flow controller calibration curves for a) CO₂ mass flow controller and b) N₂ mass flow controller

APPENDIX B: ADDITIONAL RIG EVALUATION AND REGIME TESTS

B-1 Testing of inert reactor pipe

The high pressure fixed bed reactor system used by Henning (2017) was modified for this study by replacing the $\frac{1}{2}$ " quartz reactor tube with a $\frac{3}{4}$ " Alloy C276 pipe. It was necessary to test whether the reactor pipe still remained inert after the modification. A few different tests were done at high temperatures and pressures. An experimental run using 30% CO₂ at 925°C and 20 bar was performed with and without a char sample (2N). The CO concentration curves obtained during the 2 runs are shown in Figure B1.1.

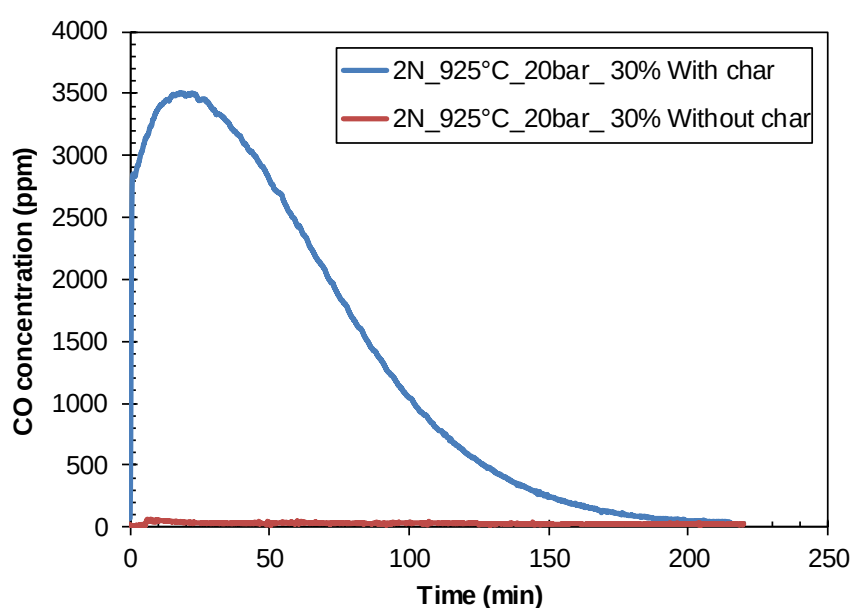


Figure B1.1: CO curves with and without char sample at 925°C 20 bar 30%

The CO formation in the absence of the char sample was a factor 100 lower, which signified the inertness of the Alloy C276 pipe.

B-2 Furnace temperature profile

To ensure a stable temperature zone in the reactor, furnace temperature profiles were determined for different compositions of reactant gas. The profiles when using pure N₂, pure CO₂ and a mixture of 30% CO₂ with the balance N₂ are shown in Figure B2.1.

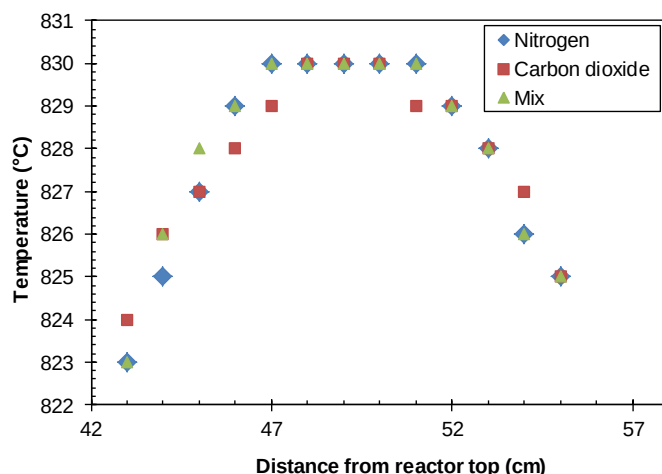


Figure B2.1: Furnace temperature profiles using different compositions of reagent gas

The temperature stable zone was observed to be 48-50 cm from the top of the reactor pipe. The char sample was loaded onto the quartz filter which was positioned 49 cm from the top of the reactor pipe. The thermocouple was placed 5 mm above the sample. This ensured that both the sample and the thermocouple were in the thermal stable area.

