Investigation of the conversion of fuels in the presence of solid oxygen carriers and the development of a plasma-assisted chemical looping system for H$_2$ production

Yaoyao Zheng
Queens’ College

A dissertation submitted for the degree of

*Doctor of Philosophy*

Department of Engineering
University of Cambridge
December 2018
Preface

This dissertation is a result of my own work that has been carried out in the Department of Engineering, University of Cambridge between October 2014 and March 2018. It includes nothing which is the outcome of work done in collaboration, except where specifically acknowledged in the text. It is not substantially the same as any that I have submitted, or, is being concurrently submitted for a degree or diploma or other qualification at the University of Cambridge or any other University or similar institution except as declared in the Preface and specified in the text. I further state that no substantial part of my dissertation has already been submitted, or, is being concurrently submitted for any such degree, diploma or other qualification at the University of Cambridge or any other University or similar institution except as declared in the Preface and specified in the text.

This dissertation contains approximately 64749 words, 95 figures and 26 tables.

Yaoyao Zheng
Department of Engineering
University of Cambridge

December 2018
Acknowledgements

First, I would like to sincerely thank my supervisor Dr Stuart A. Scott, for his unhesitating support, guidance and encouragement throughout my PhD. I would also like to express great gratitude to my advisor Prof. John Dennis, from the Department of Chemical Engineering and Biotechnology, for his precious advice on this work. I am extremely grateful to Dr Rob Grant, from Gas Recovery and Recycle limited, for his generous provision of many equipment and devices, without which I would not be able to carry out the plasma-based topics. I would also like to thank Rob for many helpful discussions with him. It has been my great pleasure to work with Drs Ewa Marek and Wenting Hu, from who I have learnt immensely in research. Sincere gratitude to Ewa and Wenting’s continuous encouragement through my research is also acknowledged.

It would not have been possible to accomplish a PhD without the help of many support staff. Hereby I would like to thank Roy Slater, Robert Leroy, Jack Graham, Juan Dickerson and John Harvey from the Department of Engineering, as well as Zlatko Saracevic from the Department of Chemical Engineering and Biotechnology. They are always with great patience to help in every possible way.

I would like to thank my colleagues: Drs Mohammad Ismal, Felix Donat, Ruinan Mao, Peng Dai; Richard Goerke, Martin Chan, Matthias Schnellmann, Paul Hodgeson, Zach Bond, Samual Gabra. I will always keep the treasurable memories of the time together at Cambridge. Thank you for bringing me joy in times of difficulty.

My studentship was kindly funded by China Scholarship Council and Cambridge Trust. Research studentship to support the writing-up stage of my PhD was also provided by Cambridge Philosophical Society. I am sincerely grateful to these funding bodies.

I thank friends from the college, the department and in Cambridge, for bringing so much enjoyment to my life here. I wish to give my deepest gratitude to my families: mum, dad, and brother, for their understanding and support for all the decisions I have made. Last but not least, I must thank my beloved boyfriend Qifeng, for his being supportive, inspiring and encouraging as always, especially in my hard times.
List of Publications & Conference Presentations

The outcome of the work described in this dissertation has been submitted to peer reviewed journals for publication, and presented or to be presented in international conferences. These include:

Publications:


2. Y. Zheng, R. Grant, W. Hu, S.A. Scott, Pyrolysis of wood pellets in the presence of oxygen carriers in a fluidised bed coupled with a DBD reactor for tar quantification, Chemical Engineering Journal. 355 (2019) 858–870. doi:10.1016/J.CEJ.2018.08.090. (This work was included in Chapter 5.0).


Conferences:


3. Dec 2015  **In situ gasification of a Polish char by CO₂ in the presence of Fe₂O₃, in a fluidised bed for chemical looping combustion.** UK-Sino Forum on Clean


Abstract

Chemical looping combustion (CLC) is an alternative technique that was originally developed for the purpose of carbon capture and storage (CCS). It employs oxygen carriers (usually transition metal oxides) to provide oxygen for the combustion of fuels in a fuel reactor. The reduced oxygen carriers can be regenerated in an air reactor. The redox property of the oxygen carriers exhibits promising capability for converting fuels for other chemical processes such as reforming, partial oxidation, and etc. This dissertation is concerned with understanding the effect of adopting typical oxygen carriers on various conversion techniques, suited for different fuels.

Combustion of a solid fuel, a Polish coal-derived char was first carried out in a fluidised bed reactor in the presence of Fe-based oxygen carriers: Fe₂O₃ and ZrO₂-supported Fe₂O₃. To avoid inefficient combustion arising from direct solid-solid reaction between the char and the oxygen carriers, CO₂ was introduced to the fluidised bed, to allow the char to be gasified in situ, prior to the reaction with the oxygen carriers. The focus of this study was to understand how the oxygen carriers affect the in situ gasification step. The results of in situ gasification in oxygen carriers were compared with those in an inert bed. Fe₂O₃ was found not to alter the gasification step, given that the gasification of the char was free of external mass transfer limitation. A numerical model, was developed to describe the gasification behaviour, as well as predicting the effect of CO on gasification. The inhibition effect of CO on char gasification seems more significant than expected.

Combustion of biomass, a type of wood pellets, by Fe₂O₃ or mayenite-supported CuO was studied in a fluidised bed, respectively. The aim was to understand how efficient the wood pellets were combusted by the oxygen carriers, as well as the distribution of the products. The products from direct thermal processing of biomass usually contain condensable volatiles, which was defined as tar here. Therefore, in addition to commercial analysers for gaseous products, a tar measurement system, based on a plasma reactor, was developed. With the developed measuring system, it was found that both Fe₂O₃ and mayenite-supported CuO were efficient for combusting biomass, particularly the latter one. The chemical looping oxygen uncoupling (CLOU) nature of CuO makes mayenite-supported CuO a promising candidate for the direct combustion of biomass, without introducing any reactive gaseous oxidant.
The final part (Chapters 6, 7 and 8) of the dissertation was focused on developing and investigating a plasma-assisted chemical looping system for H₂ production from CH₄ at mild temperatures (~ 673 K). The active oxygen carriers investigated include SrFeO₃, Fe₂O₃, and Ni-doped SrFeO₃ and Fe₂O₃. SrFeO₃ was over-reactive in such system, leading to total combustion of CH₄ to CO₂ and H₂O. The addition of Ni onto SrFeO₃, however, significantly improved the selectivity towards H₂; whilst the high reactivity was only active in the fresh cycle. Fe₂O₃ was found inert for converting CH₄ to H₂; on the other hand, doping Ni onto Fe₂O₃ to form NiO/Fe₂O₃ dramatically improved H₂ production and the reactivity maintained high for three redox cycles. The energy cost of H₂ production from the plasma-assisted chemical looping system was found comparable to that for water electrolysis.
# Table of Contents

Preface .......................................................................................................................... 3
List of Publications & Conference Presentations .......................................................... 5
Abstract ......................................................................................................................... 7

1.0 Introduction ................................................................................................................. 12
  1.1 Chemical looping combustion ................................................................................. 12
     1.1.1 Carbon capture and storage (CCS) ................................................................. 12
     1.1.2 Chemical looping combustion ................................................................. 15
     1.1.3 Oxygen carriers for CLC ............................................................................. 15
     1.1.4 Reaction between solid fuels and oxygen carriers .................................... 19
  1.2 Gasification ............................................................................................................... 20
     1.2.1 Introduction to gasification ........................................................................... 20
     1.2.2 Gasification of char with CO ................................................................. 20
  1.3 Pyrolysis .................................................................................................................... 24
     1.3.1 Introduction to pyrolysis ............................................................................. 24
     1.3.2 Pyrolysis products ...................................................................................... 26
     1.3.3 Removal of biomass tar .............................................................................. 26
  1.4 Plasma ....................................................................................................................... 29
     1.4.1 Dielectric barrier discharge (DBD) and its application on tar removal ........ 30
     1.4.2 Plasma chemistry ....................................................................................... 32
  1.5 Production of hydrogen ............................................................................................ 34
     1.5.1 Steam reforming of methane (SRM) ............................................................. 34
     1.5.2 Chemical looping reforming of CH, ............................................................. 35
     1.5.3 Plasma-involved processes for H₂ production from CH₄ ................................ 37
     1.5.4 Hydrogen production techniques based on the splitting of water ............. 39
  1.6 Objectives and structure of the dissertation ............................................................ 40

2.0 Experimental methods .............................................................................................. 42
  2.1 Introduction ............................................................................................................... 42
  2.2 Preparation of materials ......................................................................................... 42
     2.2.1 Sources and specifications of chemicals and gases ..................................... 42
     2.2.2 Preparation of materials ............................................................................. 43
  2.3 Apparatus .................................................................................................................. 47
     2.3.1 Stainless steel fluidised bed reactor ............................................................ 47
     2.3.2 Quartz tube fluidised bed reactor ............................................................... 48
     2.3.3 Quartz tube fluidised bed reactor coupled with a plasma reactor ............. 50
     2.3.4 Plasma-assisted packed bed reactor ........................................................... 55
  2.4 Characterisation of the materials ............................................................................ 57
     2.4.1 Analysis by X-Ray Powder Diffraction (XRD) ........................................... 57
     2.4.2 SEM-EDX ................................................................................................. 58
     2.4.3 Brunauer-Emmett-Teller (BET) and mercury intrusion porosimetry (MIP) .... 58

3.0 In situ CO₂ gasification of a Polish coal-derived char in the presence of FeO₃-based oxygen carriers ............................................................................................................. 59
  3.1 Introduction ............................................................................................................... 59
     3.1.1 FeO₃ reduction as source of oxygen ............................................................. 60
     3.1.2 Support material- ZrO₂ ............................................................................... 61
  3.2 Experimental methods ............................................................................................. 62
     3.2.1 Preparation of the materials ....................................................................... 62
     3.2.2 Experiments ............................................................................................... 62
6.1.2 Estimation of the mean electron energy ........................................... 139
6.2 Experiments and calculation of the parameters ..................................... 140
  6.2.1 Development of a plasma-assisted chemical reactor ......................... 140
  6.2.2 Experiments ............................................................................. 141
  6.2.3 Estimation of the parameters ..................................................... 142
6.3 Results and discussion ....................................................................... 142
  6.3.1 Understanding the electrical signals ............................................. 142
  6.3.2 CH conversion and mean electron energy ....................................... 149
6.4 Conclusions ....................................................................................... 150

7.0 H₂ production in a plasma-assisted chemical looping system in the presence of SrFeO₃δ ................................................................. 154
  7.1 Introduction ...................................................................................... 154
    7.1.1 SrFeO₃δ .................................................................................. 154
    7.1.2 H₂ production from chemical looping ......................................... 154
  7.2 Experimental methods ....................................................................... 155
    7.3 Results .......................................................................................... 156
      7.3.1 Identification of the non-stoichiometry of SrFeO₃δ ......................... 156
      7.3.2 Identification of the gaseous products ....................................... 156
      7.3.3 H₂ production from plasma-assisted redox cycle ......................... 161
      7.3.4 Results of conversion, selectivity and material balance ............... 167
  7.4 Discussion ....................................................................................... 169
    7.4.1 The effect of Ar on plasma intensity and conversion of CH₃ ............ 169
    7.4.2 Investigation of the effects of plasma catalysis and plasma heating ... 170
    7.4.3 Investigation of longer plasma discharge period in the SrFeO₃δ-packed DBD reactor ................................................................. 173
    7.4.4 Investigation of O₂ release from SrFeO₃δ in air regeneration stage ... 176
    7.4.5 Comparison of the system for H₂ generation and other industrial means of H₂ generation ........................................................................... 177
    7.4.6 Investigation of Ni on SrFeO₃δ for hydrogen production ............... 179
  7.5 Conclusions ....................................................................................... 183

8 H₂ production from partial oxidation of CH by Fe₃O₄-supported Ni-based catalysts in a plasma-assisted packed bed reactor ......................................................... 184
  8.1 Introduction ...................................................................................... 184
  8.2 Experimental methods and data analysis ............................................. 184
    8.2.1 Experiments ............................................................................. 184
    8.2.2 Data analysis ............................................................................ 185
  8.3 Results ............................................................................................. 185
    8.3.1 The results of AlO, and Fe₃O₄ ..................................................... 185
    8.3.2 The results of NiO/AlO, Ni/AlO, NiO/Fe₃O, and NiFeO/Fe₃O .......... 186
    8.3.3 XRD characterization of NiO/Fe₃O and NiFeO/Fe₃O ...................... 189
  8.4 Discussion ....................................................................................... 192
    8.4.1 Catalytic effect .......................................................................... 192
    8.4.2 Comparison to water gas shift equilibrium .................................. 197
    8.4.3 Discussion of the H₂ production in Fe₃O₄-based and SrFeO₃δ-based materials in the plasma-assisted chemical looping system ....................... 199
  8.5 Conclusions ....................................................................................... 201

9.0 Conclusion .......................................................................................... 202

10.0 Future Work ...................................................................................... 206

List of abbreviations and symbols ............................................................. 208

Reference .................................................................................................. 213
1.0 Introduction

1.1. Chemical looping combustion

1.1.1 Carbon capture and storage (CCS)

Fossil fuels are the primary energy resource worldwide [1], despite promising renewable sources of energy such as solar energy, wind energy and hydropower, which in total account for about 7% [2]. According to the report from International Energy Agency (IEA) [3], in 2015, there is still around 82% of the world energy supply derived from fossil fuels, and there has been no significant change of their share in the total energy supply in the past several decades, i.e. from 1971 to 2015. The combustion of fossil fuels, as the main approach to supply energy, however, generates a substantial amount of CO₂, which is a greenhouse gas (GHG). IPCC [4] is over 95% certain that global warming is a consequence of GHG emissions. According to IEA’s report published in 2017 [3], since the 1870s, the amount of CO₂ emitted from the burning of fossil fuels has increased dramatically and in 2015, it reached to over 35 Gt. It has been realised that in the 20th century, the global average temperature increased by 1 K [2]. The European Union has set a target of reducing GHG emission by at least 20% by 2020, based on the baseline of 1990 [3]. As one of the main greenhouse gases, CO₂ emissions should be controlled. Because of the abundance and low cost of fossil fuels, they are likely to remain an important part of the energy system for many decades to come. To continue to tap this convenient energy source without incurring the downsides, techniques to capture CO₂ produced from fossil fuel combustion processes and store it underground have been proposed. These techniques are called carbon capture and storage (CCS). Currently CCS for power plants is mainly sub-classified into three categories: pre-combustion, post-combustion, oxy-fuel combustion.

Pre-combustion

Pre-combustion capture is a technique that separates the carbon and hydrogen in the fuel prior to combustion [5]. The fuel is firstly converted into a mixed stream of gas products, known as ‘syngas’, mainly consisting of CO, H₂ and CO₂. The process is called reforming for gaseous and liquid fuels, and gasification for solid fuels. Steam is then introduced to the mixture to generate a mixed stream of CO₂ and H₂, followed by the separation of CO₂.
This finally gives a H\(_2\)-rich product stream, which can be used in many applications such as electricity generation [6]. One of its limitations is the high capital cost of the gasifier. In addition, if the gasification or reforming is by O\(_2\), a considerable amount of energy is used to drive the air separation unit to provide O\(_2\). The energy penalty for pre-combustion is about 8\% - 12\% [7,8], where the energy penalty is defined as follows.

\[
\text{Energy penalty} = 1 - \frac{\eta_{\text{with capture}}}{\eta_{\text{without capture}}}.
\]

\(\eta_{\text{with capture}}\) and \(\eta_{\text{without capture}}\) stand for power plants energy efficiency with and without carbon capture installed, respectively. The value of the energy penalty varies with the types of power plant, with pulverised coal (PC) power plants normally showing the highest energy penalty, and natural gas combined cycle (NGCC) the least [9].

**Post-combustion**

Post-combustion carbon capture separates CO\(_2\) from the exhaust gas of a conventional combustion process. CO\(_2\) is normally absorbed by a solvent (typically amine-based), and then released from the solvent to be further compressed and stored. There are also other approaches to the separation of CO\(_2\), such as membrane filtration and cryogenic separation [10]. One significant advantage of post-combustion is its suitability for retrofit in current operating power plants without causing dramatic change and affecting the conventional operations. However, this also incurs an energy penalty due to the regeneration of the solvent and gas compression, causing about an 11\% decrease in the overall efficiency (from ~39\% to ~28\%) of the power plant [9,11].

**Oxy-fuel combustion**

In oxy-fuel combustion processes, the fuel is burned in a mixture of O\(_2\) and CO\(_2\) rather than in air. The presence of CO\(_2\) in the mixture is simply to lower the temperature in the flame. This burning atmosphere results in a flue gas stream containing mainly CO\(_2\) and steam, which simplifies the capture of CO\(_2\).[12] (as the gas is free of N\(_2\)). CO\(_2\) can be captured from the mixed stream by the condensation of H\(_2\)O. The major cost and energy penalty arises from O\(_2\) production in the air separation unit. The thermal efficiency of coal-steam cycle plant decreases from ~ 44\% without capture to ~ 36\% with capture [7].
Chemical looping combustion (CLC)

Chemical looping combustion is an alternative to conventional combustion. The term ‘chemical looping’ is used to describe cyclic processes which employ oxygen carriers to provide oxygen for the conversion of fuels [13]. Oxygen carriers are typically transition metal oxides that are able to give up oxygen through reduction whilst oxidising a fuel. The reduced oxides are regenerated in air in order to be used in the next combustion cycle. A mixed flue gas stream containing CO$_2$ and steam is obtained and CO$_2$ is captured by condensation. In this system, air is only used to oxidise the reduced oxygen carriers, and would never mix with CO$_2$ produced from the reaction of the fuel and oxygen carrier. Thus, unlike conventional combustion where a substantial amount of energy is used for separating CO$_2$ and N$_2$, the CO$_2$ is not diluted with a large amount of N$_2$ in this case. A diagram of the CLC process is presented in Fig. 1-1. It involves two interconnected fluidised bed reactors, a fuel reactor and an air reactor.

![Systematic Diagram of CLC](image)

**Fuel reactor:** \[(n+\frac{m}{2}) \text{Me}_x\text{O}_y + \text{C}_n\text{H}_m \rightarrow (n+\frac{m}{2}) \text{Me}_x\text{O}_y + n\text{CO}_2 + m\text{H}_2\text{O}\] \[\text{R. 1-1}\]

**Air reactor:** \[\text{Me}_x\text{O}_y + \text{O}_2 \rightarrow \text{Me}_x\text{O}_y\] \[\text{R. 1-2}\]

Reaction R. 1-2 in the air reactor is always exothermic [14]. When two fluidised bed reactors are interconnected, the inter-transport of the solid oxygen carriers can provide...
heat for the reaction in the fuel reactor. The heated air (N\textsubscript{2} and O\textsubscript{2}), leaving the air reactor at high temperature (~ 1223 K), can be used to generate steam, or when the operation is pressurised, to drive a gas turbine. CLC has attracted great research interest in the past two decades, with work mainly focused on reactor design [15–17], oxygen carriers [18–20] and thermodynamic efficiency [21,22], mostly on gaseous fuels. Chemical looping combustion of solid fuels is investigated in this dissertation (coal-derived char in Chapter 3, and biomass in Chapter 5). The combustion of solid fuels accounts for a major portion of the world’s electricity supply. For instance, coal makes up to over 40% [23]. Solid fuel is also less expensive than oil and natural gas due to its large amount available [24]. Hence, solid fuels are expected to remain its role as a primary energy source in future decades.

1.1.2 Chemical looping combustion

CLC started with the conversion of gaseous fuels [25–28], followed by the interest in solid fuels at a later stage [14,29–31]. Leion \textit{et al}. [32] carried out work on the reactivity of several types of coals and a petroleum coke using natural mineral ilmenite, in addition to a synthetic material composed of Fe\textsubscript{2}O\textsubscript{3}/MgAl\textsubscript{2}O\textsubscript{4} in a fluidised bed reactor. The results demonstrated the viability of the application of CLC to various types of solid fuels. Both ilmenite and Fe\textsubscript{2}O\textsubscript{3}/MgAl\textsubscript{2}O\textsubscript{4} increased the gasification rate of the fuels, and they exhibited similar reactivity. Linderholm \textit{et al}. [33] published a study of CLC with solid fuel in a continuous 10 kW combustor comparing different natural minerals (ilmenite, ilmenite and lime, manganese ore, and manganese ore and lime). Manganese ore as an oxygen carrier showed a faster rate of gasification than ilmenite, and the addition of lime particles into the manganese ore improved the rate further. On the other hand, compared to CLC with gaseous fuels, the use of solid fuels is more complicated since the solid particles of fuel and oxygen carriers are difficult to separate [14]. The solid fuel inventory may follow the recycled stream of the oxygen carrier and enter the air reactor, where it can burn to produce CO\textsubscript{2} that contaminates the air stream. Therefore, in terms of solid feed, one option is to adopt an initial gasification step prior to combustion.

1.1.3 Oxygen carriers for CLC

Suitable materials for oxygen carriers should have the ability to release and capture oxygen at a temperature range of interest from ~ 1073 - 1473 K [24]. Hence, materials
suitable as oxygen carriers are usually transition metals oxides, and promising candidates ideally should have high oxygen capacity, high reactivity for redox, good resistance to mechanical force, and less likely to agglomerate. They should also be thermodynamically favoring fuel conversion to CO$_2$ and H$_2$O. Additionally, materials that are environmentally friendly and with low cost, are preferred. There are few pure oxygen carriers that meet all the criteria. Practically, other materials such as Al$_2$O$_3$ are used to support the active oxygen carriers. This helps to increase the mechanical strength of oxygen carriers [13]. Besides, due to the dilution of the oxygen carriers on the supports, side effect of sintering/agglomeration can be minimised and the overall reactivity would improve owing to the increased surface area.

Fe$_2$O$_3$, CuO, NiO and MnO$_2$-based oxygen carriers are the mostly investigated looping agents in CLC. Fe$_2$O$_3$ is abundant, cheap, shows high reactivity. It can be reduced to different states (Fe$_3$O$_4$, FeO, or Fe). In a sulphur-containing environment, using Fe-based oxygen carriers is advantageous [34]. For solid fuels like char, sulphur-containing gases such as H$_2$S and SO$_2$ are products in gasification. Sulphur-containing gases can react with oxygen carriers to form sulphates and sulphites. Depending on the oxygen carriers used, this can lead to the deactivation of the oxygen carriers. For Fe$_2$O$_3$/FeO systems, due to the thermodynamic property of the pair, iron cannot form sulphates and sulphides [34] so that deactivation caused by sulphur is not an issue for Fe$_2$O$_3$. On the other hand, there are some limitations of Fe-based materials. Usually, the reduction of Fe$_2$O$_3$ to FeO is more favoured, as it is the fastest step; further phase reduction reactions are slow, especially the phase change from FeO to Fe [26]. However, limiting reduction to Fe$_2$O$_3$ → FeO, would limit the oxygen transport capacity. In terms of supporting materials for Fe$_2$O$_3$, Al$_2$O$_3$, TiO$_2$, and ZrO$_2$ are commonly used. The direct use of Al$_2$O$_3$ with Fe$_2$O$_3$ causes the formation of FeAl$_2$O$_4$, leading to decreased rate of reduction from Fe$_2$O$_3$ to phases beyond FeO[35]. To avoid the formation of FeAl$_2$O$_4$, when exploiting Al$_2$O$_3$ as the support material, one solution is to add some additional materials, such as MgO to form MgAl$_2$O$_4$. Some researchers used Fe$_2$O$_3$/MgAl$_2$O$_4$ as the oxygen carrier for CLC, and they found good reactivity of Fe$_2$O$_3$ and inertness of the support, MgAl$_2$O$_4$ [34,36]. Alternatively, ZrO$_2$ is promising as a support due to its inertness [37].
Copper-based oxygen carriers show very high reactivity (e.g. higher than Fe-based ones) in CLC. CuO has the ability to release gaseous oxygen, and this is known as chemical looping oxygen uncoupling (CLOU). At temperatures above 1073 K, CuO starts to decompose to Cu₂O and gaseous O₂. Chuang et al. [38] tested the performance of reduction and oxidation of Cu-based oxygen carriers over multiple cycles for CLC at elevated temperatures from 1073 to 1173 K. The results show that the yield of CO₂ at 1173 K was lower than that at 1073 K. This is because between reduction and oxidation, the reactor was purged with N₂. At higher temperatures, CuO decomposed to Cu₂O and gaseous O₂ during the N₂ purging. For this reason, some of the oxygen was lost from CuO. On the other hand, the main concerns of using CuO are the agglomeration of particles and the need for low operating temperature. Cu has a melting temperature of 1358 K. For this reason, use of CuO/Cu is normally limited to below 1173 K (~ sintering temperature of Cu). To overcome this issue, support material is always necessary for CuO, when operated at high temperatures. Various methods for preparing CuO have been studied in order to minimise this phenomenon. Chuang et al. [38] compared samples of CuO supported on Al₂O₃, prepared from mechanical mixing, wet impregnation and co-precipitation methods, among which only the co-precipitated one gave no agglomeration.

Ni-based materials are another branch of materials used due to its excellent reactivity, however they are more expensive than Fe₂O₃ and CuO. Besides, environmental and health issues limit their use in the fluidised beds. Another concern is their easy deactivation by H₂S. Mn-based oxygen carriers are also of interest. Mn-based oxygen carriers have a lower cost and higher oxygen transport capacity than iron. Similar to CuO/Cu, MnO is able to release gaseous oxygen to become Mn₃O₄ [24]. However, at temperatures above 1173 K, for MnO → Mn₃O₄ + O₂(g), the equilibrium O₂ is above 21.4%, higher than the amount in air (~ 20.8%). This brings difficulty for the regeneration of the material. Normally, active Mn-based oxides are mixed with other active materials to form spinels, resulting in better properties than pure Mn-based oxides [25].

Perovskites, which can easily donate oxygen, are another group of materials suitable as oxygen carriers. They can be expressed as ABO₃, which can gradually lose oxygen whilst maintaining the perovskite structure: ABO₃ ↔ ABO₃-δ + δ/2 O₂. SrFeO₃ is one of the most studied perovskites due to its relatively low cost and high potential for losing oxygen.
The non-stoichiometry of the material, 3-δ, has been shown to be a function of temperature and pO₂ [39]. Moreover, SrFeO₃ starts releasing gaseous oxygen at temperatures as low as ~ 400°C in air [40,41], and the process is characterised by fast kinetics and good resistance to carbonation over multiple redox cycles [42].

Other materials of interest are natural minerals [43] due to their low price [33], [44]. However, the cost of preparation of the materials from raw materials and lifetime of materials should also be considered when evaluating their feasibility. The most promising natural mineral is ilmenite (FeTiO₃). The issue with ilmenite is that an activation step is needed [44]. Initial redox reactions of ilmenite show low reactivity. After several cycles of redox (normally over 10 cycles), both the porosity and reactivity of the material increases. Activated ilmenite exhibits high mechanical strength and reactivity, as well as a low tendency to agglomerate. Table 1-1 summarised the properties of the main oxygen carriers that have been discussed as above.

<table>
<thead>
<tr>
<th>Oxygen carriers</th>
<th>Reactivity</th>
<th>Cost</th>
<th>Oxygen capacity</th>
<th>Recyclability/stability</th>
<th>Health and Safety level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂O₃/Fe₃O₄</td>
<td>Medium</td>
<td>Low</td>
<td>Low</td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td>CuO/Cu</td>
<td>High</td>
<td>Medium</td>
<td>High</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>NiO/Ni</td>
<td>High</td>
<td>Medium</td>
<td>High</td>
<td>Medium</td>
<td>Low (i.e. carcinogenic)</td>
</tr>
<tr>
<td>Mn₂O₃/Mn₃O₄</td>
<td>Medium/high</td>
<td>Medium</td>
<td>Low</td>
<td>Low</td>
<td>Medium</td>
</tr>
<tr>
<td>SrFeO₃₋δ (in perovskite phase)</td>
<td>High</td>
<td>High</td>
<td>Low</td>
<td>High</td>
<td>Medium</td>
</tr>
<tr>
<td>Ilmenite</td>
<td>Medium (requires activation)</td>
<td>Low to medium (need to include processing cost)</td>
<td>Medium</td>
<td>High</td>
<td>Medium to high</td>
</tr>
</tbody>
</table>

Oxygen carriers can be prepared via several methods, typically mechanical mixing, wet impregnation and co-precipitation. The properties of the oxygen carriers can significantly vary as a result of different preparation methods used. For mechanical mixing, metal
oxides and the support material powders are simply mixed, then the particles are calcined at high temperatures (e.g. 1273 K). Impregnation methods use metal oxide precursors, usually in the form of nitrate-solution, to be deposited on a solid support material. The co-precipitation method is more complex, and it uses solutions of both the active metal and the support material, by adjusting the pH of the solution to form co-precipitates of insoluble oxide precursors. A final calcination step to convert the precursors to the oxides is also needed here. Oxygen carriers prepared by co-precipitation often exhibit better performance. Chuang et al. [38] examined the performance of Al₂O₃ supported Cu-based oxygen carriers prepared from the three methods. Only co-precipitation method produced particles with a high loading of copper, and they did not agglomerate at 1073 - 1173 K.

