

Advanced Fluidised Bed Gasification for Carbon Capture and Fuel Cell Applications

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Abstract

The rapid global economic and population growth requires consistent supply of energy. Gasification is a promising technology for processing solid fuels. One of the technology options is the integration of coal gasification with combined cycle (IGCC). As concerns over enhanced global warming have increased, more advanced technology such as integration of IGCC system with carbon capture and storage (CCS) has been proposed, such as oxyfuel IGCC. Another technology for power generation that can be used instead of IGCC is integrated gasification fuel cell (IGFC). IGFC can also be combined with oxyfuel concept to mitigate global warming. The main objectives of this work are to obtain a greater understanding of oxyfuel gasification of coal and to assess the impact of gases produced on typical materials used in fuel cells.

A laboratory scale continuous pressurised fluidised bed reactor has been modified to study CO₂ and steam (concentration up to 40%mol.) gasification of coal at 850 °C and pressures up to 10 bar_a. A second stage fixed bed reactor has been specially designed and constructed to study degradation of different solid oxide fuel cell (SOFC) anode materials (nickel/yttrium stabilised zirconium oxide (Ni/YSZ) and nickel/gadolinium-doped ceria (Ni/CGO)) after exposure to real fuel gas at 765 °C.

The main findings include: (1) C conversion decreased significantly at high pressure. This drop was mainly caused by the char deactivation through repolymerisation of the volatiles. (2) Input steam increased C conversion, as steam was more reactive

than CO₂. However, moisture from feedstock behaved differently compared to steam addition in the gasification gas. (3) Ni/CGO showed a better performance than Ni/YSZ in terms of carbon and sulphur deposition. Fuel gas from CO₂/H₂O gasification tended to form less carbon and sulphur on tested anode materials than that from CO₂ gasification.

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Declaration of Originality

I certify that all work presented in this thesis is my own and otherwise is appropriately referenced.

Xiangyi Long

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Nomenclature

CCS	Carbon capture and storage	
CF	Correction factor	
CGO	Gadolinium doped ceria	
DI	Deionised	
EDX	Energy dispersive X-ray spectroscopy	
GL	German lignite	
HTW	The high-temperature Winkler	
IGCC	Integrated Gasification Combined Cycle	
IGFC	Integrated Gasification Fuel Cell	
IR	Infrared	
NMP	1-methyl-2-pyrrolidinone	
PAHs	Polycyclic aromatic hydrocarbons	
SCGP	Shell coal gasification process	
SEC	Size exclusion chromatography	
SEM	Scanning electron microscopy	
SOFC	Solid oxide fuel cell	
TGA	Thermogravimetric analyser	
TPO	Temperature programmed oxidation	
UV	Ultraviolet	
XRD	X-ray diffraction	
YSZ	Yttria stabilised zirconia	
C_{CO_2}	CO ₂ concentration	%vol.
C_D	Drag coefficient	-
C_{H_2}	H ₂ concentration	%vol.
CI	Confidence intervals	-
conv.C	C conversion	%
conv.CO ₂	CO ₂ conversion	%
C_{oxygen}	Content of oxygen from NiO in the fresh anode material before reduction	%wt.
C_p	Specific heat	J g ⁻¹ K ⁻¹
d	Interplanar distance	nm
D_i	Internal diameter	mm

d_p	Particle diameter	m
e	Minimal wall thickness	mm
ER	Equivalence ratio	-
f	Creep strength	MPa
F_{CO_2}	Inlet CO ₂ flow rate	NL min ⁻¹
F_{coal}	Coal flow rate	g min ⁻¹
$F_{fuel\ gas}$	Fuel gas volumetric flow rate	NL min ⁻¹
F_{gas}	Flue gas volumetric flow rate	NmL min ⁻¹
F_{out}	Volumetric flow rate	NL min ⁻¹
F_{solid}	Solid material flow rate	g min ⁻¹
g	Gravity acceleration	9.81 m s ⁻²
HHV	Higher heating value	MJ m ⁻³
LHV	Lower heating values	MJ m ⁻³
n	Positive integer	-
p	Design pressure	MPa
Re_p	Particle Reynolds number	-
SD	Standard deviations	-
t	Time	min
U	Superficial velocity	m s ⁻¹
U_{mf}	Minimum fluidising velocity	m s ⁻¹
u_t	Terminal velocity	m s ⁻¹
W_{after}	Sample weight after TPO	mg
W_c	Carbon deposition	mg mg ⁻¹ reduced sample
W_{empty}	Weight of the container	g
$W_{reduction}$	Weight of the fresh sample after reduction	mg
W_{solid}	Weight of the collected material and the container	g
Δt	Time interval	min
ΔV	Gas volume difference between the time interval	NL
ϵ_{mf}	Void fraction	-
θ	Scattering angle	°
λ	Wavelength of incident ray	nm
μ	Viscosity	kg m ⁻¹ s ⁻¹

Nomenclature

ρ	Density	g L^{-1}
ρ_{CO_2}	Density of CO_2	mg mL^{-1}
ρ_g	Gas density	kg m^{-3}
ρ_s	Solid density	kg m^{-3}
ϕ_s	Sphericity	-

Chapter 1 Introduction

1.1 Background

The rapid global economic and population growth requires consistent supply of energy. According to the IEA prediction, the primary energy demand is expected to increase more than 30% between 2014 and 2040 (shown in Figure 1.1). In 2040, under the IEA's New Policies Scenario, the demands of nuclear, hydro, bioenergy and other renewables are expected to increase to 7, 3, 11 and 6% respectively of the total global primary energy demand, while the rest of the energy demand (73%) is expected to be provided by the fossil fuels (coal, oil and gas) with almost one third of each (IEA, 2016). Therefore, coal, as one of the fossil fuels and been used globally for thousands of years, and its consumption is expected to remain high for the foreseeable future (around 4000 Mtoe y^{-1}).

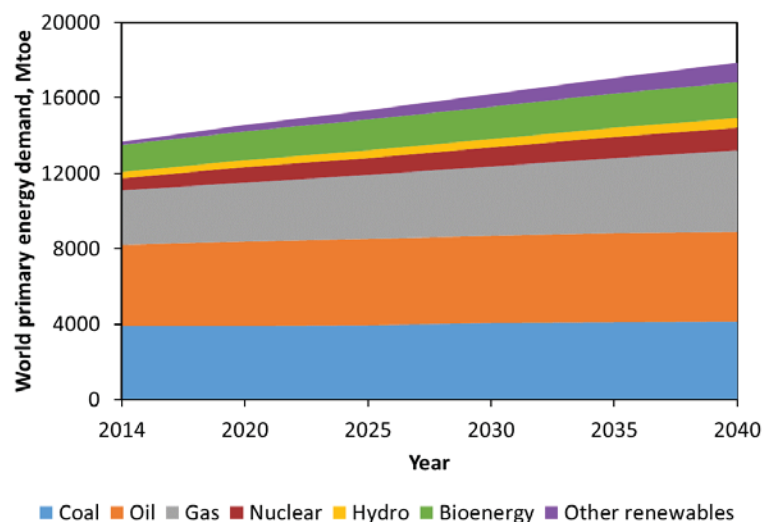


Figure 1.1 World primary energy demand by fuel in the New Policies Scenario
(adapted from IEA (2016))

The direct combustion of coal (such as stoker boilers and pulverised fuel combustion) has been the dominant way of releasing the energy in coal for over 200 years throughout the world. Pulverised fuel firing system is one of advanced coal combustion technologies. It has been developed incrementally to improve its efficiency and reduce its environmental impact over the last 75 years. However, it is now reaching its efficiency limit and is facing environmental issues. The combustion of coal can cause various environmental issues, such as the emissions of particulates, SO_x , NO_x , Hg and CO_2 (IEA, 2014). There are technologies available to deal with some of these issues, but they have an impact on the efficiency and economics of the power generation. Therefore, alternative technology options have been investigated in recent decades. Gasification of coal is not a new technology. Gasification is the conversion of carbonaceous fuel into a gaseous fuel (Higman and Van der Burgt, 2011). The overall process includes pyrolysis, hydrogenation and partial oxidation which is the dominant technology. It has been used to produce combustible gases from coal and other carbonaceous materials since the 19th Century. Coal gasification technology was first utilised for illumination more than 100 years ago. During the 1940s, it was widely used in Europe and other countries to produce gas and liquid fuels, due to a shortage of crude oil supplies (Joshi and Lee, 1996). The use of coal for these products diminished in Europe in the post 2nd world war period. However, production of liquids has continued in South Africa by Sasol using Lurgi gasifiers. One of the technology options that has been considered for the last 30 years is the combination of coal gasification with a combined cycle power generation plant. The

integration of coal gasification with combined cycle (IGCC) is a clean coal technology option that can remove or reduce the pollutant emissions. The main components for IGCC process are the gasifier, the gas turbine and the steam turbine. It is a promising technology for power generation, and its efficiency is higher than conventional coal fired power plants. During 1970s and 1980s, large gas turbine technology became available for power generation. This was partly due to the improvement of materials for the turbine blades. A gas turbine (which requires a gas at pressure) linked to a steam turbine is called a combined cycle. IGCC is the technology that utilises this turbine combination fed with fuel gas from a gasifier. The IGCC technology has been shown to have a higher efficiency than the best conventional coal fired power plants. The IGCC process first gasifies carbon-based fuels into a gaseous fuel. This pressurised gaseous fuel is cleaned whilst hot (to avoid thermal efficiency loss), and then passed through a gas turbine to generate electricity. After that, the excess heat in the flue gas is used to raise steam to drive a steam turbine.

In more recent years concerns over enhanced global warming have resulted in more advanced technology options, such as carbon capture and storage (CCS). However, this costs efficiency penalties. There are normally three routes for carbon capture including post-combustion, pre-combustion and oxyfuel. The Oxyfuel uses pure O_2 (produced by air separation unit) instead of air and produces flue gas with pure CO_2 for storage without CO_2/N_2 separation. For oxyfuel IGCC, a pure stream of CO_2 is produced at the back end of the process, part of this CO_2 is recycled back into the

gasifier as the gasification agent and temperature moderater. The heat required for the CO₂ gasification (endothermic reaction) is provided by O₂ combustion reactions.

Another technology for power generation that can be used instead of gas turbines is fuel cell. Fuel cell converts chemical energy from a fuel gas into electricity directly via electrochemical reactions. Without suffering from Carnot, thermodynamic and mechanical limitations, it provides a more efficient (generally 40 to 60%) route for electrical power generation. It is an environmental friendly technology, as it produces much less pollutant emissions compared to conventional power plants. The high resistant to contaminants and high operating temperatures (650 to 1000 °C) of solid oxide fuel cells (SOFC) allow them to integrate with gasification (Abuadala and Dincer, 2012, Gholamian et al., 2016). Therefore, the oxyfuel integrated gasification fuel cell (IGFC) provides high efficiency and low pollutant emissions.

1.2 Objectives

The objectives of this work were to obtain a greater understanding of the oxyfuel gasification of coal in a fluidised bed reactor and to assess the impact of the gases produced on typical materials used in fuel cells. The following tasks were carried out to meet these objectives.

- (1) To modify of an existing laboratory scale pressurised fluidised bed reactor to operate under pressurised oxyfuel conditions with steam flow addition, and to

construct a second stage fixed bed reactor to test SOFC anode materials and to expose them to gasification gas.

- (2) To investigate the pressure influence on oxyfuel gasification and to identify the potential reasons for changes in performance.
- (3) To study how the gasification performance changes with steam addition under pressurised oxyfuel gasification conditions.
- (4) To analyse the degradation of SOFC anode materials when exposed to gasification gas produced under a range of gasification conditions.
- (5) To make recommendations for the design and operation of large scale oxyfuel gasification facilities and integrated oxyfuel gasification with fuel cell.

1.3 Outline of the Thesis

This thesis is divided into seven chapters.

Chapter 1 introduces the background to the topic, the objectives of the project and the structure of the thesis.

Chapter 2 provides the literature survey, the ideas underlying oxyfuel gasification and the relevant developments in the field.

Chapter 3 describes the experimental details including the used materials, the pressurised fluidised bed reactor and its modifications, the experimental procedures,

and the analytical methods. In addition, the repeatability of the procedure, the mass balance and error analysis are presented in this chapter.

Chapter 4 and 5 discuss the experimental results from different operating conditions of pressurised oxyfuel gasification. They focus on different operating parameters including pressure and steam addition.

Chapter 6 describes the study of the degradation of the SOFC anode materials when exposed to fuel gas from oxyfuel gasification.

Chapter 7 summaries this project with the main conclusions and the recommendations for the future work.

Chapter 2 Literature Review

2.1 Gasification Principles

Gasification is a thermal reaction that partially oxidises solid or liquid feedstock to generate a large quantity of gaseous products (mainly H_2 and CO , with CO_2 , H_2O , CH_4 as minor components and other gaseous hydrocarbons in smaller concentrations) and solid (char, ash) and liquid (tar) products. The economic value of low- or zero-value feedstocks is increased by converting them into marketable fuels and products (Knoef and Ahrenfeldt, 2005). The products (chemicals and gaseous fuels) can be utilised to produce added-value chemicals or as a clean energy carrier (Basu, 2010).

The principal reactions that may occur during gasification are shown in Table 2.1. They involve reaction of C (which may come from a wide range of sources, e.g. coal, coke, biomass or char) with CO , CO_2 , H_2 , H_2O and CH_4 .

Table 2.1 Principal gasification reactions (Higman and Van der Burgt, 2011)

Reaction type	Reaction	ΔH , MJ kmol ⁻¹
Combustion reactions	$C + 0.5 O_2 \rightarrow CO$	-111
	$CO + 0.5 O_2 \rightarrow CO_2$	-283
	$H_2 + 0.5 O_2 \rightarrow H_2O$	-242
Boudouard reaction	$C + CO_2 \leftrightarrow 2 CO$	+172
Water gas reaction	$C + H_2O \leftrightarrow CO + H_2$	+131
Methanation reaction	$C + 2 H_2 \leftrightarrow CH_4$	-75
CO shift reaction	$CO + H_2O \leftrightarrow CO_2 + H_2$	-41
Steam methane reforming reaction	$CH_4 + H_2O \leftrightarrow CO + 3 H_2$	+206

According to Basu (Basu, 2010), a gasification process normally follows a sequence of steps including drying, pyrolysis and gasification, with the energy for the process being supplied by combustion. These steps often overlap with no clear limit between them. Figure 2.1 illustrates a potential pathway for gasification.

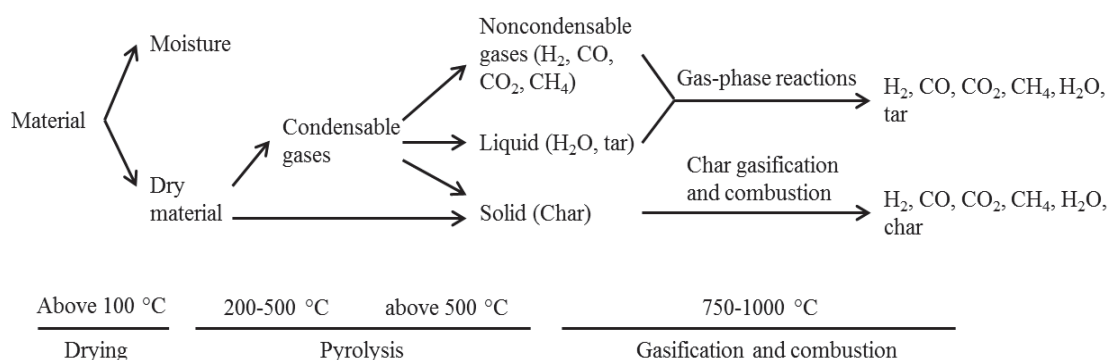


Figure 2.1 Gasification potential pathway (reproduced from Basu (2010))

The typical moisture content of coal ranges from 2%wt. to 9%wt., while the moisture content of freshly cut wood normally ranges between 30%wt. and 60%wt. (Sivek et al., 2010, Ruiz et al., 2013). For a high level of moisture content material, the energy to vaporise water is a concern, which affects the economics and efficiency of its use. Pre-treatments, such as drying, are essential for biomass to remove some moisture before it is fed into a gasifier. After a fuel enters the gasifier, the drying process takes place first. The loosely bound surface water in the material is removed irreversibly, when temperature is above 100 °C. This uses a proportion of the energy released in the gasifier to provide the energy for volatilisation.

Pyrolysis is the thermal decomposition of solid fuels in an inert atmosphere. The initial products are light and heavy condensable gases and solid char. The

conventional pyrolysis could begin at 200 °C and is completed by 500 °C. Then, with temperature above 500 °C, condensable gases may be cracked into lower-molecular-weight species including noncondensable gases (H_2 , CO, CO_2 and CH_4), liquid (tar and H_2O) and char (Higman and Van der Burgt, 2011).

Gasification step involves chemical reactions among produced gases, char and gasification agents. The most important part is char gasification, which is comprised of several reactions between char and gasification agents (O_2 , CO_2 and H_2O). During this step, solid char is converted into smaller molecular weight gases such as CO and H_2 . Reactions of char gasification are Boudouard, water gas and methanation reaction (shown in Table 2.1) depending on gasification agents. Meanwhile, the gas phase reactions including CO shift and steam methane reforming reaction are happened simultaneously.

To provide the heat demand for drying, pyrolysis and endothermic gasification reactions, exothermic combustion reactions (shown in Table 2.1) are allowed to take place in the gasifier.

The overall conversion rate of the gasification process is governed by the slowest reactions, which are the heterogeneous reactions with C including Boudouard, water gas and methanation reactions. The reaction rates of Boudouard and water gas reactions are comparable, and several orders of magnitude higher than methanation reaction (Higman and Van der Burgt, 2011). Several reaction mechanism models have been proposed for these reactions. A widely used model for Boudouard

reaction was proposed by Ergun (1956). It is a two-step process. In the first step (Reaction 2.1), an oxygen-surface complex (C(O)) is formed by CO₂ dissociation at a carbon free active site (C()) with releasing of CO. In the second step (Reaction 2.2), the oxygen-surface complex produces CO and a new carbon free active site. The second step is the rate limiting step.



The reaction rate of water gas reaction is generally considered to be faster than that of Boudouard reaction at lower temperatures. The reaction model of water gas reaction can be similar as Boudouard reaction. In the first step (Reaction 2.3), a steam molecule dissociates at a carbon free active site, and forms oxygen-surface complex with H₂ releasing. In the second step (Reaction 2.4), CO and a new carbon free active site are produced by the oxygen-surface complex. In this model, the desorption of oxygen-surface complex is the rate limiting step. Some models consider H₂ inhibition by reaction with carbon free active site forming a complex from the third step (Reaction 2.5 and 2.6). Therefore, some of the active sites can be blocked by H₂.



2.2 Feedstock for Gasification

Various types of feedstock can be used for gasification process. Some typical feedstock materials include coal, biomass, agricultural residues and industrial residues (Abuadala and Dincer, 2012). Among those feedstocks, coal and biomass are the most widely used materials for gasification processes.

2.2.1 Coal

Coal is a complex mixture of organic compounds and minerals. Geologically, it is a sedimentary organic rock (Petrakis and Grandy, 1980). It is the largest fossil resource in the world, and it plays a significant role in the global energy system (Schrag, 2007).

The rank of a coal reflects the extent to which the organic matter in the parent biomass has been altered under high pressure and moderate temperatures over geologic timescales. Peat is the first stage in this conversion to coal, although it is not classed as a coal due to high content of original plant structures. The coal rank

series can be divided into four categories namely anthracite, bituminous coal, sub-bituminous coal and lignite, as shown in Table 2.2.

Table 2.2 Classification of coals by rank (ASTM, 2017)

Class	Group	Fixed carbon (%wt.)	Volatile matter (%wt.)	High heating value (MJ kg ⁻¹)
Anthracite	Meta-anthracite	over 98%	under 2%	
	Anthracite	92-98%	2-8%	
	Semi-anthracite	86-92%	8-14%	
Bituminous	Low-volatile	78-86%	14-22%	
	Medium volatile	69-78%	22-31%	
	High volatile A	under 69%	over 31%	over 32.5
	High volatile B	under 69%	over 31%	30.2-32.5
Sub-bituminous	High volatile C	under 69%	over 31%	26.7-30.2
	A	under 69%	over 31%	24.4-26.7
	B	under 69%	over 31%	22.1-24.4
	C	under 69%	over 31%	19.3-22.1
Lignite	A	under 69%	over 31%	14.6-19.3
	B	under 69%	over 31%	under 14.6

2.2.2 Biomass

Biomass contains chemical energy stored as organic materials produced from solar energy by photosynthesis. It is an environmental friendly, carbon-neutral, energy resource. It can be separated into two main categories, namely the purpose-grown energy crops and wastes. The two kinds of energy crops are woody crops and agricultural crops. The waste types are varied, including wood residues, forestry residues, tropical crop wastes, and temperate crop wastes (Saidur et al., 2011).

The vegetable biomass mainly contains cellulose, hemicellulose and lignin and a small quantity of lipids, simple sugars, proteins, inorganic constituents, moisture and starches. Lignocellulose is the combination of lignin, cellulose and hemicellulose, which forms the dominant part of the biomass structure (Zhang et al., 2010a). The composition and proportion of lignocellulose is varied in biomass. Cellulose forms the largest part of lignocelluloses, then hemicelluloses, and followed by lignin. The difference between cellulose and hemicellulose is the different source of sugar. Lignin is an aromatic polymer, which is synthesized from phenylpropanoid precursors and there is an increasing interest in its alternative exploitation for either energy or chemical production.

2.3 Gasification Systems

2.3.1 Types of Gasifier

Based on the gas-solid contacting mode, gasifiers can be broadly divided into three types: fluidised bed, fixed bed (moving bed) and entrained flow.

Generally, moving bed gasifiers are used for low-capacity units (10 kW_{th}-10 MW_{th}), and fluidised bed gasifiers are installed in the intermediate range (5 MW_{th}-100 MW_{th}), while entrained flow are employed in the large-capacity units (>50 MW_{th}) (Basu, 2010). Detailed description of example of commercially available technologies of different types of gasifiers are discussed below.

2.3.1.1 The high-temperature Winkler (HTW) process (fluidised bed gasification)

The high-temperature Winkler process is a fluidised bed process and was developed by Rheinbraun AG of Germany in 1970s (Higman and Van der Burgt, 2011). This process operates at high pressure and high temperature (below the ash-melting point) primarily for lignite gasification, and it is also suitable for other reactive fuels (e.g. biomass). In HTW process, gasification agents are introduced into the fluidised bed reactor at different levels. Normally, the pressure of the bed is maintained at 10 bars, and the temperature is kept at 800 °C to avoid ash fusion. Additional gasification medium supplied overbed reaches the local temperature around 1000 °C to reduce the production of methane and other hydrocarbons. The gas quality produced from this process is better than that of traditional low-temperature fluidised bed gasifiers due to the reactive nature of the fuel.

2.3.1.2 Sasol-Lurgi process (moving bed gasification)

Sasol-Lurgi moving bed dry bottom gasifier first proposed by Lurgi in the 1930s (Higman and Van der Burgt, 2011) and it is one of the first practical applications of gasification. Sasol-Lurgi gasifiers are operated widely in the world, mainly in South Africa, China and the United States. It could be categorised as updraft (counter current) gasifier where the feedstock is supplied from the top, and oxidant (e.g. air or steam) moves counter-currently with the feed stock from the bottom. Solid fuel

(e.g. coal or biomass) therefore experiences drying, pyrolysis, gasification and oxidation as it continuously moves down to regimes of increasingly higher temperature. This technology is a commercially proven technology that could work with as received coal (contain moisture) at pressure up to 30 bar_a. The disadvantage of the reactor is its relatively restricted scale, high tar yield and frequent maintenance required.

2.3.1.3 Shell coal gasification process (SCGP) (entrained flow gasification)

In 1978, Shell and Koppers jointly developed a pressurised version of Koppers-Totzek process, which operates 150 t d⁻¹ in Harburg, Germany. In 1994, a 2000 t d⁻¹ Shell gasification unit was built for Demkolec in Buggenum in the Netherlands, and internationally traded coal was used as original feedstock (Higman and Van der Burgt, 2011). There are more than 30 SCGP reactors operating globally, including the first one built nearly 40 years. SCGP is an entrained flow gasification process. The temperature and pressure in the gasifier is generally 1500 °C and 30-40 bar. SCGP uses side feeding, and consists of two side-mounted burners that is the place of dried coal and oxygen injection. The fuel gas leaves the reactor from the top, while the slag leaves through an opening in the reactor bottom. A steam jacket is used to protect the reactor shell from high temperatures.

2.3.2 Advanced Gasification Systems

2.3.2.1 Integrated gasification combined cycle

IGCC plants have been identified as one of the most attractive options among other coal based power plants due to their higher thermal efficiency and low environmental impact with a better control on greenhouse gas emissions (Ahmed et al., 2017). The first demonstration of the basic IGCC concept in a commercial scale was the Cool Water Project in California, USA from 1984 to 1989. Texaco gasifier was used in that project. After that, several commercial IGCC plants were built and started operating during in 1990s. Willem Alexander IGCC Plant is one of first commercial IGCC plant across the world. It was built in Buggenum, Netherlands in 1994. The net power generation capacity can achieve 253 MW from 1998. ELCOGAS IGCC Plant in Puertollano, Spain, built in 1998, is one of the largest IGCC plant globally with the net capacity of 330 MW.

The IGCC gasifies coal and other carbon-based fuels in a high-pressure gasifier to produce syngas. The syngas is hot cleaned to remove impurities such as acidic gases (e.g. H_2S , HCl), mercury, alkali and alkaline earth metals, and other particulates. The cleaned syngas is then combusted to drive a gas turbine for electricity generation. The excess heat from the combustion of syngas is recovered through a steam turbine to produce more electricity.

The feedstock for IGCC is flexible and includes coal, biomass and waste. Moreover, the cleaned syngas from IGCC could apply to different applications (Figure 2.2) to meet different market demands. Therefore, the lower production costs could be achieved with the higher possibilities for generating profits, and the development of a system with multi-feedstock and multi-product satisfies the requirements for the market flexibility.

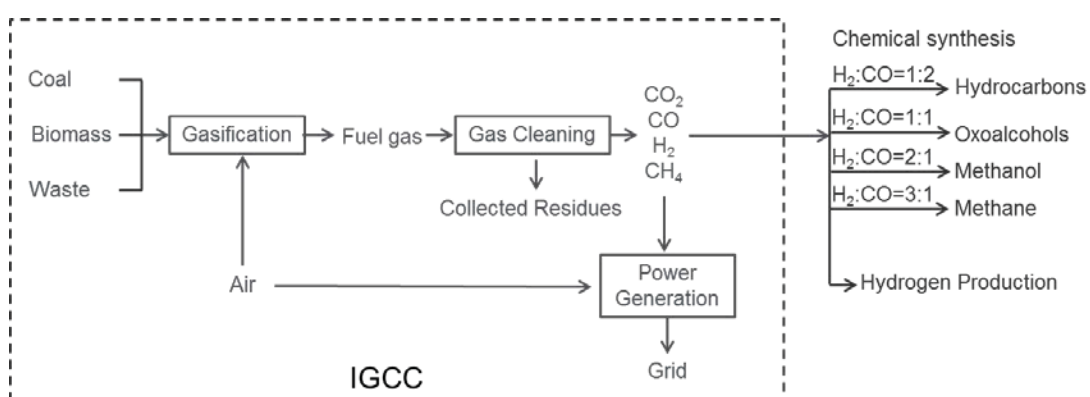


Figure 2.2 Gasification of multi-feedstock and multi-product

2.3.2.2 Oxyfuel IGCC with CO₂ recycling

Oxyfuel technology is defined as using oxygen instead of air for fuel combustion or gasification. In 1982, this concept was used to produce of pure CO₂ through oxyfuel combustion for enhanced oil recovery (Abraham et al., 1982). Later, oxyfuel pulverised coal combustion was further developed for the integration with CCS. OxyCoal from Doosan Power Systems is one of the earliest demonstration of oxyfuel combustion system with a capacity of 40MW_{th}, and it was built in Renfrew, UK in 2009. Further scale up is required before this process become commercialised. In

China, a 200 MW oxyfuel combustion plant is under development led by Shenhua Group and Dongfang Boiler Works. Oxyfuel gasification is a relatively new process developed for IGCC integrated with CCS (Oki et al., 2011). An air separation unit is introduced into the system to provide pure O_2 instead of air for both gasification and combustion. Thus, a stream of pure CO_2 can be produced after the combined gas and steam turbines and ready for carbon storage. With the CO_2 recycling, part of the produced CO_2 is recycled back into the gasifier as the both the gasification agent and temperature moderator. The basic flowsheet of this anticipated oxyfuel IGCC plant with CO_2 recycling is shown in Figure 2.3.

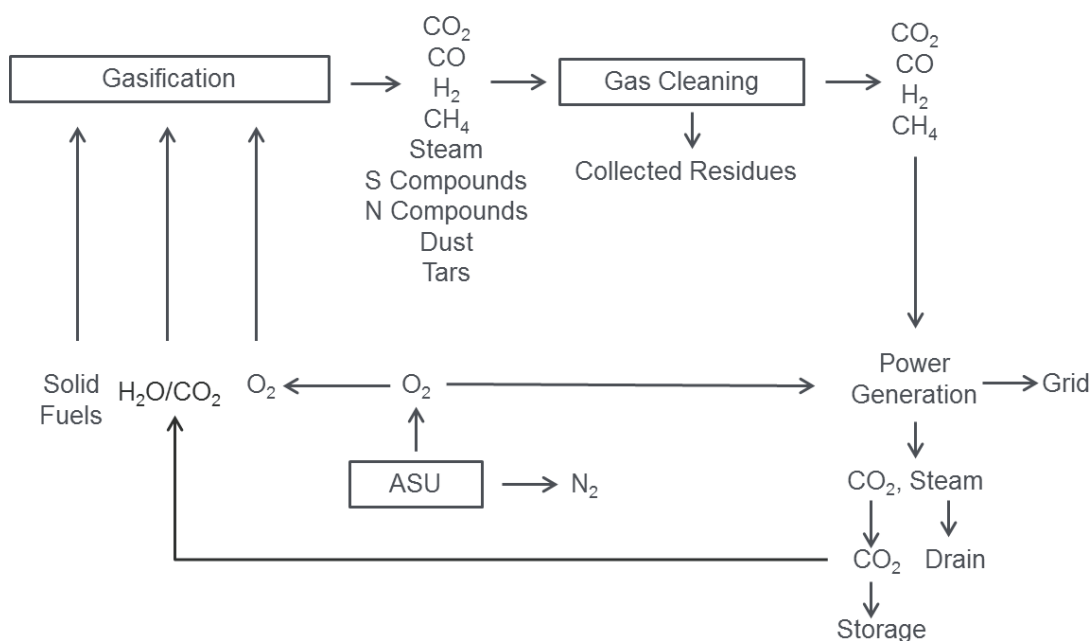


Figure 2.3 Basic flowsheet of an Oxyfuel IGCC plant with CO_2 recycling

Another technology generally is considered for carbon capture in IGCC is pre-combustion. It utilises pure O_2 and steam for gasification. After gas cleaning, the fuel gas consists CO , CO_2 , H_2 and CH_4 . CO is converted to CO_2 and produces H_2 through water gas shift reaction in a shift converter. CO_2 is then removed by a chemical or physical process with mainly H_2 left in the fuel gas. CH_4 should be removed before combustion or it should be kept at a minimum quantity through the gasification conditions. Compared to this pre-combustion IGCC process, oxyfuel IGCC does not require a shift converter or CO_2 remover.

Previous work (Spiegl, 2010) was performed in the same fluidised bed reactor used in this project. Stable operation and fuel gas compositions were achieved under a wide range of operating conditions (up to 3 MPa, 950 °C), with continuous feeding of German Lignite, Daw Mill coal and Polish coal and using CO_2/O_2 as gasification agent. That work provided a valuable insight into oxyfuel gasification concept, and it proved the reliability of the reactor running in sophisticated gasification mode under pressure.

2.3.2.3 Oxyfuel integrated gasification fuel cell combined cycle with CO_2 recycling

The solid oxide fuel cell (SOFC) generates electricity through electrochemical reactions from gaseous fuels with a higher efficiency than that can be achieved with a steam turbine based system. The SOFC operates at high temperatures that is

similar to gasification process. Thus, it is possible to integrate SOFCs with gasification plants to further enhance the process efficiency. Many researchers investigated the combined process through modelling, and have shown its feasibility (Thallam Thattai et al., 2017, Siefert and Litster, 2013, Park et al., 2011). A number of literature references have studied the performance of IGFC using simulated gasification products, while a few studies have used actual gasification products. The introduction of general information on fuel cells and review of the experimental work of the combined process of gasification and SOFC are discussed below.

2.3.2.3.1 Fuel cells

The fuel cell is defined as an electrochemical device that converts the chemically stored energy of a fuel directly into electrical energy (Abuadala and Dincer, 2010). Because of the direct conversion of the energy, the efficiency of a fuel cell (generally between 40-60%) is generally higher than that of conventional power generation systems that suffer from Carnot, thermodynamic and mechanical limitations (Seitarides et al., 2008). Hydrogen is the most commonly utilized fuel gas for fuel cells, as water is the only waste from this process (Seitarides et al., 2008).

The three main components that comprise a fuel cell are the anode, the cathode, and an electrically insulating electrolyte or membrane separating the two electrodes. The fuel gas (such as H_2 , CO and CH_4 produced from a gasifier) is introduced at the anode (negative electrode), and then diffuses towards the boundary between anode

and electrolyte. In the meantime, an oxidant (air or O_2) is continuously supplied to the cathode (positive electrode). Then, the fuel gas is oxidized and releases electrons, which travel through an external circuit to the cathode, before the electrons are accepted by oxygen atoms (Seitarides et al., 2008).

Fuel cells can be divided through their electrolyte type, operating temperature, and charge conducted mechanism. Table 2.3 shows several common types of fuel cells and their operating temperature range.

Table 2.3 Different types of fuel cell (Abuadala and Dincer, 2012)

Type of fuel cell	Temperature range
Direct methanol fuel cell	~ 60 °C
Proton exchange membrane fuel cell	~ 80 °C
Alkaline fuel cell	~ 100 °C
Phosphoric acid fuel cell	~ 200 °C
Molten carbonate fuel cell	~ 650 °C
Solid oxide fuel cell	650-1000 °C

2.3.2.3.2 Solid oxide fuel cell

SOFC uses ceramic electrolyte to conduct negative oxygen ions transferring from the cathode to the anode. Due to operating in a similar temperature range and sufficient tolerance to syngas contaminants, the SOFC can be combined with a gasification process into an integrated system, a combination which could result in a significant efficiency increase (Abuadala and Dincer, 2010, Abuadala and Dincer, 2012, Omosun

et al., 2004, Seitarides et al., 2008). Reaction 2.7 to 2.10 represent the operation of an SOFC using gaseous production from gasification processes (Seitarides et al., 2008).



The typical gas stream from gasification contains CO, H₂, CO₂, CH₄ (maybe N₂ and steam depending on the gasification medium) and various impurities including soot, H₂S and tars. There are some technical issues associated with the combined process, as the degradation of the SOFC anode caused by the chemical interaction between some of the gasification products and the anode material. One of the vital issues is the carbon deposition which can damage the integrity of the anode structure and poison the active sites of the catalyst resulting in catalytic activity reduction (Offer et al., 2009). Another issue is the decrease of catalytic activity caused by the catalytic active sites being poisoned by sulphur-containing compounds (Boldrin et al., 2014).

The tolerance of the SOFC anode to the gasification products is not yet sufficiently understood. Most researchers have studied the influence of the gasification gas species and impurities using simulated gas and model tars. Mermelstein et al. (2009a) tested carbon formation from 15 g Nm⁻³ benzene as a model tar in the fuel gas flowing over SOFC anode materials. It was found that the carbon formation

decreased sharply, when the addition of steam at concentrations in the range 1 to 2.5% (steam to carbon ratio of 0.4 to 1). However, carbon formation did not further decrease, when steam concentration increased to 7.5%. Alzate-Restrepo and Hill (2010) studied the carbon deposition from CO and H₂ mixtures on nickel/yttrium stabilised zirconium oxide (Ni/YSZ) anode at 800 °C and observed that the amount of deposited carbon increased with increasing of CO content, while more carbon was deposited over Ni/YSZ exposed to H₂/CO mixtures than to pure CO. Mermelstein et al. (2011) investigated the impact of different simulated gasification syngas mixtures with benzene as a model tar compound on a nickel/gadolinium-doped ceria (Ni/CGO) anode SOFC. At 765 °C with a current density of 300 mA cm⁻² for a 3 hours test, there was negligible impact of tar (benzene) concentrations between 2-15 g m⁻³ on anode. However, at a lower current density of 100 mA cm⁻² with 15 g m⁻³ tar load, carbon deposition was present on the anode after 3 hours. In addition, the presence of CO and CH₄ increased the carbon deposition on the anode of SOFC, and the effect of CH₄ addition was more significantly than CO addition. Boldrin et al. (2014) investigated the influence of the fuel gas and related contaminants on carbon deposition and reforming activity over SOFC anode material by exposing Ni/CGO to a simulated gasification feed containing a model tar (toluene) and a sulfur compound (CS₂) at temperatures from 600 to 765 °C. It was found that the presence of toluene in the syngas increased the amount of carbon deposits at temperatures above 700 °C, and the amount of carbon deposits decreased with sulfur contaminants above 11 ppm of H₂S. Lorente et al. (2012) compared the effects

between a real gasification tar and a model tar (toluene) with simulated fuel gas (0-2.5% H_2O /15% H_2 / N_2 balanced) on two commercially available anode materials, Ni/YSZ and Ni/CGO. It was observed that (1) less degradation of anode by carbon formation from real tar than that from model tar, (2) less amount of carbon deposited over Ni/CGO than that over Ni/YSZ, and (3) the amount of carbon deposition could be reduced by increasing the steam content in the feed gas.

The studies on the effects of the actual product gas from the gasification on SOFC are limited. Hofmann et al. (2007) tested a commercial high temperature SOFC (Ni/CGO anode) operating on wood gas from a Viking two-stage fixed bed gasifier. Before entering the SOFC, the wood gas was cleaned by desulphurization and tar removal, and treated by humidification to a steam to carbon ratio at 0.5. Their results show that there was no carbon deposition, sulphur contamination or anode microstructure change in the experiment condition during the 150 h test. Later, Hofmann et al. (2008) examined the impact of tars on Ni/CGO anode during feeding real wood gas to SOFC. The gas was cleaned from HCl, H_2S and particulates before the feeding to the SOFC membranes. According to their results, tar did not cause noticeable problems to Ni/CGO anode operation, when its content was from 0 to 3000 mg Nm^{-3} . However, when high steam content and high fuel utilization conditions were employed, the anode nickel material was oxidized and the SOFC lost its performance. In addition, carbon deposits could be formed on the inside of the functional layer of the anode, when the particulates reached the SOFC. Singh et al.

(2010) tested the performance of a Cu anode SOFC operated at 950 °C using a fuel gas from coal pyrolysis in Ar in a fixed bed reactor, at 700 to 950 °C. The results indicated that there was no degradation of the Cu anode with the presence of SO₂ and COS. The performance of the SOFC was decreased when a CO-rich fuel gas was fed due to the addition of CO₂ in the pyrolysis reactor.

2.4 Gasification Parameters

Gasification process can be affected by the gasifier operating conditions, these include temperature, pressure and different gasification agents. This section reviews the effects of these parameters on gas composition, gas yield, heating value and C conversion. The influences of such parameters on tar and char are reviewed later in Section 2.5.2 and 2.5.3, respectively.

2.4.1 Effect of Gasification Agents

Generally, the gasification agents include air (or oxygen), steam, CO₂ and mixtures of the above gases. Different gasification agents produce gases with different component concentrations. Gasification agents are chosen based on the intended application of gases produced by the gasification process.

