

Steam gasification kinetics of biochar at elevated pressures

J Schroeder



orcid.org/ 0000-0002-3652-8961

Dissertation accepted in fulfilment of the requirements for the degree *Master of Engineering in Chemical Engineering* at the North-West University

Supervisor: Prof HWJP Neomagus
Co-Supervisor: Prof RC Everson
Co-Supervisor: Prof JR Bunt

Graduation: June 2021
Student number: 25988719

Declaration of authorship

I, Jané Schroeder, hereby declare that the dissertation entitled: ***“Steam gasification kinetics of biochar at elevated pressures.”*** submitted in the fulfilment of the requirements for the degree of 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 on this, 18th day of December 2020 in Potchefstroom.

A handwritten signature in black ink, appearing to read 'J Schroeder', is written over a horizontal line.

J Schroeder (Student)

Acknowledgements

I would like to acknowledge and thank the following persons and institutions greatly for their role played throughout the project and completion of this dissertation:

- Firstly, my Heavenly Father for giving me the opportunity to study and all the blessings and grace I have received throughout my life. (*Jer 29:11: "For I know the plans I have for you," declared the Lord, "plans to prosper you and not harm you, plans to give you hope and a future."*)
- Professor Hein Neomagus for his motivation, patience, guidance and wisdom throughout this project.
- Professors John Bunt and Ray Everson for their guidance.
- Clement Mgano for his patience and advice throughout the project.
- Ted Paarlberg for his technical assistance with the high pressure reactor.
- The workshop personnel for the assistance with technical aspects of the rig.
- Andrei Koekemoer from the Sasol technology R&D department for his mentorship throughout the project.
- My loving parents, brother and Johan Maree for their support and love.
- Sasol for their financial assistance towards this project.

The work presented in this paper is based on the research support by the South African Research Chairs Initiative of the Department of Science and Technology and National Research Foundation of South Africa (Coal Research Chair Grant No. 86880). Any opinion, finding, conclusion or recommendation expressed in this material is that of the author(s) and the NRF does not accept liability in this regard.

Abstract

Coal remains a valuable resource in the generation of energy and transportation fuels, however the world's coal resources are depleting and its impact on the environment and human health raises concern. The investigation into alternative resources, such as biomass, have become more relevant, and one of the short term promising processes for biomass utilization is co-gasification with coal. In this study the steam gasification kinetics of a locally available biomass derived char at elevated pressures is investigated to further understand the possible application of biomass as gasification resource in the industry.

A waste product biomass (*eucalyptus nitens*) sample was received and charred to produce the biochar sample. A comparison between the raw biomass and biochar was completed with the use of several characterisation techniques. A mass loss of 83.4% was obtained during char preparation, while an O/C ratio of 0.66 and 0.03 and H/C ratio of 1.42 and 0.03 was obtained for biomass and biochar respectively.

For the gasification experiments, the biochar sample was prepared to a size of $-150+75\ \mu\text{m}$. The char reactivity experiments were carried out in a laboratory-scale high pressure fixed bed reactor in the temperature range of 700 to 730°C to ensure experiments are completed in the chemical reaction controlled regime. The steam partial pressure was varied from 1 to 10 bar steam, and the CO and CO₂ products were measured and used to determine the specific reaction rate of biochar.

From the obtained results it was found that the specific reaction rate increased with an increase in conversion, temperature and steam partial pressure. The increase in steam partial pressure had a significant effect on the reaction rate up to 10 bar steam, where it was observed that the formation of CO₂ contributed more to the specific reaction rate than that of CO, and that the selectivity of CO₂ increased over the entire steam partial pressure range. The effect of temperature on product selectivity was found to be less significant than that of steam partial pressure. From the comparison between biochar and coal char it was observed that the biochar had a higher reactivity than that of a typical Highveld derived coal char. Both the LH and PL models were able to accurately predict the specific reaction rate at 20% conversion, with the average error estimated at 4.1% and 3.9% respectively. The activation energy was also determined by the use of these kinetic models and the results were found to be consistent with literature. In general, progress has been made in the study of biochar as a viable option for a co-source in steam gasification, however more research is required on the processing of this alternative source in existing commercial gasifiers.

Keywords: biochar, steam, gasification, high pressure, gasification kinetics

TABLE OF CONTENTS

<i>Declaration of authorship</i>	<i>i</i>
<i>Acknowledgements</i>	<i>ii</i>
<i>Abstract</i>	<i>iii</i>
<i>List of Figures</i>	<i>vii</i>
<i>List of Tables</i>	<i>ix</i>
<i>List of symbols</i>	<i>x</i>
<i>List of abbreviations</i>	<i>xi</i>
<i>Chapter 1: Introduction</i>	<i>1</i>
1.1 Background and motivation	1
1.2 Problem statement	4
1.3 Aim and objectives	4
1.4 Scope of study	4
1.4.1. Limitations of study	5
1.5 Study outline	5
<i>Chapter 2: Literature review</i>	<i>6</i>
2.1 Introduction	6
2.2 Biomass as potential energy source	6
2.2.1. Biomass in general	6
2.2.2. Different types of biomass	6
2.2.3. Biomass availability in South Africa	8
2.2.4. Energy uses for biomass	9
2.3 Gasification	11
2.3.1. Conventional fuels and trends	11
2.3.2. Biomass gasification	12
2.4 Gasification reactions and mechanisms	14
2.5 Factors influencing gasification rate	15
2.5.1. Type of biomass	15
2.5.2. Temperature	16
2.5.3. System pressure	17

2.6	Modelling.....	22
2.6.1.	Kinetic models.....	22
2.6.2.	Structural models	24
2.7	Summary of steam gasification studies.....	25
2.8	Summary	27
Chapter 3: Sample Preparation and Characterisation		28
3.1	Introduction.....	28
3.2	Materials	28
3.3	Methods.....	29
3.3.1.	Sample preparation.....	29
3.3.2.	Characterisation techniques	30
3.4	Results and Discussion	32
3.4.1.	Chemical Characteristics	32
3.4.2.	Structural Characteristics	37
3.5	Summary	40
Chapter 4: Experimental of Gasification		41
4.1	Introduction.....	41
4.2	Materials	41
4.3	Experimental setup	42
4.4	Experimental procedure	45
4.5	Data processing.....	46
4.5.1.	CO and CO ₂ concentration	46
4.5.2.	Conversion	46
4.5.3.	Specific reaction rate.....	47
4.6	Carbon balance.....	48
4.7	Regime identification	49
4.8	Uncertainty analysis.....	51
4.9	Summary	52
Chapter 5: Results and Discussion		54
5.1	Introduction.....	54
5.2	Steam gasification reactivity	54

5.2.1.	Effect of conversion on specific reaction rate	54
5.2.2.	Effect of temperature on specific reaction rate	56
5.2.3.	Effect of steam partial pressure on specific reaction rate	57
5.3	Product distribution	59
5.3.1.	CO and CO ₂ formation	59
5.3.2.	Selectivity	60
5.3.3.	Comparison with coal.....	61
5.4	Kinetic Modeling and site occupancy	62
5.4.1.	Langmuir-Hinshelwood model	62
5.4.2.	Power law.....	65
5.4.3.	Site occupancy.....	67
5.5	Comparison between biochar and coal steam gasification	68
5.6	Summary	69
Chapter 6: Conclusions and Recommendations.....		70
6.1	Introduction.....	70
6.2	Conclusions	70
6.3	Contribution to existing field of science	71
6.4	Prospects	71
6.5	Recommendations	71
References		73
Appendix A: Char preparation.....		83
Appendix B: Experimental calibration.....		85
Appendix C: Additional rig evaluation		87
Appendix D: Error estimation calculation.....		89
Appendix E: Additional calculations		92

List of Figures

Figure 1.1: Total final energy consumption of the world from 1990-2018 (adapted from [1]).	1
Figure 1.2: Energy Consumption and Supply by source in 2016 (adapted from [7]).	2
Figure 1.3: Number of scientific publications on gasification research using either coal (Scopus keywords: coal AND gasification) or biomass (Scopus keywords: biomass AND gasification) as feedstock - Access on 16/11/2020	3
Figure 2.1: Illustration of different types of biomass	7
Figure 2.2: Plantation area by species for each province in South Africa (adapted from [29])	9
Figure 2.3: Technologies that convert biomass into different fuels(adapted from [32])	9
Figure 2.4: Number of gasifiers used by primary feedstock. (adapted from [36])	12
Figure 2.5: Schematic of a typical fixed bed gasifier(adapted from [43])	13
Figure 2.6: Effect of temperature on reaction rate and controlling mechanism(adapted from [60])	16
Figure 2.8: The effect of temperature on conversion rate during steam gasification at low pressure.(taken from [55])	17
Figure 2.9: Specific reaction rate as a function of steam partial pressure. (taken from [52]).	18
Figure 2.10: The effect of temperature on weight loss fraction at elevated pressures.(taken from [62])	19
Figure 2.11: The effect of partial pressure on the weight loss fraction at elevated pressures.(taken from [62])	20
Figure 2.12:Effect of steam partial pressure on specific reaction rate of three coal chars at 850 °C and 10% conversion.(taken from [59])	21
Figure 3.1: Raw biomass (left) and biochar (right)	30
Figure 3.2: Van Krevelen plot of biomass and Highveld coal samples	34
Figure 3.3: X-ray Fluorescence spectroscopy results	35
Figure 3.4:Fourier-transform infrared spectroscopy (FTIR) analysis results for both raw biomass and biochar	36
Figure 3.5: Scanning electron microscope analysis (SEM) analysis for raw biomass sample at a) 400 μm and b) 100 μm	37
Figure 3.6: Scanning electron microscope (SEM) analysis results for biochar sample at) 30 μm , b) 50 μm , c) 50 μm and d) 100 μm	38
Figure 3.7: Thermogravimetric analysis (TGA) results for biomass sample	39
Figure 4.1: Experimental rig	43
Figure 4.2: Gas fraction as a function of time for biochar steam gasification	46
Figure 4.3: Conversion as a function of time for biochar steam gasification	47
Figure 4.4: Specific reaction rate as a function of conversion	48

Figure 4.5: Specific reaction rate of small and large char particles at 10 bar steam for a) 750 °C, b) 740 °C and c) 730 °C	50
Figure 4.6: Specific reaction rate of small and large char particles at 1 bar steam for a) 750 °C, b) 740 °C and c) 730 °C	51
Figure 4.7: Experimental repeatability for different operating conditions for biochar at a) 700 °C 1 bar steam, b) 730 °C 1 bar steam, c) 700 °C 10 bar steam and d) 730 °C 10 bar steam.	52
Figure 5.1: Effect of conversion on the specific reaction rate at 720 °C	54
Figure 5.2: Effect of conversion on specific reaction rate at a) 700 °C, b) 710 °C and c) 730 °C	55
Figure 5.3: Effect of temperature on specific reaction rate at 20% conversion	56
Figure 5.4: Effect of steam partial pressure on specific reaction rate	57
Figure 5.5: Reaction order with steam partial pressure at different temperatures	58
Figure 5.6: Comparison of CO, CO ₂ and total carbon conversion for a temperature of a) 700 °C, b) 710 °C, c) 720 °C and d) 730 °C	59
Figure 5.7: Observed selectivity of CO and CO for various steam partial pressures and temperature of a) 700 °C, b) 710 °C, c) 720 °C and d) 730 °C	60
Figure 5.8: Arrhenius plot of Langmuir-Hinshelwood rate constants	63
Figure 5.9: Correlation between Langmuir-Hinshelwood model and experimental data with uncertainties given for the highest temperature	64
Figure 5.10: Arrhenius plot of PL parameters	65
Figure 5.11: Correlation between the power law and experimental data with uncertainties given for the highest temperature	66
Figure 5.12: Site occupancy as a function of steam partial pressure (extrapolated to 50 bar steam)	67
Figure 5.13: Comparison of biochar and coal char specific reaction rate for conversion of 4-30%	68
Figure A.1: Temperature profile of tube furnace	83
Figure B.1: HPLC pump calibration curve	85
Figure B.2: Mass flow controller calibration curve	86
Figure C.1: Concentration curves with and without char sample at 10 bar steam partial pressure and 730 °C	87
Figure C.2: CO ₂ formation from steam and CO gas	88

List of Tables

Table 2.1: Advantages and disadvantages of different gasifiers [37]	11
Table 2.2: Structural models	24
Table 2.3: Summary of steam gasification studies on biochar and high pressure coal chars	26
Table 3.1: Materials for sample preparation and characterisation	28
Table 3.2: Characterisation completed by external laboratories	30
Table 3.3: Lignocellulosic composition for raw biomass (wt% ar*)	32
Table 3.4: Proximate and ultimate results for raw and charred biomass	33
Table 3.5: Results of Energy Dispersive X-Ray Spectroscopy (wt%)	35
Table 3.6: CO ₂ gas adsorption results	39
Table 3.7: Summary of biomass and biochar characterisation	40
Table 4.1: Materials used for experiments	41
Table 4.2: Component list of experimental rig	44
Table 4.3: Carbon mass balance calculations	49
Table 4.4: Experimental operating conditions	53
Table 5.1: The ratios of $r_{s,40\%}/r_{s,10\%}$ for temperatures of 700-730 °C and steam partial pressures 1-10 bar	56
Table 5.2: Observed selectivity of biochar and coal at 2.5 and 10 bar steam partial pressure	61
Table 5.3: Langmuir-Hinshelwood rate constants for different temperatures	62
Table 5.4 : Parameters calculated for power law	65
Table 5.5: Activation energy and frequency factor from power law	65
Table A.1: Charring of biomass	83
Table D.1: Specific reaction rate at different conversions for repeated runs of 1 bar steam at 700 °C	89
Table D.2: Specific reaction rate at different conversions for repeated runs of 1 bar steam at 730 °C	89
Table D.3: Specific reaction rate at different conversions for repeated runs of 10 bar steam at 700 °C	90
Table D.4: Specific reaction rate at different conversions for repeated runs of 10 bar steam at 730 °C	90
Table D.5: Error estimation between experimental and calculated values	91
Table D.6: Quality of fit for kinetic models	91

List of symbols

Symbol	Description	Units
A	Frequency factor	$gg^{-1}s^{-1}bar^n$
$C(O)$	Carbon-oxygen surface complex	-
C_f	Free carbon active sites	-
E	Activation energy	$kJ\ mol^{-1}$
$f(P_{H_2})$	Function of hydrogen mechanism	-
k_i	Reaction rate constant	s^{-1}
k_s	Specific reaction rate constant	s^{-1}
K_i	Lumped constant of k_i	s^{-1}
m_c	Mass of carbon	g
$m_{c,0}$	Initial mass of carbon	g
$m_{s,0}$	Initial sample mass	g
MW_c	Molecular weight of carbon	$g\ mol^{-1}$
n	Apparent reaction order	-
$\dot{n}_t$	Total molar flow rate	$mol\ s^{-1}$
P_{H_2O}	Steam partial pressure	bar
r_c	Carbon conversion rate	$g\ s^{-1}$
r_s	Specific reaction rate	$g\ g^{-1}\ s^{-1}$
r_{CO}	CO reaction rate	$g\ g^{-1}\ s^{-1}$
r_{CO_2}	CO ₂ reaction rate	$g\ g^{-1}\ s^{-1}$
R	Universal gas constant	$J\ mol^{-1}\ K^{-1}$
R_c	Carbon conversion rate	$g\ s^{-1}$
t	Time	$s\ or\ min$
T	Temperature	$K\ or\ ^\circ C$
x_{ash}	Ash yield fraction	-
x_c	Carbon mass fraction	-
X	Conversion	-
X_c	Carbon conversion	-
y_{co}	CO mole fraction	-
y_{co_2}	CO ₂ mole fraction	-
Greek Symbols		
ψ	Structural parameter	-

List of abbreviations

Abbreviation or acronym	Description
ADF	Acid Detergent Fiber
ADL	Acid detergent lignin
ar	As received
BET	Brunauer-Emmet-Teller
CBM	Biochar sample
CI	Confidence interval
CTL	Coal-to-liquid
D-A	Dubinín-Astakhov
daf	Dry ash free basis
db	Dry basis
EDS	Energy Dispersive X-Ray Spectroscopy
EPC	Electronic pressure controller
FBDB	Fixed bed dry bottom
FTIR	Fourier-transform infrared spectroscopy
HPFBR	High pressure fixed bed reactor
IEA	International energy agency
ISO	International standards organisation
LOI	Loss-on-ignition
LH	Langmuir Hinshelwood
MFC	Mass flow controller
MFM	Mass flow meter
NDF	Neutral Detergent Fiber
PH ₂ O	Steam partial pressure
RBM	Raw biomass sample
RPM	Random pore model
SEM	Scanning electron microscope
SCM	Shrinking core model
SCME	School of Chemical and Mineral Engineering
TGA	Thermo-gravimetric analyser
TPD	Temperature programmed desorption
VM	Volumetric model
XRF	X-ray fluorescence

Chapter 1: Introduction

1.1 Background and motivation

The effective utilisation of energy sources has become more critical in the past decades, mainly since the world energy demand is continually increasing. This trend can be seen in Figure 1.1, where it is shown that the total energy consumption of the world increased by 34% over a 26-year time period [1]. The increasing energy demand is a result of different factors [2], which include the electricity price, the level of growth in economic production, population growth, weather patterns and technology changes.

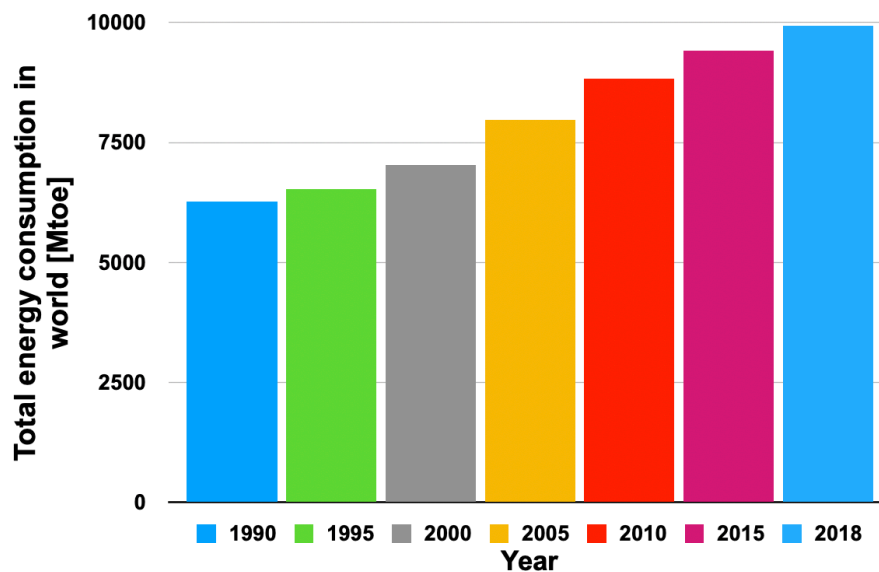


Figure 1.1: Total final energy consumption of the world from 1990-2018 (adapted from [1]).

Currently coal is the main resource used for electricity generation in South Africa, comprising of 88% of the country's energy supply in 2019 [3]. While this is the main use of coal, a significant amount is also utilized in coal-to-liquid (CTL) processes [4]. This CTL activity is used to produce synthetic fuels and other useful chemicals. In general, coal is a primary source of energy, and being seen as a major contributor of CO₂ emissions and particulate matter, with a strong impact on the environment and human health [5]. The available coal resources and quality of coal in South Africa is also depleting [6], which has resulted in exploring alternative sources as fuel for energy supplies.

These alternative sources include renewable energy sources, which are hydro-power, wind energy, geothermal energy, solar energy and biomass energy [7]. The energy consumption and energy supply by different sources are displayed in Figure 1.2 [7]. From these graphs it is evident that coal and oil recourses are largely used for energy consumption and supply

across the world. However, the use of biofuels and waste for energy source around the world is 10-11%, making it the most used renewable energy source at present. The use of biomass as renewable source of electricity has increased from 5.6% in the year 2000 to 9.2% in 2017, making it the 3rd highest renewable electricity source after wind and hydropower [8].

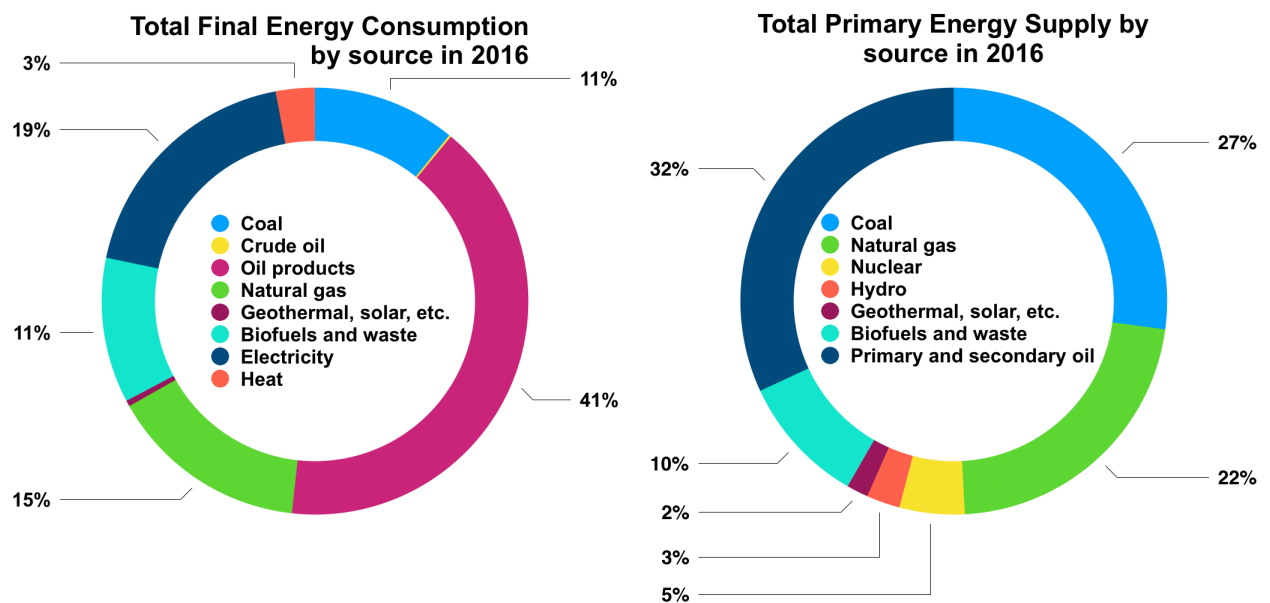


Figure 1.2: Energy Consumption and Supply by source in 2016 (adapted from [7]).

Biomass is considered an appealing alternative energy source, since it can be used to produce electricity, heat and transportation fuels [9]. This energy resource has several advantages including the potential to generate a variation of gaseous, liquid and solid fuels which can be used for various applications [9], [10], [11]. The different types of biomass can be divided into four groups namely: waste, processing residues, locally collected feedstocks and internationally traded feedstocks [10]. It can thus be comprehended why biomass is used for over 70% of all renewable energy production [9].

One of the most attractive operations for utilising biomass is gasification, because it is considered more environmentally friendly and it produces higher efficiencies than combustion and pyrolysis [9]. Gasification is the thermo-chemical conversion of carbonaceous material into a gaseous product like syngas, in an oxygen lean environment [10]. The gasification process is carried out at elevated temperatures, at atmospheric or elevated pressures and in the presence of a gasifying agent. These gasifying agents include air, oxygen, steam or mixtures of these gases [12]. Some complex chemical reactions that can influence the operation of a biomass gasifier are pyrolysis, partial oxidation of pyrolysis products, gasification of produced char, tar formation and lower hydrocarbons conversion and water-gas shifting [10].

Despite all the advantages of biomass as a gasification feedstock, some drawbacks have been considered such as high initial investment costs, food security and water management [11], [13]. Biomass gasification produces char and tar as by products, where tar is generally undesirable because it results in blockages of pipes and filters in downstream equipment [13]. Another option is to focus more on applications which are able to use mixed feedstocks, such as the co-feeding of biomass and coal. The co-gasification of these new recourses requires a comparison of the reactivity of biochar and coal.

The number of scientific publications on steam gasification using either biomass or coal as feedstock for different years are shown in Figure 1.3. An increase in both biomass and coal gasification studies is observed from the early 2000s. However, resent studies have shown more interest in biomass gasification. The major driving force for the renewed interest in biomass gasification are due to the concerns regarding climate change observed in the 1990s [11].

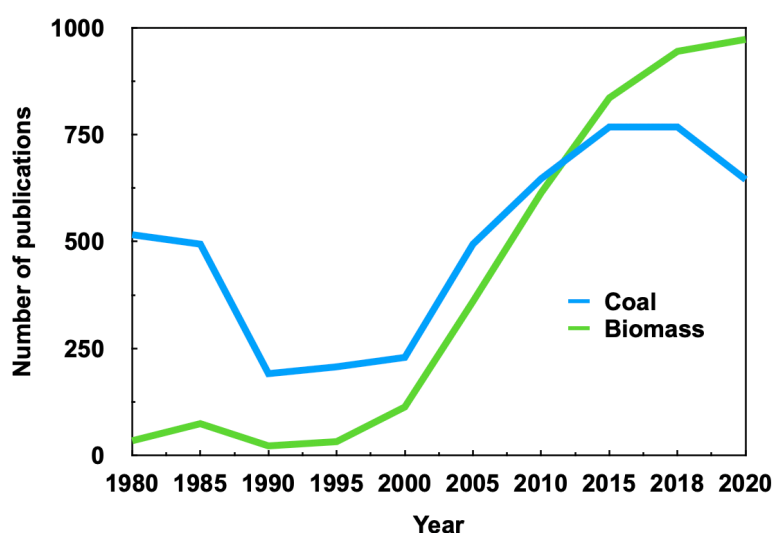


Figure 1.3: Number of scientific publications on gasification research using either coal (Scopus keywords: coal AND gasification) or biomass (Scopus keywords: biomass AND gasification) as feedstock - Access on 16/11/2020

To further understand the gasification process, the important role of biochar gasification kinetics should be considered. Commercially gasifiers operate at elevated pressures, however numerous studies on steam gasification kinetics and modelling of biomass at low pressures have been conducted. Additionally, biochar steam gasification kinetics at elevated pressures are limited making the study relevant to the field.

1.2 Problem statement

Coal is a valuable resource in the South African coal to liquid process (CTL), however the development of new technologies and concepts in coal gasification are required to combat health and environmental concerns. The investigation into alternative resources such as biomass, have become more relevant. One of the most promising processes for biomass utilization is gasification. Commercially in South Africa, the gasification process is performed at elevated pressures and in large complex gasifiers called fixed-bed dry bottom gasifiers, which is considered a technology that is fuel flexible [11]. To successfully design such a gasifier, information on gasification kinetics is necessary. In the South African context, high pressure biomass steam gasification kinetic research is lacking. Therefore, in this study the steam gasification kinetics at elevated pressures is given attention, to further understand the possible application of biomass as gasification resource in the local industry.

1.3 Aim and objectives

The aim of this study is to determine steam gasification reaction kinetics of biochar over a wide pressure range.

To assist in achieving the aim of this study, the following objectives have been defined:

- Source a locally available biomass.
- Characterise the biomass and char derived product.
- Determine the steam gasification kinetics of the biochar at elevated pressures under chemical controlled conditions.
- Model the kinetics through available models.
- Compare biomass with Highveld coal char gasification kinetics.

1.4 Scope of study

In order to achieve the objectives set for this project, the following scope was developed. The study required a series of experiments to be completed, but firstly sample sourcing and preparation was performed. Waste woodchip samples were supplied from South African Pulp and Paper Industries Limited (SAPPI). These woodchips were firstly water washed and then air dried. After drying the biomass was charred in a furnace, where after the char will be crushed and sieved to desired particle size range.

After sample preparation is completed, both the biomass and biochar samples were characterised through various characterisation techniques. Whereafter the pre-experiments were conducted. These experiments were required to ensure that all reactivity data will be obtained under reaction controlled conditions. Gasification experiments were completed using

a high pressure fixed bed reactor (HPFBR) setup, where the concentration of gaseous products (CO and CO₂) was recorded in order to determine the biochar reactivity. Experiments were conducted on the biochar sample with a set particle size range, while the temperature and steam partial pressure were varied.

Data obtained from different experimental conditions were compared and an appropriate kinetic model to describe the steam gasification kinetics of biochar was determined. Lastly, the gasification kinetics of biochar with steam were compared to that of coal char gasification with steam.

1.4.1. Limitations of study

- For this study only one type of biomass sample (woodchips) is being investigated.
- The surface area of partially converted chars was not investigated due to laboratory unavailability during COVID-19 and equipment problems.
- The study does not contain investigations of the inhibition effect of reaction products on the reaction rate of biochar.
- The influence of the heterogeneous water-gas-shift reaction on the formation of CO₂ was not investigated, and subsequently further investigations in the selectivity and reaction mechanisms were not performed.

1.5 Study outline

This study is composed of six chapters which are the introduction, literature study, characterisation, experimental, results and discussion and finally the conclusion and recommendation chapters. In Chapter two a literature study is provided on the gasification of biomass and different aspects which influence the kinetics of this reaction. The different characterisation techniques used on both the raw sample and biochar are discussed in Chapter three, as well as the results obtained from these techniques. All experimental procedures for the gasification of biochar as well as sample preparations are discussed in Chapter four. The fifth chapter of this study contains the experimental results of the biochar gasification with steam and includes the evaluation of different kinetic and structural models. The comparison between coal and biochar steam gasification is also discussed in Chapter five. The conclusions of the study as well as some additional recommendations for future studies are discussed in the final chapter.

Chapter 2: Literature review

2.1 Introduction

The following chapter provides the background on the field of research. A review on biomass as energy source, different aspects of biomass gasification and different modelling techniques is provided.

2.2 Biomass as potential energy source

2.2.1. Biomass in general

Biomass consists of stored energy, which is produced by photosynthesis, when plants absorb energy from the sun. This energy can then be released in the form of heat when biomass is combusted. Biomass is utilised in different ways, for example it can be converted to biogas or liquid biofuels, or even burned directly as fuel source [14].