1.1.4 Reaction between solid fuels and oxygen carriers
For the conversion of solid fuels in the chemical looping scheme, owing to the slow or negligible solid-solid reaction rate between oxygen carriers and the fuels, either an initial gasification step or a CLOU materials is required. For the first approach, the gasification step converts the solid fuels into gases (either in situ or ex situ), followed by the oxidation of the products by the oxygen carriers. Fe-based oxygen carriers for the in situ gasification of chars for CLC have been studied by Saucedo et al. [14]. They found that heterogeneous reaction took place between the produced CO (from gasification) and Fe₂O₃. The overall gasification rate increased, owing to the removal of CO from the char surface and the enhanced surface CO₂ concentration. This conclusion was believed to apply to the situation where the gasification step is limited by mass transfer. No catalytic effect of the oxygen carriers on the rate of gasification was observed. For the second approach, i.e. CLOU, Mattisson et al. [24] first described the phenomenon of combusting solid fuels by gaseous oxygen that released from oxygen carriers. They tested CuO/Cu₂O, MnO₂/MnO, and Co₃O₄/CoO for combustion of a petroleum coke, and found promising performance of CuO/Cu₂O and MnO₂/MnO, due to their high CLOU nature. Compared to the reaction rate in a CLC material scheme, i.e. with Fe₂O/Fe₃O₄, the rate with CuO/Cu₂O was found to be 50 times higher.
1.2 Gasification

1.2.1 Introduction to gasification

Gasification is the thermal conversion of carbonaceous matter into gaseous products containing CO, CO$_2$, and H$_2$. Gasification of solid fuels such as coal consists of two stages, starting with pyrolysis (discussed in 1.3), where moisture and volatiles leave the solid fuel under thermal effect. This is followed by the gasification of char. Pyrolysis is a fast reaction, compared to the gasification of char [45]. Therefore, char gasification is usually the rate-determining step in the overall gasification. Direct coal gasification would generate a large variety of products, mainly due to a huge number of volatiles produced under heating. This brings more uncertainty to the process. Alternatively, gasification of solid fuel derived char (from devolatisation in inert gas) significantly simplifies the process. This is particularly suitable for solid fuels such as coal, in which char usually makes up a large fraction of the fuel.

1.2.2 Gasification of char with CO$_2$

Gasification of char can either be conducted in steam or CO$_2$. In this dissertation, CO$_2$ is the gasification agent used. The gasification performance is dependent on multiple factors including char type, how the char is prepared (which affects the pore structure and surface area), particle size, gasification temperature, and gasification agent. Liu et al. [46] carried out of gasification of three chars, using CO$_2$ as the gasification agent, with temperatures ranging from 1273 to 1573 K. The three chars, which were prepared by different methods from the same parent coal, were denoted as A, B and C respectively. Char A was prepared from the pyrolysis of the parent coal with a slow heating rate (10 K/min) in a fixed bed reactor at 1173 K for 30 min. Char B was prepared by feeding the coal through in a drop tube furnace at 1373 K. Char C was prepared by firstly being demineralised with HF and HCl, followed by the same procedures as char B. Generally, the carbon conversion increased with increasing temperature. The gasification rate versus conversion varied among the three chars, as seen in Fig. 1-2. For char A, the rate decreased with increasing conversion; for char B, at 1573 K, it had a maximum rate at a conversion of ~ 0.27; for char C, at 1373 K, it had a minimum rate at a conversion of ~ 0.42, followed by an increase, whilst at a conversion of ~ 0.8, it dropped again. At higher temperatures, the rate curves always reached a maximum value (parabolic trend).
The difference in the rates was caused by variation in the structure and surface area of the char due to the preparation methods, as well as the minerals present. The coal type also has a strong influence on the reactivity of the char. Beamish et al. [47] examined the reactivity of 18 types of chars with particle size of ~ 220 µm, produced from lignite to high volatile bituminous coals in a Thermogravimetric Analyser (TGA) with CO as the gasification agent. The high volatile bituminous coal derived chars showed 20 - 30 times higher reactivity than most subbituminous coal-derived chars. The reactivity difference
between lignite coal char and subbituminous coal chars was small, despite a difference in volatile matter of \( \sim 10 \) wt.% (\( \sim 60 \) wt.% for lignite coal and \( \sim 50 \) wt.% for subbituminous coal), which indicates an insignificant effect of volatile matter on the reactivity. Char reactivity was also found to show a strong correlation with the calcium content: higher calcium content (than other metal elements including Mn, Fe, Na and P) results in higher reactivity. Additionally, the form of calcium also matters.

Amongst the several factors, the most important one affecting the gasification rate is the operating temperature. A change in temperatures can alter the rate-limiting factor in the overall reaction. The gasification process can be controlled by the reaction rate (kinetically controlled), intra-particle mass-transfer, or external mass-transfer, described as regimes I, II, and III, as follows [45].

Regime I: this is normally a low-temperature regime, where the chemical reaction rate is the rate-controlling step and the experimentally observed activation energy is the intrinsic activation energy of the reaction.

Regime II: a medium-temperature regime, where the chemical reaction is limited by intra-particle mass transfer of gas from the particle surface into the particle. The activation energy observed experimentally is about half the intrinsic activation energy.

Regime III: a high-temperature regime, where the chemical reaction is limited by external mass transfer of gas from bulk phase to the surface of the particle. In this situation, the overall gasification rate is dominated by the external mass transfer, and the experimentally obtained activation energy would be close to zero.

The effectiveness factor is introduced to take into account the effect of internal mass transfer resistance. The effectiveness factor \( \eta \) is defined as:

\[
\eta = \frac{\text{the observed reaction rate } r_{\text{obs}}}{\text{the rate without mass transfer restriction } r_{k}}, \quad \text{Equation 1-1}
\]

when \( \eta = 1 \), this means the overall reaction rate is not affected by diffusion. Thiele modulus, \( \phi \), is another dimensionless number, which was developed by Ernest Thiele
(paper: relation between catalytic activity and size of particle, 1939) to describe the relationship between diffusion and reaction rate in a porous catalyst pellet without mass transfer limitation, \( i.e. \phi = \frac{\text{reaction rate}}{\text{diffusion rate}} \). For a spherical particle and first order reaction, the following relationship between the effectiveness factor [48] and the Thiele modulus [49] can be obtained:

\[
\eta = \frac{3}{\phi} \left[ \frac{1}{\tanh(\phi)} - \frac{1}{\phi} \right],
\]

Equation 1-2

where

\[
\phi = R \sqrt{\frac{k}{D}}.
\]

Equation 1-3

\( R \) is the sphere radius, \( k \) is the volumetric rate constant and \( D \) is the diffusion coefficient. When \( \phi \) is very small (<0.1), \( \eta \) is around 1, resulting \( r_{\text{obs}} = r_s \). When \( \phi \) is much larger than 0.1, \( \eta \approx \frac{3}{\phi} \), in which case the diffusion limitation is significant, and the particle is in regime II.

Equation 1-2 should only really be applied to the case where the solid is not itself consumed by the reaction (i.e. catalytic). For non-catalytic reactions, in the limiting cases of \( \phi < 0.1 \) and for the case where the reaction rate is independent of the state of the solid, it is correct to apply Eq. 1-2. For high \( \phi \), the reactant does not reach the centre of the particle and the reaction is confined to a thin surface front which burns inwards, with material consumed at a rate of \( \frac{3}{\phi} \) times that, if the reaction was uniform throughout. Shrinking core is proposed to describe the reaction in regime II, where instead of general rate constant, an effective shrinking core rate constant

\[
k' = \eta \cdot k = \frac{3}{R} \sqrt{kD}
\]

is used, and it is only approximately correct. The reaction rate constant is a strong function of temperature. An increase in temperature increases the reaction rate constant. As a consequence, the Thiele module can increase with temperature and the effectiveness
factor decreases. Increasing particle size can also lead to a lower effectiveness factor. Therefore, changes in operating temperature and particle size can alter the controlling regime. Usually, the temperature effect is more significant. Hodge et al. [50] measured char gasification rates under CO, from 1273 to 1673 K. Observed activation energies of 78 to 156 kJ/mol at higher temperatures, and 242 to 281 kJ/mol at lower temperatures were observed, indicating internal diffusion limitations at higher temperatures. The change in the gasification rate when in different fuel sizes is often used to experimentally examine the presence of mass transfer limitation. Saucedo et al. [14] investigated different regimes of the gasification of a lignite char. At a temperature of 1173 K, changing the char particle size from 800 to 2130 µm led to a noticeable change in the rate of gasification, suggesting the effect of mass transfer limitation. While at 1073 K, it was found that the gasification rate was not a function of fuel size, implying little mass transfer effect.

1.3 Pyrolysis
1.3.1 Introduction to pyrolysis
Pyrolysis is the first step of thermal treatment of solid fuels. It is the processing of fuels in the absence of oxygen or air, and is usually used to produce char, condensable liquid fuels and gaseous products such as CO, H, CH, CO,[51]. Pyrolysis can be classified into conventional, fast and flash pyrolysis, depending on parameters mainly including operating temperature, heating rate and particle size, as indicated in Table 1-2. In pyrolysis, moisture is the first product to leave the fuel, and this happens when the temperature is above 373 K (chemisorbed water needs higher temperature). When the temperature increases further, falling in the range of 395 to 475 K, internal bond breakage and rearrangements occur and free radicals are formed [51,52]. The predominant functional groups in the products are carboxyl, carbonyl and hydroperoxide. Carbon-rich char is a main product of pyrolysis in conventional pyrolysis. If the purpose is to obtain mainly liquid and gaseous products, fast pyrolysis would be suitable; flash pyrolysis is operated to achieve primarily gas-based products [52].

Biomass (studied in Chapter 5), as a relative clean solid fuel when compared to coal, mainly consists of hemicellulose, cellulose, and lignin. The overall performance of pyrolysis is determined by the combined effect of each component’s behavior under
Hemicellulose and cellulose decompose at relatively low temperatures, compared to lignin. Hemicellulose starts to decompose at 470 K, and the process is normally completed by 530 K. The decomposition temperature of cellulose is in the range of 510 to 620 K, and that of lignin is between 550 and 770 K [51].

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Conventional pyrolysis</th>
<th>Fast pyrolysis</th>
<th>Flash pyrolysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrolysis temperature (K)</td>
<td>550 - 950</td>
<td>850 - 1250</td>
<td>1050 - 1300</td>
</tr>
<tr>
<td>Heating rate (K/s)</td>
<td>0.1 - 1.0</td>
<td>10 - 200</td>
<td>&gt; 1000</td>
</tr>
<tr>
<td>Particle size (mm)</td>
<td>5 - 50</td>
<td>&lt; 1</td>
<td>&lt; 0.240</td>
</tr>
<tr>
<td>Solid residence time (s)</td>
<td>450 - 550</td>
<td>0.5 - 10</td>
<td>&lt; 0.5</td>
</tr>
</tbody>
</table>

Pyrolysis is not a single reaction but a complicated process involving multiple physical and chemical transformations. A large variety of product species are formed during pyrolysis, and secondary reactions make the process even more complex. Pyrolysis was initially considered to consist of primary and secondary reactions [54]. For instance, biomass is firstly pyrolysed into non-condensable gases, volatiles and char, through the primary reactions. Some of the produced volatiles can further decompose into gaseous products and char through secondary reactions. Typically, primary reactions are endothermic, and secondary reactions are normally exothermic. Koufopanos et al. [55] proposed a mechanism in which biomass firstly decomposes into a mixture of gases and volatiles, and char. This is then followed by reactions between gaseous products (non-condensable gases and tar) and solid char. This approach attempts to hide the complexity of pyrolysis by grouping components into loose categories.

Miller and Bellan [56], on the other hand, suggested that different fractions of biomass (cellulose, hemicellulose and lignin) firstly produce some intermediates, which then decompose into char, gas and tar. The tar generated can further decompose to gases. Other mechanisms have been proposed to explain the effect of process conditions on both the kinetics of pyrolysis and the yields of the products [51,57], but pyrolysis is still not fully understood.
1.3.2 Pyrolysis products

The main products obtained from pyrolysis are char, non-condensable gases, and condensable volatiles (which usually become viscous tar below 473 K). Tar consists of more than 300 compounds, containing functional groups such as carboxyls, carbonyls and phenolics [58]. Due to its complicated composition, it is always a challenge to fully understand its properties because of interactions between each individual compound. The relationship between tar yield and operating conditions, however, can be determined from experimental results. Maximum tar yield occurs in a temperature range between 623 and 773 K [51,52]. When temperature increases further, heavy molecules present in the char and liquid can be further broken down, causing an increase in the overall amount of gaseous product [52]. Therefore, as temperature rises, the yield of tar is always a combined effect of more heavy carbon-based material going to tar, and certain fractions of the tar being decomposed into gaseous products. The yield of char can be maximised using a relatively low temperature and a slow heating rate. A study of the effect of temperature on bio-char yield was carried out by Rocha et al. [59]. In the low temperature range of 723 to 773 K, the gravimetric yield of char was between 12 wt.% to 14 wt.%.

When the temperature increased to above 923 K, the yield dropped significantly to < 7 wt.%.. To maximise the gaseous products, it is widely accepted that high temperatures and high heating rates would help [57,60,61]. For each individual gaseous species, the yields with temperature differ. Normally, an increase in temperature favours the production of syngas. Kantarelis and Zabaniotou [62] studied fast pyrolysis of cotton stalks in a fixed bed reactor between 673 and 1033 K. Their results showed that the overall gas yield increased with temperature; the H, content increased significantly from 18 vol% to 39 vol% of the total gaseous products as the temperature increased from 673 to 1033 K, whilst CO, dropped sharply. CH, showed a maximum yield at 773 K.

1.3.3 Removal of biomass tar

The formation of unwanted condensable products (when it is not the target product of the process, such as bio-oil), i.e. tar, is one of the main issues in the pyrolysis and gasification of biomass. Considerable efforts have been put into the reduction and removal of tar [51,63–66]. Tar removal approaches can be categorised into primary and secondary methods [67]. Primary approaches refer to those treatments inside the gasifier and aim to
reduce the formation of the produced tar from the gasification process \textit{in situ}. Secondary approaches are methods to remove the tar formed after gasification. Tar can be removed either physically or chemically. In primary approaches, since less tar is formed, it reduces the load on downstream processes. Secondary approaches are often reported to be more effective in tar removal but they normally require extra units for specific treatment [65].

- **Primary tar removal methods**

Inside a gasifier, the formation of tar can be minimised by adjusting the operating conditions, selection of proper catalysts, or modification of the gasifier design [65]. High temperatures and pressures are preferred to achieve a high conversion of biomass carbon and low tar content in the off-gas. Operating temperatures above 1073 K are usually required for gasification for a clean gaseous product stream, and higher temperatures also lead to fewer species of tar formed [68–70]. Knight [71] studied pressurised gasification of wood chips up to 21.4 bar. High pressures significantly decreased the amount of tar, and at 21.4 bar, there was nearly no phenol (which was found at lower pressures) detected. The presence of the gasification agent itself is also able to decrease the tar yield due to reforming reactions, \textit{e.g.} CO$_2$ reforming to give CH$_4$ and CO as the primary reforming products [72,73]. In the absence of catalysts, CO$_2$ normally starts to reform tar at temperatures higher than 823 K [74]. The nature of the gasification agent (\textit{e.g.} H$_2$O and O$_2$) can also affect the compositions and quantity of the gaseous products [65].

Adopting catalysts inside the gasifier is an effective way of affecting the reactions, and thus the products. The presence of catalysts can promote the gasification of char, change the compositions of gaseous products and reduce tar formation [65]. Commonly-used catalysts for tar reduction are zeolites, olivine, iron or Ni-based catalysts and dolomite [67]. Corella \textit{et al.} [75] reported a reduction of tar yield from 6.5 wt.% to 1.3 wt.% in the presence of dolomite. Corella \textit{et al.} [76] further found that dolomite did not significantly alter the amounts of the CH$_4$ and C$_2$H$_n$ produced, but increased the amount of H$_2$ and decreased the amount of CO. However, dolomite is friable, and thus not suitable for fluidised systems [65]. Olivine was shown to be more resistant, and has comparable catalytic performance to dolomite [77]. Ni-based catalysts are also reported to have good performance in tar abatement and the improving the yield of hydrogen, whilst a negative side of Ni is its easy deactivation [78]. Deactivation can be reduced by adjusting the
operating conditions, e.g. increasing the temperature, or regenerating the catalyst through burn-off if possible. In general, the catalyst to be used inside the primary reactor should meet following criteria: 1) high tar reduction efficiency; 2) high resistance to deactivation at operating temperatures (> 1073 K); 3) high mechanical strength in fluidised system. Ideally, the catalyst should also be inexpensive, less likely to sinter at the operating temperature and be easily regenerated. Nickel is attractive, in some respects, but is expensive and is a carcinogen, meaning its use in fluidised system could be problematic (owing to its loss in the fines elutriated from the bed).

- **Secondary approaches to tar removal**

Physical or mechanical removal of tar after gasifiers employs extra units to capture the tar in the downstream. These units can be a filter, cyclone, electrostatic precipitator, or scrubber etc. [67]. Physical methods normally operate at low temperatures at which the tar condenses (e.g. 473 – 573 K). Chemical approaches are aimed at completing the conversion of tar formed from the upstream into more desirable components, and they normally take place in a second reactor. Cracking techniques are more frequently used and the commonly-studied approaches include thermal cracking, catalytic cracking, plasma cracking or a combination thereof. Thermal cracking, by definition, uses a high temperature (usually above 1273 K) to crack the tar into lighter gaseous products. The catalysts used in the primary reactor for tar reduction can also be employed in the downstream to decrease the temperature needed for thermal cracking. The desired properties for catalysts in a downstream tar conversion unit are similar to those in the primary reactor, except that high mechanical strength might not be required as the catalyst bed inside the secondary tar removal reactor is normally fixed [67]. Plasma cracking, which is essentially using plasma to breakdown the tar, is usually achieved by thermal, or arc plasma (refer to 1.4 for the new terminology). It has comparable tar destruction efficiency to incineration process, making it highly attractive [79]. In addition to direct plasma cracking, other processes such as reforming of tar in waste air stream by plasma reactors to reduce the tar have also been widely studied recently, and more description regarding this is presented in 1.4.
1.4 Plasma
In recent decades, plasma has attracted intensive interest in the field of chemical engineering, due to its excellent capability of stimulating chemical reactions [80]. Plasma, known as the fourth state of matter (other states are solid, liquid and gas), is an ionised gas, where free electrons are formed as a result of ionisation. The ions and electrons coexist, with the overall plasma being neutral. The energy required for creating plasma can be from thermal heating, electric discharge, or electromagnetic fields. Plasmas are subdivided into thermal and non-thermal plasma. The latter refers to a condition where the temperature of the heavy particles, ions and electrons are the same, i.e. they are in thermal equilibrium. An electric arc is an example of thermal plasma [80]. In a non-thermal plasma the temperature of electrons is much higher than that of the heavy particles and ions, resulting in a non-equilibrium system. Practically, non-thermal plasma is more frequently used because [81]: 1) electromagnetic fields naturally transport charged species, resulting in their concentrations and energies varying in space. This means that it would be difficult to have a system in perfect thermal equilibrium; 2) it is more energy-efficient to feed the energy only to the extent that could effectively create the desired products for a particular reaction, rather than bringing the whole system to the equilibrium.

Plasma was initially mainly used for ozone generation, and it has been studied since the 19th century. In the late 1990s, researchers started to apply this technology, mainly non-thermal plasma, in the destruction of harmful compounds in air (i.e. mainly NOx) [82,83] and synthesis of products from hydrocarbons [84,85], which otherwise would require high temperature or pressure. Prieto et al. [86,87] carried out work to understand the possibility of converting heavy oils to light hydrocarbons in a plate-plate type plasma reactor using argon as a carrier gas. The heavy oil was converted into product species including CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}, C\textsubscript{3}H\textsubscript{6}, and C\textsubscript{4}H\textsubscript{10}. Their study, for the first time, demonstrated the possibility of using a plasma reactor to crack heavy oils at ambient temperature and pressure, and showed significant selectivity towards ethylene. Plasma reactors were later studied for the destruction of volatile organic compounds (VOCs), or tar as unwanted product, based on toluene, xylene and benzene as model compounds [88,89]. The group at University College London has studied a coupled fluidised bed-plasma system for gasification of waste [90–92], including the removal of tar. A plasma converter, operated at ~ 1473 K, was positioned after the gasifier to convert the products primarily to syngas.
Tar measurement was carried out off-line. The tar removal efficiency was obtained by taking the difference in the tar level before, and after the plasma converter. The system processed a continuous feed flow rate of up to 100 kg/h of waste, and showed very effective removal of tar compounds in the presence of thermal plasma. Voltage supply, fuel concentrations, carrier flow rate, distance between the two electrodes and frequency are the main factors influencing the removal efficiency. Other aspects of recent interest for employing plasma include reforming of fuels (e.g. H₂ production from CH₄, reforming in plasma reactors), surface treatment of materials, sterilisation, and etc. [80]. The application of plasma for H₂ production is described in 1.5.3. Other applications are beyond the interest of this dissertation, and thus not reviewed. Here, the operating temperatures of interest are rather low, compared to those for thermal plasma, as the focus is on non-thermal plasma. The application of such plasma to the conversion and removal of VOCs, or tar, is reviewed below.

1.4.1 Dielectric barrier discharge (DBD) and its application on tar removal

The most common configurations of non-thermal plasma used are corona discharge and dielectric barrier discharge [80]. In a corona discharge, the discharge expands from the pinpoint of the high voltage electrode to the outer space, as shown in Fig. 1-3. A corona region is a pattern of bright sparks near the pinpoint. This is also where ionisation occurs. Outside this ionisation region, the electric field is low, and current is only carried by electron drift. Only dark discharge is seen in the drift region. The plasma formed in corona discharge, therefore, has poor uniformity and contains sparks. Sparks can lead to local over-heating and noises, and thus need to be avoided in many applications.

![Illustration of corona discharge](image)

Figure 1-3 Illustration of corona discharge.
In a DBD, at least one barrier material is employed between the two electrodes. Figure 1-4 shows several typical configurations of DBD reactors including planar and cylindrical types. Typical potential change of a plate type DBD reactor is presented in Fig. 1-5. The discharge builds up on the surface of the barrier, which creates a reverse electric field. As a result, in order to have a strong enough electric field to break down the gases passing through the gap, a higher voltage is needed [93]. However, a DBD can create a more homogenous discharge by spreading micro-discharges over the electrode surface, and arcing can also be avoided by selecting proper dielectric materials. In general, DBD has two advantages over corona discharge [94]: 1) the formation of arc is avoided or lessened; 2) higher probability of collision between electron, ions and molecules due to more homogenous distribution of plasma. Popular materials used for the dielectric barrier are glass, quartz, alumina and ceramics [94].

![Figure 1-4 Typical configurations of DBD reactors.](image-url)
DBD technology was originally developed by Siemens in 1857 [93]. It involved a double-walled cylindrical glass tube, with gas flowing though the gap between the inner and outer walls. The two electrodes were positioned inside the inner tube and outside the outer tube. The purpose of this reactor was to generate ozone from atmospheric air. The Siemens tube was quickly found to be an ideal reactor for decomposing gases without excess heat. It has now become a promising technology for abatement of VOCs from waste air [88]. To improve the removal efficiency, catalysts (mostly Ag, Mn, Ce, Cu, Mn, Fe, Ni, Zn based) have been loaded within a DBD reactor [88,96–100]. Most of the experimental studies of the removal of VOCs, or tar, using DBD employ toluene, benzene, xylene, or a mixture of the three as a model compound. On the other hand, because tar consists of a wide range of compounds, besides the three above, it would be interesting to investigate the tar removal efficiency of a product stream containing actual tar compounds from thermal treatment (e.g. combustor, fluidised reactor etc.). This has been actively studied in the field of waste-to-energy [67], though more by thermal plasma approach [90–92].

1.4.2 Plasma chemistry
As an ionised gas, ionisation is always the first reaction to consider in plasma. Due to the low mass and high mobility of electrons, they are always the first to get energy from electric fields. The energy can then be transferred to all other plasma components to support ionisation, excitation, dissociation and other plasma-chemical processes. The rate
of such processes depends on the number of electrons available to transfer the energy. There are mainly five mechanisms for ionisation [101]: direct ionisation by electron impact (DIEI), stepwise ionisation by electron impact (SIEI), ionisation by collision of heavy particles (ICHP), photo-ionisation (PI) and surface ionisation (SI). DIEI is considered an important process in non-thermal discharge, where electric fields and electron energies are quite high, but the excitation level of neutral species is relatively moderate. DIEI is the ionisation of neutral and previously unexcited species (i.e. atoms, radicals, or molecules) by an electron, whose energy is high enough to stimulate the ionisation act in one collision. The ionisation occurs when the energy ∆E transferred by an incident electron with a high energy of E, to the valence electron exceeds the ionisation potential.

When the concentration of excited neutrals is high enough, the energy required for ionisation can also be directly transferred to the preliminary electronically excited neutrals by colliding with electrons, and this is known as SIEI. When the level of electronic excitation is high enough, the probability of obtaining ionisation energy for free electron is much lower than that for excited neutrals. Compared to direct electron ionisation, SIEI is composed of more than one step. Initially, neutrals need to obtain energy from an electron-neutral collision so as to become excited; and this is followed by a collision with a relatively low-energy electron to cause the actual ionisation. For the direct collision of the heavy particles (ions and neutrals), acquiring energy that is high enough for ionisation does not guarantee an effective ionisation event. This is mainly due to their low velocities. Regardless of having enough energy, it is very difficult for a heavy particle to transfer this energy to an electron (which is moving very fast) inside an atom. This suggests that heavy particles must have a high kinetic energy for ICHP.

Beside electron collision, the energy for ionisation can also be supplied by a photon. The wavelength of such photons is usually less than 100 nm (ultraviolet radiation). However, the contribution of photo-ionisation process is usually not significant in plasma systems due to low concentrations of high-energy photons. Surface ionisation is when collisions happen between electrons, ions, and photons with surfaces. The surface-related ionisation is very different from the aforementioned four mechanisms, and beyond the scope of the interest here.
1.5 Production of hydrogen

Hydrogen, is a clean energy source in the sense that it does not generate CO or CO₂ when being consumed. Its high heating value (on a mass basis) also makes it advantageous than other fuels in some applications. At 298 K and 1 atm, the heating value (lower to higher heating values) of H₂ is 120 - 142 MJ/kg, compared to 50 - 55.5 MJ/kg for CH₄, and ~ 45 MJ/kg for diesel fuel (data from Ref. [102]). There are multiple ways of producing H₂, including steam reforming of methane or other hydrocarbons, chemical looping reforming, gasification of solid fuels, reforming of oil, water splitting/dissociation through electrolysis, chemical approach or high temperature, plasma (-assisted) decomposition etc. [103]. Introduction of the main techniques relevant to this work are presented as follow.

1.5.1 Steam reforming of methane (SRM)

Steam reforming of natural gas, mainly methane, is the most common and cheapest (with an energy cost of below 160 MJ/kg of hydrogen produced [104]) industrial process used for the production of H₂. It makes up about 50% of the total H₂ production [103]. The operating temperatures of the reformer, where the main reaction (\( \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO} \)) takes place, is usually above 1073 K [105]. Catalysts can be employed in the reformer to lower the processing temperature or/and increase the yield of H₂.