Few works have been reported on comparison of different gasification agents. Gil et al. (1999) investigated the effect of some different gasification agents (including air, steam/oxygen mixture and pure steam) using pine wood chips on the gas quality

and product distribution. An atmospheric bubbling fluidised bed reactor was used in their study. According to their research, pure steam gasification had the largest hydrogen content (53-54%vol.) in gaseous products, followed by the steam/oxygen mixture gasification with hydrogen content of 25-30%vol, as the input of steam increase the extent of water gas reaction. However, the CO concentration of steam/oxygen mixture gasification was the highest, around 43-47%vol. Steam gasification had the second largest CO concentration of 21-22%vol. Air gasification gave both the lowest CO and H₂ concentrations. The lower heating values (LHV) of steam and steam/oxygen gasification were similar about 13 MJ m⁻³, while air gasification had a lower LHV of 4.5-6.5 MJ m⁻³ since the fuel gas was diluted by N₂. The gas yield for air gasification (1.7-2.0 m³ kg⁻¹ biomass d.a.f.) was relatively larger than the other two types of gasification, and tar yield was lower with 6-30 g kg⁻¹ biomass (Gil et al., 1999). Prabowo et al. (2014) compared the effect of steam and CO₂ as gasification agents on gasification of rice straw in a laboratory scale downdraft gasifier. Based on their results, CO₂ fraction in gasification agent could generally increase the CO yield and lower the H₂ yield. However, with the presence of steam in the gasification agent, the H₂ yield was largely increased.

2.4.2 Effect of Temperature

This section focuses on the studies used fluidised bed gasifiers. Generally, the gasification temperature in a fluidised bed reactor is around 700 to 1100 °C (Higman and Van der Burgt, 2011). The exact temperature depends on the properties of the

fuel. The gasification reaction rate is slow when temperature is below 700 °C. When temperature is above 1100 °C ash melting can cause agglomeration, which disrupts the operation of the fluidised bed. The reaction temperature is one of the most significant operating variables that influence the gasification process (Chaudhari et al., 2003, Yan et al., 2010, Emami Taba et al., 2012). This effect mainly depends on two factors. One is the overall reaction rate, as both chemical reaction rate and mass transfer rate are affected by temperature. According to DeGroot and Richards (1989), for steam-carbon and CO₂-carbon reactions, it is predicted that there is between a 20 and 200 fold increase in overall reaction rate, over the temperature range 750 and 950 °C. The other is the thermodynamic behaviour. The reactions are limited by thermodynamic equilibrium, although the kinetics of reaction may not be fast enough to allow equilibrium to be achieved at low temperatures. The main reaction of steam gasification is the water gas reaction, which is endothermic. The products of this reaction can be increased by increasing the reaction temperature (Xiang et al., 2009, Lv et al., 2004, Emami Taba et al., 2012). However, there are some limitations on the highest temperatures that can be used in a gasifier. These include the materials available for the gasifier construction, melting point of ash, volatile matter content of solid fuels, and production of undesirable gases (Emami Taba et al., 2012).

2.4.2.1 Effect of temperature on gas composition

Figure 2.4 shows the effect of temperature on gas composition during steam gasification in fluidised bed gasifiers, using continuous material feeding system,

reported in the literature. Table 2.4 summarizes the conditions used in these studies. According to the authors, with a temperature increase, the hydrogen content increases, while concentrations of CO₂, methane and higher hydrocarbons decrease, and CO concentration shows different trends (Karmakar and Datta, 2011, Lv et al., 2004, Turn et al., 1998, Xiang et al., 2009).

With the temperature increase, endothermic reactions (water gas reaction, steam methane reforming reaction) are enhanced, and less methane is released during pyrolysis. Therefore, hydrogen concentration is increased and methane concentration is normally decreased by increasing the temperature in gasification process (Karmakar and Datta, 2011, Lv et al., 2004, Turn et al., 1998). The study by Xiang et al. (2009) showed relatively different results of hydrogen concentration. They gasified natural coke in a fluidised bed gasifier using steam and oxygen as gasification medium. The hydrogen concentration was quite stable, when bed temperature was increased from 850 to 1000 °C. Chaudhari et al. (2001) investigated the temperature effect using steam only during the gasification of biomass-derived char in a bench scale fluidised bed gasifier. Their results show that methane concentration increase from 15.3 to 19.3%vol. from 650 to 700 °C, and then decrease to 9.9%vol. at 800 °C at a low steam flow rate. They suggested that methane might be an intermediate product, and its concentration was determined by the balance between its formation and decomposition reactions. At a lower temperature (around 650 °C), the formation rate of methane was low. When temperature was increased

about 700 °C, methane formation rate increased, and the rate of decomposition reactions of methane (such as steam methane reforming reaction) was relatively slower than its formation rate. As a result, the concentration of methane was increased. With the temperature increased further (above 750 °C), the decomposition reactions of methane became more dominant than its formation reaction and a decrease in the methane concentration was observed.

Table 2.4 Conditions of gasification experiments at atmospheric pressure in fluidised bed gasifiers

Sample	Medium	Bed material	Temperature, °C	S/B ratio ¹	ER ²	Reference
Rice husk	steam	Silica sand	650-770	1.3	0	Karmakar and Datta, 2011
Pine sawdust	steam, air	Silica sand	700-900	2.7	0.22	Lv et al., 2004
Sawdust	steam, O ₂ , N ₂	Alumina beads	750-950	1.4	0.18	Turn et al., 1998
Natural coke	steam, O ₂	Quartz sand	850-1000	3.8	0.02	Xiang et al., 2009
Biomass-deriv	steam	Quartz chips	650-800	1.09	0	Chaudhari et al., 2001

¹ Steam to biomass ratio, ² Equivalence ratio.

For steam only gasification or steam and oxygen gasification with a low equivalence ratio (ER) (e.g. 0.02), CO is mainly formed by water gas and Boudouard reactions. Both are endothermic reactions. The consumption of CO is from CO shift reaction that is an exothermic reaction (Xiang et al., 2009, Karmakar and Datta, 2011). The products of endothermic reactions and reactants of exothermic reaction are favoured with the rise of temperature, thus CO concentration is increased when temperature goes up. This is accompanied by a reduction in the content of CO₂.

Turn et al. (1998) have done experiments using sawdust for steam and oxygen gasification at equivalence ratio of 0.18. They observed that CO concentration was almost constant with increasing temperature, and suggested that it was due to the shift of equilibrium of the partial combustion reaction ($C + 0.5 O_2 = CO$) towards the left side. Lv et al. (2004) reported that the concentration of CO declined with temperatures between 700 and 900 °C at a relatively high equivalence ratio (0.22) for steam and oxygen gasification. They claimed that, with a relatively high content of input oxygen, the CO formation was mainly originated from the combustion reaction, which is exothermic. For higher hydrocarbons (such as C_2H_2 , C_2H_4 and C_2H_6), their concentrations reduced with increase of temperature, since thermal cracking and steam reforming were strengthened (Lv et al., 2004, Turn et al., 1998).

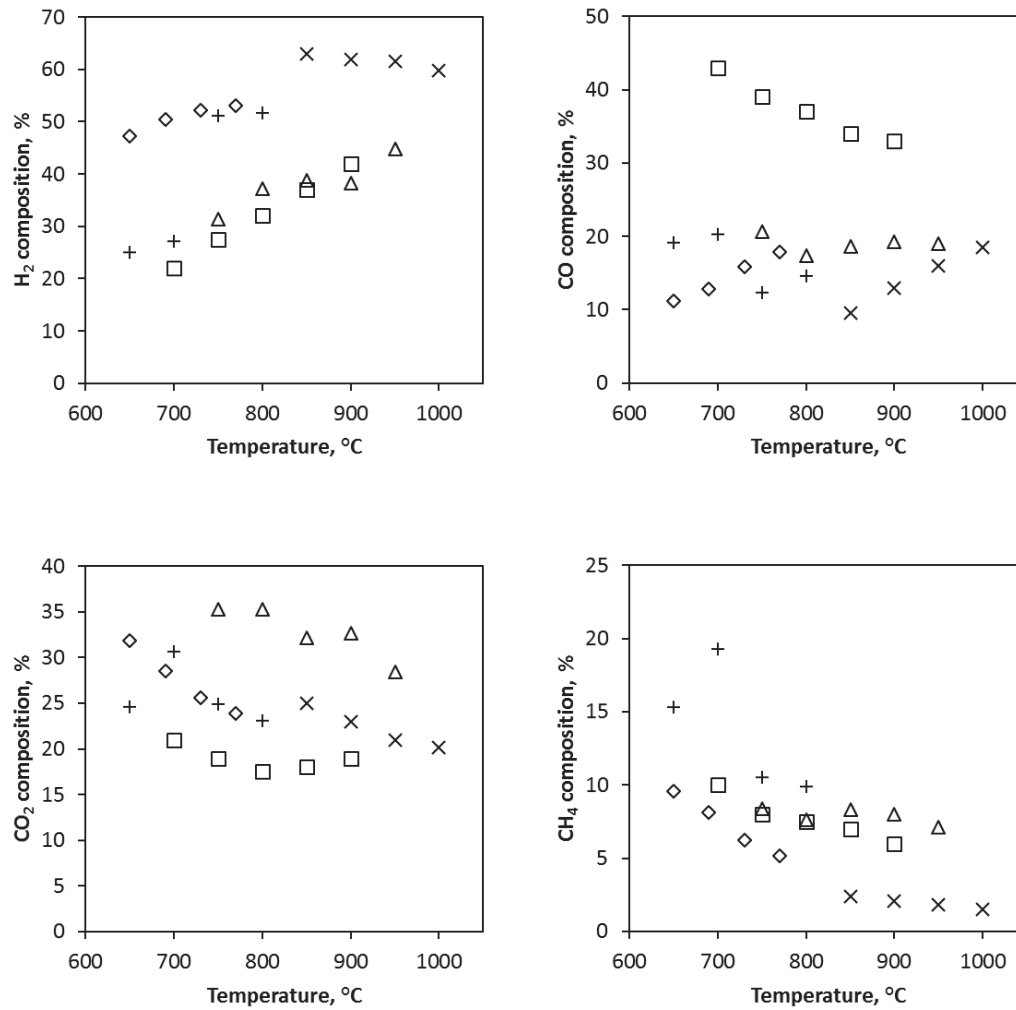


Figure 2.4 Effect of temperature on gas composition of steam gasification in continuous fluidised bed gasifiers (◇ (Karmakar and Datta, 2011), □ (Lv et al., 2004), Δ (Turn et al., 1998), × (Xiang et al., 2009), + (Chaudhari et al., 2001))

2.4.2.2 Effect of temperature on C conversion and gas yield

C conversion is defined as the percentage of total carbon content in gaseous products to total carbon content in feedstock, and gas yield is defined as total flow

rate of inert-free gaseous products to the mass flow rate of a feedstock in a dry and ash free basis (Emami Taba et al., 2012). Figure 2.5 shows the influence of temperature on C conversion and gas yield from literature data. The experimental conditions for each literature study are shown in Table 2.4. According to Figure 2.5, both C conversion and gas yield show upwards trends over a range of temperature from 650 to 1000 °C. Xiang et al. (2009) stated that there were three major reasons for these observations. Firstly, when the temperature was increased, more gas was generated during pyrolysis, which is the initial period of gas production during gasification. Then, the increase of temperature enhanced the tar cracking. Thirdly, gasification reaction rates were also favoured by temperature.

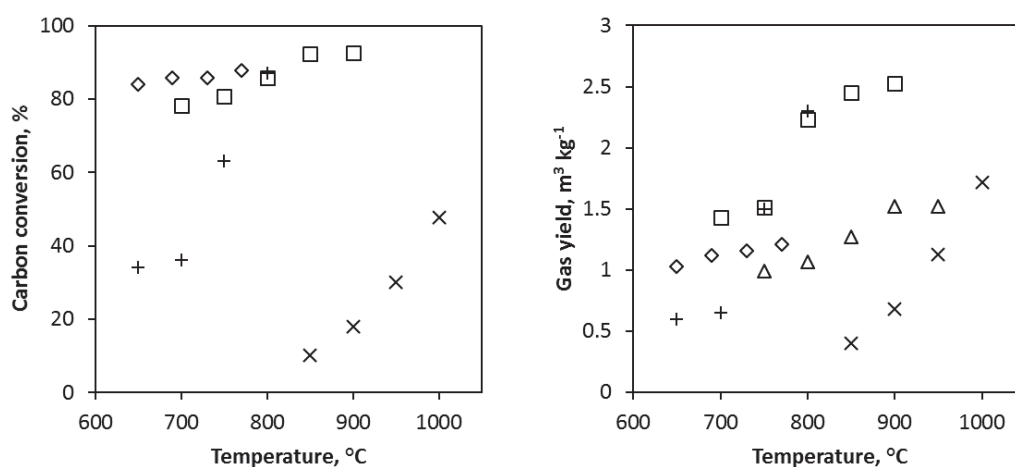


Figure 2.5 Effect of temperature on C conversion (left) and gas yield (right) of steam gasification in continuous fluidised bed gasifiers ($\diamond$ (Karmakar and Datta, 2011), $\square$ (Lv et al., 2004), Δ (Turn et al., 1998), $\times$ (Xiang et al., 2009), $+$ (Chaudhari et al., 2001))

2.4.2.3 Effect of temperature on calorific value

Calorific value is defined as the heat released by the combustion of a specific amount of fuel (Emami Taba et al., 2012). The calorific value of produced gases has contributions from the contents of hydrogen, CO and hydrocarbons (e.g. CH₄ and C₂H₄) (Lv et al., 2004). The higher heating values from some studies (Karmakar and Datta, 2011, Lv et al., 2004, Turn et al., 1998, Xiang et al., 2009, Chaudhari et al., 2001) are illustrated in Figure 2.6. With an increase of temperature, the higher heating values are slightly varied around 9 to 14 MJ m⁻³.

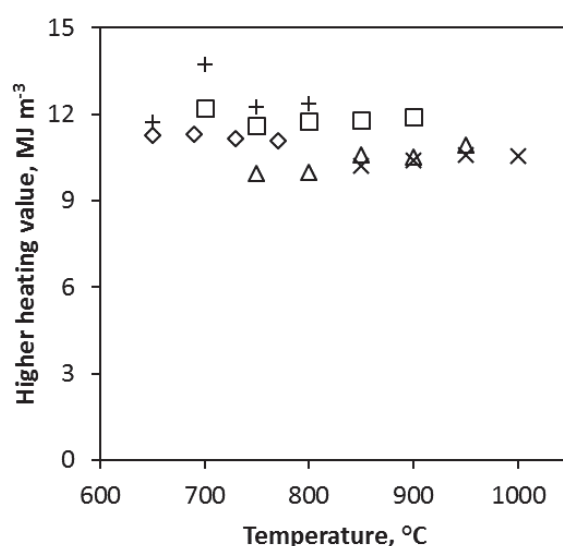


Figure 2.6 Effect of temperature on higher heating value of steam gasification in continuous fluidised bed gasifiers (◇ (Karmakar and Datta, 2011), □ (Lv et al., 2004), Δ (Turn et al., 1998), × (Xiang et al., 2009), + (Chaudhari et al., 2001))

2.4.3 Effect of Pressure

Pressurized gas generated from coal or biomass gasification potentially has a wide range of industrial applications, but only few studies have investigated the effect of pressure on gasification process. According to the research of Fermoso et al. (2010) and Kitzler et al. (2011), there was a negative effect of pressure on gasification process. However, the study of Duan et al. (2012) shows opposite results. From their results, high pressure improved both the higher heating value (HHV) of the produced gas and the C conversion of the feeding material.

Fermoso et al. (2010) gasified four different ranked coals using a mixture of steam and oxygen as gasification medium in a fixed bed gasifier at atmospheric pressure and at pressure of 1.5 MPa. Their results show that concentrations of H_2 and CO decreased, while concentrations of CO_2 and CH_4 increased with pressure increase for all four coal samples. They claimed that the char produced at the higher pressure was less reactive than that produced at atmospheric pressure. A lower extent of fuel devolatilisation occurred at high pressure, therefore a larger amount of char was formed and this had a higher and more ordered carbon structure. These changes resulted in a reduction in the C conversion at the higher pressure. Kitzler et al. (2011) used wood pellets for air gasification in a fluidised bed gasifier at pressures from 0.1 to 0.5 MPa, and they had similar results to Fermoso et al. (2010). They suggested that the main reasons for H_2 and CO decrease and increase of CO_2 and CH_4 might be the shifts of chemical equilibrium of Boudouard reaction, water gas reaction, steam

methane reforming reaction, and methanation reaction, when pressure increased. Duan et al. (2012) studied the pressure effect of Huaibei bituminous coal gasification using a gasification medium of steam and air mixture in a circulating fluidised bed reactor. In contrast to previous studies, their results show positive effect of pressure on gasification process with higher HHV and C conversion. They suggested that there might be two main reasons. On one hand, the rates of gasification reactions were increased by pressure. On the other hand, the fluidisation was better due to the coalescence and collapse of bubbles in the reactor. The bubble size decreased, when pressure was increased. This caused a longer residence time and improved gas/solid contact in the bed.

2.5 Gasification Products

The products from gasification process are divided into three kinds of species containing gas (syngas), tar (heavy condensable hydrocarbons and water soluble organics) and char (carbonaceous residue and ash).

2.5.1 Gas

Combustible gases are the major products from gasification. The main gases are H_2 , CO, CO_2 and CH_4 . A more detailed discussion of gaseous products has been given in Section 2.4.

2.5.2 Tar

Tar produced during gasification is defined as the condensable volatiles, including those in the aqueous phase escaping in the gaseous product stream (Milne et al., 1998). It is an undesirable product from gasification. It can cause several severe problems (such as fouling and blockages mainly in downstream processes (Li and Suzuki, 2009). It is also a potential environmental hazard and represents a thermal loss from the process.

2.5.2.1 Tar formation

The quantity of tar produced from solid fuels during gasification depends on several factors including fuel composition, equivalence ratio, steam to material ratio, operating temperature, pressure, residence time, particle size, and reactor design (Padban et al., 2000, Meng et al., 2011, Aljbour and Kawamoto, 2013). Figure 2.7 depicts the representative components found in condensates from wood pyrolysis with short residence time at the given temperatures. This figure illustrates the potential types of chemical mechanisms occurring at different temperatures during biomass pyrolysis. It includes dehydrogenation, aromatization, dealkylation and deoxygenation (Elliott, 1988).

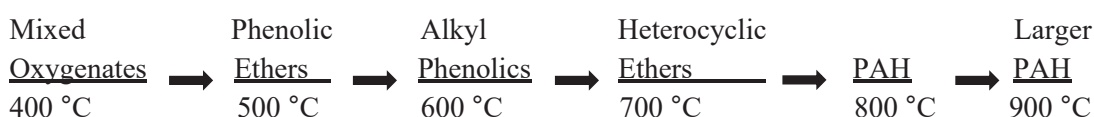


Figure 2.7 Tar maturation scheme proposed (Elliott, 1988)

Baker et al. (1988) have investigated the tar formation in different types of gasifiers. From their research, the tar yield from a fixed bed updraft gasifier was the highest, as the tars were formed in the pyrolysis zone and left the gasifier without passing through a hot zone. However, the tar yield from a fluidised bed gasifier varied depending on its gasification agent and bed temperature. (Baker et al., 1988) According to Figure 2.8, in general, tar yield decreases when temperature is raised. At the same time, the proportion of the GC detectable tar (relatively lower boiling point compounds) increases (Padban et al., 2000).

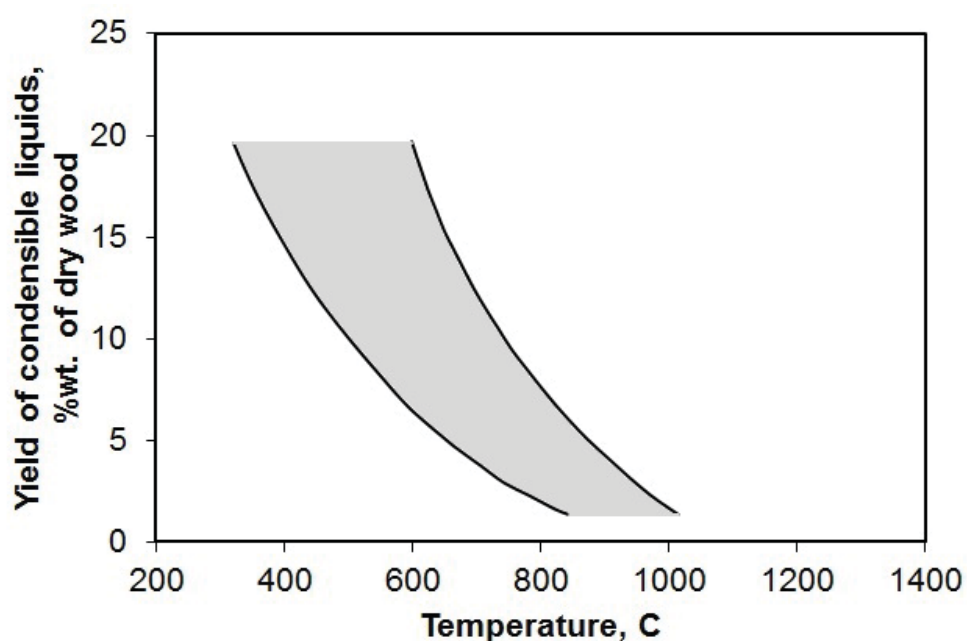


Figure 2.8 Tar yield as a function of the maximum temperature exposure (reproduced from Baker et al. (1988))

2.5.2.2 Tar properties

Based on the research of Elliott (1988), the chemical composition of the tar from biomass changes with the temperature rise. With an increase of operating temperature, both the oxygen content and hydrogen to carbon ratio decline. Elliott (1988) suggested that the changes of the elemental contents represent the conversion of the highly oxygenated tar to more thermally stable tar components with less oxygen content, and then to a highly aromatic structure through deoxygenation. Table 2.5 shows the chemical components that were found in the tars from different processing temperatures, which also demonstrates the relationship between tar composition and operating temperature.

Table 2.5 Chemical components detected in biomass tars (Elliott, 1988)

Conventional flash pyrolysis (450-500°C)	High temperature flash pyrolysis (600-650°C)	Conventional steam gasification (700- 800°C)	High temperature steam gasification (900-1000°C)
Acids	Benzenes	Naphthalenes	Naphthalene
Aldehydes	Phenols	Acenaphthylenes	Acenaphthylene
Ketones	Catechols	Fluorenes	Phenanthrene
Furans	Naphthalenes	Phenanthrenes	Fluoranthene
Alcohols	Biphenyls	Benzaldehydes	Pyrene
Complex oxygenates	Phenanthrenes	Phenols	Acephenanthrylene
Phenols	Benzofurans	Naphthofurans	Benzanthraces
Guaiacols	Benzaldehydes	Benzanthraces	Benzopyrenes
Syringols			226 MW PAHs
Complex phenolics			276 MW PAHs

2.5.2.3 Tar composition

According to Wolfesberger-Schwabl et al. (2012), the yield of tar amount decreased, when temperature was increased from 800 to 850 °C during steam gasification of wood pellets. In parallel, concentration of aromatic compounds and phenols decreased, while concentrations of naphthalene and polycyclic aromatic hydrocarbons (PAHs) increased with temperature increasing from 800 to 850 °C.

Meng et al. (2011) investigated the effect of steam to biomass ratio on the tar content through a circulating fluidised bed gasifier. They found that the total tar content declined with an increase of steam to biomass ratio from 0.9 to 1.3.

2.5.2.4 Tar reduction

Guo et al. (2013) have studied the effect of char circulation on the tar yield of herb residues gasification in a circulating fluidised bed gasifier. Their results show that the tar yield was reduced by around 50% compared to that without char circulation. They suggested that ash has a catalytic function on tar cracking, as about 60% of that is metal oxides. The tar produced during gasification could be catalysed by metal oxides from ash and decomposed on the char surface. Mun et al. (2012) examined the effectiveness of some additives (coal based activated carbon, biomass based activated carbon and dolomite) on tar removal. From their results, coal based activated carbon had a significant contribution to tar removal. They claimed that coal based activated carbon had a large surface area and large pore size, which

provided large space for tar adsorption and cracking. Wu et al. (2011) compared steam, CO₂ and O₂ used three different reforming agents for tar elimination. Steam had the higher efficiency for tar reduction, and CO₂ or O₂ presence induced the formation of OH, H and O radicals that enhanced hydrocarbon conversion.

2.5.3 Char

Char is defined as the solid carbonaceous material that remains during the thermal processing of coal or biomass (Cousins et al., 2006). It is mainly comprised of fixed carbon and ash (Sekine et al., 2006). The structure of char is important during gasification process, as it affects the mass transport of the volatile matter and later char gasification reactions. The initial char structure is related to whether swelling occurred when the original fuel was heated. The extent of the pore structure change is determined by the type of the material and the gasification condition (Yu et al., 2007).

According to Yu et al. (2007), the change of char structure is described as follow. During devolatilisation, the metaplast of a coal causes high fluidity thus the pore openings of the coal are blocked at the beginning of the plastic stage. Therefore, the volatile matter is trapped in the coal particle and forms bubbles. Later, the movement of bubbles transports the volatile matter during plastic stage, and when the number of bubbles in the coal fluid is large enough, the volatile matter diffuses into the bubbles. As a result, the bubbles increase and the coal particle swells. When

the bubbles reach the surface of the coal particle and overcome the force balance, the volatile matter is then released through the burst of bubbles.

van Heek and Mühlen (1987) studied the effect of heating rate, pressure and particle size on char structure, and their results are illustrated in Figure 2.9. Based on their study, at low pressures, low heating rate and small particles, the volatile matter formed during pyrolysis leaves the vitrain particle at its plastic stage, and then the particle shrinks again. At high pressures, high heating rate and for larger particles, it takes longer time for the volatile matter formed during pyrolysis to leave the particle, so that the size of the particle may be increased even more during plastic stage. Owing to the earlier coke formation, the outer shell of the particle solidifies before the volatile matter has released, and then the particle cannot shrink any more.

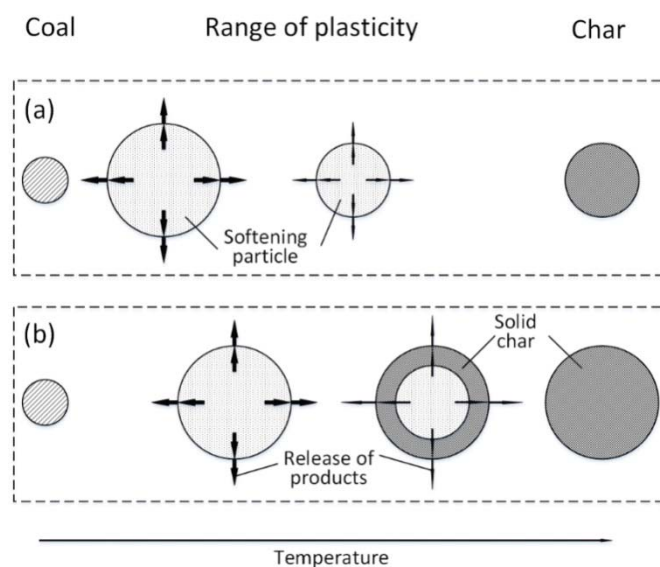


Figure 2.9 Swelling behaviour of vitrain particles at (a) low pressures and heating rate, small particles, (b) high pressures and heating rate, larger particles (reproduced from van Heek and Mühlen (1987))

According to van Heek and Mühlen (1987), durain particles had quite different behaviour compared to other kind of lithotype particles. The size of durain particle was almost half of its original size after pyrolysis (shown in Figure 2.10). The same researchers suggested that high content of exinite in durain particle caused this plastic behaviour. During pyrolysis, the coal particle decayed rapidly, and the volatile matter escaped through the soft surrounding vitrinite before the solidification of the outer shell, and then the particle shrinks again.

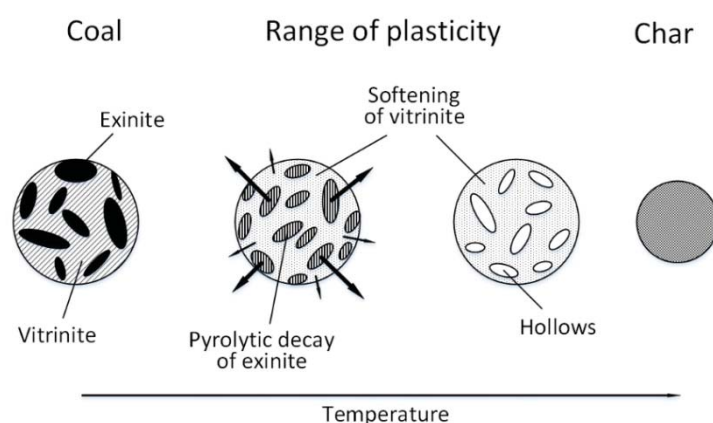


Figure 2.10 Shrinking behaviour of durain particles (reproduced from van Heek and Mühlen (1987))

Tay et al. (2013) investigated the effect of different gasification agents on char structure using FT-Raman spectroscopy. From their results, the presence of steam during gasification is significant for char structure evolution, as the relative ratio of small and large (>5 fused rings) aromatic ring structures decreased in the char. Guo et al. (2008) compared the effect of oxygen and steam on char structure during gasification. They claimed that oxygen reacted with char only on its external surface,

while steam reacted mainly on the internal surface of char (Guo et al., 2008). Zhang et al. (2011) studied the effect of volatile-char interactions on char structure during steam gasification of brown coal in a fluidised-bed/fixed-bed reactor. According to their results, the interactions between volatile and char significantly improved the conversion of small aromatic ring systems into large ones in steam gasification. They believed that H radical played an important role in the interaction of volatile and char, as it induced the condensation of aromatic ring systems through deep penetration into the char matrix. In addition, they implied that the O containing structures in char were also influenced by volatile-char interactions (Zhang et al., 2011). Sekine et al. (2006) gasified several kinds of coal chars with steam to clarify the effect of the amount and the morphology of ash on the reactivity and structure of chars. Their results demonstrated that the reactivity of char varied depending on ash content, and the graphitic carbon ratio was raised as the conversion increased (Sekine et al., 2006).

Wu et al. (2000) investigated the effect of different pressure (0.1, 0.5, 1.0 and 1.5 MPa) of pyrolysis on char structure and morphology. They found that the char character was significantly affected by the system pressure. By increasing the pressure, the char size and sphericity increased. From their cross-sectional characterization of the char particles, the majority of the char particles produced at a high pressure were of a high porosity with thin walls and network (Wu et al., 2000). Chen et al. (2008) studied also the effect of pressure (0.1 and 3 MPa) on the

behaviour of pyrolysis and gasification of four types of Chinese coal. The results show that high pressure restrained the primary pyrolysis (300-700 °C) and enhanced the secondary cracking of volatiles within the char (700-1000 °C). In addition, the gasification reactivity of char reduced as the pyrolysis pressure increased (Chen et al., 2008).

Miura et al. (1989) reviewed the factors that might control the rate of coal char gasification. For lower rank coals (C<80%wt.), the char gasification rate was mainly controlled by the catalytic effect of coal minerals (such as Ca, K, Na and Mg). However, for higher rank coal (C>80%wt.), the char gasification rate was controlled by the intrinsic reactivity of the coal.

2.7 Summary

Gasification is a thermochemical process that converts carbon-rich solid fuels into mainly gaseous products (CO, H₂, CO₂ and CH₄) and minor products of tar and char. During the gasification process, the materials undergo four steps including drying, pyrolysis, gasification and combustion. The generally used solid fuels for gasification are coal and biomass.

In this chapter, the information on the gasification performance (product yields, fuel gas heating value and C conversion) affected by different parameters including temperature, pressure and gasification medium has been summarised. The main

concepts of this project were introduced as the oxyfuel gasification with recycled CO_2 and oxyfuel integrated gasification fuel cell combined cycle. The first concept has been studied by the previous work (Spiegel, 2010) that shows stable operation and fuel gas composition achieved under a wide range of operating conditions (750 to 950 °C, up to 3 MPa) with continuous feeding of different types of coal using CO_2/O_2 as gasification agent. For the further development of this concept, it is necessary to fill the gap of the previous studies to analyse the potential reasons for the drop of C conversion at pressurised conditions and investigate the gasification performance with steam addition at different pressures. The second concept was generated from the first concept with SOFC integration. Most researchers studied the influence on SOFC performance of simulated gasification products, while only few studies investigated the effects of real gasification products. In addition, literature references describing the impact of using syngas with a high CO_2 concentration are limited. Therefore, it is necessary to study the influences of actual gasification products with high CO_2 content on the degradation of SOFC.

Chapter 3 Experimental

3.1 Introduction

The materials, experimental setup, experimental procedures, analytical methods and commissioning of the experimental setup are discussed in this chapter.

3.2 Materials

Coal, anode materials, compressed gases, deionised (DI) water, solvents, ice and dry ice pellets were the materials used in this project. The used compressed gases include CO₂ (99.8% purity), N₂ (99.998% purity), H₂ (99.99% purity) and a calibration gas mixture (1% CH₄/15% CO/15% CO₂/10% H₂ balance in N₂, 99.99% purity). All those gases were supplied by BOC Ltd. The solvents used in this study were methanol, chloroform and 1-methyl-2-pyrrolidinone (NMP).

3.2.1 Coal

The coal sample used in this study was German lignite (GL). It was supplied as part of Flexgas, a research project on fluidised bed gasification funded by the Research Fund for Coal and Steel (European Union) with partners in Italy, Spain, Austria and Portugal, and used in the previous work (Spiegel, 2010) in the fluidised bed reactor. Lignite is a major energy resource in many parts of the world. It is a low rank coal,

and it has been proven to be more reactive than many other kinds of coals for fluidised bed gasification due to its high volatile content (Li, 2004). The coal sample was pulverised and sieved to a particle size distribution of 200-300 μm , as this range was found to be the most suitable range for the feeding system (described in 3.3.4) and for the fluidising conditions (described in 3.6.1). It was stored in bottles during this project. In most conditions, the coal was used without any further pre-treatment. For some tests, it was dried prior to use as described in the corresponding chapters. The proximate analysis, ultimate analysis and calorific value of the coal are shown in Table 3.1. The proximate analysis was carried out in a thermogravimetric analyser (Pyris 1 TGA, PerkinElmer), and the other two analyses were provided by a commercial analytical laboratory¹.

Table 3.1 Analysis of German lignite

Proximate analysis (%wt., a.r.)					
Moisture		Total Volatiles		Fixed Carbon	
11.4		45.3		40.0	
Ash					
3.3					
Ultimate analysis (%wt., a.r.)					
Carbon	Hydrogen	Oxygen*	Nitrogen	Chlorine	Sulphur
57.4	4.03	20.4	0.61	0.02	0.23
Calorific Values (MJ kg ⁻¹ , d.a.f)					
HHV			LHV		
23.1			21.9		

* By difference

¹TES Bretby, Burton-on-Trent, Staffordshire, DE15 0XD, UK

3.2.2 Anode Materials

Two types of solid oxide fuel cell (SOFC) anode material: NiO/YSZ (yttria stabilised zirconia) and NiO/CGO (gadolinium doped ceria) were tested in this study. Both tested anode materials were provided with the pre-treatments including calcination and sieving by Prof N.P. Brandon's research group². The anode materials were calcined for one hour at 1300 °C in air, and sieved in a range of 125-250 µm. The main properties of the anode materials are shown in Table 3.2.

Table 3.2 Properties of the SOFC anode materials

	NiO content, wt%	BET surface area, m ² g ⁻¹
NiO/YSZ	66	6.21
NiO/CGO	60	5.60

3.3 Experimental Setup

The experimental equipment used for this project is described in this section. It can be divided into eight main process systems: gas supply, solid feeding, steam generator, fluidised bed reactor, fixed bed reactor, gas cleaning (including tar trap and other gas cleaning), online gas measurement, and incinerator. Each system is discussed in detail in this section. The experimental setup was modified from an existing laboratory scale high pressure fluidised bed gasifier. The original setup was

²Department of Earth Science and Engineering, Imperial College London, London SW7 2AZ, UK

used for oxy-fuel gasification (Spiegl, 2010). The modifications include two parts. Firstly, the steam generator was modified to provide a larger amount of steam for high pressure steam gasification. Secondly, a second stage fixed bed reactor was designed and constructed to test the degradation effects on the anode materials from SOFC.

A flow sheet of the whole process is shown in Figure 3.1. The grey dots area indicates the tube with trace heating. The area with the dashed line is the second stage fixed bed reactor. The gasification experiments were performed in the fluidised bed reactor. The fixed bed reactor is utilised for exposing anode materials to syngas from the fluidised bed gasifier to study their degradation by the gasification products. For the gasification experiments without testing anode materials, the fluidised bed reactor was directly connected to the tar trap without the fixed bed reactor. For the experiments with testing anode materials, the fluidised bed reactor was connected to the second stage fixed bed reactor followed by the tar trap.

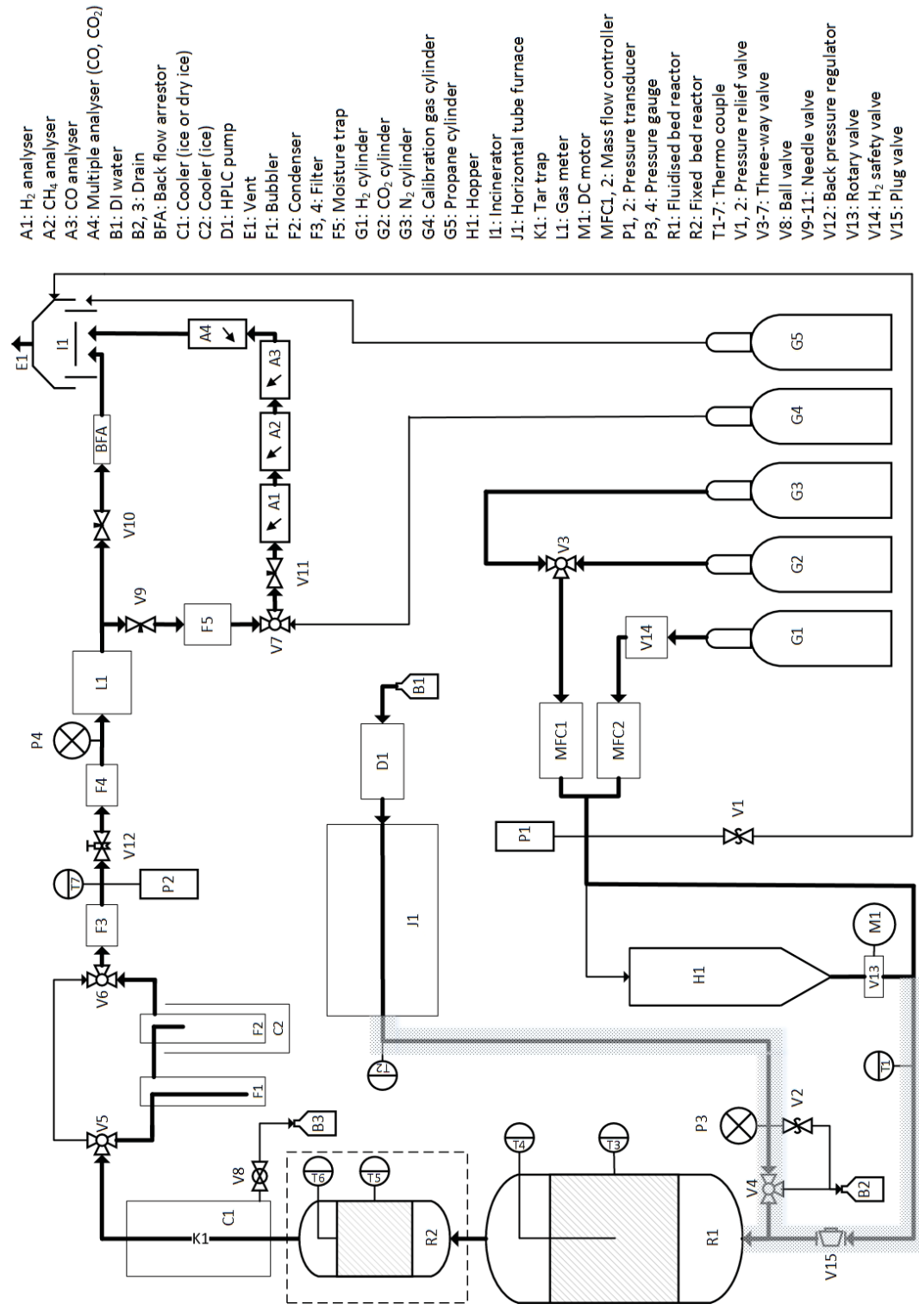


Figure 3.1 The process flow sheet

3.3.1 Fluidised Bed Reactor

The fluidised bed reactor is installed inside a cabinet ($1.72 \times 0.95 \times 1.80 \text{ m}^3$) that is made of steel sheets to protect the operator. A schematic diagram of the fluidised bed reactor is shown in Figure 3.2. The main body of the reactor is made of Incoloy Alloy 800 HT with an inside diameter of 34 mm, wall thickness of 7 mm and the length of 504 mm. This material has a high tensile strength, a high creep resistance, and it resists to high temperature corrosion. Its chemical composition is shown in Table 3.3. The reactor can operate at 1000°C at 40 bar_a and at 1050°C at 30 bar_a for a total of 1000 h before it should be replaced. The wall thickness needed to achieve this performance was determined by calculation and can be seen in Appendix 1. The reactor contains a 28 mm (i.d.) quartz tube liner placed inside of the Incoloy tube. The bottom of this quartz liner has an inverted cone shape with a hole at the base. It sits on a supporting ring, which is part of the spout feed line for both gas and solids. To ensure the quartz liner seals against the spout line, a layer of kaowool (ceramic fibre wool) is placed between the bottom of the quartz liner and the supporting ring, and a hollow cylindrical stainless steel counter weight (32 mm o.d., 12.5 mm i.d., 20 mm height) is placed on the top of the quartz liner to press the seal.