B-3 Testing of inert thermocouple

A K-type thermocouple was inserted in the Alloy C276 pipe in order to have a more accurate control on the reaction temperature. Two runs were performed using 2N char with 30% CO₂ at 900°C and 20 bar. The K-type thermocouple was inserted into the pipe for one run and removed for the next. These results were then compared to the results obtained by Henning (2017) when using the quartz tube. The results are shown in Figure B3.1.

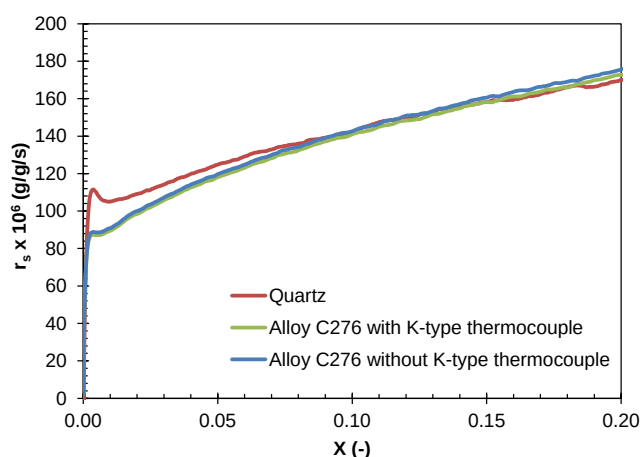


Figure B3.1: Specific reactivity of 2N char at 900°C 20 bar 30% when using a quartz or alloy C276 tube with and without a K-type thermocouple

The reaction rates deviated by no more than 3%. This proved that the Alloy C276 pipe with a K-type thermocouple inserted was inert and could thus be used for experimentation.

B-4 Isothermal particle reaction conditions

In order to validate isothermal conditions, various criteria are available for testing the lack of interphase temperature gradients such as the criterion proposed by Anderson (1963) shown in Equation B4.1.

$$\frac{r_A d_p^2 (\Delta h_{rxn})}{4k_{p,coal} T} < 0.75 \frac{T R}{E_a} \quad (B4.1)$$

In this equation the left hand side should be smaller than the right hand side if the particles are under isothermal conditions. This criterion was evaluated for the experimental runs with the highest reactivity. It was assumed that it would also be valid for the lower reactivity runs. The parameters used in the calculation are shown in Table B4.1.

Table B4.1: Reaction parameters for isothermal criterion

	2N (855°C 30 bar 30%)	4N (830°C 30 bar 30%)	5N (800°C 30 bar 30%)	Units
r_A	7.6	3.2	2.0	mol m ⁻³ s ⁻¹
Δh_{rxn}	170	170	170	kJ mol ⁻¹
E_a	261	260	253	kJ mol ⁻¹
$k_{p,coal}$	0.26			W m ⁻¹ K ⁻¹
d_p	0.5			mm
R	8.314			J mol ⁻¹ K ⁻¹

The thermal conductivities of the chars were taken from Incropera et al. (2002). The calculated values for the left and right sides of Equation B4.1 are shown in Table B4.2.

Table B4.2: Calculated values for isothermal criterion

	2N	4N	5N
Left	2.8 x 10 ⁻⁴	1.2 x 10 ⁻⁴	7.5 x 10 ⁻⁵
Right	2.7 x 10 ⁻²	2.6 x 10 ⁻²	2.6 x 10 ⁻²

The data from Table B4.2 indicates that Equation B4.1 is valid for all three chars. This confirms that the particles are under isothermal conditions.

Although the above equation is useful in determining the presence of heat transfer limitations it requires knowledge of many physical properties of the reacting sample. It is difficult to find accurate values of the required parameters due to the heterogeneous nature of coal.

Madon and Boudart (1982) introduced a different experimental technique to test for the presence of heat transfer limitations. They proposed varying the concentration of reacting material in a catalyst by mixing it with inert particles. In the absence of transport limitations the reaction rate should be proportional to the active material. If heat transfer limitation were present under the reaction conditions then diluting the catalyst with inert particles should reduce these limitations. This would affect the observed reaction rate. For the purpose of this study it means that under specific reaction conditions the reaction rate should not change when diluting the sample with an inert powder.

The presence of heat transfer limitations were thus also tested by making use of inert sand particles with a particle size distribution comparable to the char sample. The experimental run with the highest reactivity was selected for these tests (2N at 855°C 30 bar 30%). Two separate experimental runs were performed. This included a run using only the char sample and a run using a mixture of equal amounts of char and inert sand. A plot of reaction rate against conversion is shown for both runs in Figure B4.1. The two runs differed by no more than 3% which indicated the absence of heat transfer effects in the char particle. It was assumed that for lower reaction rates the char particles also remained isothermal.