In most rural areas around the world biomass is still the major energy source for cooking and heating, the reason for this is that biomass is frequently the only available source of energy and / or it is affordable [15]. In some developing countries in Africa and Asia biomass accounts for more than a third of the total energy consumption [16]. Biomass is largely available over the world making it more favourable than other fossil fuels like coal and natural gas. These fossil fuels thus require transportation which comes with some additional cost, while biomass is distributed more evenly.

Biomass consists of a wide range of different bio materials, such as wood, waste from wood and food industry, forest and agricultural residues, straw, sewage sludge, bagasse [17]. Although there are many types of biomass, it mostly consists of biopolymers like lignin, hemicelluloses and cellulose [18]. The three main elements found in biomass are carbon, oxygen and hydrogen. Some characteristics of biomass such as density, moisture content, size, heating value and shape all play a critical part in the composition of the products produced from biomass [17]. These different types of biomass result in different challenges which requires solutions for harvesting, collection, transportation, storage, gasifier operations and cleaning of the syngas after production [16].

2.2.2. Different types of biomass

The chemical and structural characteristics of the biomass can be used to determine which type of biomass is best suited for the different fuel applications [19]. Currently 67% of biomass classified as residues and waste and 33% of lignocellulosic energy crops are being used for heating purposes in both domestic and industrial areas [20]. The generation of electricity

utilizes up to 50% of energy crops, residues and waste [20]. Biomass can be divided into four main categories which are wood and agricultural residues, solid waste, landfill gas and alcohol fuels. These categories are further discussed in this section.

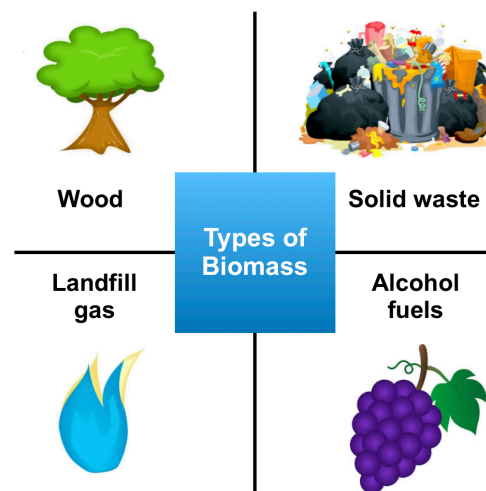


Figure 2.1: Illustration of different types of biomass

Wood and Agricultural residues

Wood as a biomass resource can be obtained from forests or in the waste produced by wood processing. Examples of this biomass type includes woodchips, wood pellets, palm kernel shell and sawdust [12]. Virgin wood can be utilized by burning it directly to heat up buildings, to produce process heat required in the industry as well as to generate electricity.

Agricultural biomasses are typically waste materials produced from food crop production, which includes field residues and processing residues. Agricultural residues do not compete for land reserved for food crops, which implies that it does not threaten the food supply. Field residue is straw from grains, while processing residues are bagasse, chaff, cobs and husks. These residues can be used to produce different biofuels such as cellulosic ethanol, bio-crude and other liquid biofuels [14].

Energy crops are high-yield crops which are grown for specific energy applications. Different examples of this class include; *Hybrid eucalyptus*, *Jatropha*, *Pongamia*, and perennial grasses, i.e. *Miscanthus* and *Napier grass* [12]. These biomasses are mainly used to generate electricity when burnt and to produce biofuels such as biogas.

Solid waste

Solid waste biomass includes food waste and industrial waste. A third of the food produced globally for human consumption is currently lost, discarded or uneaten, which means there is a lot of different ways to obtain this biomass type [21]. Food waste typically includes animal

fat, residues from drink or food manufacturing. Through the use of fermentation technologies biofuels such as food waste biodiesel, ethanol, hydrogen and methane can be produced [21].

Industrial waste is a by-product of some manufacturing or industrial processes. Garbage produced by the industry is also considered a biomass type, since this waste can be burnt to produce heat energy which is used in waste-to-energy plants [22].

Landfill gas and Anaerobic digestion

A landfill site is where waste material is buried under ground. These buried waste products produce gas, which can be obtained through piping systems [23].

The gas obtained from landfills contain a mixture of carbon dioxide and methane. The use of this gas results in a reduction of the methane gas that can contribute to the greenhouse effect. The methane in the gas can be used to produce electricity, heat and transport fuels. The use of landfill gas thus helps prevent global warming and reduces the need for additional energy imports in certain countries [24].

Anaerobic digestion is another method used to produce biomass. This process converts the organic matter of different waste materials into biogas, biosolids and liquor. It is considered an energy efficient and environmentally friendly process that is used for energy production and waste minimisation [25].

Alcohol fuels

Waste from food crops like wheat and corn can be used to produce a variety of liquid fuels including ethanol and methanol [22]. These alcohols are used in the production of alternative fuels [23]. Wastewater is another waste produced by the industrial sector. These waters contain different sugars and starches, which has the potential to be anaerobically digested to produce biogas or to be fermented to produce ethanol [24].

2.2.3. Biomass availability in South Africa

Although there are many different types of biomass feedstocks, the two main classes of biomass resource availability are based on forestland and agricultural land [26]. The primary forest resources are obtained from logging residues and excess biomass from timberlands. There are five groups in which the different forest resources are categorized i.e. logging residue, fuel treatments, fuelwood, forest products industry and urban wood residues and forest growth biofuels [26].

According to Petrie and Macqueen (2013) South Africa has significant potential in the biomass energy sector due to its 42 million ha of natural woodland and 1.35 million ha of plantation [27]. Resource surveys carried out in the Western Cape province indicate that 150 000 t.p.a

of unwanted trees can be harvested in the next 20 years [28]. The plantation area in use in each of South Africa's provinces are displayed in Figure 2.2. Mpumalanga and KwaZulu-Natal are the two main provinces which contribute to the total plantation area of South Africa [29]. South Africa has the capability of producing 94 Mt of biomass per annum [30], making the use of biomass as energy source in South Africa a viable option.

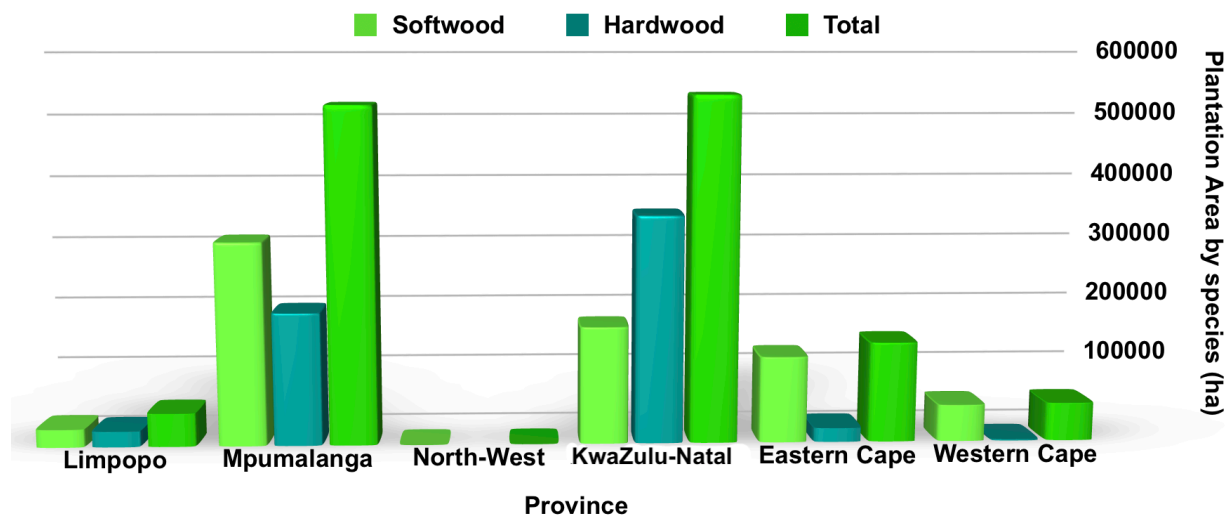


Figure 2.2: Plantation area by species for each province in South Africa (adapted from [29])

2.2.4. Energy uses for biomass

Biomass as energy source is used in different oxidative and non-oxidative thermochemical applications which include pyrolysis, combustion and gasification [31].

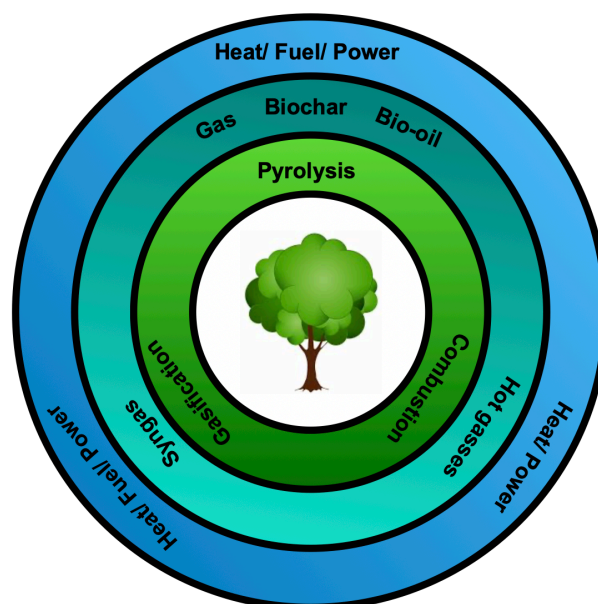


Figure 2.3: Technologies that convert biomass into different fuels(adapted from [32])

Pyrolysis

Pyrolysis is the thermochemical application which is most studied because this process has the ability to produce gas, liquid and solid biofuels [32]. The pyrolysis process involves the degradation of lignocellulosic components found in biomass in inert conditions at specific heating conditions [31]. The quantity of each product formed from pyrolysis is influenced by the composition of the biomass as well as different operating conditions such as heating rate, temperature, residence time and catalyst type [31]. To reduce tar formation in other thermochemical processes, pyrolysis is recommended as a pre-treatment [32]. It has been reported that the pyrolysis of biomass at temperatures below 300 °C results in the formation of char and the reduction of molecular weight, CO and CO₂. While pyrolysis temperatures of 300-500 °C favours the formation of tar [33]. In general pyrolysis is a favourable option for recycling biomass and energy recovering since it is related to value-added product generation, lower NO_x and SO_x emissions and less tar formation [31].

Combustion

In general combustion is the rapid oxidation of fuel accompanied by the production of heat energy. For combustion to occur three sources are required namely oxygen, fuel and heat [34]. Combustion is a widely used oxidative thermal process for energy-related applications [31]. An example of these applications are waste-to-energy plants which generate electricity with the aid of steam turbines. Biomass is also used as an alternative fuel in wood-fired stoves to produce heat energy, however the use of combustion under uncontrolled conditions could result in air pollution by releasing flue gas into the atmosphere [31].

Gasification

One of the most favourable utilization processes of biomass is gasification, since it provides a high process efficiency and high potential for the use of biomass [35]. Gasification is a thermal process where organic components of biomass are oxidized by a gasifying medium such as air, steam, limited oxygen and carbon dioxide at elevated temperatures [31]. An advantage of gasification is that it offers flexibility regarding the use of different feed materials as well as the fact that it can generate different products. Biomass can thus be used to produce syngas through the gasification process, which can then be used to produce different kinds of energy, energy carriers and chemicals i.e. heat, biofuels, hydrogen and biomethane [16].

2.3 Gasification

2.3.1. Conventional fuels and trends

The gasification industry around the world is considered large since there are more than 272 gasification plants in operation with 686 gasifiers [36]. One of the most favourable gasification applications is the production of chemicals, for example 25% and over 30% of the world's ammonia and methanol are being produced by gasification respectively [36]. In the industry different types of gasifiers are used for different applications. For small scale power and heat generation downdraft and updraft fixed bed gasifiers were developed. Bubbling fluidised bed systems are preferred for medium to large scale gasification plants that generate power. For larger capacities and production of fuels and chemicals pressurized systems are favoured [11]. The advantages and disadvantages of gasifier types are displayed in Table 2.1[37].

Table 2.1: Advantages and disadvantages of different gasifiers [37]

Gasifier type	Advantages	Disadvantages
Fixed bed downdraft	• Produces clean gas (less tar and ash) • Easier to control than updraft • Low sensitivity for fines from fuel • Requires minimal tar clean-up • Reduces need for cyclone separator • Simple and low-cost	• Fuel specific • Fuel must have low moisture content • Lower efficiency • Impractical for scale-up
Fixed bed updraft	• Effective heat transfer • Ability to process high moisture fuel • Less sensitive to ash contained in fuel • Less complex fuel preparation required • High cold gas efficiency • Simple and low-cost	• Higher tar production • Not suitable for scale-up • Ability to handle fines from fuel is limited • Requires controlled feed size distribution
Bubbling fluidized bed	• Uniform temperature distribution • Fuel flexibility and wide range particle size acceptability • Scale-up possible	• Large bubbles can be a problem result of gas bypassing through bed

	• Ash can be removed easily from reactor • High heat transfer rates and load flexibility • Possible to use catalyst to increase tar conversion	• Short residence time, results in reactions not reaching chemical equilibrium • High tar formation
--	--	--

The primary feedstock for gasification is coal and according to the graph from Figure 2.4, it will remain the dominant fuel for the future [36] [38]. Gasifiers have the ability to capture energy from several sources such as coal, petroleum coke, crude-oil, gas, biomass and waste. The number of gasifiers used for these different feedstocks worldwide are displayed on a logarithmic scale in Figure 2.4 [35].

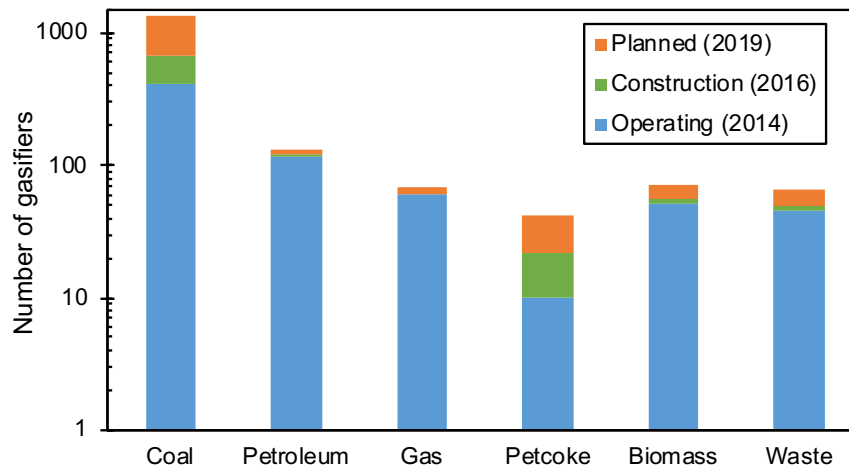


Figure 2.4: Number of gasifiers used by primary feedstock. (adapted from [36])

2.3.2. Biomass gasification

Commercially in South Africa, the gasification process is performed in fixed-bed dry bottom (FBDB) gasifiers [39]. Coal is fed at the top of the gasifier, which uses a lock-hopper system, while the reactant gas (gasifying agent) is introduced at the bottom and flows upwards. A temperature drop in the reactor occurs due to the counter-current operation, which results in 4 characteristic zones as shown in Figure 2.5. As the coal descends through the reactor, it is first dried and de-volatilised which results in char, whereafter the char enters the gasification zone and finally the residual char is burnt to ash [39]. The gasification term refers to the gasification zone inside the gasifier which converts the residues produced by the pyrolysis step into syngas [40]. The main reason for investigating the gasification kinetics is that the gasification zone is the rate limiting step in the process [41] [42].

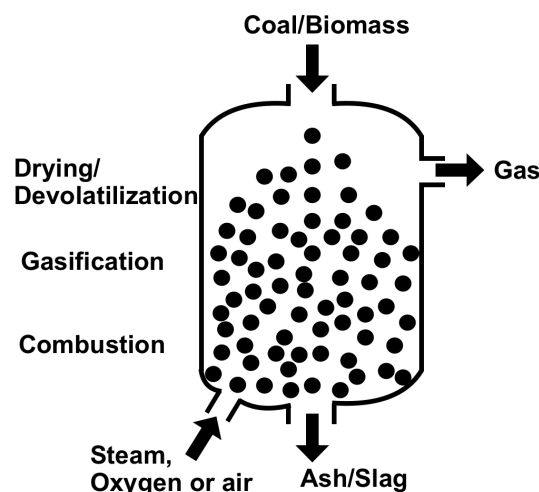


Figure 2.5: Schematic of a typical fixed bed gasifier(adapted from [43])

In the gasification zone a gasifier agent or gas is introduced to the system [44]. For a FBDB gasifier H_2O and O_2 are used as reagent gases in the industry, however CO_2 , steam, O_2 -steam, CO_2 -steam and O_2 -steam- CO_2 are used for laboratory scale studies regarding reaction kinetics [12]. Various studies have been completed on the char gasification reaction with these gases, however some noted that the use of steam resulted in faster reactions than the use of CO_2 [45] [46] [47]. Ahemd and Gupta (2011) found that the average reaction rate for woodchip char steam gasification was almost twice than that of CO_2 [41].

The main constituents of biomass (cellulose and hemicellulose) results in biomass being more reactive than coals which then leads to lower required gasification temperatures [26]. In the biomass gasification industry small fixed bed updraft and downdraft technologies are preferred to generate heat and power. For the production of fuels and chemicals, large entrained flow gasifiers are favoured [11].

The use of biomass as gasifier feedstock also plays an important role in reducing emissions of CO_2 , NO_x and SO_x [19] [48]. Biomass has several advantages as gasification fuel such as:

- Converting waste products into high value products,
- Reduction of landfill space required for disposal of solid wastes,
- Reduction in methane emissions from landfills,
- The risk of groundwater contamination from landfills are reduced and;
- Ethanol production from non-food sources are possible [37].

The utilization of biomass has some drawbacks which include the seasonal availability, lower energy density and high moisture content [49].

2.4 Gasification reactions and mechanisms

During the gasification process biomass is converted to different gaseous products, the conversion of these products involves the following reactions [50]:

Char gasification reaction:



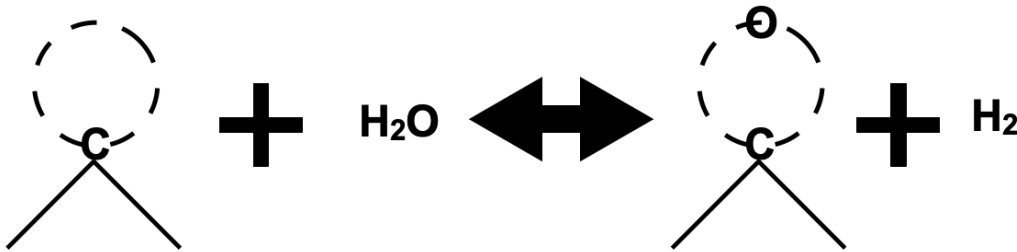
Water gas shift reaction:



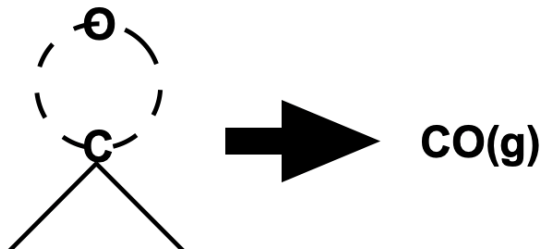
Boudouard reaction:

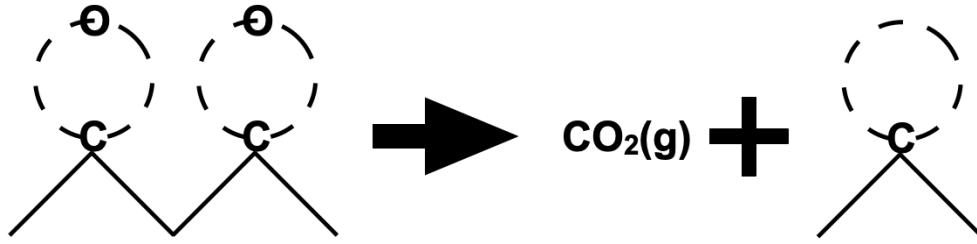


It is believed that during the char gasification reaction (R-1), CO is mainly formed from the surface of the char [51]; the formation of CO₂ is less certain. Akhtar *et al.* (2019) found that CO₂ can be formed by either the water gas shift reaction or from the char surface in the same manner as the CO is formed. The first mechanism suggested for the C(O) and H₂ formation is illustrated below [51], [52], [53]:



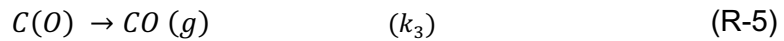
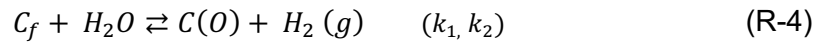
Where the intermediate formation of the adsorbed carbon-oxygen surface complex is considered the rate-limiting step during the biochar steam reaction and the free active sites are formed after the H₂ is released from the carbon active sites [51]. The formation of CO and CO₂ is illustrated by the following two mechanisms:





Where the CO gas is formed from the adsorbed carbon-oxygen surface complex and the formation of CO₂ results in free active sites being formed.

Another commonly used reaction mechanism for carbon gasification with steam is suggested by Ergun and Reif which does not consider the formation of CO₂[52] [53]:



Where C_f is the free active site and $C(O)$ is an adsorbed carbon-oxygen surface complex. This mechanism is used to produce the simplest form of a Langmuir-Hinshelwood model to represent experimental data obtained. The use of this Langmuir-Hinshelwood model is further discussed in Section 2.6.1.

2.5 Factors influencing gasification rate

It has been proven that the char gasification rate is affected by several factors which include the biomass type, the chemical and physical properties of the char, char preparation conditions and operating conditions such as temperature and pressure [54] [52] [55] [56]. All these factors are discussed in further detail in this section.

2.5.1. Type of biomass

For this study only one type of biomass will be considered (woodchips), however previous studies have investigated the influence that the type of feedstock will have on the gasification process. Sattar *et al.* (2014) investigated steam gasification of four different biomass feedstocks and found that biochar, derived from wood, produced the highest quantity of syngas between wood, rapeseed, sewage sludge and *miscanthus* biochar [54].

The reaction rate is also influenced by the different biomass types. When only considering woody biomass samples for steam gasification it has been found that the content of inorganic elements mainly influences the reaction rate. According to Dupont *et al.* (2011) the increase in conversion resulted in a higher inorganic element content which then increases the samples

catalytic or inhibitor effect [57]. A summary completed by Klose and Wölki (2005) compared the different reaction rates during steam gasification at 0.1 MPa using various biomass chars [52]. They reported that barley had the largest reaction rate and poplar had the lowest value, however other feedstocks such as bark, maple, straw and pine had similar reaction rates. It has been reported that barley has a higher hemicellulose and lower cellulose and lignin content than poplar [58]. Irmak *et al.* (2013) reported that the difference in lignocellulosic composition of these biomass samples can be a reason for the variation in gasification efficiency [59].

2.5.2. Temperature

Temperature has a large impact on biomass gasification kinetics [12] [55]. This operating parameter can be controlled at laboratory scale as well as in the industry, however temperature becomes a function of several elements in the industry [10]. The effect that temperature has on the reaction rate is displayed in Figure 2.6 [60]. The reaction rate moves from the chemical reaction controlled regime to pore diffusion controlled or external mass transfer controlled regimes with an increase in temperature.

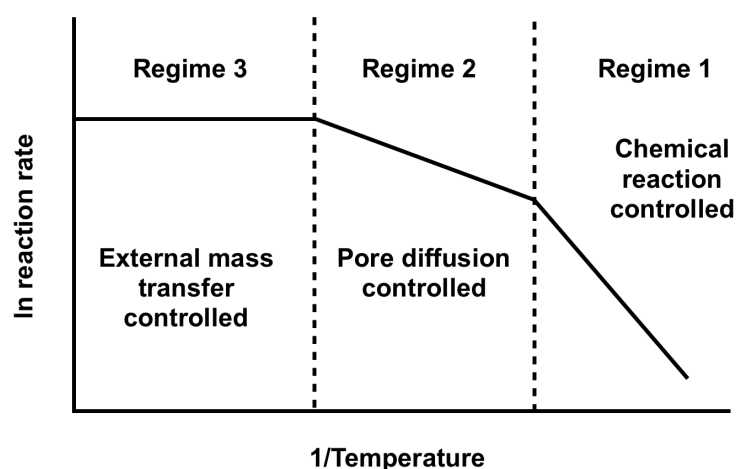


Figure 2.6: Effect of temperature on reaction rate and controlling mechanism(adapted from [60])

At lower temperatures (below 1000 °C) the chemical reaction is the rate limiting step [60]. The type of biochar will influence the temperature range where the transition from one regime to the next will occur. From the graph it is clear that both Regime 1 and Regime 2 are more effected by the increase of temperature, while for Regime 1 the effect is more significant. Therefore, lower temperatures can provide chemical controlled conditions while higher temperatures will result in diffusion limitations.

2.5.3. System pressure

The effect of steam partial pressure on the gasification rate has been found to be significant, however more studies have been completed on lower steam partial pressure than elevated pressures. The effect of low and high pressure steam gasification with regards to operating conditions such as temperature and steam partial pressure are discussed further in this section.

Low pressure steam gasification

Temperature

According to Ahmad *et al.* (2016) an increase in reaction temperature will result in an increase in reaction rate [12]. In Figure 2.7 the effect of temperature on the conversion rate is displayed for a pinewood sawdust derived char. In this study on wood chip derived biochar, the time required to achieve 0.95 conversion was reduced by increasing the gasification temperature by 100 °C [55]. This trend is also found in other studies, where the reactivity increased by nine times with a 200 °C increase [56].

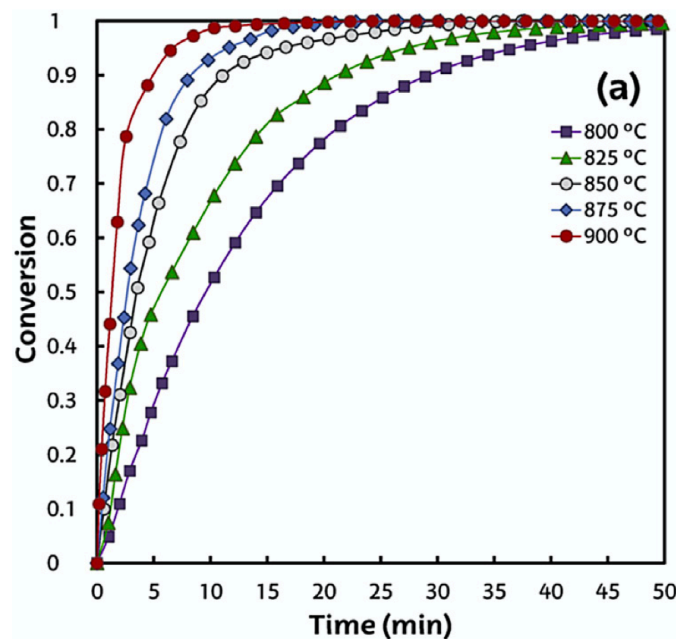


Figure 2.7: The effect of temperature on conversion rate during steam gasification at low pressure.(taken from [55])

Steam Partial Pressure

Various studies on the influence of steam partial pressure on the gasification kinetics of biochar at low pressures have been completed [41] [52] [55] [56] [61]. This was achieved by either changing the concentration of the steam at a constant system pressure or by changing the total system pressure at a constant steam concentration.

The effect of steam partial pressure on the reaction rate has been found to be less prominent than that of temperature [55]. In a study completed by Ahmed and Gupta (2011) an insignificant effect of steam partial pressure on woodchip derived char gasification was found. The steam partial pressure was varied between 0.6 and 1.5 bar at 900 °C in a fixed bed reactor [41]. However, other authors observed a significant effect of steam partial pressure on the biochar reaction rate at low pressures [52] [56] [61].

In Figure 2.8 the influence of steam partial pressure on the specific reaction rate of biochar is observed [52]. In this study two different biochar samples were investigated. The reaction rate increased with an increase in steam partial pressure for both samples, however the beech wood char has a more pronounced increase than the oil palm shell char. As the steam partial pressure increases the influence on the oil palm shell char reaction rate becomes less significant.

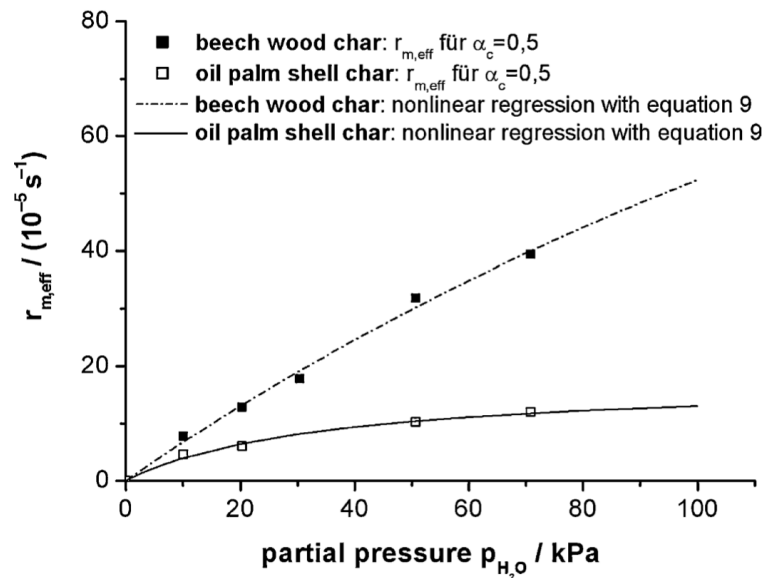


Figure 2.8: Specific reaction rate as a function of steam partial pressure. (taken from [52])

Van de steene *et al.* (2011) found that if the partial pressure of steam is increased from 0.1 to 0.4 atm the gasification rate was 3 times faster [56]. While Guizani *et al.* (2013) observed a 2.5 times increase in the char reactivity of beech wood chips by increasing the steam concentration from 10% to 30% [61].