The reactor is sealed and connected to the system by two flanges at each end. The inner flanges are attached the reactor by half moon rings, which are fitted in the machined grooves in the reactor shell near both edges. The inner and outer flanges are fixed together by 8 stainless steel bolts (M 10, 50 mm) on each end. The flange is sealed by placing a copper gasket (48 mm o.d., 37 mm i.d., 2 mm thickness, CU35, FTI Ltd.) between the end of the reactor and the outer flange. The centres of the

outer flanges are welded with a 5/16 inch (7.9 mm) fitting bored through and 5/8 inch (15.9 mm) straight unions (Swagelok) respectively. These unions are connected to the upstream spout line and downstream second stage reactor or the tar trap. The pressure of the reactor is controlled by a back pressure regulator (maximum 103 bar, Tescom Corporation) installed after the tar cleaning system, which is downstream of the reactor shown in Figure 3.1 with the label V12. The reactor pressure is measured by two pressure transducers (Series 2000, Basingstock). One is placed before the fluidised bed reactor and the other is placed before the back pressure regulator.

Table 3.3 The chemical composition of Incoloy Alloy 800 HT

Element	Percentage, %
Ni	30 – 35
Cr	19 – 23
Fe	39.5
C	0.06 – 0.1
Mn	1.5
S	0.015
Si	1
Cu	0.75
Al*	0.15 – 0.6
Ti*	0.15 – 0.6

* Al + Ti: 0.85-1.20%

The reactor shell is resistance heated to provide the heat for gasification, which is normally provided from O₂ combustion in the industrial scale. A K-type thermocouple is placed on the centre of the outside surface of the heating zone for temperature monitoring and controlling. To reduce the heat loss, the reactor body is thermally insulated by several layers of Superwool 607 HT sheet. Power is supplied by a series of three transformers including a variable transformer (200-250 V, 32 A

max.), and two fixed step-down transformers (with the coil ratio of 250/48 and 230/10 respectively). The final output from the transformers is 1.7-2 V and maximum power is 8 kW. The reactor is clamped by two electrodes. The top electrode is connected to the transformer by copper bars fixed on the cabinet. The bottom electrode is mobile and connected using 32 insulated copper cables to allow the thermal expansion of the reactor. To avoid overheating of the cables, the connections (between the electrode and cables) are cooled by wrapping with 1/8 inch (3.2 mm) copper tubing with a continuous water flow.

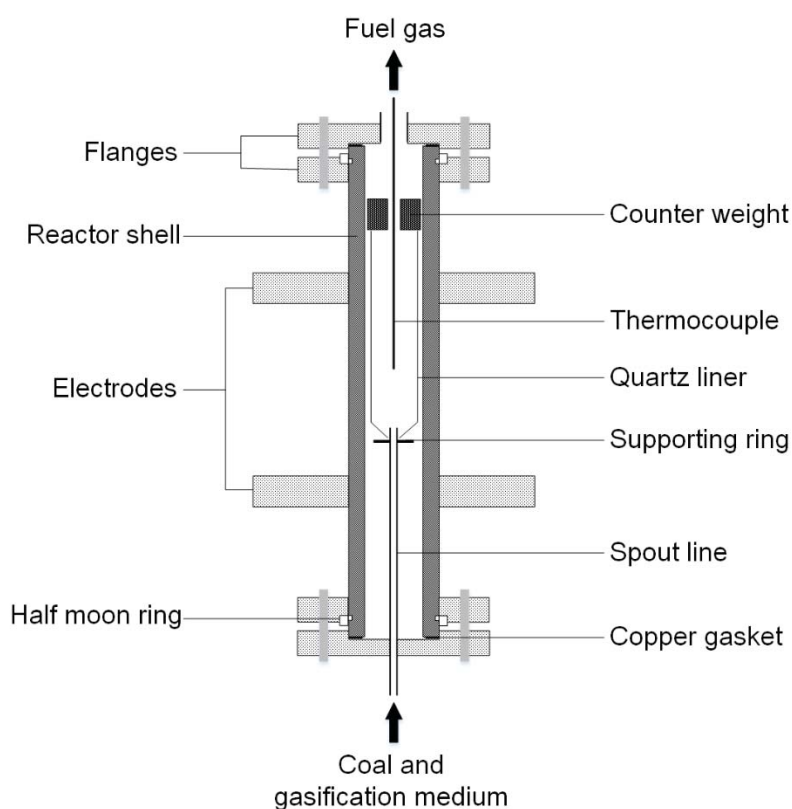


Figure 3.2 Fluidised bed reactor

3.3.2 Construction of the Fixed Bed Reactor

To assess the degradation of anode materials used in SOFC when exposed to a gasifier fuel gas, a fixed bed reactor was designed and constructed. It was placed as a second stage reactor downstream from the fluidised bed gasifier, so that the gas products and the vaporised tars could directly pass through the fixed bed.

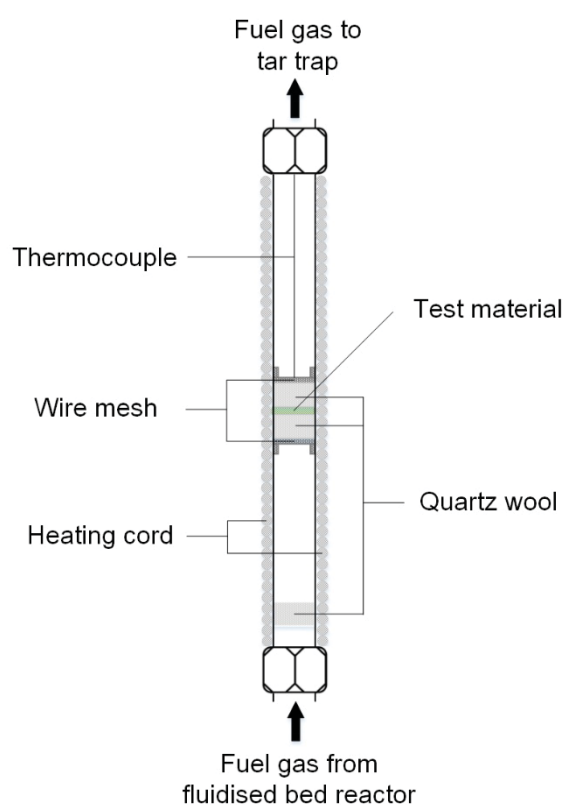


Figure 3.3 The second stage fixed bed reactor

The fixed bed reactor is made of a 11.6 inch (about 295 mm) stainless steel tube with 5/8 inch (15.9 mm) o.d. and 0.049 inch (1.2 mm) wall thickness. As shown in Figure 3.3, the fixed bed of anode material is located at the midpoint of the reactor tube, and consists of two pieces of stainless steel wire mesh and two layers of quartz wool (exposed up to 1050 °C, Azpack). The tested materials were placed between the

quartz wool, which was clamped by the two pieces of wire mesh. A K-type thermocouple attached on top of the fixed bed is used to measure the bed temperature, and to hold the bed in place as the gas flows up the reactor. A quartz wool plug is inserted into the inlet of the reactor, to trap the char particles from the fluidised bed reactor and to avoid any interaction between the chars and the anode materials. No blockage was occurred by this quartz wool plug. This reactor is heated using a heating cord (800 W, 115 V, working up to 800 °C, HC504X1, Barnstead/Electrothermal) controlled by a temperature feedback controller (output voltage 50 V). The feedback signal is provided by a K-type thermocouple placed on the centreline of the outer surface of the reactor tube. Outside the heating cord, layers of Superwool are wrapped around the reactor tube for insulation and to reduce the heat loss.

3.3.3 Steam Generator

The current steam generator (Figure 3.4) is composed of an HPLC pump (CM4000 multiple solvent delivery system, LDC/Milton Roy), a horizontal tube furnace (1 kW, Carbolite Furnaces) and trace heating lines. A previous setup used FGS051-060 heating tape as the energy source to evaporate water into steam. As the maximum output voltage for the temperature controllers was 50 V due to laboratory safety regulations, the maximum power supplied by the heating tape was 54 W. Thus, the maximum steam flow was limited. Instead of using the heating tape, the current setup uses the horizontal tube furnace with a power of 1 kW as the energy source. The main advantage of the current setup is the improvement of the maximum steam flow rate by 18 times.

Inside the tube furnace, a 1/2 inch (12.7 mm) stainless steel tube (0.035 inch (0.89 mm) wall thickness) is fitted as the chamber for water evaporation. A K-type thermocouple is placed in the centre of the chamber to monitor the steam temperature. The HPLC pump is connected to one end of the chamber by a 1/16 inch (1.6 mm) stainless steel tube to provide DI water at a controlled flow rate. The other end of the chamber is connected through a 1/4 inch (6.4 mm) stainless steel tube to a three-way valve. A pressure gauge and a pressure relief valve are installed on the 1/4 inch connecting tubing to release the pressure in case of blockage. One side of the three-way valve connects to the spout line near the bottom of the fluidised bed reactor, and another side leads to the drain. The steam line between the tube furnace to the bottom of the fluidised bed reactor, and the tubes between the bottom of the reactor and the start point of the solid feeding are heated by heating tapes (310 W, 120 V, working up to 480 °C, FGS051-060, Omega Engineering). These tubes with the trace heating are illustrated as the grey dots area in Figure 3.1. The trace heating prevents any solid feed blockages caused by steam condensation that makes the solid fuels bind together and clog in the feeding tube. The steam generator was tested and produced a stable flow of steam after approximately 2 min of water injection, and all the injected water evaporated instantly.

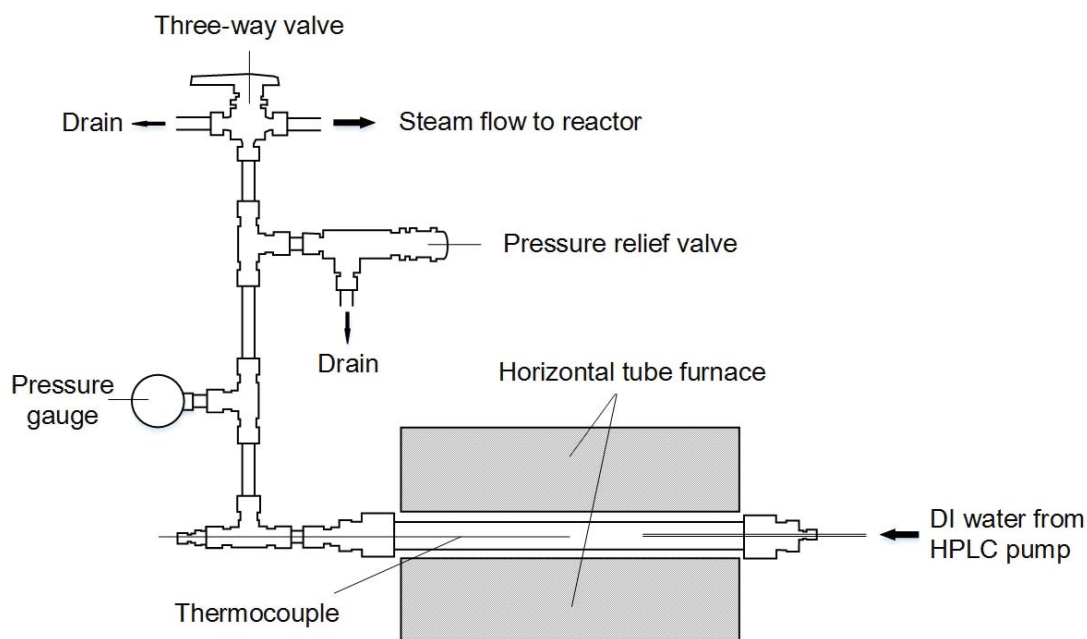


Figure 3.4 Steam generator

3.3.4 Solid Feeding

The feeding system consists of a hopper, a shaker, a rotary valve and a variable speed DC motor. The flow rate of the feeder depends on the bulk density of the feeding materials. The operating flow rate range for the German lignite is from 0.7 to 5.4 g min⁻¹, below which the feeder cannot provide a stable flow. The minimum flow rates of the carrier gas (CO₂) for coal feeding are 0.9, 2.7 and 4.2 NL min⁻¹ at 1, 5 and 10 bar_a respectively. These flow rates were determined by calculating the terminal velocities for coal particles at 20 °C using the method shown in 3.6.1. The minimum carrier gas flow rate at atmospheric pressure was tested, and the result matched the calculated data. From previous studies (Paterson et al., 2002) using this feeder, the most suitable size range of the material particles is from 200 to 300 µm.

All the feeding lines are made of stainless steel and can be operated at elevated pressure. The hopper stores a known weight of the feed material and is directly connected to the rotary valve, which connects to the spout line. The top of the hopper also connects to the spout line to equalise pressure, in order to have a free flow of the solid material. The rotary valve was modified from a 1/4 inch plug valve (SS-4P4T, Swagelok). The passage through the plug valve was blocked in the centre to form two cups back to back. The handle of the plug valve was removed and attached to the DC motor to provide a continuous rotation. The fuel first fills a cup as it passes the feed line from the hopper, then, as the valve rotates further, it drops from the cup into the high velocity gas flow, and is transferred at high velocity into the spout of the fluidised bed reactor. The flow rate is controlled by the rotation speed, which is adjusted by the input voltage for the motor. There were two motors used during the tests with different maximum rotation speeds. The motor with lower rpm provides a flow rate range from 0.7 to 3.6 g min⁻¹ linear with the input voltage. The motor with higher rpm provides a flow rate range from 3.5 to 5.4 g min⁻¹ proportional to the input voltage. The calibrations of the flow rate against the input voltage for the DC motor can be found in Appendix 2.

3.3.5 Gas Supply

Pure CO₂, N₂ and H₂ were provided from gas cylinders supplied by BOC used in these experiments. As the experiments with CO₂ were operated at up to 10 bar_a and with N₂ and H₂ were operated at atmospheric pressure, the CO₂ is provided at 20 bar_a from the gas cylinder and both N₂ and H₂ are provided at 6 bar_a. CO₂ and N₂ are connected to one mass flow controller with flow rate ranges of 0-13 NL min⁻¹

and 0-19 NL min⁻¹, respectively. H₂ was connected to another mass flow controller with the flow rate from 0 to 0.86 NL min⁻¹. Both mass flow controllers were supplied by Brooks Instruments. The actual flow rate of the gas was found to be different from the value indicated by the control panel of the mass flow controller. The gas flows for CO₂ and N₂ were calibrated through a bubble meter. The calibration curves are shown in Appendix 3. The H₂ flow was converted from the correction factor (CF) that was calculated based on a manufacturer provided formula (Equation 3.1).

$$CF = \frac{Cp_1\rho_1}{Cp_2\rho_2} \quad \text{Equation 3.1}$$

Where Cp (J g⁻¹ K⁻¹) is the specific heat, ρ (g L⁻¹) is density, 1 is gas calibrated, and 2 is gas to be measured.

3.3.6 Tar Trap and Gas Cleaning

The tar trap (shown in Figure 3.5) is a 5/8 inch stainless steel tube surrounded by and welded to a cylindrical stainless steel container with the top open. Depending on the experimental conditions, the container can be filled with ice or dry ice for cooling the fuel gas and condensing the tar. The bottom of the container is welded with a 1/4 inch stainless steel tube with a ball valve (Swagelok) to drain the melted ice. Inside the tar trap, a piece of rectangle wire mesh sheet (200×500 mm²) is rolled and inserted to improve the contact surface area with the tar. In the outlet of the tar trap, a ball of glass wool (extra fine, Assistant) is located to trap tar mist and avoid the char particles entering downstream equipment.

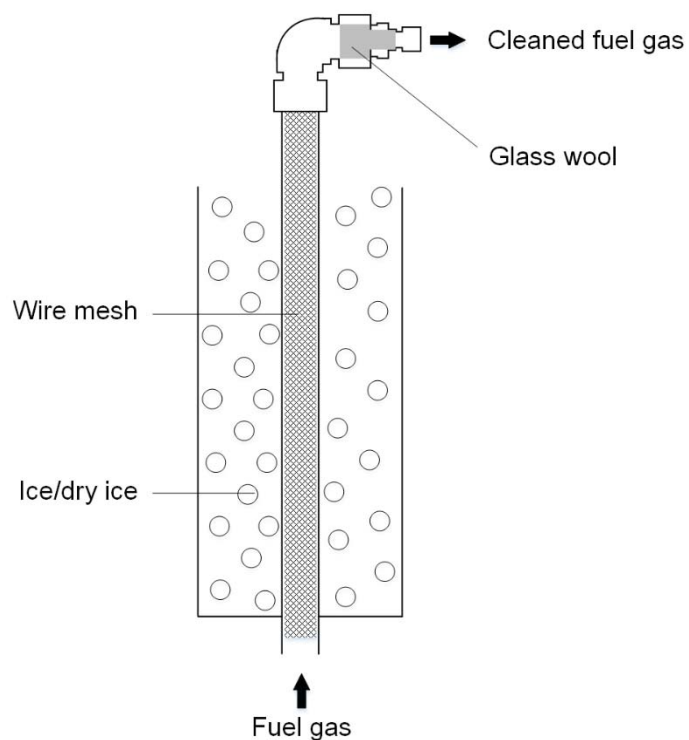


Figure 3.5 Tar trap

Other parts of the gas cleaning system include a bubbler, a condenser, a high pressure filter (0.3 μm element pore size, GE-15K-FC-03, Swagelok) and an atmospheric pressure filter (Balston filter element 100-12-BQ, Parker Hannifin Ltd.), as shown in Figure 3.1. The bubbler and the condenser (shown in Figure 3.6) are made of stainless steel to operate under elevated pressure. The bubbler work with the same principle as the Dreschel bottle, which allow the inlet gas pass through the contained liquid before it escape to the outlet. The bubbler contains 4.5 mL DI water, and the gas inlet immersed under the water surface. The condenser is empty with an ice-water bath outside. The fuel gas passes through the DI water in the bubbler to remove NH_3 and H_2S , and then flows through the condenser to collect the steam vapour. The high pressure filter is located after the condenser for capturing any

traces light tars left to provide a clean gas for the pressure transducer, back pressure regulator and gas analysers. The temperature upstream from the back pressure regulator is measured by a K-type thermocouple. It has been demonstrated that the fuel gas was cooled down to the ambient temperature using this gas cleaning train. After the back pressure regulator, the atmospheric pressure filter is placed for further moisture and trace tar capture.

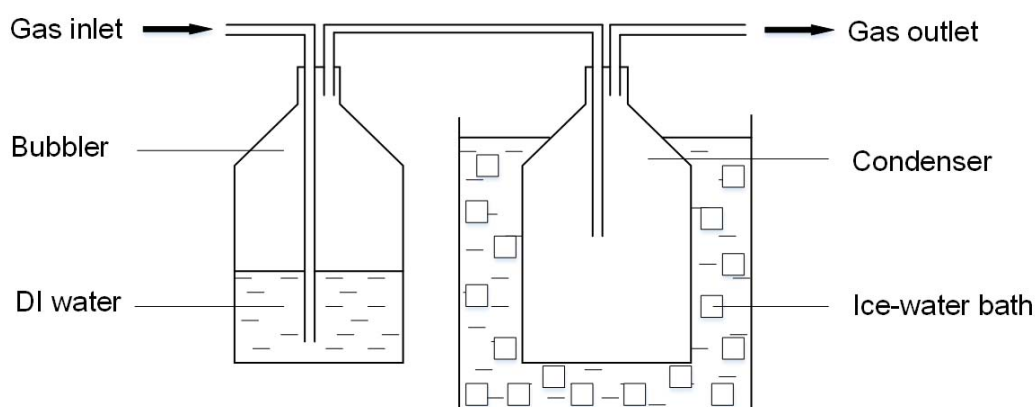


Figure 3.6 Bubbler and condenser

3.3.7 Online Gas Measurements

A gas meter (Model G4, Metrix Grupa Apator) and four online gas analysers (one each for CO, CH₄, H₂ and a multi-gas analyser for CO₂ and CO) are installed after the gas cleaning system. After passing through the gas meter, the gas stream splits into two streams. One stream flows through a moisture trap packed with silica gel for further drying, then to the four gas analysers in series, before the gas is vented. The remainder of the fuel gas stream goes to the incinerator.

3.3.8 Incinerator

A propane burner is installed to burn the fuel gas and flue gases flow into a vent. A backflow arrestor (RF53N, Witt Gas Techniques Ltd) is located on the end of the gas line to avoid any backflow caused by the high flame velocity from the burning of the fuel gas.

3.4 Procedures

This section describes the procedures of the gasification experiments and the anode material tests. In general, the experimental procedure has five steps including rig assembly, leak testing, reactor heating up, reaction and shut down. The detailed procedure description for each step is given below.

3.4.1 Gasification Experiments

There are three similar experimental procedures for the gasification runs. The first procedure was used for CO₂ gasification at atmospheric pressure. The second one was for CO₂ gasification at high pressure. The third one was for CO₂ and steam gasification.

3.4.1.1 CO₂ gasification at atmospheric pressure

The rotary valve for the feeder was disassembled and cleaned in order to have a consistent feeding. The O-rings of the valve were replaced if necessary. The valve

was then assembled and connected back to the DC motor. The German lignite sample was weighed (60g) (Sartorius CPA3245, $d=0.1$ mg) and placed in the feeding hopper. Then the hopper was sealed and connected to the gas supply and to the bottom of the fluidised bed reactor. The bottom flange of the reactor was assembled and sealed with a copper gasket. The quartz liner was placed inside the reactor shell and sat on the spout line. Between the spout line and the quartz liner, the piece of kaowool blanket was placed as a seal. A counter weight was placed on the top of the quartz liner. Then, the top flange was closed and sealed by the copper gasket. The mass flow controller was set for a CO_2 flow at 2 NL min^{-1} . 60 g of sand (Merck Chemicals Ltd, sea sand purified by acid and calcined) was added into the quartz liner, where it was fluidised by the gas flow. A piece of $200 \times 500 \text{ mm}^2$ wire mesh was cut and inserted into the tar trap, and a ball of glass wool was placed on the outlet of the tar trap. The tar trap was then placed on the top of the reactor, and the outside of the tar trap was filled with ice in order to condense tars. The reactor was then insulated by several layers of superwool to reduce the heat loss. The gas outlet of the tar trap was connected to the bubbler, which was filled with 4.5 mL DI water. The bubbler was then connected to the condenser, which was immersed in a water-ice bath. The outlet of the condenser was connected to filters, the back pressure regulator, the gas meter, online gas analysers, and the incinerator.

After assembly, the equipment and gas line upstream from the back pressure regulator were leak tested. By controlling the back pressure regulator, the rig was pressurised to 5 bar_a with CO_2 . A leak detector was used to check for leaks from the reactor, the gas line, the feeding system and the tar trap. After sealing all the

connections of the rig, the reactor was then depressurised slowly to atmospheric pressure.

After the leak test, the cooling water for the electrodes was switched on. Then, the main power and the transformers were switched on. The Lab View programme was opened for controlling and recording the temperatures of the reactor, and recording the data from the analysers. Both the reactor wall and bed temperatures were recorded, and the reactor temperature was controlled by the wall. The temperature of the reactor wall was set 50 °C higher than the desired temperature of the reactor based on the experience. The reactor was then heated up to 20 °C higher than the desired temperature due to an approximate 30 °C difference of temperature between the wall and the bed. During the heating up period, the online gas analysers were calibrated by passing through the calibration gas mixture.

When the required temperature was reached, the inlet gas was set to the desired flow rate by the mass flow controller. Then, the propane cylinder was opened and the incinerator was ignited. When the temperatures of both the wall and the bed were stabilised, the feeding motor was turned on and set to the desired coal flow rate. The vibrator for the hopper was turned on. At the start of the run, the bed temperature dropped sharply by approximately 20 °C due to endothermic reactions in the reactor. The power of the resistance heater was slightly adjusted to ensure the bed temperature reached the desired condition. During the run, the ice for the tar trap was regularly checked and refilled. The data of the fuel gas concentration was recorded automatically in the computer, and the reading of the gas meter was recorded manually every two minutes.

The run was finished when the hopper was emptied. This was indicated by the concentrations in the fuel gas (except CO₂) starting to decrease and the bed temperature increasing sharply. The time of each run depended on the coal flow rate, as 60 g of coal was placed in the hopper for every experiment. The power supply and the transformers were switched off. Then, the cooling water for the electrodes was switched off. The mass flow controller for the inlet gas was set back to 2 NL min⁻¹, and the propane for the incinerator was turned off. The reactor was cooled down to around 50 °C, then the flow of CO₂ was turned off and the plug valve below the spout line was closed. Then the reactor was disassembled. The bed material and tar were recovered for further analysis.

3.4.1.2 Gasification at high pressure

The rig assembly and the test procedure for the gasification experiments at high pressure were the same as those for atmospheric pressure (shown in Section 3.4.1.1). However, the leak test, heating up and shut down steps were slightly different as described below.

The leak test was carried out at 5 bar above the desired operating pressure. For the heating up step, the set temperature of the wall was 100 to 150 °C higher than the desired temperature depending on the experimental pressure and coal feeding rate. As the CO₂ and steam flow rates were higher at high pressure experiments, and they required higher energy input to reach the desired temperature. As both Boudouard and steam char reactions are endothermic reactions, larger coal feeding rates caused higher energy demand. Therefore, the temperature difference between the reactor wall and bed was increased in order to increase the heat transfer rate. During the

heating up, the gas flow rate and the system pressure were increased to the desired conditions in steps to ensure the fluidisation of the bed. When the run was finished, the inlet gas flow rate was decreased to 2 NL min⁻¹ and system was depressurised to atmospheric pressure in steps.

3.4.1.3 CO₂ and steam gasification

For the gasification with steam addition, the rig assembly was the same as for the gasification with only CO₂ apart from the connection of the steam generator and steam line. During the heating up stage, the horizontal tube furnace for the steam generator was turned on and set to 400 °C. All the trace lines between the tube furnace and the bottom of the reactor and between the start point of the coal feeding and the bottom of the reactor were insulated and heated to 300 °C by the heating tapes. When the furnace and the trace lines reached the set temperature, the HPLC pump was turned on and set to the desired water flow rate, with the formed steam vented to the drain. When the steam was being generated continuously (which took around 2 minutes), the steam was diverted into the reactor before the coal feeding was started. After the run, the steam was switched back to the drain by the three-way valve, and the tube furnace and trace heating were turned off.

3.4.2 Gasification Experiments with Anode Material Test

For testing the anode materials, the procedure was similar to that used for the gasification experiments. The differences are described below. The rig was assembled in a similar way, with the second stage fixed bed reactor placed between

the fluidised bed reactor and the tar trap. A small piece of wire mesh and some quartz wool were weighed and placed halfway up the fixed reactor tube. 100 mg of tested anode material was placed on the quartz wool, and then it was covered by another layer of quartz wool and wire mesh. The fixed bed reactor was then installed between the fluidised bed reactor and the tar trap. A thermocouple was placed halfway along the fixed bed reactor wall to control its temperature. Then the fixed bed reactor was wrapped by a heating cord, and several layers of superwool for insulation. During the heating up period, a N_2 flow of 2 NL min^{-1} was used. When the fixed bed was heated to the desired temperature of $765\text{ }^{\circ}\text{C}$, a small stream of steam and H_2 were injected into the fixed bed reactor passed through the fluidised bed reactor in order to have a gas mixture of $2.5\%H_2O/10\%H_2/N_2$ for the material reduction. The reduction was carried out for 90 min. After that, the inlet gas was switched to the desired gas composition for the gasification in the fluidised bed reactor. The gasifier was operated using the procedure described above. When the run finished, the reactors were cooled down with a 2 NL min^{-1} gas flow of $15\%H_2/N_2$ to reduce the anode materials.

3.5 Analytical Methods

Different analyses were carried out on: (1) fuel gas from the gasification tests, (2) tar from the gasification tests, (3) anode materials, and (4) coal. The fuel gas volumetric flow rate was measured by a dry gas meter and component concentrations were analysed by several online gas analysers. The weight of the tar was measured and

the molecular size distribution of the tar was analysed by a size exclusion chromatography (SEC). The fresh anode materials were analysed by X-ray diffraction (XRD). After exposure to gasification fuel gases, anode materials were studied by temperature programmed oxidation (TPO), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). The property of coal was examined by thermogravimetric analysis (TGA).

The amount of each product at thermodynamic equilibrium of experimental conditions was calculated using Aspen Plus based on the Gibbs free energy minimisation.

3.5.1 Fuel Gas Analysis

3.5.1.1 Dry gas meter

A dry gas meter (Model G4, Metrix Grupa Apator) was used to measure the volumetric flow rate of the fuel gas. It was calibrated by passing CO₂ with different known volumetric flow rates from the mass flow controller. The calibration curve is shown in Appendix 4. The gas meter measures the gas volume directly. The data from the gas meter was recorded every 2 min during the experiments. The volumetric flow rate (F_{out} , NL min⁻¹) was calculated based on Equation 3.2.

$$F_{out} = \frac{\Delta V}{\Delta t} \quad \text{Equation 3.2}$$

Where Δt (min) is the time interval, and ΔV (NL) is the gas volume difference between the time interval.

3.5.1.2 Online gas analysers

The main gas products in the fuel gas were measured by four online gas analysers, including a CO analyser (ADC), a CH₄ analyser (ADC), a H₂ analyser (Hitech K1500) and a multi-gas analyser (Servomex Xentra 4200) for CO and CO₂. The measuring ranges are shown in Table 3.4. The accuracies of all these analysers are $\pm 1\%$ of measured value. The analysers were calibrated with a certified calibration gas mixture (1%CH₄/15%CO/15%CO₂/10%H₂ balance in N₂) and a pure CO₂ gas before each run.

Table 3.4 Range of the online gas analysers

	Range
CO ¹	0 - 60%
CH ₄	0 - 20%
CO ²	0 - 25%
CO ₂	0 - 100%
H ₂	0 - 100%

¹ ADC, ² Servomex Xentra 4200

The analysers used for measuring CO, CO₂ and CH₄ are infrared (IR) gas analysers. An infrared light source emits radiation within the IR range and this passed through the gas sample into the detector. The gas to be detected absorbs specific wavelengths in the IR range, and the absorption is proportional to the gas concentration within the equipment measuring range. The readings from IR analysers are pressure sensitive. To ensure the gas stream was at atmospheric pressure or close to it, it was directly connected to the vent after the analysers to avoid any pressure build up. In addition, a pressure gauge was placed before the analysers for monitoring.

The H₂ analyser uses thermal conductivity for the measurement, and it can determine the H₂ concentration in binary or pseudo-binary gas mixture. However, there are four main compounds (CO, CO₂, H₂ and CH₄) in the fuel gas. The thermal conductivities of these gases are shown in Table 3.5. It can be seen that H₂ has a relative high thermal conductivity. The information from the supplier shows that a measurement error of 0.08% (abs.) for H₂, if 1% of CH₄ is also present. The maximum CH₄ concentration obtained from the experiments is 2.7%. Thus, the maximum error for H₂ from CH₄ is 0.22% (abs.), which is not significant. Since CO has a similar thermal conductivity to N₂ (shown in Table 3.4), it is assumed that CO has the same influence as N₂ on H₂ measurement. A cross-calibration curve of H₂ against N₂ was built by using mixtures of N₂ and CO₂ with different concentrations as the analyser was calibrated in CO₂. The detailed method of the calibration and the calibration curve are shown in Appendix 5. A correction factor for CO (or N₂) was obtained and applied to the H₂ concentration in the final results.

Table 3.5 Thermal conductivity (NIST, 2017)

Thermal conductivity at 20 °C, W m ⁻¹ K ⁻¹	
H ₂	0.182
CO ₂	0.016
CH ₄	0.034
CO	0.026
N ₂	0.025

3.5.1.3 Further calculations

After obtaining the fuel gas flow rate and the fuel gas concentrations, further gasification parameters including the CO₂ conversion, higher heating value (HHV), the CO/H₂ ratio and the C conversion can be determined by following equations.

The CO₂ conversion (conv._{CO₂}, %) was calculated by Equation 3.3.

$$conv_{CO_2} = \frac{CO_2 \text{ flow rate in inlet gas} - CO_2 \text{ flow rate in outlet gas}}{CO_2 \text{ in inlet gas}} \times 100\% \quad \text{Equation 3.3}$$

HHV of the fuel gas (HHV_{fuel gas}, MJ m⁻³) (shown in Equation 3.4) was calculated by the sum of the HHV of each gas (HHV_{CO}, HHV_{H₂}, HHV_{CH₄}, MJ m⁻³) times its volumetric concentration (C_{CO}, C_{H₂}, C_{CH₄}, %vol.).

$$HHV_{fuel\ gas} = HHV_{CO} \times C_{CO} + HHV_{H_2} \times C_{H_2} + HHV_{CH_4} \times C_{CH_4} \quad \text{Equation 3.4}$$

The C conversion (conv._C, %) to gas products excluding tars was calculated by Equation 3.5.

$$conv_C = \frac{\text{mole of C in outlet gas} - \text{mole of carbon in inlet gas}}{\text{mole of C in the coal}} \times 100\% \quad \text{Equation 3.5}$$

3.5.2 Tar Analysis

3.5.2.1 Tar measurement

The amount of the tar released from the gasification process was determined by washing the tar trap with 400 mL of a solvent mixture of chloroform and methanol (volume ratio of 4:1). Then, a vacuum filter was used to remove the particles from

the solution and a rotary evaporator operating at 60 °C at atmospheric pressure was used to remove the solvent. When the solution was reduced to approximately 20 mL, it was transferred to a weighed glass bottle. After that, the bottle was placed in an oven (Carbolite) at 45 °C overnight. The weight was measured after 2 hours leaving the tar with the cap open for stabilisation. However, during this evaporation and drying process, some low boiling tar was lost. The weight of the tar in the bubbler and condenser was also measured and found to be below 5% of the tar collected in the tar trap. Generally, the amount of tar was equal to 0.1 to 0.3% of coal fed. Thus, measuring the tar only in the tar trap gives an error around 0.005-0.015% (abs.), which was not significant.

3.5.2.2 Size exclusion chromatography

SEC was used to determine the molecular size distribution of the sample. In SEC, a sample is dissolved in a solvent, and the solution is injected into a column packed with porous particles. The molecules of the sample are eluted from the column by an eluent, generally the same as the solvent for the sample. With the molecular size decreasing, the elution time of the molecule increases, as the molecules with the smaller size stay for a longer time in the pores of column packing. Large molecules are not retained by the packing and pass through the column more quickly.

In this study, the solvent used was 1-methyl-2-pyrrolidinone (NMP), and the column used was a mixed-D column (Polymer Laboratories, Church Stretton UK) packed with polystyrene and polydivinylbenzene. During the test, a diluted tar was passed through the column preheated to 80 °C with an NMP flow at 0.50 mL min⁻¹. The

eluted material was detected by ultraviolet (UV) absorption at wavelengths of 270 and 300 nm using a Diode Array detector.

3.5.3 Anode Material Analysis

3.5.3.1 X-ray diffraction

XRD is a non-destructive analytical technique that determines the crystal structure and chemical composition of a compound. If the wavelengths of X-ray are similar to the distances between planes in a crystal lattice, the crystalline material can function as diffraction gratings. XRD analysis is on the basis of a crystalline material and the constructive interference of monochromatic X-rays. When the collimated monochromatic X-rays are generated and directed to the crystalline sample, the constructive interference (and diffracted rays) can be produced. These diffracted X-rays are produced by the interaction between the incident rays and the sample if Bragg's Law (Equation 3.6) is satisfied (Warren, 1969). Then these diffracted X-rays are detected and processed. By comparison of the produced diffraction pattern with the standard reference patterns, the crystalline form of the sample can be identified.

$$n\lambda = 2d \sin \theta \quad \text{Equation 3.6}$$

Where n is a positive integer, λ (nm) is the wavelength of incident ray, d (nm) is the interplanar distance, and θ (°) is the scattering angle.

In this work, XRD of fresh anode materials were analysed by X'Pert from PANalytical. The X-ray generator was set at 40 kV for tension and at 40 mA for current. The scan range was from 5 to 89.9998° and the scan step size was 0.05°.

3.5.3.2 Temperature programmed oxidation

TPO was used to determine the properties of the deposited carbon on the anode materials. It was carried out in an AutoChem II Chemisorption Analyzer (Micromeritics) and the flue gas was detected by a mass spectrometry (Cirrus 2, MKS Instruments). Around 30 mg of the sample was placed in a U shaped quartz tube, and it was held in position by some quartz wool. The sample was heated up to 985 °C at 10 °C min⁻¹ in a gas flow of 2% O₂ balance Ar at 30 NmL min⁻¹, and the mass intensities of the CO₂ and O₂ in the exit gas were measured.

The amount of deposited carbon was measured by the produced CO₂ amount during the TPO test. The carbon deposition (W_c , mg mg⁻¹ reduced sample) can be calculated from the following Equations 3.7 and 3.8.

$$W_c = \frac{\frac{12}{44} \times \int_0^t C_{CO_2} F_{gas} \rho_{CO_2} dt}{W_{reduction}} \quad \text{Equation 3.7}$$

$$W_{reduction} = W_{after} \times (1 - C_{oxygen}) \quad \text{Equation 3.8}$$

Where C_{CO_2} (%vol.) is CO₂ concentration measured from the mass spectrometer, F_{gas} (NmL min⁻¹) is the flue gas flow rate, ρ_{CO_2} (mg mL⁻¹) is the density of CO₂, t (min) is time, W_{after} (mg) is the sample weight after TPO, $W_{reduction}$ (mg) is the weight of the fresh anode material after reduction, and C_{oxygen} (%wt.) is the content of oxygen from NiO in the fresh anode material before reduction.

3.5.3.3 Scanning electron microscopy and energy dispersive X-ray spectroscopy

SEM was used to determine the microstructure of the anode materials, and EDX was used to provide the qualitative and quantitative element distribution on the material surface. In SEM, a focussed beam of electrons scans the surface of the sample, and the secondary and backscattered electron signal is detected to produce high resolution images (Kuo, 2007). A Phenom Pro desktop SEM was used in this study, and the accelerating voltage was 15 kV. The anode material samples were adhered on the carbon conductive tabs that were adhered on an aluminium stub. The stub was then placed inside the SEM chamber for analysis.

3.5.4 Coal Analysis

3.5.4.1 Thermogravimetric analysis

TGA is a method that measures the mass of a sample over time during temperature changing. A Pyris 1 TGA from PerkinElmer was used for the proximate analysis of the coal sample. The proximate analysis measures the contents of moisture, volatile matter, fixed carbon and ash of coal. About 5 mg of sample was placed on the sample holder, and TGA was operated of the program below:

- (1) Switch the gas to N₂ at 40 ml/min, and hold for 10 min at 50°C,
- (2) Heat from 50 °C to 110 °C at 10 °C/min,
- (3) Hold for 30 min at 110 °C,
- (4) Heat from 110 °C to 900 °C at 10 °C/min,

- (5) Hold for 30 min at 900 °C,
- (6) Cool from 900 °C to 800 °C at 10 °C/min,
- (7) Hold for 10 min at 800 °C,
- (8) Switch the gas to air at 40 ml/min, and hold for 40 min at 800 °C.

The moisture was evaporated during steps (1) to (3). The volatile matter was released during steps (4) to (7). The fixed carbon was measured from the mass loss during step (8). The remaining mass after step (8) was the ash.

3.5.5 Thermodynamic Equilibrium Modelling

Aspen Plus (Aspen Technology, Inc.) was used to calculate the products composition at thermodynamic equilibrium of the experimental conditions. It is a software designed to build a process model and simulate the model. An Aspen Plus process model can be built and operated by the following steps: (1) Define the process flowsheet by defining and connecting the unit operations and process streams. (2) Specify the chemical components, the physical properties of the chemical components and mixtures, the conditions (e.g. flow rate, temperature and pressure) for the components of feed streams, and the operating conditions for the unit operations. (3) Run the simulation to generate product concentrations (Aspen, 2012).