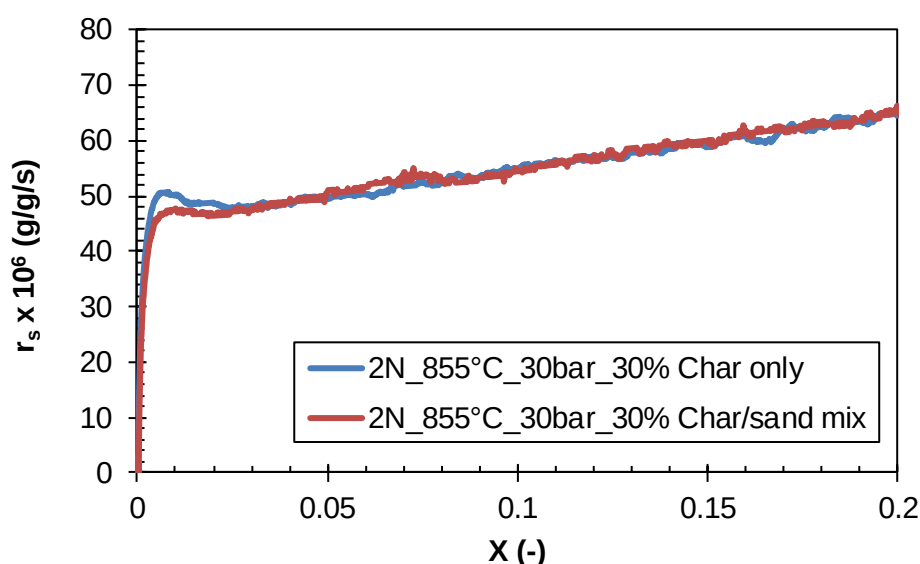


Figure B4.1: Specific reactivity of 2N at 855°C 20 bar 30% with char and char/sand mix

B-5 Operating conditions tests

Particle size tests

The effect of char particle size on the specific reactivity was evaluated in order to test for the presence of internal diffusion limitations. The results for 2N char at 855°C and 4N char at 830°C are shown in Figure B5.1 a-b respectively.

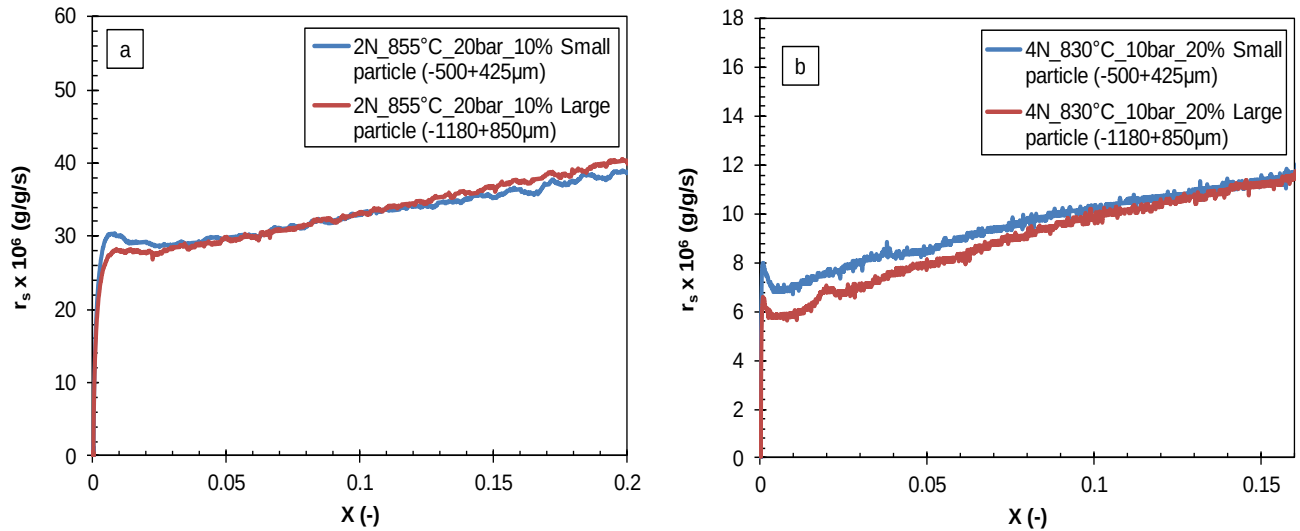


Figure B5.1: Specific reactivity of small and large char particles of a) 2N at 855°C 20 bar 10% and b) 4N at 830°C 10 bar 20%

The specific reaction rate of the small and large char sample deviates by no more than 5% at 855°C and it is concluded that internal diffusion limitations are negligible at temperatures of 855°C and below for 2N char.