The research on SRM dates back to 19th century, when SRM over Ni-based catalyst was first reported and patented [106]. Later on, in the early 20th century, other catalysts, including iron, cobalt, promoted nickel, alkali, and alkaline earths were found effective in reducing the operating temperature of SRM [106]. Owing to the good performance of Ni-based catalysts, SRM over Ni for H₂ production has been widely investigated and utilised. Some catalysts such as rhodium and ruthenium, have been reported more catalytically active for SRM [107]; while their applications are limited by the high cost. For these reasons, Ni-based catalysts are more practically used. However, deactivation of Ni, is often an issue in the reforming of hydrocarbons. The deactivation mainly results from oxidation of Ni to NiO, poisoning of the surface active sites, or coking over the Ni-based materials [108]. A significant amount of work has been carried out to eliminate the deactivation of Ni. Alkali was found helpful for suppressing the formation of coke, as it could neutralise the acidic sites active for cracking on the support, and promote the
reaction between coke and steam [108]. Other methods for eliminating the coking include selection of appropriate supports, and modification of the characteristics of the material such as particle size, surface area, and etc. [109]. In terms of the oxidation of Ni for deactivation, Matsumura and Nakamori [110] studied SRM over Ni catalyst on various supports (i.e. silica, $\gamma$-alumina, and zirconia) at 773 K, much lower than the temperature for conventional SRM. Metallic phase Ni on the silica and zirconia were obtained by reducing the calcined (prepared at 973 K) materials in H$_2$ at 773 K; whilst Ni/$\gamma$-alumina was only obtained by reduction at a higher temperature, 973 K. When reforming by steam at 773 K, the activity of Ni/silica was found to decrease due to the oxidation of nickel, similarly, Ni/$\gamma$-alumina particles were also partially oxidised; Ni/ZrO$_2$ was found the most effective in H$_2$ production, and no significant deactivation was observed. The accumulated hydroxyl groups on the surface of the ZrO$_2$ support was believed to be responsible for the high yield of H$_2$. From the perspective of the processing parameters, to improve the purity of H$_2$ in the product stream and eliminate carbon from SRM, a high steam to CH$_4$ ratio can be adopted. For this reason, the ratio of H$_2$O to CH$_4$ as feedstock is usually controlled at 2.5 to 3 [111].

In addition to the participation of catalysts, a water-gas shift step (H$_2$O + CO $\rightarrow$ H$_2$ + CO$_2$) is usually employed downstream for SRM plants to increase the yield of H$_2$. Due to the exothermic nature of the water-gas shift reaction (WGSR), it is usually operated at temperatures of around 673 K. As a whole, H$_2$ production from CH$_4$ steam reforming plants often requires multiple stages, making the process more appropriate for large scale H$_2$ production and not requiring high H$_2$ purity.

1.5.2 Chemical looping reforming of CH$_4$

Chemical looping reforming techniques have been studied, following the rise of research interest in CLC. Similar to CLC, the reforming techniques under the chemical looping concept normally requires two inter-connected reactors, with an operating temperature usually above 973 K [112,113]. There are two schemes for employing chemical looping technology for the reforming of methane, or other hydrocarbons [13]. The first is to integrate reforming (e.g. with steam) process with chemical looping combustion (SR-CLC), as first proposed by Ryden and Lyngfelt [114]. In this process, SR of hydrocarbons to H$_2$-rich gas would take place in a tubular reactor through conventional catalytic
processes. It differs from conventional reforming by employing a CLC system to provide heat for the reformer (positioned inside a fluidised bed) externally. The reduced oxygen carriers were sent to an air reactor for re-oxidation, similar to conventional CLC. The second scheme is auto-thermal chemical looping reforming (a-CLR). The generation of H₂ from CH₄ by oxygen carriers takes place in the fuel reactor; and re-oxidation of the reduced oxygen carriers happens in a separate regeneration reactor. Instead of regeneration of the materials in air for CLC, CO₂ or steam is usually used for the re-oxidation as this helps improve the yield of H₂. Another advantage of using steam is that it allows high purity H₂ to be produced.

Compared to SR-CLC, a-CLR has the advantage of avoiding the need for a complex or extra unit to supply heat for the reforming process. However, it has high requirements for the oxygen carriers to be used. A good selectivity of oxygen carrier for the generation of H₂-rich gas is a crucial criterion for material screening. The commonly used oxygen carriers are not much different from those for CLC, mainly including Fe-, Cu-, Ni-, Mn-based metal oxides, and mixed oxides [115]. Ni-based oxygen carriers showed very high selectivity towards H₂-rich gas [116], which is similar to conventional SRM; whereas direct use of Fe-, Cu- and Mn- based oxygen carriers resulted in total combustion, giving mostly CO₂ and H₂O. It was found that the addition of a small portion of NiO (i.e. 1%) into Fe₂O₃ can significantly improve the yield of H₂ and CO [117]. Other than conventional oxygen carriers, some perovskites were also found to show promising results for the partial oxidation of CH₄, for H₂ and syngas production. Such perovskites include La,Sr,Fe,Co,O₃,La,Sr,FeO₃,LaFeO₃ and etc. [112]. As found in the study [112], the addition of a small amount of NiO (~ 5%) onto the perovskite structure was found significantly improved H₂ yield, similar to the synergistic effect of adding NiO to Fe₂O₃. On the other hand, the preparation of such perovskite structures is costly and time-consuming. The non-stoichiometry in the obtained samples is also very hard to control, which brings the difficulty in maintaining high homogeneity of bed materials from different batches.

In general, the production of H₂ from chemical looping reforming currently is under research stage, though intensive work on this has been ongoing. The application of this technology at an industrial scale still requires more effort. Most of the current research has been focused on material selection and preparation. Whilst, holistic understanding of the actual energy and financial cost for the application of such technology is important for determining the feasibility of the technology.
1.5.3 Plasma-involved processes for H\textsubscript{2} production from CH\textsubscript{4}.

Conventional thermo-catalytic technologies for H\textsubscript{2} production from CH\textsubscript{4} are more suited for large scale production due to the need of large equipment size or complex operating systems, and usually high metal/metal oxides capacity. For small and medium-scale H\textsubscript{2} production, other approaches could be more advantageous. In such a scenario, the concept of using plasma for hydrogen production becomes increasingly attractive. The application of plasma for H\textsubscript{2}-rich gas production from CH\textsubscript{4} can be mainly classified into three categories: 1). direct cracking of CH\textsubscript{4}; 2). reforming of CH\textsubscript{4}; 3). partial oxidation of CH\textsubscript{4} [101]. For the first approach, plasma is used to directly dissociate CH\textsubscript{4} into H\textsubscript{2} and carbon black (soot). The H\textsubscript{2} can be collected, whereas the carbon in solid phase usually remains inside the reactor. This process results in CO-rich gas products, and ideally the carbon black should be collected as a useful product.

Practically, complete collection of the solid carbon is difficult, especially when catalysts are employed to assist the cracking, leading to energy loss (in carbon) and deactivation of the catalyst. The accumulation of solid carbon inside the plasma reactor, depending on the form of carbon, can also be problematic. The accumulated carbon can potentially affect the electric field and consequently affect the formation of plasma. Furthermore, the highly endothermic nature of the cracking reaction, which requires a substantial amount of energy input, also limits the use of such scheme for H\textsubscript{2} production [118].

Compared to the direct decomposition of CH\textsubscript{4}, the other two approaches, reforming and partial oxidation of CH\textsubscript{4}, by plasma, have been studied to a wider extent, particularly in non-thermal plasma reactors, e.g. DBD reactors [101,119–122]. For the reforming process in plasma, it is essentially putting the conventional reforming of CH\textsubscript{4}, either in CO or steam, in a plasma-assisted reactor. The advantage of such process is that it allows the reforming process to happen at low temperature, where the selectivity towards H\textsubscript{2}-rich gas is favored, but the reaction rate can be speeded up by plasma. The adoption of catalysts, usually solid particles, not only improves the conversion and H\textsubscript{2} production, but also helps easier formation and stabilisation of plasma. Tu et al. [123] studied dry reforming of methane (DRM) over a Ni/Al\textsubscript{2}O\textsubscript{3} catalyst in a DBD reactor. The bed material fully packed the plasma discharge zone. It was found that by adding the catalyst pellets, the discharge mode switched from filamentary micro-discharge to predominant surface discharge on the catalyst surface (and a small zone of micro-discharges between the catalyst and the quartz wall). This change in the discharge mode should be beneficial as
it increases the chances of chemical interaction between the gas phase and solid surface. The breakdown voltage, which is the minimum voltage required for a system/substance to become conductive, also decreased significantly when the bed was fully packed. Besides, the use of Ni-based catalyst significantly improved the yield of H₂, giving an increased H₂/CO mole ratio from 0.84 to 2.53. Additionally, the presence of Ni was found to widen the distribution of discharge across the bed, suggesting the conductive Ni active sites help the spread and expand the discharge over the catalyst surface. When introducing the catalysts, the position of packed catalytic zone is also important. Wang et al. [124] at Tsinghua University studied the effect of three packing modes of the commercial catalyst Ni/Al₂O₃ in a DBD system for DRM from 573 to 773 K. The three contact modes were a) catalyst (fixed by quartz wool on the two sides) positioned in the downstream of the plasma discharge zone in the reactor, where the plasma discharge was not externally heated; b) catalyst positioned just next to the plasma discharge zone, where both the plasma discharge zone and the catalyst were externally heated; c) the catalyst zone and discharge zone fully overlapped each other and externally heated. The results showed that mode c) exhibited the best conversion of CH₄, as well as the selectivity to CO and H₂. Similar to conventional reforming approaches, carbon deposition was commonly found in reforming in DBD reactors. The group at Tsinghua University [119] further studied the effect of introducing steam into the CO, reforming of CH₄ in the DBD reactor, and found that the addition of steam helped reduce the degree of carbon deposition. They considered the removing effect due to the steam gasification of the solid carbon. On the other hand, the endothermic nature of the reforming process means that it also requires external energy input. The other drawback is that the use of a reforming gas (CO₂, or H₂O) causes burden on later separation process, and reduces the purity of H₂.

For the partial oxidation of CH₄ in similar non-thermal plasma reactors, where typically a gaseous oxygen stream is fed to the reactor, it exhibits the advantage of its exothermic nature of the oxidation process [101]. The need of a pure oxygen stream requires some oxygen-making process, and this increases the energy penalty. However, if the oxygen can be supplied for the oxidation of CH₄ from a solid, and the solids can be regenerated for the continuous or cycling production of H₂, this would be very promising for H₂ production. This is essentially a chemical looping system. Such a concept of a plasma-assisted chemical looping system for H₂ production is therefore proposed and demonstrated in Chapters 6, 7 and 8.
1.5.4 Hydrogen production techniques based on the splitting of water

H₂ production from fossil fuels, such as the SRM and chemical looping reforming of methane, always generates environmental emissions, such as CO₂. This leads to the need of looking for H₂ production from a clean and abundant resource, and this concept is known as ‘green hydrogen production’ [103]. Water, as a rich resource on the earth, can be a promising candidate. In the past several decades, there has been a large body of work on H₂ production from water splitting. The most mature technique that has been used is the water electrolysis. ~ 3.9% of the total H₂ production worldwide is from water electrolysis [125], and it is currently the most common industrial process for generating pure hydrogen [103]. Water is decomposed to H₂ and O₂ by an external circuit. Typical electrolysers for water electrolysis are solid oxide (SOE), alkaline (AE), and polymer electrolyte membrane electrolysers (PEME), where AE is the most mature technique and usually produces hydrogen with a purity over 99.8%. Catalyst such as platinum, are often adopted to improve the rate of electrolysis. The main limitation for expanding the application of this technology is its high cost. This not only comes from the electricity (which has probably come from a fossil fuel, and thus greener than expected) and the expensive catalyst, but also some pre-treatment process. The electrolysers are sensitive to the purity of water used, otherwise, side reactions would dominate in electrolysis. For this reason, purification prior to the actual electrolysis is required, leading to a significant increase in the operating cost of this technology [126].

Thermal decomposition of water, which uses heat to split water into H₂ and O₂, has also been studied for H₂ production. This approach requires extremely high temperature, which is normally above 2500 K, and only at above 3000 K is the decomposition significant (> 50% conversion of water) [127]. This brings technical difficulty for the separation of H₂ and O₂. The membranes for the separation cannot stand such high temperature, thus the mixed H₂ and O₂ requires cooling before being separated. Materials, therefore, become the main constraint limiting the application of this technology. Another technique for water splitting for H₂ production is the S-I cycle, a thermochemical way for obtaining H₂ from water. The cycle requires following steps of R. 1-3 to R.1-6 [103].

\[
\text{H}_2\text{SO}_4(aq) \overset{(573 \text{ to } 773 \text{ K})}{\longrightarrow} \text{H}_2\text{O}(g) + \text{SO}_3(g) \quad \text{R. 1-3}
\]
A big advantage of S-I cycle it that it avoids the need for catalysts and separation membranes. It is operated at reasonable temperature range and requires low energy input. However, the technical and commercial viability needs further confirmation. There are many other water splitting techniques such as photocatalytic approach, high-temperature electrolysis, dark fermentation and etc. [103], where most of them are currently under R&D stage, with their practical application limited by the extremely high cost or low energy efficiency.

1.6 Objectives and structure of the dissertation

The aim of the dissertation was to investigate the conversion of various fuels in the presence of oxygen carries, so as to understand how the oxygen carriers would affect the conversion of fuels in situ. Depending on the type of fuels, the conversion techniques and so as the operating conditions could vary. For the solid fuels like coal char, as direct solid-solid reaction between the oxygen carriers and the fuel is impossible, a gasification step, or CLOU material is needed. Here, CO₂ gasification of a Polish coal-derived char was carried out prior to the reaction with the oxygen carriers. The focus of this study was on the influence of the oxygen carriers on the gasification rate. For biomass, as under thermal treatment (i.e. pyrolysis), multiple phases of products can be generated, and these include non-condensable gases (e.g. CO, CO₂, CH₄ etc.), condensable volatiles, and char. The non-condensable and condensable products usually react with the oxygen carriers directly. For biomass, as the composition of char is usually low and under such scenario, it is possible to employ oxygen carriers such as Fe₂O₃ to achieve good conversion of the pyrolysis products. For purely gaseous fuels such as CH₄, chemical looping combustion of CH₄ at operating temperatures at above 800°C have been studied to a wide extent including total combustion and chemical looping for H₂ production from CH₄ can be obtained. Lowering the operating temperature for the conversion of gaseous fuels by oxygen carriers becomes attractive in this case, particularly for H₂-rich gas production, where the forward water-gas shift reaction is favored, leading to more production of H₂.
This initiated the idea of using plasma-assisted system for the purpose of decreasing the operating temperature but still allows the chemical reactions to take place. This constitutes the second part (i.e. chemical looping conversion of fuels at mild temperatures, as presented in chapters 6, 7, and 8) of the dissertation. A plasma-assisted chemical looping system at mild temperatures for H₂ production from CH₄ was proposed and investigated. The aim was to have a system which

(1) could be operated at milder temperature (e.g. ≤ 773 K) than those for conventional H₂ production techniques,
(2) could achieve H₂ production in a single step,
(3) would run comparable energy penalty in reference to other existing H₂ production techniques (e.g. 320 to 510 MJ/kg for water electrolysis).

The structure of this dissertation is as follows. Chapter 2 illustrates the experimental set-up used in this work, and describes the methodologies of material preparation, experimental procedures and sample characterisation. Chapter 3 presents in situ CO₂ gasification of a Polish coal-derived char in the presence of Fe-based oxygen carriers. A kinetic model to describe the CO₂ gasification of the char was developed in Chapter 4. In addition to understanding the rate of char gasification by CO₂, Chapter 4 further investigated the inhibition effect of CO on CO₂ gasification. Chapter 5 focuses on understanding the effect of oxygen carriers (Fe₂O₃ and mayenite-supported CuO) on the distribution of products from biomass pyrolysis, and the effect of CO₂ on product distribution. For this work a new method of measuring tars was developed, making use of a plasma reactor in the sample line for tar conversion. Chapters 6 to 8 presents the investigation on the development of a plasma-assisted packed bed chemical looping system for H₂ production, wherein Chapter 6 focuses on understanding of the electrical signal of the developed plasma-assisted reactor, Chapter 7 focused on testing H₂ production with the developed system packed with SrFeO₅, a highly active chemical looping agent. Based on the preliminary results on Chapter 7, Chapter 8 further investigated H₂ production with the system packed with Fe-based and Ni-doped oxygen carriers. Finally, conclusions from the current work as well as recommendations for future work are drawn in Chapter 9.
2.0 Experimental methods

2.1 Introduction
The source of chemicals and gases used for experiments, methods for the preparation and characterisation of the materials, the apparatus employed for the research and typical experimental procedures are described in this chapter. Due to the wide range of experimental conditions used in this study, more detailed descriptions about individual experimental conditions and investigations are presented in corresponding chapters.

2.2 Preparation of materials

2.2.1 Sources and specifications of chemicals and gases
Lists of chemicals and gases with specifications are presented in Tables 2-1 and 2-2 respectively. The gases used were supplied by BOC.

Table 2-1 List of chemicals used with specifications from suppliers.

<table>
<thead>
<tr>
<th>Molecular Formula</th>
<th>Specifications</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$-Al$_2$O$_3$</td>
<td>3 mm pellets</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Al(OH)$_3$</td>
<td>Reagent grade, &lt; 5 $\mu$m</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>CaCl$_2$</td>
<td>$\geq 97.0%$, granulated</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Ca(OH)$_2$</td>
<td>$\geq 98%$, &lt; 5 $\mu$m</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>CuO</td>
<td>$\geq 98%$, &lt; 10 $\mu$m</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>$\geq 99.8%$</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>&gt; 95 wt%, &lt; 10 $\mu$m</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>Fe(NO$_3$)$_3$∙9H$_2$O</td>
<td>ACS reagent, $\geq 98$ wt%</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>HNO$_3$</td>
<td>$\geq 99.5%$</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>H$_2$O (de-ionised)</td>
<td>&lt; 1 $\mu$s/cm</td>
<td>Using Pure Lab Prime purifier (ELGA Lab water)</td>
</tr>
<tr>
<td>NaOH</td>
<td>Pellets, extra pure</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Ni(NO$_3$)$_2$∙6H$_2$O</td>
<td>$\geq 98.5%$</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>SrCO$_3$</td>
<td>$\geq 98%$</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Zr(OH)$_4$</td>
<td>$\geq 97$ wt%</td>
<td>Sigma-Aldrich</td>
</tr>
</tbody>
</table>

Table 2-2 List of gases used with grade information from BOC.

<table>
<thead>
<tr>
<th>Gas species</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>$\geq 99.995%$</td>
</tr>
<tr>
<td>N$_2$</td>
<td>$\geq 99.998%$</td>
</tr>
<tr>
<td>Ar</td>
<td>$\geq 99.998%$</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>$\geq 99.5%$</td>
</tr>
<tr>
<td>5 vol% H$_2$ in N$_2$</td>
<td>$\geq 99.999%$</td>
</tr>
<tr>
<td>CO</td>
<td>$\geq 99.90%$</td>
</tr>
<tr>
<td>10 vol% CO in N$_2$</td>
<td>$\geq 99.99%$</td>
</tr>
</tbody>
</table>
2.2.2 Preparation of materials

- Chemicals and sand

Information regarding the materials used in this work including oxygen carriers, fuels and various sand is described in this section. Synthesis of oxygen carriers used methods including mixing, dry-impregnation and co-precipitation.

\(\text{Fe}_2\text{O}_3\)

\(\text{Fe}_2\text{O}_3\) particles were prepared by solid mixing. It started from the granulation of \(\text{Fe}_2\text{O}_3\) powders using de-ionised (DI) water as a binder, with a mass ratio of 10:1 for \(\text{Fe}_2\text{O}_3\) powder to DI water. After mixing in a commercial mixer, the resulting granules were sieved to appropriate size and calcined in air at 1273 K for 6 h in air. Information on the exact fraction size is presented in appropriate sections.

Mayenite-supported \(\text{CuO}\)

Wet mixing approach was employed to prepare mayenite-supported \(\text{CuO}\), following the protocol described by Hu et al. [128]. Typically, 5.61 g of \(\text{Ca(OH)}_2\) and 8.85 g of \(\text{Al(OH)}_3\) powders were mixed with 200 ml of DI water in a 1 L beaker. The resulting slurry was stirred on a hotplate at 313 K for 2 h. 15.00 g of \(\text{CuO}\) powder was then added to the mixture. Further mixing for 20 h was performed, and the obtained mixture was dried in ventilated air at 353 K for 48 h. The dried cake was then crushed and calcined in air at 1273 K for 6 h. The obtained granules were finally sieved to 355 - 425 \(\mu\)m. The resulting mayenite-supported \(\text{CuO}\) particles contain 60 wt% \(\text{CuO}\), 23 wt% \(\text{Al}_2\text{O}_3\), and 17 wt% \(\text{CaO}\).

\(\text{ZrO}_2\)

\(\text{ZrO}_2\) particle was prepared from zirconium (IV) hydroxide \(\text{Zr(OH)}_4\). \(\text{Zr(OH)}_4\), powder was firstly wetted and bound by DI water. The mass ratio of \(\text{Zr(OH)}_4\), to DI water was about 1:4 (i.e. 20 g \(\text{Zr(OH)}_4\), requires around 80 ml DI water). The mixture was agitated with a magnetic stirrer at 353 K for 30 minutes, until a relative homogenous state was observed. The temperature was then increased to 393 K for 4 h to remove the water. Simultaneously, agitation was maintained to avoid phase separation. The resulting \(\text{Zr(OH)}_4\), was dried (without agitation) at 393 K for another 5 h, followed by calcination in air at 1273 K for 6 h. \(\text{Zr(OH)}_4\), would decompose into \(\text{H}_2\text{O}\) and \(\text{ZrO}_2\) at temperatures above 773 K [129].
Therefore, ZrO₂ particles were obtained and finally sieved to a size fraction of 180 μm - 355 μm.

**NiO/Fe₂O₃ and NiFe₂O₄/Fe₂O₃.**
Dry-impregnation method was used to prepare NiO/Fe₂O₃ and NiFe₂O₄/Fe₂O₃. Nickel nitrate hexahydrate, Ni(NO₃)₂·6H₂O, was mixed with Fe₂O₃ (prepared from solid mixing, with particle size of 600 - 850 μm), followed by the addition of DI water to just dissolve the nitrate. The resulting mixture was stirred at 313 K for 20 min, followed by drying at 398 K for 12 h. The dried mixture was then calcined in air at 823 K for 5 h to form NiO/Fe₂O₃, or at 1123 K for 5 h to produce NiFe₂O₄/Fe₂O₃. In both cases, the molar ratio of Ni to the total metal (i.e. Ni + Fe) was about 1:10.

**Al₂O₃, Ni/Al₂O₃, and NiO/Al₂O₃.**
The preparation of Al₂O₃ started with γ-Al₂O₃ pellets being crushed to a size fraction of 600 - 850 μm. The resulting particles were then calcined in air at 1273 K for 6 h. The preparation of NiO/Al₂O₃ followed the same protocol (i.e. dry-impregnation) as that for NiO/Fe₂O₃. The prepared NiO/Al₂O₃ was divided into two equal portions. One portion was used as prepared, i.e. NiO/Al₂O₃. The other portion was reduced in 5 % H₂ at 1073 K for 30 min to obtain Ni/Al₂O₃. Similarly, the resulting Al₂O₃-supported Ni-based particles had a sieve size of 600 - 850 μm, with a Ni to total metal molar ratio of 1:10.

**SrFeO₃-δ and NiO/SrFeO₃-δ.**
SrFeO₃-δ was prepared via solid mixing. Stoichiometric amounts of SrCO₃ and Fe₂O₃ (0.72 mol and 0.36 mol respectively, molar ratio of 2:1) were mixed, and followed by the addition of ethanol, C₂H₅OH, as a binder to improve mixing. The resulting mixture was then ball milled for 3 h at 25 Hz, followed by drying in air at 323 K for 24 h. The resulting particles were calcined in air at 1273 K for 19 h. The preparation of NiO/SrFeO₃-δ followed the dry-impregnation method as for NiO/Fe₂O₃ and NiO/Al₂O₃. The obtained particles were sieved to 600 – 850 μm with a Ni to total metal molar ratio of 1:10.
ZrO$_2$-supported Fe$_3$O$_4$

ZrO$_2$-supported Fe$_3$O$_4$, containing 65 wt% Fe$_3$O$_4$ and 35 wt% ZrO$_2$, was prepared by co-precipitation method. Zirconium (IV) hydroxide power, Zr(OH)$_4$, was firstly ‘dissolved’ in deionised water at 343 K for about 10 minutes to form 0.1 M Zr(OH)$_4$ solution/ dispersion. Around same volumetric amount of 0.5 M nitric acid was slowly added into Zr(OH)$_4$, dispersion. The dispersion was agitated at 343 K for 2 h. Fe(NO$_3$)$_3$·9H$_2$O was then added into the acidic solution (pH = 0.5). NaOH was later added to the solution of nitrates, resulting in precipitates formed in a pH environment of 9.8 ± 0.2. The precipitate was stirred for a further 10 minutes, before aging at room temperature without stirring for another 2 h. Afterwards, the precipitate was washed with DI water until its ionic conductivity fell below 100 $\mu$S cm$^{-1}$, and pH to around 7 to eliminate the presence of free Na$^+$. Then the precipitates were dried in air at 383 K for 40 h. The dried cake was calcined at 1273 K for 6 h, followed by crushing and sieving to the desired particle size fraction (180 - 355 µm).

Silica and alumina sand

Both the received silica sand and alumina sand were washed with DI water, followed by drying at 353 K for 24 h. The particles size fraction for use were 250 - 350 µm for silica sand, and 355 – 425 µm and 600 – 850 µm for alumina sand (for appropriate use).

The material and bulk densities of each material were measured. The bulk density was determined from the weight of a known volume of material. To obtain the material density, the voidage was measured by slowly adding water to a packed bed of sample just to the surface and recording the volume of water added.

- **Solid fuels**

Polish coal-derived char

The coal char was derived from a Polish coal, a brown lignite coal, kindly provided by Institution for Chemical Processing of Coal. Proximate and ultimate analysis data are provided by the institution, as presented in Tables 2-3 and 2-4.
Table 2-3 Proximate analysis of the coal.

<table>
<thead>
<tr>
<th></th>
<th>ad (air-dry) wt%</th>
<th>daf (dry ash free) wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>14.0 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>Volatile</td>
<td>38.09 ± 0.17</td>
<td>53.35 ± 0.25</td>
</tr>
<tr>
<td>Fixed carbon (balanced)</td>
<td>43.31</td>
<td></td>
</tr>
<tr>
<td>Ash</td>
<td>14.6 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>Higher heating value (HHV)</td>
<td>18466 ± 83 kJ/kg</td>
<td></td>
</tr>
<tr>
<td>Lower heating value (LHV)</td>
<td>17471 ± 101 kJ/kg</td>
<td></td>
</tr>
</tbody>
</table>

Table 2-4 Elemental analysis.

<table>
<thead>
<tr>
<th>Element</th>
<th>wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>48.4 ± 0.6</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>2.99 ± 0.27</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.56 ± 0.15</td>
</tr>
<tr>
<td>Oxygen</td>
<td>19.9 ± 0.69</td>
</tr>
<tr>
<td>Sulphur</td>
<td>0.9 ± 0.04</td>
</tr>
</tbody>
</table>

The received Polish coal was air dried for 48 h, followed by mechanical size reduction and sieving to size fraction of 1000 - 2240 μm. Then, the char-making process was carried out in a stainless-steel reactor (illustrated in Fig. 2-1.), fed with 1 L alumina sand (350 - 425 μm, with a material density of 3950 ± 70 kg/m³) as the fluidising bed. N<sub>2</sub> was used to fluidise the bed at a flow rate of around 300 ml/s (all the flow rates in this thesis are expressed at 293 K and 1 atm). The superficial gas velocity was ~ 0.27 m/s, with a ratio of superficial velocity to minimum fluidising velocity, U/U<sub>mf</sub>, of ~ 4.8 (refer to 2.3.1 for the determination of U<sub>mf</sub>). The bed was operated at 1173 K, and the sieved coal was continuously fed into the reactor at a feeding rate of 200 mg/s. The produced volatiles from the reactor were burned in ambient air by a burner, which was positioned above the top of the reactor, as shown in Fig. 2-1. The whole feeding process took about one hour, and the reactor was maintained at 1173 K for another hour to keep relative homogeneity of the solid product. The reactor was then cooled down to ambient temperature in flowing N<sub>2</sub>. The obtained coal char was sieved into desired size fractions including 300 – 425 μm, 425 - 600 μm, 600 - 850 μm, and 850 - 1180 μm. They are stored in sealed bottles and chances of contact with air before use were minimised.
Wood pellets
The received wood pellets were crushed and sieved to a size fraction of 4.0 - 4.2 mm. They were air dried at ambient environment for 24 h prior to use. The elemental analysis results of the wood sample are presented in Table 2-5.

Table 2-5 Elemental analysis.

<table>
<thead>
<tr>
<th>Element</th>
<th>wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>46.33</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>6.12</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.00</td>
</tr>
<tr>
<td>Oxygen (balanced)</td>
<td>47.55</td>
</tr>
</tbody>
</table>

2.3 Apparatus
Experimental set-ups employed and developed include a stainless-steel fluidised bed reactor, a quartz tube fluidised bed reactor, a quartz tube fluidised bed coupled with plasma reactor in the downstream, and a plasma-assisted packed bed reactor. The configurations, and experimental procedures for running each set-up, are described below.