High pressure steam gasification

Steam gasification studies using biochar at elevated pressures are more limited than that of low pressure gasification.

Temperature

The significance of temperature on the gasification rate of biochar is discussed in more detail in Section 2.5.3, the effect that high pressure will add to this reaction condition will be evaluated in this section.

A study completed on the steam gasification of maple and jack pine wood chars at 21.7 bar, investigated the effect that temperature will have on the weight loss of these chars [62]. In Figure 2.9 the results of varying the temperature between 815 °C and 704 °C at a steam partial pressure of 10.85 bar are shown.

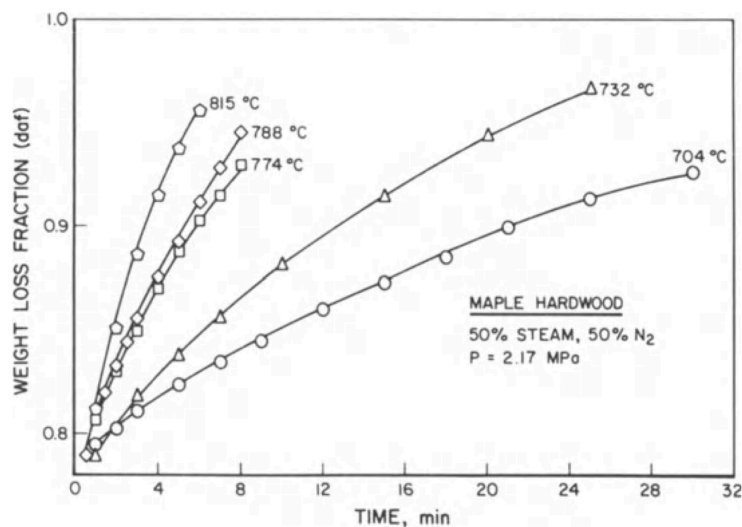


Figure 2.9: The effect of temperature on weight loss fraction at elevated pressures.(taken from [62])

At elevated temperatures the weight change occurs more rapidly than at lower temperatures. This implies that an increase in pressure will result in an increase of gasification rate. Similar results were obtained for the jack pine wood char, indicating that the impact of temperature on weight loss is significant for both char samples [62].

The effect that an increase in temperature has on low- and high pressure steam gasification are relatively similar, seeing that for both conditions an increase in temperature will result in an increase in gasification rate.

Steam partial pressure

The investigation of the effect of steam gasification on biochar reaction rate at elevated pressure has not been widely studied. However, a study completed by Nandi and Onischak (1985) on maple and jack pine evaluated the effect of steam partial pressure by changing the total system pressure at a constant steam concentration. The results from varying the partial pressure of steam between 0.85 and 10.85 bar are shown in Figure 2.10. In this study it was

concluded that the effect of steam partial pressure on the gasification rate was significant for steam partial pressures higher than 3.95 bar [62].

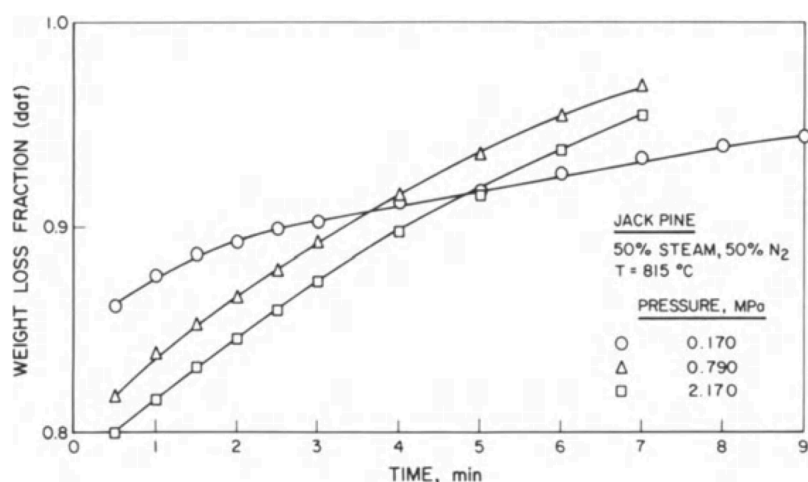


Figure 2.10: The effect of partial pressure on the weight loss fraction at elevated pressures.(taken from [62])

Considering the data reported in Figure 2.10, the effect of steam partial pressure endures for longer time periods when at elevated steam partial pressure. For an increase of steam partial pressure an increase in gasification rate is expected, however the effect of this reaction condition at elevated pressures for biochar has not yet been studied in detail which further motivates the importance of this study.

The limited studies on biochar reactivity at elevated steam partial pressure, leads to an investigation into elevated steam gasification of other carbon materials and predictions of high steam partial pressure gasification of biochar. A study investigated the steam gasification of polyvinylchloride (PVC) coke at 1000 °C and a total system pressure of 10 bar, while changing the concentration of steam. An increase of steam partial pressure from 0.55 bar to 4.3 bar resulted in an increase of gasification rate [63].

Another carbon source to consider is coal char. Studies using coal char at elevated steam partial pressures have found that an increase in steam partial pressure results in an increase in reaction rate as shown in Figure 2.11 [64] [65] [66]. Sha *et al.* (1990) found that the reaction rate started to increase more slowly at steam pressures above 10 bar [65], which suggests a form of saturation. Another study reported this saturation effect at elevated pressures and found that this behaviour is affected by temperatures [66].

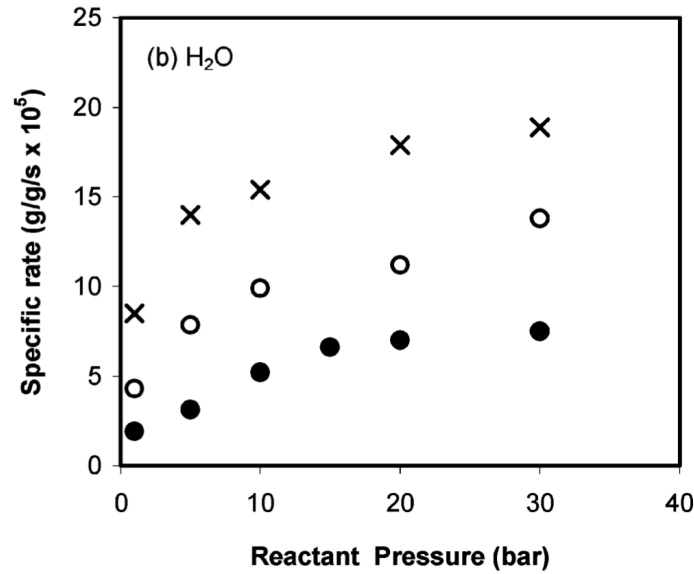


Figure 2.11: Effect of steam partial pressure on specific reaction rate of three coal chars at 850 °C and 10% conversion. (taken from [59])

The saturation effect on the specific reaction rate can be explained by the estimation of site occupancy. Site occupancy or surface coverage is able to express the desorption of intermediate surface complexes and it has been reported that the desorption can affect the apparent reaction rate [64]. Roberts and Harris (2006) reported that the site occupancy of Australian coal derived char can be estimated by using an empirical method constructed from the reaction mechanisms which are described by the Langmuir-Hinshelwood (LH) expressions and temperature programmed desorption (TPD). The estimation of the site occupancy can be described with the equation given in 2-1 [64]:

$$\theta = \frac{\frac{k_1}{k_3} p_{H_2O}}{1 + \frac{k_1}{k_3} p_{H_2O}} \quad (2-1)$$

Where θ is the site occupancy, $\frac{k_1}{k_3}$ are the rate constants for corresponding reactions and the p_{H_2O} is the steam partial pressure. The study on coal derived char reported that the site occupancy increased with an increase in steam partial pressure from 1-30 bar for both LH and TPD methods used [64]. This indicates that the reactive surface of the char becomes more saturated with surface complexes at elevated steam partial pressures [45], [64], [67]. Which suggests that the further increase of steam partial pressure will result in an unaffected specific reaction rate and the saturation effect is observed. This can be predicted for biomass derived char as well.

2.6 Modelling

Information regarding the kinetics of biochar gasification with steam is essential in understanding the phenomena occurring inside the reactor and for designing the process. The gasification process is significantly affected by the physicochemical properties of the char, the steam partial pressure, the gasification temperature and the particle size [68].

The gasification process can be divided into three main regimes according to the temperature, steam partial pressure and the char particle size [69]. Regime 1 usually occurs at lower temperatures as shown in Figure 2.6 in Section 2.5.2. In Regime 1 the gas temperature and concentration on the surface sites of the char are equal to those in the bulk gas, resulting in chemical reaction controlled conditions. While Regime 2 is considered the transition regime and the rate limiting step for this regime is pore diffusion. Regime 3 occurs at high temperatures and its rate limiting step is external mass transfer [53]. Experiments must be performed in Regime 1 (chemical reaction controlled) to ensure that the kinetics can be determined in the absence of mass transfer. This is then further used in particle and reactor models to predict the industrial gasification process.

There are two different types of models that are used to describe the conversion of a char particle, these are kinetic models and structural models. The two main models to consider for kinetic modelling are the Langmuir-Hinshelwood model and power law.

2.6.1. Kinetic models

Langmuir-Hinshelwood model

The Langmuir-Hinshelwood kinetics are used to describe either single- or dual-site mechanisms [70]. This model describes the adsorption of 2 molecules onto a surface, that then react and desorbs to form a product. The mechanisms suggested in Section 2.4 leads to the Langmuir-Hinshelwood rate expressions. This model describes the dependency of the reaction rate on the partial pressure and reaction temperature well [52]. The most simple form of the Langmuir-Hinshelwood takes reactions R-4 and R-5 into account for steam gasification [53]. This leads to the following rate equation:

$$r_s = \frac{k_1 P_{H_2O}}{1 + \frac{k_1}{k_3} \cdot P_{H_2O}} \quad (2-2)$$

Where k_1 is the rate constant for reaction 4 and k_3 is the rate constant for reaction 5 and both these rate constants follow the Arrhenius law. The P_{H_2O} refers to the steam partial pressure.

Equation 2-2 suggests that the H_2 formation has no significant effect on the reaction rate due to the low concentrations of H_2 formed [71].

When considering the effect of hydrogen inhibition on the reaction rate the Langmuir-Hinshelwood formulation becomes the following:

$$r_s = \frac{k_1 P_{H_2O}}{1 + \frac{k_1}{k_3} \cdot P_{H_2O} + f(P_{H_2})} \quad (2-3)$$

The reactivity between chars and steam is known to decrease in the presence of hydrogen. The term $f(P_{H_2})$ refers to a function which depends on the selected mechanism. Most studies assume that the oxygen exchange mechanism represents the inhibition of hydrogen, which leads to the reversible reaction in R-9 [53].

Studies have determined steam gasification kinetics without considering hydrogen inhibition mechanisms, the following equation was used [72] [71]:

$$r_s = \frac{K_1 P_{H_2O}}{1 + K_2 P_{H_2O} + K_3 P_{H_2}} \quad (2-4)$$

However, the term $K_3 P_{H_2}$ was assumed to be $K_3 P_{H_2} \approx 0$, due to the relatively low hydrogen concentration being formed during steam gasification [71]. If this is assumed, there is no variance in eq. 2-2 and 2-4.

Power law

The power law is a popular model used for modelling the intrinsic reaction rates of char gasification. This nth order kinetic model gives allowance for the effect of state of conversion. The power law is consider to be more accurate in representing the reaction rates at medium to high conversions [71].

The rate equation is described by:

$$r_s = k_s (P_{H_2O})^n \quad (2-5)$$

Where the rate constant is assumed to follow the Arrhenius equation shown below:

$$k_s = A \exp \left(\frac{-E}{RT} \right) \quad (2-6)$$

2.6.2. Structural models

Structural models are intended to describe the internal solid matrix or internal pore structure and the changes occurring during the char conversion process [73]. The three structural models most frequently used are the Grain model, the Random Pore model and the Volumetric Model. These char conversion models are summarised in the following table [74].

Table 2.2: Structural models

Model	Equation
Grain Model	$\frac{dX}{dt} = k_{GM}(1 - X)^{2/3}$
Random Pore Model	$\frac{dX}{dt} = k_{RPM}\sqrt{1 - \psi \ln(1 - X)}$
Volumetric Model	$\frac{dX}{dt} = k_{VM}(1 - X)$

Another model not displayed in the table above is the Shrinking Core Model (SCM). This model was developed by Yagi and Kunii (1961), which assumes that a reaction occurs at the surface of an unreacted core [75]. The model consists of a structural factor which is dependent on the porosity and initial surface area of the char sample. The SCM has been proven to provide a good representation of gasification reactivity, if internal diffusion is neglected by assuming that the core of the char has a low internal porosity [76].

The Grain Model (GM) assumes that the char particle is a combination of smaller spherical grains where the reaction then occurs at the external surface of the char which moves within the particle, while the Volumetric model (VM) assumes a homogeneous reaction throughout the whole particle [53]. Both the GM and VM describe a decrease in reaction rate with an increase of conversion [74].

The Random Pore Model (RPM) describes the change occurring in the pores of the char structure during char conversion [53]. The RPM assumes that the reaction surface contains overlapping cylindrical pores which increase to a certain conversion and then start to come together to form one mass and collapse. Ahmed and Gupta (2011) found that the RPM provided a good representation of the reaction rate for woodchip char during steam gasification. An average rate constant of 0.065 and structural parameter (ψ) of 9.00 over a range of steam partial pressure was reported [41].

2.7 Summary of steam gasification studies

The results of various biochar and coal char steam gasification studies have been discussed in this chapter. A summary of these studies is shown in Table 2.3. For the summary table mostly studies using a woody biomass type was considered.

The different structural models used by authors to describe the biochar steam gasification reactivity are the Shrinking Core Model (SCM), Homogeneous model (HM) and Random Pore Model (RPM). Popular kinetic models used are the power law (PL) and the Langmuir-Hinshelwood model (LH), although the LH model is used more often.

The TGA is the most popular analysis technique used by the different authors. The operating conditions were varied over a range of 700-1150 °C for temperature and 0.1-60 bar for steam partial pressure. The various authors observed activation energies ranging from 112.6-300 kJ/mol. While the reaction order was determined between the values of 0.34 and 1.5.

Table 2.3: Summary of steam gasification studies on biochar and high pressure coal chars

Study	Material used	Analysis Technique	Temperature (°C)	Partial Pressure (bar)	Model	E (kJ/mol)	Reaction order
Morin, Pécate and Hémati, (2018)	Beech wood stick	Fluidised bed reactor	700-850	0.1-0.7	SCM	123	0.62
Lopez et al.,(2016)	Pinewood sawdust	Conical spouted bed reactor	800-900	0.2 -1.0	HM, SCM, RPM	188.2, 196, 190.3	0.340, 0.351, 0.344
Nilsson et al., (2014)	Olive tree char	Fluidised bed reactor	760-900	0.2-0.4	LH, PL	137	0.8-1.5
Woodruff and Weimer (2013)	Switchgrass char	Modified fixed bed reactor	1000-1150	0.19; 0.67 and 0.9	LH, RPM	112.6	NR
Ahmed and Gupta, (2011)	Yellow pine woodchips	Reactor chamber	900	0.6; 0.9; 1.2 and 1.5	RPM	NR	NR
Dupont et al., (2011)	21 different types of wood chips	TGA	750-900	0-0.27	SCM	167	0.6
Roberts and Harris (2006)	Coal char	High pressure TGA	850 °C	1-30	LH	-	0.4-0.5
Klose and Wölki (2005)	Beech wood and oil pail shell	TGA	740-790	0.1-1.0	LH	200-300	NR
Sha et al., (1990)	Three different coal chars	Pressurized thermal balance	850 & 900	1.2-31	LH	-	Approaches zero
Mühlen et al., (1985)	Coal char	Fluidised bed gasifier	800-1000	1-60	Derived model	-	NR
Nandi and Onischak (1985)	Maple and Jack Pine	TGA	704-815	0.85-10.85	-	164-266	NR

2.8 Summary

Biomass is a valuable resource that is widely available across the world and has various applications. The use of biomass in coal-to-liquid processes are being investigated due to the world's coal resources and its quality becoming more depleted. Gasification is a vital part of the coal-to-liquid process and the gasification of biomass has some uncertainties. Several studies on biochar gasification have been completed at different temperature ranges, however the effect of elevated pressure on the gasification rate of biochar is lacking. In South Africa gasification occurs in a fixed bed reactor at elevated temperature and pressure. This leads to the investigation of biochar gasification at elevated pressure.

Previous authors have found that both temperature and pressure influence the biochar gasification rate. However, in order to predict biochar gasification rate at elevated steam partial pressure coal char gasification studies were considered. From the results obtained, it has been found that the increase of the reactant partial pressure has a notable effect on the reaction rate up to partial pressures of 20 bar.

Chapter 3: Sample Preparation and Characterisation

3.1 Introduction

For the gasification kinetic experiments biochar was used and in the following chapter the char preparation and biomass and biochar characterisation are discussed. In Section 3.2, the materials used to complete the char preparation and characterisation are listed. The analysis methods applied to prepare and characterise the properties of the biomass and biochar samples are discussed in Section 3.3. Section 3.4 contains the results and discussion of both samples, followed by a summary of the biomass and biochar properties in Section 3.5.

3.2 Materials

The materials listed in Table 3.1 were used for sample preparation and in-house characterisation. A waste product (woodchips) from the plant genus *Eucalyptus nitens* was supplied by the South African Pulp and Paper Industries Limited (SAPPI). This sample was used to produce the biochar sample.

Table 3.1: Materials for sample preparation and characterisation

Chemicals & Liquids:			
Name	Supplier	Detail	Uses
Tap water	NWU Potchefstroom	None	Water wash of biomass sample.
Deionised water	NWU Potchefstroom	Obtained from water laboratory in SCME.	Water wash of biomass sample.
Potassium bromide	Sigma-Aldrich	Purity: > 99%	Fourier-transform infrared spectroscopy (FTIR) analysis.
Gases:			
Name	Supplier	Detail	Uses
Nitrogen	Afrox South Africa	Purity: > 99.999%	Charring process and Thermogravimetric analysis (TGA)
Carbon dioxide	Afrox South Africa	Purity: > 99.9%	CO ₂ adsorption

Equipment:			
Name	Supplier	Detail	Uses
Three phase horizontal furnace	Lenton	model no: TMH16/75/610	Charring process
Ceramic heating boats	Ceradvance engineering ceramics	Custom made	Charring process
Ball mill	NWU Potchefstroom	Custom made	Crushing of biochar to desired particle size
Sieves	Labotec Ltd	Sizes ranging from 75 to 800 μm .	Sieving of biochar sample to obtain desired particle size
Surface area and porosity analyser	Poretech CC	Model name: Micrometrics ASAP 2020	CO ₂ adsorption
Vertical tube furnace	Elite Thermal Systems	Model no: TSV15/50/180	Thermogravimetric analysis (TGA)
FTIR analyser	Shimadzu	Model name: Shimadzu IRAffinity-1	Fourier-transform infrared spectroscopy (FTIR) analysis

3.3 Methods

The methods used for sample preparation and characterisation are discussed in this section. In the case that characterisation analysis was completed by external laboratories, the respective method or standard is given.

3.3.1. Sample preparation

Approximately 18 kg of the raw biomass sample was washed twice with tap water and then once with deionised water before air-drying the sample for three days. The raw biomass was then cone and quartered by continually dividing the raw biomass sample into 4 sub-samples to produce a representative sample of 670 g for characterisation. The remaining biomass was used to produce the biochar in a three phase Lenton horizontal furnace, at 950 °C using a heating rate of 10 °C/min and a N₂ flow rate of 2 Nl/min. The temperature profile of the furnace is given in Appendix A-1, which indicates where the effective isothermal zone is located and where the ceramic boats were placed.

Pictures of the bio material before and after charring are shown in Figure 3.1. In general, it was observed that the biomass sample on the left has a larger volume than that of the biochar sample, which is expected due to the reduction in mass from the charring processes. There is a colour change from a light brown to a dark black in the two samples and the biochar sample became more brittle than the biomass sample.



Figure 3.1: Raw biomass (left) and biochar (right)

For the production of 1 kg of biochar, 40 charring runs were completed, with an average weight loss of 83.1 wt% (see Appendix A-2 for more detail). The biochar samples were cone and quartered by hand into 4 equal samples of ± 250 grams each. Three of these samples underwent size reduction to $-150+75\mu\text{m}$ by using a ball mill and sieve sizes $+150\mu\text{m}$ and $+75\mu\text{m}$. All biochar samples were stored in airtight plastic bags, flushed with N_2 and stored inside a fridge which is kept at a constant temperature of 3.5°C .

3.3.2. Characterisation techniques

Several analyses were performed, where some standardised methods were used by external laboratories, as summarised in Table 3.2.

Table 3.2: Characterisation completed by external laboratories

Property	Standard	Operational laboratory
Fibre analysis		
Neutral detergent fiber (NDF)	ASM 060	Agricultural Research Council
Proximate analysis		
Moisture content (wt%)	ISO 11722 : 1999	Bureau Veritas Testing and
Ash (wt%)	ISO 1171:2010	Inspections South Africa
Volatile matter (wt%)	ISO 562:2010	
Fixed carbon (wt%)	By difference	
Ultimate analysis		
Carbon (wt%)	ISO 12902 – CHN	Bureau Veritas Testing and
Hydrogen (wt%)	ISO 12902 – CHN	Inspections South Africa
Nitrogen (wt%)	ISO 12902 – CHN	

Oxygen (wt%)	By calculation	
Sulphur (wt%)	ISO 19579:2006	
Mineral analysis		
X-ray fluorescence analysis	ISO 13909-4: 2001	Bureau Veritas Testing and Inspections South Africa

The raw data obtained from the fibre analysis was used to determine the hemicellulose and cellulose content of the raw biomass sample. The following equations are used for these calculations [77]:

$$\text{Hemicellulose}(\text{wt}\%) = \text{NDF} - \text{ADF} \quad (3-1)$$

$$\text{Cellulose}(\text{wt}\%) = \text{ADF} - \text{ADL} \quad (3-2)$$

The Acid Detergent Lignin (ADL) value obtained from test results was assumed to be equal to the total mass percentage of lignin in the sample [77].

The other analysis techniques used for characterisation were completed at the North-West University and are discussed in further detail in the following sections.

Fourier-transform infrared spectroscopy (FTIR)

Fourier-transform infrared spectroscopy (FTIR) analysis was completed using a Shimadzu IRAffinity-1 at the School of Chemical and Minerals Engineering laboratories at North-West University. Each sample was diluted in potassium bromide powder in a ratio of 1:10 and mixed using a mortar and pestle. After the sample is mixed, a small amount of sample (50 to 100 ng) was placed in the sample plate and placed inside the Shimadzu IRAffinity-1[78].

Scanning electron microscope analysis (SEM)

The surface morphology of both the biomass and biochar samples were captured using a Quanta FEG 250 Environmental Scanning electron microscope (ESEM). In order to improve the conductivity of the samples, they were pre-treated with a carbon coating using a sputter coater. While capturing the pictures a visual inspection was done on both samples. These analyses were completed at the Laboratory of Electron Microscopy (LEM) of the North-West University.

Thermogravimetric analysis (TGA)

A home built Thermogravimetric analysis (TGA) was carried out at the School of Chemical and Minerals Engineering laboratories of the North-West University [79]. Approximately 2 g of raw biomass sample was placed in the sample holder and then the vertical tube furnace is lowered over the sample. Technical grade N₂ is fed to the system with a flow rate of 2 Nl/min, while the temperature of the furnace is set to reach 950 °C with a heating rate of 5 °C/min.

Data was logged every 2 seconds using a RADWAG PS 750/c/2 balance and Advantech VISIDAQ computer software.

CO₂-adsorption

Surface analysis was completed by determining the CO₂ surface area using the Micrometrics ASAP 2020 surface area and porosity analyser at the North-West University. Prior to the CO₂ adsorption process, approximately 0.5 g of sample was degassed under vacuum (10 µmHg) at 380 °C for 24 hours. The CO₂ adsorption analysis was completed in an ice-water bath at 0 °C. The ASAP 2020 v4.01 software automatically obtained the adsorption data. The Brunauer–Emmet –Teller (BET), Dubinin-Astakhov (D-A) and Horvath–Kawazoe (H-K) methods were used to acquire the median pore width, maximum pore volume and surface area of the sample [80].

3.4 Results and Discussion

The results obtained from chemical and structural analyses are discussed in this section for both the biomass and biochar samples.

3.4.1. Chemical Characteristics

Lignocellulosic composition

The fibre analysis results are used to determine the lignocellulosic composition of the biomass sample as discussed in Section 3.3.2 and displayed in Table 3.3.

Table 3.3: Lignocellulosic composition for raw biomass (wt% ar*)

	Hemicellulose	Cellulose	Lignin
Raw biomass	11.1	58.9	19.1

*ar-as received

The biomass sample shows a high cellulose content, while the hemicellulose and lignin contribute only a third of the biomass composition. The lignocellulosic composition of the raw biomass sample is similar to that found other studies for hardwood samples [80], [81], [82], [83]. It has been observed that forest residues generally have hemicellulose content of 13.0 – 39.0 wt% while agricultural residues and energy crops have 18.0 – 35.0 wt% and 15.0 – 32.2 wt% respectively [82]. When comparing the hemicellulose content of 11.1 wt% to these values, the biomass sample tends more to the forest residue classification.

The cellulose content of the sample correlates well with other forest residue cellulose values found in literature which range from 23.7 – 59.7 wt% [80], [81], [82], [83]. Agricultural and forest biomass generally have higher lignin content than that of energy crops. The typical lignin

composition for forest residues range from 18.1 – 34.0 wt% [77], [82], [83]. Materials with a high lignin content generally make the pre-treatment process of biomass more difficult [82].

Ultimate and Proximate analysis

The ultimate and proximate analysis results for the raw biomass (RBM) and biochar (CBM) are presented in Table 3.4. The charring process of the biomass resulted in an increase of fixed carbon content and a decrease in the volatile matter. The results further indicate a decrease in oxygen and hydrogen content, while carbon content is increased. This then leads to a significant decrease in H/C and O/C ratios for the biochar.

Table 3.4: Proximate and ultimate results for raw and charred biomass

Proximate Analysis (wt% adb*)	RBM	CBM
Ash	1.0	2.4
Volatile matter	79.6	4.2
Fixed carbon	10.1	91.9
Moisture content	9.3	1.5
Ultimate Analysis (wt% daf*)		
Carbon	45.5	94.6
Hydrogen	5.4	0.2
Nitrogen	0.05	0.6
Total Sulphur	0.04	0.03
Oxygen	39.8	4.4
H/C	1.42	0.03
O/C	0.66	0.03

*adb – air dry basis, daf – dry ash free

Using the data obtained from the ultimate analysis, a Van Krevelen plot is made to compare the molar H/C and O/C ratios of the biomass with that of a typical Highveld coal used in another study [67] and being used as comparison to coal in the reactivity study. The results are shown in Figure 3.2.

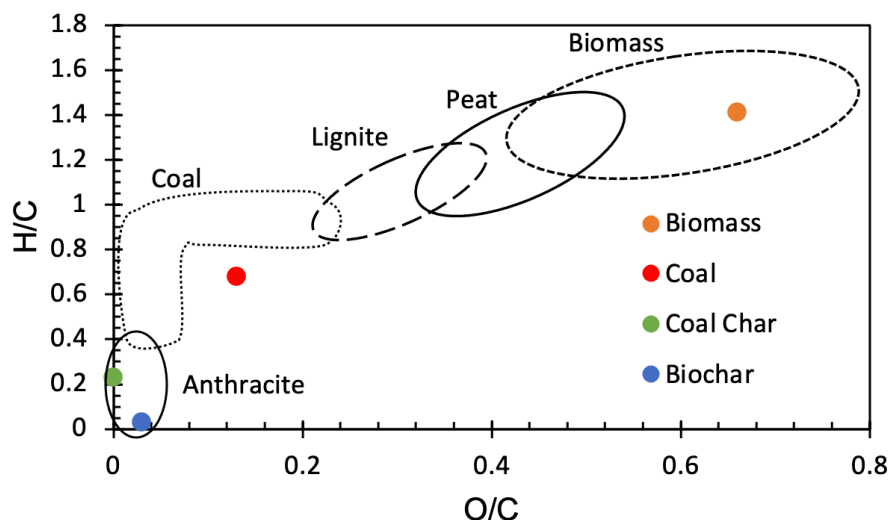


Figure 3.2: Van Krevelen plot of biomass and Highveld coal samples

According to this diagram, the H/C and O/C ratios of the biomass sample fall in the range to be classified as a biomass. The biochar sample has low ratios of H/C and O/C which classifies it as an anthracite. While the coal char, with which the reactivity of the biochar will be compared to, also showing an anthracite classification. The major difference between the biochar and coal char samples is the oxygen content of the biochar sample which is higher than that of the coal.

X-ray fluorescence analysis (XRF)

In Figure 3.3, the results obtained from X-ray Fluorescence spectroscopy are displayed. The use of the XRF analysis allows for the detection of major and trace elements in rocks, minerals, and sediment [84].

The four major elements detected from the analysis were Si, Fe, Ca and S, which correlate well with values obtained from literature for woody chars [49]. The content of the Si species in woody ash has been found to be lower (7.33 wt% [85] and 8.84 wt% [86]) than the 25 wt% obtained for the biomass sample. The high amount of Si species in the sample indicates that sand may be present in the sample. The amount of Al in the biomass sample is relatively high compared to literature values which range from not detected to 2.3 wt% [49] [85] [86]. However, in a study done on inorganic elements of biomass, higher Al values for barley straw have been reported [87].