For the 4N char the initial reaction rate of the smaller char particle is about 14% faster compared to the large particle which suggests a small effect of diffusion limitations during the early stages of conversion. Between 10% and 20% conversion the reaction rates differ by no more than 5%. The kinetic data will be taken at 10% conversion where the reaction is observed to be free of diffusion limitations.

B-6 Carbon mass balance

The calculated amount of carbon converted ($m_{c,cal}$) was determined by weighing the char sample before and after gasification as discussed in Section 3.3.4.2. The experimental carbon converted ($m_{c,exp}$) was determined as follows:

The carbon conversion rate (r_c) was determined at each time interval of the experimental CO concentration curve.

$$r_c = \frac{y_{CO}}{2} \times \dot{n} \times MW_C \text{ [g/s]} \quad (\text{B6.1})$$

Where y_{CO} is the fraction of CO (-), $\dot{n}$ is the molar flow rate (mol/s) and MW_C the molecular weight of carbon (g/mol).

Next, the total amount of carbon converted ($m_{c,exp}$) at each time interval was calculated by Equation B6.2.

$$m_{c,exp}(t) = \int_0^t r_c \text{ dt [g]} \quad (\text{B6.2})$$

A comparison of the calculated carbon converted as well as the experimental carbon converted for the high temperature run (2N 875°20 bar 30%) and other randomly selected runs are shown in Table B6.1.

Table B6.1: Carbon mass balance calculations for randomly selected runs

Run	$m_{c,cal}$ (daf) (g)	$m_{c,exp}$ (daf) (g)	Absolute Error (%)
2N 875°C 20 bar 30%	0.1557	0.1709	9
4N 830°C 10 bar 5%	0.0329	0.0350	6
4N 830°C 20 bar 30%	0.0312	0.0308	1
5N 780°C 30 bar 30%	0.0339	0.0319	6
4N 830°C 20 bar 10%	0.0263	0.0281	7
4N 830°C 30 bar 20%	0.0276	0.0287	4
5N 800°C 30 bar 30%	0.0258	0.0242	7
5N 780°C 30 bar 10%	0.0543	0.0520	4
5N 790°C 10 bar 20%	0.0378	0.0368	3
4N 830°C 20 bar 30%	0.0310	0.0308	1
2N 830°C 10 bar 20%	0.0272	0.0298	9

The maximum error was shown to be < 10%.

APPENDIX C: ERROR ESTIMATION

C-1 Repeat runs

The specific reaction rate at various conversions is shown in Table C1.1 for the runs using 5% CO₂ and in Table C1.2 for the runs with 30% CO₂. The confidence interval for each run was calculated with Equation C1.1 (Devore and Farnum, 2005).

$$\bar{x} \pm (t \text{ critical value}) \frac{s}{\sqrt{n}} \quad (\text{C1.1})$$

With $\bar{x}$ the sample mean, s the sample standard deviation and n the sample size (3 in this case). The t critical value is based on a 95% confidence level and equals 4.303 for 2 degrees of freedom. The confidence intervals at different conversions are shown in Table C1.1 and Table C1.2. The average error on a 95% confidence level was determined to be 6%.

Table C1.1: Specific reaction rate at different conversions for different runs of 4N at 830°C 30 bar 5%

	$r_s \times 10^6$ (g/g/s)					
X (-)	Run 1	Run 2	Run 3	Average	Standard deviation	Confidence Interval
0.05	7.2	7.0	7.4	7.2	0.2	7.2 ± 0.5
0.10	8.3	8.1	8.6	8.3	0.3	8.3 ± 0.7
0.15	9.5	9.2	9.6	9.4	0.2	9.4 ± 0.5
0.20	10.2	10.0	10.5	10.2	0.3	10.2 ± 0.7

Table C1.2: Specific reaction rate at different conversions for different runs of 4N at 830°C 30 bar 30%

	$r_s \times 10^6$ (g/g/s)					
X (-)	Run 1	Run 2	Run 3	Average	Standard deviation	Confidence Interval
0.05	19.6	19.1	18.9	19.2	0.4	19.2 ± 0.9
0.10	23.0	22.4	22.3	22.6	0.4	22.6 ± 0.9
0.15	26.1	25.4	25.3	25.6	0.4	25.6 ± 1.1
0.20	28.5	27.7	27.4	27.9	0.6	27.9 ± 1.5