2.3.1 Stainless steel fluidised bed reactor
An electrically-heated, stainless-steel (316) fluidised bed reactor was used for the preparation of the coal-derived char at 1173 K. Figure 2-1 is a schematic diagram of the set-up. The stainless-steel tube (i.d. 78 mm, 1130 mm in height), loaded with 1 L alumina sand, was surrounded by electrical heating coils, which were PID controlled via a K-type thermocouple immersed in the fluidised bed. N, for fluidisation passed through a windbox, a distributor with 37 evenly distributed identical holes (diameter of 0.4 mm), and then to the main body of the bed. An electrical feeder was housed to the top of the tube to feed the coal continuously. A slotted lid with two holes (i.e. one allowing products, and the other for thermocouple to go through), sited on the top of the reactor. A burner was positioned above the top of the reactor to burn off any volatiles, before their entering the extraction system.
2.3.2 Quartz tube fluidised bed reactor

An open-ended quartz tube fluidised bed reactor was used for the investigation of the gasification of the Polish coal-derived char in various bed materials, as well as the study of the CO inhibition effect on the char gasification. A diagram describing the set-up is shown in Fig. 2-2. The quartz tube (i.d. 29 mm), with a porous distributor, was loaded with appropriate solid materials (silica sand, Fe₂O₃, or ZrO₂-supported Fe₂O₃) and externally heated by an electrical furnace. The temperature of the bed was measured by a K-type thermocouple, operated by a PID controller. Flows of gases (N₂, Air, CO or/and CO₂) were controlled by rotameters and solenoid valves (allow for an easy switching of the gases) controlled to enter the quartz reactor. Char sample was introduced from the top of the reactor in batch. The gas at the reactor outlet was sampled and dried by CaCl₂ before entering the gas analyser, Fourier transform infrared (FTIR, Perkin Elmer 100) analyser.

Figure 2-1 Set-up of the stainless steel fluidised bed reactor.
For a typical gasification experiment, 20 ml solid particles (silica sand, Fe₂O₃, or ZrO₂-supported Fe₂O₃) were fed into the reactor in cold. The reactor was then heated up to the desired operating temperature (from 1123 to 1248 K). The bed in the heating up stage was fluidised by air at 50 ml/s. As the operating temperature was reached, the fluidising gas switched from air to N₂ at the same flow rate for 5 min to remove potential oxygen. This was followed by gas switching to the gasification agent, CO₂, at a volumetric concentration from 20% to 100% (balance N₂), at a total flow rate of 50 ml/s. For the investigation of the effect of CO on the gasification of Polish char, the fluidising gas changed from N₂ to a mixed gas stream of 20% CO₂ and various CO concentrations (balance N₂), with other conditions being the same. The fluidised bed was expected to operate in a bubbling regime. The minimum fluidisation velocity of the bed, Uₘᵢ, was estimated from the correlation provided by Wen and Yu [130]:

\[ Re_{mf} = \sqrt{1135.7 + 0.0408 N_{Ga}^{-3.7}}. \]

Where the Reynolds number, \( Re_{mf} \) is a function of the minimum fluidisation velocity, \( Uₘᵢ \), the particle diameter, \( d_p \), the dynamic viscosity, \( \mu \), and the density of the fluidising gas, \( \rho_f \):

\[ Re_{mf} = \frac{\rho_f U_{mf} d_p}{\mu} \]

and the Galileo number, \( N_{Ga} \), is obtained by

\[ N_{Ga} = \frac{d_p^3 \rho_f (\rho_s - \rho_f) g}{\mu^2}, \]

where the \( \rho_s \) represents the density of the solid particles and \( g \) is the acceleration due to gravity. The particles used here were 250 – 355 µm for silica sand, 180 – 250 µm for Fe₂O₃, and ZrO₂-supported Fe₂O₃, with corresponding particle densities of 2600 ± 50 kg/m³, 2800 ± 60 kg/m³, and 2160 ± 80 kg/m³. The diameter of the particles, \( d_p \), used for obtaining \( U_{mf} \) was taken as the mean average of the upper and lower limit of the sieve size. The resulting ratios of the superficial velocity to the minimum fluidisation velocity, \( U/Uₘᵢ \), were between 6.6 - 9.0, for different materials under various operating temperatures. The dynamic viscosity and density of the fluidising gas at temperatures up to 1248 K were extrapolated from NIST Chemistry WebBook [131].

Typically, 0.04 g Polish char, with a particle size fraction of 600 - 850 µm, was dropped to the fluidised bed from the top. This much larger char size (than those for the fluidising
bed particles) allowed easy separation of bed materials from remaining char ash. [CO] and [CO₂] were measured by FTIR. The whole gasification time allowed for completion under various conditions was between around 900 s to over 3000 s, depending on the gasification temperature and the type of the solid particles in bed. The response time of the sampling system and the analyser, defined as the time taken to respond from 5% to 95% of a full step change, was 3 s, negligible when compared to the gasification time needed here.

Figure 2-2 Set-up of the quartz tube fluidised bed reactor.

2.3.3 Quartz tube fluidised bed reactor coupled with a plasma reactor
The investigation of the processing of biomass (wood pellets) in the presence of alumina sand and oxygen carriers of 355 - 425 µm, was carried out in a fluidised bed reactor, coupled with a dielectric barrier discharge (DBD) reactor in the downstream for online quantification of tar produced from the upstream. The material density values were 3950 ± 70 kg/m³ for alumina sand, 2900 ± 100 kg/m³ for Fe₂O₃, and 2000 ± 80 kg/m³ for mayenite-supported CuO. The effect of CO₂, i.e. 18% CO₂ (balance N₂), on the product distribution from thermal treatment, which is essentially the gasification of the wood, was also investigated in the same set-up. Figure 2-3 presents a schematic diagram of the set-up. The fluidised bed is the quartz tube reactor as described in 2.3.2. The gaseous product from the fluidised bed was sampled to the DBD reactor. The sampling line from the fluidised bed to the DBD reactor, together with the DBD reactor, was externally heated by heating tapes (Omega, STH051) to prevent any tar condensation. A trap, immersed in
ice water and consisting of a tube packed with CaCl₂ and ceramic beads, and plugged with glass wool at each end (not shown in Fig. 2-3), was placed after the DBD reactor, before the pump to trap tar and water. The gas was then analysed by a FTIR (ThermoFisher Scientific, NICOLET iS10) and a paramagnetic oxygen analyser (ABB, EL3020).

The configuration of the DBD reactor (cross sectional view) is shown in Fig. 2-4. It consisted of two metal electrodes, with the high voltage electrode being a stainless-steel rod (diameter of 25.0 mm, length of 80 mm) and the ground electrode being a stainless-steel tube (i.d. 36.0 mm), and a dielectric quartz tube (i.d. 26.0 mm, o.d. 30.0 mm). The quartz tube just covered the inside high voltage electrode, resulting a gap (3.0 mm) between the outer surface of the quartz tube and the inner surface of the ground electrode, to allow the sampled gas to flow through. The 80 mm long, and 3.0 mm gap regime was where plasma was regenerated. The DBD reactor was sealed by two Teflon end-caps, which also provided electrical insulation and support for the electrodes. Alternating voltage ranging from 13.2 to 15.2 kV (peak to peak) at a frequency of ~ 22 kHz was supplied to generate plasma via a plasma generator (PVM500-2500, Information Unlimited). The determination of the dissipated plasma power in the DBD reactor was described below.

Figure 2-3 Set-up of a quartz tube fluidised bed reactor coupled with a plasma reactor in the downstream for the quantification of tar from upstream.
Figure 2-4 Configuration of the plasma reactor for the quantification of tar from upstream.

Specific energy density (SED) was used to characterise the density of plasma energy within the reactor and is given by

$$ SED = \frac{P}{Q}, $$

where $P$ is the power input (W), $Q$ is the gas flow rate (L/s) passed through the reactor. The power input is related to the frequency $f$ of the ac supply by

$$ P = E \times f. $$

The energy input per cycle $E$ is [93]

$$ E = \int_{0}^{t} V(t) I(t) dt = \int_{0}^{t} V(t) dq, $$

where $V(t)$ is the voltage and $I(t)$ is the current. Thus, the power can be determined from the $V$-$q$ Lissajous diagram. The voltage was measured using a high voltage probe (TESTEC, 1000:1, 30 kV, 50 MHz) with the sensing head connected to the high voltage electrode. The charge was obtained from the voltage (Tektronix probe, P6015A, 1:1) across a $1 \mu F$ capacitor, connected in series between the reactor ground electrode and earth. Both the voltage and charge signals were collected simultaneously using an oscilloscope (Tektronix, TDS 3012) in X-Y mode. Figure 2-5 is a typical $V$-$q$ Lissajous curve from one experiment. The energy input was obtained by taking the area enclosed by the curve.
For a typical experiment, the fluidised bed was loaded with 20 ml of bed material \((i.e.\) alumina sand, \(\text{Fe}_2\text{O}_3\), or mayenite-supported \(\text{CuO}\)) and fluidised by pure \(\text{N}_2\) at a flow rate of \(~3\ \text{L/min}\). The temperature of the bed varied from 773 to 1173 K, giving a \(U/U_{mf}\) of 1.7 to 3.4 in alumina sand, 3.0 to 5.8 in mayenite-supported \(\text{CuO}\), and 2.2 to 4.3 in \(\text{Fe}_2\text{O}_3\).

The air stream entering the sampling line was set at 0.45 L/min, and the total flow rate of the sampling line was set at 0.90 L/min. The temperatures of the sampling line and the DBD reactor were kept at 573 K and 523 K, respectively. After each experiment, the fluidising gas was switched from \(\text{N}_2\) to air to burn off the char (produced from in \(\text{N}_2\)). Any produced \(\text{CO}\) and \(\text{CO}_2\) from the burn-off was measured to quantify the char. For every experiment, \(0.0538 \pm 0.0004\ \text{g}\) of wood was fed. Sufficient bed material was provided in each batch experiment to allow full conversion of the carbon content in wood to \(\text{CO}_2\), assuming \(\text{Fe}_2\text{O}_3\) was reduced to \(\text{Fe}_3\text{O}_4\), or \(\text{CuO}\) to \(\text{Cu}_2\text{O}\). The duration of the experiment was set to be equal to the pyrolysis time for the fuel, assuming that this can be determined by noting when \(\text{CH}_4\) was no longer detected. Each experiment was repeated three times. For the experiments using 18% \(\text{CO}_2\), as the fluidising agent, alumina sand was used as the bed material, whilst all other conditions were kept identical.
The quantification of the tar produced from the fluidised bed, was carried out by taking the difference in the signals from the FTIR between two runs: with the plasma on, and off, meaning that two separate experiments were performed with other conditions being the same. Here, tar was defined as any carbon-containing gaseous species except CO, CO$_2$, and CH$_4$. The aim was to develop a method to allow the total quantification of tar; whilst the composition of the tar can be of interest, it was not a focus of the current study. The difference in signals of CH$_4$, CO and CO$_2$ with plasma either on or off was used to account for the carbon content in the tar being burned in the plasma. To obtain a real-time signal would require two sampling lines in parallel, one with plasma and one without. Here, for the sake of proof of principle, only one sampling line was used and the experiment repeated to allow the difference to be determined. Assuming that tar can be converted to CO, CH$_4$, and CO$_2$ completely, the amount of carbon in the tar entering the sampling system is given by:

$$m_{C,tar} = \sum_{i=\text{CO, CO}_2, \text{or CH}_4} m_{i,\text{on}}^o - \sum_{i=\text{CO, CO}_2, \text{or CH}_4} m_{i,\text{off}}^o,$$

where $m_{i,\text{on}}^o$ and $m_{i,\text{off}}^o$ are respectively the mass of carbon in the carbon-containing species $i$ (CO, CO$_2$, or CH$_4$) that enters the sampling system with the plasma being on or off, respectively. Here, $m_{i,\text{on}}^o$ and $m_{i,\text{off}}^o$ were determined by taking the integral of the rate of species $i$ that enters the sampling system and detected by FTIR, with plasma running $R_i(t)$ over pyrolysis time from $t_0$ to $t_\alpha$:

$$m_i = \int_{t_0}^{t_\alpha} R_i(t) \, dt.$$

The above equation gives the mass of carbon entering the sampling system over the duration of an experiment. To obtain the total amount of carbon in each species, for instance in tar, the ratio of the total gas flow rate in the fluidised bed, $F_{FB}$, to the flow rate into to the sampling line $F_{\text{sampling}}$ was used:

$$M_{\text{C,tar}} = m_{\text{C,tar}} \times \frac{F_{FB}}{F_{\text{sampling}}},$$

where $M_{\text{C,tar}}$ is the total amount carbon in the tar produced in the fluidised bed.

Following each experiment, the residual amount of carbon remaining in the bed was measured by burning off in air. The carbon balance was calculated by:

$$m \% = \frac{(\sum_i m_i^{\text{off}} + m_{\text{C,burn-off}} + m_{\text{C,tar}}) \times \frac{F_{FB}}{F_{\text{sampling}}}}{M_{\text{C,total}}} \times 100\%$$

54
\[ M_{C,\text{total}} = M_{\text{wood, total}} \times x_C, \]

where \( M_{\text{wood, total}} \) is the total mass of wood fed into the FB, and \( x_C \) is the weight fraction of elemental carbon in the wood. \( M_{C,\text{total}} \) is the total carbon content in the wood fed. \( m_{C,\text{burn-off}} \) is the amount of carbon in the char determined from air burn-off, after pyrolysis time \( t_a \):

\[
m_{C,\text{burn-off}} = \int_{t_a}^{t_b} R_{\text{CO, burn-off}} + R_{\text{CO}_2,\text{burn-off}} \, dt,
\]

where \( R_{\text{CO, burn-off}} \) and \( R_{\text{CO}_2,\text{burn-off}} \) are the rates of production of CO and CO\(_2\) (expressed as equivalent mass of carbon and corrected for dilution in the sampling system) during burn-off from \( t_a \) to \( t_b \).

The yield of gaseous species \( i \), of tar, \( Y_{\text{tar}} \), of char, \( Y_{\text{char}} \) can be calculated respectively from:

\[
Y_i = \frac{m_{(i,\text{off})} \times F_{\text{FB}}}{M_{C,\text{total}}} \times \frac{F_{\text{sampling}}}{M_{C,\text{total}}}
\]

\[
Y_{\text{tar}} = \frac{M_{C,\text{tar}}}{M_{C,\text{total}}}
\]

\[
Y_{\text{char}} = \frac{m_{(C,\text{burn-off})} \times F_{\text{FB}}}{M_{C,\text{total}}} \times \frac{F_{\text{sampling}}}{M_{C,\text{total}}}
\]

### 2.3.4 Plasma-assisted packed bed reactor

A DBD-plasma-assisted packed bed reactor was developed and used for the investigation of \( \text{H}_2 \) production from CH\(_4\) in a plasma-assisted chemical looping system. Figure 2-6 illustrates the designed set-up, where a quartz tube (i.d. 25.0 mm, o.d. 28.0 mm) acted as the reactor as well as a part of the dielectric material between the two electrodes. A co-axial stainless-steel rod (diameter of 12.0 mm) within the quartz tube formed the high voltage electrode (supported by a cap and the distributor of the quartz tube). A stainless-steel mesh wrapped around the outer surface of the quartz tube, formed the ground electrode, enclosing a height of 20 mm. The gap between the quartz tube and the high voltage rod surface (6.5 mm) was the plasma discharge zone, packed with the oxygen carriers (a volume of 7.5 ml), where the packing is also part of the dielectric material. The system was operated at atmospheric pressure, and externally heated. Ac power was supplied to the DBD reactor and the applied voltage, frequency and plasma power can be
obtained via an oscilloscope, as described in 2.3.2. The gas (pure CH$_4$, pure Ar, mixed stream of CH$_4$ and Ar, or air depending on specific experiment) inflow entered the bed from the bottom of the reactor at an appropriate flow rate (refer corresponding chapters for the exact values), low enough to prevent fluidisation. In some experiments, the emitted ultraviolet and visible (UV-Vis, 200 to 800 nm) light from excited species was measured by an UV-Vis spectrometer (HAMAMATSU, TM-UV/VIS: C10082CA). An optical fibre was positioned inside the quartz tube reactor above the plasma region, where the UV-Vis light can be captured, but not too close to affect the plasma activity. The signal transferred through the fibre to the spectrometer. The sampled gas from the DBD reactor was dried before entering the analysers. For the experiment with pure CH$_4$ as the gas inflow, an extra N$_2$ dilution stream was mixed with sampled gas, resulting a stream of ~20% CH$_4$ in N$_2$ (refer to Fig. 2-6 and Chapter 6, 6.2.2). H$_2$ and O$_2$ were measured by a thermal conductivity analyser (ABB, Caldos27) and a paramagnetic oxygen analyser (ABB, magnos206), respectively. Other carbon-containing gas species were measured by a FTIR (MKS Instruments - MultiGas™) analyser. To minimise the flammability of the flue gas from the set-up, it was burned in Bunsen burner before entering the extraction system.
2.4 Characterisation of the materials

2.4.1 Analysis by X-Ray Powder Diffraction (XRD)
XRD analysis was performed using an Empyrean PANalytical diffractometer. A typical diffractogram was collected in the range of $2\theta$, which is defined as the angle between the incident beam and the detector, from $5^\circ$ to $80^\circ$ using Cu $K_\alpha$ radiation with a voltage of 40 kV and current of 40 mA, providing X-rays with characteristic wavelengths at 1.5406 Å and 1.5444 Å with an intensity ratio of 2:1. In a typical scan, the size of the samples were reduced to below 50 µm by manual grinding with a mortar and pestle. The powder was carefully packed into and filled full a sample holder disc to produce a flat surface, before being loaded into the diffractometer. The diffractometer was set up in a Bragg-Brentano geometry where the sample was fixed, whilst both the source and the detector rotated along the goniometer circle simultaneously. The scan step size was 0.0167°, with a continuous scan speed of 0.0278 °/s. The spectra obtained were manually compared with those from Inorganic Crystal Structure Database (ICSD) as a primary approach for
phase identification, together with the use of the software Material Analysis Using Diffraction (MAUD) as an auxiliary method (for confirmation).

### 2.4.2 SEM-EDX

The surface and internal morphologies, together with the determination of chemical elements of samples, were studied using scanning electron microscope with energy dispersive X-ray spectroscopy (SEM/EDX). The analysis was performed with TESCAN MIRA3 FEG-SEM combined with Oxford Instruments Aztec Energy X-maxN 80 EDS system at an accelerating voltage of 15 kV, working distance of 14 mm and 1000x magnification.

### 2.4.3 Brunauer-Emmett-Teller (BET) and mercury intrusion porosimetry (MIP)

The surface area and pore size distribution of the samples were measured by a TriStar 3000 (Micrometrics, Series No. 1001) gas adsorption analyser. In a typical analysis, sample particles were firstly degassed in vacuum at room temperature. This was followed by N₂ purging into the sampling chamber isothermally at 77 K, with the absolute pressure increasing from 0.01 to 1 bar. Then the gas was withdrawn to a pressure of 0.14 bar. The amount of N₂ adsorbed and desorbed was recorded as a function of pressure. The specific surface area of the particles was then estimated using the Brunauer-Emmett-Teller (BET) theory [132]. The pore size distribution and volume (for pore size smaller than 200 nm) were calculated from the Barrett-Joyner-Halenda (BJH) model [133]. Alternatively, the pore-related parameters including pore size and volume are also measured by MIP. Characterisation of the porosity by this method is achieved by applying a pressure to a sample that is immersed in mercury. The measurement was performed in an AutoPore IV 9500 Automated Mercury Porosimeter. In a typical test, the injection pressure was raised from 0.10 to 60000.00 psia (0.007 to 4136.854 bar). The contact angle, surface tension, and density for Hg in these tests were 130°, 0.485 N/m and 13.54 g/mL, respectively.
3.0  *In situ* CO$_2$ gasification of a Polish coal-derived char in the presence of Fe$_2$O$_3$-based oxygen carriers

3.1  Introduction

As outlined in Chapter 1, CLC of solid fuels requires either (1) CLOU oxygen carriers, or (2) a separate gasification step prior to the combustion of the gasification products by conventional CLC oxygen carriers. The latter approach can be carried out *in situ* or *ex situ*. *In situ* CO$_2$ gasification of a Polish coal-derived char in a fluidised bed reactor in the presence of typical Fe$_2$O$_3$-based oxygen carriers is studied in this chapter. The presence of oxygen carriers on CO$_2$ gasification of a Polish char is to be understood. Saucedo *et al.* [14] carried out an experimental and numerical modelling study on the effect of Fe$_3$O$_4$ on the gasification of a German lignite char. Their results showed a much-improved rate of CO$_2$ gasification in the presence of Fe$_3$O$_4$, compared to the gasification in inert sand, as shown in Fig. 3-1. The gasification of the lignite char itself was found to be limited by external mass transfer. The improved gasification rate was explained by assuming that the Fe$_3$O$_4$ removed the inhibition effect of CO on gasification by removing the accumulated CO on the char particle surface via combustion. The re-generated reagent (from combustion of CO by Fe$_3$O$_4$), CO$_2$, improved the surface CO$_2$ concentration, and thus positively influenced the gasification. The current research investigates the effect of oxygen carries on another type of char, and hopefully free of external mass transfer limitation. Extrapolating the results by Saucedo *et al.*, for a solid fuel free of external transfer limitation, the oxygen carriers should not influence the char gasification step, given that catalytic effect of the oxygen carriers is insignificant. The aim of this research is to verify the mechanism for the fuels without mass transfer limitation.
Figure 3-1 Gasification of Hambach lignite coal, $m_{\text{coal}} \sim 0.15 \text{ g}, d_p = +710, -1000 \mu\text{m}$ in 12.5 mol% CO$_2$, balance N$_2$, at 1073, 1123 and 1173 K in a of silica sand or Fe$_2$O$_3$. The figure was reproduced from Ref. [14]. For copyright issue, the figure is removed here.

The work starts by studying CO$_2$ gasification of a Polish char (lignite char) in silica sand for the identification of the controlling regime of the gasification, and to provide a baseline. Then, the replacement of silica sand by Fe-based oxygen carriers allows the investigation of the effect of oxygen carriers on gasification.

### 3.1.1 Fe$_2$O$_3$ reduction as source of oxygen

Fe$_2$O$_3$, as a cheap and abundant metal oxide with good reactivity, has a great potential for industrial applications of CLC. Research on the kinetics of Fe$_2$O$_3$ reduction has progressively developed from a single-step reduction mechanism [134] where Fe$_2$O$_3$ is directly reduced to Fe, to the complex mechanism that has taken into account all the four phases (haematite, magnetite, wustite and metallic iron) [135]. A list of the reduction reactions of Fe-O system by CO is presented below.

\[
\begin{align*}
3 \text{ Fe}_2\text{O}_3 + \text{ CO} & \rightarrow 2 \text{ Fe}_3\text{O}_4 + \text{ CO}_2 & \text{R-3.1} \\
\text{Fe}_2\text{O}_3 + \text{ CO} & \rightarrow 3 \text{ FeO} + \text{ CO}_2 & \text{R-3.2} \\
\text{FeO} + \text{ CO} & \rightarrow \text{ Fe} + \text{ CO}_2 & \text{R-3.3}
\end{align*}
\]
In a CO-rich reducing environment, haematite (Fe₂O₃) is subsequently reduced to magnetite (Fe₃O₄), wustite (FeO), and finally iron (Fe). The final state of hematite in the reduction process depends on the ratio of CO/CO₂ in the gases surrounding the material and the temperature. The thermodynamic phase equilibrium of the Fe-O system at temperatures of interest for gasification (~ 1000 - 1400 K) is presented in Fig. 3-2. For temperatures above 1000 K, a phase transition of Fe₂O₃ → Fe₃O₄ has a partial pressure ratio of CO₂ to CO, \( \frac{P_{CO_2}}{P_{CO}} \), at equilibrium of higher than \( 10^4 \), meaning that the presence of Fe₂O₃ will permit nearly full combustion of CO. FeO → Fe is believed to be the slowest step [48], [136,137] and usually avoided in CLC of solid fuels.

![Phase diagram of Fe₂O₃ to Fe from 1000 to 1400 K.](image)

Figure 3-2 Phase diagram of Fe₂O₃ to Fe from 1000 to 1400 K. Giddings and Gordon [138] data source for the partial pressure of oxygen was used for the phase boundaries containing wustite (FeO), then a conversion from oxygen partial pressure to the ratio of CO₂ to CO was made by using the Gibbs free energy of CO combustion (CO + \( \frac{1}{2} \) O = CO₂) computed from MTDATA software [139] using SGTE database. For the phase boundary of Fe₂O₃ to Fe₃O₄, data from NASA database was used.

### 3.1.2 Support material- ZrO₂

Support materials, such as the most commonly used Al₂O₃, tend to interact with Fe₂O₃ (to form e.g. FeAl₂O₄ for Fe₂O₃ and Al₂O₃). FeAl₂O₄ is unreactive, resulting a negative impact on the overall performance of the material [37]. Usually, an inert support that helps improve the mechanical strength and only dilutes the active metal oxides is desirable.
ZrO₂ is selected as a support material for Fe₂O₃ due to its inertness to Fe₂O₃. Liu et al. [37] carried out chemical looping H₂ production using Fe₂O₃/ZrO₂, and found no evidence of ZrO altering the thermodynamics of Fe-O system. It is initially expected that ZrO should also be inert in ZrO₂-supported Fe₂O₃ for gasification; whilst its actual performance is investigated in this chapter.

3.2 Experimental methods

3.2.1 Preparation of the materials

The fuel, Polish char (with a particle size fraction of 600 – 850 µm), was derived from the devolatilisation of a Polish coal, as described in 2.2.2. CO₂ gasification of the char in silica sand was first studied to provide fundamental understanding of CO₂ gasification of the fuel. Then the bed material was switched to two active oxygen carries respectively: Fe₂O₃ and ZrO₂-supported Fe₂O₃ (65 wt.% Fe₂O₃). The particle size fractions used for each bed material were 180 – 250 µm for Fe₂O₃, 180 – 355 µm for ZrO₂-supported Fe₂O₃, and 250 – 355 µm for silica sand. Fe₂O₃ was prepared from the granulation of the commercial Fe₂O₃ powder with DI water, and ZrO₂-supported Fe₂O₃ was prepared by co-precipitation. Detailed procedures for the preparation of the two oxygen carriers as well as the silica sand were described in 2.2.2. The surface area of the prepared char, Fe₂O₃ and ZrO₂-supported Fe₂O₃ was measured by BET method, as described in 2.4.3, which are 307.14, 0.25, and 1.18 m²/g, respectively.

3.2.2 Experiments

Gasification of the char in silica sand in a quartz tube fluidised bed reactor from 1123 to 1248 K with CO₂ concentration varying from 20% to 100% (balance N₂) was first investigated. For a typical experiment, ~ 0.04 g of char was added into fluidised bed from the top of the reactor. Investigation of the gasification in the presence of active oxygen carriers were carried out only in 20% CO₂, with temperature ranging from 1123 to 1248 K. ~ 0.1 g char, instead of 0.04 g, was added into the fluidised bed for a typical experiment when in Fe₂O₃-based oxygen carriers. This was to amplify the obtained signals, without affecting the mixing behaviour in the fluidised bed (i.e. the rate was normalised, and no evidence of mixing was observed). For all gasification experiments here, the volume of the bed (unfluidised) was ~ 20 ml and the fluidising gas flowrate was at 50 ml/s (leading to a U/Uₘ between 6.6 – 9.0, depending on bed materials and temperatures), and the
operating pressure of the fluidised bed was at atmospheric. The detailed description of the experimental set-up and procedures were illustrated in 2.3.2. It should be noted that here, the effect of the change in the flow rate on the gas compositions due to the reaction inside the fluidised bed, was considered negligible.

3.3 Results

3.3.1 Reproducibility of the gasification experiment

Each single experiment was repeated for at least another two times to ensure the reliability of the results. Figures 3-3 to 3-4 show two runs of char gasification in silica sand at 1173 K in 100% CO₂, on two separate days. The results show good agreement of the two runs, indicating high reproducibility of the gasification experiments. Carbon balance, defined as the ratio of the increased amount of carbon in gaseous phase to the amount of carbon in the char fed into the reactor, fell between 95% and 104%, implying high reliability of the experimental data obtained. The gasification rate (i.e. rate of production of CO per unit mass of carbon) firstly reached a peak (1.4%) at a conversion, X, of 0.2, and then gradually dropped to zero. The conversion of carbon, X, was defined by the initial mass of char fed into the reactor \( m_0 \), the accumulated increased amount of carbon in the gaseous phase \( m_t \), and the fraction of carbon in the char (0.484 as seen in Table 2-4):

\[
X = \frac{m_t}{m_0 \times 0.484}.
\]

Figure 3-3 Carbon conversion of gasification of the char over time by 100% CO₂ at 1173 K in the quartz-tube silica sand-loaded fluidised bed of two experimental runs. ~ 0.042 g char with a particle size fraction of 600 – 850 µm was added into the bed in a single run.
Figure 3-4 Rate of gasification (rate of production of CO per unit mass of carbon) of the char over conversion by 100% CO, at 1173 K in the quartz-tube silica sand-loaded fluidised bed of two experimental runs. ~ 0.042 g char with a particle size fraction of 600 – 850 µm was added into the bed in a single run.
3.3.2 Effect of temperature on char gasification

Figures 3-5 to 3-7 show the results of gasification of the char in 100% CO$_2$ with the operating temperatures from 1123 to 1248 K. The results are presented in mole fraction of CO over time, rate of gasification over conversion $X$, and normalised rate ($\frac{\text{Rate of gasification}, R_{g}'}{\text{Initial rate of gasification}, R_{g,0}}$) over conversion $X$, respectively.