A RGibbs reactor model was used in the modelling, as it is based on Gibbs free energy minimisation. Gibbs free energy is minimised when a system reaches equilibrium at constant temperature and pressure. Therefore, the products composition from this reactor model represents it at thermodynamic equilibrium.

3.6 Commissioning of the Experimental Setup

This section is divided into five parts. The first part demonstrates the fluidisation conditions including the calculations of minimum fluidising velocity and terminal velocity. The second part describes the steady fuel composition. The third part discusses the mass balance of the system. The fourth part shows the experimental repeatability. The final part describes the experimental errors associated with different items of equipment and the overall errors for the gas composition and C conversion.

3.6.1 Fluidisation Conditions

This section discusses the minimum fluidising velocity and terminal velocity, and briefly describes the pressure drop and temperature distribution of the fluidised bed.

For fluidisation, the superficial velocity (U , m s^{-1}) has to be higher than the minimum fluidising velocity (U_{mf} , m s^{-1}). As there was no recirculating system available for the fluidised bed reactor, the superficial velocity should be lower than the terminal velocity (u_t , m s^{-1}) to minimise carryover of the particles.

The minimum fluidising velocity depends on the properties of the solid particles and the fluidising medium. The calculations were based on Equation 3.9 (D. Kunii, 1991).

$$\frac{1.75}{\varepsilon_{mf}^3 \phi_s} \left(\frac{d_p U_{mf} \rho_g}{\mu} \right)^2 + \frac{150(1-\varepsilon_{mf})}{\varepsilon_{mf}^3 \phi_s^2} \left(\frac{d_p U_{mf} \rho_g}{\mu} \right) = \frac{d_p^3 \rho_g (\rho_s - \rho_g) g}{\mu^2} \quad \text{Equation 3.9}$$

Where d_p is particle diameter (m), ε_{mf} is void fraction, ϕ_s is sphericity, ρ_g is gas density (kg m^{-3}), ρ_s is solid density (kg m^{-3}), μ is viscosity ($\text{kg m}^{-1} \text{s}^{-1}$), g is gravity acceleration (9.81 m s^{-2}).

The values of gas density and viscosity were obtained from NIST Webbook (NIST, 2017). The data of void fractions and sphericities of sand and char were taken from D. Kunii (1991).

The calculated minimum fluidising velocities for different particle sizes as a function of operating conditions at 850°C are shown in Table 3.6. For a particular particle size, it was observed that the differences between the minimum fluidising velocities were negligible in the pressure range from 1 to 10 bar_a. When the particle size increased, the minimum fluidising velocities increased. The minimum fluidising velocities using CO_2 as the fluidising gas were slightly lower than those using steam. The superficial velocities were set to be higher than the minimum fluidising velocities at all the experimental conditions

Table 3.6 Minimum fluidising velocity (U_{mf}) and superficial velocity (U) at 850 °C

Gasification medium		Type	Particle size, μm	Pressure, bar _a		
				1	5	10
$U_{\text{mf}}, \text{ m s}^{-1}$	CO_2	Sand	200	0.023	0.023	0.023
			300	0.038	0.038	0.038
		Char	200	0.019	0.019	0.019
			300	0.040	0.040	0.039
	Steam	Sand	200	0.024	0.024	0.024
			300	0.039	0.039	0.039
		Char	200	0.020	0.020	0.020
			300	0.041	0.041	0.041
$U, \text{ m s}^{-1}$				0.248	0.074 to 0.187	0.093

The terminal velocity can be estimated from fluid mechanics by Equation 3.10 (D. Kunii, 1991). According to Equation 3.10, particles with lower densities and smaller sizes have lower terminal velocities. Thus, the terminal velocities of the 200 μm char particles are the lowest among char and sand particles with sizes from 200 to 300 μm . Therefore, the superficial velocity should be lower than the terminal velocities of the 200 μm char to avoid particle entrainment from the bed. The terminal velocities were calculated based on Equations 3.10 to 3.13.

$$u_t = \left[\frac{4d_p(\rho_s - \rho_g)g}{3\rho_g C_D} \right]^{0.5} \quad \text{Equation 3.10}$$

where C_D is drag coefficient. In general, it can be determined according to Equation 3.11 (D. Kunii, 1991).

$$C_D = \frac{24}{Re_p} \left[1 + (8.1716e^{-4.0655\phi_s}) Re_p^{0.0964+0.5565\phi_s} \right] + \frac{73.69(e^{-5.0748\phi_s}) Re_p}{Re_p + 5.378e^{6.2122\phi_s}} \quad \text{Equation 3.11}$$

Where Re_p is particle Reynolds number and it is defined as shown in Equation 3.12.

$$Re_p = \frac{\rho_g u_t d_p}{\mu} \quad \text{Equation 3.12}$$

In order to solve these equations to calculate the terminal velocity, a formula (Equation 3.13) was deducted from Equation 3.10 and 3.12.

$$C_D = \frac{4d_p^3(\rho_s - \rho_g)\rho_g g}{3Re_p^2 \mu^2} \quad \text{Equation 3.13}$$

As the drag coefficient in both Equation 3.10 and Equation 3.12 should be equal, the Excel Solver (Microsoft Office) was used to find a Reynolds number that fulfilled the conditions to produce the drag coefficient with the same value. Afterward, the terminal velocity can be derived by applying the drag coefficient to Equation 3.10.

The terminal velocities for 200 μm char at 850 °C under different conditions are shown in Table 3.7. It can be seen that the terminal velocities reduced when system pressure went up from 1 to 10 bar_a. The terminal velocities in CO₂ were lower than those in steam. The superficial velocities were below the terminal velocities under the experimental conditions used in this project.

Table 3.7 Terminal velocity (u_t) of 200 μm char and superficial velocity (U) at 850 °C

Gasification medium		Pressure, bar		
		1	5	10
u_t , m s ⁻¹	CO ₂	0.49	0.38	0.33
Re_p		1.06	4.11	7.16
C_D		32.38	10.85	7.17
u_t	Steam	0.56	0.45	0.40
Re_p		0.51	2.06	3.65
C_D		61.36	18.73	11.90
U , m s ⁻¹		0.25	0.07 to 0.19	0.09

The pressure drop across the fluidised bed was between 0.3 to 0.5 bar_a under the experimental conditions. The temperature distribution in the bed was determined during previous studies (Spiegl et al., 2010) with this reactor. The result shows the good mixing in the fluidised bed. The test was performed with 60 g of sand at 700 °C, the bed height was 110 mm. From the bottom to the height of 20 mm, the temperature was increased from 685 to 705 °C. Then, from 20 mm to the top of the bed, the temperature was quite stable with only 5 °C increase. When the fluidising gas flow rate increases, the bed may transfer from bubbling fluidisation to slugging. As the reactor is narrow and long, when gas bubbles rise, they coalesce and grow eventually large enough to spread across the reactor and become slugging (D. Kunii, 1991). As the bubble/slug reaches the freeboard, the solids will rain back down into the bed. Therefore, the fluidisation is unlikely to be regular or smooth, but it does provide a turbulent mixing environment.

In addition, 60 g of sand was used as the bed material during the experiments due to its effective mixing with the coal particles. This was proved by previous studies (Cousins et al., 2006) carried out with this reactor.

3.6.2 Steady Fuel Gas Composition

A steady fuel gas composition was reached during all the experimental runs. Figure 3.7 shows a typical measured fuel gas composition detected by the online gas analysers during an example gasification experiment. Time 0 indicates the start of coal feeding. During the initial period, the temperature of the fluidised bed reactor was constantly adjusted by the power to the resistance heater to compensate for the sudden heat loss from the coal injection (caused by coal heating up and the

endothermic reaction in the bed) and to achieve a steady bed temperature. After around 20 min in the case shown in Figure 3.7, a steady gas composition was achieved.

However, the bed was not operated under a steady state, as the unconverted char and the ash from the coal were accumulated in the bed. As a result, the ash and C concentrations increased with time during each run. Although the C concentration increased, after injection into the reactor, the char reactivity decreased sharply, and it became inert within a short residence time. The concentration of the reactive C did not increase with time after the start-up period. Therefore, the increase of ash and inert C did not affect the fuel gas reaching a steady composition, which is important to compare the gasification performance under different operating conditions.

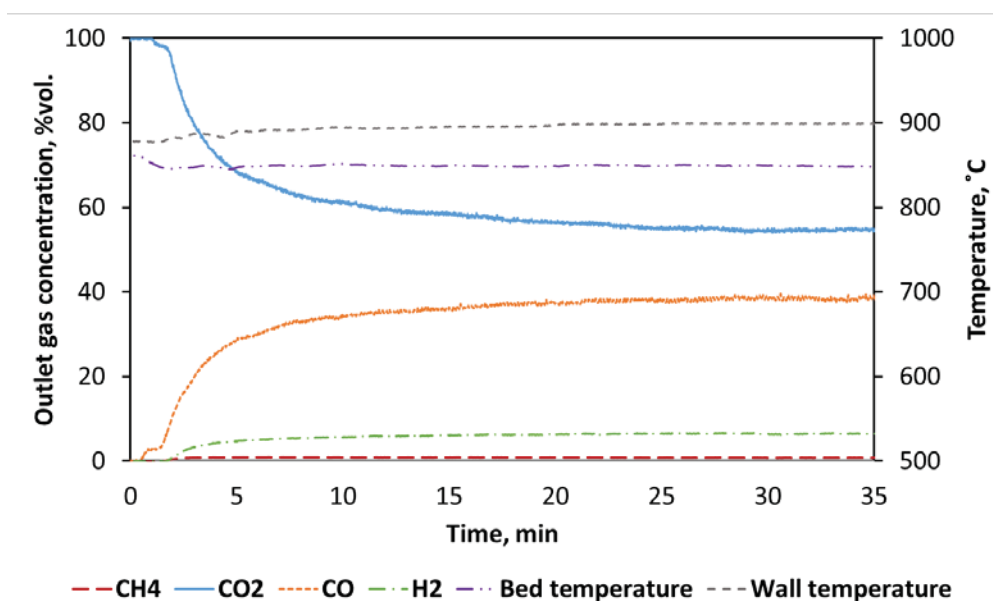


Figure 3.7 Fuel gas composition during CO₂ gasification at 850 °C at atmospheric pressure with CO₂ flow rate at 2.39 NL min⁻¹ and German lignite flow rate at 1.04 g min⁻¹

The fuel gas composition was taken as the average value from the steady gas composition period for all the experiments. Due to the errors from the analysers and calibration gas, the sum of the measured fuel gas concentrations was not exactly 100%. Normally, it was from 100 to 103%, and it was 100.4% for the sample run in Figure 3.7. The final results were normalised to 100%.

3.6.3 Mass Balance

The mass balance was calculated at two situations. Firstly, an overall mass balance was calculated starting from the coal injection until all the fuel gas was released from the bed for a sample experiment. Secondly, a mass balance at the steady fuel gas composition was calculated for another sample experiment. The details are shown below.

3.6.3.1 Overall mass balance

An overall mass balance of 94% was calculated for a sample experiment at 850 °C at 5 bar_a using 20% H₂O and 80% CO₂ as the gasification medium. The quantities of the reactants flowing into the reactor and the quantities of the products are shown in Table 3.8. There are several reasons for the mass balance not closing. (1) The amount of the reacted water was overestimated. As the measured output water amount was significant smaller than the real amount. The output water was collected in the bubbler and the condenser. The total weight was measured after the run. During the reactor cool down, a stream of gas passed through this water for about 3 to 4 h, so a large amount of water was lost by saturating the gas stream. (2) There were errors for the amount of the gas products. The fuel gas weight was determined

by the sum of the volume of each gas products times its density. The fuel gas volume was recorded in every 20 s. However, during the start-up period, the fuel gas concentrations changed sharply. It gave an error while calculating the volume of each gas in this 20 s. (3) The amount of char was underestimated. The char was measured by the weight difference between the collected char bed and the initial sand bed. The char bed was collected after the experiment from the bottom of the reactor through the spout line. The bed cannot be fully retrieved as there was always some leftover between the base of the quartz liner and the spout injection point. (4) Some light tars might be lost if they could not be trapped in the tar trap, the bubbler or the condenser. Some collected tars might be lost during the solvent evaporation to weigh the tar. (5) Only the four main fuel gas compounds were measured. Some minor gaseous products including some hydrocarbons (such as C_2H_6 and C_2H_4), H_2S and NH_3 were not measured.

In addition to the mass balance, a C balance of 97% and a H balance of 55% were estimated and shown in Table 3.8. As there was no data for both the compositions of char and tar. It was assumed that char only consisted of C and ash, and the composition for tar was the same as the original coal. The assumption of the tar composition gave a small error, as tar should be comprised of C and H (but mostly C), however tar only occupied 0.2% of the total weight. The data of the C balance and H balance suggests that the loss of water from the filters, by saturating the cooling gas flow after each test (the first reason discussed above) should be the main loss of the mass balance.

Table 3.8 The quantity of reactants and products of gasification at 850 °C at 5 bar_a using 20% H₂O and 80% CO₂ as the gasification medium

	Constituent	Weight, g	Weight of C, g	Weight of H, g
Reactants	Coal	60.0	34.4	2.4
	Water	31.6	0.0	3.5
	CO ₂	382.8	104.4	0.0
	Total	474.4	138.8	5.9
Products	Char	10.2	6.7	0.0
	Fines in tar trap	2.4	1.6	0.0
	Tar	0.2	0.0	0.0
	Water	15.5	0.0	1.7
	CO ₂	344.1	93.8	0.0
	CO	71.4	30.6	0.0
	CH ₄	1.8	1.4	0.4
	H ₂	1.1	0.0	1.1
	Total	446.8	134.2	3.3
Mass balance		94%	97%	55%

3.6.3.2 Mass balance at the steady fuel gas composition

A mass balance of 99% was calculated at the steady fuel gas composition of gasification at 850 °C at 5 bar_a with CO₂ flow rate at 9.01 NL min⁻¹ and dried coal flow rate at 1.37 g min⁻¹. As there was no steam addition and the feedstock was dried, the errors from the water collection (the first reason in 3.6.3.1) could be reduced. In addition, as the measurement was taken at the steady fuel gas composition, the error from total gas amount (the second reason in 3.6.3.1) measuring disappeared. However, the char, fines in the tar trap and tar were collected after the experiment. An assumption was made that those components

were generated evenly during the run. The flow rates of reactants and products at the steady fuel gas composition are shown in Table 3.9.

Table 3.9 The flow rates of reactants and products at the steady fuel gas composition of gasification at 850 °C at 5 bar_a with CO₂ flow rate at 9.01 NL min⁻¹ and dried coal flow rate at 1.37 g min⁻¹

	Constituent	Flow rate, g min ⁻¹
Reactants	Coal	1.37
	CO ₂	16.35
	Total	17.72
Products	Char	0.37
	Fines in tar trap	0.07
	Tar	0.01
	Water	0.14
	CO ₂	14.08
	CO	2.88
	CH ₄	0.03
	H ₂	0.01
	Total	17.58
Mass balance		99%

3.6.4 Experimental Errors and Repeatability

This section describes the source of the errors including temperature measurement, pressure transducer, mass flow controller, steam generator, solid feeder, gas meter, calibration gas and online gas analysers. The error propagation method was used to calculate overall errors for the gas composition and C conversion. The last part of this section describes the experimental repeatability and the method used for calculating the error bars in this thesis.

3.6.4.1 Equipment errors

Temperature measurement: All the temperatures in the system were measured by K-type thermocouples with an accuracy of $\pm 0.4\%$ of measured value. The operating temperatures of the fluidised bed and the fixed bed were 850 and 765 °C, which gave an error of ± 3.4 and 3.1 °C respectively. The temperature of the fluidised bed can be controlled within ± 5 °C of the desired temperature at atmospheric pressure, and ± 5 to 15 °C of the desired temperature at elevated pressures. This is caused by the slow response of the system. The fixed bed was controlled within ± 1 °C of the experimental condition.

Pressure transducer: The accuracy of the pressure transducers is ± 0.1 bar. The system pressure was controlled within ± 0.1 bar of the desired pressure by the back pressure regulator.

Mass flow controller: The mass flow controllers gave an accuracy of $\pm 1\%$ of reading. As the actual flow rate was found to be different from the set point, the mass flow controllers were calibrated by a bubble meter for each used gas. However, this introduced errors from the bubble meter (accuracy: ± 10 mL) and human reaction time (0.45 s (Thorpe et al., 1996)). The gas flow errors from the calibration can be calculated based on Equation 3.14, using the same method from Dogru et al. (Dogru et al., 2002). This equation applies to calculate the error of the multiplication of two factors. A gas flow of 7.2 NL min⁻¹ was calculated with a calibration error of $\pm 6.9\%$ and a total error of $\pm 7.0\%$ (by Equation 3.15) including the equipment error. The H₂ flow was not calibrated by the bubble meter, as it can rapidly diffuse through the soap bubble resulting in an incorrect low flow rate measurement. Instead, it was

calibrated by a conversion factor which gave a relatively large error. However, H₂ was only used for reducing the anode materials, and a 10% H₂ flowed for 90 min ensuring the full reduction. This does not affect the experimental results.

$$\frac{\Delta F}{F} = \left[\left(\frac{\Delta V}{V} \right)^2 + \left(\frac{\Delta t}{t} \right)^2 \right]^{0.5} \quad \text{Equation 3.14}$$

$$\Delta C = [\Delta A^2 + \Delta B^2]^{0.5} \quad \text{Equation 3.15}$$

Where $C = A + B$, and A and B are independent.

Steam generator: The error from the steam generator was caused by the HPLC pump with an accuracy of $\pm 1\%$ of reading.

Solid feeder: The feeding rate of the solid feeder was controlled by the DC motor, the rotary speed of which can be accurately controlled by the input voltage. The calibrations of the coal flow rate against input voltage were carried out at ambient condition. However, the actual flow rate was affected by several factors: (1) The experimental pressure may slightly increase the flow rate. As the bulk density of the coal was slightly increased by pressure, and the volume of the cups in the feeder was unchanged, the mass flow rate of the coal slightly increased. Even for experiments at atmospheric pressure, there was a pressure drop across the fluidised bed, the feeder was still under a pressure of 0.3 to 0.5 bar_a. (2) The resistance between the drive shaft and the rotary valve caused by the friction of the worn seals reduced the coal flow rate. The friction of the worn seals increased during the feeding process. This results in a decreasing coal flow rate during a run. To reduce this effect, the rotary valve was cleaned and the seal O rings were replaced with new ones after each experiment. To evaluate the error of the solid feeder, another method was used to

measure the average solid flow rate by weighing the inventory in the hopper and measuring the feeding time. This method is not subject to a significant error. The error of the solid feeder was maximum $\pm 5\%$ of the set flow.

Gas meter: The accuracy of the gas meter is ± 0.1 NL. The error of the measured volumetric gas flow was calculated using the same method for mass flow controller from Equation 3.14. A volumetric gas flow of 10.9 NL min^{-1} was calculated with an error of $\pm 1.2\%$ of measured value.

Calibration gas: The accuracy of the gas mixture is $\pm 2\%$ of the certified value. The maximum error of each gas mixture is shown in Table 3.10. To maintain the consistency, the same cylinder of calibration gas was used for all the experiments.

Table 3.10 Maximum error of calibration gas

	CH ₄ , %	CO ₂ , %	H ₂ , %	CO, %
Certified value	1	15	10	15
Absolute error, $\pm$	0.02	0.3	0.2	0.3

Online gas analysers: The accuracies of the online gas analysers are $\pm 1\%$ of the measurement. However, more errors were introduced by the calibration gas and normalising the gas composition. As the errors from the online gas analyser and calibration gas were independent, an error contains these two factors with a value of $\pm 2.2\%$ can be calculated by Equation 3.15. To consider the error from normalising, the sum of the gas concentrations was maximum at 103%. For each gas component, an error was calculated at $\pm 3.7\%$ of the reading (same method using Equation 3.15).

3.6.4.2 Overall errors for gas composition and C conversion

The overall error for C conversion can be calculated based on the errors from each instrument including gas meter, H₂ analyser, mass flow controller and solid feeder. The C conversion was calculated based on Equation 3.5, and it can be derived to Equation 3.16.

$$C_{conv.} = \frac{[F_{fuel\ gas}(1-C_{H_2})-F_{CO_2}]\times 12}{F_{coal}\times 22.4\times 0.574} \times 100\% \quad \text{Equation 3.16}$$

Where $F_{fuel\ gas}$ (NL min⁻¹) is the fuel gas volumetric flow rate, C_{H_2} (%vol.) is H₂ concentration, F_{CO_2} (NL min⁻¹) is the inlet CO₂ flow rate, and F_{coal} (g min⁻¹) is the coal flow rate.

As there were four factors affecting the error in the C conversion, it was difficult to calculate it in one step. The overall error was calculated by introducing the factors sequentially. If the two factors were in a multiple relationship, the error was calculated according to Equation 3.14. If the two factors were in an additive relationship, the error was calculated based on Equation 3.15.

The overall errors in the gas composition and C conversion of an example experiment were calculated and presented in Table 3.11. This experiment was performed at 850 °C at 5 bar_a with a CO₂ flow rate at 7.2 NL min⁻¹, DI water flow rate at 1.4 mL min⁻¹ and a coal flow rate at 3.9 g min⁻¹. This discussion assumes random errors and no bias in the measurement.

Table 3.11 The overall error of the gas composition and C conversion for CO₂ gasification at 850 °C at 5 bar_a with CO₂ flow rate at 7.2 NL min⁻¹, DI water flow rate at 1.4 mL min⁻¹ and German lignite flow rate at 3.9 g min⁻¹

	CO, %	CO ₂ , %	H ₂ , %	CH ₄ , %	C _{conv} , %
Value	32.7	54.7	10.8	1.8	62.6
Relative error, ± of measurement	3.7%	3.7%	3.7%	3.7%	8.4%
Absolute error, ±	1.2	2.0	0.4	0.1	5.3

3.6.4.3 Experimental repeatability

To determine the repeatability of the experimental setup, an experimental run was carried out five times. These experiments were carried out at the same condition as the example experiment for system error calculations in Table 3.11 (850 °C at 5 bar_a with a CO₂ flow rate at 7.2 NL min⁻¹, DI water flow rate at 1.4 mL min⁻¹ and a coal flow rate at 3.9 g min⁻¹). The experimental results (the dry fuel gas composition, flow rate, C conversion and tar production), their mean values, the standard deviations (SD), and 95% confidence intervals (CI) are shown in Table 3.12. It can be observed that the standard deviations are relatively small. All the error bars in this thesis were calculated of 95% confidence interval. It is assumed that SD/mean is a constant. For the measurements without repeat, the error bars were calculated as $\pm 1.96 \times \text{measured value} \times \text{SD/mean}$.

Table 3.12 Repeatability of the experimental procedure

Run	Fuel Gas Composition (dry)				$F_{\text{fuel gas}},$ NL min ⁻¹	$C_{\text{conv}}, \%$	Tar, %
	CO, %	CO ₂ , %	H ₂ , %	CH ₄ , %			
1	29.6	57.5	10.8	2.1	10.9	59.2	0.18
2	32.7	54.7	10.8	1.8	11.0	62.6	0.15
3	34.0	55.9	8.2	1.8	10.8	64.4	0.16
4	34.0	55.4	8.8	1.8	10.8	64.0	0.14
5	32.3	57.3	8.5	1.8	11.0	68.0	0.15
mean	32.5	56.2	9.4	1.9	10.9	63.7	0.16
SD¹	1.8	1.2	1.3	0.1	0.1	3.2	0.02
95% CI²	32.5±1. 6	56.2± 1.1	9.4± 1.1	1.9± 0.1	10.9± 0.1	63.7± 2.8	0.16± 0.01

$$^1\text{SD} = \sqrt{\frac{\sum_{i=1}^N (x_i - \bar{x})^2}{N-1}}$$

$$^295\% \text{ CI} = \bar{x} \pm \frac{1.96\text{SD}}{\sqrt{N}}$$

Chapter 4 Effect of Pressure on Gasification Performance

4.1 Introduction

Fluidised bed gasifiers can be operated at elevated pressures, as this reduces the equipment size for a particular output or can raise the output for a given reactor size. In addition, many application routes for the gasification (such as Fischer-Tropsch and methanol synthesis) require pressurised syngas. These can affect the economics in terms of both capital and operating costs.

As mentioned in chapter 2, there is conflicting information in the literature on the impact of raising the operating pressure: some literature suggests that the C conversion increases with pressure (Duan et al., 2012), whereas other literature suggests the opposite effect (Fermoso et al., 2010, Peralta et al., 2005).

In this chapter, the influence of pressure on the gasification performance (fuel gas composition, heating value, C conversion and tar production) in a fluidised bed reactor are investigated. The main finding from the results is the significant reduction of C conversion at elevated pressures. The potential causes, including suppression of volatile release from the coal particles, char deactivation, changes in the fluidisation characteristics in the bed, and thermodynamic equilibrium were studied in this chapter. The aims have been to understand the performance of the overall process under elevated pressure, and to understand the potential causes of the C conversion caused by the pressure.

This chapter consists of four parts. The first part describes the experimental conditions. The second part shows the overall impacts on gasification performance from the pressurised conditions. The third part discusses the potential causes of the decreases of C conversion at elevated pressure. The final part summarised the main conclusions.

4.2 Experimental Conditions

All the gasification experiments were performed at 850 °C using pure CO₂ as gasification agent and German lignite as the fuel. The detailed experimental conditions are shown in Table 4.1 and 4.2. The data from the fluidised bed reactor was taken the average value from the steady gas composition. The error bars were calculated from the measurement errors discussed in Chapter 3.

To study the overall influence of pressure on gasification, the experiments run 1, 2 and 3 (shown in Table 4.1) were carried out. The pressures tested were 1, 5 and 10 bar_a. In this fluidised bed reactor, when the system pressure increases, it is impossible to keep all other parameters constant. As the pressure increased, the gas density increased. If keeping the same coal and CO₂ mass flow rate, the volumetric flow rate of CO₂ decreased at high pressure, then the superficial velocity (U) decreased. Thus, the gas residence time increased. In addition, the minimal fluidising velocity (U_{mf}) was almost no difference at each tested pressure (calculated in Chapter 3). As a result, the ratio of U/U_{mf} decreased. However, it is difficult to keep the same coal and CO₂ mass flow rate for both 1 and 10 bar_a experiments. If performing an experiment at 10 bar_a under the conditions suitable for experiment at 1 bar_a, the

superficial velocity would be too low to carry the coal particles for the material feeding (the minimal gas flow rate for coal feeding was calculated in Chapter 3). If conducting an experiment at atmospheric pressure using the coal and CO₂ flow rates suitable for 10 bar_a experiment, the superficial velocity would be too large and the char would be entrained out of the reactor without being reacted properly in the bed. Therefore, the flow rates of coal and CO₂ were kept the same only for 5 and 10 bar_a experiments. Another coal and CO₂ flow rates were used for the experiment at 1 bar_a, while the mole ratio of inlet CO₂ to C in the coal (CO₂/C) was kept constant at 2. The same approach has been used by other studies (Valin et al., 2010, Mayerhofer et al., 2012). According to the Boudouard reaction, the stoichiometric ratio of CO₂ to C is 1, therefore, there was 100% excess CO₂ at the inlet to the gasifier.

Table 4.1 Gasification conditions at 850 °C in the fluidised bed reactor

Run	Pressure, bar _a	Sample preparation	Coal _{in} , g min ⁻¹	CO ₂ _{in} , NL min ⁻¹	n[CO ₂]/[C]	U/U _{mf}
1	1	As received	1.04	2.39	2	10
2	5	As received	3.90	9.01	2	8
3	10	As received	3.90	9.01	2	4
4	5	Dried	1.37	3.57	2	3
5	5	Dried	1.37	4.50	3	4
6	5	Dried	1.37	9.01	5	8
7	5	Dried	1.72	9.01	4	8
8	5	Dried	3.40	9.01	2	8

To understand the effect of change in the fluidisation characteristics on C conversion, experimental run 4 to 6 (Table 4.1) were conducted. The experiments were performed at 5 bar_a using dried coal as the feedstock to avoid any interaction with the moisture from the coal. The coal feeding rate was kept constant at 1.37 g min⁻¹.

The CO₂ flow rate was varied from 3.57 to 9.01 NL min⁻¹, which caused a variation in the U/U_{mf} ratio from 3 to 8.

To study the deactivation of char caused by high coal feeding rate in the fluidised bed, the experimental run 6 to 8 were carried out with different dried coal flow rates from 1.37 to 3.40 g min⁻¹, while the CO₂ flow rate was kept constant to have the same fluidisation condition (U/U_{mf} ratio at 4).

In order to understand the effect of suppression of volatile release from the coal, the data of pyrolysis and gasification experiments produced from a high pressure wire mesh reactor was used for comparison³. A wire mesh reactor can be used to study the thermal process (pyrolysis and gasification) of solid fuels at a wide range of conditions. This reactor is a relative small scale bench reactor, and allows the study of single variable while keeping other parameters constant. It can be used to investigate the behaviour of particles in a near mono-layer and therefore the impact on the results from the reactor is negligible. The schematic diagram of the wire mesh reactor is shown in Figure 4.1. About 5 mg of solid fuel particles are placed between the two layers of wire mesh. These particles are evenly distributed to minimise contact. The wire mesh is connected between two electrodes and acts as a resistance heater. The temperature, pressure, heating rate and holding time can be accurately controlled. This reactor has the ability to go up to 2000 °C at 30 bar_a, and the heating rate can go up to 10000 °C s⁻¹. During the experiments, a gas flow passes through the mesh, and sweeps away the volatiles from the reaction zone into a tar

³The data from high pressure wire mesh reactor was obtained by Dr. Cesar Berruenco in this laboratory.

trap placed on the top of the wire mesh reactor. The tar is cooled down by liquid nitrogen or dry ice depending on the experimental conditions.

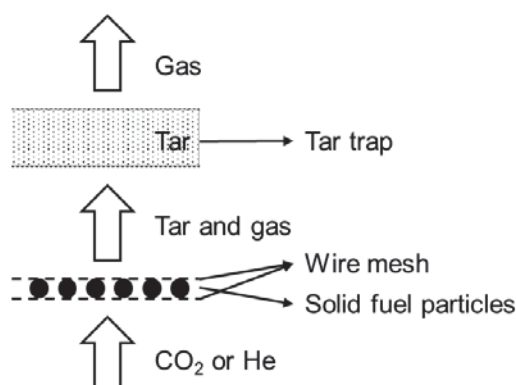


Figure 4.1 Schematic diagram of the wire mesh reactor

Table 4.2 Experimental conditions in the wire mesh reactor with the heating rate at 1000 °C s⁻¹ and holding time of 60 s

Run	Pressure, bar _a	Gas
9	1	He
10	5	He
11	10	He
12	1	CO ₂
13	5	CO ₂
14	10	CO ₂

The experimental conditions for the wire mesh experiments are shown in Table 4.2. The runs from 9 to 11 were the pyrolysis experiments at 1, 5 and 10 bar_a with He as the inert sweep gas. The runs from 12 to 14 were the CO₂ gasification experiments. All the wire mesh experiments were carried out at 850 °C using German lignite. The heating rate and holding time were kept constant at 1000 °C s⁻¹ and 60 s respectively.

4.3 CO₂ Gasification at Different Pressures

This section describes the overall impact from pressure on the gasification performance.

4.3.1 The Effect of Pressure on Gas Composition, Gas Yield and Heating Value

Figure 4.2 shows the data for the fuel gas yields against total pressure.

When the pressure increased, and H₂ yield decreased slightly from 0.22 to 0.15 m³ kg⁻¹ coal. The H₂ was produced from the pyrolysis, steam-char reaction, water gas shift reaction, steam CH₄ reforming reaction, and steam tar reforming reaction, while consumed from methanation reaction. The steam was provided by the moisture from the coal (12%), and it was around 6%vol. in the inlet gas stream. As CH₄ and tar concentrations were very low, less than 2 and 0.5% respectively, H₂ was mainly generated from the pyrolysis, steam-char reaction, water gas shift reaction. With the pressure increasing, the equilibrium of the steam-char reaction was shifted to the reactants side, and the methanation reaction was shifted to the products side, both of which resulted in the reduction of H₂.

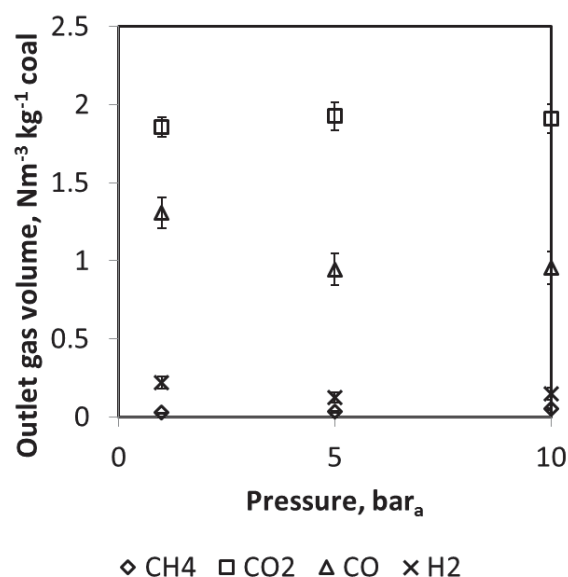


Figure 4.2 Fuel gas yields during CO₂ gasification of German lignite at 850 °C at different pressures (the outlet gas volume of CO₂ includes CO₂ fed)

CO₂ was the inlet fluidising gas, and it is also one important product component. The CO₂ in the outlet stream cannot be distinguished between the unreacted inlet CO₂ (Boudouard reaction) and that produced by pyrolysis and water gas shift reaction. However, the amount of the reacted CO₂ was much larger than the produced CO₂. Therefore, CO₂ conversion was calculated (Equation 3.2) to represent the change of CO₂. The results are shown in Table 4.3. It can be seen that the CO₂ conversion drops from 19 to 17% with the increase in the system pressure from 1 to 5 bar_a, and kept constant from 5 to 10 bar_a. As the pressure increased, the Boudouard reaction shifted to the reactants side and less CO₂ was consumed. In addition, the extent of Boudouard reaction was reduced, since the char produced at high pressure was less reactive. This has been observed by other literature (Chen et al., 2008, Saxena, 1990, Peralta et al., 2005). This may be because the residence time

of the volatile release from the coal particle was increased at high pressure. Some of this volatile repolymerised on the char to form secondary char.

Table 4.3 CO₂ conversion during CO₂ gasification of German lignite at 850 °C at different pressures

Pressure, bar _a	1	5	10
CO ₂ conversion, %	19	17	17

The CO yield decreased from 1.31 to 0.95 m³ kg⁻¹ coal, when pressure increased from 1 to 5 bar_a. Then, it kept constant at 5 and 10 bar_a. As steam, CH₄ and tar (steam-char, CH₄ and tar reforming reactions) were relatively small amount, CO was mainly produced from Boudouard reaction and pyrolysis. Assume the amount of CO produced from the Boudouard reaction was correlated to the reacted CO₂ amount. So, CO from the Boudouard reaction was twice the amount of the reacted CO₂, and the remaining CO was from pyrolysis. The calculated CO distribution is shown in Figure 4.3. It can be seen that more than 60% of CO was produced from the Boudouard reaction. This assumption underestimates the amount of CO produced from the Boudouard reaction, as the actual reacted CO₂ was much more and it was counteracted by the produced CO₂. The amount of the produced CO₂ cannot be acquired. Thus, this distribution can only tell the roughly proportion of the source of the CO, and the trends of the CO yield from each reaction (Boudouard reaction and pyrolysis) are not unreliable.

The CH_4 yield increased from 0.03 to 0.05 $\text{m}^3 \text{kg}^{-1}$ coal, when the pressure increased. CH_4 was generated from the pyrolysis, methanation reaction, and consumed from the steam CH_4 reforming reaction. With the increase of the pressure, both methanation and steam CH_4 reforming reactions shifted to CH_4 side.

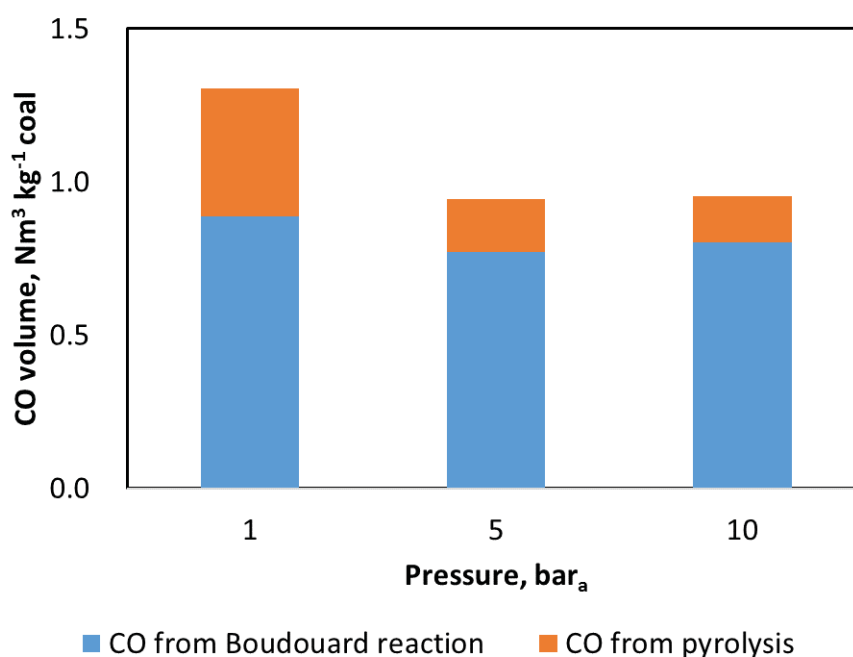


Figure 4.3 CO distribution during CO_2 gasification of German lignite at 850 °C at different pressures

The concentrations of CO_2 , CO , H_2 and CH_4 in the fuel gas during the gasification of German lignite at 850 °C, at different process pressures (1, 5, 10 bar_a) are shown in Figure 4.4. The concentration trend of each gas is similar as the trends shown on Figure 4.2 for the gas yields. With increasing pressure from 1 to 10 bar_a, the concentration of CO and H_2 decreases from 38 to 31% and 6 to 5% respectively. However, the concentration of CH_4 slightly goes up from 0.9 to 1.7%. For CO_2 concentration, as mentioned above, the produced CO_2 and feeding CO_2 cannot be distinguished. Thus, the CO_2 concentration shown in Figure 4.4 includes both the

unreacted inlet CO_2 and the produced CO_2 , and the value increases when the process pressure increased from atmospheric to high pressure. This is because more CO_2 was remained and less fuel gas was produced (from Figure 4.2).

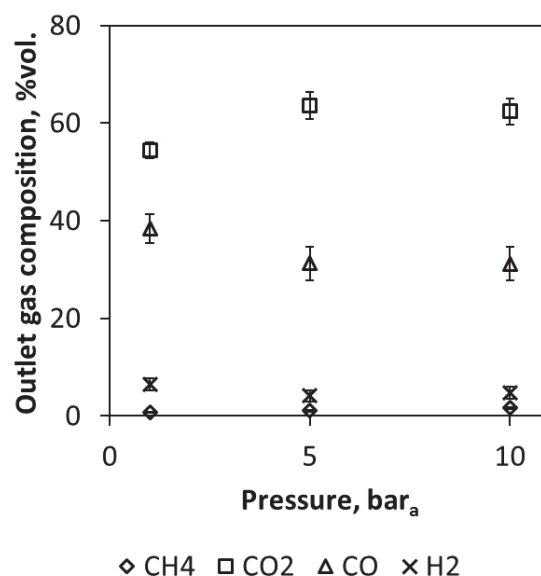


Figure 4.4 Fuel gas composition (dry basis) during the CO_2 gasification of German lignite at 850 °C at different pressures (the concentration of CO_2 includes CO_2 fed)

The higher heating value of dried outlet gas from CO_2 gasification of German lignite at 850 °C is shown in Figure 4.5. The higher heating value (HHV) was calculated according to Equation 3.3. From the Figure 4.5, it can be seen that the HHV of the fuel gas changed from 6 to 5 MJ m^{-3} with the increase in total pressure. This HHV was reasonable compared to other studies (Kurkela and Ståhlberg, 1992, Fermoso et al., 2009). This variation is due to the decrease of CO and H_2 concentration and increase of CH_4 concentration.