C-2 Modelling error calculation

Algorithm used by the *nlparci* function in MATLAB:

Firstly the fitted parameters matrix is obtained from the least squares method using the *lsqcurvefit* function.

$$P = \begin{bmatrix} A \\ E \\ n \end{bmatrix} \quad (C2.1)$$

The Jacobian matrix J is then calculated

$$J = \begin{bmatrix} \frac{\partial f}{\partial k_0}(P', x) \\ \frac{\partial f}{\partial E}(P', x) \\ \frac{\partial f}{\partial n}(P', x) \end{bmatrix} \quad (C2.2)$$

Next, the variance on the residuals (r) is calculated

$$\sigma_r = \frac{1}{N - k} \sum_{i=1}^N r_i^2 \quad (C2.3)$$

$$\text{With } r_i = y_i - f(P', x_i) \quad (C2.4)$$

N is the number of data points, k the number of parameters (3 in this case), x is the x-data in the model (CO₂ partial pressure) and y is the y-data (experimental reaction rate).

The covariance matrix is then calculated

$$\text{Cov}(P) = \sigma_r (J^T J)^{-1} \quad (C2.5)$$

Where T stands for transposing and the upper script -1 for the inverse matrix.

Finally the error estimates on the parameters (s_p) are calculated by the point-wise square root of the covariance matrix

$$s_p = \begin{bmatrix} s_A \\ s_E \\ s_n \end{bmatrix} = \sqrt{\text{Cov}(P)} \quad (\text{C2.6})$$

The modelling parameters and confidence intervals reported by MATLAB is shown in Table C2.1.

Table C2.1: Modelling parameters with confidence intervals reported by MATLAB for different chars

Parameter	2N	4N	5N	Units
E	261 ± 20	260 ± 26	250 ± 30	kJ/mol
n	0.45 ± 0.02	0.56 ± 0.03	0.51 ± 0.04	-

The uncertainty on each parameter for the different chars based on a 95% confidence interval is shown in Table C2.2, Table C2.3 and Table C2.4.

Table C2.2: Error estimation on power law modelling parameters for 2N

Parameter	2N	Error (%)
E	261 ± 20	8
n	0.45 ± 0.02	4

Table C2.3: Error estimation on power law modelling parameters for 4N

Parameter	4N	Error (%)
E	260 ± 26	10
n	0.56 ± 0.03	5

Table C2.4: Error estimation on power law modelling parameters for 5N

Parameter	5N	Error (%)
E	250 ± 30	12
n	0.51 ± 0.04	8

From the tables, the average modelling uncertainty for the parameters E and n is 10% and 6% respectively. The repeatability uncertainty (6%) was added to the modelling uncertainty to give an estimated maximum uncertainty on the parameters E and n of <15% and <10% respectively.

APPENDIX D: EXTENDED EXPERIMENTAL RESULTS

D-1 Surface area analysis

The micropore surface area results for 2N, 4N and 5N are shown in Table D1.1, Table D1.2 and Table D1.3 respectively.

Table D1.1: Micropore surface area of 2N char at different partial pressures and conversion

Conversion	Micropore surface area (m ² /g)		
	0.1 bar	1.5 bar	9.0 bar
Char	189 ± 9	189 ± 9	189 ± 9
0.1	275 ± 14	315 ± 16	334 ± 17
0.2	282 ± 14	357 ± 18	392 ± 20

Uncertainties based on maximum surface area deviation (See Section 3.5.2)

Table D1.2: Micropore surface area of 4N char at different partial pressures and conversion

Conversion	Micropore surface area (m ² /g)		
	0.1 bar	1.5 bar	9.0 bar
Char	139 ± 7	139 ± 7	139 ± 7
0.1	202 ± 15	263 ± 13	268 ± 13
0.2	224 ± 11	290 ± 15	308 ± 15

Uncertainties based on maximum surface area deviation (See Section 3.5.2)

Table D1.3: Micropore surface area of 5N char at different partial pressures and conversion

Conversion	Micropore surface area (m ² /g)		
	0.1 bar	1.5 bar	9.0 bar
Char	170 ± 9	170 ± 9	170 ± 9
0.1	251 ± 13	289 ± 15	300 ± 15
0.2	298 ± 15	292 ± 15	341 ± 17

Uncertainties based on maximum surface area deviation (See Section 3.5.2)