![Mole fraction of the char over time](image1)

Figure 3-5 Mole fraction of the char over time by 100% CO$_2$ from 1123 to 1248 K in the silica sand-loaded fluidised bed. ~ 0.042 g char with a particle size fraction of 600 – 850 µm was added into the bed.

![Rate of gasification](image2)

Figure 3-6 Rate of gasification of the char over conversion by 100% CO$_2$ from 1123 to 1248 K in the silica sand-loaded fluidised bed. ~ 0.042 g char with a particle size fraction of 600 – 850 µm was added into the bed.
According to Fig. 3-5, temperature exhibited a positive effect on the measured CO in the sampled product stream. The peak of the mole fraction of CO reached the highest at 1248 K, giving a value of ~ 0.023, and the lowest peak was 0.007 at 1123 K. The residence time of the analyser, FTIR, is ~ 3 s, which is negligible compared to the gasification time (e.g. 400 s for the gasification at 1248 K, and over 1500 s for that at 1123 K); thus, the effect of gas mixing on FTIR signal can be ignored. The trends of gasification rate curves, as shown in Fig. 3-6, are similar to the mole fraction curves. In a typical gasification experiment, the gasification rate always increased to a peak value when the conversion \( X \) reached between 0.1 and 0.2. Figure 3-7 presents the normalised rate, \( \frac{R_g}{R_{g,0}} \), the ratio of the gasification rate to the initial gasification rate (at \( t = 0 \)), over conversion \( X \). In the kinetically controlled regime this plot should give \( f(X) \), which describes the pore structure evolution and change in rate as conversion increases. A change in the shape of \( f(X) \), would give indication of a change in the controlling regime, or imply that the gasification is in the mass transfer limited regime. The results shown here did not reveal significant variation in the trend of \( f(X) \) curves, suggesting no strong evidence for a change in the temperature range studied. This shape of \( f(X) \) can be explained by the change in pore structure [14,140] that in the beginning period of gasification, the
chemical reaction was slow enough to allow the CO$_2$ diffuses into the particle. The pore size first increased to a threshold, below which it led to an increase in the total surface area and active sites and thus the rate of production of CO gradually reached to a maximum. Increase in the pore size above the threshold value led to a decrease in the total surface area due to coalesce of the pores, resulting in the decrease in the gasification rate.

### 3.3.3 Effect of CO$_2$ concentration on char gasification

Results of the effect of CO$_2$ concentration from 20% to 100% in the temperature range from 1123 to 1248 K were presented in Figs. 3-8 to 3-11. The increase in the CO$_2$ concentration, in general, promoted the gasification. According to Figs. 3-11 and 3-13, the maximum rate of production of CO in the gasification experiments with CO$_2$ content from 20% to 100% always fell into a char conversion range between 0.1 and 0.2 both at 1248 K, and this is also representative for the results at other temperatures.

![Figure 3-8 Mole fraction of CO from the gasification of the char over time with CO$_2$ concentration from 20% to 100% at 1123 K in the silica sand-loaded fluidised bed. ~0.042 g char with a particle size fraction of 600 - 850 µm was added into the bed.](image)
Figure 3-9 Rate of gasification of the char over conversion with CO$_2$ concentration from 20% to 100% CO$_2$ at 1123 K in the silica sand-loaded fluidised bed. ~ 0.042 g char with a particle size fraction of 600 - 850 µm was added into the bed.

Figure 3-10 Mole fraction of CO from the gasification of the char over time with CO$_2$ concentration from 20% to 100% CO$_2$ at 1248 K in the silica sand-loaded fluidised bed. ~ 0.042 g char with a particle size fraction of 600 - 850 µm was added into the bed.
3.3.4 The effect of Fe$_2$O$_3$ on in situ char gasification

Gasification in the presence of oxygen carriers were performed in 20% CO$_2$ from 1123 to 1248 K. The presence of Fe$_2$O$_3$ consumed CO produced from in situ gasification, and generated CO$_2$. Therefore, the additional CO$_2$ measured by the FTIR resulted from a combination of char gasification and combustion of CO by Fe$_2$O$_3$. To improve the CO$_2$ signals (distinguishable from the background CO$_2$ level) detected by the FTIR, the amount of the char fed to the bed was increased to ~ 0.1 g (still in the range where the gasification was not affected by the amount of char fed). The final reduced phase of Fe$_2$O$_3$ should be limited by the ratio of CO$_2$ to CO in the bed. It was noticed that in the work carried out here, a CO$_2$ to CO ratio larger than 15 (refer to Fig. 3-2) over the gasification time was always obtained. This ensures that Fe$_2$O$_3$ should only be reduced to the magnetite phase, Fe$_3$O$_4$.

To express the gasification rate of the char, different from the measured overall change in CO, the consumption of CO by the oxygen carriers to generate CO$_2$ should be considered. For char gasification only (in silica sand):

\[ R_{\text{CO}_2, \text{silica}} = -r. \]
The overall rate of production of CO: \( R_{CO,\text{silica}} = 2r \).

For char gasification in the presence oxygen carrier:

The overall rate of production of CO: \( R_{CO_2,oc} = -r + r_{oc} \).

The overall rate of production of CO: \( R_{CO,oc} = 2r - r_{oc} \).

\( r_{oc} \) is the rate of production of CO, from the reaction between the CO and oxygen carriers.

Rate of char gasification (based on production of CO) can be expressed as

\[ 2r = 2 \times (R_{CO_2,oc} + R_{CO,oc}) \]

Figure 3-12 gives an example of the CO and CO\(_2\) measured from gasification in silica sand at 1223 K. For carbon gasification in CO\(_2\), consuming one mole of CO should generate two moles of CO, which was also observed in Fig. 3-12. In Fig. 3-13, rate of CO in Fe\(_2\)O\(_3\), CO\(_2\) in silica sand and in Fe\(_2\)O at 1223 K were presented. Good carbon balances between 97\% to 105\% were obtained in the Fe\(_2\)O beds.

![Graph showing rate of gasification per unit mass of carbon](image)

Figure 3-12 \( R_{CO,\text{silica}} \) and \( R_{CO_2,\text{silica}} \) at 1223 K, where the rates here represent the overall rate of production of CO, and CO\(_2\) per unit mass of carbon of carbon in a bed of silica sand.
Figure 3-13 \( R_{CO,oc} \), \( R_{CO_2,oc} \) and \( R_{CO_2,silica\ sand} \) at 1223 K, where \( R_{CO,oc} \) and \( R_{CO_2,oc} \) here represent the overall rate of production of CO and CO\(_2\) per unit mass of carbon of carbon in a bed of Fe\(_2\)O\(_3\), respectively, and \( R_{CO_2,silica\ sand} \) is the overall rate of production of CO\(_2\) in a bed of silica sand.

Figures 3-14 to 3-16 show the comparison of overall char gasification rates (based on the total production of CO per unit mass of carbon) in silica sand and Fe\(_2\)O\(_3\) at different temperatures, and no significant difference in the rates in the two beds were observed.
3.3.5 The effect of ZrO$_2$-supported Fe$_2$O$_3$ (FeZr) on in situ char gasification

Figure 3-17 shows the rate of CO in FeZr, CO$_2$ in FeZr and silica sand, and the overall gasification rate (based on total CO production rate per unit mass of carbon). Figures 3-18 to 3-20 present the comparisons of the overall gasification rate in silica sand, and FeZr at 1123, 1173 and 1248 K, respectively. Different from the results in a bed of Fe$_2$O$_3$, clear differences in the rates at each temperature were found, where the gasification rate was in silica sand was always higher. The carbon balances (over the period until no change in
mole fractions of each gas was observed) in FeZr were 84%, 81% and 79%, corresponding to each temperature from 1123 to 1248 K. The results seem to suggest an inhibition effect of FeZr on the char gasification, leading to some unreacted carbon remaining in the bed.

Figure 3-17 $R_{CO,oc}$, $R_{CO_2,oc}$, $R_{CO_2, silica sand}$ and the overall rate of gasification at 1123 K and by 20% CO$_2$, where $R_{CO,oc}$ and $R_{CO_2,oc}$ represent the overall rate of production of CO, and CO$_2$ per unit mass of carbon of carbon in a bed of FeZr and $R_{CO_2, silica sand}$ is the overall rate of production of CO in a bed of silica sand.

Figure 3-18 Overall gasification rate over time by 20% CO at 1123 K in beds of silica sand and FeZr.
3.4 Discussion

3.4.1 Kinetic evaluation of the gasification of the char (in silica sand)
In this work, prior to investigating the gasification performance in the presence of active oxygen carriers, understanding of whether the gasification of Polish char was affected by mass transfer limitation is necessary. The measured gasification rate was first compared with the external mass transfer rate, which is also the maximum rate...
approachable for gasification reaction. If the rate is limited by the diffusion of the reactant to the surface, the maximum rate can be estimated based on Eq. 3-1 [141]:

\[
R_{\text{max}} = 2 \times \frac{Sh}{1.102} \times ([\text{CO}_2]_{\text{bulk}} - [\text{CO}_2]_{\text{surface}}) \times D_{\text{CO}_2} \times \frac{6}{d_p^2 \times \rho},
\]

Equation 3-1

The surface concentration of CO\(_2\) is close to zero when the reaction is totally controlled by external mass transfer. The constant 1.102 is introduced to account for the fact of the non-equiomolar counter diffusion [142]. Sherwood number (a dimensionless number describing the ratio of convection mass transfer rate to that of diffusive mass transfer), Sh, of the reacting char particle in the fluidising situation was obtained from the correlation [141]

\[
Sh = 2\varepsilon_{mf} + 0.69 \left(\frac{U_{mf} \ell}{v \varepsilon_{mf}}\right)^{1/2} \left(\frac{v}{D_{\text{CO}_2}}\right)^{1/3},
\]

Equation 3-2

where \(\varepsilon_{mf}\) is the voidage at incipient fluidisation, \(v\) is the kinematic viscosity of fluidising gas, \(d\) is the diameter of the reacting particle, and \(D_{\text{CO}_2}\) is the diffusivity of CO\(_2\) in a gas mixture. Table 3-1 compares the maximum char gasification rate observed from the experiments and the limiting maximum rates, at different temperatures. For example, at 1123 K, the maximum gasification rate by 20% CO\(_2\) is \(2.1 \times 10^{-4}\) mol s\(^{-1}\) g\(^{-1}\), whereas the corresponding limiting rate of 0.0090 mol s\(^{-1}\) g\(^{-1}\) is significantly faster. At the highest temperature 1248 K, the limiting rate is \(~0.0097\) mol s\(^{-1}\) g\(^{-1}\), and this is still more than five times the maximum gasification rate, which is \(1.8 \times 10^{-3}\) mol s\(^{-1}\) g\(^{-1}\). The significant differences in the rates suggest that the gasification of the char was less likely to be influenced by external mass transfer.

Table 3-1 \(R_{\text{max}}\) at different temperatures by 20% CO\(_2\).

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>[CO(<em>2)](</em>{\text{bulk}}) (mol/m(^3))</th>
<th>(D) (m/s)</th>
<th>Sh</th>
<th>(R_{\text{max}}) (mol s(^{-1}) g(^{-1}))</th>
<th>(R_{\text{max,measured}}) (mol s(^{-1}) g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1123</td>
<td>2.1686</td>
<td>0.00017</td>
<td>1.5605</td>
<td>0.0090</td>
<td>2.1 \times 10^{-4}</td>
</tr>
<tr>
<td>1148</td>
<td>2.1213</td>
<td>0.00017</td>
<td>1.5576</td>
<td>0.0091</td>
<td>3.7 \times 10^{-4}</td>
</tr>
<tr>
<td>1173</td>
<td>2.0761</td>
<td>0.00018</td>
<td>1.5550</td>
<td>0.0093</td>
<td>5.5 \times 10^{-4}</td>
</tr>
<tr>
<td>1198</td>
<td>2.0328</td>
<td>0.00019</td>
<td>1.5522</td>
<td>0.0094</td>
<td>8.9 \times 10^{-4}</td>
</tr>
<tr>
<td>1223</td>
<td>1.9912</td>
<td>0.00019</td>
<td>1.5495</td>
<td>0.0095</td>
<td>1.3 \times 10^{-3}</td>
</tr>
<tr>
<td>1248</td>
<td>1.9514</td>
<td>0.00020</td>
<td>1.5468</td>
<td>0.0097</td>
<td>1.8 \times 10^{-3}</td>
</tr>
</tbody>
</table>
The value of the slope from Arrhenius plot would give indication of the controlling regime of a reaction. The gasification of the solid fuel can usually be described as:

\[ r = k'(T, C)f(X), \]

where \( k'(T, C) \) is the effective rate constant, which is a function of gas concentration \( C \) and temperature \( T \). Assuming that the overall CO gasification of the char obeys the Arrhenius law \( (k = Ae^{-\frac{E}{R_\text{ideal}T}}) \), Eq. 3-3 can be obtained

\[ r = G(C)Ae^{-\frac{E}{R_\text{ideal}T}}f(X), \quad \text{Equation 3-3} \]

where \( A \) is the frequency factor, \( E \) is the effective activation energy, \( R_\text{ideal} \) is the ideal gas constant. By taking the natural logarithm of Eq. 3-3, and apply the initial gasification rates, \( R_{g,0}' \), the following equation was obtained:

\[ \ln\left( R_{g,0}' \right) = \ln(A \cdot G(C)) - \frac{E}{R_\text{ideal}T}. \]

For constant gas concentrations, the effective activation energy \( E \) can be obtained from the slope of the Arrhenius plot \( \ln\left( R_{g,0}' \right) \) versus \( 1/T \). Arrhenius plot of the initial gasification rate for different CO \(_2\) concentrations was shown in Fig. 3-21. The values of various parameters of the trendlines for the Arrhenius plots are presented in Table 3-2. According to Fig. 3-21, the data points of the initial gasification rates for different CO \(_2\) concentrations were well fitted to linear lines, with high values of R-squared values, \( R^2 \), as shown in Table 3-2. This further indicates no clear change in the controlling regime from 1123 to 1248 K. The observed activation energy, \( E \), was calculated from the slope of the trendline, and the frequency factor, \( A \), was obtained from the intercept. Activation energy values between 196 to 216 kJ mol\(^{-1}\), and frequency factor values between \( 6.2 \times 10^4 \) mol s \(^{-1}\)g \(^{-1}\) to \( 1.67 \times 10^5 \) mol s \(^{-1}\)g \(^{-1}\) were obtained for CO \(_2\) concentrations from 20% to 100%. The apparent activation energy estimated here is close to those reported in literature for CO \(_2\) gasification of other lignite chars, which were around 190 kJ mol\(^{-1}\) [143,144]. Therefore, it is reasonable to believe that intra-particle mass transfer limitation is less of our concern here.
Figure 3-21 Arrhenius plot of the natural logarithm of the initial gasification rate versus the inverse of temperature from 1123 to 1248 K for CO concentrations from 20% to 100%.

Table 3-2 Values for the parameters of the trendlines in for the Arrhenius plots in Fig. 3-23.

<table>
<thead>
<tr>
<th></th>
<th>100% CO</th>
<th>80% CO</th>
<th>60% CO</th>
<th>40% CO</th>
<th>20% CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept $\ln(A)$</td>
<td>13.82</td>
<td>12.81</td>
<td>13.34</td>
<td>13.78</td>
<td>14.33</td>
</tr>
<tr>
<td>Slope $\frac{-E}{R_{\text{ideal}}}$, (K)</td>
<td>-24612</td>
<td>-23575</td>
<td>-24356</td>
<td>-25052</td>
<td>-26025</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.991</td>
<td>0.993</td>
<td>0.994</td>
<td>0.996</td>
<td>0.993</td>
</tr>
</tbody>
</table>

### 3.4.2 Gasification in the presence of Fe$_3$O$_4$

The discussion in 3.4.1 suggest that gasification of Polish char was mainly controlled by intrinsic chemical kinetics from 1123 to 1248 K. Based on Saucedo et al.’s results in Ref.[14] that the overall gasification rate was improved by the presence of Fe$_3$O$_4$, due to the removal of surface CO, given that gasification was limited by mass transfer. In the current study, for the kinetically controlled gasification of Polish char, Fe$_3$O$_4$ did not have much effect on the char gasification rate, i.e. the overall gasification rates between in silica sand and Fe$_3$O$_4$ beds were very comparable. This is consistent with the mechanism extrapolated from the study by Saucedo et al. that the removal of CO by Fe$_3$O$_4$ so as to improve the gasification rate is mainly effective when the gasification is external mass
transfer limited. On the other hand, the presence of Fe₂O₃ increased the CO₂ concentration due the combustion of the produced CO, which might improve the gasification rate; however, the increased amount (i.e. between 0.2% to 0.7% in 20% CO₂, depending on the temperature) is negligible compared to the bulk 20% CO₂ gasification environment.

According to Fig. 3-11, a significant amount of CO was still observed in the presence of Fe₂O₃, suggesting relatively slow combustion of produced CO from the gasification step. For the application of CLC for CCS, chemical looping oxygen carriers with higher oxidation activity, are needed in this case.

### 3.4.3 Gasification in the presence of FeZr

Based on the results in 3.3.4, over the whole temperature range, gasification of Polish char in FeZr exhibited lower rates than those in silica sand and Fe₂O₃ beds. This suggests some ‘inhibition’ effect in the presence of FeZr, either chemically or physically. The chemical reactivity of the prepared FeZr was first investigated by comparing the reduction of FeZr and Fe₂O₃ by CO.

- **Comparison of the reduction between FeZr and Fe₂O₃ by 10% CO**

The reduction experiment was carried out in a quartz tube fluidised bed reactor at 1173 K, as described in 2.3.2. Around 8 g of FeZr or Fe₂O₃ particles were fed into the bed. The feed gas, 10% CO in N₂, was introduced into the reactor at a flowrate of 1.8 L/min. Figures 3-22 and 3-23 show mole fractions of CO, CO₂, and the sum of the two in the reduction. The produced CO₂ should only come from the oxidation of CO. Therefore, the sum of the mole fractions of CO and CO₂ should always be around 0.1 through the whole reduction period, as seen in Figs. 3-22 and 3-23. For FeZr, the experiment was terminated at ~ 550 s due to de-fluidisation of the bed; whilst for Fe₂O₃, up to 1000 s, there was no significant de-fluidisation. Significant difference in the reduction behavior was observed in the two beds. Three stages were seen in the reduction of FeZr, which are t = 0 to t = 80 s (stage 1), t = 80 to t = 300 s (stage 2), t = 300 to t = 500 s (stage 3), and t > 500 s, respectively. Assuming that the three stages correspond to the phase transitions of reduction of Fe₂O₃ (i.e. Fe₂O₃ → FeO, FeO → FeO, and FeO → Fe) in FeZr (given that ZrO will not lose oxygen), the oxygen balances (defined as the ratio amount of increased oxygen in the gas phase to the estimated amount of oxygen released from phase
reduction) were obtained as follow: 0.98 for stage 1, 0.94 for stage 2, and 0.18 for stage 3. The first two stages exhibit good oxygen balances, indicating the presence of appropriate phase transitions. Apparently, the reduction from wustite, FeO, to Fe has not completed. In the bed of FeO, however, there was no separation of stages. FeO also seems to be less reactive than FeZr for CO reduction. This probably can be partly explained by the larger BET surface area of FeZr.

It is also suspected that carbon deposition from CO via $2\ CO \rightarrow C + CO_2$, onto the solids, could lead to a lower amount of CO measured at the outlet. Direct identification of the deposited carbon was difficult here, whilst there is some evidence showing that at least no significant carbon deposition occurs. For carbon deposition from CO, the stoichiometric ratio of the consumption of CO to the production of CO$_2$ is 2, and for FeO reduction in CO, this ratio is 1. If carbon deposition is significant during reduction, the ratio should fall between 2 and 1. The experimental data gave a ratio of around 1 over the whole reduction period, suggesting little carbon deposition. It seems that the low CO amount and the apparent gasification rate in the gasification experiments are highly likely to have resulted from other factors.

Figure 3-22 FeZr reduction by 10% CO in fluidised bed at 1173 K.
Investigation of the low carbon balance in char gasification in FeZr

Char gasification in FeZr shows lower carbon balance (79% to 84%), suggesting some carbon remaining in the fluidised bed. The possible amount of carbon left inside the bed was examined by air burn-off. Air was used to burn the bed after CO$_2$ gasification of the char at 1173 K and 1248 K for 2000 s. After the completion of CO$_2$ gasification, the gas was firstly switched to N$_2$ to flush out any CO$_2$ remaining in the bed. The N$_2$ purge took about 60 s, before being switched to air for burning off. For reference, the CO$_2$ gasification – N$_2$ – air experiments were also carried out in silica sand bed and in FeZr without adding char into the bed (blank experiment).
Figure 3-24 Air burning-off of the fluidised beds after CO\textsubscript{2} gasification. The experimental curve labelled ‘blank’ in FeZr bed at 1173 K means no char was fed into the fluidised bed in the CO\textsubscript{2} gasification stage.

Figure 3-24 shows the CO\textsubscript{2} mole fraction during the air burn-off (from t = 6 s). For the char gasification in silica sand at 1173 K, there is no CO\textsubscript{2} peak, meaning that all the carbon in the char was gasified. However, in the FeZr bed with char fed in the gasification stage, two peaks (a small peak, followed by a bigger one) were always observed. In the blank experiment in FeZr, where no char was added, a small peak was found. At 1173 K, the amount of carbon in CO\textsubscript{2} during the air burn-off accounted for 19\% of the total carbon (as char) fed into the FeZr bed; at 1248 K, the value was 16\%. These data balance the lower carbon balances previously reported for char gasification in FeZ, implying that FeZr was causing some carbon remaining during gasification. There are two possible reasons for this: (1) FeZr is inhibiting the gasification of char thus causing some carbon in the char unreacted; (2) there was some carbon deposition from the CO produced. (2) was thermodynamically unstable, as CO carbon deposition on iron-based materials have been reported \cite{145,146} only at low temperatures (below 1073K). Carbon deposits would react with iron to form iron carbides and free carbon, depending on specific operating temperatures. For the carbon deposition from 2 CO → C + CO\textsubscript{2}, at the lowest gasification temperature 1123 K, P\textsubscript{CO}/P\textsubscript{CO\textsubscript{2}} is ~ 0.06 \cite{147}, and the value decreases with increasing temperature. This theoretically rules out the possibility of (2) at gasification temperatures studied (where P\textsubscript{CO}/P\textsubscript{CO\textsubscript{2}} \gg 1). Alternatively, (2) might become possible if the thermodynamics is different: e.g. CO bound to zirconia.
Comparison of char gasification between in pure ZrO₂ and silica sand

So far, the results seem to suggest an ‘inhibition’ effect of FeZr on CO₂ gasification of Polish char. Further investigation on the effect of ZrO₂ was carried out by performing char gasification in ZrO₂ (prepared from Zr(OH)₄ powder, the detailed preparation method is presented in 2.2.2). Figure 3-25 presents the comparison of char gasification by 20% CO₂ in ZrO₂ and silica sands at 1173K. Same amount of char (~0.1 g ± 0.004 g) was added to the beds. According Fig. 3-25, the amount of CO produced in silica sand was much higher than that in ZrO₂. Char gasification in silica sand finished at around 1800 s; while in ZrO₂, after 6000 s (not shown in this Fig. 3-25), there was still CO detected. The difference is also a function of temperature. At the highest temperature of 1248 K, the maximum rate in ZrO₂ is about two thirds of the latter; at the lowest temperature of 1123 K, the difference is about a factor of 7.

![Graph showing mole fraction of CO during char gasification](image)

Figure 3-25 Mole fraction of CO of char gasification by 20% CO₂ at 1173 K in ZrO₂ and silica sand beds, respectively.

Based on the above results, it seems that the presence of ZrO₂ could be the main reason accounting for decreased apparent char gasification rate in FeZr. However, it is still unclear by which mechanism ZrO₂ affects the char gasification. Maitre and Lefort [148] studied the reaction between solid carbon and ZrO₂ at temperatures above 1600 K, where zirconia carbide was formed. Though this temperature is much higher than the
temperatures studied here, it is widely recognised [148,149] that an intermediate product zirconium oxycarbide Zr(C,O) was formed prior to the transformation to ZrC, and the formation temperature for zirconium oxycarbide is still unclear. XRD characterization of fresh ZrO₂, ZrO, which has experienced CO₂ gasification, and ZrO, which has experienced gasification and followed by air oxidation have been carried out. For the gasified and oxidised samples, they were quenched to room temperature for testing. The results showed no difference between the three samples, which indicates less likelihood of the formation of zirconium carbide. Further work on this could be focused on the interaction between ZrO for CO to investigate whether the apparent inhibition effect was due to the product CO being absorbed by the ZrO.

3.5 Conclusions

The main results from the investigation carried out in this chapter are summarised below:

a) CO₂ gasification of Polish char in the temperature range from 1123 to 1248 K was found to be free of external mass transfer limitation. The high apparent activation energy found, between 196 to 216 kJ mol⁻¹, suggests that it is mostly likely to be in the kinetically controlled regime.

b) The presence of Fe₂O₃ was found to have no significant effect on the gasification of the char, mainly due to the face that gasification of the char was not influenced by external mass transfer (i.e. the external mass transfer rate is more than 5 times higher than the maximum rate of gasification over conversion).

c) The results of char gasification in ZrO₂-supported Fe₂O₃ (FeZr) showed a much decreased apparent rate of gasification of Polish char, compared with sand. Auxiliary experiments were carried out to explore the reason behind. Results of reduction of FeZr and Fe₂O₃, respectively in 10% CO (balance N₂) show that CO reacted much faster with FeZr, indicating that the reduction of FeZr by CO is fast enough. Further investigation of char gasification in pure ZrO₂ was carried out and it showed that the apparent rate of char gasification in ZrO₂ was much lower than that in silica sand, suggesting an ‘inhibition’ effect of ZrO₂ on char gasification, and the inhibition effect decreases with increasing temperature. However, the mechanism of ZrO₂ for ‘inhibiting’ the gasification requires further investigation. Future work could focus on the interaction between ZrO₂ surfaces and CO.
4.0 Numerical study of CO$_2$ gasification of Polish char and the investigation of the CO inhibition effect on gasification

4.1 Introduction

Experimental investigation of the gasification of a Polish char was carried out in Chapter 3. The results suggested that the gasification of the char was mainly controlled by chemical kinetics (perhaps with some influence of intra-particle diffusion). A numerical model for the gasification is developed in this chapter. The kinetic parameters to be substituted into the numerical model were obtained based on the gasification results in Chapter 3. More importantly, this chapter aims at understanding the effect of CO on CO$_2$ gasification by intentionally introducing some CO into the fluidised bed.

4.1.1 Mechanisms of CO$_2$ gasification of carbon and the effect of CO

The effect of the gasification product, CO, on reaction kinetics has been studied in literature [150–152]. Any attempt to understand the underlying mechanism requires the gasification itself free of mass transfer limitation. For intrinsic kinetics, the models can be categorised into two kinds: chemical reactions mainly take place on the surfaces for nonporous particles, and reactions initiate on pore surfaces within the solid for porous particles [140]. For instance, the unreacted shrinking core model applies to relatively non-porous particles, where the rate-limiting step that can be one of the following: diffusion through a fluid film surrounding the solid particle, diffusion through the ash/inert solid layer, and chemical reaction at the core surface [153]. The volumetric model, on the other hand, is applied to porous particles and when the intrinsic reaction rate is relatively slow [154]. The reaction rate can be considered uniform throughout the reacting particle. The random pore model is suitable for situations where reaction depends strongly on the total internal surface area of the pores [140]. The results shown in Chapter 3 show periods of increase in the observed rates as the conversion increased in the initial stage, is a typical example of the gasification of porous particle and the increase in the rate is largely because of the increase in the surface area due to pore evolution [14,140].