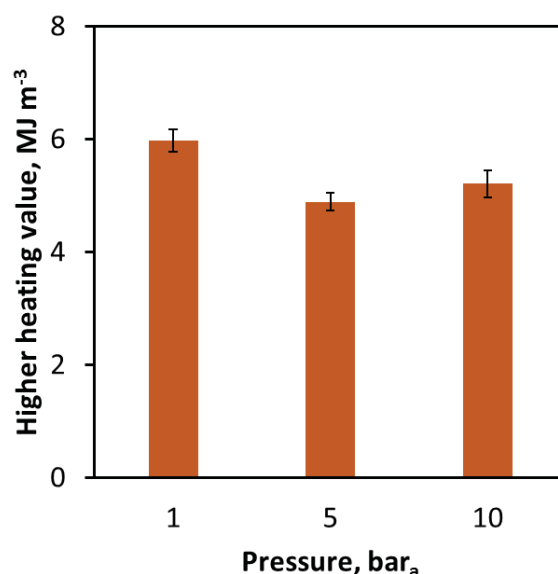


Figure 4.5 Higher heating value of dried outlet gas from CO₂ gasification of German lignite at 850 °C at different pressures

4.3.2 The Effect of Pressure on Tar

Figure 4.6 gives the data of released tar during gasification at different pressure. The generation of tar yields is a result of competition among production and consumption of tar. The primary tar is formed from the thermal decomposition of coal structure, and it can only be affected by the temperature and holding time at the temperature. Then, during the release of the primary tar, it may be repolymerised to produce secondary char, or cracked to produce lighter tars and gases. The transportation of the tar out of the particle may be influenced by the pressure (Gavalas, 1982). It can be seen that the released tar increased from 0.25 to 0.48% with the pressure increasing from 1 to 10 bar_a. This result agrees with some studies (Mayerhofer et al., 2012, Bai et al., 2014, Luo et al., 2016, Sathe et al., 2002). However, the results from the literature have not been consistent, as the pressure

impact on tar yield is complicated. During the volatile release, when the system pressure increased, the pressure around the surface of the coal particle increased. Two consequences may exist. First, the diffusion of the volatiles through the pores to the particle surface was slower, thus the residence time of the volatiles increased. As a result, the extent of the thermal cracking and repolymerising reactions increased and the amount of the released tar could be decreased. Second, since the diffusion rate of the volatiles reduced, the accumulated volatiles (especially light gases) might build up the pressure inside the coal particle rapidly, faster than the diffusion, resulting a forced flow due to the pressure gradient (Sathe et al., 2002). This forced flow could carry the volatiles out of the particle. Therefore, the residence time of the volatiles in the coal particle could be reduced, and the tar yield was increased. This phenomenon is based on the porous structure of the coal particle. As the coal used in this study was lignite, which is normally nonplastic coal. This type of coal almost retains its porous structure during pyrolysis with limited extent of swelling and melting (Saxena, 1990).

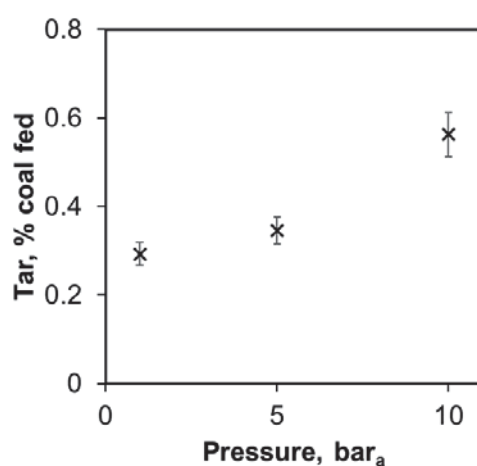


Figure 4.6 Tar released as percent of coal fed during CO₂ gasification at different pressures

Figure 4.7 shows the SEC results of the tars produced from gasification at different pressures. It can be observed that tars produced at 5 and 10 bar_a had a similar size distribution. The proportion of the smaller molecular weight tar compounds was larger at pressurised conditions than that at atmospheric pressure condition. The proportion of the larger tars was smaller from higher pressure experiments than that from the experiment at atmospheric pressure. This can be explained by (1) the increase of the reaction rate of the thermal cracking (including hydrocracking and steam/CO₂ reforming) of the tar in the bed and the freeboard as the pressure increased, (2) due to reduced superficial velocity at high pressure, the residence time of the volatiles in the bed and freeboard increased and gave longer time for thermal cracking. Therefore, larger tar compounds tended to crack to form lighter tar compounds.

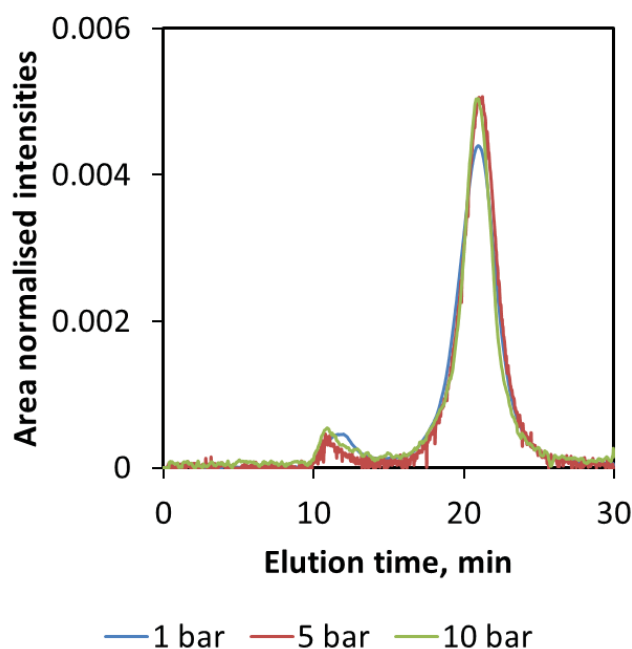


Figure 4.7 Area normalised SEC chromatogram of tar produced under different pressures

4.3.3 The Effect of Pressure on C Conversion

Figure 4.8 shows the C conversion at 850 °C, at different process pressures. The C conversion was calculated using Equation 3.4. It indicates how much carbon in the coal was transferred into gas. The loss of C conversion is mainly in the unreacted char, produced tar and soot. The value is corrected for inlet C in the CO₂. The formation of gaseous C from the lignite is a result of gasification and pyrolysis.

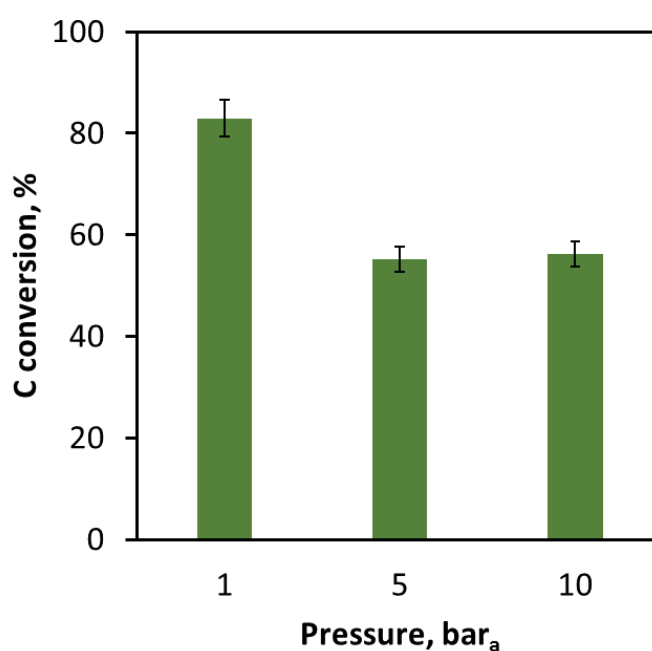


Figure 4.8 C conversion of CO₂ gasification of German lignite at 850 °C as a function of pressure

From Figure 4.8, the C conversion dropped significantly from 83% to 56% from 1 to 5 bar_a, but did not change much between 5 and 10 bar_a. Although there were some agglomerates observed in the char bed collected from pressurised experiments, steady gas composition can be achieved during those runs. Therefore, fluidisation

was not affected by those agglomerates. There are several potential reasons for this observation.

Firstly, due to the pressure increase, the release of volatiles from the fuel particles could be retarded due to the increased external pressure and this could have led to deposition of secondary char within the particles, which reduced their reactivity.

Secondly, U/U_{mf} ratio was reduced when the system pressure increased. There were two impacts. (1) The reduced superficial velocity increased the gas residence time in the bed. (2) The fluidised bed could be transferred from turbulent fluidisation to bubbling fluidisation, resulting a smaller bubble size in the bed. Both two aspects helped the mass transfer of the gasification gas from the bubble phase to the emulsion phase. As the most gasification reaction happened in the emulsion phase because of poor gas solid contacting in the bubble phase. These might cause the C conversion increased, as more gasification gas was around the fuel particles.

Thirdly, when the pressure increased, the coal flow was increased from 1 to 5 bar_a and kept constant from 5 to 10 bar_a. As it was mentioned before that it was impossible to change only the pressure in the fluidised bed. The increase of coal flow rate caused high volatile concentration in the fluidised bed. There were two consequences. Firstly, as the volatile concentration around the coal particles was increased, the diffusion of the volatile through the pore of the coal particle to the surface was retarded. More secondary reactions including thermal cracking and repolymerising could happen. Secondly, during this volatile releasing from the bed, it contacted with coal particles and secondary reactions could happen on the coal particle surface. With the increase of the volatile concentration, the extent of these

reactions increased. In both situations, the repolymerising reaction produced secondary char covered the original char. This secondary char was in highly graphite structure with low reactivity. Therefore, the further reactions of the char were prevented, and the C conversion could be reduced.

Fourthly, as the pressure increased, the equilibrium of the Boudouard reaction was shifted to the reactants side, resulting less char reaction.

Fifthly, at high pressure, the partial pressures of CO and H₂ were higher than those at atmospheric pressure, so CO and H₂ inhibition might have contributed to the effect. When comparing the concentrations at 5 and 10 bar_a, the CO concentrations were quite similar, but the pressure was doubled. Therefore, the CO partial pressure at 5 bar_a was half of that at 10 bar_a. If the CO inhibition had a large influence, then the C conversion at 10 bar_a should be lower than that at 5 bar_a. However, the results of C conversion at 5 and 10 bar_a did not show much difference. Therefore, the CO inhibition cannot be the main reason for C conversion decrease. H₂ concentration had a similar trend as CO concentration, the same reason could apply to H₂ as well. Thus, the H₂ inhibition also cannot be the main reason for decline of C conversion.

4.4 Potential Reasons for C Conversion Decrease

As described above, the decrease of C conversion at high pressure might have been caused by several factors, including suppression of volatile release from the coal particles, char deactivation, changes in the fluidisation characteristics in the bed, thermodynamic equilibrium, and H₂ and CO inhibition. Since the H₂ and CO

inhibition should not be the main reasons in this case, all other factors have been discussed in detail in the following sections to gain a greater understanding of the principal reason for the drop of C conversion at high pressure.

4.4.1 Effect of Suppression of Volatile Release

Figure 4.9 shows the previous work conducted in the WMR. As the volatiles are swept away from the char by a large gas flow in the WMR, the results from WMR determine the intrinsic particle behaviour at pressurised conditions. The data shows the gas, tar and volatile yields from pyrolysis and the total weight loss from the gasification of German lignite at different pressures from 1 to 10 bar_a. According to the graph, the volatile yield from pyrolysis was slightly decreased from 53.5 to 51.6%, with the increase of gas yield and the decrease of tar yield. This can be explained by the suppression of volatile release with the pressure increasing. As a result, the residence time of the volatile in the pore of the coal particles increased. The improved gas yield and reduced tar yield caused by the enhanced extent of the cracking reaction. However, only 2% drop of the total volatile yield indicates that the extent of the repolymerising reaction (to form unreactive secondary char) seemed not be much improved. The results of the weight loss in gasification includes the loss of pyrolysis step and gasification. It can be observed that the weight loss was slightly decreased with the increase in pressure. Therefore, the impact of the secondary char formation by the volatile release suppression was relatively small. The sharp decrease in C conversion as the pressure was raised from 1 to 5 bar_a in the fluidised bed reactor cannot be explained by the suppression of volatile release under high pressure.

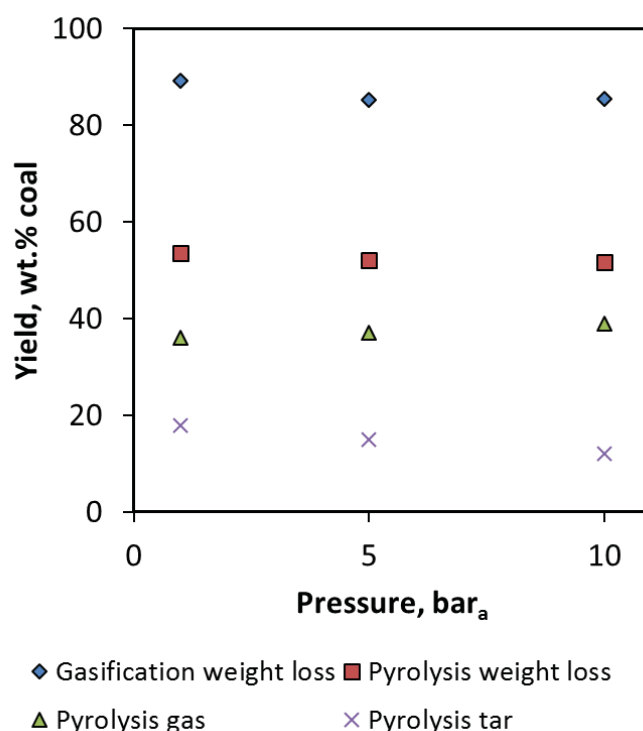


Figure 4.9 Volatile yield from gasification (with CO₂) and pyrolysis (with He) of German lignite at 850 °C with the heating rate at 1000 °C and 60 s holding time at different pressures from wire mesh reactor

4.4.2 Effect of Fluidisation Conditions

The data of the fuel gas yield of CO₂ gasification of German lignite at different fluidisation conditions is shown in Figure 4.10. According to the Figure 4.10, H₂ yield and CH₄ yield were constant and relatively small, while the U/U_{mf} ratio increases. Because there was no moisture from the coal as the coal was dried, and there was no steam injection. H₂ and CH₄ were mainly produced through pyrolysis step, and H₂ could be consumed through the reverse water gas shift reaction as the large amount of input CO₂ to produce CO and H₂O. Only around 30% of fuel-H was converted into H₂ and CH₄ and the remaining was in the char, tar and produced H₂O. This shows

that pyrolysis step was not influenced by the change of fluidisation condition. The yield of CO increased slightly, which might be due to the increase of CO₂ input. However, when the inlet CO₂ increased, the gas superficial velocity was increased. On one hand, the CO₂ concentration in the emulsion phase might decreased by the poor mass transfer due to the reduced overall surface area caused by the larger bubble size. On the other hand, the mass transfer of the CO₂ from the bubble phase into the emulsion phase might be enhanced by the high CO₂ concentration in the bubble phase. The result represents the competition of these two influences. The small increase of the CO yield shows the CO₂ in the emulsion phase slightly improved. Thus, the Boudouard reaction was pushed towards the products side and the reaction rate was increased as well. Table 4.4 shows the CO₂ conversion at different fluidisation conditions. As the U/U_{mf} ratio was increased from 3.0 to 7.5, the CO₂ conversion decreased from 32 to 24%. This drop was caused by two reasons: (1) The CO₂ residence time was reduced. (2) Although the amount of the reacted CO₂ was slightly increased, the increased amount of the input CO₂ was much higher.

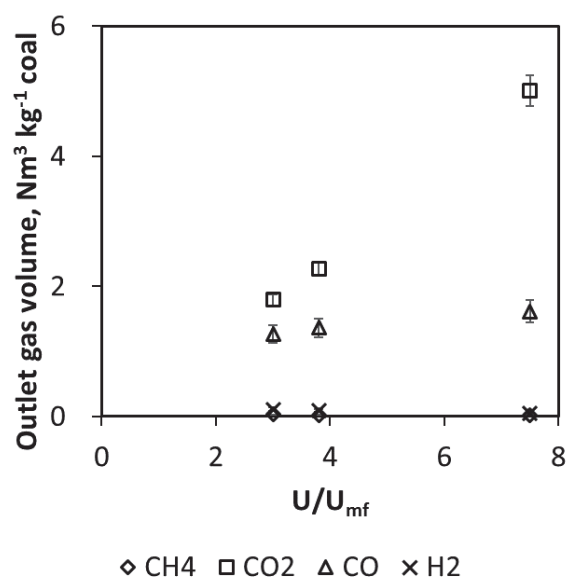


Figure 4.10 Fuel gas yield during the CO₂ gasification of German lignite at 850 °C at 5 bar_a with dried GL flow rate at 1.37 g min⁻¹ at different fluidisation conditions (the outlet gas volume of CO₂ includes CO₂ fed)

Table 4.4 CO₂ conversion of CO₂ gasification of German lignite at 850 °C at 5 bar_a with dried GL flow rate at 1.37 g min⁻¹ at different fluidisation conditions

U/U _{mf}	3.0	3.8	7.5
CO ₂ conversion, %	32	31	24

Figure 4.11 shows the fuel gas composition during the CO₂ gasification of German lignite at different fluidisation conditions. This figure shows that the concentrations of CO, H₂ and CH₄ decreased, while the concentration of CO₂ increased from 56 to 75%, when U/U_{mf} ratio was increased. This was mainly because the amount of the increase in the unreacted CO₂, and this CO₂ diluted the other gases and made all other gases show decreasing trends.

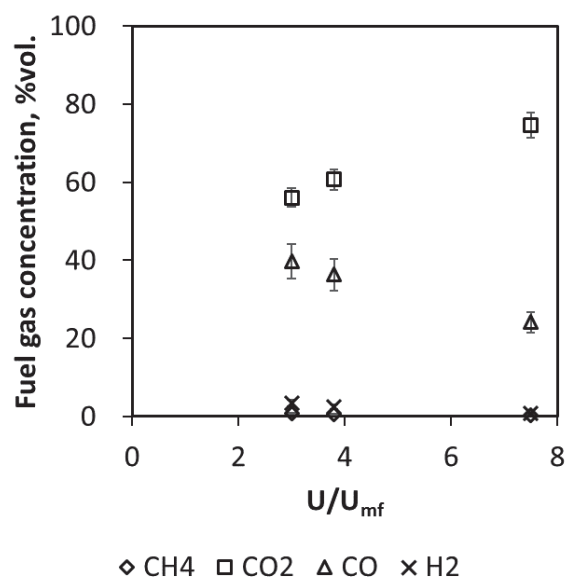


Figure 4.11 Fuel gas composition (dry basis) during the CO₂ gasification of German lignite at 850 °C and 5 bar_a with dried GL flow rate at 1.37 g min⁻¹ at different fluidisation conditions (the concentration of CO₂ includes CO₂ fed)

Figure 4.12 shows the results for released tar at different fluidisation conditions. According to the figure, the released tar was almost constant around 0.2% at tested fluidisation conditions. This result agrees the previous discussion that the pyrolysis step did not affect by the fluidisation condition. Figure 4.13 shows the SEC results of the tar produced at different fluidisation conditions. It can be observed that the proportion of the smaller tar decreased with the increase of U/U_{mf} ratio. As the reduce of the gas residence time, residence time of the volatiles in the bed and freeboard decreased. Thus, less large tar molecules cracked to form smaller tars.

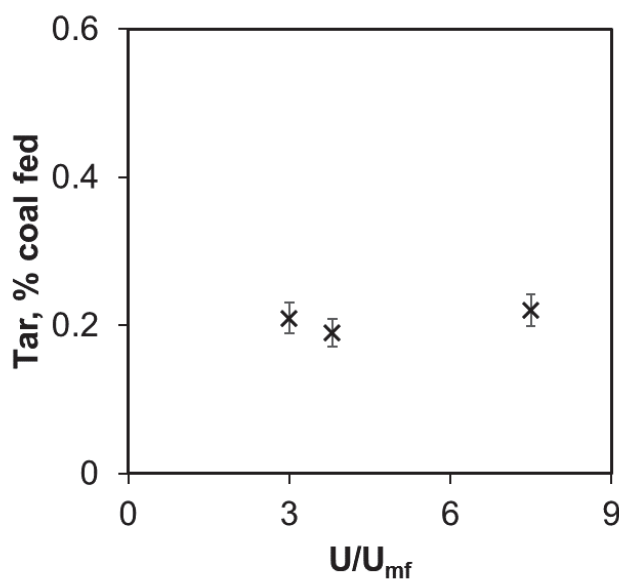


Figure 4.12 Tar released as percent of coal fed during CO_2 gasification at $850\text{ }^\circ\text{C}$ at 5 bar_a with dried GL flow rate at 1.37 g min^{-1} at different fluidisation conditions

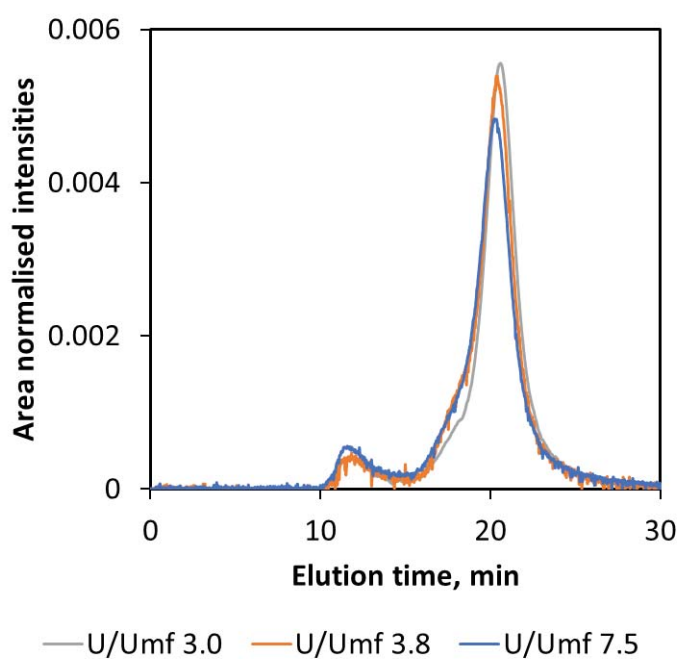


Figure 4.13 Area normalised SEC chromatogram of tar produced at $850\text{ }^\circ\text{C}$ at 5 bar_a with dried GL flow rate at 1.37 g min^{-1} at different fluidisation conditions

The C conversion data of CO₂ gasification of German lignite at different fluidisation conditions is shown in Figure 4.14. The change in the U/U_{mf} ratio from 3.0 to 7.5 will have altered the fluidising conditions in the bed. As discussed above, when increased the U/U_{mf} ratio, the residence time of the gas was decreased and the bubble size was increased, while the concentration of the input gas in the bubble phase was increased. As a result, the concentration of the gasification gas in the emulsion phase was slightly increased. However, this small increase did not affect much on the C conversion, which remained relatively constant with values of 73% at U/U_{mf} ratio of 3.0 and 78% at U/U_{mf} ratio of 7.5. Therefore, within this experimental range, the influence of fluidisation condition on the C conversion is relative small.

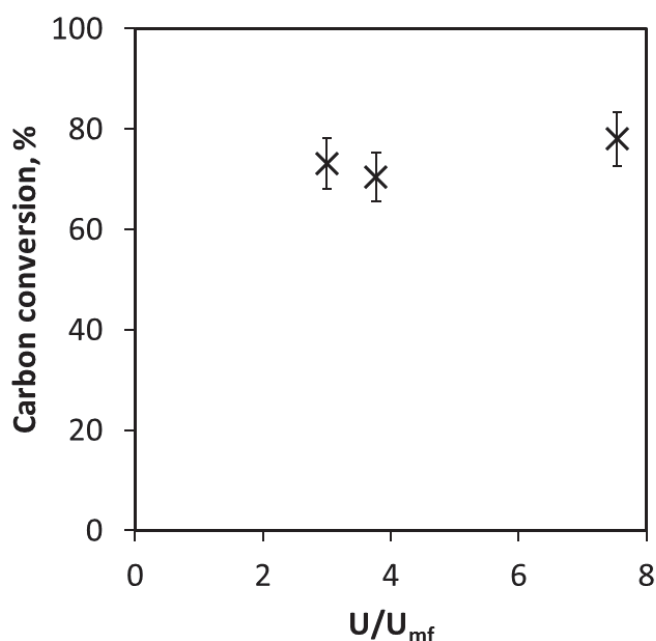


Figure 4.14 C conversion of CO₂ gasification of German lignite at 850 °C at 5 bar_a with dried GL flow rate at 1.37 g min⁻¹ at different fluidisation conditions

4.4.3 Effect of Char Deactivation

The fuel gas yields at different coal flow rates are shown in Figure 4.15. The left figure shows the fuel gas flow rate and the right figure shows the volume per gram of coal. Figure 4.16 shows the dry gas concentration, with similar trends as the fuel gas flow rate.

The flow rates of produced H_2 and CH_4 were increased proportionally as more coal was injected. Since these two products were mainly from the pyrolysis at these conditions, and the change of coal flow rate did not have any influence. Thus, the production of H_2 and CH_4 in the volume per gram of coal should be constant at each coal flow rate. This can be observed in the right graph of Figure 4.15.

The CO flow rate was slightly increased while CO_2 flow rate was decreased. Both the CO and CO_2 produced from pyrolysis should be linearly increased with the coal flow rate, while the CO production and CO_2 consumption from the Boudouard reaction were more complicated. As the inlet CO_2 flow rate was constant when changing the coal flow rate, the bubble size should be equal, resulting a similar CO_2 concentration in the emulsion phase. As the coal flow rate increased, the bed height might be increased. However, as the high superficial velocity and narrow bed diameter, the fluidised bed might be in a slugging or a turbulent fluidising condition, the bed height did not affect the gas residence time. In addition, more coal particles were in the emulsion phase. The overall surface area of the coal particles was improved and provided a larger surface area for the Boudouard reaction. Thus, the extent of the Boudouard reaction was enhanced, and more CO was produced and less CO_2 was remained. In terms of the CO produced per gram of coal, it was slightly decreases.

As the CO_2 concentration was constant with more coal particles in the emulsion phase, the amount of CO_2 molecules surrounded by one coal particle was decreased. So, less CO was produced per gram of coal. The change of CO_2 is illustrated in Table 4.5. With the increase of coal flow rate, the CO_2 conversion slightly increases from 24 to 28%. This was because the input CO_2 flow rate was constant, and the amount of the reacted CO_2 was increased.

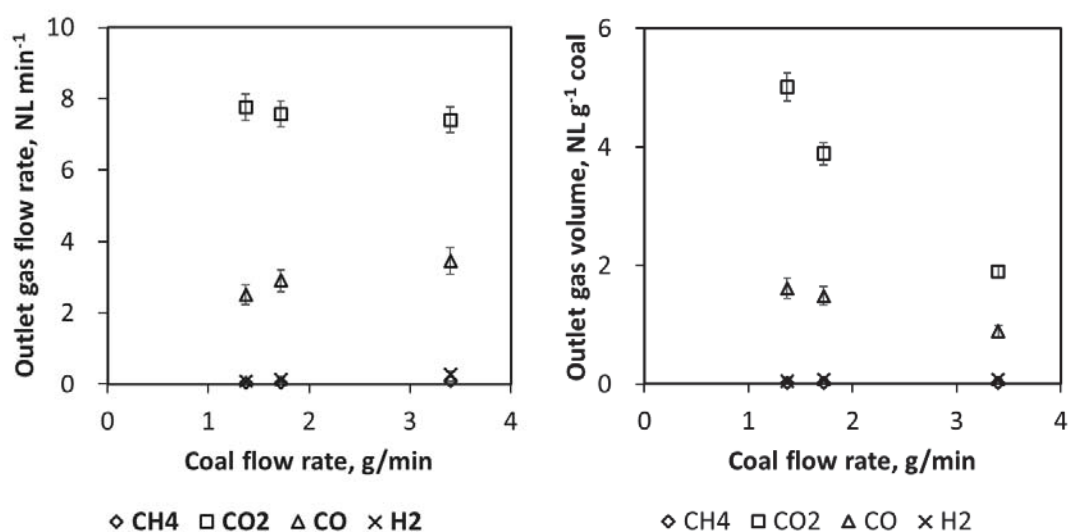


Figure 4.15 Fuel gas yield of CO_2 gasification of German lignite at 850 °C at 5 bar_a with CO_2 flow rate at 9.01 NL min⁻¹ at different coal flow rate (the outlet gas volume of CO_2 includes CO_2 fed). Left: fuel gas flow rate. Right: fuel gas volume per gram of coal.

Table 4.5 CO₂ conversion of CO₂ gasification of German lignite at 850 °C at 5 bar_a with CO₂ flow rate at 9.01 NL min⁻¹ at different coal flow rate

Coal flow rate	1.4	1.7	3.4
CO ₂ conversion, %	24	26	28

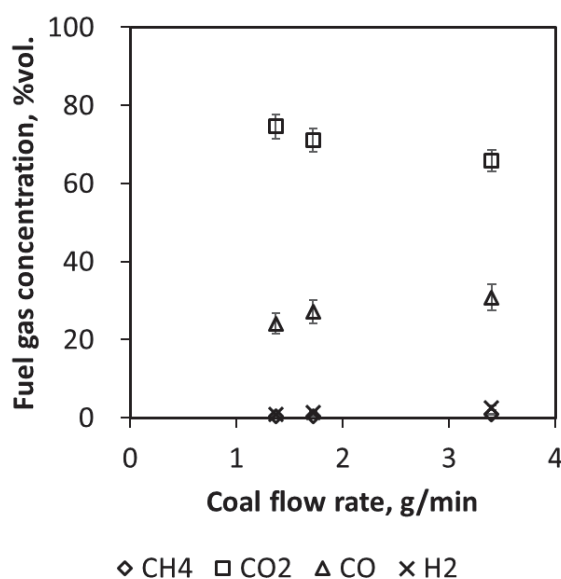


Figure 4.16 Fuel gas composition (dry basis) of CO₂ gasification of German lignite at 850 °C at 5 bar_a with CO₂ flow rate at 9.01 NL min⁻¹ at different coal flow rate (the concentration of CO₂ includes CO₂ fed)

Figure 4.17 shows the tar yield increased when the coal flow rate increased. As the pyrolysis did not affect by the coal flow rate, the volatile flow rate increased proportionally with the increase of coal flow rate. The concentration of the volatile was increased. Firstly, the increased volatile flow rate might reduce the residence time in the bed and freeboard, and resulted less secondary reactions of the volatile. Secondly, as discuss earlier, the increased volatile concentration could enhance the

secondary reactions both inside the pore and on the outer surface of the coal particles.

Figure 4.18 shows the SEC results of the tars produced at different coal flow rate. It can be seen that no clear difference among those tars. This might due to the two consequences by improving the volatile concentration were counteractant.

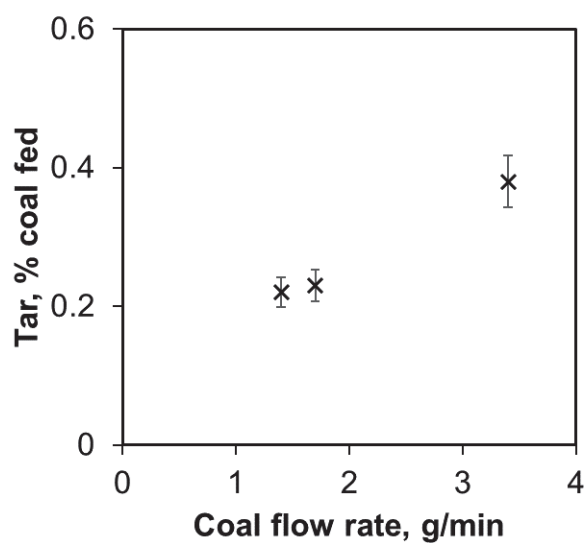


Figure 4.17 Tar released as percent of coal fed during CO₂ gasification at 850 °C at 5 bar_a with CO₂ flow rate at 9.01 NL min⁻¹ at different coal flow rate

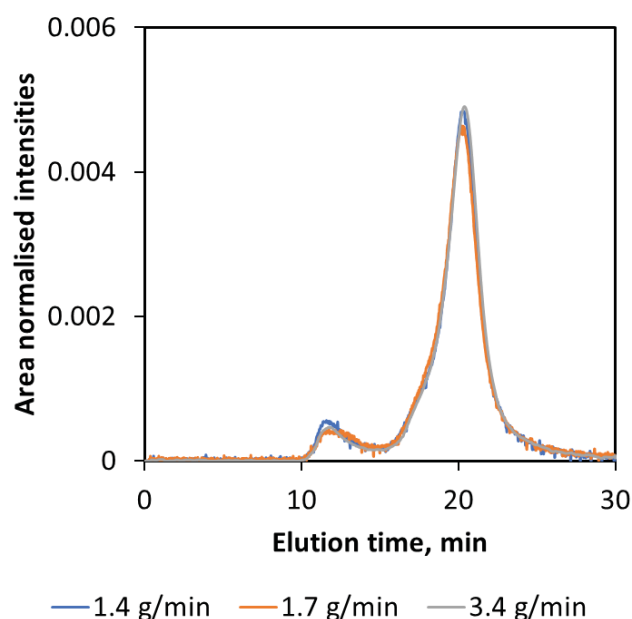


Figure 4.18 Area normalised SEC chromatogram of tar produced at 850 °C at 5 bar_a with CO₂ flow rate at 9.01 NL min⁻¹ at different coal flow rate

Figure 4.19 shows the C conversion at different coal flow rates. With coal flow rate increasing, C conversion decreased sharply. As discussed above, the volatile concentration in the fluidised bed increased by the improve of coal flow rate. This high concentration of volatile around the coal particles slowed down the diffusion of volatile from the pore to the particle surface. Thus, the residence time of the volatile inside coal particles was increased with more chance of the repolymerising reaction to produced unreactive secondary char to avoid further gas char reactions, and also the structure of the char could change. In addition, the repolymerising reaction on the surface of the coal was also improved by high volatile concentration. However, this secondary char produced on the coal surface was tended to be soot and could be removed from the bed. Therefore, the extent of char deactivation is correlated to

coal flow rate in the fluidised bed. This result shows that the char deactivation had a large impact on the decrease of the C conversion at high pressure.

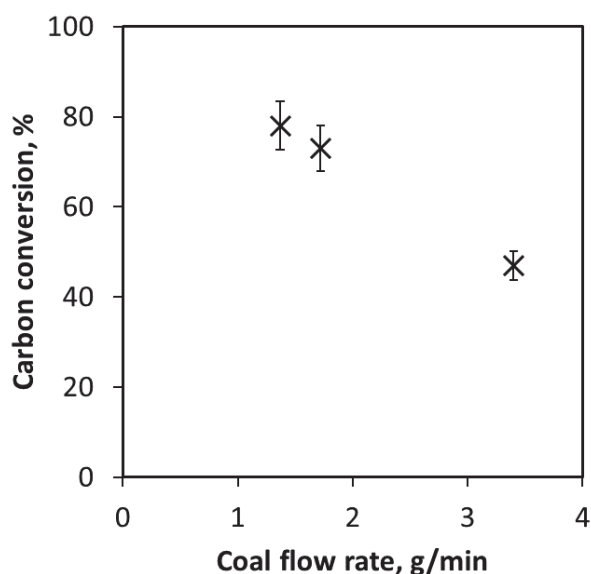


Figure 4.19 C conversion of CO₂ gasification of German lignite at 850 °C at 5 bar_a with CO₂ flow rate at 9.01 NL min⁻¹ at different coal flow rate

4.4.4 Effect of Thermodynamic Equilibrium

The comparison of the experimental data and the calculated data in the thermodynamic equilibrium is shown in Figure 4.20. The data from the thermodynamic equilibrium was calculated using Aspen Plus based on the Gibbs free energy minimisation. The input for the calculation was C and CO₂, and the output was CO, CO₂, H₂, CH₄ and water. However, water was not included in the comparison, as it was not measured in the fuel gas during the experiments. Each gas component from the experimental data shows the same trend as the calculated data, while the results from the experiments were far from the thermodynamic equilibrium. According to the equilibrium data, with the pressure increasing, both the CO and H₂

yields decrease while the production of CO_2 and CH_4 increase, as the shift of equilibrium to the less gas molecules side. However, this effect was small from 1 to 10 bar_a. Comparing the data between the experiments and the equilibrium calculation, the CO and H_2 yields from the experiments were much lower than the calculated results, as the char was deactivated in the fluidised bed without a full conversion. The CO_2 was much more from the experiments than from the calculation, due to the large amount of unreacted CO_2 . The CH_4 yield was higher in the experimental data. This may be because the gas residence time was not long enough for the gas products to reach their equilibrium values, and char could be deactivated in the bed.

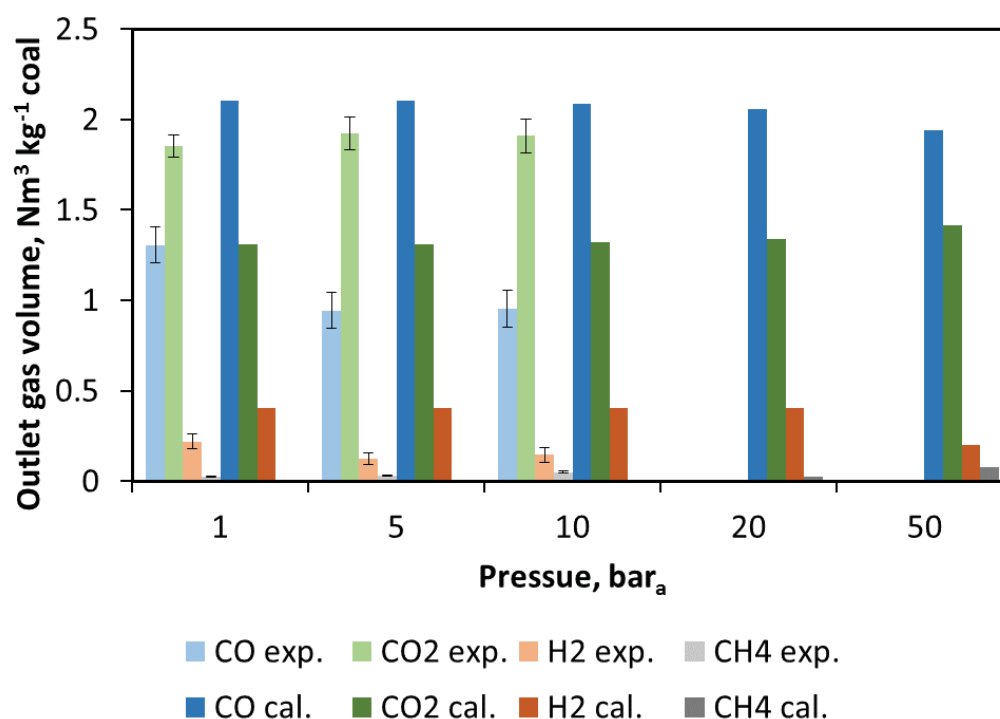


Figure 4.20 Outlet gas volume from experiments and thermodynamic equilibrium calculations of CO_2 gasification at 850 °C at different pressure

4.5 Conclusions

It was observed that C conversion decreased significantly from 83% to 56% when the pressure increased from 1 to 5 bar_a, and then kept nearly constant between 5 and 10 bar_a. In principle, the reduction of C conversion at elevated pressure could be caused by several factors, including suppression of volatile release from the coal particles, char deactivation, changes in the fluidisation characteristics in the bed, thermodynamic equilibrium, and H₂ and CO inhibition. As the partial pressure of CO at 5 bar_a was half of that at 10 bar_a, the C conversion at 10 bar_a should be lower than that at 5 bar_a if the CO inhibition had a large impact. However, the results show C conversion at 5 and 10 bar_a were similar. Therefore, the CO inhibition cannot be the main reason for C conversion decrease. H₂ concentration had a similar trend as CO concentration. The same reason also applies to H₂. Thus, the H₂ and CO inhibition should not be the main reason in this case. All other potential reasons have been experimentally studied.

- (1) The results from the wire mesh reactor show only 2% drop in the total volatiles released by pyrolysis between 1 and 10 bar_a, indicating that the sharp drop of C conversion is not a reflect of intrinsic particle behaviour. Therefore, C conversion reduction with pressure in the fluidised bed reactor cannot be explained by the suppression of volatile release under high pressure.
- (2) The influence of the changes in the fluidisation characteristics in the bed cannot be the main reason for the decrease of C conversion at pressurised conditions. Due to the fact that C conversion remained relatively constant in the

experimental range, with the change of U/U_{mf} ratio from 3 to 7.5. The yield of CO increased slightly, although the amount of CO_2 input had been largely increased. The small increase of the CO yield indicated that the concentration of CO_2 in the emulsion phase slightly improved. This was caused by the competition of two phenomena. As the input CO_2 increased, the gas superficial velocity was increased. On one hand, the CO_2 concentration in the emulsion phase decreased by the poor mass transfer due to the reduction overall surface area caused by the larger bubble size. On the other hand, the mass transfer of the CO_2 from the bubble phase into the emulsion phase was enhanced by the increase of CO_2 concentration in the bubble phase. This small increase of CO_2 concentration in the emulsion phase had a negligible impact on the C conversion.