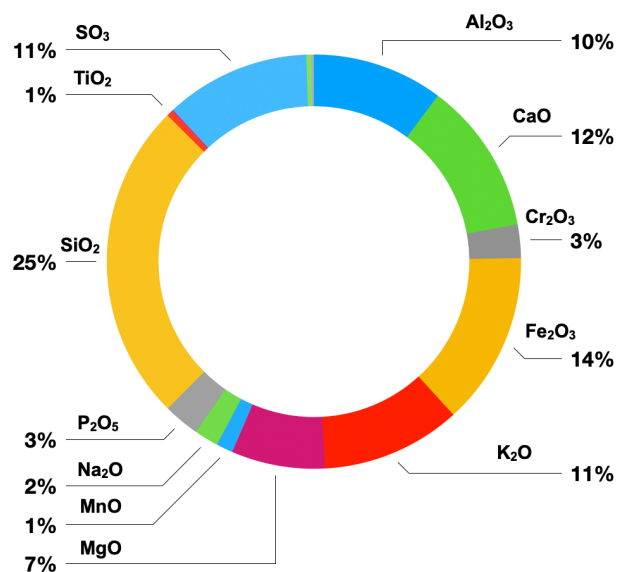


Figure 3.3: X-ray Fluorescence spectroscopy results

Energy Dispersive X-Ray Spectroscopy (EDS)

The elemental composition of the samples were also determined by Energy Dispersive X-Ray Spectroscopy (EDS) analysis and the results are displayed in Table 3.5. The results from the analysis indicate that both samples consist of the two main components which are carbon and oxygen.

The relative high detection limits of this characterisation technique resulted in only carbon and oxygen being considered. The difference in the EDS results and results obtained from the ultimate analysis for the biochar sample is less than 2 wt% for both carbon and oxygen content. However, the ultimate analysis results for the raw biomass has a larger difference in both the carbon and oxygen content which are 11 wt% and 5 wt% lower respectively.

Table 3.5: Results of Energy Dispersive X-Ray Spectroscopy (wt%)

Sample	C	O
RBM	56	44
CBM	93	6

The O/C ratio calculated from the EDS is 0.59 and 0.048 for the biomass and biochar respectively. These values are comparable to the values obtained from the ultimate analysis which are 0.66 for biomass and 0.030 for biochar and do not affect the Van Krevelen plot classifications.

Fourier-transform infrared spectroscopy (FTIR)

The results obtained from the FTIR spectra analysis for both samples are shown in Figure 3.4. The peaks for the raw biomass sample that are between 1000-1500 cm^{-1} indicate -CO groups, while the peaks between 1500-2000 cm^{-1} indicate both -C=O and C=C groups [88] [89]. The raw biomass sample also contains -CH and -OH groups identifiable by the peaks at 2700 cm^{-1} and 3300 cm^{-1} respectively [88] [89].

The biochar sample displays peaks at 700 cm^{-1} which indicate aromatic C-H stretching. The biochar's graph has peaks between the 1500-2000 cm^{-1} range, similar to that of the biomass sample, which are indicative of aromatic C=C stretching [90]. There are differences in the graphs for both samples, indicating that the functional groups have changed from the raw sample to the biochar sample. The first difference observed is the biochar peak at 700 cm^{-1} which indicates the presence of adjacent aromatic hydrogen in the biochar [90]. The biochar's plot flattens more than the raw biomass plot, this correlates with results found in literature [91]. The plateau from the biochar results indicate that functional groups of -CO, -C=O, -CH and -OH have been removed from the sample due to charring.

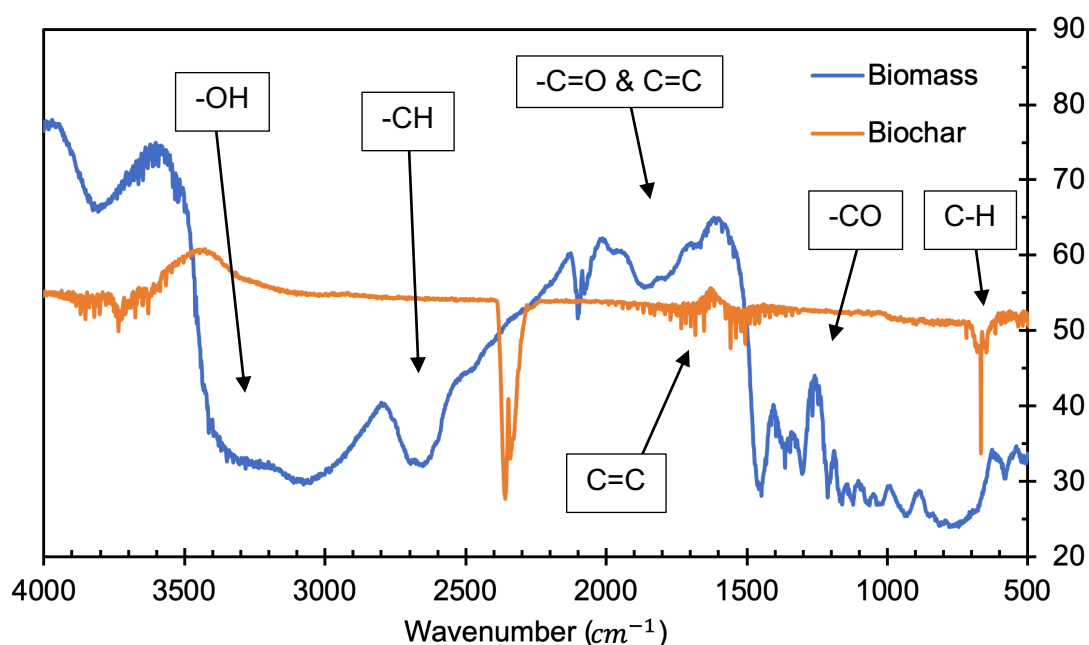


Figure 3.4: Fourier-transform infrared spectroscopy (FTIR) analysis results for both raw biomass and biochar

3.4.2. Structural Characteristics

Scanning electron microscope analysis (SEM)

The figures obtained from the SEM analysis, for both the raw biomass and biochar are displayed in Figure 3.5 and 3.6. From the raw biomass figures (Figure 3.5 a-b), the main structural form of the woody sample can be seen, with both the vertical and horizontal fibres [85]. Mechanical damage to the woody sample is detected from the figures due to the curve shape of the sample at ends (indicated by the circles). This damage might be a result of the hammer mill used to reduce the particle size of the raw biomass sample.

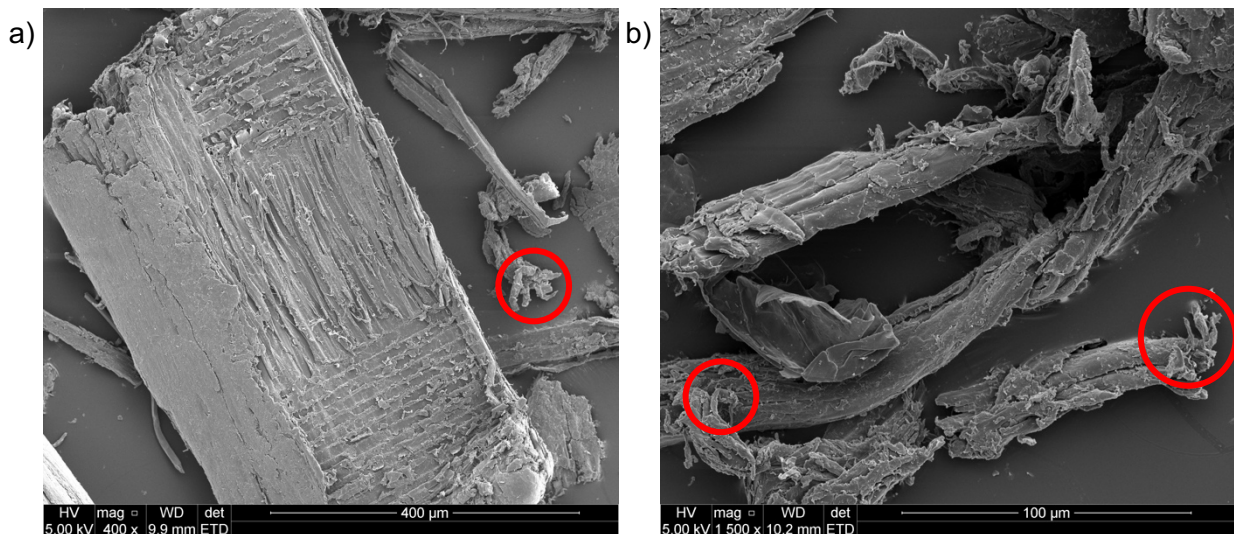


Figure 3.5: Scanning electron microscope analysis (SEM) analysis for raw biomass sample at a) 400 µm and b) 100 µm

The main observation from the biochar figures (Figure 3.6 a-d), is that the sample is more brittle and shows more small breakages and cracks than the raw sample (as shown by the circles). Ash is observed from the biochar figures as well as the same woody structure from the raw biomass figures. The biochar has a more homogeneous structure than that of the raw biomass, which is seen from Figure 3.6 c), where the different layers which are present in the raw biomass are 'grown' together in the biochar.

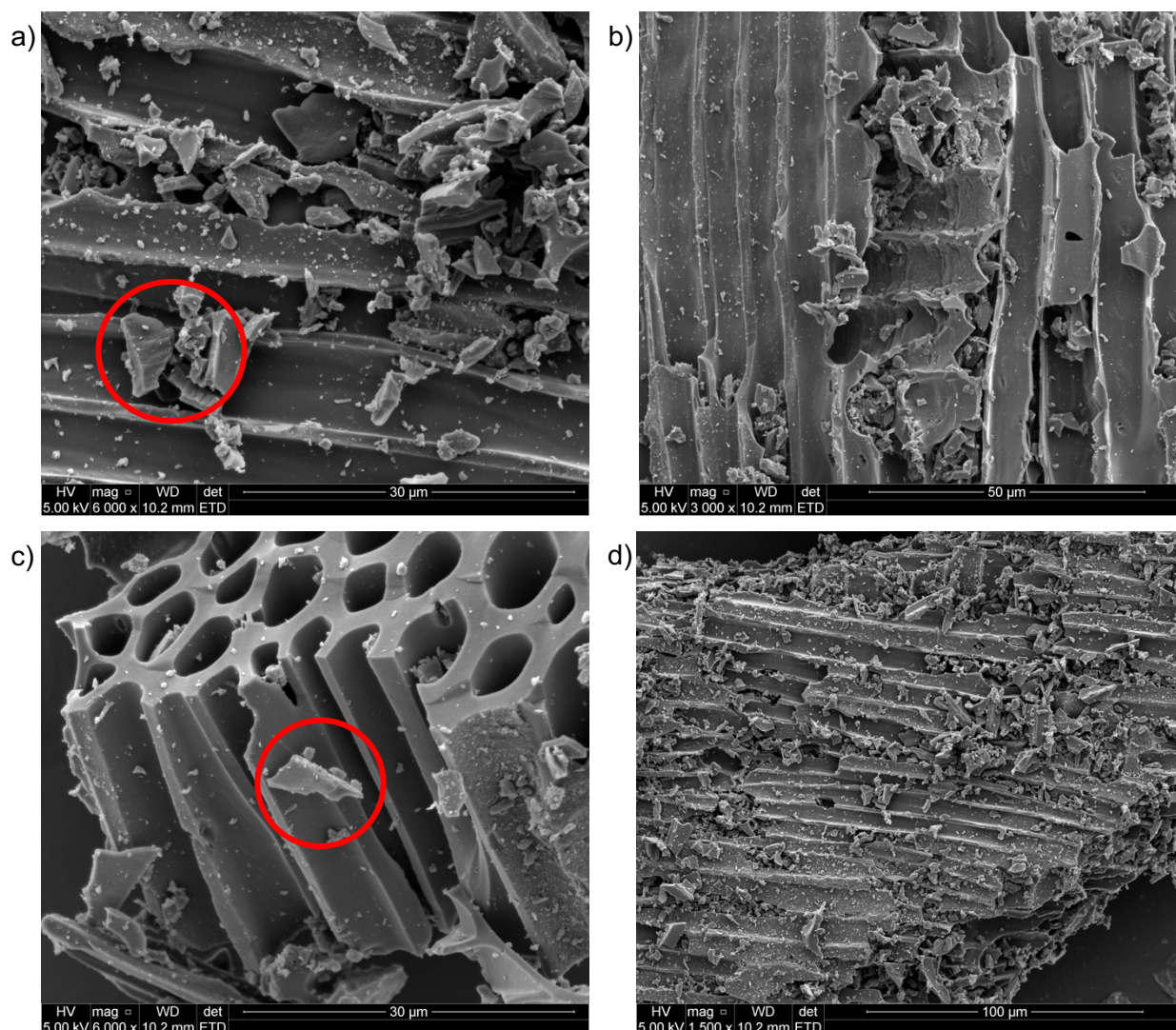


Figure 3.6: Scanning electron microscope (SEM) analysis results for biochar sample at a) 30 μm , b) 50 μm , c) 50 μm and d) 100 μm

Thermogravimetric analysis (TGA)

A thermogravimetric analysis (TGA) was completed on the raw biomass sample and the results are shown in Figure 3.7. From the graph it is seen that most of the mass loss occurs between the 300 and 440 $^{\circ}\text{C}$ range, which is an indication of the moisture content and volatile matter being reduced from the sample.

According to the proximate analysis the difference in volatile matter between the raw biomass sample and the biochar is 83.4 wt%, which correlates with the value of mass loss observed from the TGA data (more than 80 wt%). The mass loss of 83 wt% obtained from the charring runs also correlate with the TGA results which indicates a mass yield of less than 20 wt%.

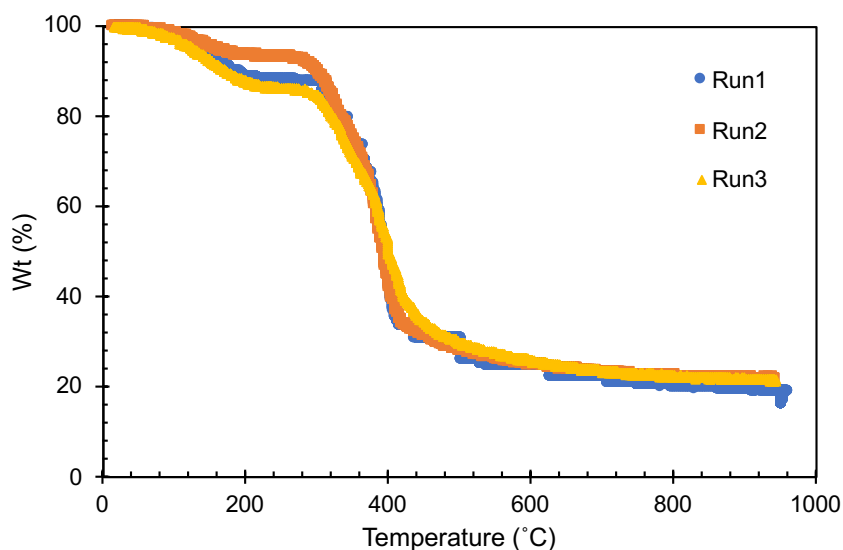


Figure 3.7: Thermogravimetric analysis (TGA) results for biomass sample

CO₂ gas adsorption

A summary of the CO₂ gas adsorption results is displayed in Table 3.6.

Table 3.6: CO₂ gas adsorption results

Parameter	Technique	Biochar
SA (m ² /g)	BET method	331
Micropore SA (m ² /g)	Dubinin-Astakhov	466
Average pore width (Å)	Horvath-Kawazoe	3.7

SA - surface area

The surface area determined by the BET method is in the range of the unreacted biochars studied by other authors on woody/plant base derived chars [91], [92], [93]. In a study on steam gasification of miscanthus derived chars produced at 800°C, the author found a micropore SA of 476.7 m²/g [92]. This value is in agreement with results obtained for the biochar micropore SA using the DA-method. It is known that chars are porous materials where the surface area of the inner pore walls are larger than the external surface area [94]. This results in different reaction rates for different chars with the same external surface area. It is assumed that the biochar surface is dominated by micropores because the average pore width is less than 20 nm [83] [84]. The internal surface area can be related to the characteristics of these micropores, which in return affects the gasification rate [67].

3.5 Summary

Various characterisation techniques were used to compare the biomass and biochar samples. In general, it was found that the carbon content in the biomass sample increased due to the charring procedure. Functional groups such as -CO, -C=O, -CH and -OH identified in the biomass sample became less prominent in the biochar sample. While the biochar sample becomes more brittle than the raw biomass sample, even though the structural form remains constant for both samples. From the TGA the biomass sample losses +/- 80% of the total mass which correlate well with the sample mass produced during sample preparation of the biochar. From comparing the results with that found in literature, it can be concluded that the biomass and biochar samples correlates with other woody/plant based biomass and biochar materials. A summary of the biomass and biochar characterisation is shown in Table 3.7.

Table 3.7: Summary of biomass and biochar characterisation

Parameter	Biomass	Biochar
<i>Fibre analysis (wt%)</i>		
Hemicellulose	11.1	ND
Cellulose	58.9	ND
Lignin	19.1	ND
<i>Proximate analysis (wt%-adb)</i>		
Ash	1.0	2.4
Volatile matter	79.6	4.2
Fixed carbon	10.1	91.9
Moisture content	9.3	1.5
<i>Ultimate analysis (wt%-daf)</i>		
Carbon	45.5	94.6
Hydrogen	5.4	0.2
Nitrogen	0.05	0.6
Total Sulphur	0.04	0.03
Oxygen	39.8	4.4
<i>Gross calorific value (MJ/kg)</i>		
CV	18.1	30.4
<i>Micropore surface area (m²/g-daf)</i>		
D-A method	ND	477

Chapter 4: Experimental of Gasification

4.1 Introduction

The experimental methods used during the experimentation are discussed in this chapter. In Section 4.2, the materials used to conduct the experiments are described, which includes the chemicals and gases used. The high pressure reactor setup is described in Section 4.3 followed by the description of the operation procedures in Section 4.4. The methods used to process the data obtained from experiments are discussed in Section 4.5. The rig was assessed by conducting a mass balance which is described in Section 4.6, while in Section 4.7 the regime identification is discussed. This chapter ends with an uncertainty analysis in Section 4.8.

4.2 Materials

A summary of all the materials used to complete experimentation is given in Table 4.1.

Table 4.1: Materials used for experiments

Biochar		
Name	Supplier	Detail
Biochar	SAPPI	<i>eucalyptus nitens</i> woodchips (prepared as detailed in Section 3.3.1)
Chemicals		
Name	Supplier	Detail
Methanol	Sigma-Aldrich	Used as solution for HPLC pump, Purity: > 99.9%
Iso-propanol	Rochelle Chemicals	Used for cleaning pump filter. Purity: > 99.7%
De-ionised water	Immuno-Vet Services	Used as feed to the steam generator. Ultra-high purity
Gasses		
Name	Supplier	Detail
Nitrogen	Afrox South Africa	Used as calibration gas for analyser and inert gas during gasification experiments Purity: > 99.999%
Carbon dioxide (calibration gas)	Afrox South Africa	Used as calibration gas for analyser Concentration: 1041ppm, balance N ₂

Name	Supplier	Detail
Carbon monoxide (calibration gas)	Afrox South Africa	Used as calibration gas for analyser Concentration: 1650ppm, balance N ₂
<i>Other</i>		
Name	Supplier	Detail
Molecular sieves	Sigma-Aldrich	UOP type 3Å molecular sieves (3.2 mm pellets), used for the moisture trap.

4.3 Experimental setup

A high pressure fixed bed gasification rig (laboratory scale reactor) is used to carry out all reactivity experimental work. The schematic representation and list of components are displayed in Figure 4.1 and Table 4.2 respectively. All gases used for experiments are stored in high pressure cylinders and the water used to produce steam is stored in a sealed container. A constant nitrogen pressure supply throughout experiments is ensured by pressure regulator with gauge pressure of 0-52 bar (3). The HPLC water pump has its own pressure gauge and volumetric flow controller to feed the steam to the reactor. Calibration on the flow of the pump is detailed in Appendix B-1. The mass flow controller (5) is used to control the nitrogen gas flow to the system and the calibration is given in Appendix B-2.

The mixture of steam and nitrogen gas enters a 93 cm $\frac{3}{4}$ " scheduled 40 alloy C276 pipe reactor (12). An evolution on the reactivity of the pipe with steam is detailed in Appendix C-1. Inside the pipe reactor is a sample bed (14) which is supported by a porous quartz filter disc with an average pore size of 15-40 μm . A vertical spilt-tube furnace (13) is used as heating source for the reactor. The furnace is equipped with a N-type thermocouple and Eurotherm PID (model 201) temperature controller, to measure and control the temperature inside the furnace. The effective heat length of the pipe reactor is ± 40 cm at the centre, with a 5 cm isothermal zone [97]. A 3 mm K-type thermocouple (11) is located inside the reactor, which is placed ± 5 mm above the sample bed and is used to take temperature readings during experimental runs.

Additional heating wires located between the reactor and the condenser unit (16) are maintained at a temperature of 250 °C, and this is monitored using a K-type thermocouple. The condenser unit (16) consists of 3 containers located inside an ice-bath constructed at the NWU-Potchefstroom campus. After the products formed from experimental runs flow through the condenser unit, the gases are then carried through a moisture trap (17), to remove

moisture remaining in the product gas. Further, the effluent flows through a filter (18) with a 15 μm aperture to remove any excess particles, which protects the downstream equipment.

An electric pressure controller (EPC) is installed downstream of the filter to maintain the total system pressure. Downstream of the EPC (20), a thermal mass flow meter (22) is installed to determine the total flow of product gas through the EPC towards the gas analysers. Both the EPC and MFM readings are logged during experiments to ensure reaction conditions remain constant. A RS-232 data interface is used to communicate between these instrumentation units and the computer. These measurements were logged using the Flow Plot software designed for Bronkhorst High Tech instruments.

The stream is split into an analysis stream and purge stream. The analysis stream flows through a rotameter, which monitors the flow rate (maximum flow of 1 NL/min) towards the non-dispersive infra-red (NDIR) analysers (24) (25). Fractions of both CO and CO₂ in the product gas is measured by the analysers and logged every 3 seconds. The data logged is then saved in Excel by using Excel VBA coding. Both analysers are calibrated before experimental runs using both calibration gases.

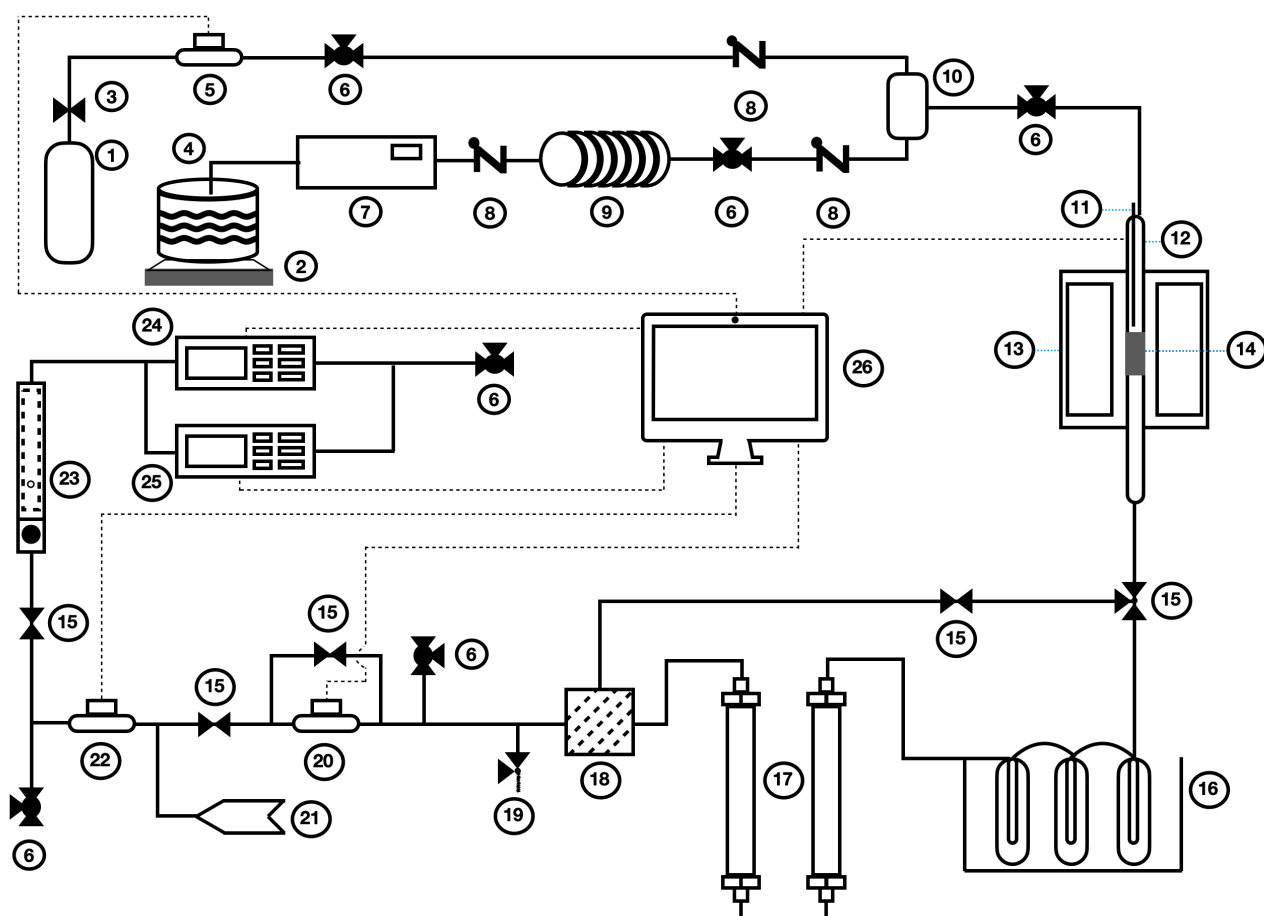


Figure 4.1: Experimental rig

Table 4.2: Component list of experimental rig

Number	Name	Model	Description
1	Nitrogen gas cylinder	Afrox Baseline 5.0	-
2	Scale	Vibra AB3202	3200 g capacity
3	Pressure regulator	-	-
4	Water reservoir	-	Glass container (1000 ml)
5	Nitrogen mass flow controller	Bronkhorst type EI-Flow	0.000-5.000 NL/min
6	Purge	-	-
7	HPLC pump	Chrome-tech LS-Class pump	Flow rate: 0.000-4.999 ml/min Pressure: ambient to 49 MPa
8	Check valve	-	-
9	Steam generator	Thermon SA cartridge elements	Ambient to 450 °C
10	Mixing point	-	-
11	K-type thermocouple	-	-
12	Reactor pipe	Multi-alloys C276 alloy	Ambient to 120 bar & 1000 °C
13	Furnace	Carbolite VST 12/100/200	Ambient to 1200 °C
14	Sample bed	-	Porous quartz frit (pore size - 40+15 µm)
15	Valve	-	-
16	Steam condenser	-	2.5 L capacity
17	Moisture trap	-	Filled with UOP type 3Å molecular sieves
18	Filter	-	-
19	Pressure safety release valve	-	-
20	Electronic pressure controller	Bronkhorst type EI-Press	Ambient to 80 bar
21	Calibration gas	Afrox	CO 1650ppm balance N ₂ CO ₂ 1041ppm balance N ₂
22	Thermal mass flow meter	Bronkhorst type EI-Flow	0-2.0 NL/min
23	Rotameter	-	-
24	CO analyser	ADC MGA3000 analyser	NDIR: 50-5000 ppm
25	CO/CO ₂ analyser	Venus pro (P0256-8000)	NDIR CO: -250 – 5500 ppm NDIR CO ₂ : -250 – 5500 ppm
26	Computer	-	-

4.4 Experimental procedure

At the start of an experimental run, a biochar sample between 0.3-0.5 g was weighed and placed on top of the quartz filter disc located inside the tubular reactor. After the reactor is reconnected to the rig, nitrogen was introduced to the system. The nitrogen flow rate is controlled by the mass flow controller, which is set to the desired set point using the Flow View software on the computer.

Heating wires located prior to the mixing chamber are set to $105 (\pm 2) ^\circ\text{C}$ and the steam generator temperature has a set point of $360 (\pm 12) ^\circ\text{C}$. Before switching on the HPLC pump, the purge valve located downstream from the steam generator is opened. The water flow rate was then set using the HPLC pumps user interface and steam starts flowing from the purge line to ensure actual flow.

Prior to each run, the furnace was set to a desired reaction temperature. Once this temperature has been reached the furnace was closed over the pipe reactor. The required reaction temperature at the sample bed was monitored by the thermocouple located inside the reactor. Nitrogen was used to flush the biochar sample to ensure an inert environment inside the reactor. After a flushing period of 30 min, the reactor was pressurised to the required pressure of that specific experiment.

The desired pressure was set using the Flow View software on the computer, which communicates with the EPC to control the total system pressure. The ice bath where the condensers are located, was filled with ice. Once the isobaric and isothermal conditions were reached the steam was introduced into the system by closing the purge valve located downstream from the steam generator. Thereafter the data logging was started on the computer. The ice level was monitored throughout each experiment to ensure that the water contained inside the product gas was condensed before flowing through downstream equipment.

After the gasification reaction was finished, the logging software and steam pump were switched off. This was followed by the depressurisation of the system, by bypassing the EPC and opening the purge valve downstream from the MFM. Once the total system pressure was below 5 bar the water is removed from the condensers. Then the system was further depressurised to a pressure below 1 bar. The reactor can now be removed from the furnace and allowed to cool down to room temperature before closing the nitrogen flow. Lastly, the reactor pipe was removed from the rig and the remaining sample collected from the reactor.