To account for this effect, the rate $R'_{g}$ can be expressed as [137,155–157]:

$$R'_{g}(X) = R'_{g,0} \times f(X), \quad \text{Equation 4-1}$$

where $R'_{g,0}$ is the initial rate, when the pore parameters are at initial conditions. The function $f(X)$ is the term introduced to describe the change in pore structure over the
conversion of carbon of the particle. It should be noted that $R'_{g}(X)$ should be a function of local conversion, which will vary across the particle. For example, for a spherical particle, there can be radial gradient in gas concentrations if intra-particle mass transfer limitation exists. Saucedo et al. [14] proposed the idea of using an arbitrary function, $f(X)$, which can be experimentally determined in the kinetically controlled regime. For simplicity, the local conversion, $X$, was replaced by an average conversion across the particle. This was later improved by Dai et al. [158] by using the local conversion within a particle. The idea of implementing an experimentally determined $f(X)$ instead of using a mathematical pore model for $f(X)$ was continued in this work. The advantage is that it avoids the process of selecting between different models that may give a good fit to experimental results.

The mechanism of carbon-carbon dioxide gasification, which determines the intrinsic reaction rate expression, can consist of multiple elementary steps [159] including

$$
\begin{align*}
C_f + CO_2 (g) & \rightleftharpoons C(CO_2) \\
C_f + C(CO_2) & \rightleftharpoons C(CO)_A + C(O) \\
C_f + C(O) & \rightleftharpoons C(CO)_B \\
C(CO)_A & \longrightarrow CO(g) + nC_f \\
C(CO)_B & \longrightarrow CO(g) + nC_f \\
C_f + C(O) & \rightleftharpoons C(CO)_C
\end{align*}
$$

, where $C_f$ represents a free active carbon site, $C(CO_2)$ and $C(O)$ are the carbon site occupied by CO, and an oxygen atom respectively. $C(CO)$ represents the site occupied by CO, with the subscripts A, B and C indicating the sites formed via different reactions. A very complex rate expression would result if all proposed reactions were taken into account.

On the other hand, an application of Langmuir-Hinshelwood mechanism to describe the C-CO$_2$ reaction kinetics, results in the rate expression as [150,151,160] follow

$$
R'_{g} = \frac{k_{a}N_{1}P_{CO_2}}{(1+k_{b}P_{CO}+k_{c}P_{CO_2})}, \quad \text{Equation 4-2}
$$
where $k, k_a, k_b,$ and $k_c$ are the rate or ratio of rate constants, $N_t$ is the total number of active sites. Equation 4-2 is consistent with a subset of the above elementary reactions [160], and two commonly recognised gasification mechanisms, (Mechanism A [150,151,161,162] and Mechanism B [15], below), with different meanings of $k, k_a$ and $k_c$ [164].

Mechanism A:

$$C_f + CO_2 (g) \xleftrightarrow{k_1 \over k_{-1}} C(CO) + C(O) \quad \text{R.4-1}$$

$$C(CO) \xrightarrow{k_2} CO(g) + nC_f \quad \text{R.4-2}$$

Mechanism B:

$$C_f + CO_2 (g) \xrightarrow{k_1} C(CO) + C(O) \quad \text{R.4-3}$$

$$C_f + CO(g) \xleftrightarrow{k_2 \over k_{-2}} C(CO) \quad \text{R.4-4}$$

$$C(CO) \xrightarrow{k_3} CO(g) + nC_f \quad \text{R.4-5}$$

In mechanism A, CO retards the gasification due to the reaction of chemisorbed oxygen with gaseous CO to generate CO$_2$. In mechanism B, the retardation happens via the adsorption of CO on a free active carbon site. Debates over the two mechanisms will not be reviewed here but can be found elsewhere [165]. In general, mechanism A, also known as the Ergun’s mechanism, has been studied to a wider extent. The above mechanisms were fitted to the experimental data at pressures of CO up to 1 atm. At higher pressures, up to 40 atm, Blackwood and Ingeme [160] found their data to be best fitted with a rate expression as

$$R'_g = k_a N_t p_{co_2} + \frac{k_b N_t p_{co_2}^2}{(1+k_c p_{co_2}+k_d p_{co})}. \quad \text{Equation 4-3}$$

Studies focusing on high CO partial pressure in a gasification environment have been carried out to a lesser extent in previous work. The amount of produced CO from C-CO$_2$ gasification is usually too low to exhibit its effect on the gasification rate. Only when the partial pressure of CO in the system reach certain amount, does it become possible to
validate the CO term in rate expressions. In this study, CO was intentionally introduced to the system at different concentrations to investigate its effect on gasification. A numerical model based on Mechanism A was developed to describe the gasification of Polish char. The literature reported values of the activation energy of R.4-1, 95 kJ/mol [161], was used as the starting point for the fitting of other kinetic data. The kinetic data, obtained by taking the initial conditions at different temperatures and CO concentrations were substituted into the model to fit the experimental results.

4.2 Experimental methods
The experimental investigation was carried out in a quartz tube reactor loaded with silica sand, the same as the one used for Chapter 3, in a bubbling fluidised bed, as described in 2.3.2. CO with various concentrations (0.5%, 1%, or 3.5%) mixed with 20% CO$_2$ (balance N$_2$) was used as the fluidising gas. The temperature investigated was from 1148 to 1248 K. Around 0.04 g of Polish coal derived char (the same fuel used in Chapter 3) was fed into the fluidised bed for every single experiment. The product gas was sampled and analysed by a FTIR. Refer to 2.3.2 for more detailed experimental conditions.

4.3 Theory of the numerical model
As described in Chapter 3, gasification of Polish char was mainly controlled by chemical kinetics. However, there was no strong evidence showing that the gasification is purely free of intra-particle diffusion limitation. A numerical model, containing both the kinetic part and the intra-particle diffusion is developed. Assuming that the gasification is totally free of intra-particle diffusion limitation, the obtained kinetic parameters can be directly substituted into the model. Good fitting of the modelled results with the experimental results imply the validity of the assumption. The intra-particle diffusion part in the model should not affect the results if gasification is free of diffusion limitation. Otherwise, the experimental results would be underestimated, and the presence of the diffusion part in the model would then increase the difference between the experimental and modelling results. The intrinsic kinetics of the model is developed based on the Ergun’s two-step mechanism [161], and the diffusion part is built from Cylindrical Pore Interpolation Method (CPIM) [166], a method based on Maxwell Stefan equations for describing multicomponent diffusions.
4.3.1 Intrinsic kinetics of gasification in CO, based on Ergun’s mechanism

(Mechanism A)

In Chapter 3, kinetic data based on Arrhenius law was obtained. However, this can only be thought as a preliminary treatment of the experimental results. CO gasification of carbon, known as the Boudouard reaction (R. 4-6), is better described by Ergun’s two step (R. 4-1 and 4-2) mechanism [161], which is also widely recognised.

\[ C + CO_2 \leftrightarrow 2CO \]  
R. 4-6

By applying a pseudo steady state assumption for the concentration of \( C(O) \), the rate of the production of CO can be expressed as [161]

\[ R'_{g,o} = \frac{2c_2(k_{CO_2} - \frac{p_{CO_2}^2}{K_P})}{p_{CO_2}^2 + \frac{k_2}{k_1} + \frac{k_1}{k_2} + \frac{k_1}{k_1} \times p_{CO}}. \]  
Equation 4-4

The term \( \frac{p_{CO}^2}{K_P} \) was later introduced to account for the reversibility of step two in Mechanism A [165]. In this expression, \( k_i \) represents rate constant per active site with an activation energy of \( E_i \); \( p_{CO_2} \) and \( p_{CO} \) are partial pressures of CO and CO, respectively; \( c \) is the concentration of active sites per unit mass of carbon; \( K \) is the equilibrium constant.

In this chapter, the experimental data were retreated to obtain kinetic data based on Eq. 4-4. The equation shows that the overall rate does not follow the Arrhenius law, while individual steps do. Ergun [167] found the equilibrium constant for R.4-1, and the activation energy of \( c k_2 \) by carrying out experiments for three types of carbons:

\[ K_1 = \frac{k_1}{k_{-1}} = 4150 \times \exp \left( \frac{E}{R_{ideal}T} \right) \]  
Equation 4-5

\[ E_{ck_2} = 247 \text{ kJ/mol}, \]  
Equation 4-6

where \( E \) was found to be -95 kJ/mol, \( K_1 \) is the equilibrium constant of R. 4-1. \( K_1 \) was found to be only a function of temperature, regardless of the type of carbon. Likewise, the activation energy of \( c k_2 \) was independent of carbon types. If the concentration of active site is independent of temperature, and \( k \) changes exponentially with \( 1/T \), this indicates that \( k \) is the same for each of all types of carbon. The primary property accounting for the differences in reactivity between carbons is the variation of the number of active sites per unit mass of carbon, \( c \). It is not possible to directly measure the rate
constants $k_1$ and $k_2$, without measuring the concentration of active sites $c$ of the char [161]. $c$ also changes as the gasification proceeds, which can be expressed as a function of $X$, the conversion of the char. $f(X)$ was obtained experimentally from the regime, which has the least mass transfer effect (i.e. at 1123 K) if there is any.

### 4.3.2 Intra-particle mass transfer

For the diffusion part of the numerical model, it assumes: 1) a spherical porous carbon particle with cylindrical pores of uniform pore diameter; 2) negligible temperature variation within the particle; 3) negligible internal pressure variation from the centre to the surface; 4) the fluxes $J$ can be linked via the reaction stoichiometry with a constraint that $N_2$ is stagnant, i.e. $J_{CO} = -2J_{CO_2}$, and $J_{N_2} = 0$. This last assumption is only valid if the gas concentrations are assumed to be in steady state throughout, which is not overly restrictive given that the time constant needed here to establish a steady state was about in milliseconds (i.e. the time constant for diffusion is estimated from $\frac{R^2}{D}$, where $R$ is the radius of the particle, and $D$ here is the diffusion coefficient of $CO_2$), i.e. much shorter than the time to fully convert the particle.

A material balance on the gaseous species within the spherical reacting char particle gives:

$$\frac{dy_a}{dt} = \frac{R_{ideal}T}{\rho} \left( \frac{1}{r^2} \left( \frac{d(r^2J_a)}{dr} \right) - r_g \right), \quad \text{Equation 4-7}$$

where $y_a$ is the molar fraction of component $a$, $r$ is the radial coordinate and $a = 1$ for CO, 2 for $CO_2$ and 3 for $N_2$. $R_{ideal}$ is the ideal gas constant. The reaction term is

$$r_g = \frac{v_a}{2} \times R'_g(X) \times \rho_{ln} \quad \text{Equation 4-8}$$

$$R'_g(X) = R'_{g,0} \times f(X). \quad \text{Equation 4-9}$$

$R'_g(X)$ and $R'_{g,0}$ are respectively the rate of gasification at a conversion $X$ and zero, in mol s$^{-1}$ g$^{-1}$ and $v_a$ is the stoichiometric coefficient for species $a$. $r_g$ is the gasification rate per unit volume of carbon, in mol s$^{-1}$ m$^{-3}$. The rate of change of local conversion then be obtained by
\[
\frac{dx}{dt} = R'_g(X) \times \frac{M_{\text{carbon}}}{2},
\]

Equation 4-10

where \(M_{\text{carbon}}\) is the molar mass of carbon, in g mol\(^{-1}\).

The overall gasification is non-equimolar and \(N_2\) is present as a third gas species, thus a simple binary diffusion model for description is inappropriate. CPIM, which describes diffusion of multi-components, and accounts for the effects on pore size, is applied [166]. The model is simplified here by noting that CO produced from the gasification by CO\(_2\) is at low concentrations, thus the pressure gradient term in the original CPIM is eliminated.

The pseudo steady assumption means that \(J_1 = -2J_2\), and \(J_3 = 0\); so that only the flux of CO needs to be calculated. Now, the diffusion terms have the following forms:

\[
\frac{dy_1}{dr} = \frac{\tau^2 R_{\text{ideal}}}{\epsilon P} \left[ y_{12} \left( \frac{(D_A)_{23}}{(D_A)_{12}} \right) - y_{12} \left( \frac{(D_A)_{12}}{(D_A)_{13}} \right) \right] \quad \text{Equation 4-11}
\]

\[
\frac{dy_2}{dr} = \frac{\tau^2 R_{\text{ideal}}}{\epsilon P} \left[ y_{21} \left( \frac{(D_A)_{13}}{(D_A)_{12}} \right) - y_{21} \left( \frac{(D_A)_{12}}{(D_A)_{23}} \right) \right] \quad \text{Equation 4-12}
\]

\[
\frac{dy_3}{dr} = \frac{\tau^2 R_{\text{ideal}}}{\epsilon P} \left[ y_{31} \left( \frac{(D_A)_{13}}{(D_A)_{12}} \right) + y_{32} \left( \frac{(D_A)_{12}}{(D_A)_{23}} \right) \right], \quad \text{Equation 4-13}
\]

where \(y_i\) is the molar fraction of species \(i\), \(J_i\) is the molar flux, \((D_A)_{ij}\) is the molar diffusivity. \(\epsilon\) and \(\tau^2\) are the porosity and the tortuosity factor of the particle, respectively. \(P\) is the total pressure. \((D_A)_{ij}\) is obtained by interpolating between the extremes of continuum and Knudsen flow:

\[
\frac{1}{(D_A)_{ij}} = \frac{1}{(D_K)_{i}} + \frac{1}{(D_B)_{ij}}. \quad \text{Equation 4-14}
\]

\((D_K)_{i}\) and \((D_B)_{ij}\) are the Knudsen diffusivity and the molecular diffusivity, respectively. \((D_K)_{i}\) and \((D_B)_{ij}\) are given by:

\[
(D_K)_{i} = \frac{d_{\text{pore}}}{3} \sqrt{\frac{8R_{\text{ideal}}}{\pi M_i}} \quad \text{Equation 4-15}
\]
\[(D_B)_{ij} = \frac{1.00 \times 10^{-8} \rho^{1.75} \left( \frac{1}{M_i} + \frac{1}{M_j} \right)^{1/2}}{p \left( \sum_i v'_{\alpha} \right)^{1/2} + \left( \sum_j v'_{\alpha} \right)^{1/2}}. \quad \text{Equation 4-16}\]

For estimating \((D_B)_{ij}\), which was determined by Fuller et al. [168] is used. \(d_{\text{pore}}\) is the pore diameter, \(M_i\) is the molar mass of species \(i\), \(v'_{\alpha}\) is the atomic diffusion volume of an element in species \(i\), or \(j\). In this study, Knudsen diffusion, \((D_k)_i\), was found the rate limiting step that governs the overall molar diffusion, \((D_A)_{ij}\), \(i.e.\) the values of \((D_B)_{ij}\) are usually more than twice those of \((D_k)_i\).

The porosity \(\varepsilon\) and pore diameter \(d_{\text{pore}}\) change with conversion of the carbon \(X\), which could affect the diffusion. The correlations of porosity and pore diameter proposed by Dai et al. [158] are used in the study, assuming that the crossover between uniform pore channels can be neglected, and the enlargement of pores occurs only in a radial direction:

\[
\frac{\varepsilon(r)}{\varepsilon_o} = \left( \frac{d_{\text{pore}}}{d_{\text{pore, o}}} \right)^2 \quad \text{Equation 4-17}
\]

\[
d_{\text{pore}} = d_{\text{pore, o}} \sqrt{\frac{(\varepsilon_o + X(1 - \varepsilon_o))/\varepsilon_o}{}}. \quad \text{Equation 4-18}
\]

\(\varepsilon_o\) and \(d_{\text{pore, o}}\) are respectively the initial porosity and pore diameter. The values are determined by N\(_2\) adsorption and mercury intrusion porosimetry in Table 4-1.

The model assumes following initial and boundary conditions:

For \(t = 0\):

\[P_{\text{co}}(r) = P_{\text{co, bulk}}, \ P_{\text{co}_2}(r) = P_{\text{co}_2, bulk}, \ X(r) = 0\]

For \(r = 0\):

\[J_{\text{co}}(t) = 0, \ J_{\text{co}_2}(t) = 0\]

For \(r = R\):

\[P_{\text{co}}(t) = P_{\text{co, bulk}}, \ P_{\text{co}_2}(t) = P_{\text{co}_2, bulk}\]

, where \(P_{\text{co, bulk}}\) and \(P_{\text{co}_2, bulk}\) are respectively the partial pressure of CO and CO\(_2\) in the bulk phase, \(R\) is the radius of the particle.
4.3.3 Solution of the model

Parameters of the char particles were listed in Table 4-1. The tortuosity value was assumed to be the reciprocal of the porosity, as suggested by Bhatia and Perlmetter [169].

Table 4-1 Model parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial porosity $\varepsilon_o$</td>
<td>0.69</td>
</tr>
<tr>
<td>Initial pore diameter $d_{pore,o}$</td>
<td>160 nm</td>
</tr>
<tr>
<td>Tortuosity factor $\tau^2$</td>
<td>1.43</td>
</tr>
<tr>
<td>Surface area</td>
<td>240 m$^2$/g</td>
</tr>
<tr>
<td>Pore volume</td>
<td>1.44 cm$^3$/g</td>
</tr>
</tbody>
</table>

The pseudo-steady assumption for the gas phase allows the equations describing the diffusion to be simplified. By substituting $J_1 = -2J_2$ into Eq. 4-11, gives

$$\frac{dy_1}{dr} = \frac{\tau^2RT_1}{\varepsilon P} \left[ \frac{-2y_1}{\alpha_{A21}} - \frac{y_2}{\alpha_{A12}} - \frac{y_3}{\alpha_{A13}} \right].$$  \hspace{1cm} \text{Equation 4-19}

This assumption reduces the number of gas phase species, which need to be solved, to one, since $J_1 = -2J_2$, and $y_1 + y_2 + y_3 = 1$, which is valid when the generated CO concentration is relatively low. Despite a pseudo-steady state in the gas phase being assumed, the model was solved firstly by discretising the gas and solid phase balance equations, and marching forward in time (finite difference method) the time-dependent mass balance equations. The model was solved in Matlab using ODE15s.

4.4 Results

4.4.1 Experimental investigation of the effect of CO on char gasification

Experiments of introducing CO along with the gasification agent, 20% CO, were carried out at temperatures from 1148 to 1248 K. Typical experimental results of gasification at various CO concentrations (0%, 0.5%, 1%, and ~ 3.5% CO) at 1173 K, were presented in Fig. 4-1. Apparently, the presence of CO significantly decreased the gasification rate. Around 0.5% of CO decreased the gasification rate to about half of the rate when no CO
was introduced. Interestingly, further increase in the CO amount did not lead to significant drop in the gasification rate: the rates with 1% CO and 3.4% CO were comparable and not much lower than that in the presence of 0.5% CO.

Figure 4-1 Gasification of Polish char in a fluidised bed at 1173 K by a mixed stream of CO, CO₂, and N₂, where CO₂ was always at 20% and CO from 0% to 3.4% CO (balance N₂).

4.4.2 Determination of the kinetic data based on Ergun’s equation

By rearranging the rate expression of gasification Eq. 4-4, and neglecting the term \( \frac{p_{co}^2}{K_p} \), Eq. 4-20 is obtained. At \( X = 0 \), \( ck_1 \) and \( ck_2 \) are obtained from the slope and intercept of the rearranged equation. Substituting \( p_{co_2}, p_{co} \) at \( X = 0 \), and varying \( \frac{k-1}{k_1} \) (based on varying a value of activation energy between -92 to -98 kJ/mol [161]), the slope and intercept were determined by having the least squared value of the initial rates. Table 4-2 gives the obtained kinetic parameters results, and the activation energy of \( \frac{k-1}{k_1} \) is -93 kJ/mol (by fitting). These experimentally obtained kinetic parameters (i.e. \( ck_1, ck_2 \) and \( k/k_1 \)), which were the main variables for the numerical model at different operating conditions, were substituted into the model to predict the gasification profiles.

\[
\frac{p_{co_2}}{k_{g,o}} = \frac{1}{2ck_2} \left( p_{co_2} + \frac{k-1}{k_1} p_{co} \right) + \frac{1}{2ck_1} \quad \text{Equation 4-20}
\]
Table 4-2 Kinetic results of char gasification based on Ergun’s equation, from the experimental data of CO concentrations varying from 20% to 100%.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$ck_1$ (mol s⁻¹ g⁻¹ bar⁻¹)</th>
<th>$ck_2$ (mol s⁻¹ g⁻¹)</th>
<th>$k/k_1$ (bar)</th>
<th>$k/k_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1123</td>
<td>4.863x10⁻⁴</td>
<td>2.336x10⁻⁴</td>
<td>0.4804</td>
<td>5.083</td>
</tr>
<tr>
<td>1148</td>
<td>6.248x10⁻⁴</td>
<td>4.678x10⁻⁴</td>
<td>0.7487</td>
<td>4.092</td>
</tr>
<tr>
<td>1173</td>
<td>1.660x10⁻⁴</td>
<td>4.845x10⁻⁴</td>
<td>0.2919</td>
<td>3.324</td>
</tr>
<tr>
<td>1223</td>
<td>3.488x10⁻⁴</td>
<td>1.050x10⁻³</td>
<td>0.3011</td>
<td>2.251</td>
</tr>
<tr>
<td>1248</td>
<td>6.317x10⁻⁴</td>
<td>1.815x10⁻¹</td>
<td>0.2873</td>
<td>1.874</td>
</tr>
</tbody>
</table>

Based on the values of $ck_1$ and $ck_2$ shown in Table 4-2, the corresponding activation energies, $E_{ck_1}$ and $E_{ck_2}$ are obtained, which are -244 and -176 kJ/mol respectively. The values of $E_{2ck_1}$ and $E_{2ck_2}$ are within the value ranges reported previously in literature [14,170], and the overall value of overall activation energy of gasification would fall into the range between -244 and -176 kJ/mol, similar the range of values estimated from Arrhenius law, which is between 196 to 216 kJ/mol. The high value of the activation energy also suggests less likelihood of being limited by the diffusion for gasification.

4.4.3 Comparison of experimental and model results based on Ergun’s equation

- Validation of model

The model assumes a fixed radius, but this is only valid when the local conversion at the boundary does not reach 100%. Figure 4-2 gives the computed local conversion as a function of dimensionless time (defined as the ratio of the ongoing gasification time to the total time required for the completion of the gasification). It shows that the difference in the local conversion between the center and the surface boundary at 1173 K is not as significant as that at 1248 K. Under these conditions, the local conversion at the center was predicted to be ~ 0.98 when the outer surface reached the conversion of unity (and when the particle boundary would begin to move). Therefore, for this Polish char, the entire char particle is almost fully converted before a moving boundary appears, characteristic of the gasification not being limited by diffusion through the particle.
Figure 4-2 Local conversion profiles of the modelled (based on Ergun’s mechanism) results from gasification of Polish char by 20% CO$_2$ at (a) 1173 K, and (b) 1248 K.

- **Modelled results based on Ergun’s equation**
  $f(X)$ that could describe the change in pore structure is obtained experimentally at 1123 K. Gasification at 1123 K, which is the lowest operating temperature in this study, should
be of least mass transfer limitation, if there is any. Experimental gasification of char particles of a wide range of sizes (from 250 to 1180 µm) was performed to confirm that it is not mass transfer limited, as shown in Fig. 4-3. No noticeable difference in obtained rates was observed, indicating the gasification being fully kinetically controlled at 1123 K.

![Gasification of Polish char in FB at 1123 K, by 100% CO₂, with different particle size fractions, in µm.](image)

The $f(X)$ expression obtained at 1123 K was then applied to the model to compute experimental results at all temperatures. Figure 4-4 presents the comparison of the rate of gasification under different operating conditions (whilst no CO was intentionally introduced into the reactor at this stage) between experimental and modelled results. It shows good agreement between the experimental and modelled data from 1123 to 1248 K, and at various CO concentrations.
Figure 4-4 Comparison of experimental and model (based on Ergun’s mechanism) results of gasification with conditions (a). at 1123 K, by 20% CO₂, (b). at 1123 K, by 60% CO₂, (c). at 1123 K, by 100% CO₂, (d). at 1173 K, by 20% CO₂, and (e). at 1248 K, by 20% CO₂.

The comparison of the concentration of CO within the char particle over gasification were modelled, with results at 1123 K and 1248 K were shown in Fig. 4-5. The concentration of CO depends on the rate at which it is produced by the reaction and the rate at which it
diffuses from the particle. As illustrated in Fig. 4-5a, at 1123 K, the local CO mole fraction at the particle centre firstly increases to a maximum (~ 0.021) from an initial value of ~ 0.018, followed by a gradual decrease to zero. As the temperature increases to 1248 K (Fig. 4-5b), the change in the [CO] at the centre was from 0.135, to 0.150, and to 0. The corresponding maximum deviations from the boundary value to the centre of CO, (not shown here) is 0.07, i.e. 0.2 at the boundary and 0.13 at the centre. From the deviation in the concentration of CO, across the particle, no significant influence from diffusion was expected, yet the large changes in CO concentration might have still imposed some diffusion limitation. For a system, in which the reaction rate is a non-linear function of both the product and the reactant, the effect of diffusional resistance depends on the sensitivity of the rate to the concentration of these species. The large amount of CO that builds up (suggested by Fig. 4-5b) and the lack of apparent limitation on the gasification indicates that the gasification rate is relatively insensitive to the concentration of CO. The form of the Ergun expression and the values of the constants used, mean that the apparent kinetics are not greatly affected by a large CO concentration.

4.4.4 The effect of CO
The modelled (i.e. based on Ergun’s expression), and experimental results of gasification agreed reasonably well in the cases presented previously, in which the background levels of CO in the experiments were small. However, as shown in Fig. 4-6, when CO was present in the fluidising gas, the fitting was very poor for both the two concentrations of CO. The modelled results significantly over-estimated the gasification rates.

Figure 4-5 Modelled (based on Ergun’s mechanism) CO mole fractions inside the char particle gasified by 20 % CO, at (a). 1123 K, and (b). 1248 K.
4.5 Discussion

4.5.1 Refitting the results based on different CO concentrations

The model, based on Ergun’s mechanism, fitted well with the experimental data without any intentionally introduced CO in the background; whilst it over-estimates the experimental data when CO was applied. It should be aware that the kinetic data used for the model was obtained from the experimental results at various temperature and CO concentrations from 20% to 100%. For these conditions, the measured initial CO concentrations were low, and their effect on the estimation of kinetic data might not be significant. The obtained kinetic data, in this case, might only suit for low CO concentrations at a wide range of CO concentrations. This means the only term that describes the inhibition effect of CO, \( \frac{k_1}{k_{-1}} \), might have been underestimated, and the underestimated effect only becomes significant and noticeable when [CO] is significant. Therefore, to be able to predict the conditions with 1% and ~3.5% CO in the background gas, the kinetic data were re-fitted by taking into account all levels of CO at different CO concentrations. Table 4-3 gives the refitted kinetic data, based on Ergun’s mechanism.

The activation energy of \( \frac{k_{-1}}{k_1} \) obtained this time was -108 kJ/mol (with a fixed the pre-exponential factor \( A = 4150 \)), much higher the originally obtained - 93 kJ/mol. The much higher values of \( \frac{k_{-1}}{k_1} \) from the re-fitting, as shown in Table 4-3, suggests more pronounced effect of CO inhibition. Figure 4-7 presents the results based on the re-fitted kinetic data at various conditions at 1173 K. Much improved fitting of the experimental results was obtained with the new kinetic data for all the conditions, compared to Fig. 4-6.
Table 4-3. Re-fitted kinetic data based on CO at various concentrations.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$c_k$</th>
<th>$c_{k'}$</th>
<th>$k/k_1$</th>
<th>$k_{1}/k_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1148</td>
<td>0.0061</td>
<td>0.0002</td>
<td>0.036</td>
<td>19.699</td>
</tr>
<tr>
<td>1173</td>
<td>0.0196</td>
<td>0.0003</td>
<td>0.017</td>
<td>15.478</td>
</tr>
<tr>
<td>1223</td>
<td>0.0176</td>
<td>0.0008</td>
<td>0.046</td>
<td>9.842</td>
</tr>
<tr>
<td>1248</td>
<td>0.0466</td>
<td>0.0013</td>
<td>0.027</td>
<td>7.956</td>
</tr>
</tbody>
</table>

Figure 4-7 Gasification results using the re-fitted kinetic data at 1173 K in (a). 20% CO$_2$ + 0% CO, (b). 20% CO + 1% CO, (c). 20% CO + 3.4 % CO, and (d). 60% CO + 1% CO.