- (3) The change of thermodynamic equilibrium was not the main reason for the drop of C conversion at high pressure, by comparing the experimental results with the data calculated at thermodynamic equilibrium. The trend of each gas component from experimental results are the same as the calculated ones, while the experimental results are far from thermodynamic equilibrium. This is due to the short residence time of gas and deactivation of char in the bed.
- (4) The drop of the C conversion was mainly caused by the char deactivation caused by the repolymerising reaction of the volatiles in the pores of the char particles, which led to the deposition of secondary char and structure change of the char. This effect was enhanced by the volatile concentration, which was correlated to the solid fuel feeding rate and the reactor size. With coal flow rate increasing, the volatile concentration in the fluidised bed increased. This high concentration of

volatile around the coal particles slowed down the diffusion of volatile from the pore to the particle surface. Thus, the residence time of the volatile inside coal particles was increased with more chance of repolymerisation to produced unreactive secondary char to stop further gas char reactions, and the structure of the char could change as well. This effect could be further investigated by char characterisation through morphology, chemical composition and surface area. The results show that the char deactivation had a large impact on the decrease of the C conversion at high pressure. Therefore, it is important to consider the solid feeding rate corresponding to the reactor size when design large scale plants using similar type of gasifier, as C conversion would need to be maximised to reduce C losses.

Chapter 5 Effect of Steam on Gasification Performance

5.1 Introduction

Steam is widely used as a gasification agent in gasifiers. The literature shows that there are several benefits to be gained from its use. One of the most important advantages is that the introduction of steam improves the production of H_2 (Xiao et al., 2017, Prabowo et al., 2014, Sheeba et al., 2013). In addition, the rate of char-steam reaction is faster than that of char- CO_2 reaction (DeGroot and Richards, 1989, Yang and Wong, 1983), which enables a large throughput or reduces the gasifier size with the same throughput. There are two routes for the addition of steam into the gasification process: injection of steam in the fluidisation gas and evaporation of the moisture from the feedstock. Many literature studies concern the influence of the first type of steam addition into the gasification process (Smolinski, 2011, Yan et al., 2010, Zhou et al., 2005), but only few literature studies cover the effect of the moisture from the feedstock (Kaewluan and Pipatmanomai, 2011). In addition, these studies were mainly performed at atmospheric pressure.

In this chapter, the effect of different ways of adding steam into the gasifier on the performance (fuel gas composition, heating value, CO/H_2 ratio, C conversion and tar production) at elevated pressure is described. There are three objectives of these experiments. Firstly, to study the influence of steam concentration on the steam/ CO_2 gasification. Secondly, to understand the performance of the steam/ CO_2 gasification

at elevated pressure. Last, to see the different performance by using the steam produced from different routes (water injection and moisture of the feedstock).

This chapter is divided into three parts. In the first part, the overall experimental conditions are described. The second part discusses the results from two modes of steam addition: (1) influence of adding steam into the fluidisation medium, (2) influence of the moisture of the feedstock and the comparison with the steam injection on the gasification performance. The last part is the summary of the main findings.

5.2 Experimental Conditions

All the experiments were carried out at 850 °C using German lignite as the feedstock. Purified acid-treated sea sand was the bed material for the fluidised bed reactor. The detailed experimental conditions are shown in Table 5.1. The experimental repeatability is shown in Section 3.6.4. The experiments were carried out around 15 to 60 min (60 g of coal gasified for each experiment and the experimental duration varied depending on the coal feeding rate) and results were taken from the average of the steady gas composition at each condition, and the error bars were the calculated errors shown in 3.6.5.

To investigate the influence of adding steam on the gasification performance, experiments 1 to 9 (shown in Table 5.1) were carried out. Both neat CO₂ and CO₂/steam mixtures were used as the gasification medium. The total mole ratio of

CO₂ and steam to carbon from coal ((CO₂+H₂O)/C) was kept constant at 2:1. The steam flow was controlled by a calibrated HPLC pump. The steam input (0, 0.36, 0.72 mL min⁻¹) shown for these tests was that added into the system from the water injected by the HPLC pump. It does not include that formed from the moisture (equal to 0.13 mL min⁻¹ of water at set coal flow rate) in the coal. The mole ratios of H₂O/CO₂ in the inlet gas flow were 0/100, 20/80 and 40/60. The experiments were conducted at 1, 5 and 10 bar_a.

To understand the effect of the moisture from the solid fuel on the gasification process, three types of experiments (run 10 to 18 in Table 5.1) were performed using German lignite (moisture content: 12%wt.). For the first type of experiments, the coal sample was dried. This sample was prepared by putting the original German lignite in an oven at 110 °C overnight to remove all the moisture from the sample. This effectiveness of the drying process was checked by TGA. The second type of experiments used the dried coal and injected steam in the fluidising gas. In this condition, the coal was dried in the same method used for the first type of experiments, and the amount of steam injected into the system was equal to that formed from the moisture content of the solid fuel. This simulated the moisture flowing into the system from the feedstock. The last type of experiments was utilised the original coal sample containing moisture. The experiments were carried out at 5 bar_a. The feeding rate of the coal was slightly different between the dried coal and the original coal, in order to keep the same feeding rate of carbon. This set of experiments was performed under three different fluidisation conditions (with U/U_{mf} from 3.0 to 7.5), as it was observed that the moisture effect was not constant at different U/U_{mf} ratios.

The gasification performance was determined by the fuel gas yield, fuel gas composition, heating value, CO/H₂ ratio and C conversion. The produced tar was also collected and analysed by SEC. The detailed analytical methods and calculations are shown in Section 3.5.

Table 5.1 Experimental conditions

Run	Pressure, bar _a	Sample preparation	Coal _{in} , g min ⁻¹	CO _{2 in} , L min ⁻¹	H ₂ O _{in} , mL min ⁻¹	H ₂ O _{in} ¹ , %	H ₂ O _{total} ² , %	$\eta[\text{CO}_2+\text{H}_2\text{O}]/[\text{C}]$	U/U _{mf}
1	1	As received	1.04	2.39	0.00	0	6	2	10.0
2	1	As received	1.04	1.91	0.36	20	25	2	10.0
3	1	As received	1.04	1.43	0.72	40	44	2	10.0
4	5	As received	3.90	9.01	0.00	0	6	2	7.5
5	5	As received	3.90	7.20	1.36	20	25	2	7.5
6	5	As received	3.90	5.40	2.71	40	44	2	7.5
7	10	As received	3.90	9.01	0.00	0	6	2	3.8
8	10	As received	3.90	7.20	1.36	20	25	2	3.8
9	10	As received	3.90	5.40	2.71	40	44	2	3.8
10	5	Dried	1.37	3.57	0.00	0	0	2	3.0
11	5	Dried	1.37	3.57	0.18	6	6	2	3.0
12	5	As received	1.55	3.57	0.00	0	6	2	3.0
13	5	Dried	1.37	4.50	0.00	0	0	3	3.8
14	5	Dried	1.37	4.50	0.18	5	5	3	3.8
15	5	As received	1.55	4.50	0.00	0	5	3	3.8
16	5	Dried	1.37	9.01	0.00	0	0	5	7.5
17	5	Dried	1.37	9.01	0.18	3	3	5	7.5
18	5	As received	1.55	9.01	0.00	0	3	5	7.5

¹ Percentage of steam in the inlet gas stream

² Percentage of steam in the reactants including the moisture from the feedstock

5.3 Effect of Steam Concentration and Pressure

The gasifier performance with different $\text{H}_2\text{O}/\text{CO}_2$ ratios and different pressures is described and discussed in this section.

5.3.1 Effect of Steam Concentration and Pressure on Gas Composition, Yield and Heating value

The influence of adding steam on the fuel gas concentration is shown in Figure 5.1. The concentrations were measured on a dry basis, as the fuel gas was dried before the analysis. The trends of fuel gas concentration against inlet $\text{H}_2\text{O}/\text{CO}_2$ ratio are the same at each tested pressure and the same as the trends for the fuel gas yield (shown in Figure 5.2). With increasing steam input concentration, H_2 and CH_4 concentrations increased, while the CO concentration decreased slightly at 1 bar_a and remained almost constant at 5 and 10 bar_a. The total fuel gas yield was reduced by the increase of steam concentration. Owing to the increase of H_2 and CH_4 yields (shown in Figure 5.2) and decrease of total fuel gas yield, the measured concentrations of H_2 and CH_4 increased. The actual changes in yield of each gas component are discussed in detail below.

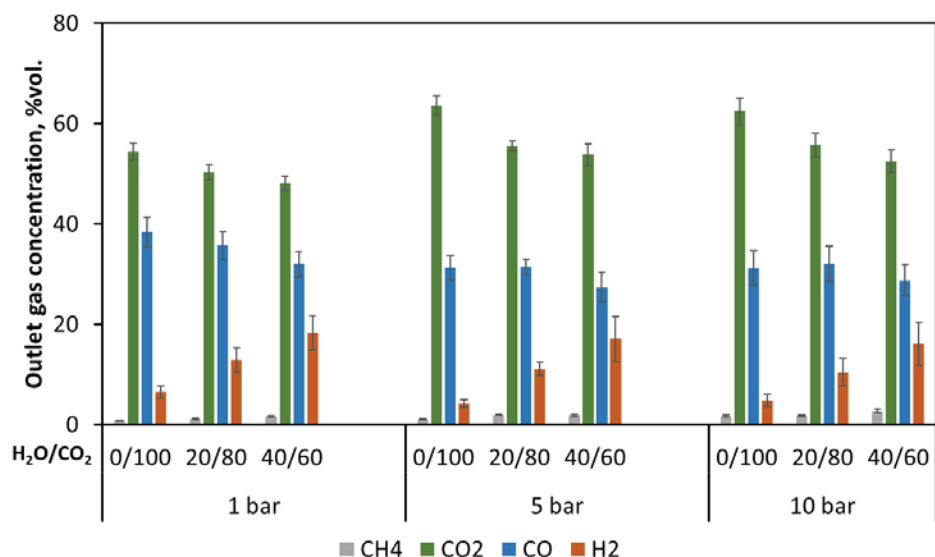


Figure 5.1 Fuel gas concentration of CO₂/H₂O gasification of German lignite at 850 °C at different pressure (the outlet gas concentration of CO₂ includes CO₂ fed) (a) 1 bar_a, (b) 5 bar_a, (c) 10 bar_a.

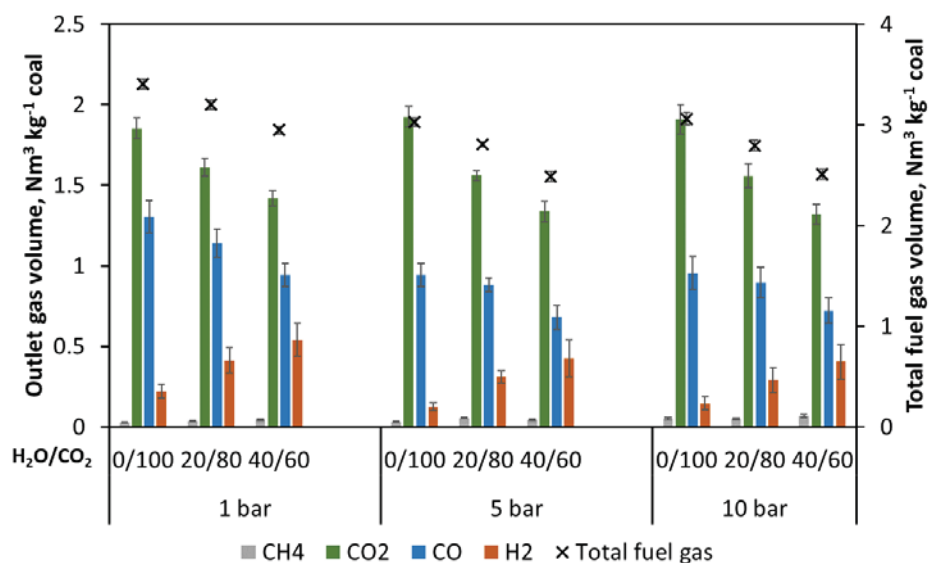


Figure 5.2 Fuel gas yield of CO₂/H₂O gasification of German lignite at 850 °C at different pressure (the outlet gas volume of CO₂ includes CO₂ fed) (a) 1 bar_a, (b) 5 bar_a, (c) 10 bar_a.

The CH₄ yields were slightly increased with the increase in the steam concentration at different experimental pressures. The CH₄ was produced during pyrolysis and by the methanation reaction, but can be consumed through the steam methane reforming reaction. With increase of inlet H₂O concentration from 0 to 40%, the CH₄ production from pyrolysis might be increased from the thermal cracking from the volatiles, as the tar yield was decreased (shown in Figure 5.7). However, the increase of CH₄ was about 0.02 L g⁻¹ coal (0.013 g g⁻¹ coal), and the decrease of tar yield was around 0.0005 to 0.0039 g g⁻¹ coal. Therefore, the increase of CH₄ was not mainly from pyrolysis but from methanation reaction, due to the increase of H₂ concentration. This must have been a more dominant effect than any change to the steam methane reforming reaction.

The H₂ yield increased from 0.2 to 0.5 m³ kg⁻¹ at atmospheric pressure, and from 0.1 to 0.4 m³ kg⁻¹ at both 5 and 10 bar_a, when the inlet steam concentration increased from 0 to 40%. H₂ can be produced through different reactions in the gasifier, including steam-char reaction, water gas shift reaction, steam methane reforming reaction, pyrolysis and steam-tar reforming reaction. Meanwhile, it can be consumed by the methanation reaction. As the methanation reaction was more dominant than the steam methane reforming reaction (discussed above), and there was a very low methane concentration (less than 3% in Figure 5.2) in the produced gas and a very small tar production (less than 1% in Figure 5.9), the H₂ was mainly produced from steam-char reaction, water-gas shift reaction and pyrolysis. Therefore, when the steam concentration increased, the H₂ yield increased due to the enhancement of steam-char reaction and water gas shift reaction.

However, the CO yield decreased from 1.3 to 0.9 m³ kg⁻¹ at 1 bar_a and from 0.9 to 0.7 m³ kg⁻¹ at 5 and 10 bar_a with the increasing of input steam concentration. This may be because the Boudouard reaction is partially replaced by the steam-char reaction due to the partial replacement of CO₂ by steam. In addition, the extent of water gas shift reaction was increased, as the kinetics was increased and the equilibrium was shifted to the products side when increased steam concentration and decreased CO₂ concentration in the inlet gas flow.

CO₂ conversion (calculated by Equation 3.3 in Section 3.5.1.3) as a function of CO₂/H₂O ratio and pressure is shown in Figure 5.3. CO₂ was consumed through the Boudouard reaction, and it could be produced through the water gas shift reaction and pyrolysis, so the overall effect is a balance between these opposing influences. The extent of pyrolysis was constant at the different ratio of gasification agents, as the coal feed rate was not changed. In the experiment using 60% CO₂ and 40% H₂O as gasification medium at 1 bar_a, the CO₂ conversion was negative. This indicates more CO₂ was produced through pyrolysis and water gas shift reaction than was consumed by the Boudouard reaction. The CO₂ conversion decreased with the rise of steam concentration. There are two possible reasons: (1) the extent of Boudouard reaction was reduced as more active steam was injected to compete for the active sites for reaction with char, (2) CO₂ was increased by the equilibrium shift of water gas shift reaction to the products side.

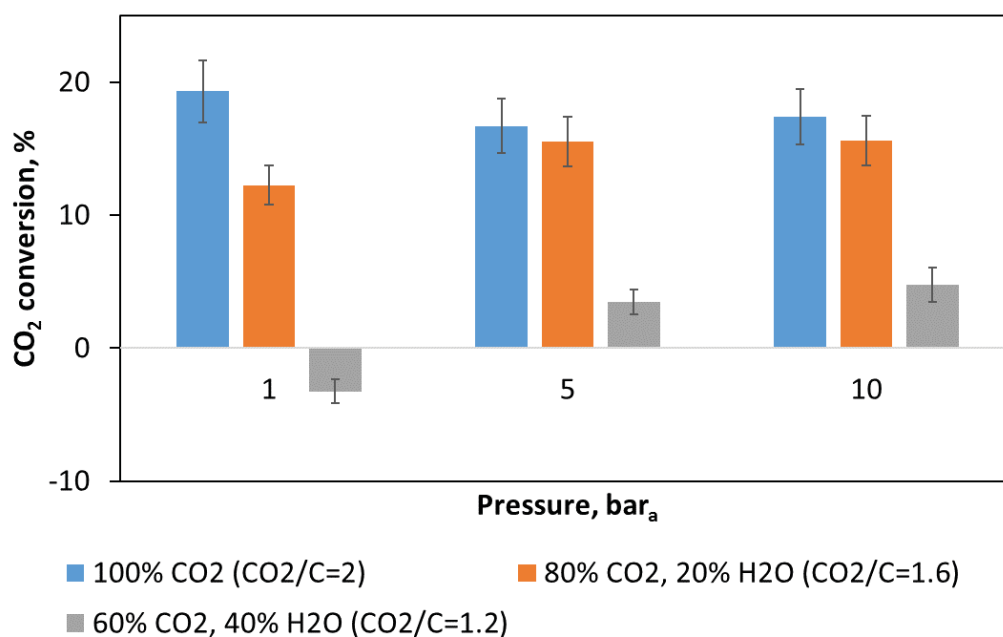


Figure 5.3 CO₂ conversion of CO₂/H₂O gasification of German lignite at 850 °C at different pressure

Figure 5.4 shows the data of higher heating value of the dry products from CO₂/H₂O gasification. The higher heating value was in the range 5 to 7 MJ m⁻³, which is about the average value compared to 4 to 12 MJ m⁻³ from the literature (Kang et al., 2017, Herdel et al., 2017, Xiang et al., 2009, Lv et al., 2004, Karmakar and Datta, 2011). At all tested pressures, there is an increasing trend in the higher heating value with the rise in the inlet steam concentration. This is mainly due to the increase of the hydrogen concentration. With the pressure increasing, the higher heating value had a slightly decrease due to the decrease of the combustible gas concentration in the fuel gas.

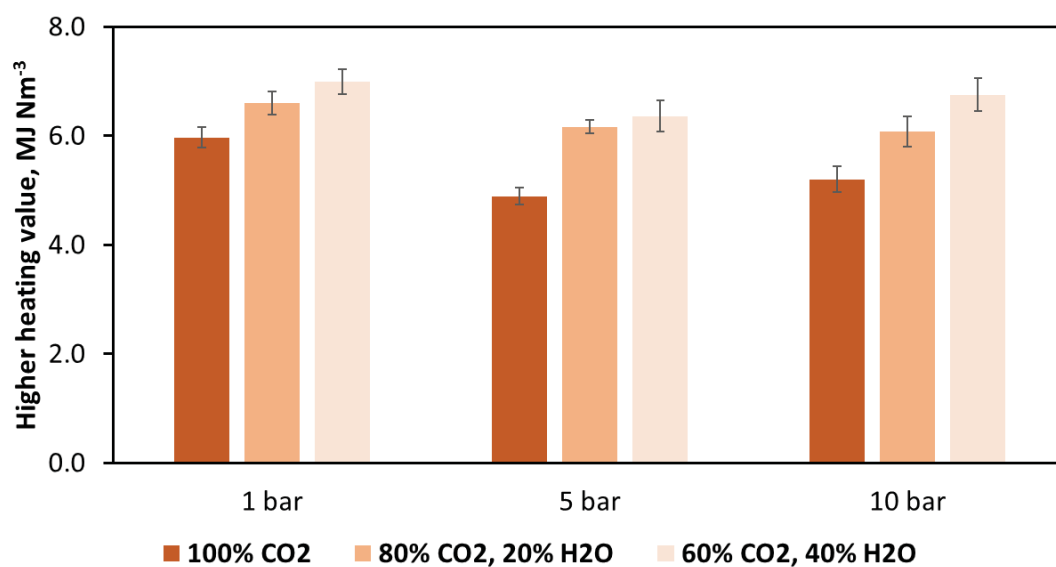


Figure 5.4 Dry gas higher heating value of CO₂/H₂O gasification of German lignite at 850 °C at different pressure

The CO/H₂ ratio of the produced gas from CO₂/H₂O gasification is shown in Figure 5.5. When the steam concentration increased, the CO/H₂ ratio dropped due to the growth of the H₂ concentration and reduction of the CO concentration. It can be seen that the CO/H₂ ratio can be adjusted within the experimental range studied by changing the ratio of H₂O/CO₂ in the inlet stream.

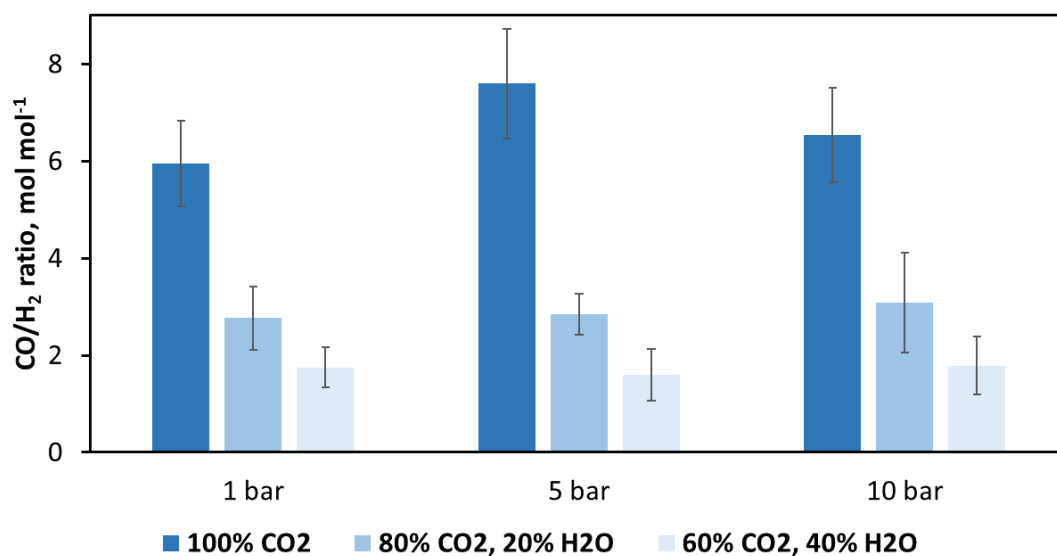


Figure 5.5 CO/H₂ ratio of the produced gas from CO₂/H₂O gasification of German lignite at 850 °C at different pressure

5.3.2 Effect of Steam Concentration and Pressure on the C Conversion

The C conversion is an important parameter for the gasification process. It illustrates the efficiency of the utilisation of the solid fuel as it influences the energy output per unit size, which in turn affects the capital and operating costs. The C conversion of CO₂/H₂O gasification at different pressures is shown in Figure 5.6. This shows that the C conversion increased when the steam input was increased from 0 to 40%. At atmospheric pressure, the C conversion increased from 83 to 96%. At elevated pressure, (5 and 10 bar_a), the C conversion went up from around 55 to about 65%. The increase of the C conversion is mainly because the steam is more reactive than CO₂ and the reaction rate of the steam-char reaction is faster than that of the Boudouard reaction. Although using steam requires additional energy to produce

steam from water by comparison with using CO_2 , it is still desirable to replace some of CO_2 with steam in the gasification agents to achieve higher C conversion in some case. The drop of the C conversion from atmospheric to high pressure was mainly due to the deactivation of char. The detailed discussion of this can be found in Chapter 4.

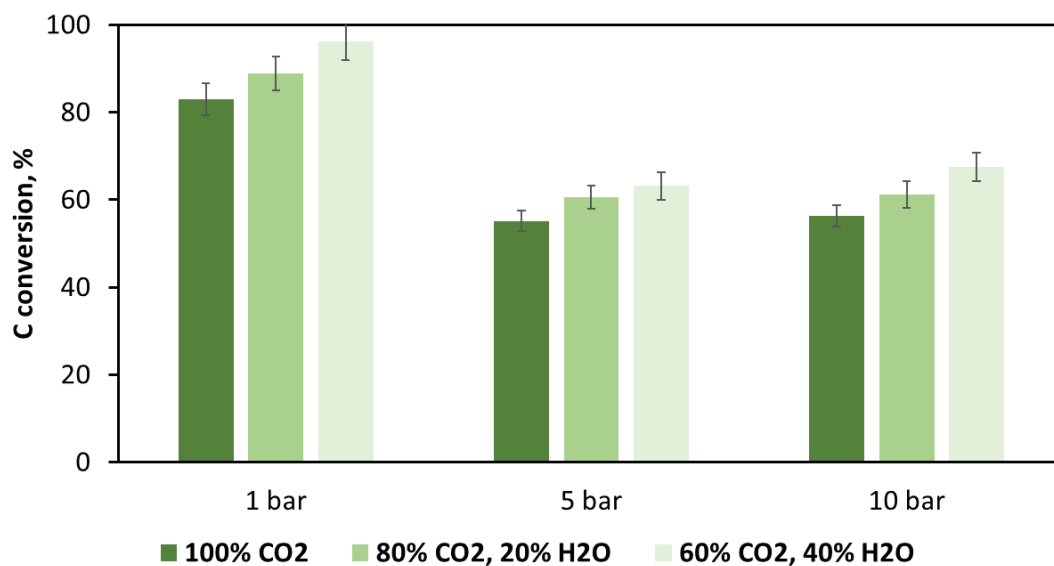


Figure 5.6 C conversion of $\text{CO}_2/\text{H}_2\text{O}$ gasification of German lignite at 850 °C at different pressure

5.3.3 Effect of Steam Concentration and Pressure on Tar

The influence of the inlet steam concentration on the tar formation is discussed in this section. The tar yield and molecular size distribution of the tar are shown in Figure 5.7 and Figure 5.8 respectively.

5.3.3.1 The yield of tar

The tar production during CO₂/H₂O gasification with different steam concentrations under different system pressures are shown in Figure 5.7 and Figure 5.8. Figure 5.7 gives the data of tar yield, and Figure 5.8 shows the tar concentration in the fuel gas if the tar was uniformly distributed over the run. It can be observed that the tar yield was below 0.6% and concentration was below 1.6 g Nm⁻³ in the fuel gas at every tested condition. The tar production in this study was small compared with 15 g Nm⁻³ that is normally used as reference value for fluidised bed gasifiers (Liu and Aravind, 2014). At each experimental pressure, there is a decreasing trend of the tar production with the increasing of steam concentration. At atmospheric pressure, the tar yield dropped from 0.25 to 0.20%, when the steam concentration increased from 0 to 40%. At 5 bar_a, the tar yield decreased from 0.30 to 0.18%. When the system pressure was 10 bar_a, the reduction of the tar yield was the largest from 0.48 to 0.09% with the increasing of steam concentration. Similar results can be found in some studies (Wu et al., 2011, Meng et al., 2011). This decrease of tar yield was mainly because of the tar steam reforming reaction (shown in Equation 5.1). With the increasing of the steam concentration, the reaction rate of the tar steam reforming reaction was increased. As a result, the tar yield should be reduced. Wu et al. (2011) also suggested that more OH radicals were produced as the steam concentration increased, and this rose the oxidation rate of tars. However, when the pressure was increased, the trends of the tar yield with and without steam addition were different. When no steam was added into the system, the tar yield increased with increasing pressure from 1 to 10 bar_a, which has been discussed in Section 4.3.2. In contrast,

when steam (both 20 and 40%) was added in the inlet stream, the tar yield reduced with the system pressure increase. As the release of the volatiles might be retarded by the pressure, the residence time of the volatiles from the pore to the char surface was increased and the extent of the thermal cracking of the volatiles was enhanced. These different trends suggest that the presence of steam can affect the routes for tar formation and destruction in the gasifier.



where C_mH_n represents the tar, which can be a mixture of different types of high molecular weight compounds.

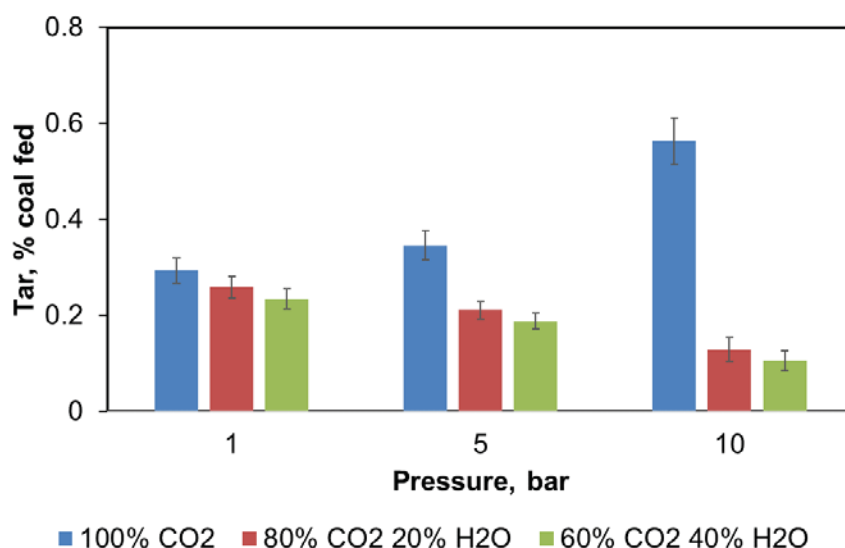


Figure 5.7 Tar released as percent of coal (dry-ash free basis) fed during CO₂/H₂O gasification at different pressure

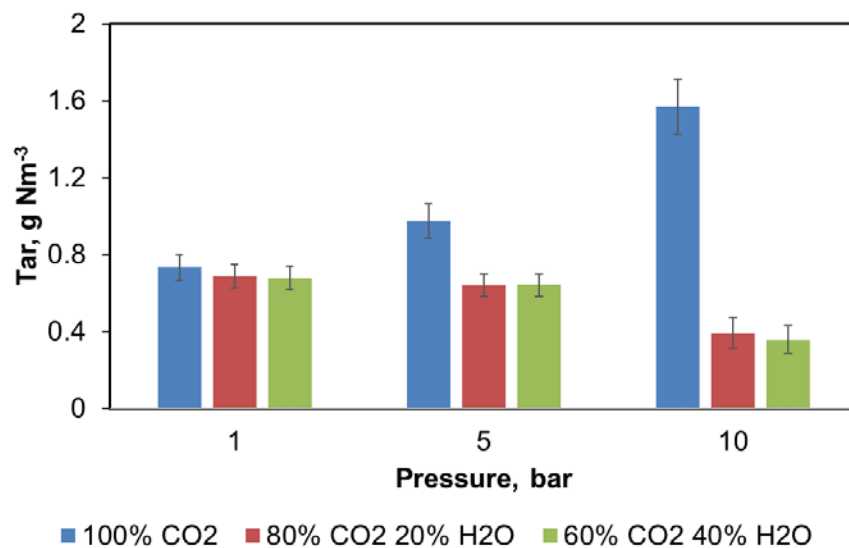


Figure 5.8 Amount of tar released in the fuel gas during CO₂/H₂O gasification at different pressure

5.3.3.2 SEC analysis of tar

The SEC analysis results of tars from different ratio of H₂O/CO₂ gasification at different process pressure is shown in Figure 5.9.

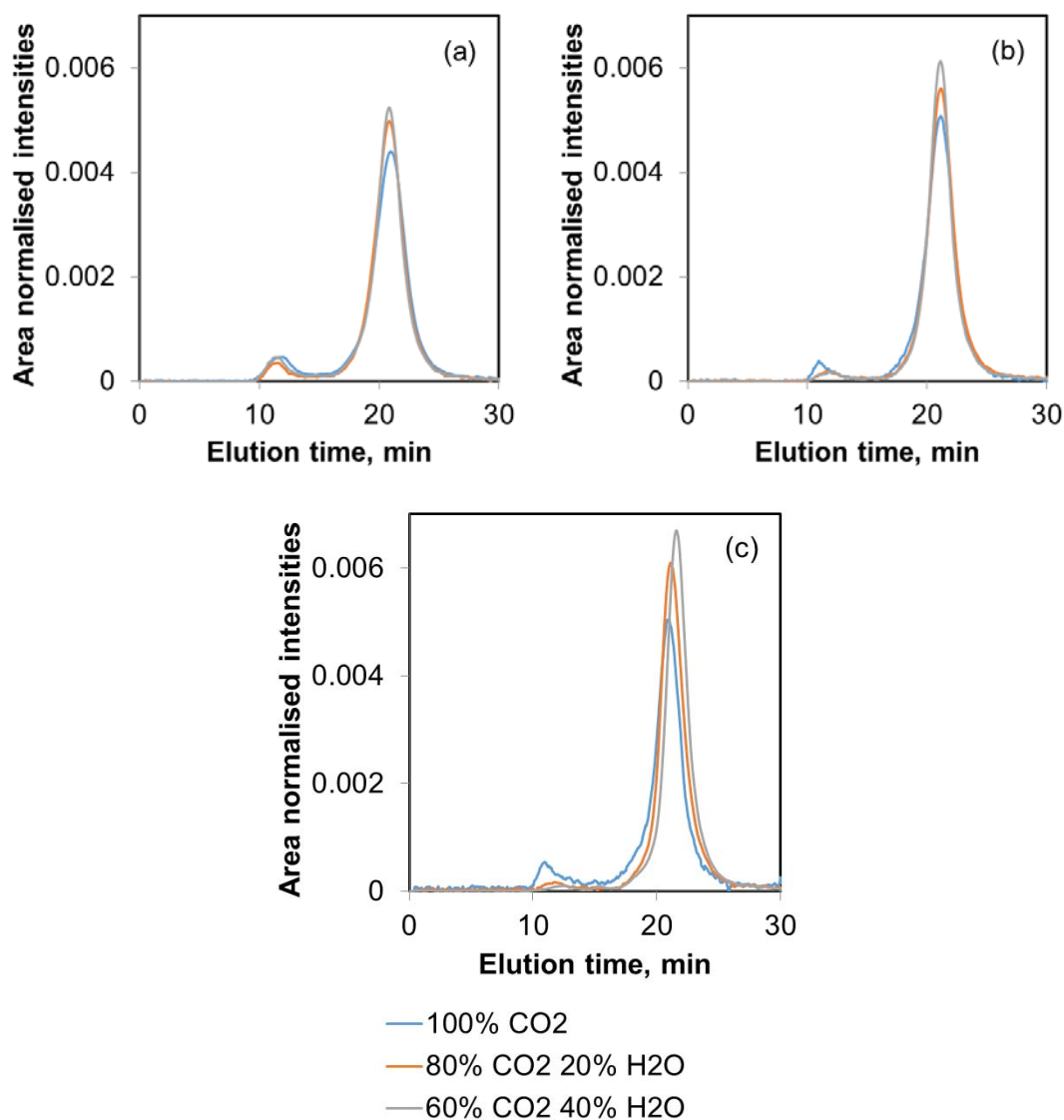


Figure 5.9 Area normalised SEC chromatogram of tar produced with different steam concentrations during $\text{CO}_2/\text{H}_2\text{O}$ gasification at different pressures ((a): 1 bar_a, (b): 5 bar_a, (c): 10 bar_a)

At each tested pressure (1, 5, 10 bar_a), the tar collected from the experiments with a higher steam concentration has a larger intensity area in the peak at longer elution times. This suggests that the tar produced from the gasification environment with a higher steam concentration has a higher concentration of smaller molecules. This

may be because steam reacted with the large primary tar molecules to form smaller molecular size tars and this effect increased with the inlet steam concentration.

5.4 Effect of the Moisture

The effect of steam produced from the moisture in the solid fuel itself on the gasification process and a comparison of the effect of this source of steam with that added separately are discussed in this section. It was observed that the moisture effect was not constant at different U/U_{mf} ratios. Therefore, the impact of the U/U_{mf} are also discussed here.

5.4.1 Effect of Moisture on Gas Composition, Yield and Heating value

Figure 5.10 shows the yields of the produced gas ((a): H_2 , (b): CH_4 , (c): CO_2 , (d): CO) from the CO_2 gasification with dried coal, dried coal with steam (equivalent amount as moisture) and the original coal (contains 12%wt. moisture at ambient temperature and pressure) as a function of U/U_{mf} .

Figure 5.10 (a) shows that, with U/U_{mf} of 3.0, the H_2 yield from the original coal (i.e. containing moisture) was higher than that from the dried coal and the dried coal with steam addition. The difference between these results suggests that the steam from the moisture in the coal can react more effectively with the char. This can be explained that due to the high heating rate ($1000\text{ }^{\circ}\text{C s}^{-1}$), the moisture and coal particle were heated up to the temperature for steam-char reaction before this

steam escaping from the pore of the particles. The reaction between the additional steam and the coal is affected by the mass transfer of the steam from the bubble phase to the emulsion phase. This will limit the reaction of the additional steam. For the gasification with the dried coal, there was no steam input, thus the H_2 was mainly produced from pyrolysis of the volatiles in the fresh fuel. With the increase of the U/U_{mf} ratio, the residence time of the gases in the fluidised bed decreased and therefore, there was less time for reaction. This reduced the H_2 concentration, together with a dilution effect by the extra fluidising gas. The overall effect of these changes was to cause a progressive reduction in the H_2 concentration and the disappearance of any effect of the moisture in the fuel.

Figure 5.10 (b) shows the change of CH_4 production. The CH_4 yield was higher from the gasification of the coal with moisture than that from the dried coal and the dried coal with steam. CH_4 was mainly produced by the methanation reaction and by pyrolysis. The CH_4 yield from the test with coal containing moisture was higher than that with the dried coal and with added steam. This can be observed for the tests with different U/U_{mf} ratios, although the effect does decrease at the higher values. When the moisture in the fuel evaporates instantly in the reactor, the coal particle may break into small particles. The CH_4 production from the pyrolysis can be improved by reducing the particle size (Septien et al., 2012). With the ratio of U/U_{mf} increasing, the CH_4 yield from the dried coal and the dried coal with steam kept relatively stable. This is owing to the constant production of CH_4 from pyrolysis at different U/U_{mf} ratio.

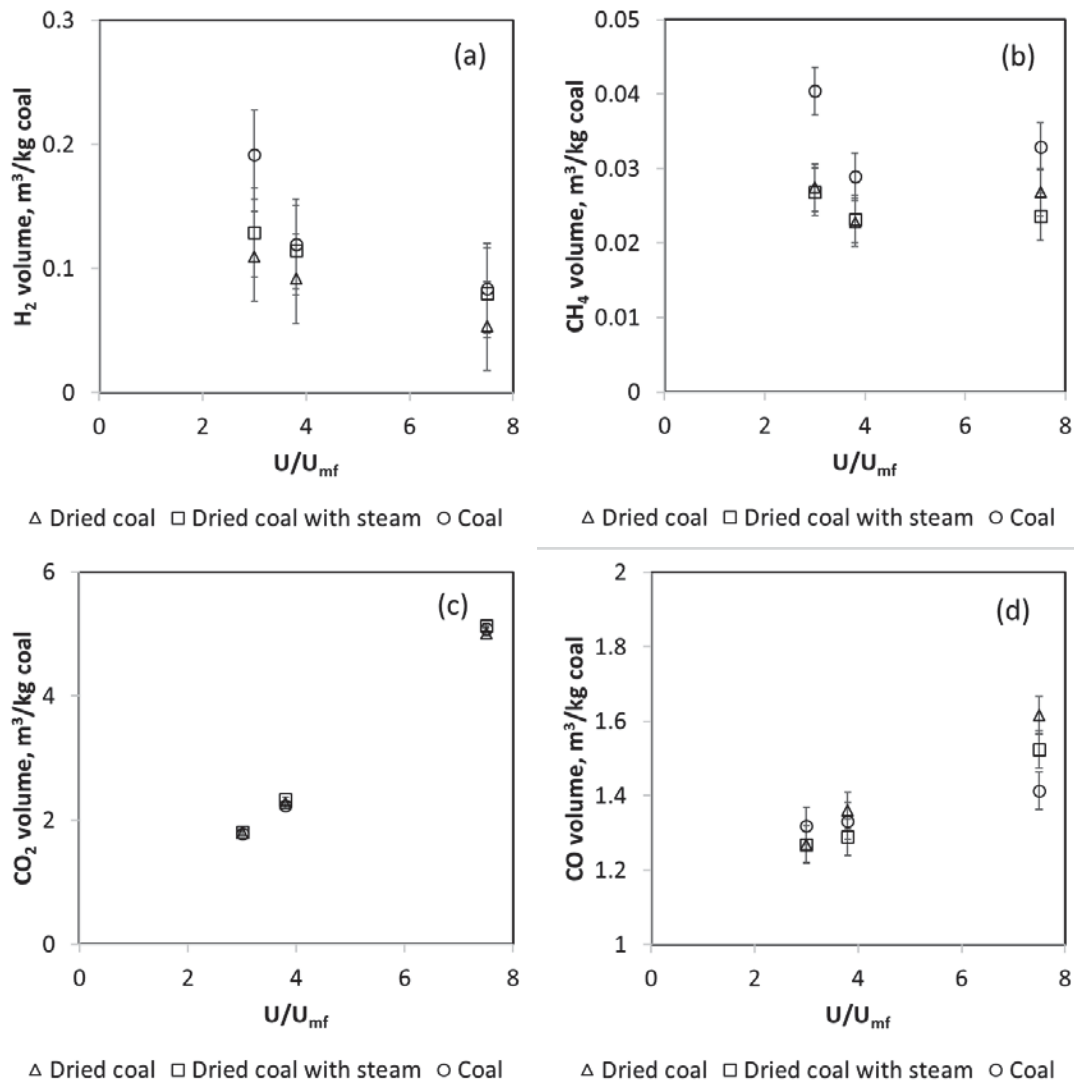


Figure 5.10 Fuel gas volume of CO_2 gasification at $850\text{ }^\circ\text{C}$ at 5 bar_a of German lignite in different conditions at different U/U_{mf} (a): H_2 , (b): CH_4 , (c): CO_2 , (d): CO (the outlet gas volume of CO_2 includes CO_2 fed)

Figure 5.10 (c) shows the data of the CO_2 volume in the outlet gas stream. There was no change of the CO_2 volume in the outlet gas stream among the different coal conditions. The CO_2 volume was increased with the increase of the U/U_{mf} ratio, because the CO_2 amount was expressed as the release volume per coal weight, and the input CO_2 was increased while the coal feeding rate was constant.