4.5 Data processing

4.5.1. CO and CO₂ concentration

After an experimental run is completed the raw data obtained is imported to Excel where the fraction of CO and CO₂ are then plotted over time. The fractions of both CO and CO₂ were logged every three seconds, which resulted in a visibly continuous line on the plot although individual measurements were taken. To illustrate the data processing method, a high pressure and complete conversion run were performed. This experiment was carried out at 720 °C and a total pressure of 20 bar with 50% steam (10 bar steam partial pressure). The results of the experimental run are displayed in Figure 4.2a and Figure 4.2b.

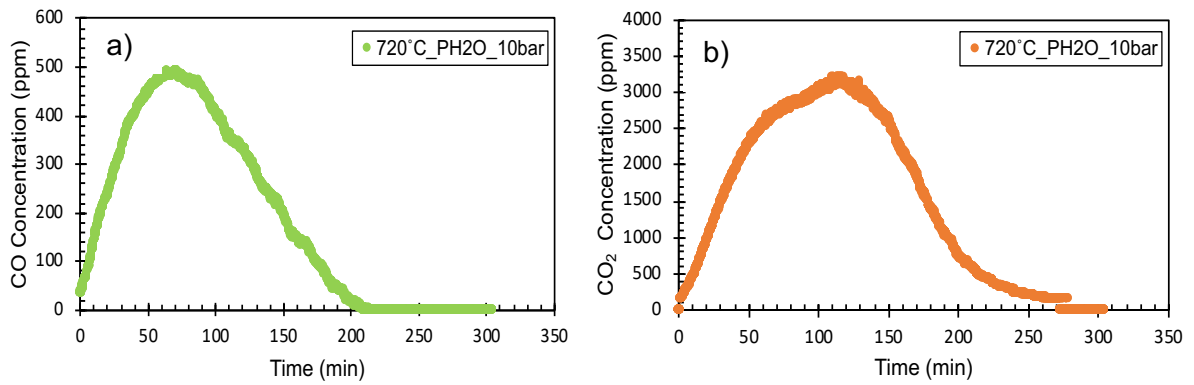


Figure 4.2: Gas fraction as a function of time for biochar steam gasification

Comparing the two graphs it can be observed that the CO₂ is the more dominant product. Both Figure 4.2a and Figure 4.2b show a graduate increase and decrease in concentration. The peak concentration of CO is reached before the peak concentration of CO₂ is reached.

4.5.2. Conversion

After the concentrations of both products are obtained, the amount of carbon reacting with steam per second was determined using reaction stoichiometry and the product gas flow rate. The following equation is used to calculate the carbon conversion at each time interval:

$$r_c = (y_{CO} + y_{CO_2})(\dot{n}_t)(MW_c) \quad (4-1)$$

Where y_{CO} and y_{CO_2} are the fraction of CO and CO₂ respectively, $\dot{n}_t$ is the total molar flow rate and MW_c is the molecular weight of carbon. Thereafter, the amount of carbon remaining in the sample is determined by calculating the amount of carbon reacted at each time interval. Equation 4-2 was used to calculate the carbon reacted after time (t).

$$\Delta m_c(t) = \int_0^t r_c dt \approx \frac{\Delta t}{2} [Rc(t_0) + 2Rc(t_1) + \dots + 2Rc(t_{n-1}) + Rc(t_n)] \quad (4-2)$$

Where Δt is equal to 3 seconds, which is the time interval between each reading. Equation 4-3 was used to determine the total amount of carbon in the unconverted sample ($m_{c,o}$).

$$m_{c,o} = m_{s0}(1 - x_{ash})(x_c(daf)) \quad (4-3)$$

m_{s0} is the initial sample mass, x_{ash} the fraction of ash yield and $x_c(daf)$ the carbon fraction on a dry ash free basis obtained from the ultimate and proximate analysis. Lastly, the conversion is calculated on a dry ash free basis using Equation 4-4.

$$X(t) = \frac{\Delta m_c(t)}{m_{c,o}} \quad (4-4)$$

The conversion plot for the experiment carried out at 720 °C and a total pressure of 20 bar with 50% steam is displayed in Figure 4.3.

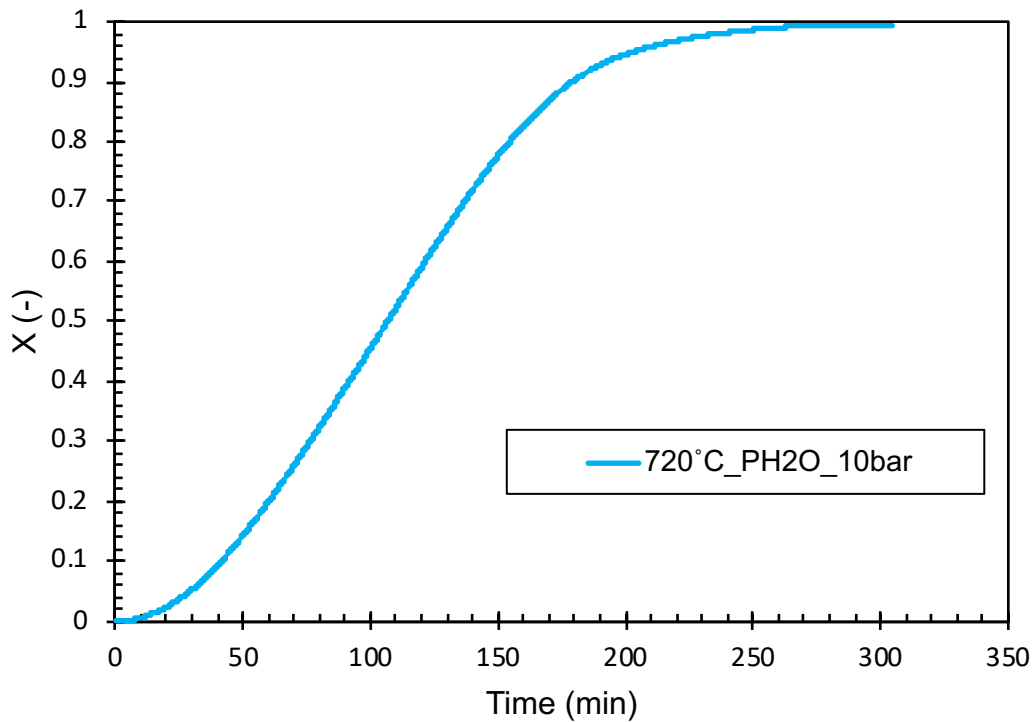


Figure 4.3: Conversion as a function of time for biochar steam gasification

4.5.3. Specific reaction rate

After calculating the carbon conversion rate (r_c), it is normalised with the amount of unreacted carbon in the biochar sample at the reaction time. This normalised reaction rate is termed as the specific reaction rate (r_s). The same normalisation technique was used by other authors to describe the specific reaction rate of steam gasification [46] [56]. The specific reaction rate is given by Equation 4-5.

$$r_s = \left(\frac{1}{1-X} \right) \left(\frac{dX}{dt} \right) \quad (4-5)$$

In Figure 4.4, the specific reaction rate of the 20 bar and 50% steam gasification at 720 °C is plotted as a function of conversion.

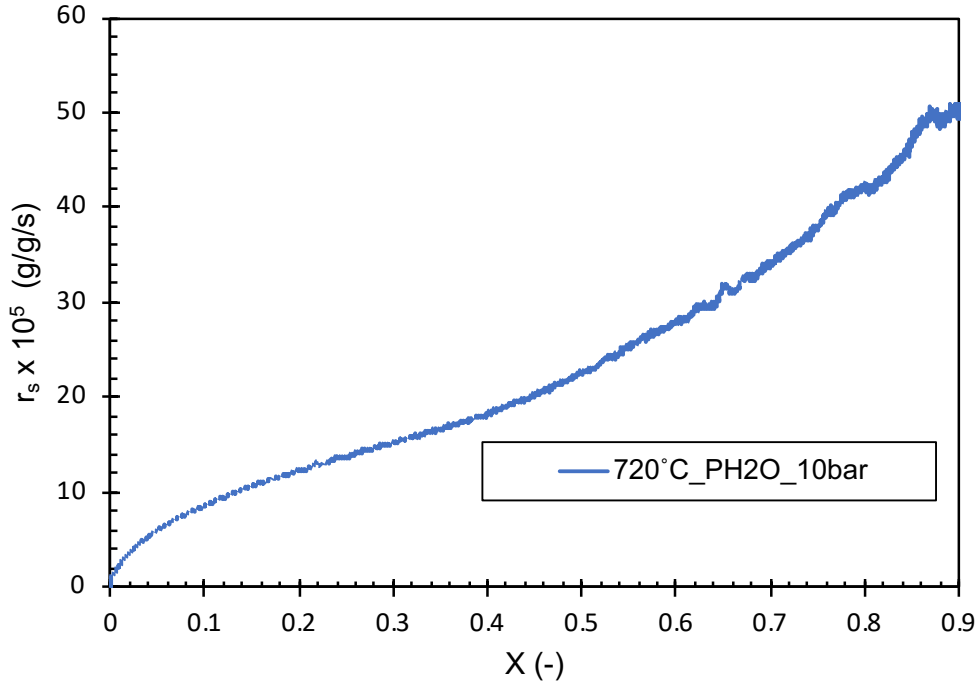


Figure 4.4: Specific reaction rate as a function of conversion

For the discussion of kinetics, the specific reaction rate at 20% conversion was determined in order to obtain a better relation of kinetics at different operating conditions. A conversion of 20% was chosen, because it is close to initial characteristics and compensates for the residence time from experimental procedure.

4.6 Carbon balance

The accuracy of the system was also tested by performing various full conversion steam gasification experiments. The initial mass, temperature, total pressure and steam concentrations were varied to evaluate the carbon mass balance over a range of conditions. The initial carbon mass inside the sample ($m_{c,cal}$) was hereby determined using Equation 4-3.

The initial amount of carbon was compared to the amount of carbon converted ($m_{c,exp}$), which was calculated from the CO and CO₂ concentration curves obtained during experiments. These results are shown in Table 4.3.

Table 4.3: Carbon mass balance calculations

Temperature (°C)	Total pressure(bar)	Steam partial pressure(bar)	$m_{c,cal}$ (daf) (g)	$m_{c,exp}$ (daf) (g)	Mass balance closure (%)
760	Ambient	50 %	0.2283	0.2436	93
760	Ambient	50 %	0.3646	0.3349	92
760	2	1	0.4567	0.4593	99
720	20	10	0.2751	0.2673	97
720	20	10	0.2743	0.2729	99
720	30	20	0.2308	0.2221	96
690	30	20	0.4557	0.4482	98

The maximum deviation obtained was smaller than 9%. This value indicates that the amount of carbon calculated using the results obtained from the biochar characterisation agrees well with the amount of carbon converted calculated from the concentration curves obtained from experiments.

In general, the calculated amount of carbon in the sample is larger than of the converted carbon during an experiment. The converted carbon is determined by only measuring the CO and CO₂ fractions, and other gasses such as CH₄ were not considered. This could be the reason for the small deviation, and under prediction of carbon in the feed. However, at elevated pressure the formation of CH₄ is expected to be more, which is not observed here. It was therefore concluded that the use of only CO and CO₂ analysers are sufficient in terms of determining the carbon reactivity from these experiments.

4.7 Regime identification

The operating conditions were chosen to represent industrial conditions (high pressure), however as noted from the literature review to investigate the intrinsic reaction kinetics the experiments should be completed in the chemical reaction controlled regime. To ensure these experimental conditions, several experimental runs were completed at different temperatures, pressures and using different particle sizes.

To investigate the influence of particle size on the conversion rate a biochar sample is prepared under the same conditions as described in Section 3.3.1 with a particle size range of -500+425 μm . The specific reaction rates were determined for both the -150+75 μm and -500+425 μm samples at each operating condition. Firstly, the samples were gasified at an elevated pressure of 20 bar with 10 bar partial pressure steam at various temperatures.

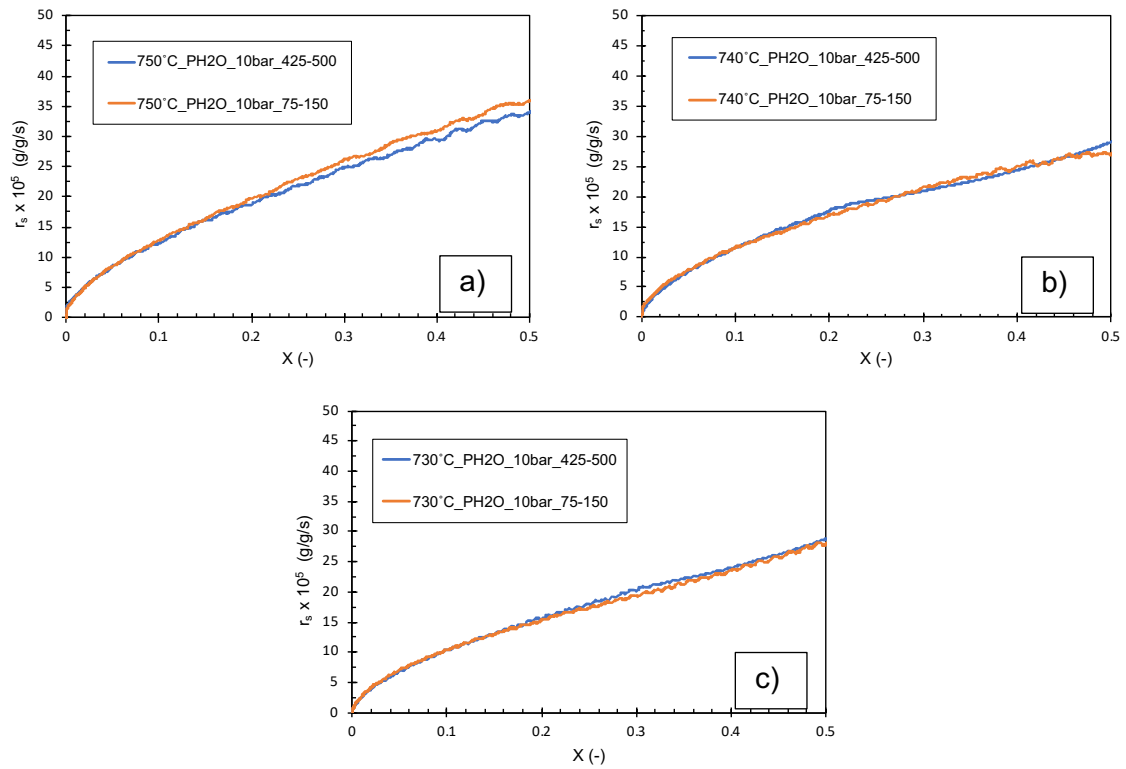
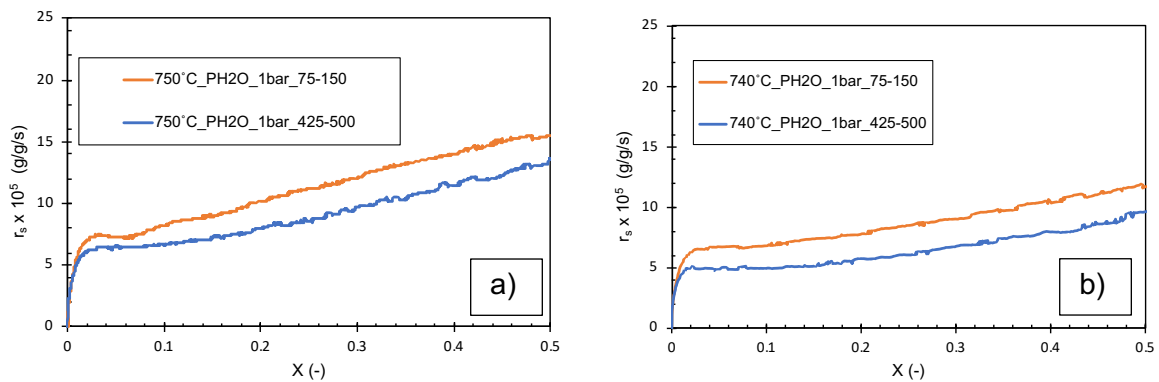


Figure 4.5: Specific reaction rate of small and large char particles at 10 bar steam for a) 750 °C, b) 740 °C and c) 730 °C

When comparing the graphs from Figure 4.5a to Figure 4.5c the specific reaction rate is not affected by the particle size. It is assumed to be in the chemical controlled reaction regime for all temperatures below 750°C at 20 bar with 10 bar steam partial pressure. The influence of particle size is further tested at the lowest pressure of 2 bar and 1 bar steam partial pressure to ensure that all experimental runs are also here operated in the chemical controlled regime.



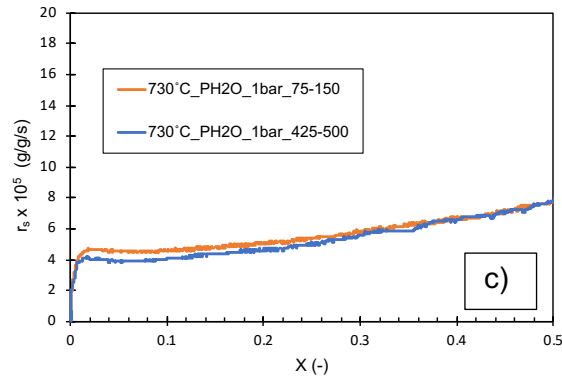
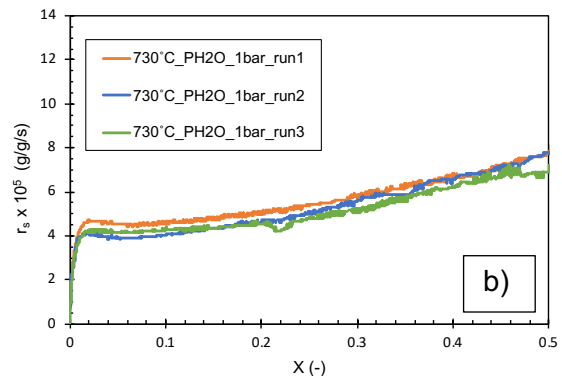
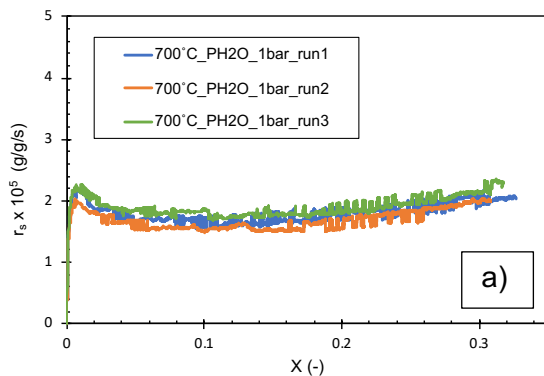


Figure 4.6: Specific reaction rate of small and large char particles at 1 bar steam for a) 750 °C, b) 740 °C and c) 730 °C

The graphs from Figure 4.6a and Figure 4.6b indicate that the specific reaction rate is affected by particle size, and are smaller for the larger particle size. By decreasing the temperature from 740 °C to 730 °C the effect of particle size on the reaction rate becomes insignificant. The percentage difference between the small and large particle reaction rates were determined and it indicated that the difference at 1 bar for 750 °C and 740 °C was larger than 16%. It is therefore assumed that at a temperature of 730 °C and below, the operating conditions for this pressure range (1-10 bar steam partial pressure) will be in the chemical reaction controlled regime.

4.8 Uncertainty analysis

In order to determine the experimental repeatability, three experimental runs were completed at the same operating conditions. These repeated runs were completed at some extremes of the operating conditions in order to ensure experimental repeatability throughout all the experimental runs. These experimental results are shown in Figure 4.7a-d.



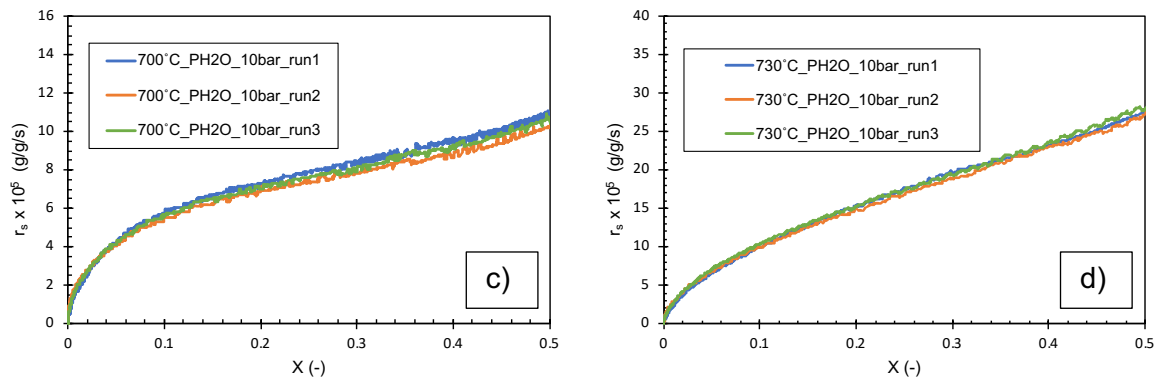


Figure 4.7: Experimental repeatability for different operating conditions for biochar at a) 700 °C 1 bar steam, b) 730 °C 1 bar steam, c) 700 °C 10 bar steam and d) 730 °C 10 bar steam.

To determine the experimental error a t-distribution with 95% confidence interval was used, and detailed calculations are shown in Appendix D-1. The experimental uncertainty obtained for the 700 and 730 °C at 1 bar steam partial pressure was 18% and 14% respectively. While an average uncertainty of 8% and 6% were obtained for 10 bar steam partial pressure at 700 and 730 °C. These results suggest that the repeatability at lower pressures are less than that of higher pressure, which is mainly caused by the relative low gas concentrations, that are then measured closest to the detection limit of the gas analysers (CO: -250 ppm to 5500 ppm and CO₂: -250 ppm to 5500 ppm). However, the results indicate good repeatability throughout experimental operating conditions.

4.9 Summary

Several biochar gasification tests were conducted at various temperatures and pressures to ensure scientific and repeatable experimentation. An inspection of the carbon balance indicated that the use of only a CO and CO₂ analyser is sufficient for an effective determination of the char reactivity. Other gasification tests were completed in order to determine the operating conditions of the experiments under chemical reaction controlled conditions.

From the variation of particle size, temperature and pressure the operating temperature for chemical reaction controlled conditions was determined to be equal to or less than 730 °C. A sample mass of about 0.3 g biochar, with particle size range -150+75 µm, was used for experiments.

A summary of the experimental operating conditions and variables are shown in Table 4.4.

Table 4.4: Experimental operating conditions

Parameter	Gasification conditions
Sample mass	~ 0.3 g
Particle size	-150+75 μm
Total flow rate (STP)	2 NL/min
Steam to N ₂ ratio	1:1
Reaction temperature	700-730 °C
Steam partial pressure	1-10 bar
Total system pressure	2-20 bar

Chapter 5: Results and Discussion

5.1 Introduction

Steam reactivity gasification experiments were carried out at 4 different temperatures and 5 different partial pressures of steam with a constant molar steam to nitrogen ratio of 1:1. The steam gasification reactivity is presented in Section 5.2, where the effect of conversion, temperature and steam partial pressure is discussed. The product formation from biochar and the comparison with coal is given in Section 5.3. In Section 5.4, two kinetic models: the Langmuir-Hinshelwood and Power law model are used to model the obtained reactivity results and the quality of fit (QOF) for both models are discussed. A further comparison with coal reactivity is discussed in Section 5.5 and a summary of the results is given in Section 5.6.

5.2 Steam gasification reactivity

5.2.1. Effect of conversion on specific reaction rate

Figure 5.1 illustrates the specific reaction rate for a conversion of 4 up to 50% for different steam partial pressures (1-20 bar) at 720 °C.

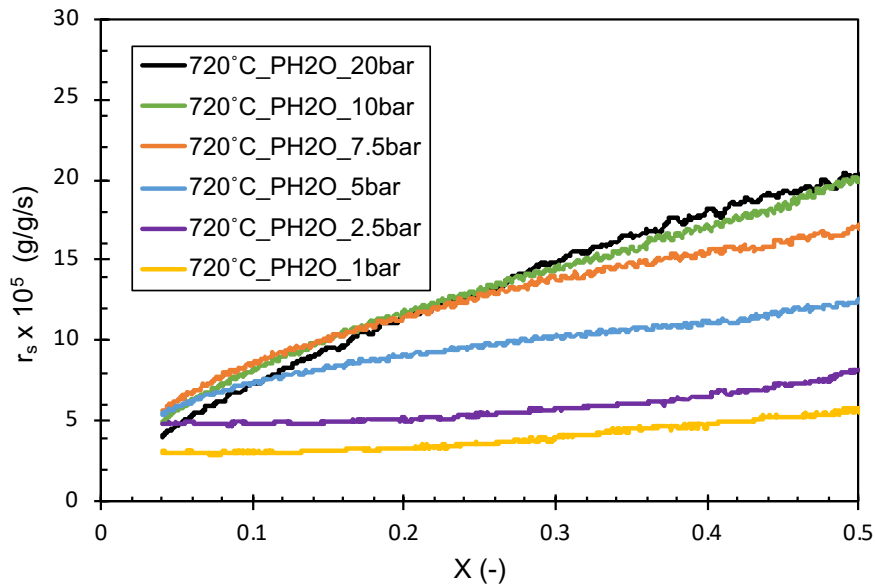


Figure 5.1: Effect of conversion on the specific reaction rate at 720 °C

From Figure 5.1, it is observed that the specific reaction rate increases with an increase in steam partial pressure as well as conversion. The increase in conversion has a more significant effect on the reactivity at elevated pressures (5-20 bar) than at lower pressures (1 and 2.5 bar). However, a form of saturation on the reaction rate is observed at elevated steam partial pressures, where the effect of partial pressure above 10 bar disappears. Previous studies of coal char steam gasification at steam partial pressures above 10 bar

indicated no notable increase in specific reaction rate [64], [65], [45], which is in agreement with the results obtained here. It has been reported that this is a result of an increase in the site occupation to almost complete coverage [45], [46], [65], [67]. Roberts and Harris (2006) reported that for coal steam gasification an increase in steam partial pressure resulted in an increase of the quantity of the surface complexes which again resulted in an increase in the reaction rate [64]. The insignificant change above 10 bar hereby implies that the active char sites are mostly covered and that a further increase from 10 bar steam partial pressure will have a less significant effect on the specific reaction rate.

On the basis of these findings, the experiments were confined to partial steam pressures of 1 – 10 bar in the further discussions. The steam partial pressure for other temperatures (700, 710 and 730 °C) are varied between the range of 1-10 bar steam and are shown in Figure 5.2.

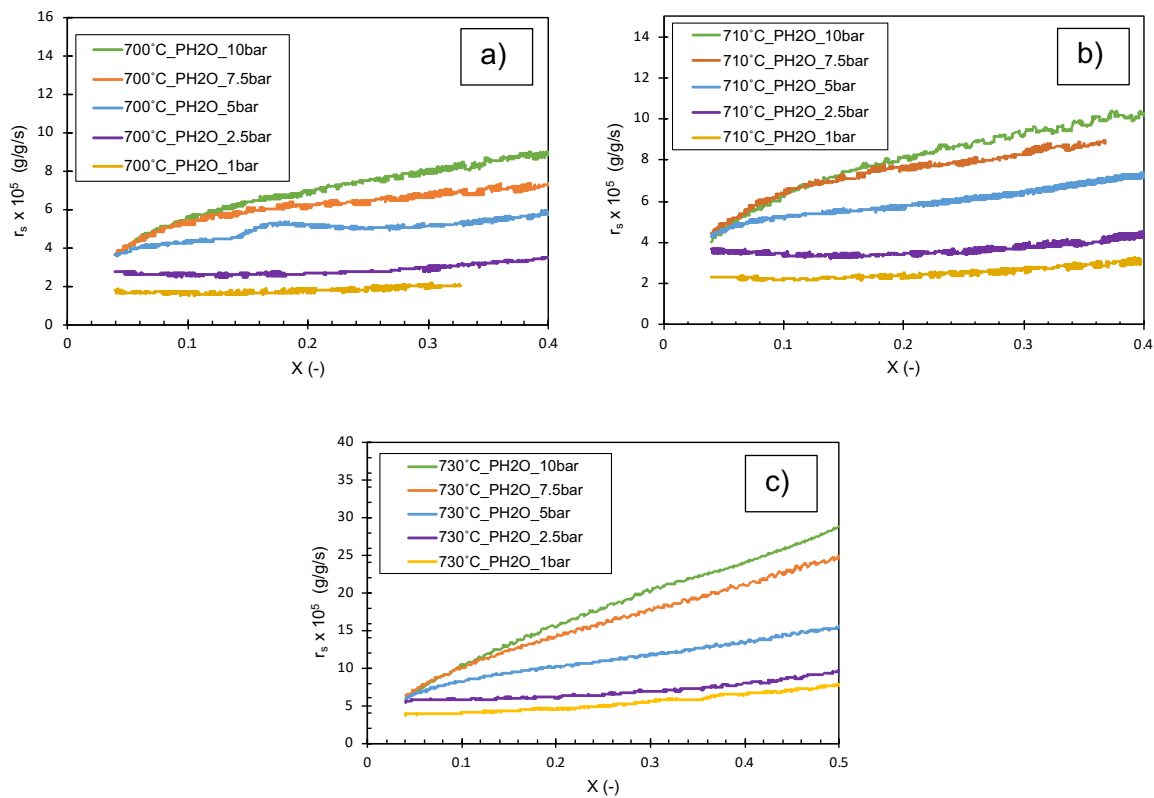


Figure 5.2: Effect of conversion on specific reaction rate at a) 700 °C, b) 710 °C and c) 730 °C

In Figure 5.2, it is seen that the specific reaction rate increases with an increase of conversion throughout all steam partial pressures. This is ascribed to pore development, associated with conversion which is also reported for coal char [46], [67]. For biomass, Ahmed and Gupta (2011) reported a similar increase in reaction rate with conversion up to 30% [41].

The magnitude by which the reaction rate increases over conversion is affected by steam partial pressure and reaction temperature. This trend is further investigated for a conversion range of 10 to 40% and the results are shown in Table 5.1.