4.5.2 Rate expression based on a three-step mechanism

A new rate expression based on a three-step mechanism is deduced as follow. The intra-particle mass transfer in the model remains the same as previously described. The new
mechanism is a combination of Mechanisms A (Ergun’s) and B. It differs from Ergun’s mechanism by taking into account the situation when CO gas molecules can block the active sites to form C(CO):

\[ CO_2(g) + C_f \xrightarrow{k_1} CO(g) + C(O) \]
\[ C(O) \xrightarrow{k_2} CO(g) + nC_f \]
\[ CO(g) + C_f \xrightarrow{k_3} C(CO). \]

By applying assumptions from the Langmuir adsorption isotherm [171], and at steady state, the rate of formation of \( C(O) \) equals the rate of disappearance of \( C(O) \):

\[
\frac{d\theta_1}{dt} = k_1 p_{CO_2} (1 - \theta_1 - \theta_2) - k_{-1} p_{CO} \theta_1 - k_2 \theta_1 = 0.
\]

Similarly, for \( C(CO) \):

\[
\frac{d\theta_2}{dt} = k_3 p_{CO} (1 - \theta_1 - \theta_2) - k_{-2} \theta_2 = 0.
\]

\( \theta_1 \) and \( \theta_2 \) are respectively the surface active coverage by \( C(O) \) and \( C(CO) \).

The rate of carbon transfer per unit mass of carbon from solid phase to the gas phase is then \( R'_{g} = c k_2 \theta_1 \), giving a final rate expression of

\[
R'_{g} = \frac{2ck_2 \times p_{CO_2}}{p_{CO_2} + \left(\frac{k_{-1}}{k_1} + \frac{k_2}{k_1} K_3\right) \times p_{CO} + \frac{k_{-1}}{k_1} K_3 \times p_{CO}^2 + \frac{k_2}{k_1} K_3 \times p_{CO}} f(X),
\]

Equation 4-21

where

\[ K_3 = \frac{k_2}{k_{-3}}. \]

To obtain the values of the kinetic terms, Eq. 4-19 is rearranged into:

\[
\frac{p_{CO_2}}{R_{g}} = \frac{1}{2ck_2} \left( p_{CO_2} + \left(\frac{k_{-1}}{k_1} + \frac{k_2}{k_1} K_3\right) p_{CO} + \frac{k_{-1}}{k_1} K_3 \times p_{CO}^2 \right) + \frac{1}{2ck_1}.
\]

Equation 4-22
This new rate expression has an extra term describing the inhibition effect of CO, depending on the square of the partial pressure of CO. By taking the slope and the intercept of $\frac{P_{CO_2}}{RT_g}$ versus $(p_{CO_2} + \left(\frac{k_{-1}}{k_1} + \frac{k_2}{k_1}K_3\right)p_{CO} + \left(\frac{k_{-1}}{k_1}K_3p_{CO}^2\right)$, $2ck_2$ and $2ck_1$ are obtained. The kinetic data are obtained by achieving least squared values of the initial rates. $k_1/k_2$ and $K_3$ are constrained to follow the Arrhenius relation. Table 4-4 presents the values of the kinetic data for the new equation, and the new modelled results, in comparison to the experimental results, are shown in Fig. 4-8.

Table 4-4 Kinetic results of char gasification based on the new rate equation.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$c_k$</th>
<th>$c_k$</th>
<th>$k_1/k_2$</th>
<th>$k_1/k_2$</th>
<th>$K_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1148</td>
<td>0.0054</td>
<td>0.00022</td>
<td>0.0405</td>
<td>19.751</td>
<td>0.570</td>
</tr>
<tr>
<td>1173</td>
<td>0.0087</td>
<td>0.00034</td>
<td>0.0366</td>
<td>15.470</td>
<td>0.558</td>
</tr>
<tr>
<td>1223</td>
<td>0.0096</td>
<td>0.00082</td>
<td>0.0897</td>
<td>9.954</td>
<td>0.535</td>
</tr>
<tr>
<td>1248</td>
<td>0.0371</td>
<td>0.0012</td>
<td>0.0337</td>
<td>8.090</td>
<td>0.524</td>
</tr>
</tbody>
</table>

![Graphs]
According to Fig. 4-8, good fitting of the experimental data with the results from the three-step mechanism, was achieved for various combinations of CO and CO$_2$ concentrations. Comparing Figs. 4-7 and 4-8, the new rate equation model even gave a slightly better fit for the conditions at 20% CO$_2$ + 1% CO. At this stage, it is difficult to determine which rate expression is significantly better for describing the gasification of Polish char, but both show higher sensitivity to the presence of CO than the results based on Ergun’s mechanism with no introduction of CO. The mole fractions of CO across the radius of a char particle over gasification by 20% CO$_2$ modelled from the three conditions: Ergun’s mechanism with kinetic data obtained at no introduction of CO, Ergun’s mechanism with kinetic data involving introduction of CO, and three-step mechanism, were compared and shown in Fig. 4-9. The mole fractions of CO inside the char particle from Fig. 4-9b and 4-9c are much lower than the one from Ergun’s mechanism with kinetic data obtained without CO addition experiments (Fig. 4-9a). However, the modelled overall gasification rates of the char particle from the three conditions all fitted well of the experimental data, as shown in Figs. 4-4d, 4-7a, and 4-8a, indicating higher sensitivity to CO locally with the latter two situations.
Figure 4-9 Modelled CO mole fraction across the radius of the char particle over gasification by 0 % CO and 20 % CO, at 1173 K, based on (a). Ergun’s mechanism with kinetic data obtained at no introduction of CO, (b). Ergun’s mechanism with the kinetic data obtained involving the introduction of CO, and (c). three-step mechanism.

The local gasification rate across the char particle from the three-step mechanism was also presented to understand the effect of local CO on the gasification rate. Figure 4-10 shows the local rates under various introduced CO concentrations at 1173 K. Some difference, whilst not significant, in the gasification rate between the particle center in the initial period was observed when gasified by 20% CO (no introduced CO), as shown in Fig. 4-10a, corresponding to the case when a maximum of ~ 3% accumulation of CO in the particle center and 0% at the surface in Fig. 4-9c. This indicates less effect of the [CO] gradient on the local gasification rate in the beginning of gasification. The overall gasification rate, as shown in Fig. 4-8a, also seems to be similar to the roughly averaged local gasification rates from the center to the surface. In the later stage of gasification, larger differences in the local rate across the particle were observed in Fig. 4-10a. This probably mainly resulted from the difference in local conversion, caused by the differences in local $f(X)$ values.
When there is the intentionally introduced CO in the background (1% and 3.4%), as seen in Fig. 4-10b and 4-10c, the presence of the high [CO] in the background significantly decreased the local rates across the radius. Furthermore, the rates in the center decreased to much lower values than the rate of in the presence of 3% locally produced CO (Figs. 4-9c and 4-10a). This indicates a higher sensitivity of the gasification rate to the externally added CO rather than locally self-produced CO. In addition, the rate gradients across the particle when CO was intentionally introduced in Fig. 4-10b and 4-10c, are lower than over the whole gasification period. The dimensionless radius here was defined as the ratio of distance between a radial position and the particle center, over the initial radius of the particle.

![Diagram](image1)

**Figure 4-10** Local gasification rate (modelled based on the three-step mechanism) across the radius of the char particle over gasification time at 1173 K, in 20% CO, mixed with (a) 0% CO, (b) 1% CO, and (c) 3.4% CO as gasification agent.

Investigation of the effect of the intentionally introduced CO in the background on the gasification rates is carried out here. Roberts and Satterfield [172] defined a modified Thiele modulus, for a reaction with a rate expressed as:
\[ r = \frac{k_{\text{pA}}}{1+K_A p_A + \sum_i K_i p_i}, \]  

Equation 4-23

where \( l \) is used to denote any reaction product other than the reactant A. According to Eqs. 4-4, 4-8, 4-9 and 4-23, the following relations can be obtained

\[ k = c k_1 \rho_m \times f(X) \]

\[ K_A = \frac{k_1}{k_2} \]

\[ K_l = \frac{k_1}{k_2}. \]

The modified Thiele modulus by Roberts and Satterfield is:

\[ \phi_m = L (k'' \frac{R_{\text{ideal}T}}{D_{\text{co2}}^{\text{eff}}})^{1/2}, \]

where

\[ k'' = \frac{k}{\omega} \]

\[ \omega = 1 + K_l [p_{\text{co},s} + (2p_{\text{co},s} D_{\text{co2}}^{\text{eff}} / D_{\text{co}}^{\text{eff}})]. \]

\( D_{\text{co2}}^{\text{eff}} \) and \( D_{\text{co}}^{\text{eff}} \) are the effective diffusivity of CO and CO, \( p_{\text{co},s} \) and \( p_{\text{co2},s} \) refer to the partial pressures of CO and CO, at the particle surface. \( L \) refers to the characteristic length of a particle. Without the addition of CO to the system, the surface CO partial pressure, \( p_{\text{co},s} \), is always zero (the boundary condition used in the study), as a result, \( p_{\text{co},s} \) in the denominator of the \( \phi_m \) can be removed. Whereas, when CO is added to the fluidising agent, the presence of \( p_{\text{co},s} \) results in a decrease of \( \phi_m \). This means that the addition of CO suppresses the rate gradient across the particle. As seen in Fig. 4-10, the change of externally introduced CO from 0% to 3.4% CO results in a decrease of concentration gradient across the particle. With higher level of CO present on the surface, the local rate at the center becomes more sensitive to the surface high CO concentration. The boundary condition of high CO restrained the overall gasification of the particle.
4.6 Conclusions

The main results from the numerical study of the gasification of Polish char and the investigation of the inhibition effect of CO are summarised as follow:

a). A numerical model based on Ergun’s two step mechanism and the kinetic data obtained without the addition of CO to the system, was used to fit the experimental gasification results. It gave good fit of the experimental results of gasification at various CO₂ concentrations (without CO introduced externally) at different temperatures. However, the model significantly over-estimated the gasification rates when CO was intentionally added.

b). By including the experimental results of adding CO, new kinetic data from Ergun’s mechanism was obtained. With the re-fitted data, the fitting of the experimental results was significantly improved. The higher $\frac{k_{-1}}{k_1}$ values for Ergun’s two step mechanism suggest enhanced inhibition effect of CO. Based on a fixed pre-exponential factor $A$ ($A=4150$), an activation energy of $\frac{k_{-1}}{k_1}$ of -108 kJ/mol was obtained for the newly fitted kinetic data, much higher than the previously suggested ~ -95 kJ/mol.

c). A new rate expression developed from a three-step mechanism was developed, and it has an extra term (depending on the square of $p_{CO}$) describing the inhibition effect of CO. The model based on this three-step mechanism fitted well of the experimental data both without and with (i.e. 1 % and 3.4 % CO) the introduction of CO.

d). The study showed more pronounced inhibition effect of CO than expected, especially when CO was intentionally introduced in the system, along with the gasification of CO₂. According to the modified Thiele modulus, the added CO suppresses the rate gradient across the particle. This is probably the main reason for the gasification rate being more sensitive to the surface CO concentration than the local produced CO.
5.0 Development of a combined system of fluidised bed and a plasma reactor for the quantification of biomass-derived tar and investigation of the effect of oxygen carriers and the presence of CO₂ on biomass product distribution

5.1 Introduction

The effect of Fe-based oxygen carriers on CO₂ gasification of a clean solid fuel, a Polish coal-derived char, has been studied in Chapter 3. Practically, raw fuels, instead of devolatised fuels, would be used directly in industries. Direct use of un-pretreated solid fuels such as coal and raw biomass, would make the process more complicated, introducing multiple phases of products under thermal treatment, including gaseous products such as CO, CO₂, organic acids, condensable volatiles, and solid char.

CLC of liquid fuels has been studied only recently and has been normally based on model compounds due to the complexity of liquid fuels or tar. Mendiara et al. [173] investigated tar (toluene) removal by selective reforming in a chemical looping system (in TGA and a lab-scale fixed bed reactor), using four oxygen carriers (60% NiO/MgAl₂O₄, 40% NiO/NiAl₂O₄, 40% Mn₃O₄/Mg-ZrO₂, and FeTiO₃). The study compared the extent of carbon deposition of toluene on the four oxygen carriers. 40% NiO/NiAl₂O₄ and 40% Mn₃O₄/Mg-ZrO₂ were reported to have good reactivity with toluene, but 40% NiO/NiAl₂O₄ showed a high tendency for carbon deposition. They also found that the addition of H₂O reduced carbon deposition. However, the characterization of the products (apart from the deposited carbon) from the reaction between the oxygen carriers and toluene were not mentioned in this study; therefore it is not clear how these oxygen carriers further affect the distribution of the products. Ryden et al. [174] investigated CLC of kerosene with Ni-, Mn-, Cu- and Fe-based oxygen carriers in continuous operation. They reported 95% - 99% conversion of the fuel carbon converted to CO₂. CLC of solid fuels such as raw biomass or coal, rather than the derived char has been studied to a lesser extent. Some work [175–177] on char has been carried out in inter-connected fluidised CLC systems with continuous operation. However, the quantification of the amounts or character of the volatile matter and tar produced (other than CH₄) has not been undertaken. The effect of oxygen carriers on tars is not fully understood, and, it would be helpful to understand how the product distribution varies under thermal treatment (pyrolysis), and in the presence of different oxygen carriers.
This chapter aims to understand the effect of oxygen carriers on the processing of biomass, which is renewable and cleaner than raw coals, in a fluidised bed. In particular, the effect of oxygen carriers on the distribution of products under thermal treatment (pyrolysis) is examined. In addition, how the presence of gasification agent, CO₂, affects the distribution of the product is studied, and compared with the effects of oxygen carriers. The main challenge for the current study was the quantification of the condensable volatile product (liquid fuels), referred as tar in this work. Therefore, an online continuous tar measurement system needs to be first developed.

### 5.1.1 Tar measurement system

For the continuous quantification of the tar produced from the upstream, an online tar measurement system, based on the conversion of tar to light carbon-containing gaseous products at mild temperatures is developed. Dielectric barrier discharge (DBD) is a promising technique to achieve this conversion. DBD reactors have been widely studied for the abatement of VOCs [88,96,97,99]. In the current study, a DBD reactor was developed to convert the tar produced to species such as CO and CO₂, which enables the quantification of the tar to be achieved by measuring these non-condensable carbon-containing species. If the developed system is successful in the quantification of the tar, the investigation of the product distribution from biomass pyrolysis and gasification/reforming in the presence of oxygen carriers can then be carried out. In the current study, two typical oxygen carriers: Fe₂O₃, and CuO (supported on mayenite) were selected as the oxygen carriers.

### 5.2 Experimental methods

Pyrolysis of a biomass fuel, wood chips, was carried out in a quartz tube reactor, as described in 2.3.3. The pyrolysis results from a bed of active oxygen carrier (Fe₂O₃ or mayenite-supported CuO) were compared with the reference conditions in alumina sand. The temperature range of interest was from 773 to 1173 K. In addition to the fluidising pyrolysis gas being N₂, the effect of the presence of gasification agent CO₂ (~18% CO₂) on the distribution of product from the fluidised is investigated. The CO₂ experiments were carried only in alumina sand bed. The products generated from the fluidised bed including non-condensable gases, condensable volatiles and solid char were measured by different approaches. Non-condensable gases were measured by FTIR, the condensable
volatiles (referred as tar here), was measured by the tar quantification system. The quantification of char was performed by burning off the bed with air after the pyrolysis or gasification stage. For the quantification of the tar, a plasma reactor was developed and positioned downstream of the fluidised bed. For every experiment, two single runs with plasma reactor on and off (other conditions kept the same), were carried out to allow quantify the tar. A side stream of air was introduced into the plasma reactor and converted the tar into light carbon-containing gaseous species (when plasma on) that were measurable by FTIR. The difference in the signals detected by the FTIR in the two runs indicated the amount of the carbon content in the tar from the upstream. The oxygen level in the sampling line was measured by a paramagnetic oxygen analyser (ABB, EL3020). For a typical experiment, around 20 ml of bed material was fed into the quartz tube and fluidised with a flow at 3 L/min. To avoid the condensation of the tar before it reaches the plasma reactor, both the sampling system and the plasma reactor were externally heated to 573 and 523 K, respectively. More detailed experimental conditions are presented in 2.3.3.

5.3 Results

5.3.1 Tar measurement

- Identification of the product species

DBD plasma is effective in activating chemical reactions, and even N₂ (as an inert gas for most conventional chemical reactions) can react easily with other species by plasma effect. Understanding the effect of plasma on some reference gas conditions is important. Figure 5-1 shows the IR spectra (from FTIR) in the following gases passing through to the DBD reactor: pure N₂ or air/N₂ mixture (~ 8.3 vol% oxygen). The gas passing through the FB was N₂ in both cases. Additionally, the effect of plasma on the gases containing product of wood pyrolysis from the fluidised bed was also examined. In Fig. 5-1, the significant peaks at around 630 - 710 cm⁻¹, 2280 - 2380 cm⁻¹, and 3580 - 3770 cm⁻¹ are the typical peaks of CO₂. The main species detected from plasma running in N₂ was CO₂ (< 100 ppm). The CO₂ peaks in N₂ might have come from contamination in the system or have been an artefact of the background subtraction. No nitrogen-containing species were detected by the FTIR. When the stream of air joined the N₂ and was passed through the plasma reactor, the products detected were N₂O, NO₂, NO, and CO₂. In Fig. 5-1, only the main peaks of NO and NO are marked, because the secondary peaks overlapped those
for CO, CH, and CO₂. Ozone is often formed in plasma reactor in the presence of air [178], but was not observed here. This might be due to the excess of N₂ and the external heating of the plasma reactor. It could be that any ozone produced quickly decomposed in the heated environment and reacted with N₂ to form more stable species such as NO, NO₂ or NO₃. This is in agreement with the findings of Huu et al. [97]. They studied methane removal using a plasma-catalytic hybrid reactor, showing that increasing the temperature of a plasma reactor significantly decreased the ozone concentration in the product stream, e.g. with a clear ozone signal at 303 K to no signal detected at 573 K.

![Figure 5-1 Spectrum of species in different gaseous environment in the presence of plasma discharge with FB fluidised in pure N₂ (SED of 1027 J/L).](image)

When wood chips were fed into the fluidised bed, the pyrolysis products entered the sampling system. A comparison between the spectra with wood fed into a fluidised bed of alumina sand at 873 K with the plasma on and off, is presented in Fig. 5-2. With the plasma running, the products after the plasma reactor, and having passed through the cold trap, were mainly N₂O, NO₂, NO, CO₂, CH₄ and CO. Whereas, the main gaseous products without downstream plasma running, were CO, CO₂, and CH₄. Some other absorption peaks at ~ 950, 1700, and 3050 cm⁻¹ were also observed without plasma running. They seem to match the peaks of acetic acid, CH₃COOH. The fact that no acetic acid signal was detected in the plasma-treated case suggests that plasma converted the acetic acid to other species, mostly likely CO or/and CO₂. The plasma reactor also seems to have converted some of CH₄ due to lower intensity of CH₄ signals observed with plasma running. It should also be remembered that any heavier hydrocarbons, which do pass
through the sampling system unconverted, would be removed before the FTIR by the cold trap.

![Figure 5-2 Spectrum of gaseous products with/without plasma running with wood fed into the fluidised bed (in N\textsubscript{2}) of alumina sand at 873 K (SED of 1027 J/L).](image)

- **Characterisation of the flow**
  
The change in composition of the gases can change appreciably the total flow rate through the sample line. In particular, the generated tar (without plasma running) appeared to block the sampling line, leading to an increased pressure drop, and causing a change in the total flow rate through the line. To resolve the issue, correction of the change in the flow was applied. For the condition without plasma running, the oxygen introduced by the side air stream can be treated as the tracing element for the estimation of the total flow in the sampling line. Whilst in the case with plasma running, the oxygen was consumed in the plasma reactor for the conversion of the tar. In this case, some model tar compounds were assumed to estimate the amount of oxygen consumed in the DBD reactor and thus work back to the total flow rate in the sampling line.

  **Without plasma**
  
The air flow, $F_{air}$, introduced to mix with the product flow sampled from the fluidised bed was controlled by a variable area flow meter and assumed to be constant at 0.45 L/min. When there was no plasma (*i.e.* oxygen was not consumed), the oxygen in the air...
flow was used as a tracer. The total flow rate in the sampling line during the experiment, $F_{\text{total}}$, could therefore be obtained by

$$F_{\text{total}} = \frac{F_{\text{air}} \times 0.21}{x_{O2}}.$$  
Equation 5-1

Here, $x_{O2}$ is the mole fraction of oxygen detected by the ABB analyser, with 0.21 being the measured mole fraction of oxygen in the supplied laboratory air. If no change in sampled gas flow occurred, the “ideal” mole fractions of product species detected by the analyser would be

$$x_{i,\text{ideal}} = \frac{F_{FB,\text{initial}} \times y_i}{F_{FB,\text{initial}} + F_{\text{air}}},$$  
Equation 5-2

$$x_i = \frac{F_{FB} \times y_i}{F_{FB} + F_{\text{air}}}. $$  
Equation 5-3

In Eq.5-2, $x_{i,\text{ideal}}$ is the “ideal” mole fraction of the product species $i$ detected by the analyser, assuming negligible change in the total flow rate due to change in the pressure drop. $F_{FB,\text{initial}}$ is initial flow rate of the gas stream that entered to the sampling line and $y_i$ is the mole fraction of species $i$ in the gas flow from the fluidised bed. For the non-ideal case, where the flow rate from the fluidised bed upstream changed due to condensation or trapping of tar or water in the sampling line, $F_{FB}$, would be lower than $F_{FB,\text{initial}}$, leading to lower measured mole fractions of the product species $i$, $x_i$. By combining Eqs.5-2 and 5-3, the rearrangement gives

$$x_{i,\text{corrected}} = \frac{x_i \times F_{\text{total}} \times F_{FB,\text{initial}}}{F_{\text{total,initial}} \times F_{FB}},$$

where

$$F_{\text{total}} = F_{FB} + F_{\text{air}}.$$  

Corrected, “ideal” mole fractions of the product species were used for the calculation of yields.
Figure 5-3 shows the results of wood pyrolysis in a fluidised bed of FeO at 873 K, without plasma running. The oxygen, which was expected to be inert, increased a little when the wood was fed into the bed. The corrected CO₂ curve based on the measured oxygen curve is very similar to that before correction, suggesting that the change in the flow did not have a significant effect on the concentration of CO₂ measured. A similar observation was made when using other gases and at different temperatures. In the gas environment of CO₂, however, there was a significant difference between the measured and corrected mole fraction profiles of the product species. Figure 5-4 compares the results without and with the correction of the total flow rate when no plasma was running. According to Fig. 5-4a, when the wood chips were fed into the fluidised bed, a sharp increase in [CO] and [CH₄] were seen. After t = 25 s, the fraction of CO₂ started to drop to below the initial stable background level (from 0.088 to 0.068). At the same time, the measured mole fraction of O₂ increased from 0.094 to 0.118 and stabilised at 0.118, unless the flow was manually adjusted. The correlated change (~ 1:1) in the mole fraction of CO₂ and O₂ strongly suggests that this change might be due to change in the flow rate in the sampling line. With the correction of the total flow, as shown in Fig. 5-4b, the mole
fraction of CO, and O₂ (after pyrolysis) returned to the initial stable levels. In terms of CO and CH₄, no significant difference in the mole fraction curves between the two cases was observed.

Figure 5-4 Mole fractions of each gas species from FB at 773 K, fluidised by 18% CO₂, without plasma running: (a). before, and (b). after correction for the changes in the flow rate. Note that the wood was fed into the fluidised bed at t = 7 s.
With plasma

In the case when there is plasma discharge, oxygen was consumed for converting the tar and no longer used as a tracer. In order to correct for changes in the dilution, the oxygen concentration before the plasma reactor was required. It was assumed that the drop in the measured oxygen level is all used to burn the tar and possibly convert CO to CO\(_2\). Assuming that the tar is oxygen-free, then the difference in total O content in the CO and CO\(_2\) between the experiments with and without plasma all comes from the oxygen being consumed. Oxygen is also being consumed to produce water during tar combustion, and this amount depends on the chemical formula of the tar:

\[
C_xH_y + \left(x + \frac{1}{4}y\right)O_2 = xCO_2 + \frac{1}{2}yH_2O.
\]

The amount of oxygen consumed for converting the carbon in tar to CO and CO\(_2\), \(F_{O_2,C}\), is

\[
F_{O_2,C} = \left(\frac{1}{2}F_{CO,\text{on}} + F_{CO_2,\text{on}}\right) - \left(\frac{1}{2}F_{CO,\text{off}} + F_{CO_2,\text{off}}\right).
\]

Here \(F_{O_2,C}\) is the molar flow rate of oxygen consumed for burning the carbon content of tar, \(F_{CO,\text{on}}\) and \(F_{CO_2,\text{on}}\) are respectively the mole flow rates of CO and CO\(_2\), with plasma running, and \(\text{off}\) indicates the condition without plasma. Taking into account the stoichiometry of the tar, \(F_{O_2,\text{tar}}\), the mole flow rate of oxygen consumed burning the tar is

\[
F_{O_2,\text{tar}} = F_{O_2,C} \times \left(1 + \frac{\frac{1}{2}y}{x}\right).
\]

The flow of oxygen through the sampling line, in the absence of combustion, is then

\[
F_{O_2} = F_{O_2,\text{tar}} + F_{O_2,\text{measured}}.
\]

Figure 5-5 shows the comparison of flowrates of the mole fractions from pyrolysis of wood chips in a bed of FeO\(_2\) at 873 K of before and after correction. In Fig. 5-5a, the measured oxygen level significantly decreased when the wood was fed into the bed. All the three tar compounds could restore the oxygen profile to the inlet of the plasma reactor, to close to the initial value, among which the correction based on pure carbon appeared to be the best. However, a tar compound usually contains some hydrogen. The fact that
pure carbon could restore the oxygen profile best is a combined effect of: 1) the tar itself might be mainly aromatics, which has very high C to H ratio; 2) the tar might contain some oxygen, which would lead to an over-estimation of the oxygen consumed for burning the carbon content in the tar; 3) incomplete combustion in the plasma reactor; 4) fluctuation in the background flow itself.

Figure 5-5b gives the corrected CO₂ mole fraction based on an oxygen level restored using pure carbon tar compound. There is little difference between the corrected and the measured values, suggesting that with plasma running there is no need to correct for changes in dilution in the sampling line with N₂ in the fluidised bed; qualitatively, very little change in flow was observed when the plasma was active.
Figure 5-5 Mole fraction of CO$_2$ from pyrolysis of wood chips at 873 K in a Fe$_2$O$_3$ bed with plasma discharge (a). measured oxygen mole fraction and calculated mole fraction at the inlet to the plasma reactor, based on different tar compound; (b). comparison of the CO$_2$ before and after correction of the flow. Note that the plasma was turned on at $t = 10$ s, and wood was fed into the FB at $t = 20$ s.
Figure 5-6 Mole fraction profiles of different species from wood processing at 773 K, with the bed fluidised in 18% CO₂, with plasma running: (a). before correction (b). ideal oxygen mole fraction based on different tar model compounds, and (c). after correction.
based on carbon as the tar model. Note that the plasma was turned on at \( t = 55 \) s, and wood was fed into the fluidised bed at \( t = 144 \) s.

The results from an experiment with the plasma active and with the fluidised bed in 18\% CO\(_2\) are shown in Fig. 5-6. When plasma was active, after wood processing in the fluidised bed and the reactions in the plasma reactor, there was an increase in the oxygen level, together with a decrease in the CO\(_2\) level. As seen in Fig. 5-6a, the level of oxygen dropped during the reaction period when the plasma was active. To be able to correct the flow rate, the oxygen profile needs to be ‘returned’ to the condition where O\(_2\) was ‘not consumed’ for tar combustion. According to Fig. 5-6b, all the three tar compounds can restore the oxygen profile reasonably well. Figure 5-6c presented the corrected product mole fractions based on an oxygen level restored using pure carbon tar compound. With correction, after the wood processing, the mole fraction of CO\(_2\) returned to the background level.

- **The effect of plasma power**

  The plasma power input would affect the type of products after the DBD reactor and the conversion efficiency of the tar in plasma discharge. The effect of the supplied power on the destruction or conversion of the carbon-containing compounds inside the plasma reactor was investigated. This was carried out with the fluidised bed loaded with mayenite-supported CuO in pure N\(_2\) at 873 K. The reason for testing the system in the mayenite-supported CuO bed was that it is more reactive than Fe\(_2\)O\(_3\) for combustion and thus expected to result in less tar from the fluidised bed. Therefore, mayenite-supported CuO requires the most sensitive measurements. Figure 5-7 gives the mole fraction of primary carbon-containing species leaving the plasma reactor after a batch of wood chips has been added, as a function of increasing plasma input power (from 0 to 17.1 W, corresponding to SED values from 0 to 1027 J/L). The time taken for completing pyrolysis in each experiment was reproducible (~30 s), as shown in Fig. 5-7. It can be seen that as SED increased, the mole fraction of CO increased accordingly, while CO\(_2\) was not affected significantly. The apparent rate of production of CH\(_4\) decreased with the increase in the plasma power. This suggests that when the tar was transported into the hot plasma reactor, most of the tar was converted to CO. Meanwhile, some of the CH\(_4\) produced from pyrolysis, was burned and probably converted to CO or CO\(_2\). Huu et al.
[97], and Baylet et al. [179] both have investigated CH₄ conversion using DBD. Under operating conditions similar to the current study (> 473 K, and a gas mixture of N/O₂/CO₂ in the plasma reactor, and a similar DBD geometry), they found CH₄ in plasma was converted primarily into CO, and a small proportion of CO₂.