Figure 5.10 (d) shows the production of CO. At U/U_{mf} ratio at 3 and 3.8, the CO yields from different coal conditions were similar. While at the higher ratio of U/U_{mf} (7.5), the CO yield from the coal with moisture was the lowest. When the U/U_{mf} ratio increased, the CO yield was increased. As the input CO_2 was increased, the equilibrium of the Boudouard reaction was shifted to the products side to produce more CO. However, the gas residence time was reduced with the increase of U/U_{mf} ratio, thus both the Boudouard and steam-char reactions could be affected to form less CO. In addition, the amount of CO produced from pyrolysis should be constant due to the same coal flow rate.

The fuel gas composition from the tests with the different forms of steam input are shown in Figure 5.11. It is clear that there was no significant change of the fuel gas concentration from different coal conditions at each tested U/U_{mf} ratio, although there were some changes in the fuel gas yield (discussed above). This was mainly due to the dilution caused by the large amount of excess CO_2 . When compare the results at different fluidisation condition, the CO_2 concentration show the increasing trends with the increase of the U/U_{mf} ratio. This is due to the fact that CO_2 was the fluidisation and gasification medium, and the increasing amount of CO_2 was injected into the system to change the fluidisation condition.

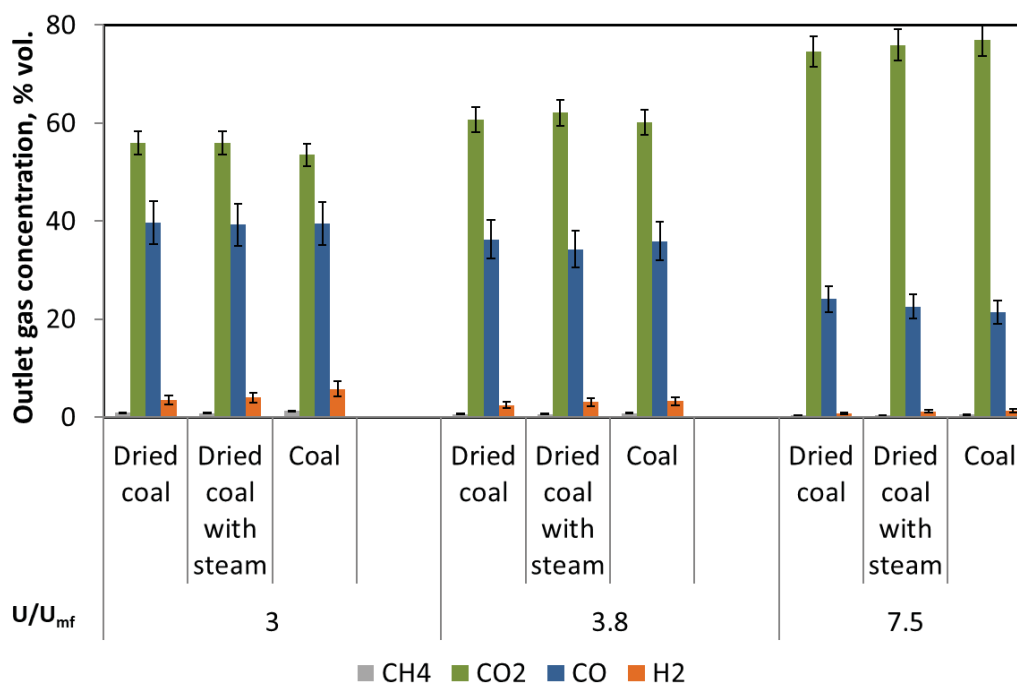


Figure 5.11 Fuel gas concentration (dry basis) of CO₂ gasification at 850 °C at 5 bar_a of German lignite in different basis at different U/U_{mf} (the outlet gas concentration of CO₂ includes CO₂ fed)

5.4.2 Effect of Moisture on C Conversion

The data of the influence of the moisture from the coal on the C conversion at different fluidisation conditions is shown in Figure 5.12.

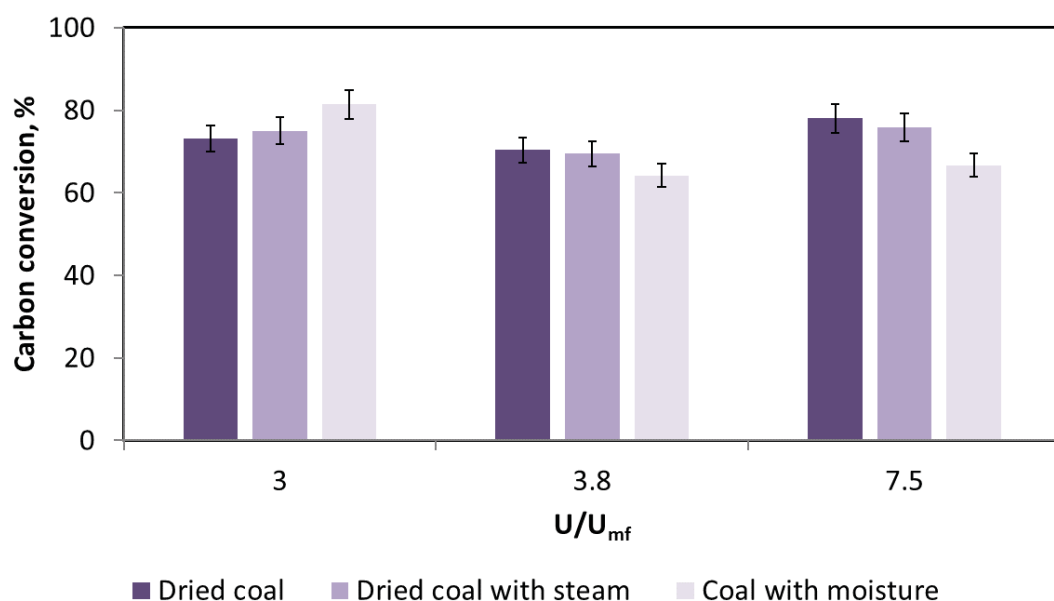


Figure 5.12 C conversion of the CO₂ gasification at 850 °C at 5 bar_a of German lignite in different basis at different U/U_{mf}

At all the three tested fluidisation conditions, when injecting a very small amount of steam (same as the moisture content) into the gasification system, the C conversion of the dried coal was not improved, and there was almost no difference between the C conversion of the dried coal and that of the dried coal with steam. When comparing the C conversion of the dried coal with steam to that of the coal with moisture, an influence of the moisture in the coal is apparent. With a U/U_{mf} of 3, the moisture from the coal shows a positive effect. The C conversion of the coal with moisture is 6% higher than that of the dried coal with steam. In contrast, at the higher ratios of U/U_{mf} ($U/U_{mf} = 3.8, 7.5$), the moisture from the coal shows a negative effect. There was an approximate 5 to 9% drop of C conversion when comparing the coal with moisture to the dried coal with steam at U/U_{mf} ratio at 3.8 and 7.5 respectively. This change in the C conversion might be due to the fragmentation of the coal particles caused by the moisture. When the air-dried coal

was injected into the fluidised bed reactor, the moisture in the coal particles heats up and expands instantly, breaking the coal particles into fragments. At a low U/U_{mf} ratio, these fragments stayed into the fluidised bed reactor and the C conversion increased due to their smaller particle size. However, at a high U/U_{mf} , these fragments might be entrained out of the reactor with the gas by the high superficial velocity. Due to the low residence time, these fragments had not been fully reacted. Therefore, the C conversion decreased in this situation. In this set of experiments, the results of the ratio of U/U_{mf} at 3 and 3.8 are quite different. Although there is only 0.8 difference between the U/U_{mf} ratios, the influence of the moisture of the coal on the C conversion shows an opposite effect. This was because the terminal velocity of the fragments might be between these two superficial velocities. For the fragments, the terminal velocity is much lower than the original coal particle as the decrease of the particle size. Thus, from the original U/U_{mf} ratio at 3 to 3.8, the fragments may transfer from a fluidisation condition to a terminal velocity condition. The terminal velocities at different particle size were calculated (method is shown in Chapter 3) and shown in Table 5.2. The ratio of u_t/U_{mf} was calculated to compared with U/U_{mf} ratio. U_{mf} was calculated for sand which was the majority of the bed, and it was not changed during the gasification. It can be observed that the terminal velocity decreased proportionally with the decrease of particle size. From the calculation, when U/U_{mf} ratio was at 3.8, the particles whose size below 58 μm were easily entrained by the gas.

Table 5.2 Calculated terminal velocity of char at 5 bar_a 850 °C with different particle size ($U_{mf} = 0.025 \text{ m s}^{-1}$, original coal particle size was 200 to 300 μm)

Particle size, μm	Terminal velocity u_t , ms^{-1}	u_t/U_{mf}
200	0.38	14.9
160	0.30	12.0
120	0.23	8.9
80	0.14	5.5
58	0.10	3.8
40	0.06	2.2

5.5 Conclusions

The conclusions of this chapter are divided into two parts based on the steam addition routes. Steam was added into the gasification system through steam injection into the fluidisation gas and evaporation of the moisture from the feedstock.

- (1) When steam concentration in the inlet gas stream increased, the production of H_2 and CH_4 increased, while the production of CO decreased and the CO_2 conversion decreased, as expected. The potential benefits of increasing steam concentration include: the H_2/CO ratio in the products can be adjusted in order to satisfy different synthesis routes, the heating value and the C conversion are increased, and the yield of the produced tar is reduced.
- (2) The influence of the moisture on the gasification performance was related to the ratio of U/U_{mf} in the fluidised bed reactor. At a low U/U_{mf} ratio (3.0), the H_2 production was improved and the C conversion was enhanced by the moisture

from the coal compared to steam addition with the amount to replace moisture. At high U/U_{mf} ratios (3.8 and 7.5), there was no difference in the H_2 production from the coal with and without moisture presence, and the C conversion was decreased by the moisture from the coal. The difference between the results of H_2 yield at low U/U_{mf} ratio suggests that the steam from the moisture in the coal can react more effectively with the char. This can be explained by due to the high heating rate ($1000\text{ }^{\circ}\text{C s}^{-1}$), the moisture and coal particle were heated up to the temperature for steam-char reaction before this steam escaping from the pore of the particles. The reaction between the additional steam and the coal is affected by the mass transfer of the steam from the bubble phase to the emulsion phase. This limits the reaction of the additional steam. The changes in the C conversion might be due to the fragmentation of the coal particles caused by the moisture. After the injection of air-dried coal into the fluidised bed reactor, the moisture in the coal particles heats up and expands instantly that breaking the coal particles into fragments. These fragments stayed into the fluidised bed reactor at low U/U_{mf} ratio, so the C conversion increased as smaller particle size. However, these fragments could be entrained out of the reactor with the gas by the high superficial velocity at high U/U_{mf} ratio. Therefore, the C conversion decreased. Due to the low residence time, these fragments had not been fully reacted.

Chapter 6 Effect of Gasification Products on Degradation of Anode Materials used in SOFC

6.1 Introduction

One of the potential uses for fuel gas is generating power in solid oxide fuel cells (SOFC). A combined gasification and SOFC process has the potential for a higher efficiency than can be achieved in a conventional power station (Zhang et al., 2010b). However, one of the main issues of concern with the combined process is the degradation of the SOFC anode materials, caused by carbon and sulphur (Offer et al., 2009) released from the fuel into the fuel gas. Carbon can be formed from different gasification products, such as CO, CH₄ and tar. Ni is used as the electro-catalyst for most anodes in SOFC, and it is very active for carbon deposition and this reduces the number of catalytic active sites and damages the anode structural integrity (Alzate-Restrepo and Hill, 2010, Offer et al., 2009, Mermelstein et al., 2011). In addition, the catalytic activity can be reduced by the sulphur-containing compounds in the fuel gas, which poison the active sites (Kavurucu Schubert et al., 2012, Laycock et al., 2011, Boldrin et al., 2014). Therefore, it is important to understand the factors affecting the degradation caused by carbon and sulphur.

Most of the literature references describe studies to investigate these effects using simulated gas (Lorente et al., 2012) and model tar compounds (Mermelstein et al., 2009b). In this work, the influence of real gasification products, including fuel gas and tar, on the degradation of anode materials has been studied. It has focused on

the change of degradation with different gasification media, and compares the performance of two types of anode materials (Ni/YSZ and Ni/CGO).

6.2 Experimental Conditions

The tests were conducted in a two-stage reactor. The first stage was the continuous fluidised bed gasifier described in previous sections and the second stage was a fixed bed reactor, designed and built as part of this work, which held the test anode materials. The gasification was performed at 850 °C using CO₂ and CO₂/H₂O as the gasification media and German lignite (1.04 g min⁻¹) as the solid fuel. The fixed bed was heated at 765 °C for blank, Ni/YSZ and Ni/CGO tests, and exposed to the gasification products directly from the gasifier. All the experiments were carried out at atmospheric pressure for 58 min. The experimental conditions for the anode material tests are shown in Table 6.1. It has to be noted that experimental Run 1 and 2 were carried out without the fixed bed reactor, and the gasifier was directly connected to the tar trap. The products from the gasifier before entering the fixed bed can be measured from these two experiments.

Table 6.1 Experimental conditions for anode material tests at 765 °C for 58 min among the products of gasification of German lignite (1.04 g min⁻¹) at 850 °C, at atmospheric pressure

Run	Second stage condition	Gasification media		
		CO ₂ , NL min ⁻¹	H ₂ O, mL min ⁻¹	H ₂ O, %
1	No fixed bed	2.39	0.00	0
2	No fixed bed	1.43	0.72	40
3	Blank	2.39	0.00	0
4	Blank	1.43	0.72	40
5	Ni/YSZ	2.39	0.00	0
6	Ni/YSZ	1.43	0.72	40
7	Ni/CGO	2.39	0.00	0
8	Ni/CGO	1.43	0.72	40

6.3 XRD Analysis of Anode Materials

The XRD patterns of NiO/YSZ and NiO/CGO samples are shown in Figure 6.1 and Figure 6.2 respectively. It can be observed that there was no carbon presence in the fresh anode materials.

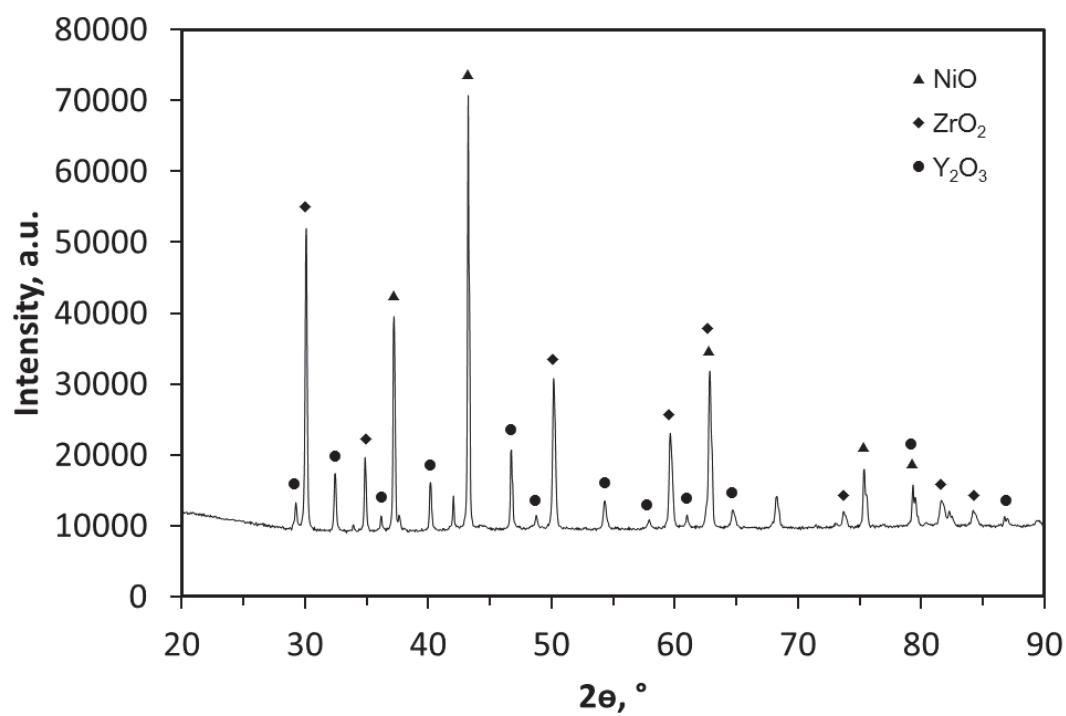


Figure 6.1 XRD pattern of NiO/YSZ

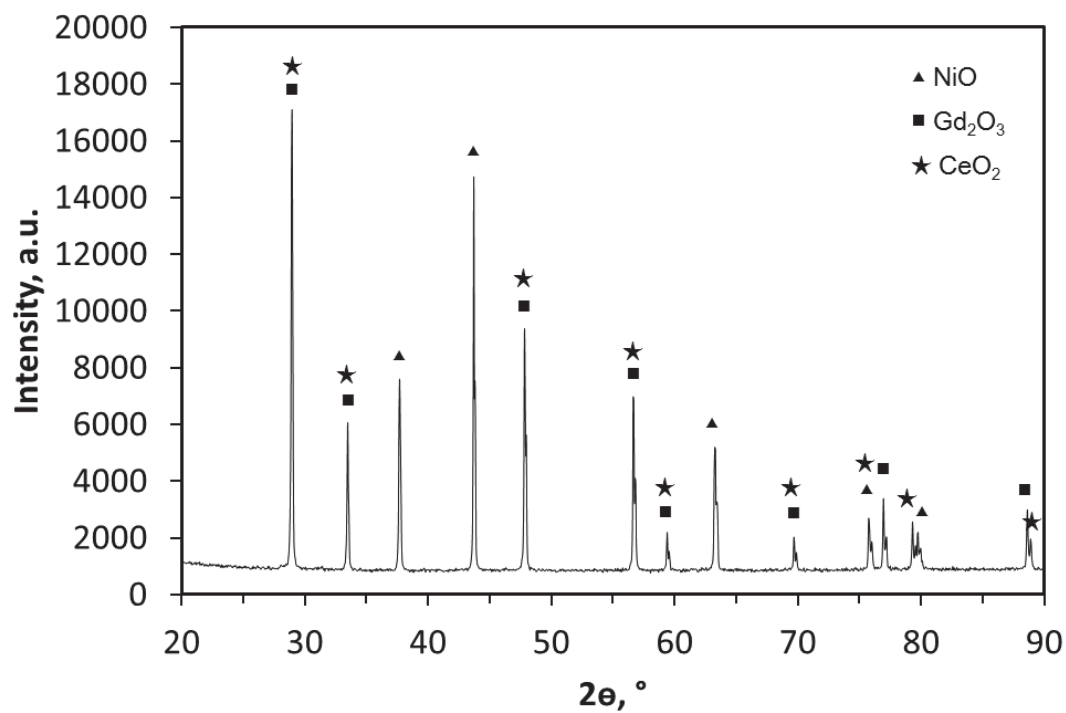


Figure 6.2 XRD pattern of NiO/CGO

6.4 Fuel Gas Composition for the Anode Tests

The tests (shown as Run 1 to 2 in Table 6.1) without the fixed bed reactor enabled the determination of the inlet fuel gas composition to the second stage for testing the anode materials. Table 6.2 shows the dry gas concentrations and flow rate from the gasifier. As the steam concentrations were not measured in the gasification products, the amount of steam in the fuel gas was estimated by assuming that the production of steam was negligible during gasification using 100% CO₂ and the increment of H₂ by gasification with 60%CO₂/40%H₂O originated from the input steam. The calculated concentrations of the fuel gas, including steam, are shown in Table 6.3.

Table 6.2 Composition and total flow rate of the dry gas products from coal gasification at 850 °C using different gasification media

Gasification medium	CH ₄ , %mol.	CO ₂ , %mol.	CO, %mol.	H ₂ , %mol.	Total flow rate, NL min ⁻¹
100% CO ₂	0.8	54.4	38.4	6.4	3.51
60% CO ₂ 40% H ₂ O	1.6	48.2	32.0	18.3	3.07

Table 6.3 Calculated composition of the fuel gas, including steam, from coal gasification at 850 °C using different gasification media

Gasification medium	CH ₄ , %mol	CO ₂ , %mol	CO, %mol	H ₂ , %mol	H ₂ O, %mol
100% CO ₂	0.8	54	38	6	0
60% CO ₂ 40% H ₂ O	1.3	40	26	15	17

From Table 6.2 and Table 6.3, it can be observed that the concentrations of H₂, CH₄ and steam increased while those of CO and CO₂ decreased with the input of steam

to the gasification medium. The detailed discussion of this influence is given in section 5.3.1.

Figure 6.3 shows the concentration and the SEC chromatograms of the produced tar under different gasification conditions. The tar concentrations in Figure 6.3 (a) were calculated from the total tar collected during each test, using the assumption that the same amount of tar was released during each time increment. It can be seen that the concentration of tar was reduced and the fraction of the smaller size molecules in the tar increased, when steam was added. These changes were mainly due to the shift of equilibrium and increase of reaction rate of the steam tar reforming reaction to the products side (detailed discussion can be found in section 5.3.3).

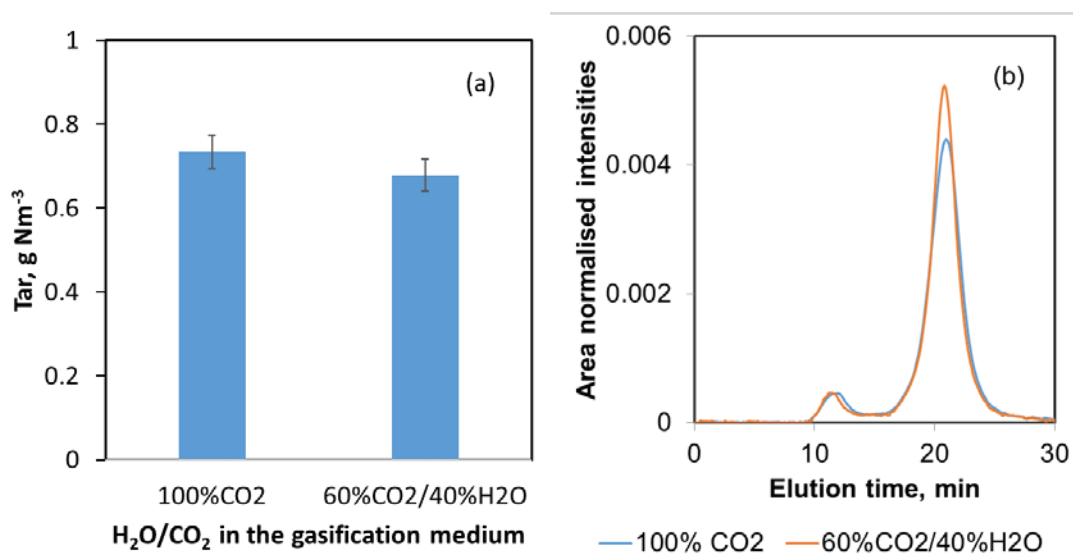


Figure 6.3 Tar produced from coal gasification at 850 °C using different gasification medium ((a): tar concentration (b): area normalised SEC chromatogram of tar.

6.4 Effect of Gasification Medium on Carbon Deposition

The amount of carbon deposited on the anode materials and nature of this carbon were analysed by TPO, and the results are shown in Figure 6.4 and Figure 6.5 respectively. It can be observed in Figure 6.4 that Ni/CGO showed a better performance than Ni/YSZ as less carbon was deposited on Ni/CGO under the experimental conditions. This is in agreement with previous work by Lorente et al. (2013) and Mermelstein et al. (2009a). It can be explained by the behaviour of ceria, which can resist carbon deposition (Zhu and Deevi, 2003). For both materials, the carbon deposition decreased when steam was added to the gasification medium. The carbon deposited on the anode materials was mainly from three sources, CO (Reaction 6.1), CH₄ (Reaction 6.2) and tar (Reaction 6.3). However, the presence of steam can reduce the carbon deposition (Finnerty et al., 1998, Lorente et al., 2012). In addition, Mermelstein et al. suggested that the carbon deposition decreased with the addition of CO₂ in the fuel gas (Mermelstein et al., 2011). With the addition of steam to the gasification medium, CO concentration decreased, steam concentration increased (shown in Table 6.3) and tar concentration decreased (Figure 6.3) in the fuel gas, which resulted in a decrease in the carbon deposition. Meanwhile, as CH₄ concentration increased and CO₂ concentration decreased, the carbon deposit can be increased (Mermelstein et al., 2011). Therefore, the amount of carbon deposited was governed by these competing effects.

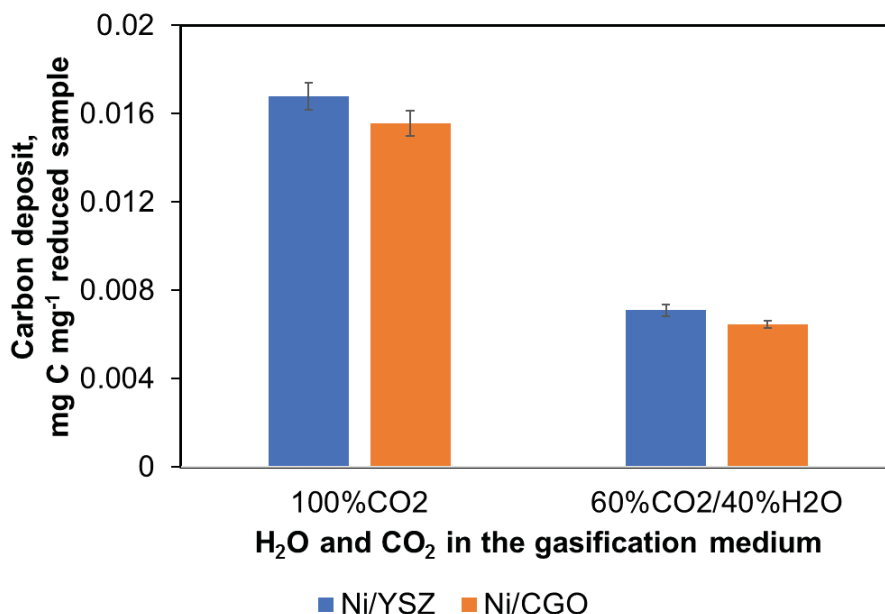


Figure 6.4 Amount of carbon deposited over Ni/YSZ and Ni/CGO exposed at 765 °C for 58 min to fuel gas from coal gasification at 850 °C using different gasification medium

Figure 6.5 shows the TPO analyses of the two anode materials exposed to the gasification products from different gasification media. The TPO profiles were different between the two anode materials. For Ni/YSZ (Figure 6.5 (a)), there are four peaks at temperatures of 230, 320, 370-410 and 570 °C. When there was no steam in the gasification medium, the peaks at 370-410 and 570 °C were mainly formed on the Ni/YSZ. When the gasification medium was CO₂/steam in the gasifier, the area of

all the peaks decreased, which represented the decrease of carbon deposition. For Ni/CGO (Figure 6.5 (b)), there were three peaks around 320, 430 and 580 °C on the TPO profile. When exposed to the fuel gases from the gasification with pure CO₂ and a mixture of CO₂/H₂O, the first peak (at 320 °C) was predominant for Ni/CGO. From the comparison of the two anode materials, the carbon removal temperature from Ni/YSZ was more dispersed (from 320 to 570 °C) and that from Ni/CGO was more concentrated around 320 °C. It indicates that carbon deposited on Ni/CGO was easier to be removed. The broad peaks in the TPO profiles may indicate a distribution of carbon types (Bartholomew, 2001).

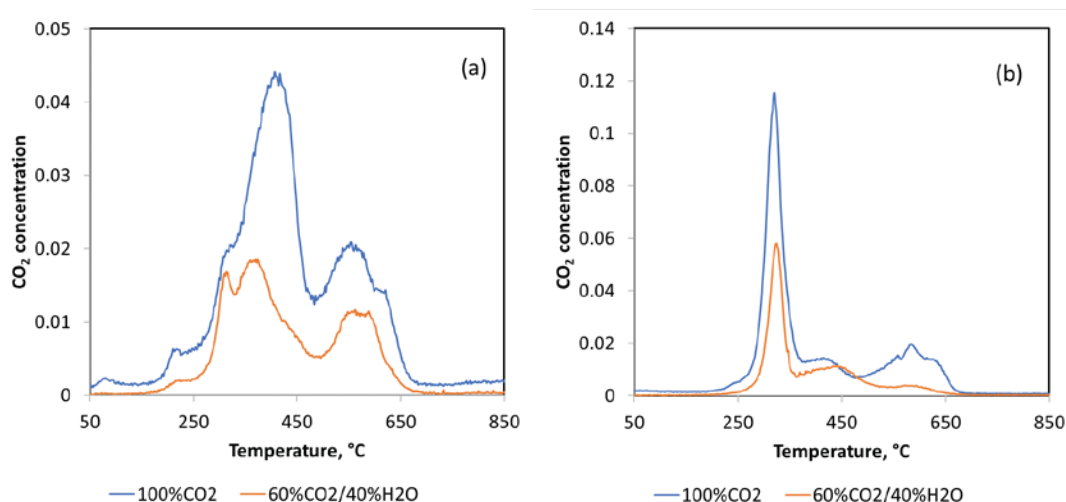


Figure 6.5 TPO of (a) Ni/YSZ and (b) Ni/CGO exposed at 765 °C for 58 min to fuel gas from coal gasification at 850 °C using different gasification medium

6.5 SEM and EDX Analysis of the Anode Materials

The influence of exposure to syngas produced at the different gasification conditions on the morphology of the anode materials was examined by SEM. Figure 6.6 and

Figure 6.7 show the SEM images of the original anode materials and the reduced anode materials after exposure to fuel gas from different gasification conditions. From Figure 6.6, it can be observed that the Ni/YSZ had a less porous structure after exposure to the gasification products than the original material. From Figure 6.7, no obvious structure change of Ni/CGO after exposure to gasification products can be seen. It suggested that Ni/CGO had a better performance in keeping its microstructure than Ni/YSZ.

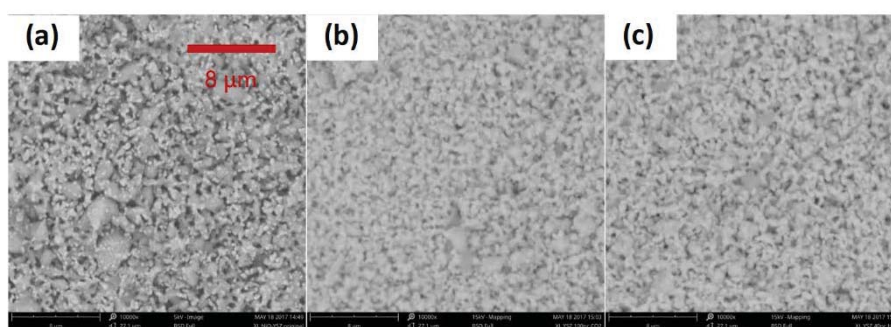


Figure 6.6 SEM images of the particle surface of (a) original NiO/YSZ and Ni/YSZ after exposing to the fuel gas from gasification with different gasification medium: (b) 100% CO₂, (c) 60%CO₂/40%H₂O

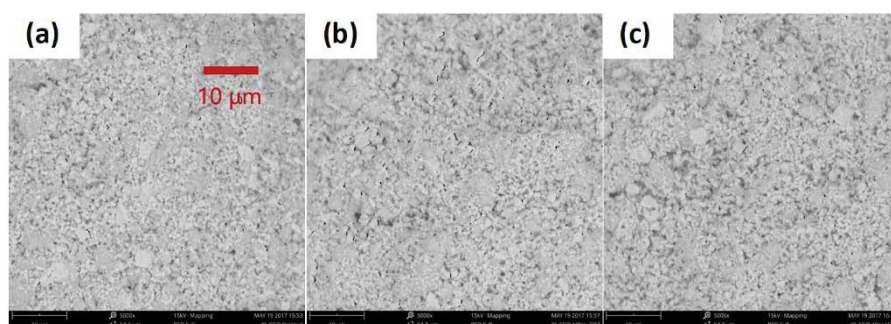


Figure 6.7 SEM images of the particle surface of (a) original NiO/CGO and Ni/CGO after exposing to the fuel gas from gasification with different gasification medium: (b) 100% CO₂, (c) 60%CO₂/40%H₂O

The EDX analysis of the two anode materials under different conditions are shown in Figure 6.8 and Figure 6.9. According to Figure 6.8 (b)-(c) and Figure 6.9 (b)-(c), there were sulphur-containing compounds formed on the anode materials after exposure to the fuel gas from coal gasification, while no sulphur was found on the original NiO/YSZ and NiO/CGO. The sulphur compounds in the fuel gas were mainly H_2S and with much lower concentration of COS (Hanaoka et al., 2013). With the presence of H_2S , bulk nickel sulphide species can be formed, such as Ni_3S_2 (Offer et al., 2009). The atomic concentrations of sulphur are shown in Table 6.4. It must be noted that at least three spots were analysed for each sample, and the average values and the standard deviation are shown. It can be observed that the sulphur concentrations were significantly different depending on the exposing conditions. Both type of anode materials had much less sulphur deposits when exposed to fuel gas from gasification with CO_2 /steam than those exposed to fuel gas from CO_2 gasification. The sulphur concentrations were similar on both anode materials exposed to fuel gas from CO_2 gasification. However, sulphur concentration on Ni/CGO was lower than that of Ni/YSZ when exposed to fuel gas from $\text{H}_2\text{O}/\text{CO}_2$ gasification. In addition, some nickel sulphide particles were observed in the samples of Ni/YSZ exposed to CO_2 gasification and CO_2 and H_2O gasification, and sample of Ni/CGO exposed to CO_2 gasification, but not for sample of Ni/CGO exposed to $\text{CO}_2/\text{H}_2\text{O}$ gasification. This suggests that CGO is more resistant to sulphur than YSZ when exposed to fuel gas from $\text{CO}_2/\text{H}_2\text{O}$ gasification. An example of nickel sulphide particle is shown in Figure 6.10. The EDX analysis shows that only nickel and sulphur were present whereas no element from supports was showing.