Table 5.1: The ratios of $r_{s,40\%}/r_{s,10\%}$ for temperatures of 700-730 °C and steam partial pressures 1-10 bar

Steam partial pressure (bar)	700 °C	710 °C	720 °C	730 °C
1	1.22	1.45	1.59	1.62
2.5	1.29	1.31	1.36	1.37
5	1.34	1.40	1.51	1.63
7.5	1.40	1.39	1.81	2.08
10	1.64	1.64	2.09	2.33

From the values in Table 5.1, it is confirmed that the factor increases with both temperature and steam partial pressure over a conversion of 10-40%. The factor increases from 1.22 at the lowest operating conditions to a factor of 2.33 at the highest operating conditions. These results can be ascribed to pore development and the increase of surface complexes with increase of steam partial pressure. Similar observations were reported for coal derived char with CO₂ gasification, where the pore volume and surface area of the char increased with higher CO₂ partial pressure [98].

5.2.2. Effect of temperature on specific reaction rate

The effect of temperatures ranging from 700 to 730 °C on the specific reaction rate for different steam partial pressures are illustrated in Figure 5.3. For the analysis of the kinetics, the specific reaction rate at 20% conversion is further used to obtain a kinetic relation at different operating conditions.

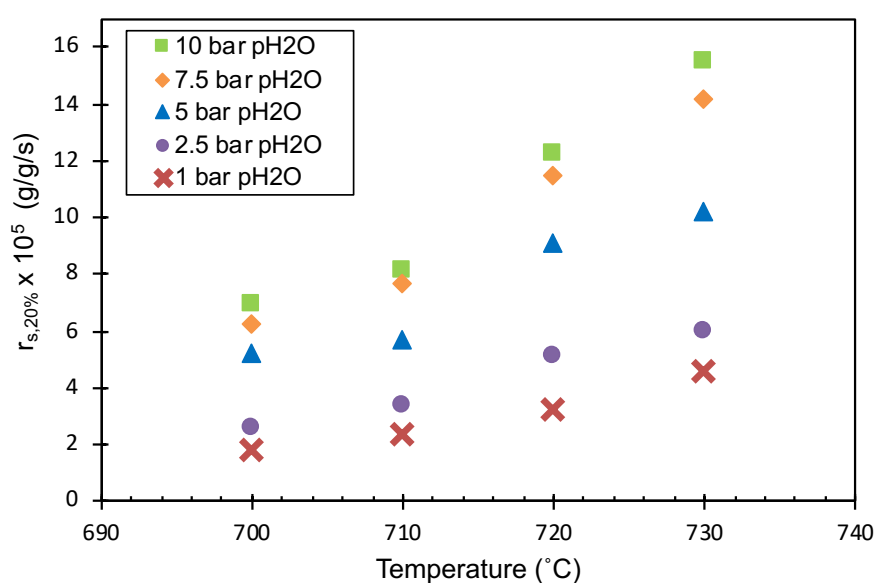


Figure 5.3: Effect of temperature on specific reaction rate at 20% conversion

Over a steam partial pressure range of 1-10 bar, it was found that the specific reaction rate increased exponentially with an increase of temperature. This strong temperature dependence is in agreement with results found in literature where the increase of temperature also followed an Arrhenius type of increase [12], [55], [56], [62]. These results were reported for different biomass feedstocks which include, sawdust derived chars [55], pine woodchips [56], maple hardwood and jack pine derived chars [62].

At a steam partial pressure of 1 bar and temperature increase of 30 °C, the specific reaction rate increased with a factor of 2.5, while at 10 bar steam partial pressure it increased with a factor of 2.2. Similar results were obtained in a study on steam gasification of maritime pine woodchips, which reported that the reactivity increased by a factor of 9 with a temperature increase from 800-1000 °C [56].

5.2.3. Effect of steam partial pressure on specific reaction rate

The effect of steam partial pressure on the specific reaction rate at 20% conversion, for 700 to 730 °C are displayed in Figure 5.4.

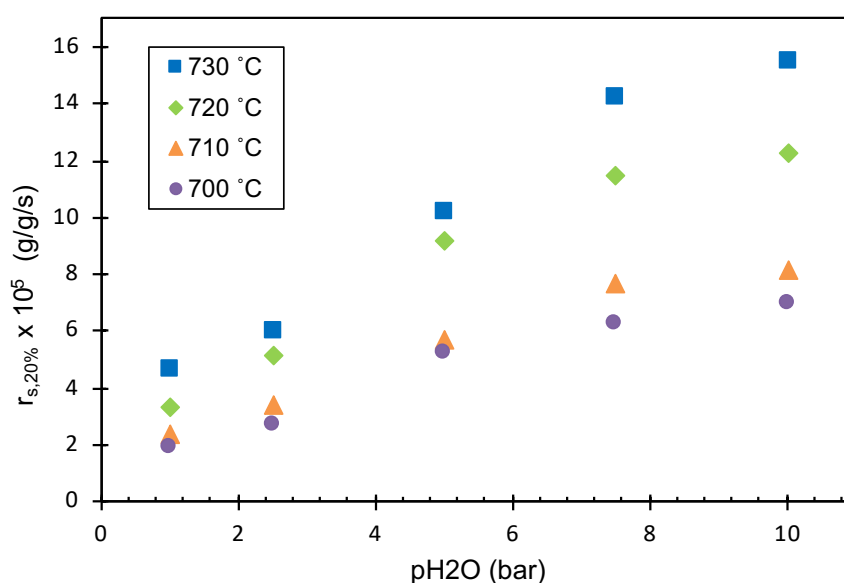


Figure 5.4: Effect of steam partial pressure on specific reaction rate

In general, the specific reaction rate increases with an increase of steam partial pressure over the entire temperature range. Both Van de steene *et al.* (2011) and Guizani *et al.* (2013) reported the same trend for maritime pine [56] and beech wood chip [61] steam gasification, which is in accordance with the results reported. Other studies have reported that faster char conversion is achieved by increasing the steam partial pressure up to 1.5 bar [41], [53].

From Figure 5.4, it is seen that the increase in reaction rate between lower steam partial pressures is larger than that between higher steam partial pressures. The reaction rate is increased with an average of 30% between 5 and 7.5 bar steam, while the increase between 7.5 and 10 bar steam is an average of 8%. The start of the saturation effect on biochar reactivity at elevated steam partial pressures is seen here. This trend has been reported for steam gasification of coal char [64], as discussed in Section 5.2.1.

In order to directly evaluate the observed reaction order with steam partial pressure, the natural logarithmic of both the steam partial pressure and specific reaction rate at 20% conversion were plotted. The results for the temperature range of 700-730 °C are shown in Figure 5.5.

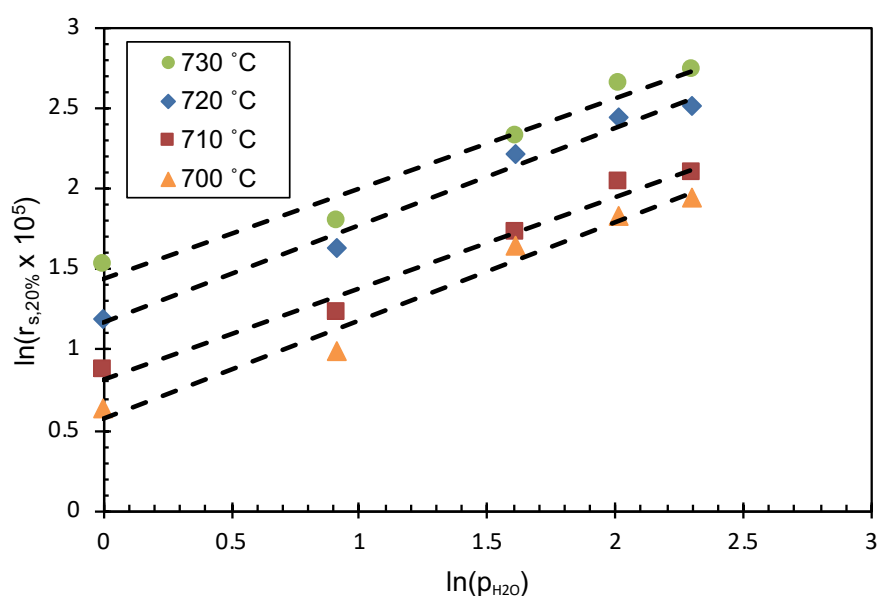


Figure 5.5: Reaction order with steam partial pressure at different temperatures.

The experimental data shown in Figure 5.5 follows a power law trend, while the difference in reaction orders throughout the partial pressure range remains similar. The observed reaction order decreased from 0.61 to 0.56 with a temperature increase from 700 to 730 °C.

These results indicate that the reaction order is not significantly affected by temperature under Regime I (chemical reaction controlled) conditions. Nilsson *et al.* (2014) investigated the gasification kinetics of olive tree pruning derived chars at 0.2-0.4 bar steam partial pressure and reported that the reaction order was affected by varying the temperature between 760 and 840 °C. However, this temperature range is higher than the 700-730 °C investigated, which might result in reaction conditions in Regime II.

5.3 Product distribution

The product formation of CO and CO₂ is investigated by comparing the rate of formation of both products to the specific reaction rate in Section 5.3.1 and the selectivity of the products in Section 5.3.2.

5.3.1. CO and CO₂ formation

The CO and CO₂ fractions are used to calculate the conversion rate of CO and CO₂. These conversion rates are compared to the rate of total carbon conversion (r_c). The results at 20% total carbon conversion are shown in Figure 5.6.

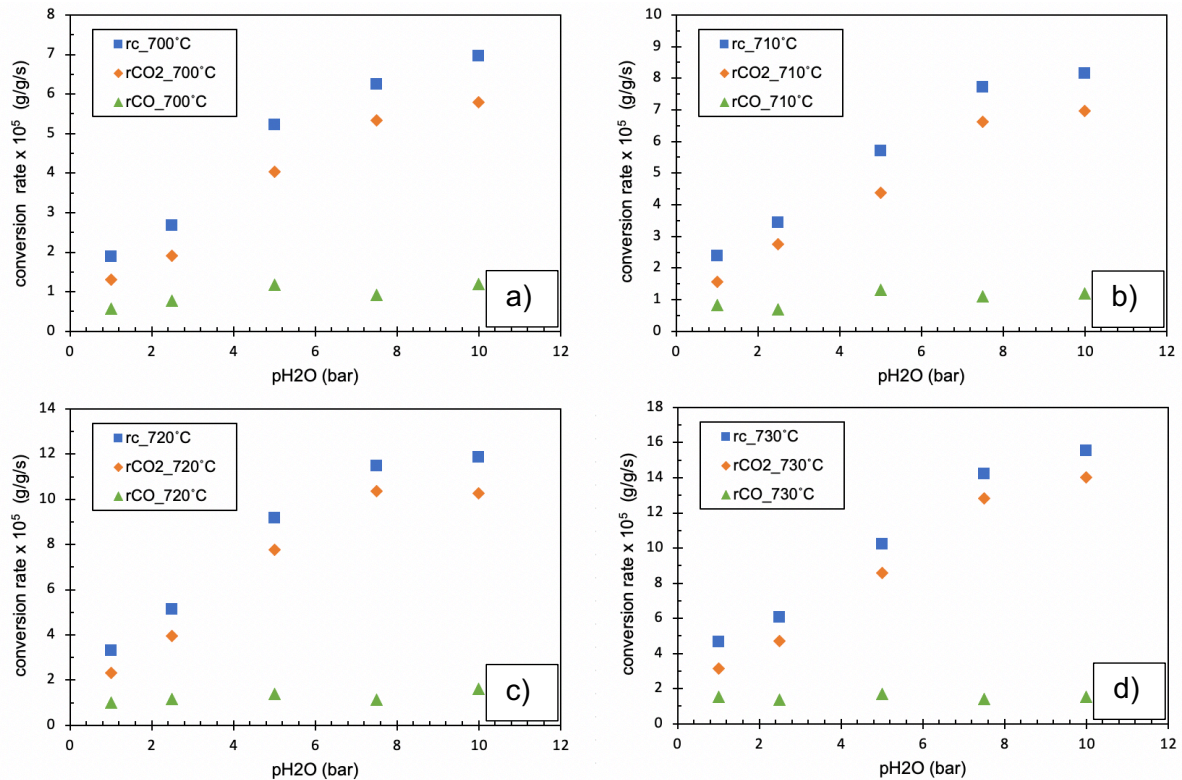


Figure 5.6: Comparison of CO, CO₂ and total carbon conversion for a temperature of a) 700 °C, b) 710 °C, c) 720 °C and d) 730 °C

In Figure 5.6, it is seen that the CO₂ conversion rate contributes more to the total carbon conversion rate than that of CO. Smolinski *et al.* (2011) studied the steam gasification of energy crop biomass derived chars at 700 °C and reported that biochar produced 3 times more CO₂ than CO, which confirms the higher CO₂ formation also observed from the results [99]. The difference in the CO₂ conversion rate and CO conversion rate becomes larger with an increase in steam partial pressure. The increase in CO₂ can be attributed to an increase in adsorbed intermediates as a result of the increase in steam partial pressure. However, this occurs until a steam partial pressure of 7.5 bar due to the smaller difference in carbon conversion rate between 7.5-10 bar steam. This ratio can be influenced by the water gas shift

reaction, and although it was shown that the homogenous conversion rate of this reaction is small (see Appendix C-2 for detail), the reaction can still be catalysed by the char and therefore no further mechanistic conclusions were made from these observations.

5.3.2. Selectivity

In order to further investigate the favored product formed from steam gasification, the selectivity of the CO and CO₂ are calculated. The results for selectivity at 20 % conversion at various steam partial pressures and temperatures are shown in Figure 5.7 a) to d).

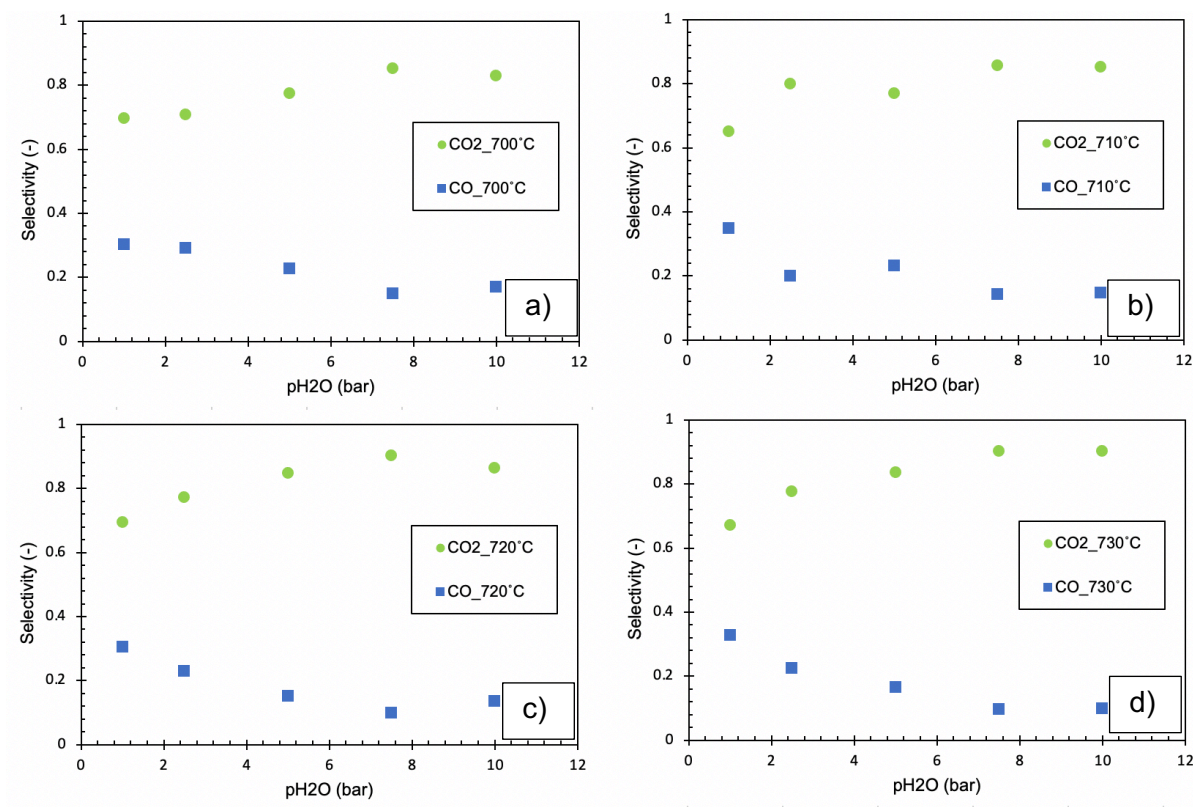


Figure 5.7: Observed selectivity of CO and CO₂ for various steam partial pressures and temperature of a) 700 °C, b) 710 °C, c) 720 °C and d) 730 °C

The results from Figure 5.7 suggest that the formation of CO₂ is favoured for the entire temperature range investigated. The selectivity of CO₂ at 10 bar steam increased from 0.83 to 0.90 with a temperature increase of 30 °C, while the CO selectivity is decreased from 0.17 to 0.10. The influence of steam partial pressure on the selectivity is larger than that of temperature, however the effect of temperature on the CO and CO₂ ratio becomes less significant with an increase in steam partial pressure. Selectivity of CO₂ increased with a factor of 1.3 over the steam partial pressure range investigated, while the CO selectivity decreased with a factor of 0.3.

It is observed throughout the steam partial pressure range, that the formation of CO₂ is larger than that of CO. This observation was found to be consistent with results in literature regarding

steam gasification of biochar [54], [100]. In contrast, a study on steam gasification of elephant grass derived biochar reported that the CO/CO₂ ratio increased at temperatures of 800-950 °C [101]. However, another study reported that the increase of temperature from 750-900 °C resulted in an increase in CO₂ concentration and decrease in CO concentration [100].

Sattar *et al.* (2014) investigated the syngas formation from steam gasification of various biochar samples at 850 °C. They observed that the formation of CO₂ was larger than CO for both sewage sludge and wood pellet derived chars [54]. According to Sattar *et al.* (2014), the increase of CO₂ is the result of two major factors, one of which is the fact the carbon content in the char decreases over time while the steam flow rate remains constant. This results in a higher steam to carbon (S/C) ratio and it has been observed by other authors that higher S/C ratios can suppress the formation of CO [102]. The second factor is the carbon reduction in char which ensures that the Boudouard reaction occurs less frequent, resulting in less CO formation [54]. However, a study on polyvinylchloride coke steam gasification at 1000 °C and steam partial pressure up to 4.3 bar, reported that the CO₂ formation was attributed to the homogeneous gas phase water gas shift reaction [63]. This is also found to be the case in the results shown here.

5.3.3. Comparison with coal

The product formation from biochar and coal char are compared by investigating the selectivity of CO and CO₂ at a conversion of 20%. Both the biochar and coal samples were gasified at 2.5 bar and 10 bar steam partial pressure, while the biochar was at a temperature of 730 °C and coal at 740 °C. The results are displayed in Table 5.2.

Table 5.2: Observed selectivity of biochar and coal at 2.5 and 10 bar steam partial pressure

Steam partial pressure (bar)	Selectivity to CO	Selectivity to CO ₂
Coal char		
2.5	> 0.99	< 0.01
10	0.36	0.64
Biochar		
2.5	0.22	0.78
10	0.11	0.89

From Table 5.2, it is observed that formation of CO₂ is larger for biomass at 2.5 bar and 10 bar steam partial pressure than that of the coal. Similar results were reported by Loha *et al.* (2011), where rice husks, sugarcane bagasse, rice straw and groundnut shell steam

gasification were compared to coal [102]. For coal char steam gasification at a partial pressure of 2.5 bar the formation of CO₂ was below the detection limit of the gas analyser, which resulted in a selectivity of < 0.01. The selectivity of CO₂ for both biochar and coal char increased with an increase in site coverage due to an increase of steam partial pressure or to the heterogeneous water gas shift reaction. Although no direct mechanistical conclusions can be drawn from this, the product distribution from biochar differs significantly from that of coal char.

5.4 Kinetic Modeling and site occupancy

The Langhuir-Hinshelwood model as well as the power law kinetic models are used to evaluate the specific reaction rate at 20% carbon conversion. The Langmuir-Hinshelwood model is discussed in Section 5.4.1 followed by the power law in Section 5.4.2.

5.4.1. Langmuir-Hinshelwood model

The equations discussed in Section 2.6.1 lead to a proposed rate equation for biochar gasification, which is a form of the Langmuir-Hinshelwood rate equation used for modelling experimental data. Previous studies have indicated that the effect of the inhibition product gas (H₂) has an insignificant influence on the reaction rate, due to the differential operation of the reactor, and the rate equation used for calculations was derived as [52] [71]:

$$r_s = \frac{[C_t]k_1p_{H_2O}}{1 + \frac{k_1}{k_3}p_{H_2O}} \quad (5-1)$$

The least-square method was used to determine the rate constants in the above-mentioned equation. This is discussed in further detail in Appendix E-1. The rate constants determined for different temperatures are displayed in Table 5.3.

Table 5.3: Langmuir-Hinshelwood rate constants for different temperatures

	700 °C	710 °C	720 °C	730 °C
$[C_t]k_1 (bar\ s)^{-1}$	1.7×10^{-5}	2.1×10^{-5}	3.2×10^{-5}	3.6×10^{-5}
$\frac{k_1}{k_3} (bar^{-1})$	0.14	0.15	0.16	0.13

The Arrhenius plot of the LH rate constants are shown in Figure 5.8. The values from Table 5.3 and Figure 5.8 show that the $[C_t]k_1$ rate constant increases with a temperature increase, while the ratio of $\frac{k_1}{k_3}$ does not significantly change. The rate constants shown in Table

5.3 were used, with a constant value of 0.15 for $\frac{k_1}{k_3}$, to determine the activation energy (E_1), which is calculated as 214 kJ mol^{-1} .

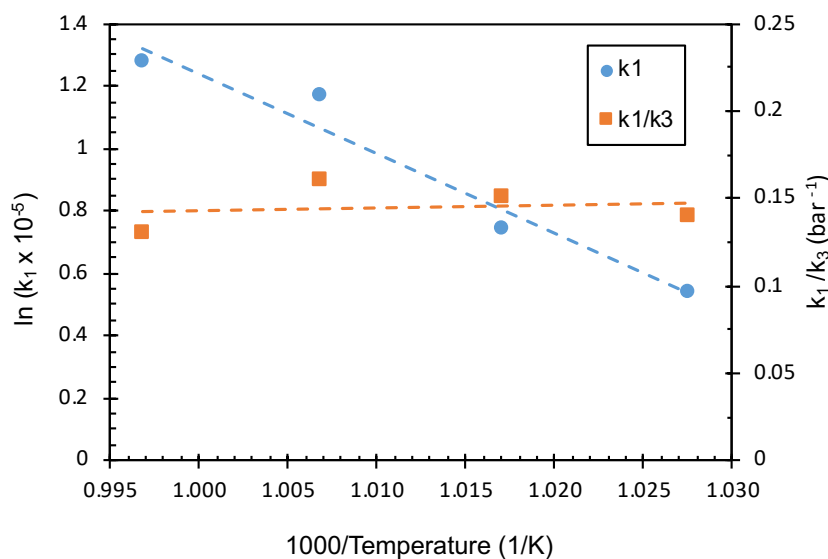


Figure 5.8: Arrhenius plot of Langmuir-Hinshelwood rate constants

The activation energy is in the range of values obtained from literature [52], [55], [62]. Activation energies of beech wood char and oil palm shell char was determined as 196 kJ mol^{-1} and 299 kJ mol^{-1} by Klose and Wölki (2005), which indicate that the type of biomass used for steam gasification can also influence the activation energy. Nandi and Onischak (1985) found activation energies of $170\text{--}177 \text{ kJ mol}^{-1}$ for high pressure steam gasification of maple and jack pine chars. In a study of switchgrass derived char, the steam gasification kinetics were described with the use of the LH model [72]. They used the Arrhenius equation to determine the activation energy and enthalpy, and obtained values of $112.6 \text{ kJ mol}^{-1}$ and $-37.3 \text{ kJ mol}^{-1}$ respectively [72]. However, these experiments were conducted at elevated temperatures of $1000\text{--}1150^\circ\text{C}$, which suggest mass transfer limitations resulting in the relative low value for the observed activation energy.

The parameters given in Table 5.3 were used to compare the LH model with the experimental data obtained at a conversion of 20%. The results are displayed in Figure 5.9.

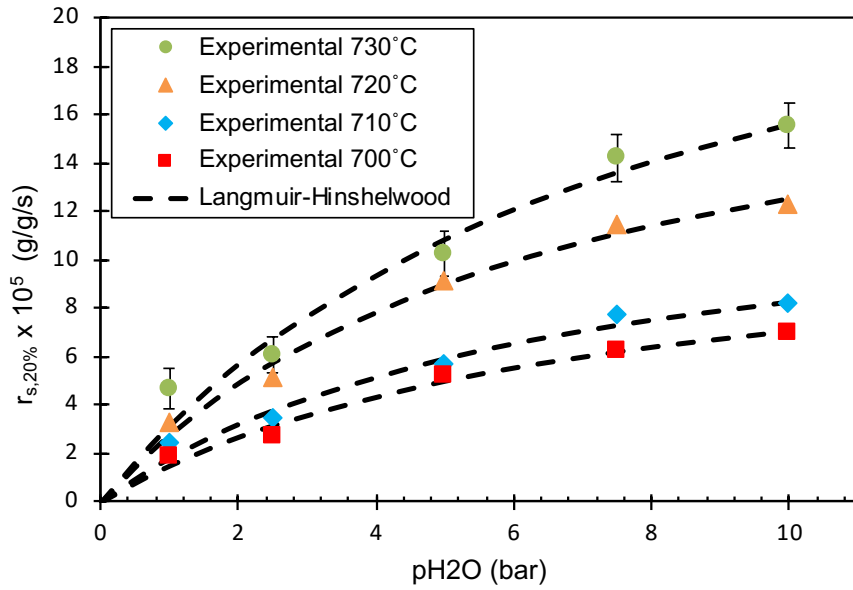


Figure 5.9: Correlation between Langmuir-Hinshelwood model and experimental data with uncertainties given for the highest temperature

From Figure 5.9, it is observed that the model shows an adequate correlation to the experimental values obtained. However, the LH model deviates more at 730 °C than the other temperatures. This is shown with the error estimation (more detail in Appendix D-2), where the maximum error of 4.9% and the minimum error of 3.9% is observed at 730 and 700°C respectively. The uncertainties shown in Figure 5.9 are largest at low temperatures and pressures, this can be the result of the measurements being taken at the bottom range of the gas analyser. The uncertainty of the experiments is dependent on steam partial pressure, since the uncertainties decrease with an increase in steam partial pressure.

Other authors that investigated biomass gasification observed that the Langmuir-Hinshelwood model described the experimental data quite well for steam partial pressures of 0.1-1 bar [52], [72]. Roberts and Harris (2006) investigated a coal char at elevated steam partial pressures and observed that the Langmuir-Hinshelwood model provides with a suitable fit for steam pressures up to 30 bar. These findings are in agreement with the results shown in Figure 5.9. The quality of fit (QOF) between the experimental and modelled values for the entire temperature range is an average of 91% (further detail given in Appendix D-3), which indicates that the model can accurately describe the experimental data over the selected pressure and temperature range.

5.4.2. Power law

The power law was used to model the experimental data using equations discussed in Section 2.6.1. The kinetic parameters for the power law were determined with the least squared method (more detail in Appendix E-1). The calculated parameters are shown in Table 5.4.

Table 5.4 : Parameters calculated for power law

	700 °C	710 °C	720 °C	730 °C
$k_s (s^{-1})$	1.8×10^{-5}	2.2×10^{-5}	3.4×10^{-5}	3.9×10^{-5}
n	0.60	0.58	0.58	0.60

The Arrhenius plot of the calculated PL rate constant is shown in Figure 5.10 for the temperature range of 700-730 °C.

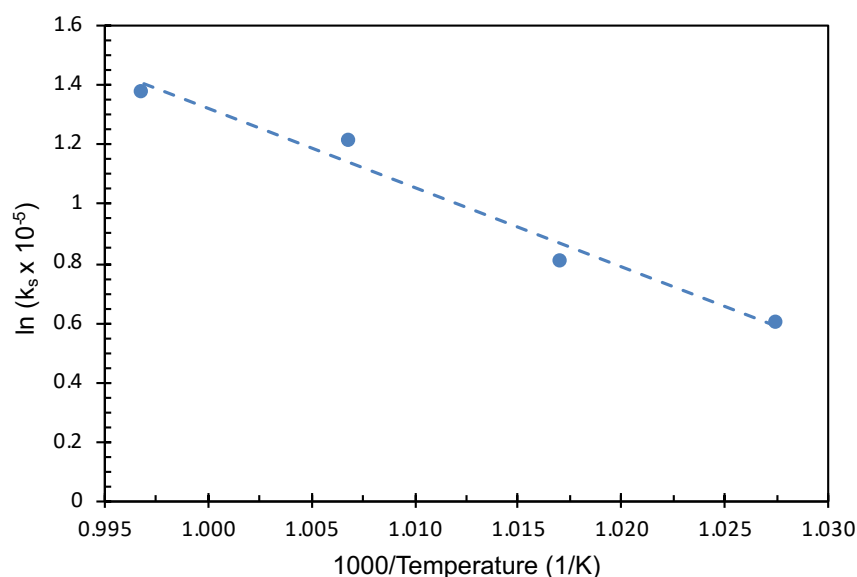


Figure 5.10: Arrhenius plot of PL parameters

The reaction rate constants from Table 5.4 were used to calculate the activation energy and frequency factor displayed in Table 5.5.

Table 5.5: Activation energy and frequency factor from power law

Parameter	
$E (kJ mol^{-1})$	222
$A (gg^{-1}s^{-1}bar^n)$	1.8×10^7

The parameters shown in Table 5.4 and Figure 5.10 show that the rate constant k_s is dependent on the temperature, while the reaction order is constant with an average of 0.59. Barrio *et al.* (2001) found similar values for steam gasification of wood char at steam partial

pressure of 0.05-1 bar. They found that the reaction order for birch and beech chars were 0.57 and 0.51 respectively, which correlate well with values shown in Table 5.5 [103]. Other studies on biomass steam gasification reported reaction order values of 0.6-1.5 [53], [57], [71]. A study on the steam gasification of wood char, using the n^{th} order reaction model, reported activation energies of 211 and 237 kJ mol^{-1} at 50% conversion [103]. These values are in agreement with the value reported in Table 5.6.

The parameters given in Table 5.5 were used to compare the power law model with the experimental data obtained at a conversion of 20%. The results are displayed in Figure 5.11.

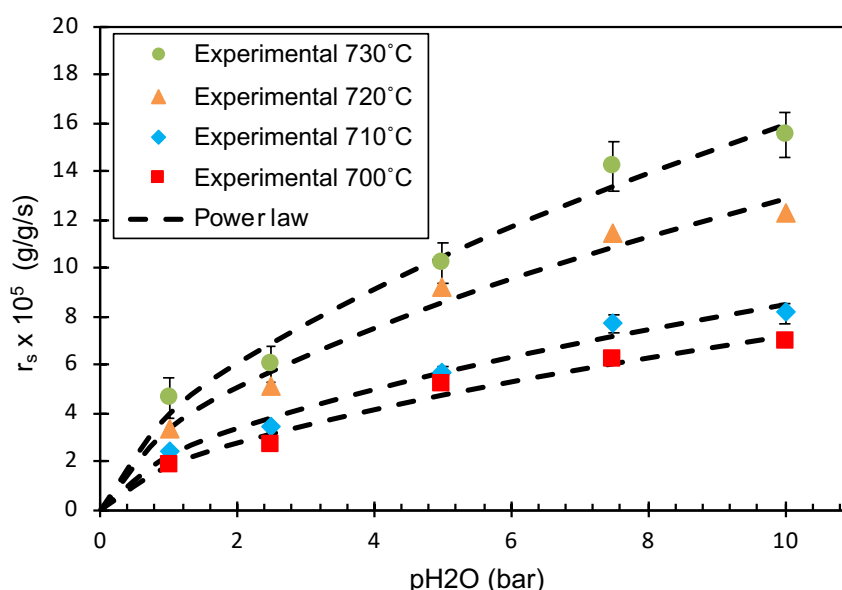


Figure 5.11: Correlation between the power law and experimental data with uncertainties given for the highest temperature

From Figure 5.11, it is seen that the predicted values from the power law provide a good correlation to the experimental values. However, the modelled values become less accurate at lower temperatures. The estimated error between the modelled and experimental values are 4.2% and 3.8% at 700 and 730 °C respectively. The quality of fit (QOF) between the experimental and modelled values is 93% for the entire temperature range (further detail given in Appendix D-3). This suggests that the power law can accurately predict the experimental values throughout the specified temperature and pressure range.

An insignificant difference in the QOF between the LH model and power law is observed. However, the LH model provides a more fundamental insight in the reaction of biochar and steam, which results in the LH model being the more appropriate model to use for kinetic modelling.

5.4.3. Site occupancy

The degree of saturation or site occupancy was determined by using the total concentration of active sites and absorbed surface complexes. The ratio of these parameters are based on the LH rate expression and are then calculated as given by equation 5-2 [64], [67]:

$$\theta = \frac{\frac{k_1}{k_3} p_{H_2O}}{1 + \frac{k_1}{k_3} p_{H_2O}} \quad (5-2)$$

The site occupancy (θ) was estimated by using the rate constants calculated from the LH model in Section 5.4.1. The results are shown in Figure 5.12.

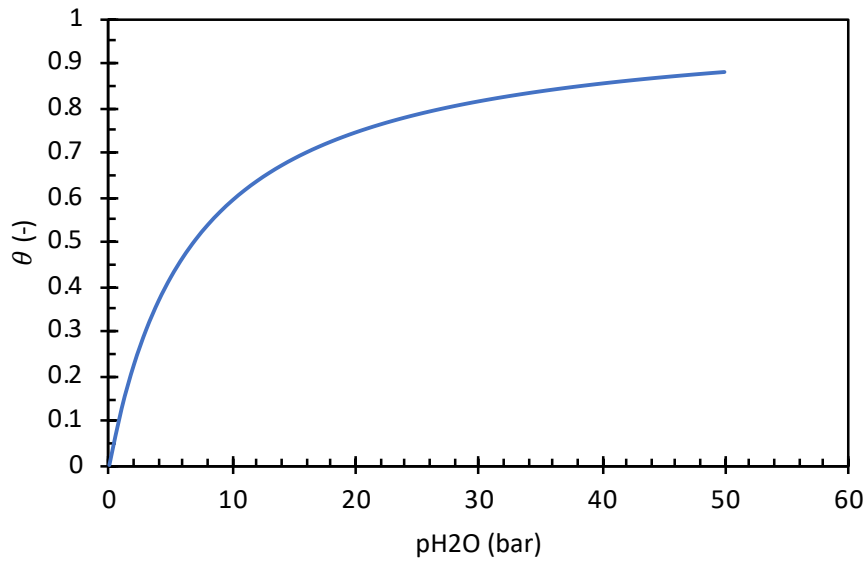


Figure 5.12: Site occupancy as a function of steam partial pressure (extrapolated to 50 bar steam)

From Figure 5.12, the site occupancy was observed to increase with an increase in steam partial pressure. Roberts and Harris (2006) reported similar results for coal derived char over a steam partial pressure range of 1-30 bar, using kinetic data from the LH model and TPD method. They reported that the quantity of available surface sites increased more rapidly up to 10 bar steam [64], which is in agreement with the results observed in Figure 5.12.

The site occupancy increases less strongly at higher steam partial pressures, indicating the saturation of active sites. This results in an unaffected reaction rate with steam partial pressure increase, as observed in Section 5.2.1. This has been reported for coal char steam gasification at elevated pressures [64], [67]. Figure 5.12 also shows a typical Langmuir-Hinshelwood behaviour.

5.5 Comparison between biochar and coal steam gasification

The data for the steam gasification of coal char was obtained by a previous student at the North-West University [67]. The specific reaction rate of the coal and biochar is evaluated at 740 °C and 10 bar steam partial pressure. This comparison over a conversion of 4-30% is displayed in Figure 5.13.

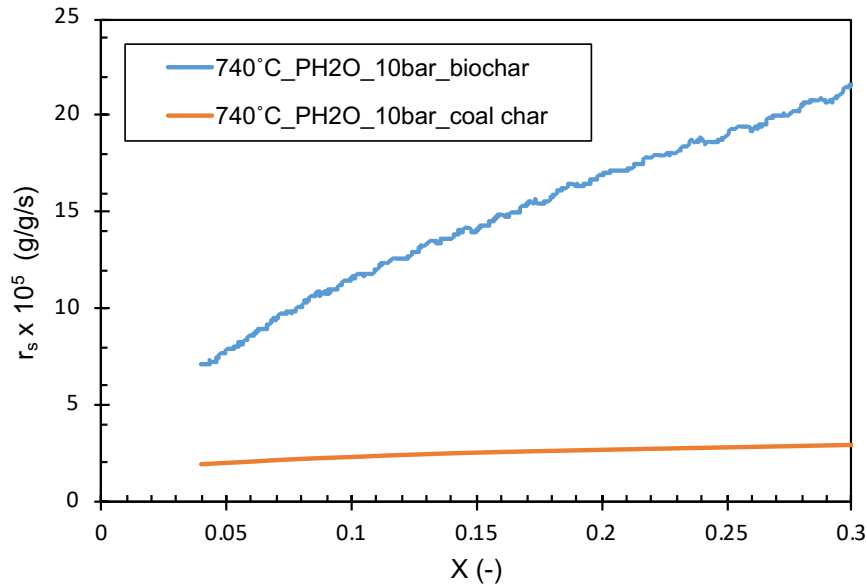


Figure 5.13: Comparison of biochar and coal char specific reaction rate for conversion of 4-30%

From Figure 5.13, it is seen that the reaction rate of the biochar is significantly higher than that of the coal char at the same operating conditions. This is in agreement with results found in literature, that indicate that biomass is more reactive than coal [26] [99]. The main reason for the higher specific reaction rate of the biochar is that it has a larger surface area. The biochar shows an initial surface area of 477 m²/g (Table 3.7), while the coal char's surface area is 257 m²/g [67]. It has also been reported that the pores of biomass derived chars are relatively larger and better accessible than those of coal chars [94].

The rate constant $\frac{k_1}{k_3}$ was observed to be constant for the biochar and the Highveld coal char with values of 0.15 and 0.13 respectively [67]. These values obtained for biomass char here are similar, which might indicate that the chemical nature of the two chars are similar, which again can be a result of the relative high charring temperature, and probably similar aromaticities (not measured here). Roberts *et al.* (2015) showed similar observations when comparing inertinite and vitrinite coal chars [104].

The specific reaction rate at 5% conversion of biochar is 4 times that of the coal char, however this factor increases to 7 at 30% conversion. This indicates that the specific reaction rate of biochar increases more with conversion than that of coal probably due to a faster pore

development in the biochar. According to the H/C and O/C ratios in Section 3.4.1, both samples were characterised as anthracite, although the biochar has a higher oxygen content and the coal char a higher hydrogen content.

5.6 Summary

The investigation of biochar reactivity at elevated steam partial pressure under Regime I reaction conditions was completed. The effect of temperature on the specific reaction rate was found to be significant for a temperature increase of 30°C. With the increase of steam partial pressure, it was observed that the specific reaction rate increased until a partial pressure of 10 bar was reached. These findings correlate with results obtained from literature.

The product formation of CO and CO₂ was also investigated, and it was found that the formation of CO₂ was favoured under the specific operating conditions. The conversion rate of CO₂ was observed to be larger than that of CO, while the CO₂ rate increased with steam partial the CO rate had insignificant changes. When comparing the product formation with coal char, it was found that biochar had larger selectivity towards CO₂ than coal char at 2.5 and 10 bar steam partial pressures.

Both the LH and power law kinetic models were used to predict the specific reaction rate. Solving the kinetic parameters for both models, resulted in values that are in agreement with values obtained from literature. The action energy was found to be equal to $214 \pm 17 \text{ kJ mol}^{-1}$ and $222 \pm 18 \text{ kJ mol}^{-1}$ for the LH and PL models respectively. The LH and PL models were able to predict the experimental values with an average error of 4% each.

Chapter 6: Conclusions and Recommendations

6.1 Introduction

In this study, the steam gasification reactivity for a waste woodchip derived biochar with - 150+75 μm particle size range was investigated. The biomass and biochar samples were both characterised using various characterisation techniques. It was found that the biomass sample showed a low lignin content compared to other forest residue samples and a low ash value of 2.4 wt%. The prepared biochar sample underwent gasification experiments at chemical controlled operating conditions in a nitrogen, steam atmosphere of 1:1. The steam partial pressure was varied between 1 and 10 bar steam. By the product analysis of CO and CO₂ only, the specific reaction rate and product selectivity was investigated. The main conclusions drawn from the results obtained and contributions made to the existing field are discussed in Section 6.2 and Section 6.3 respectively. Lastly, prospects and all recommendations for future studies are discussed in Section 6.4 and Section 6.5.

6.2 Conclusions

The biochar reactivity was found to be dependent on conversion, temperature and steam partial pressure. An increase in all these factors resulted in an increase of the biochar specific reaction rate. However, the biochar reactivity was only significantly affected by steam partial pressure up to 10 bar steam.

The formation of CO₂ from biochar was found to be significantly higher than that of CO. The increase in both temperature and steam partial pressure resulted in more CO₂ formation and a somewhat constant CO formation. The effect on CO and CO₂ formation became less notable at elevated temperatures and steam partial pressures. However, the CO₂ formation from biochar gasification was found to be larger than that of coal char at both 2.5 and 10 bar steam. The overall reactivity of biochar was found to be at least 4 times that of a typical Highveld coal char, which could be partly attributed to the high initial internal surface area of the biochar. The $\frac{k_1}{k_3}$ rate constants from both the biochar and coal char were found to be similar, suggesting that these chars have similar chemical nature.

Both the LH and PL kinetic model predicted the specific reaction rate within a 5% difference of the actual experimental values. Activation energies determined from the Langmuir-Hinshelwood and power law models, 214 and 222 kJ mol^{-1} respectively, were found to correlate well with values obtained from literature. The saturation effect found on the specific

reaction rate was confirmed with the site occupancy estimation, which indicated a strong partial pressure dependence at lower steam partial pressures and a reduced effect at elevated pressures.

6.3 Contribution to existing field of science

The following contributions were made to the existing field of biochar steam gasification:

- The determination of a locally sourced biochar reactivity in the chemical reaction controlled operating conditions at elevated steam partial pressures up to a partial steam pressure of 10 bar.
- The comparison of biochar reactivity with a typical Highveld coal at elevated steam partial pressures.

6.4 Prospects

The coal resources in South Africa are getting depleted and the use of biomass as a co-source for gasification is promising. Although the use of biomass as a single source was investigated in this project, some progress towards this objective has been made. The use of biomass instead of coal in commercially operated gasifiers will affect the operation of these gasifiers since biochar was found to react much faster than coal char. However, the investigation of co-feeding locally sourced biomass with coal will advance the knowledge required for implementing the source in commercially operated gasifiers. The behavior of charred biomass, either as pure feed, or more realistically, co-fed with coal should still be studied on a commercial scale to evaluate this alternative fuel further.

6.5 Recommendations

Reviewing the investigations conducted and conclusions made from this study, the following recommendations are made for future steam char reactivity studies:

- Investigate the steam gasification reactivity of different types of biochar as well as coal-biochar blends at elevated pressures.
- Investigate the effect of the water-gas-shift reaction at elevated pressure to determine reaction mechanisms occurring during steam gasification of biochar.
- Determine the surface area of partially reacted biochar at different conversions from steam gasification at elevated pressures in order to investigate pore development,

and have a better understanding of the reaction mechanism, and the relation of specific reaction rate and conversion.

- Study the inhibition effect of products such as CO and H₂ at elevated pressures in order to obtain a better understanding of biochar reactivity and effects on kinetic modelling.

References

- [1] I. E. Agency, "World Energy Balances 2018," 2018. [Online]. Available: <https://webstore.iea.org/world-energy-balances-2018>. [Accessed: 20-Mar-2019].
- [2] L. M. Platchkov and M. G. Pollitt, "The economics of energy (And electricity) demand," *Futur. Electr. Demand Cust. Citizens Loads*, no. April, pp. 17–47, 2012, doi: 10.1017/CBO9780511996191.005.
- [3] IEA - International Energy Agency, "Data and statistics - Explore energy data by category, indicator, country or region," *iea*, 2020. [Online]. Available: <https://www.iea.org/data-and-statistics?country=WORLD&fuel=Energy supply&indicator=TPESbySource>.
- [4] D. of Energy, "Coal resources: Overview," 2015. [Online]. Available: http://www.energy.gov.za/files/coal_frame.html. [Accessed: 04-Mar-2019].
- [5] J. Gasparotto and K. Da Boit Martinello, "Coal as an energy source and its impacts on human health," *EnergyGeosci.*, 2020, doi: <https://doi.org/10.1016/j.engeos.2020.07.003>.
- [6] G. J. De Korte, "Processing low-grade coal to produce high-grade products," *J. South. African Inst. Min. Metall.*, vol. 115, no. 7, pp. 569–572, 2015, doi: 10.17159/2411-9717/2015/v115n7a2.
- [7] I. E. Agency, "Renewables 2017," 2018. [Online]. Available: <https://www.iea.org/fuels-and-technologies/renewables>. [Accessed: 20-Mar-2019].
- [8] World bioenergy association, "Global Bioenergy Statistics 2019," *World Bioenergy Assoc.*, p. 58, 2019.
- [9] I. L. Motta, N. T. Miranda, R. Maciel Filho, and M. R. Wolf Maciel, "Biomass gasification in fluidized beds: A review of biomass moisture content and operating pressure effects," *Renew. Sustain. Energy Rev.*, vol. 94, no. May, pp. 998–1023, 2018, doi: 10.1016/j.rser.2018.06.042.
- [10] M. La Villetta, M. Costa, and N. Massarotti, "Modelling approaches to biomass gasification: A review with emphasis on the stoichiometric method," *Renew. Sustain. Energy Rev.*, vol. 74, no. January, pp. 71–88, 2017, doi: 10.1016/j.rser.2017.02.027.
- [11] A. F. Kirkels and G. P. J. Verbong, "Biomass gasification: Still promising? A 30-year global overview," *Renew. Sustain. Energy Rev.*, vol. 15, no. 1, pp. 471–481, 2011, doi: 10.1016/j.rser.2010.09.046.
- [12] A. A. Ahmad, N. A. Zawawi, F. H. Kasim, A. Inayat, and A. Khasri, "Assessing the

- gasification performance of biomass: A review on biomass gasification process conditions, optimization and economic evaluation,” *Renew. Sustain. Energy Rev.*, vol. 53, pp. 1333–1347, 2016, doi: 10.1016/j.rser.2015.09.030.
- [13] Y. Hu *et al.*, “Investigation of Biomass Gasification Potential in Syngas Production: Characteristics of Dried Biomass Gasification Using Steam as the Gasification Agent,” *Energy and Fuels*, vol. 34, no. 1, pp. 1033–1040, 2020, doi: 10.1021/acs.energyfuels.9b02701.
- [14] U. S. Energy Information Administration, “Biomass Explained,” 2019. [Online]. Available: https://www.eia.gov/energyexplained/?page=biomass_home). [Accessed: 30-May-2019].
- [15] D. Miah, R. Ahmed, and M. B. Uddin, “Biomass fuel use by the rural households in Chittagong region, Bangladesh,” *Biomass and Bioenergy*, vol. 24, no. 4–5, pp. 277–283, 2003, doi: 10.1016/S0961-9534(02)00173-3.
- [16] S. Heidenreich and P. U. Foscolo, “New concepts in biomass gasification,” *Prog. Energy Combust. Sci.*, vol. 46, pp. 72–95, 2015, doi: 10.1016/j.pecs.2014.06.002.
- [17] S. K. Sansaniwal, M. A. Rosen, and S. K. Tyagi, “Global challenges in the sustainable development of biomass gasification: An overview,” *Renew. Sustain. Energy Rev.*, vol. 80, no. March 2016, pp. 23–43, 2017, doi: 10.1016/j.rser.2017.05.215.
- [18] F. H. Isikgor and C. R. Becer, “Lignocellulosic biomass: a sustainable platform for the production of bio-based chemicals and polymers,” *Polym. Chem.*, vol. 6, no. 25, pp. 4497–4559, 2015, doi: 10.1039/c5py00263j.
- [19] F. Rosillo-Calle, “A review of biomass energy – shortcomings and concerns,” *J. Chem. Technol. Biotechnol.*, vol. 7, no. 91, pp. 1933–1945, 2016.
- [20] M.-L. van der Walt, J. van den Berg, and M. Cameron, “State of Renewable Energy in South Africa,” 2017.
- [21] S. Li and X. Yang, “Biofuel production from food wastes,” in *Handbook of Biofuels Production*, 2016, pp. 617–653.
- [22] National Energy Education Development, “Biomass at a Glance 2008,” *NEED Proj.*, pp. 12–15, 2008.
- [23] The Earth Project, “The Main Types of Biomass Energy,” 2016. [Online]. Available: <https://theearthproject.com/biomass-energy-types/>. [Accessed: 31-Mar-2020].
- [24] Clean Energy Ideas, “8 Examples of Biomass,” 2019. [Online]. Available:

<https://www.clean-energy-ideas.com/biomass/bioenergy/8-examples-of-biomass/>.

[Accessed: 31-Mar-2020].

- [25] E. Uçkun Kiran, K. Stamatelatou, G. Antonopoulou, and G. Lyberatos, "10 - Production of biogas via anaerobic digestion," in *Handbook of Biofuels Production (Second Edition)*, Second Edition., R. Luque, C. S. K. Lin, K. Wilson, and J. Clark, Eds. Woodhead Publishing, 2016, pp. 259–301.
- [26] D. Klass, "Biomass for renewable energy, fuels, and chemicals.," in *Biomass for renewable energy, fuels, and chemicals*, San Diego: Academic Press, Ed. 2007, pp. 289–303.
- [27] B. Petrie and D. Macqueen, "South African biomass energy: little heeded but much needed.," *IIED Brief. Pap. - Int. Inst. Environ. Dev.*, no. 17165, pp. 4-pp, 2013.
- [28] E. Lombard, "Replacing coal with wood chips," 2020. [Online]. Available: <http://www.timberiq.co.za/2020/01/23/replacing-coal-with-wood-chips/>. [Accessed: 30-Mar-2020].
- [29] Department of Transport, "KwaZulu-Natal Freight Transport Data Bank," 2008. [Online]. Available: http://www.kzntransport.gov.za/public_trans/freight_databank/kzn/industries/forestry/index_xml.html. [Accessed: 20-Mar-2020].
- [30] P. W. H. E. van Zyl and P. B. Prior, "South Africa Biofuels IEA Taskgroup 39 Progress Report," vol. 27, no. 21, 2009.
- [31] S. Y. Foong *et al.*, "Valorization of biomass waste to engineered activated biochar by microwave pyrolysis: Progress, challenges, and future directions," *Chem. Eng. J.*, vol. 389, no. February, p. 124401, 2020, doi: 10.1016/j.cej.2020.124401.
- [32] R. Kumar *et al.*, "Lignocellulose biomass pyrolysis for bio-oil production: A review of biomass pre-treatment methods for production of drop-in fuels," *Renew. Sustain. Energy Rev.*, vol. 123, no. May 2019, 2020, doi: 10.1016/j.rser.2020.109763.
- [33] F. Shafizadeh, "Introduction to pyrolysis of biomass," *J. Anal. Appl. Pyrolysis*, vol. 3, no. 4, pp. 283–305, 1982, doi: 10.1016/0165-2370(82)80017-X.
- [34] NASA, "Combustion," 2015. [Online]. Available: <https://www.grc.nasa.gov/WWW/K-12/airplane/combst1.html>. [Accessed: 29-Apr-2020].
- [35] J. Ahrenfeldt, T. Thomsen, U. Henriksen, and L. Clausen, "Biomass gasification cogeneration – A review of state of the art technology and near future perspectives,"

- Appl. Therm. Eng.*, vol. 50, no. 2, pp. 1407–1417, 2013.
- [36] Global Syngas Technologies Council, “The gasification industry,” 2020. [Online]. Available: <https://www.globalsyngas.org/resources/the-gasification-industry/>. [Accessed: 30-Apr-2020].
 - [37] A. K. Agarwal, U. Pradesh, A. Pandey, and D. Scientist, *Coal and Biomass Gasification: Recent Advances and Future Challenges*. 2018.
 - [38] L. Baowen, “Increased understanding of gasification,” *Cornerstone*, vol. 2, no. 3, pp. 6–12, 2014.
 - [39] J. R. Bunt and F. B. Waanders, “Identification of the reaction zones occurring in a commercial-scale Sasol-Lurgi FBDB gasifier,” *Fuel*, vol. 87, no. 10–11, pp. 1814–1823, 2008, doi: 10.1016/j.fuel.2007.11.012.
 - [40] M. Dudyrński, J. C. Van Dyk, K. Kwiatkowski, and M. Sosnowska, “Biomass gasification: Influence of torrefaction on syngas production and tar formation,” *Fuel Process. Technol.*, vol. 131, pp. 203–212, 2015, doi: 10.1016/j.fuproc.2014.11.018.
 - [41] I. I. Ahmed and A. K. Gupta, “Kinetics of woodchips char gasification with steam and carbon dioxide,” *Appl. Energy*, vol. 88, no. 5, pp. 1613–1619, 2011, doi: 10.1016/j.apenergy.2010.11.007.
 - [42] J. A. Ruiz, M. C. Juarez, M. P. Morales, P. Munoz, and M. A. Mendivil, “Biomass gasification for electricity generation : Review of current technology barriers,” *Renew. Sustain. Energy*, vol. 61, no. 18, pp. 174–183, 2013.
 - [43] A. Dutta and B. Acharya, “16 - Production of bio-syngas and biohydrogen via gasification,” in *Handbook of Biofuels Production*, R. Luque, J. Campelo, and J. Clark, Eds. Woodhead Publishing, 2011, pp. 420–459.
 - [44] Z. A. B. Z. Alauddin, P. Lahijani, M. Mohammadi, and A. R. Mohamed, “Gasification of lignocellulosic biomass in fluidized beds for renewable energy development: A review,” *Renew. Sustain. Energy Rev.*, vol. 14, no. 9, pp. 2852–2862, 2010, doi: 10.1016/j.rser.2010.07.026.
 - [45] H. J. . Mühlen, K. H. Van Heek, and H. Jüntgen, “Kinetic studies of steam gasification of char in the presence of H₂ , CO₂ and CO.,” *Fuel*, vol. 64, no. 7, pp. 944–949, 1985.
 - [46] D. G. Roberts and D. J. Harris, “Char gasification with O₂, CO₂, and H₂O: Effects of pressure on intrinsic reaction kinetics,” *Energy and Fuels*, vol. 14, no. 2, pp. 483–489, 2000, doi: 10.1021/ef9901894.

- [47] S. Kajitani, S. Hara, and H. Matsuda, "Gasification rate analysis of coal char with a pressurized drop tube furnace," *Fuel*, vol. 81, no. 5, pp. 539–546, 2002, doi: 10.1016/S0016-2361(01)00149-1.
- [48] L. Emami Taba, M. F. Irfan, W. A. M. Wan Daud, and M. H. Chakrabarti, "The effect of temperature on various parameters in coal, biomass and CO-gasification: A review," *Renew. Sustain. Energy Rev.*, vol. 16, no. 8, pp. 5584–5596, 2012, doi: 10.1016/j.rser.2012.06.015.
- [49] L. D. Mafu, H. W. J. P. Neomagus, R. C. Everson, G. N. Okolo, C. A. Strydom, and J. R. Bunt, "The carbon dioxide gasification characteristics of biomass char samples and their effect on coal gasification reactivity during co-gasification," *Bioresour. Technol.*, vol. 258, no. December 2017, pp. 70–78, 2018, doi: 10.1016/j.biortech.2017.12.053.
- [50] M. Shahbaz, S. yusup, A. Inayat, D. O. Patrick, and M. Ammar, "The influence of catalysts in biomass steam gasification and catalytic potential of coal bottom ash in biomass steam gasification: A review," *Renew. Sustain. Energy Rev.*, vol. 73, no. November 2015, pp. 468–476, 2017, doi: 10.1016/j.rser.2017.01.153.
- [51] M. A. Akhtar, S. Zhang, and C. Z. Li, "Mechanistic insights into the kinetic compensation effects during the gasification of biochar in H₂O," *Fuel*, vol. 255, no. July, 2019, doi: 10.1016/j.fuel.2019.115839.
- [52] W. Klose and M. Wölki, "On the intrinsic reaction rate of biomass char gasification with carbon dioxide and steam," *Fuel*, vol. 84, no. 7–8, pp. 885–892, 2005, doi: 10.1016/j.fuel.2004.11.016.
- [53] M. Morin, S. Pécate, and M. Hémati, "Experimental study and modelling of the kinetic of biomass char gasification in a fluidized bed reactor," *Chem. Eng. Res. Des.*, vol. 131, pp. 488–505, 2018, doi: 10.1016/j.cherd.2017.09.030.
- [54] A. Sattar, G. A. Leeke, A. Hornung, and J. Wood, "Steam gasification of rapeseed, wood, sewage sludge and miscanthus biochars for the production of a hydrogen-rich syngas," *Biomass and Bioenergy*, vol. 69, pp. 276–286, 2014, doi: 10.1016/j.biombioe.2014.07.025.
- [55] G. Lopez, J. Alvarez, M. Amutio, A. Arregi, J. Bilbao, and M. Olazar, "Assessment of steam gasification kinetics of the char from lignocellulosic biomass in a conical spouted bed reactor," *Energy*, vol. 107, pp. 493–501, 2016, doi: 10.1016/j.energy.2016.04.040.
- [56] L. Van de steene, J. P. Tagutchou, F. J. Escudero Sanz, and S. Salvador, "Gasification of woodchip particles: Experimental and numerical study of char-H₂O, char-CO₂, and

- char-O₂ reactions,” *Chem. Eng. Sci.*, vol. 66, no. 20, pp. 4499–4509, 2011, doi: 10.1016/j.ces.2011.05.045.
- [57] C. Dupont, T. Nocquet, J. A. Da Costa, and C. Verne-Tournon, “Kinetic modelling of steam gasification of various woody biomass chars: Influence of inorganic elements,” *Bioresour. Technol.*, vol. 102, no. 20, pp. 9743–9748, 2011, doi: 10.1016/j.biortech.2011.07.016.
- [58] D. Kim, “Physico-Chemical Conversion of Lignocellulose: Inhibitor Effects and Detoxification Strategies: A Mini Review,” *Molecules*, vol. 23, p. 309, 2018, doi: 10.3390/molecules23020309.
- [59] S. Irmak, M. Kurtuluş, A. Hasanoğlu Hesenov, and O. Erbatur, “Gasification efficiencies of cellulose, hemicellulose and lignin fractions of biomass in aqueous media by using Pt on activated carbon catalyst,” *Biomass and Bioenergy*, vol. 49, pp. 102–108, 2013, doi: 10.1016/j.biombioe.2012.12.016.
- [60] A. Tremel, T. Haselsteiner, C. Kunze, and H. Spliethoff, “Experimental investigation of high temperature and high pressure coal gasification,” *Appl. Energy*, vol. 92, pp. 279–285, 2012, doi: 10.1016/j.apenergy.2011.11.009.
- [61] C. Guizani, F. J. Escudero Sanz, and S. Salvador, “The gasification reactivity of high-heating-rate chars in single and mixed atmospheres of H₂O and CO₂,” *Fuel*, vol. 108, pp. 812–823, 2013, doi: 10.1016/j.fuel.2013.02.027.
- [62] S. P. Nandi and M. Onischak, “Gasification of Chars Obtained from Maple and Jack Pine Woods,” in *Fundamentals of Thermochemical Biomass Conversion*, R. P. Overend, T. A. Milne, and L. K. Mudge, Eds. Dordrecht: Springer Netherlands, 1985, pp. 567–587.
- [63] K. J. Hüttinger and W. F. Merdes, “The carbon-steam reaction at elevated pressure: Formations of product gases and hydrogen inhibitions,” *Carbon N. Y.*, vol. 30, no. 6, pp. 883–894, 1992, doi: 10.1016/0008-6223(92)90011-K.
- [64] D. G. Roberts and D. J. Harris, “A kinetic analysis of coal char gasification reactions at high pressures,” *Energy and Fuels*, vol. 20, no. 6, pp. 2314–2320, 2006, doi: 10.1021/ef060270o.
- [65] X.-Z. Sha, Y. Chen, J. Cao, Y.-M. Yang, and D. Ran, “Effects of operating pressure on coal gasification,” *Fuel*, vol. 69, no. 5, 1990.
- [66] H. J. Mühlen, K. H. van Heek, and H. Jüntgen, “Kinetic studies of steam gasification of

- char in the presence of H_2 , CO_2 and CO ,” *Fuel*, vol. 64, no. 7, pp. 944–949, 1985, doi: 10.1016/0016-2361(85)90149-8.
- [67] L. C. Mgano, “Evaluation of coal char gasification kinetics and pore development in high pressure steam and carbon dioxide,” North-West University, 2020.
 - [68] M. Morin, S. Pécate, and M. Hémati, “Kinetic study of biomass char combustion in a low temperature fluidized bed reactor,” *Chem. Eng. J.*, vol. 331, no. May 2017, pp. 265–277, 2018, doi: 10.1016/j.cej.2017.08.063.
 - [69] J. Szekely, J. W. Evans, and H. Y. Sohn, *Gas-solid reactions*. New York: Academic Press, 1976.
 - [70] H. S. Fogler, “Steps in a Catalytic reaction,” in *Elements of chemical reaction engineering*, 2014, p. 668 and 732–733.
 - [71] S. Nilsson, A. Gómez-Barea, D. Fuentes-Cano, and M. Campoy, “Gasification kinetics of char from olive tree pruning in fluidized bed,” *Fuel*, vol. 125, pp. 192–199, 2014, doi: 10.1016/j.fuel.2014.02.006.
 - [72] R. Bryan Woodruff and A. W. Weimer, “A novel technique for measuring the kinetics of high-temperature gasification of biomass char with steam,” *Fuel*, vol. 103, pp. 749–757, 2013, doi: 10.1016/j.fuel.2012.09.035.
 - [73] C. Di Blasi, “Combustion and gasification rates of lignocellulosic chars,” *Prog. Energy Combust. Sci.*, vol. 35, no. 2, pp. 121–140, 2009, doi: 10.1016/j.pecs.2008.08.001.
 - [74] L. D. Mafu, “Chemical and structural changes of biomass during pyrolysis and the influence on gasification reactivity in coal -biomass blends,” North West University, 2018.
 - [75] S. YAGI and D. KUNII, “Fluidized-solids reactors with continuous solids feed—I: Residence time of particles in fluidized beds,” *Chem. Eng. Sci.*, vol. 16, pp. 264–371, 1961.
 - [76] R. C. Everson, H. W. J. P. Neomagus, H. Kasaini, and D. Njapha, “Reaction kinetics of pulverized coal-chars derived from inertinite-rich coal discards: Gasification with carbon dioxide and steam,” *Fuel*, vol. 85, no. 7–8, pp. 1076–1082, 2006, doi: 10.1016/j.fuel.2005.10.016.
 - [77] M. Phanphanich and S. Mani, “Impact of torrefaction on the grindability and fuel characteristics of forest biomass,” *Bioresour. Technol.*, vol. 102, no. 2, pp. 1246–1253, 2011, doi: 10.1016/j.biortech.2010.08.028.