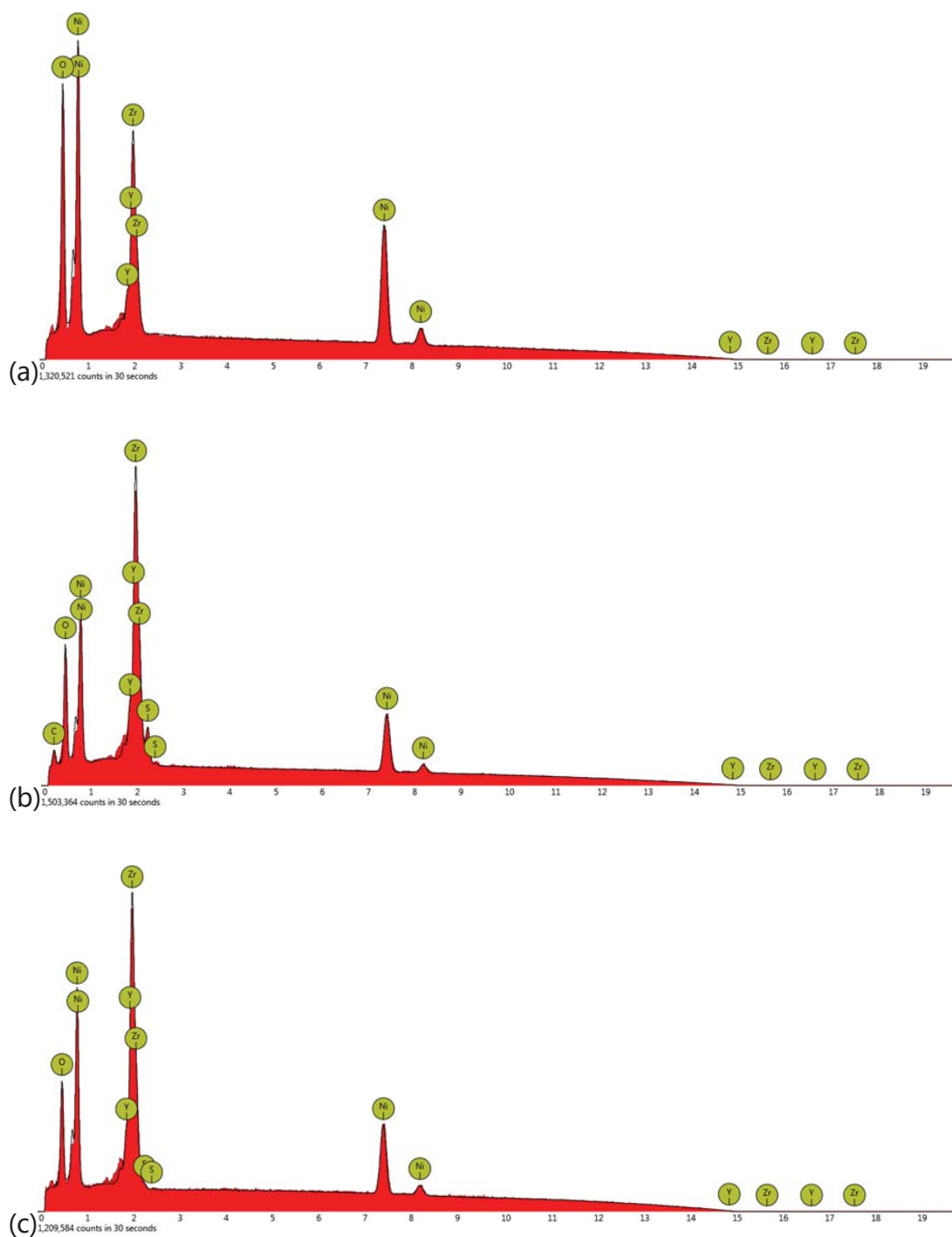


Figure 6.8 EDX analysis of (a) original NiO/YSZ and Ni/YSZ after exposing to the fuel gas from gasification with different gasification medium: (b) 100% CO₂, (c) 60%CO₂/40%H₂O

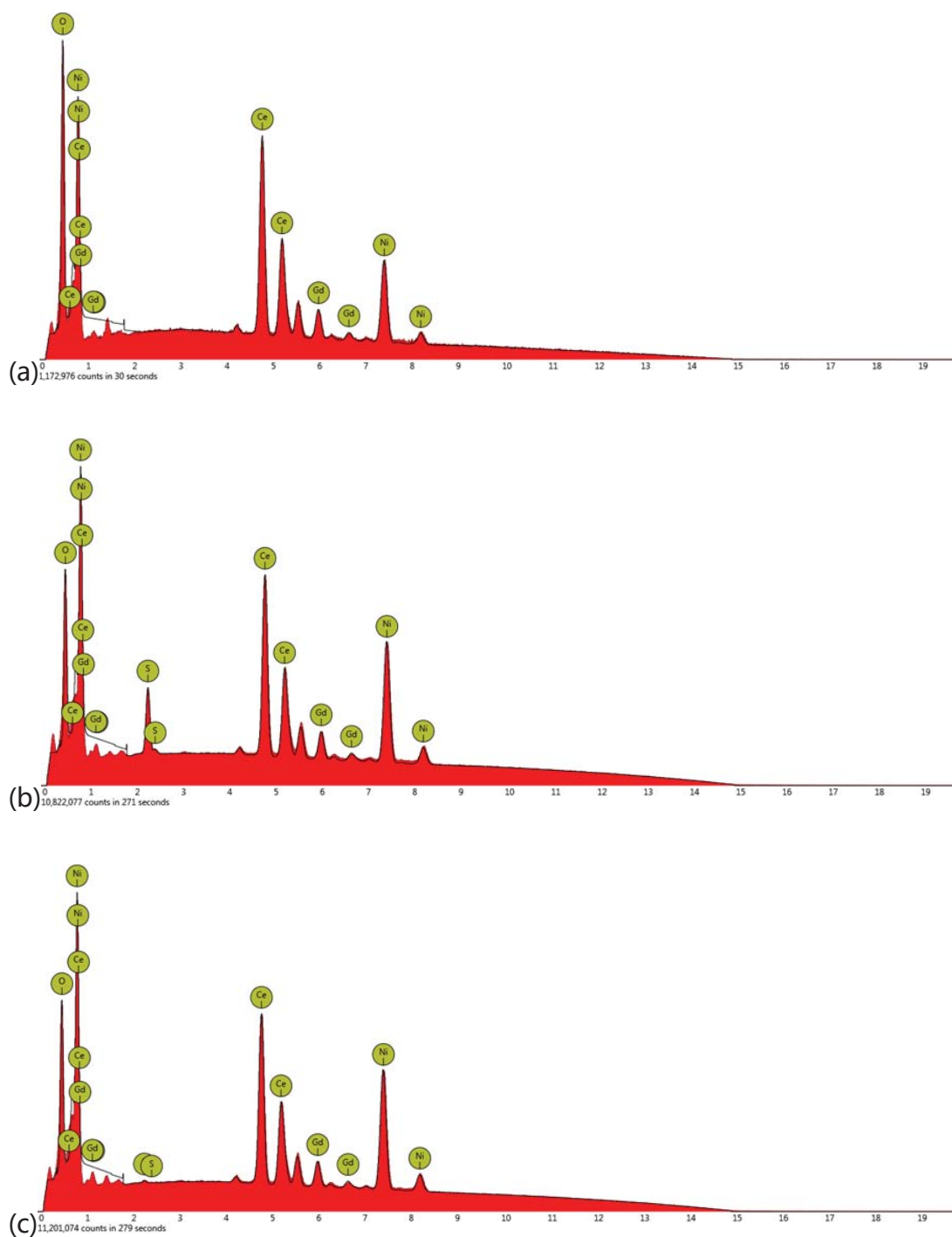


Figure 6.9 EDX analysis of (a) original NiO/CGO and Ni/CGO after exposing to the fuel gas from gasification with different gasification medium: (b) 100% CO₂, (c) 60%CO₂/40%H₂O

Table 6.4 Atomic concentration of sulphur from EDX analysis of anode materials exposed to the fuel gas from gasification with different gasification medium, pure CO₂ and a mixture of CO₂ and H₂O

	100% CO ₂ , %mol.	60%CO ₂ /40%H ₂ O, %mol.
Ni/YSZ	5±3	0.7±0.2
Ni/CGO	5±2	0.2±0.1

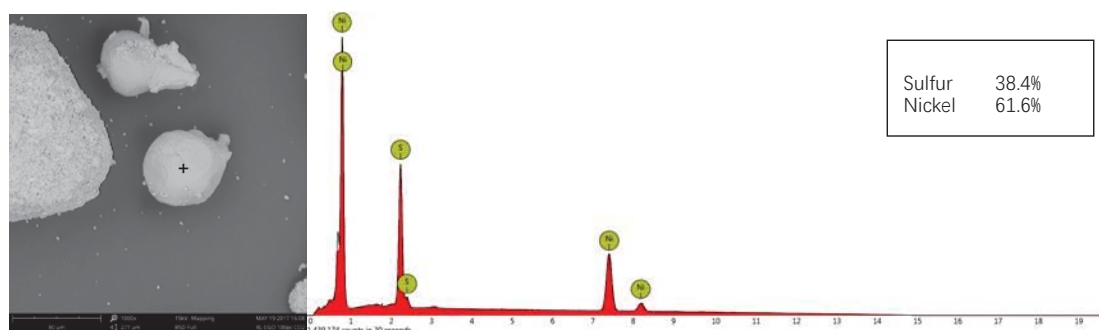


Figure 6.10 SEM image (left) and EDX analysis (right) of a nickel sulphide particle in the sample of Ni/CGO exposed to the fuel gas from CO₂ gasification

6.6 Influence on the Produced Tar

The changes in the nature of the tar after exposure to the anode materials are discussed in this section. The products from the runs without fixed bed reactor represented the initial gasification products before exposing to anode material. The blank runs were conducted for different gasification conditions with quartz wool and wire mesh as the bed in the second stage reactor, but without placing anode materials. Figure 6.11 shows the total amount of tar before and after exposing to the anode materials. It can be seen that the amount of tar reduced after passing through

the fixed bed reactor. By comparison with the blank runs, less tar collected after exposure to both anode materials for both gasification conditions. This can be explained by the tar cracking over nickel in the anode materials. Slightly less tar was collected after exposing to Ni/CGO than Ni/YSZ, which suggested that Ni/CGO had a better performance in terms of tar cracking.

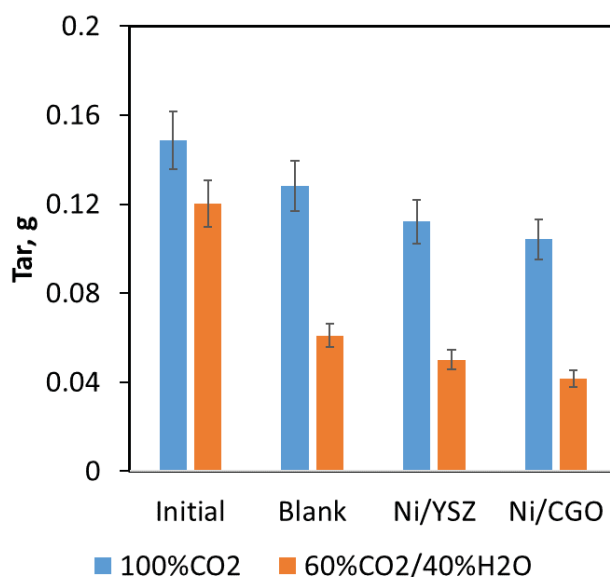


Figure 6.11 Amount of the collected tar after 58 min experiments

SEC chromatograms of tar before and after exposing to Ni/YSZ and Ni/CGO at different gasification conditions are represented in Figure 6.12. In all cases, there are two peaks in the SEC chromatograms with a small peak (around 10-15 min) and a large peak (around 15-25 min). The peak at earlier elution time represents the material with larger molecular size, while the peak at later elution time corresponds to the material with relatively smaller molecular size. As the chromatograms were area normalised, the area of the peak determines the proportion of the material of different molecular size. From Figure 6.12, the second peak of tar increased after exposing to anode materials, which means that the proportion of the smaller

molecular size compounds increased in tar. This was because the tar underwent cracking reaction over nickel to form smaller molecular weight compounds. The chromatograms are almost identical for the tar exposing to Ni/YSZ and Ni/CGO. From the comparison between Figure 6.12 (a) and (b), the tar produced from $\text{CO}_2/\text{H}_2\text{O}$ gasification had more small-size compounds and less large-size compounds than tar produced from CO_2 gasification. This can be explained by the input of steam, which promoted the steam reforming of tar to produce smaller compounds.

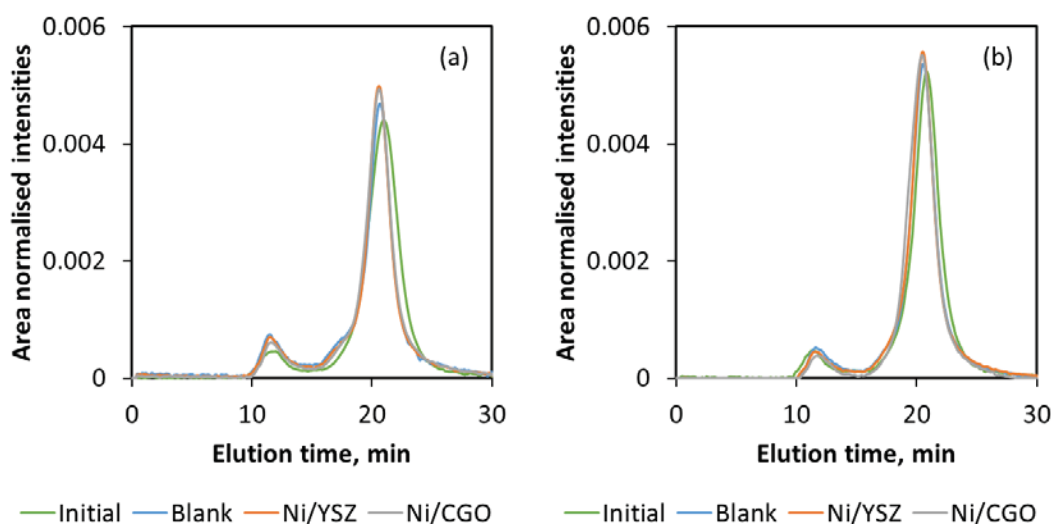


Figure 6.12 Area normalised SEC chromatograms of tar from gasification with different gasification medium ((a) 100% CO_2 and (b) 60% CO_2 /40% H_2O) before and after exposing to anode materials

6.7 Influence on the Produced Gas

The fuel gas compositions before and after exposing to anode materials are shown in Figure 6.13. The compositions of the fuel gas were different with less CO_2 and

more CO, after passing through the fixed bed reactor. As the temperature was reduced from 850 (in fluidised bed) to 765 °C (in fixed bed), the thermodynamic equilibrium constants of the gas phase reactions were changed. Meanwhile, tar was cracked in the fixed bed reactor and more gas was produced. When the fuel gas from CO₂ gasification was exposed to the anode materials, the composition did not change much compared to the blank run. This might be because the extent of the reactions on the anode material was low. The gas compositions from CO₂ and H₂O gasification were different after exposing to anode materials. Compared to the blank run, the CO₂ concentration decreased while the CO concentration increased after exposure to the anode materials. One reason for the increase in CO could be that the increase of steam improved the extent of steam tar reforming reaction over the nickel surface. In addition, CO concentration in the fuel gas was much higher after exposing to Ni/CGO than Ni/YSZ.

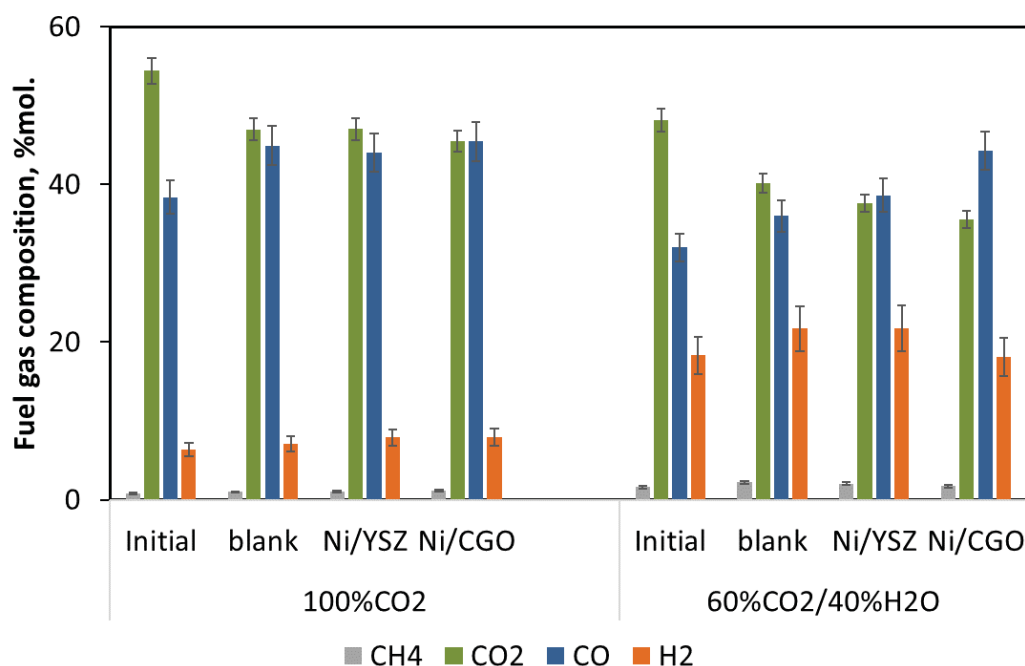


Figure 6.13 Dried fuel gas composition of gasification with different gasification medium before and after exposing to anode materials (Ni/YSZ and Ni/CGO)

6.8 Conclusions

The impacts of the real gasification products on the degradation of two types of anode materials (Ni/YSZ and Ni/CGO) used in SOFC have been compared. Ni/CGO shows a better performance in terms of carbon deposition. Compared to Ni/YSZ, less carbon tends to form on Ni/CGO, and this carbon can be removed at a lower temperature.

Sulphur components in the fuel gas does attack the anode materials, and might form nickel sulphide. The extent depends on the anode structure and the composition of the fuel gas (which is determined by the fuel and the fluidising gas

composition). Ni/CGO is more resistant to sulphur than Ni/YSZ, when steam is present in the fluidising gas.

The influence of different fuel gases (including tar and steam) from gasification with different gasification media (pure CO₂ and a mixture of 60%CO₂/40%H₂O) has been studied. The main differences in the fuel gas between these two gasification conditions are less CO and tar and more steam from the gasification with CO₂ and H₂O mixture than from the gasification with pure CO₂. The results indicate less carbon and sulphide formation when the anode material is exposed to the fuel gas from CO₂/H₂O gasification.

Chapter 7 Summary, Conclusions and Recommendations for Future Work

7.1 Summary

An existing laboratory scale continuous pressurised fluidised bed reactor has been modified to operate under pressurised oxyfuel conditions with high steam flow rate addition. The main modification has involved the use of a horizontal tube furnace for the steam generator, rather than heating tapes, to provide a larger heating capability for water evaporation to steam and enabling larger steam concentrations to be used. A second stage fixed bed reactor has been specially designed and constructed for testing SOFC anode materials exposed to real fuel gas. This fixed bed reactor has been installed directly downstream of the fluidised bed gasifier, and it uses quartz wool and wire mesh for holding the anode materials in place.

The modified continuous fluidised bed reactor has been successfully commissioned for CO₂ and steam gasification experiments of coal at 850 °C and pressures up to 10 bar_a. The two-stage system has also been commissioned at atmospheric pressure for CO₂ and steam gasification at 850 °C in the first stage reactor and with the presence of different SOFC anode materials (Ni/YSZ or Ni/CGO) at 765 °C in the second stage reactor.

The effects of pressure and steam addition on oxyfuel gasification performance have been investigated. The effect of pressure has been studied at 850 °C from 1 to 10 bar_a. Two different routes of adding steam have been studied at 850 °C, with

pressures up to 10 bar_a. These are steam injection (up to 40%mol.) in the fluidisation gas and evaporation of the moisture (about 12%wt.) from the feedstock (about 3 to 6%mol. in the fluidising gas) into the gasifier. The compositions, yields, higher heating values and CO/H₂ ratios of the fuel gases have been obtained. The amount of released tar and its SEC chromatogram have been acquired. The C conversions have been calculated, and the potential reasons for the observed C conversion drop at high pressure gasification operation have been analysed. It was observed that CO and H₂ concentrations decreased at pressurised gasification (at 5 and 10 bar_a) compared to atmospheric gasification. The C conversion decreased from 1 to 5 bar_a, and kept relative constant from 5 to 10 bar_a. With the system pressure increasing from 1 to 10 bar_a, the released tar increased from 0.25 to 0.48% of coal fed. From SEC analysis, the molecular size distribution of tars from pressurised gasification were similar. By comparison with tar from atmospheric pressure, the proportion of the smaller molecular weight tar compounds was larger and the proportion of the larger tars was smaller from tars from high pressure gasification. With increase of steam concentration in the gasification agent, the production of H₂ increased, while the production of CO decreased. In addition, the C conversion was increased, and less tar was produced. The moisture from coal reacted differently compared to the steam addition into the fluidising gas. The C conversion was improved by moisture at low ratio of U/U_{mf}, but decreased by moisture at high ratio of U/U_{mf}.

The degradation of two SOFC anode materials (Ni/YSZ and Ni/CGO) following exposure to actual fuel gas and tar has been investigated. The influence of different fuel gases (including tar and steam) from gasification with different gasification

media (pure CO₂ and a mixture of 60%CO₂/40%H₂O) has been studied. The amount of carbon formation, TPO, SEM images and EDX have been obtained and examined. It was found that the carbon deposition and amount of sulphur on anode materials were lower when exposed to fuel gas from steam/CO₂ gasification than that exposed to CO₂ gasification. In addition, less carbon and sulphur was deposited on Ni/CGO than Ni/YSZ after exposure to the fuel gas from both CO₂ and steam/CO₂ gasification. The deposited carbon on Ni/CGO can be removed at a lower temperature (around 320 °C) compared to that on Ni/YSZ.

7.2 Conclusions

The main conclusions of this project are:

- (1) **Gasification pressure:** It was observed that the C conversion decreased significantly from 83% to 56% when the pressure was raised 1 to 5 bar_a, and then remained nearly constant between 5 and 10 bar_a. The drop in C conversion at elevated pressure might in principle have been caused by several factors, including suppression of volatile release from the coal particles, char deactivation, changes in the fluidisation characteristics in the bed, thermodynamic equilibrium, and H₂ and CO inhibition. As the partial pressure of CO at 5 bar_a was half of that at 10 bar_a, the C conversion at 10 bar_a should be lower than that at 5 bar_a if the CO inhibition had a large impact. However, the results show C conversion at 5 and 10 bar_a were similar. Therefore, the CO inhibition cannot be the main reason for C conversion decrease. The same reason also applies to H₂. Thus, the H₂ and CO inhibition should not be the main reason in this case. All other potential

reasons have been experimentally studied. (I) The results from the wire mesh reactor show only 2% drop in the total volatiles released by pyrolysis between 1 and 10 bar_a, indicating that the drop is not a reflect of intrinsic particle behaviour. Thus, the suppression of volatile release under high pressure cannot be the explanation for the decrease of C conversion at elevated pressure in the fluidised bed reactor. (II) The influence of the changes in the fluidisation characteristics in the bed cannot be the main reason for the decrease of C conversion at pressurised conditions. Due to the fact that C conversion remained relatively constant in the experimental range, with the change of U/U_{mf} ratio from 3 to 7.5. Although the concentration of the gasification gas in the bubble phase of the fluidised bed was increased by input CO₂ flow rate increasing (caused by increase of U/U_{mf} ratio), the concentration of the gasification gas in the emulsion phase was slightly increased. This was proved by the small increase of the CO yield in the fuel gas. This small increase of CO₂ in the emulsion phase had negligible impact on the C conversion. (III) The change of thermodynamic equilibrium was not the main reason for the drop of C conversion at high pressure, by comparing the experimental results with the data calculated at thermodynamic equilibrium. The trend of each gas component from experimental results are the same as the calculated ones, while the experimental results are far from thermodynamic equilibrium. This is due to the short residence time of gas and deactivation of char in the bed. (IV) The drop of the C conversion was mainly caused by the char deactivation caused by the repolymerising reaction of the volatiles in the pores of the char particles, which led to the deposition of secondary char and structure change of the char. This effect was enhanced by the volatile concentration, which

was correlated to the solid fuel feeding rate and the reactor size. Therefore, it is important to consider the solid feeding rate corresponding to the reactor size when design large scale plants using similar type of gasifier, as C conversion would need to be maximised to reduce C losses.

- (2) **Steam addition in the gasification:** Steam was added by steam injection into the fluidisation gas and by evaporation of the moisture from the feedstock. With increase of the steam concentration in the gasification inlet, the production of H_2 and CH_4 increased, while the production of CO decreased and the CO_2 conversion decreased, as expected. The potential benefits of increasing steam concentration include: the H_2/CO ratio in the products is raised, the heating value and the C conversion are increased, and the yield of the produced tar is reduced. The influence of the moisture on the gasification performance was related to the ratio of U/U_{mf} in the fluidised bed reactor. At a low U/U_{mf} ratio, the H_2 production was improved and the C conversion was enhanced by the moisture from the coal compared to steam addition with the amount to replace moisture. At a high U/U_{mf} ratio, there was no difference in the H_2 production from the coal with and without moisture presence, and the C conversion was decreased by the moisture from the coal. This is because the moisture from the feedstock behaved differently compared to the steam injection. The increase of H_2 yield at low U/U_{mf} ratio might be because the steam from the moisture in the coal can react more effectively with the char. With the high heating rate ($1000\text{ }^{\circ}\text{C s}^{-1}$) for the coal, the moisture and coal particle were heated up to the temperature for steam-char reaction before this steam escaping from the pore of the particles. However, the reaction between the additional steam and the coal is affected by the mass

transfer of the steam from the bubble phase to the emulsion phase. This limits the reaction of the additional steam. The change in the C conversion might be due to the fragmentation of the coal particles caused by the moisture. The moisture in the coal particles heated up and expanded instantly after injection into the reactor, and the coal particles broke into fragments. These fragments stayed into the fluidised bed reactor at low U/U_{mf} ratio, and C conversion increased due to their smaller particle size. However, these fragments might be entrained out of the reactor with the gas by the high superficial velocity at high U/U_{mf} ratio. The C conversion decreased in this situation, as these fragments had not been fully reacted due to the low residence time.

- (3) **SOFC anode material degradation:** The impacts of the real gasification products (from CO_2 and 60% CO_2 /40% H_2O gasification) on the degradation of two types of anode materials (Ni/YSZ and Ni/CGO) used in SOFC have been compared. With 58 min exposure time, both carbon and sulphur in the fuel gas attacked both anode materials. Ni/CGO shows a better performance than Ni/YSZ in terms of carbon and sulphur deposition. Less carbon tended to form on Ni/CGO, and this can be explained by the behaviour of ceria which can resist carbon deposition. In addition, the formed carbon on Ni/CGO was easier to be removed than Ni/YSZ. The removal temperature of carbon on Ni/CGO was more concentrated around 320 °C, while that of carbon on Ni/YSZ was more dispersed from 320 to 570 °C. The main differences in the fuel gas between these two gasification conditions are less CO and tar and more steam from the gasification with CO_2 /steam mixture than from the gasification with pure CO_2 . The results indicate less carbon

deposition and sulphide formation occurred when the anode material exposed to the fuel gas from gasification with $\text{CO}_2/\text{H}_2\text{O}$ than with pure CO_2 .

The data obtained from this work indicate that good gasification performance can be achieved from oxyfuel gasification (with high CO_2 concentration in gasification medium) in a fluidised bed reactor at both atmospheric and pressurised conditions. In order to achieve a high C conversion for the economic benefit at pressurised conditions, the solid feeding rate corresponding to the reactor size needs to be considered to reduce/avoid char deactivation. Adding steam can also be used to improve C conversion, while it needs to consider the energy required to produce steam from water. The results from anode material tests show that there were C and S deposition on anode materials after exposure to fuel gas from gasification. However, the deposition can be reduced when there is current passing through. Therefore, it is difficult to deduce if the amount of C and S deposit by fuel gas from gasification can actually affect the SOFC performance, and if the fuel gas requires to be cleaned before entering the fuel cell.

7.3 Recommendations for Future Work

Based on the study completed for this project, the following areas are suggested for future investigation.

- (1) Char characterisation could be carried out in order to understand the decrease of char reactivity at elevated pressure gasification conditions.

- (2) In this work, the effect of moisture from the feedstock to provide steam was investigated. Air dried lignite contains 12% of moisture and this produced around 3-6%mol. of steam in the gasifier. The feedstock could be specially treated (such as surface drying the raw feedstock to preserve the internal moisture) to obtain different moisture content, and the comparison could be studied.
- (3) A kinetic model development could be interesting for further understanding of the participant reactions and assist process optimisation.
- (4) There was some degradation of the anode materials after exposing to gasification products. The exposed anode materials could be compared with fresh materials to test their electricity generation potentials. In addition, the impacts of the fuel gas on working anodes could be studied. This could guide if it is necessary to have a gas cleaning system upstream the fuel cell to preserve their integrity.
- (5) The regeneration of the anode materials after gasification product exposure could be studied. It is important to understand this process as the anode material are expensive and have a substantial impact on the economic feasibility of this route for power generation.
- (6) The effect of exposure time to the anode materials could be investigated. This could give an indication for the fuel cell performance in realistic long exposure times.

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Appendices

Appendix 1 Calculation for the Minimum Wall Thickness

The minimal wall thickness (e, mm) for the Incolloy reactor can be calculated based on High Pressure Safety Code (Cox et al., 1975) and BSI PD 5500 (BSI, 2015) using Equation A.1.

$$e = \frac{pD_i}{2f - p} \quad \text{Equation A.1}$$

where p (MPa) is the design pressure, D_i (mm) is the internal diameter, and f (MPa) is the creep strength.

The creep strength of the Incolloy Alloy 800 HT can be found from Figure A.1.

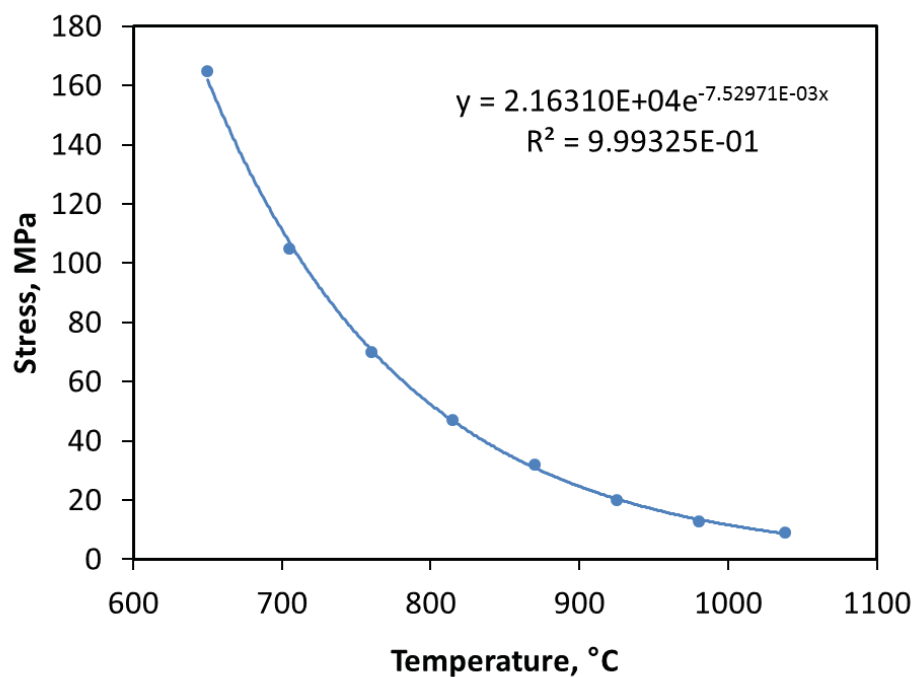


Figure A.1 The creep strength for 1000 h of Incolloy Alloy 800HT (Incolloy, 1986)

The calculated minimal wall thickness against design pressure at both 1000 and 1050 °C are shown in Figure A.2.

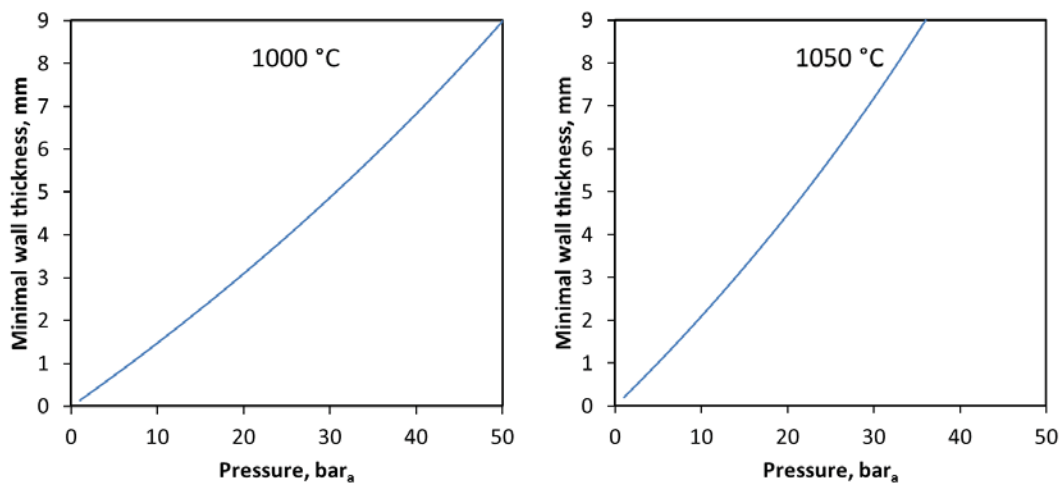


Figure A.2 Required minimum wall thickness for design pressure for 1000 h. (left: 1000 °C, right: 1050 °C)

Appendix 2 Calibration of the Solid Feeder

The flow rate of the solid feeder was controlled by a DC motor that was connected to a variable transformer (0 - 15 V). By change the output voltage from the transformer, the solid feeding rate can be adjusted. To calibrate the flow rate against the voltage, the transformer was first set to a required voltage, then the output material (in this case German lignite) was collected in a pre-weighed container for 1 min, after that the weight of the collected material and the container was measured. The material flow rate (F_{solid} , g min⁻¹) could be calculated from Equation A.2. This procedure was repeated twice for each flow rate, and the average value was taken. The calibration of the solid flow rate against the voltage is shown in Figure A.3.

$$F_{solid} = \frac{W_{solid} - W_{empty}}{\Delta t} \quad \text{Equation A.2}$$

Where W_{solid} (g) is the weight of the collected material and the container, W_{empty} (g) is the weight of the container, and Δt (min) is the time interval that is 1 min in this case.

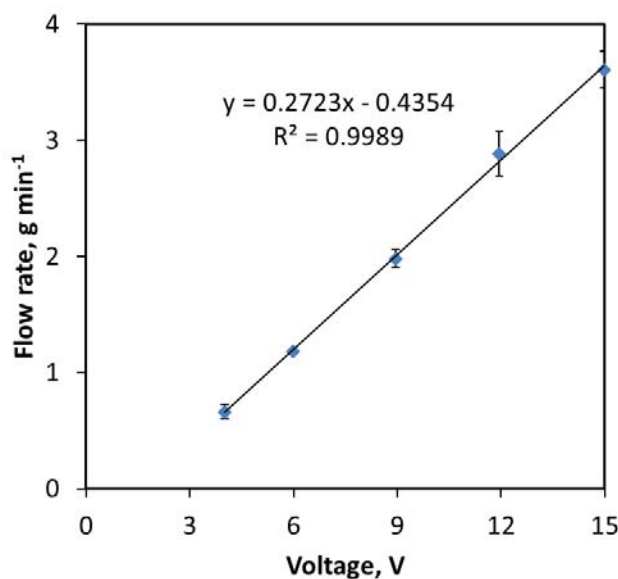


Figure A.3 Calibration of the solid feeder

Appendix 3 Calibration of the Mass Flow Controller

The mass flow controller for CO_2 and N_2 were calibrated by a 2000 mL bubble meter. The bubble meter consists of a calibrated glass tube fixed with a squeeze bulb at the bottom that filled with soap solution. It determines the gas flow rate by using a stopwatch to time the gas to move the soap bubble through a known volume between two marks (Levy, 1964). The calibrations were carried out at cylinder pressures at 20 and 6 bar_a for CO_2 and N_2 respectively. The measurement was taken three times for each flow rate, and the average value was used. The calibration curves for CO_2 and N_2 are shown in Figure A.4.

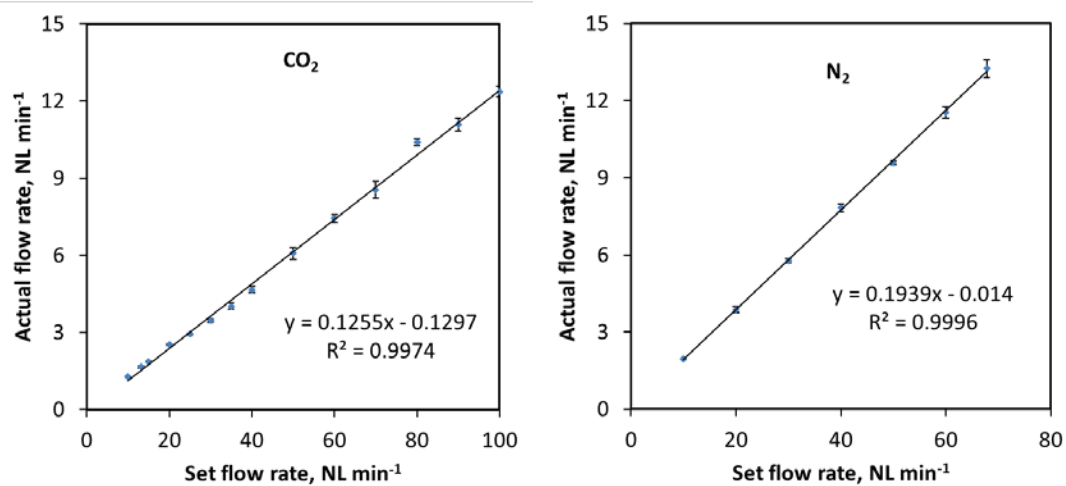


Figure A.4 Calibration of the mass flow controller for CO₂ (left) and N₂ (right)

Appendix 4 Calibration of the Dry Gas Meter

The dry gas meter is calibrated by passing a CO₂ gas stream with different known volumetric flow rates from the mass flow controller. The volumetric flow rate from the gas meter was measured by taking the gas volume readings between a known time interval. In this calibration, the reading of the gas volume (NL) was taken at 1 min intervals. The difference between these two gas volumes is the volumetric flow rate (NL/min) measured from the gas meter. The measurement for each set flow rate was repeated twice, and the average value was used. The calibration curve of the gas meter is shown in Figure A.5.

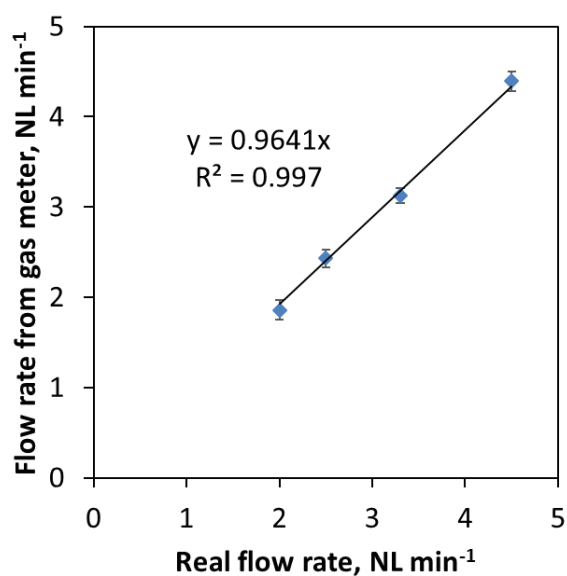


Figure A.5 Calibration of the dry gas meter

Appendix 5 Calibration of the H₂ analyser

As discussed in 3.5.1.2, the H₂ analyser determines the H₂ concentration in binary or pseudo-binary gas mixtures. In this study, the H₂ analyser was calibrated in CO₂. The measured fuel gas consisted of four main gas compounds including CO, CO₂, H₂ and CH₄. Thus, it is important to know the impact of CO and CH₄ on the reading of H₂ analyser. According to the information from the supplier, there is a measurement error of 0.08% (abs.) for H₂ with presence of 1% CH₄. The maximum CH₄ concentration obtained from the experiments is 2.7%. Therefore, the maximum error for H₂ from CH₄ is 0.22% (abs.), which is not significant. However, the CO concentration was around 20 to 40% from the experimental data. A cross calibration of H₂ against CO concentration was necessary. As the H₂ analyser measures the concentration through the thermal conductivity of the gas, and N₂ has a similar thermal conductivity with CO (shown in Table 3.5), the impact of CO on the H₂ analyser can be obtained by conducting the cross calibration of N₂ on H₂ analyser.

The cross calibration H₂ against N₂ concentration was carried out in four steps. First, a pure stream of CO₂ was passed through the H₂ analyser to give the 0 concentration of H₂. Then, a calibration gas of 10% H₂ in CO₂ was passed. A two-point calibration of signal against H₂ concentration was obtained, and shown in Figure A.6 (left). After that, gas mixtures of N₂ and CO₂ with different concentrations were passed through the H₂ analyser. The signal of measured H₂ against different N₂ concentration is shown in Figure A.6 (right). Finally, the H₂ signal in Figure A.6 (right) was converted to its concentration from Figure A.6 (left). The final cross

calibration of N₂ on H₂ analyser is shown in Figure A.7. The correlation factor is 0.1097 of N₂ on H₂ analyser (0.1097% showing on H₂ analyser if 1% N₂ presence).

Assume the differences in impacts between CO and N₂ on the H₂ analyser were negligible, the final H₂ concentration in the fuel gas was corrected by eliminating the CO impact using the correlation factor obtained from Figure A.7.

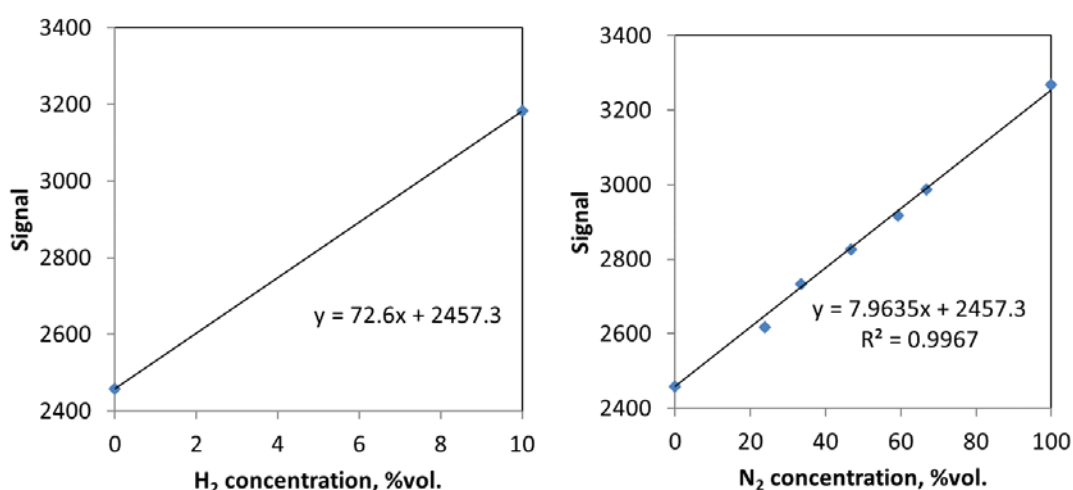


Figure A.6 Signal on H₂ analyser of flow of H₂ (left) and N₂ (right)

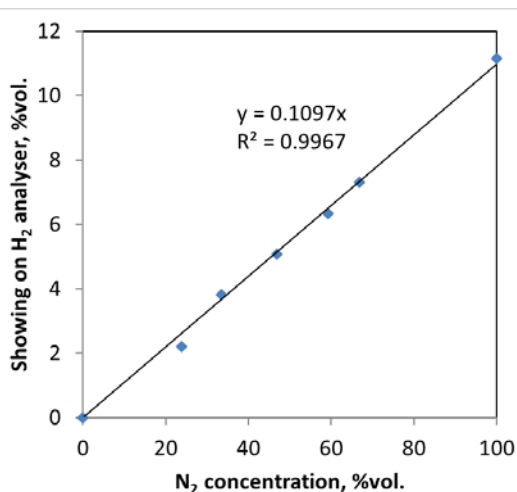


Figure A.7 Cross calibration of N₂ showing on H₂ analyser