- [78] Shimadzu Corporation, "Instruction Manual: UV-2401PC/2501PC User's System Guide," 2009.
- [79] S. Coetzee, H. W. J. P. Neomagus, J. R. Bunt, and R. C. Everson, "Improved reactivity of large coal particles by K_2CO_3 addition during steam gasification," *Fuel Process. Technol.*, vol. 114, pp. 75–80, 2013, doi: 10.1016/j.fuproc.2013.03.041.
- [80] L. D. Mafu, H. W. J. P. Neomagus, R. C. Everson, M. Carrier, C. A. Strydom, and J. R. Bunt, "Structural and chemical modifications of typical South African biomasses during torrefaction," *Bioresour. Technol.*, vol. 202, pp. 192–197, 2016, doi: 10.1016/j.biortech.2015.12.007.
- [81] S. Nanda, P. Mohanty, K. K. Pant, S. Naik, J. A. Kozinski, and A. K. Dalai, "Characterization of North American Lignocellulosic Biomass and Biochars in Terms of their Candidacy for Alternate Renewable Fuels," *Bioenergy Res.*, vol. 6, no. 2, pp. 663–677, 2013, doi: 10.1007/s12155-012-9281-4.
- [82] A. Pandey, C. Larroche, E. Gnansounou, S. K. Khanal, C. G. Dussap, and S. Ricke, *Biomass, Biofuels, Biochemicals: Biofuels: Alternative Feedstocks and Conversion Processes for the Production of Liquid and Gaseous Biofuels*. Elsevier Science, 2019.
- [83] G. Duman, M. A. Uddin, and J. Yanik, "The effect of char properties on gasification reactivity," *Fuel Process. Technol.*, vol. 118, pp. 75–81, 2014, doi: 10.1016/j.fuproc.2013.08.006.
- [84] Science Education Resource Center, "Geochemical Instrumentation and Analysis," 2020.[Online].Available:https://serc.carleton.edu/research_education/geochemsheets/techniques/XRF.html. [Accessed: 21-May-2020].
- [85] P. Nanou, H. E. Gutiérrez Murillo, W. P. M. Van Swaaij, G. Van Rossum, and S. R. A. Kersten, "Intrinsic reactivity of biomass-derived char under steam gasification conditions-potential of wood ash as catalyst," *Chem. Eng. J.*, vol. 217, pp. 289–299, 2013, doi: 10.1016/j.cej.2012.12.012.
- [86] J. Alvarez, G. Lopez, M. Amutio, J. Bilbao, and M. Olazar, "Evolution of biomass char features and their role in the reactivity during steam gasification in a conical spouted bed reactor," *Energy Convers. Manag.*, vol. 181, no. October 2018, pp. 214–222, 2019, doi: 10.1016/j.enconman.2018.12.008.
- [87] C. Dupont *et al.*, "How inorganic elements of biomass influence char steam gasification kinetics," *Energy*, vol. 109, pp. 430–435, 2016, doi: 10.1016/j.energy.2016.04.094.

- [88] C. E. Brewer, K. Schmidt-Rohr, J. A. Satrio, and R. C. Brown, "Characterization of Biochar from Fast Pyrolysis and Gasification Systems," *Environ. Prog. Sustain. Energy*, vol. 28, no. 3, pp. 386–396, 2009, doi: 10.1002/ep.
- [89] S. Kloss *et al.*, "Characterization of Slow Pyrolysis Biochars: Effects of Feedstocks and Pyrolysis Temperature on Biochar Properties," *J. Environ. Qual.*, vol. 41, no. 4, pp. 990–1000, 2012, doi: 10.2134/jeq2011.0070.
- [90] D. Özçimen and A. Ersoy-Meriçboyu, "Characterization of biochar and bio-oil samples obtained from carbonization of various biomass materials," *Renew. Energy*, vol. 35, no. 6, pp. 1319–1324, 2010, doi: 10.1016/j.renene.2009.11.042.
- [91] L. D. Mafu *et al.*, "Chemical and structural characterization of char development during lignocellulosic biomass pyrolysis," *Bioresour. Technol.*, vol. 243, pp. 941–948, 2017, doi: 10.1016/j.biortech.2017.07.017.
- [92] H. Tian, Q. Hu, J. Wang, L. Liu, Y. Yang, and A. V. Bridgwater, "Steam gasification of Miscanthus derived char: the reaction kinetics and reactivity with correlation to the material composition and microstructure," *Energy Convers. Manag.*, vol. 219, no. April, p. 113026, 2020, doi: 10.1016/j.enconman.2020.113026.
- [93] P. Liu *et al.*, "Effects of Biochar Amendment on Chloropicrin Adsorption and Degradation in Soil," *Energies*, vol. 12, no. 3, pp. 146–159, 2019.
- [94] P. Basu, *Biomass Gasification, Pyrolysis and Torrefaction: Practical Design and Theory*. 2013.
- [95] J. G. Speight, *The Chemistry and Technology of Coal*, Third Edit. Taylor & Francis, 2012.
- [96] K. S. Sing, "Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity," *Pure Appl. Chem.*, vol. 57, no. 4, pp. 603–619, 1985.
- [97] S. M. Gouws, "The influence of carbon dioxide on the gasification rate of Highveld coal chars at elevated pressures," North-West University, 2017.
- [98] S. M. Gouws, H. W. J. P. Neomagus, D. G. Roberts, J. R. Bunt, and R. C. Everson, "The effect of carbon dioxide partial pressure on the gasification rate and pore development of Highveld coal chars at elevated pressures," *Fuel Process. Technol.*, vol. 179, pp. 1–9, 2018, doi: <https://doi.org/10.1016/j.fuproc.2018.05.027>.
- [99] A. Smoliński, N. Howaniec, and K. Stańczyk, "A comparative experimental study of

- biomass, lignite and hard coal steam gasification,” *Renew. Energy*, vol. 36, no. 6, pp. 1836–1842, 2011, doi: 10.1016/j.renene.2010.12.004.
- [100] J. Li, Y. Yin, X. Zhang, J. Liu, and R. Yan, “Hydrogen-rich gas production by steam gasification of palm oil wastes over supported tri-metallic catalyst,” *Int. J. Hydrogen Energy*, vol. 34, no. 22, pp. 9108–9115, 2009, doi: <https://doi.org/10.1016/j.ijhydene.2009.09.030>.
- [101] S. D. Ferreira, I. P. Lazzarotto, J. Junges, C. Manera, M. Godinho, and E. Osório, “Steam gasification of biochar derived from elephant grass pyrolysis in a screw reactor,” *Energy Convers. Manag.*, vol. 153, pp. 163–174, 2017, doi: <https://doi.org/10.1016/j.enconman.2017.10.006>.
- [102] C. Loha, P. K. Chatterjee, and H. Chattopadhyay, “Performance of fluidized bed steam gasification of biomass - Modeling and experiment,” *Energy Convers. Manag.*, vol. 52, no. 3, pp. 1583–1588, 2011, doi: 10.1016/j.enconman.2010.11.003.
- [103] M. Barrio, B. Gøbel, H. Rimes, U. Henriksen, J. E. Hustad, and L. H. Sørensen, “Steam Gasification of Wood Char and the Effect of Hydrogen Inhibition on the Chemical Kinetics,” *Prog. Thermochem. Biomass Convers.*, pp. 32–46, 2001, doi: 10.1002/9780470694954.ch2.
- [104] M. J. Roberts, R. C. Everson, H. W. J. P. Neomagus, G. N. Okolo, D. Van Niekerk, and J. P. Mathews, “The characterisation of slow-heated inertinite- and vitrinite-rich coals from the South African coalfields,” *Fuel*, vol. 158, pp. 591–601, 2015, doi: 10.1016/j.fuel.2015.06.006.
- [105] J. L. Devore and N. R. Farnum, *Applied Statistics for Engineers and Scientists*. Thomson Brooks/Cole., 2005.

Appendix A: Char preparation

A-1 Temperature profile of charring furnace

Before the charring process could start an isothermal zone must be identified inside the three phase Lenton horizontal furnace. This was achieved with the use of a 150 cm K-type thermocouple under operating conditions of 950°C and 2 NL/min nitrogen flow. A temperature distribution of the furnace was completed and shown in Figure A.1.

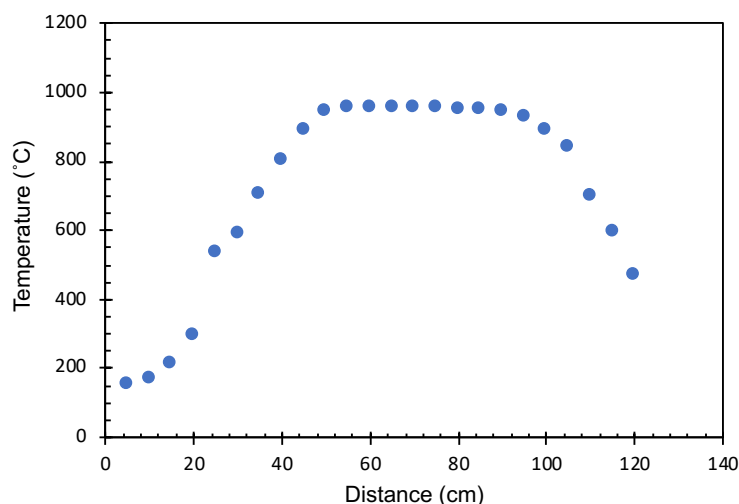


Figure A.1: Temperature profile of tube furnace

The graph from Figure A.1 indicates that the ceramic sample holder must be located 55 cm from the measured side. The effective heating zone has a length of 350 mm in the centre of the furnace, which implies that two sample holders can be placed inside the furnace at the same time.

A-2 Biomass pyrolysis

Biomass pyrolysis was done on 40 batches of the represented biomass sample and the results of the mass loss are summarised in Table A.1

Table A.1: Charring of biomass

Charring run	Initial mass (g)	Final mass (g)	Mass loss (wt.%)
1	50	8.7	82.6
2	50.5	8.4	83.4
3	70.8	11.9	83.2
4	155.3	26.2	83.1
5	156.9	26.5	83.1
6	153.7	24.8	83.9

Charring run	Initial mass (g)	Final mass (g)	Mass loss (wt.%)
7	150.9	24.3	83.9
8	153.2	28.2	81.6
9	154.4	27.7	82.1
10	154.2	26.6	82.7
11	156.3	26.5	83.0
12	155.3	26.9	82.7
13	155.4	27.2	82.5
14	154.2	27.6	82.1
15	152.8	27.8	81.8
16	156	28.1	82.0
17	155.6	27.7	82.2
18	154.9	26.6	82.8
19	154.5	28.3	81.7
20	153.2	27.4	82.1
21	154.2	28.2	81.7
22	154	27.1	82.4
23	155.4	26.3	83.1
24	154.6	25.3	83.6
25	154.7	24.3	84.3
26	153.5	23.4	84.8
27	153.5	25.9	83.1
28	152.1	22.6	85.1
29	155.5	27.3	82.4
30	153.6	26.9	82.5
31	155.4	26.3	83.1
32	153.4	26.9	82.5
33	154.9	25.8	83.3
34	153.1	24.7	83.9
35	153.8	22.4	85.4
36	154.9	24.4	84.2
37	156.8	23.4	85.1
38	153.8	23.3	84.9
39	155.5	23.9	84.6
40	153.8	26.4	82.8

The average mass loss during the charring processes was 81.3 wt%.

Appendix B: Experimental calibration

B-1 HPLC Calibration

The HPLC pump was used to provide the pressure of steam and to pump de-ionised water to the steam generator during experimental runs. The pump has the capability to provide a liquid flow rate of 0-4 ml/min with 0.001 accuracy and pressure of 1-49 MPa.

The flow rate of the water was calibrated by pumping the water into a 100 ml graduated glass cylinder and measuring the time at a specific volume. The pump set-point was varied from 0.4-2 ml/min with increments of 0.2 ml/min at atmospheric conditions. This method was carried out 3 times to ensure the accuracy of the pump. The data obtained was used to calculate the calibration curve displayed in Figure B.1.

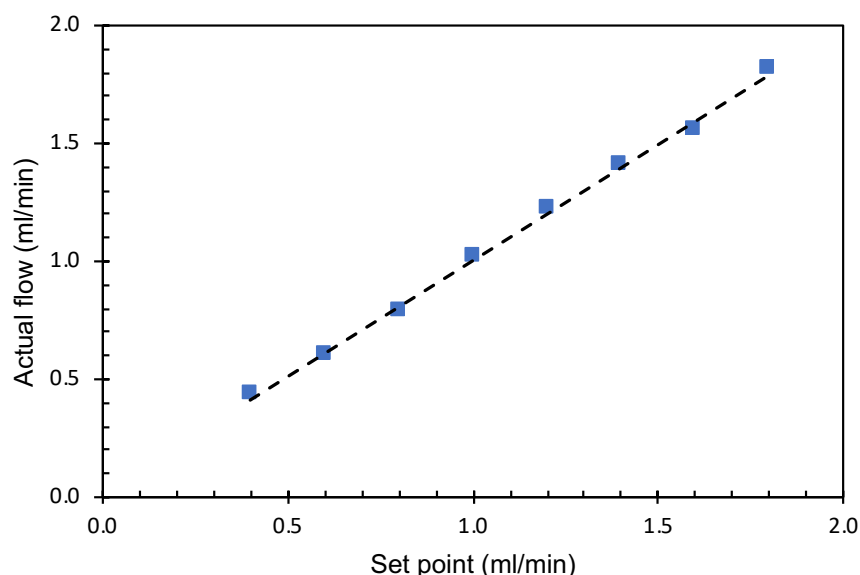


Figure B.1: HPLC pump calibration curve

B-2 Mass flow controller calibration

The mass flow controller (MFC) is used to supply the system with N_2 flow during experiments. The controller is capable of supplying a flow rate of 0 to 5 NL/min. The MFC was calibrated using a bubble flow meter with increments of 50 ml at atmospheric conditions. The actual flow rate was determined over a MFC set point range of 0.2-2.5 NL/min. The data obtained is converted to standard flow (NL/min) using a standardised pressure of 1 atm and temperature of 0 °C. These values were used to obtain the calibration curve in Figure B.2.

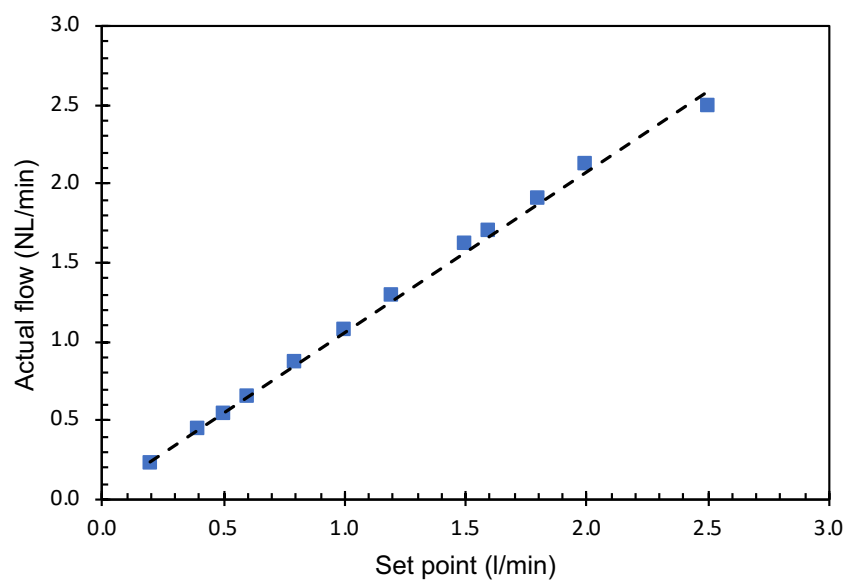


Figure B.2: Mass flow controller calibration curve

Appendix C: Additional rig evaluation

C-1 Test of inert pipe reactor

Experimental runs at an elevated temperature and pressure were done to determine if the pipe reactor is inert. An experimental run at 10 bar steam partial pressure and 730°C was completed with and without the biochar sample. The concentration curves of both the CO and CO₂ are shown in Figure C.1.

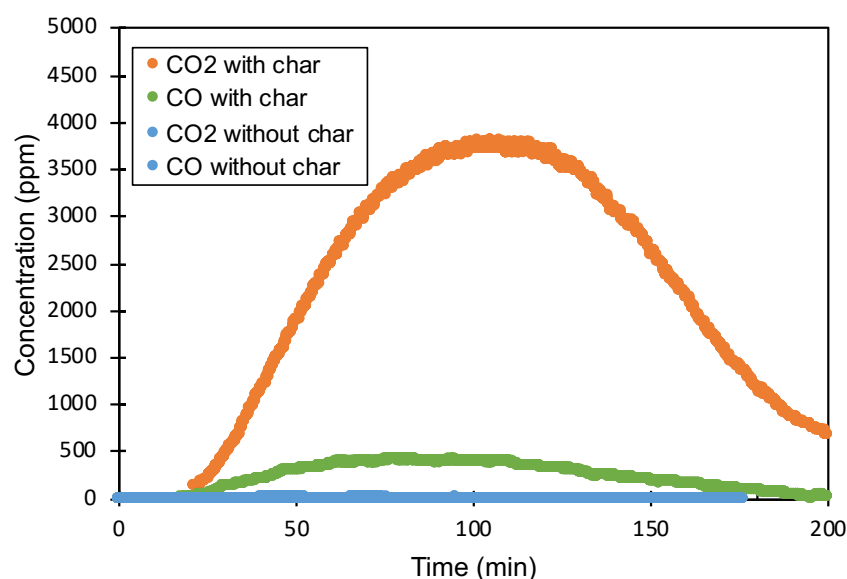


Figure C.1: Concentration curves with and without char sample at 10 bar steam partial pressure and 730°C

The CO and CO₂ formation without the biochar sample was insignificant when compared to the CO and CO₂ formation with biochar sample. This implied that the pipe reactor is inert for experimental runs.

C-2 Test of CO₂ formation from steam and CO gas

In order to determine the effect of the water gas shift reaction on the carbon conversion a CO₂ formation test was completed. The CO calibration gas, with a 1650 ppm CO concentration, was mixed with steam in a ratio of 1:1. The experiment was carried out at a temperature of 730 °C and 1 bar steam partial pressure. A higher steam partial pressure could not be investigated due to the CO low pressure gas supply. The results obtained are shown in Figure C.2.

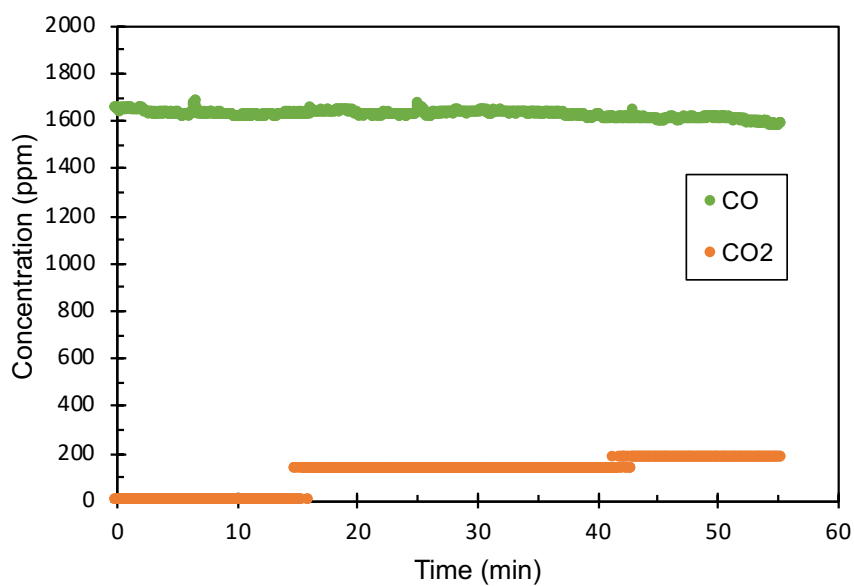


Figure C.2: CO₂ formation from steam and CO gas

The highest CO₂ concentration value reached is 170 ppm, while the CO concentration decreases from 1648 ppm to 1590 ppm. However, these results are insignificant to dismiss the effect of the water-gas-shift reaction.

Appendix D: Error estimation calculation

D-1 Repeatability of runs

Four different operating conditions were chosen, and three experimental runs were completed at each condition. These conditions are 1 bar steam partial pressure at 700 and 730 °C and 10 bar steam partial pressure at 700 and 730 °C. The t-distribution method was used to calculate the confidence interval using the following equation [105]:

$$CI = \bar{x} \pm t_{critical\ value} \left(\frac{s}{\sqrt{n}} \right) \quad (D-1)$$

Where $\bar{x}$ is the average of the repeated runs, $t_{critical\ value}$ is a value based on a specific confidence interval and degrees of freedom, s is the standard deviation of the experimental runs and n is the number of repeated runs. The $t_{critical\ value}$ for a confidence level of 95% and 2 degrees of freedom is 4.303. The confidence interval at various conversions for different repeat runs are shown in Table D.1 to Table D.4.

Table D.1: Specific reaction rate at different conversions for repeated runs of 1 bar steam at 700 °C

X (-)	r_{s,run1} (g/g/s)	r_{s,run2} (g/g/s)	r_{s,run3} (g/g/s)	$\bar{x}$ (g/g/s)	s	CI
0.1	1.6	1.5	1.9	1.6	0.2	1.6 ± 0.5
0.2	1.9	1.6	1.8	1.8	0.2	1.8 ± 0.4
0.25	2.0	1.8	1.9	1.9	0.1	1.9 ± 0.2
0.3	1.9	2.0	2.1	2.0	0.1	2.0 ± 0.3

Table D.2: Specific reaction rate at different conversions for repeated runs of 1 bar steam at 730 °C

X (-)	r_{s,run1} (g/g/s)	r_{s,run2} (g/g/s)	r_{s,run3} (g/g/s)	$\bar{x}$ (g/g/s)	s	CI
0.1	4.3	4.1	4.6	4.3	0.3	4.3 ± 0.7
0.2	4.5	4.7	5.0	4.7	0.3	4.7 ± 0.6
0.3	5.1	5.6	5.8	5.5	0.4	5.5 ± 0.9
0.4	6.2	6.6	6.8	6.5	0.3	6.5 ± 0.7

Table D.3: Specific reaction rate at different conversions for repeated runs of 10 bar steam at 700 °C

X (-)	$r_{s,run1}$ (g/g/s)	$r_{s,run2}$ (g/g/s)	$r_{s,run3}$ (g/g/s)	$\bar{x}$ (g/g/s)	s	CI
0.1	5.8	5.4	5.6	5.6	0.2	5.6 ± 0.4
0.2	7.1	7.0	7.0	7.0	0.1	7.0 ± 0.1
0.3	8.4	7.8	8.0	8.1	0.3	8.1 ± 0.8
0.4	9.6	8.7	9.3	9.2	0.5	9.3 ± 1.3

Table D.4: Specific reaction rate at different conversions for repeated runs of 10 bar steam at 730 °C

X (-)	$r_{s,run1}$ (g/g/s)	$r_{s,run2}$ (g/g/s)	$r_{s,run3}$ (g/g/s)	$\bar{x}$ (g/g/s)	s	CI
0.1	10.4	9.9	10.3	10.2	0.2	10.2 ± 0.6
0.2	15.4	14.9	15.5	15.3	0.3	15.3 ± 0.8
0.3	19.3	18.9	20.2	19.5	0.7	19.5 ± 1.6
0.4	23.6	23.0	24.0	23.5	0.5	23.5 ± 1.3

D-2 Error estimation of experimental data and models

The parameters for the kinetic models were calculated using the experimental data and the results obtained from these calculations were further investigated using a relative/deviation error. This error was determined by the following equation:

$$error (\%) = \left[\frac{\sqrt{\frac{\sum_{i=1}^n (r_{exp,i} - r_{calc,i})^2}{n}}}{r_{exp,max}} \right] \times 100 \quad (D-2)$$

Where n is the number of data points, $r_{exp,i}$ and $r_{calc,i}$ are the experimental and calculated values at a specific point and $r_{exp,max}$ the maximum experimental value of the data range.

This method provided an estimated error of deviation between the experimental and calculated data which can be caused by the experimental error. The errors for each model at different temperatures were calculated and are displayed in Table D.5. The average error for both the LH and PL model was 4%.

Table D.5: Error estimation between experimental and calculated values

	700 °C	710 °C	720 °C	730 °C
Languir-Hinshelwood	3.9 %	4.2 %	3.2 %	4.9 %
Power law	4.2 %	3.7 %	3.9 %	3.8 %

D-3 Quality of fit

In order to quantify the accuracy of the kinetic models ability to predict the reaction rate of experimental values the quality of fit (QOF) was used. The equation used to determine the QOF is shown below.

$$QOF (\%) = \left[1 - \frac{\sum_{i=1}^n \frac{|r_{exp,i} - r_{calc,i}|}{r_{exp,i}}}{n} \right] \times 100 \quad (D-3)$$

Where the parameters are the same as described in Appendix D-2. The QOF was determined for the temperature range of 700 to 730 °C and are displayed in Table D.6. The values indicate that the PL was a better fit than the LH model, although the average difference in QOF between the two models are 2%.

Table D.6: Quality of fit for kinetic models

	700 °C	710 °C	720 °C	730 °C
Languir-Hinshelwood	91 %	91 %	93 %	89 %
Power law	93 %	94 %	94 %	92 %

Appendix E: Additional calculations

E-1 Determination of model parameters

For both the Langmuir-Hinshelwood and power law kinetic models the least squared method was used to determine the kinetic parameters. This method uses a minimisation equation as seen in equation E-1.

$$Min = \sum_{i=1}^n (r_{exp,i} - r_{calc,i})^2 \quad (E-1)$$

Firstly, the reaction rate was calculated with guessed values for the kinetic parameters and then the squared difference between the experimental and calculated values. The sum of these squared values (eq. E-1) is minimised with the Microsoft Excel add in SOLVER function. This provides with an approximation of the kinetic parameters for the models.