Figure 5-7 Mole fraction of carbon-containing gaseous species detected (with dilution by air) at 873 K in FB for different SED values of the plasma reactor, (a) CO, (b) CO₂, (c) CH₄.
Figure 5-8 Overall mole fraction profiles of carbon-containing gaseous species (CO + CO₂ + CH₄) detected (with dilution by air) with the fluidised bed at 873 K, under different SED values of the DBD reactor.

Figure 5-8 illustrates the overall mole fraction of all carbon-containing species (CO, CO₂, and CH₄) detected by FTIR. The measurement system has ~ 18 seconds residence time (time taken for the FTIR signal change from 5% to 95% of full response to a step change). Any difference between the curves would suggest a difference in the amount of carbon in the tar being converted in plasma. No obvious deposits of tar were observed in the cold trapping tube. The amount of carbon without plasma discharge was the lowest, and the other three with plasma were higher. On the other hand, the increase in the plasma power from 400 to 1027 J/L did not lead to a clear difference in the measured carbon amount, but higher plasma power seems to cause conversion of CH₄ to CO or CO₂, as suggested in Fig. 5-6 (c). The results indicate that most of the produced tar in fluidised bed has been combusted (or converted to methane) in the presence of plasma at low power, further increase in the power did not result in a clear increase in the overall rate of conversion to (CH₄ + CO + CO₂), but the conversion of CH₄ to CO or CO₂. Table 5-1 presents the overall carbon balances at different plasma power ratings, where the carbon balance was defined as the ratio of total amount of carbon in the carbon-containing products (gases + char that measured by air burn-off after processing in N₂), as expressed in 2.3.3. The carbon balances do not reach 100%; this is probably due to some condensation of tar in the sampling tube. It was found that higher temperature in the fluidised bed led to better carbon balance, as shown in Table 5-2, suggesting either easier conversion of higher temperature-produced tar (from the fluidised bed) in the DBD reactor, or less
condensation of tar in the sampling system as it produced from hotter bed. The investigations of the effects of temperature and bed materials in the following sections were all carried out with a plasma SED of 1027 J/L.

Table 5-1 Total carbon as CO, CO₂, and CH₄, under different plasma SED (base on pure carbon as the tar compound).

<table>
<thead>
<tr>
<th>SED (J/L)</th>
<th>Total carbon balance (air-dried)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (no plasma)</td>
<td>0.73±0.02</td>
</tr>
<tr>
<td>400</td>
<td>0.89±0.02</td>
</tr>
<tr>
<td>685</td>
<td>0.90±0.03</td>
</tr>
<tr>
<td>776</td>
<td>0.92±0.02</td>
</tr>
<tr>
<td>900</td>
<td>0.93±0.02</td>
</tr>
<tr>
<td>1027</td>
<td>0.94±0.02</td>
</tr>
</tbody>
</table>

Table 5-2 Total carbon balance under various operating conditions (based on pure carbon as the tar compound).

<table>
<thead>
<tr>
<th>Bed material</th>
<th>FB temperature (K)</th>
<th>Carbon balance</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂ fluidised bed with alumina sand</td>
<td>773</td>
<td>0.86±0.02</td>
</tr>
<tr>
<td></td>
<td>873</td>
<td>0.88±0.03</td>
</tr>
<tr>
<td></td>
<td>973</td>
<td>0.96±0.02</td>
</tr>
<tr>
<td></td>
<td>1073</td>
<td>0.99±0.02</td>
</tr>
<tr>
<td></td>
<td>1173</td>
<td>1.04±0.01</td>
</tr>
<tr>
<td>N₂ fluidised bed with Fe₂O₃</td>
<td>773</td>
<td>0.85±0.03</td>
</tr>
<tr>
<td></td>
<td>873</td>
<td>0.88±0.03</td>
</tr>
<tr>
<td></td>
<td>973</td>
<td>0.98±0.02</td>
</tr>
<tr>
<td></td>
<td>1073</td>
<td>0.94±0.03</td>
</tr>
<tr>
<td></td>
<td>1173</td>
<td>1.01±0.02</td>
</tr>
<tr>
<td>N₂ fluidised bed with mayenite-supported CuO</td>
<td>773</td>
<td>0.91±0.03</td>
</tr>
<tr>
<td></td>
<td>873</td>
<td>0.94±0.01</td>
</tr>
<tr>
<td></td>
<td>973</td>
<td>0.96±0.02</td>
</tr>
<tr>
<td></td>
<td>1073</td>
<td>0.99±0.02</td>
</tr>
<tr>
<td></td>
<td>1173</td>
<td>0.97±0.03</td>
</tr>
<tr>
<td>N₂ fluidised bed with mayenite-supported Cu₂O</td>
<td>773</td>
<td>0.92±0.03</td>
</tr>
<tr>
<td></td>
<td>873</td>
<td>0.96±0.02</td>
</tr>
<tr>
<td></td>
<td>973</td>
<td>0.98±0.03</td>
</tr>
<tr>
<td></td>
<td>1073</td>
<td>1.00±0.02</td>
</tr>
<tr>
<td></td>
<td>1173</td>
<td>0.99±0.03</td>
</tr>
<tr>
<td>CO₂ fluidised bed with alumina sand</td>
<td>773</td>
<td>0.83±0.03</td>
</tr>
<tr>
<td></td>
<td>873</td>
<td>0.86±0.02</td>
</tr>
<tr>
<td></td>
<td>973</td>
<td>0.87±0.04</td>
</tr>
<tr>
<td></td>
<td>1073</td>
<td>0.97±0.03</td>
</tr>
<tr>
<td></td>
<td>1173</td>
<td>0.98±0.03</td>
</tr>
</tbody>
</table>
5.3.2 Pyrolysis of wood in alumina sand

Figure 5-9 shows the yield of each carbon-containing species including gaseous species, tar and char from wood pyrolysis in a fluidised bed of alumina sand from 773 to 1173 K. The error bars show the range of results for three repetitions. Alumina sand is relatively inert, thus chemical interaction with the wood particle is expected to be minimal. According to Fig. 5-9, an increase in the operating temperature improved the production of gases. The yield of CH\(_4\), increased from less than 0.1% to 1.9% on a weight basis from 773 to 1073 K, with a maximum value of 2.5% at 973 K. A sharp increase in CH\(_4\) yield was observed when further increasing the temperature from 1073 to 1173 K; at the same time, there was a decrease in the yield of tar (the tar yield increased gradually from 773 to 1073 K, followed by a drop from 1073 to 1173 K). This suggests that the significantly increased amount of CH\(_4\), might come from the cracking of tar from 1073 to 1173 K. The yield of char was determined from the CO and CO\(_2\) produced during the burn-off period after pyrolysis. The char content gradually decreased from ~29% to ~17% from 773 to 1173 K, probably due to its decomposition as the temperature increased.

![Figure 5-9 Mass fraction of different carbon-containing product species in a bed of alumina sand from 773 to 1173 K with a fluidising gas of N.](image)

5.3.3 Pyrolysis of wood in the presence of Fe\(_2\)O\(_3\)

The results of pyrolysis of wood chips in the presence of Fe\(_2\)O\(_3\) is presented in Figure 5-10. Comparing the results from Fig. 5-9, the yields of CO are similar in alumina sand and Fe\(_2\)O\(_3\) from 773 to 973 K; beyond 973 K, the amount of CO produced in the Fe\(_2\)O\(_3\) bed dropped. As discussed in Chapter 3, the presence of Fe\(_2\)O\(_3\) mainly affects the gaseous products by reacting with CO around the surface of the char particle , and no evidence of
catalytic effect of Fe₂O₃ was found. The decrease in the CO from 973 K here is most likely due to the combustion of the CO by Fe₂O₃. The yield of tar is also found lower in Fe₂O₃ from 873 to 1173 K, whilst the yield of CO₂ is much higher. This indicates that the tar produced from wood pyrolysis started to be converted by Fe₂O₃ when the temperature exceeds 773 K, and most of the tar was combusted to CO₂. From 773 to 1073 K, the yield of CH₄ in Fe₂O₃ is higher than that in alumina sand; whilst at 1173 K, the value is lower. It seems that CH₄ is also a product from the reaction between tar and Fe₂O₃ from 773 to 1073 K. When the temperature increased to 1173 K, Fe₂O₃ became highly reactive with CH₄, resulting in its decrease. This is somewhat consistent with the findings in literature [180,181] that the conversion of CH₄ by Fe₂O₃-based materials usually occurred at temperatures above 1123 K, depending on the composition, preparation method and particle size of the material. The char yields in the beds of alumina sand and Fe₂O₃ are similar, indicating no direct solid-solid reaction between char and Fe₂O₃.

![Figure 5-10 Mass fraction of different carbon-containing species in a bed of Fe₂O₃ from 773 to 1173 K with a fluidising gas of N₂.](image)

**5.3.4 Pyrolysis of wood in the presence of mayenite-supported CuO**

Figure 5-11 shows results from a bed of mayenite-supported CuO. Comparing Figs. 5-11 and 5-9, mayenite-supported CuO seems to be effective in converting pyrolysis products in situ. The products of pyrolysis were converted mainly to CO₂, especially at 1173 K, where CO₂ constitutes of ~ 87 % of the products. Comparing the results with the pyrolysis in Fe₂O₃, mayenite-supported CuO exhibited higher reactivity for combustion of the pyrolysis products. Similar to Fe₂O₃ and alumina sand, there seems to have been no
significant solid-solid reaction between mayenite-supported CuO and char from 773 K to 1073 K. However, when the temperature reached 1173 K, mayenite-supported CuO consumed most of the char generated. This high reactivity of CuO at 1173 K mainly comes from the change in the form of oxygen supply. CuO tends to release significant amount of gaseous oxygen [182] and form CuO: CuO → Cu₂O + O₂. The effect of released oxygen from CuO at higher temperatures is further discussed in 5.4.2. At temperatures below 1073 K, this effect can be ignored. Thus, at 1173 K, both gas-gas reaction between gaseous pyrolysis products and released oxygen, and solid-gas reaction between char and the released oxygen were taking place.

Figure 5-11 Mass fraction of different carbon-containing products species in a bed of mayenite-supported CuO from 773 to 1173 K with a fluidising gas of N₂.

5.3.5 The effect of CO₂ on the distribution of products from wood

The results of wood processing in a fluidised bed of alumina sand supplied with 18% CO₂ (balance N₂) are shown in Fig. 5-12. As the change in the CO₂ was obtained by taking the difference of the experimentally measured CO₂ profile and the inlet CO₂ concentration (i.e. 18% CO₂), the negative mass fraction means an overall consumption of CO₂. According to Figs. 5-12 and 5-9, at the lowest temperature, 773 K, the distribution of the products shows no significant difference between pure N₂ and 18% CO₂, indicating little effect of the presence of CO₂ to the pyrolysis products at such temperature. A clear difference appeared when the bed temperature was increased to 973 K. An overall consumption of CO₂ in the fluidised bed, together with decreased tar yield and increased CO and CH₄ (compared to the yields in N₂), was observed. The consumption of CO₂ is
mainly due to the reforming of tar produced \textit{in situ}, and the main products from this reaction are CO and CH. Further increases in the temperature led to more consumption of CO and generation of CO and CH. In terms of the char yield, from 773 to 973 K, there seems to be no difference in the products in the two gaseous environments; however, from 1073 K, the char yield in 18\% CO\(_2\) is lower than that in N\(_2\). This is probably caused by the gasification of the char, which takes place at the same time as the pyrolysis of the wood. Gasification of the char generated CO, leading to an increase in the CO yield. The starting temperature for char gasification found here, 1073 K, was also comparable to the temperature conducted for the gasification of Polish char (refer to Chapter 3). Unlike the conditions at lower temperatures, the char yield would be very sensitive to the time span (pyrolysis time) selected once the gasification of the char starts: the longer the time, the higher the proportion of carbon in the char is converted to CO. The yield of CO and char at 1073 and 1173 K in Fig. 5-12 was determined by defining the end of pyrolysis as being when CH\(_4\) was no longer detected. At this point, the fluidising gas was quickly switched to pure N\(_2\).

![Figure 5-12 Distribution of each product species in a bed of alumina sand fluidised by 18\% CO\(_2\). The negative CO\(_2\) mass fraction indicates the consumption of background CO\(_2\).](image)

5.4  Discussion

5.4.1  Carbon balance in the two fluidising gas environment

The carbon balances of the conversion of the wood chips in the two fluidising agents are presented in Table 5-2. Both N\(_2\) and 18\% CO\(_2\) gave high carbon balances, but the values in N\(_2\) at each temperature was even nearer to closure. The lower carbon balance in 18\%
CO, could mainly come from the shift in the CO, level in the background. Although the correction of the flow was conducted and the CO, mole fraction after correction is more reliable for the determination of tar and CO, there still might be some limitations. Firstly, for the correction, it was assumed that the air flow rate was constant so that the oxygen could be used as a tracer. Practically, it is hard to control the flow rate perfectly and any fluctuation in the air flow rate would result in the shift in the CO, background. For the experiments with no CO, in the background, changes in the air flow rate were less of a problem because the background level would always be nearly zero. Secondly, when the plasma was turned on, the tar compound was assumed to be oxygen-free and even the best fit did not return the oxygen mole fraction curve to a perfectly stable one, meaning that the corrected oxygen is not a perfect ‘tracer’. Thirdly, the effect on the sampling flow rate due to CO, splitting in the plasma reactor was not taken into account when characterising the flow. These accumulated errors probably caused the less ideal carbon balance in 18% CO,. Generally, to improve the carbon balance, a well-engineered system that could control the flow rate (e.g. feedback control loop of the flow to the analysers) more accurately, and more precise flow measurements is required. However, this is difficult as flow measurement devices generally require clean gases, and often the calibration of the flow device depends on species present (here both the sampled gas and the injected air must be controlled).

When the plasma was running in N2/air mixed environment, the product species detected were primarily NO,. In the presence of CO, it was found that CO and O, were also generated, as seen in Fig. 5-6. When the plasma was turned on, there was a quick drop in the CO, background level (from a mole fraction of 0.088 to 0.084), correspondingly the [CO] increased from 0.000 to 0.005 and [O2] increased from 0.094 to 0.096. The change in the mole fractions in the different species suggests that reaction of CO, splitting, CO, → CO + O, might have taken place when the plasma was running in the CO2/air mixed gas environment. As reported by Yap et al. [183], non-thermal plasma can promote the highly endothermic reaction of CO, splitting. Whether there was a significant effect of the generation of some O, from CO, splitting on the other reactions taking place in the DBD reactor is indicated in Fig. 5-13. Fig. 5-13 summarised the results of the change in the mole fraction of CO and CO, from the two fluidising gases in a bed of alumina sand at 773 K, when plasma was active. The higher background level of CO in the 18% CO, comes from the splitting of CO,. At 773 K, there was minimal tar reforming in the
fluidised bed (refer to Fig. 5-12). If the reactions taking place in the plasma reactor in the
two gaseous environments are the same, the CO and CO\textsubscript{2} signals after dropping in the
wood chips, should follow the same patterns. According to Fig. 5-13, however, there was
more significant rise of CO, and lower rise of CO \textit{(i.e. from} \textit{t = 52 s, after the initial drop
of CO) in a bed fluidised by CO\textsubscript{2} (the sums of change in the two product species are
similar in the two gas conditions). This seems to suggest a conversion of the sampled CO
(from the upstream) to CO\textsubscript{2} in the DBD reactor when running in CO/air mixed
atmosphere. The conversion of CO to CO\textsubscript{2} might be from the reaction between the CO in
the sampled gas and the oxygen generated by the dissociation of CO\textsubscript{2} in plasma. The
temperature (523 K) for the conversion of CO to CO\textsubscript{2} in the plasma reactor is much lower
than the auto-ignition temperature of CO (882 K). This reaction, however, can be initiated
in a DBD reactor if singlet O\textsubscript{2}, which is an excited species and was found to be a product
from CO\textsubscript{2} splitting in plasma [184], is generated. One of the possible routes for the
dissociation of CO\textsubscript{2} is to excite CO\textsubscript{2} to vibrational levels of the ground excited state [185].
Provided with energy just exceeding the threshold for dissociation, CO\textsubscript{2} dissociates into
ground electronic state CO and singlet oxygen. Starik \textit{et al.} [186] studied the influence
of singlet oxygen molecules on homogenous charge compression ignition (HCCI)
combustion and found a much diminished temperature needed for combustion in the
presence of singlet oxygen. The concentration of by-product CO also significantly
decreased. This strongly suggests that some CO might have been combusted by singlet
O in the current study.
5.4.2 Reactivity of products

The order of reactivity of pyrolysis products including CO, CH, and tar, with the active bed materials could be determined by comparing the results in Figs. 5-9, 5-10, and 5-11. According to Figs. 5-9 and 5-10, at the lowest temperature, 773 K, the presence of Fe$_2$O$_3$ caused a slight decrease in CO and tar yields; the yield of CH$_4$ increased a little, probably due to tar decomposition. The comparison suggested that CO and tar are more reactive than CH$_4$ for combustion/conversion. Comparing the product distribution at 773 K in the bed of alumina sand and mayenite-supported CuO, as shown in Figs. 5-9 and 5-11, there was a clear increase in the yield of CO and a decrease in CO, while no drop in the tar yield in mayenite-supported CuO was observed. In this case, CO is considered to react more readily with active bed materials. An order of the reactivity of pyrolysis products with the oxygen carriers can then be obtained: CO > tar > CH$_4$.

Both the active bed materials and the presence of CO$_2$ help tar abatement inside the fluidised bed within the short residence time (~ 1s), as shown in Fig. 5-14. The increase in the temperature improves the conversion of tar. The effect of oxygen carriers for tar reduction is more significant than CO$_2$, and mayenite-supported CuO is especially effective at high temperatures. Mayenite-supported CuO is a promising material for in
situ tar reduction in a fluidised bed reactor; it also shows great potential as an oxidant for the direct combustion of biomass.

Figure 5-14 Tar conversions in different fluidised bed conditions.

5.4.3 The effect of released oxygen from CuO on product distribution

Figure 5-15 shows the phase diagram of the Ca-Al-Cu-O system (which is identical to the Cu-O phase diagram, for the range of compositions over which the aluminum and calcium bind preferentially into calcium aluminates). At 1073 K, the oxygen mole fraction at atmospheric pressure produced by CuO is about 0.0016; at 1173 K, it reaches 0.018. Thus, at 1173 K, there can be both gas-gas reaction between gaseous pyrolysis products and released oxygen, and solid-gas reaction between char. Whether it was the released gaseous oxygen from CuO that led to the significant drop in the tar yield from 1073 to 1173 K, was investigated by performing pyrolysis of the wood chips in the bed of mayenite-supported CuO. The particles were prepared from mayenite-supported CuO, by first fluidising the bed in N₂ at 1173 K until no oxygen was detected. Fluidised in N₂, which is assumed to have an O₂ partial pressure of 1 × 10⁻⁵ bar, CuO decomposes to Cu₂O; further decomposition to Cu was avoided either by its own equilibrium with the trace amount of O₂ with the ambient and/or the slow reaction kinetics. For a typical group of experiments, the prepared Cu₂O was divided into five equal portions, for pyrolysis at each temperature from 773 to 1173 K, with and without plasma (i.e. two individual runs for one portion). The amount of oxygen available in the Cu₂O was always in excess of that needed for complete combustion of the fuel (i.e. a maximum of 0.88 g of Cu₂O is needed for every 0.0538 g wood). At each temperature, between the two runs, the Cu₂O
was not regenerated. Although the bed material was not regenerated prior to the second run, repeated experiments by switching the order of the two runs (i.e. without and with plasma running) showed that the results were not influenced by the conversion of the oxygen carrier. After two runs at each temperature, the bed was burned off in air to quantify the amount of char. The amount of char at each temperature can be obtained by taking half of carbon content in CO and CO$_2$ generated during burn-off. Figure 5-16 shows the results in mayenite-supported Cu$_2$O. Comparing the mole fractions of CO, tar and CH$_4$ in Figs. 5-11 and 5-16, the reactivity of Cu$_2$O and CuO for the conversion of CO and tar are similar from 773 to 973 K. More CH$_4$ was detected in CuO, indicating that CuO is more reactive than Cu$_2$O towards CH$_4$. When the temperature reached 1073 K, the yield of tar in CuO dropped whilst that in Cu$_2$O still remained high. At 1173 K, the difference is more significant in that both tar and char still contribute a big portion to the total yield in a Cu$_2$O bed, but not in CuO. The clear difference observed at 1073 and 1173 K suggests that gaseous oxygen from CuO is very likely to be the primary cause for the reduction of char and tar at 1173 K.

Figure 5-15 Equilibrium phase diagram of Ca-Al-Cu-O system (refer to 2.2.2 for the composition of the system) from 773 to 1273 K, where the phases of Ca and Al are not shown in the figure. The diagram was generated from MTDATA software [139] using NPL database.
5.4.4 Methods for tar measurement

In the current study, to quantify the tar produced at one experimental condition, two identical experiments were required, with and without plasma discharge. To have exactly the same experimental conditions, the wood mass, flow rate, $N_2$ to air ratio of the two experiments need to be strictly controlled. The results showed good repeatability of the approach, but it is time-consuming and does not give an instantaneous online measurement. Other ways of carrying out the tar measurement were also attempted. Firstly, the idea of using two sampling lines was tested. The sampling line from the fluidised bed to the point where the air was introduced was unchanged, after the air mixing, the stream was divided into two, with 50% of the flow going to a “blank” reactor with the same dimensions as the plasma reactor prior to an analyser, the other going to the plasma reactor prior to FTIR. The difference between the signals from the two analysers indicates the amount of tar entering each sampling line. This method simplified the experimental procedure, as only one experiment was needed to measure the tar yield. However, practically, it was difficult to control the flow conditions in the two sampling lines to be exactly the same. Although the two sampling lines were engineered to be the same, any tiny variation between the two flow rates led to significant differences in the results. The error caused by the difference in calibration, and residence time of the two analysers could not be neglected. Secondly, the plasma was pulsed on and off plasma during one experiment. However, the idea was quickly found unsuitable for the experiment because this method requires a sufficiently fast response of the plasma reactor.

Figure 5-16 Mass fraction of different carbon-containing products species in a bed of mayenite-supported Cu$_2$O from 773 to 1173 K.
(i.e. on/off), compared to the pyrolysis time. The plasma system has ~ 5 seconds response delay when turning on or off, which is not sufficiently short compared to ~ 40 seconds pyrolysis time here. However, for a continuous process in which changes took longer, this method would be suitable. Alternatively, a bypass line could be introduced around the plasma reactor. The plasma reactor could then be kept running, allowing the gas to be (periodically) sent to the analyser directly or alternatively via the plasma reactor. This would allow two curves to be obtained from the FTIR in one experimental run. However, this method would be limited by the response time of the valves and the analyser. For the short experiments carried out here, using two experiments was found to be more practical, however, if the pyrolysis was continuous, using gas switching or turning the plasma on or off may be more practical.

5.4.5 Apparent rate of tar production

The plasma system used in this study allows direct on-line measurement of tar generated during fuel processing. As Fig. 5-17 illustrates, the difference in the curves between plasma on and off accounts for the tar converted. Here, good carbon balances are obtained for most conditions (as shown in Table 5-2) and no clear evidence of tar was found in the trapping tube after the plasma reactor, indicating that for most conditions, tar condensation in the sampling line and tar remaining after plasma reactor were negligible. Assuming that all the tar can be cracked and converted to CO, CO$_2$, and CH$_4$ in the plasma reactor, the rate of the conversion of tar, $R_{\text{conversion,tar}}$, can be obtained as follow

$$R_{\text{conversion,tar}} = R_{\text{production,tar in FB}} \times \frac{F_{\text{sampling}}}{F_{\text{FB}}} \times \frac{F_{\text{sampling}}}{(F_{\text{sampling}} + F_{\text{air}})}$$

$F_{\text{air}}$ is the flow rate of air introduced into the sampling system prior to plasma reactor, $R_{\text{conversion,tar}}$ is the rate of tar cracking/conversion by plasma, and $R_{\text{production,tar in FB}}$ is the rate of production of tar from the fluidised bed. The rate curves are proportional to the mole fraction curves obtained. Figure 5-17 presents the mole fraction profile of tar cracking/conversion from a mayenite-supported CuO bed at 873 K with the DBD reactor having a SED of 1027 J/L, from which the apparent rate of tar production can be predicted. A true tar production profile over time can be further estimated by deconvolution of the system, assuming a continuous stirred tank reactor (CSTR, to
account for the ~ 18 seconds residence time) plus a plug flow reactor (PFR). Further work on this was not displayed in this study.

Figure 5-17 Mole fraction of tar based on the detection by FTIR, with the fluidised bed at 873 K, a SED of 1027 J/L in a bed of mayenite-supported CuO.

5.5 Conclusions

The main findings from the investigating the effect of oxygen carriers and CO$_2$ on the product distribution from wood chips in a fluidised bed are as follow:

(a) A plasma system for the on-line continuous quantification of tar was developed and placed in the downstream of a fluidised bed. The plasma system was found to be effective for tar conversion. The method for tar quantitation worked well and gave carbon balances close to unity. The apparent rate of tar production over time could also be obtained. Though further characterisation work was required to establish true rate profile, it provides a promising solution for the kinetic study of the generation of tar. Improvements to the response time of the gas analysers, and better control of the flow rates would allow more rapid measurements of the rates of tar production.

(b) For the pyrolysis of the wood chips, it was found that higher temperature promoted the production of gaseous products. Tar was the primary product from
pyrolysis from 773 to 1173 K. When the bed temperature increased above 1073 K, the tar formed cracked to CH₄ (from 50 wt% at 1073 K to 45 wt% at 1173 K).

(c) Fe₂O₃ and mayenite-supported CuO were found to be effective for *in situ* reduction of tar in the fluidised bed. The decreased tar was mostly combusted to CO₂. The reactivity of mayenite-supported CuO for the reaction with the pyrolysis products was higher than Fe₂O₃, and particularly effective for the conversion of tar and char at 1173 K due to its oxygen uncoupling property, resulting ~ 87% CO₂ in the products. The results showed promising feasibility of CLC/CLOU of biomass, without any active fluidising agent.

(d) With CO₂ fluidising the bed, the tar released from the biomass could be dry-reformed *in situ* at temperatures above 973 K. The reforming products were mainly CH₄ and CO. The char derived from the biomass started to be gasified in CO₂ at 1073 K.

### 6.0 Development of a plasma-assisted packed bed reactor for H₂ production from CH₄

#### 6.1 Introduction

The DBD reactor developed for the quantification of tar measurement via tar cracking and combustion in Chapter 5, has revealed the potential of fuel conversion at low operating temperatures in such a plasma discharge system. The aim of the current chapter is to design a plasma-assisted reactor that allows for the conversion of gaseous fuel, in this case, CH₄. The electrical characteristics of the system and the controlling parameter for the conversion of CH₄ are to be investigated. As a preliminary study, the two packing materials: alumina sand, which is widely considered inert and low dielectric constant material, and SrFeO₃₋δ, a reactive oxygen carrier with a higher dielectric constant, are studied.

#### 6.1.1 Electric discharge

An ideal DBD reactor is supposed to generate silent glow discharge; however, in reality,
current pulses are often observed in DBD applications. A discharge that contains a significant amount of current pulses is characterised as filamentary discharge. However, these filaments are transient states and exit only for a short time [187]. When ac voltage is applied to a DBD reactor, there are periods with discharges (when the voltage inside the gas gap is high enough to initiate breakdown and maintain a discharge), and without discharges (when the gap voltage falls below the value). The Lissajous figure is a useful tool for understanding the plasma properties. Figure 6-1 shows a resulting charge-voltage Q-V Lissajous figure of a DBD system when applied with sinusoidal voltage. Depending on the shapes, there are several types of Lissajous figures usually seen in a DBD system [187]:

1) A straight line in a Lissajous plot represents an ideal capacitance. The capacitive load has a current wave form leading the voltage, and thus the voltage and current peaks are not in phase.

2) For a resistive load, the current and voltage are in phase, and it results in an ellipse, and this normally indicates the presence of residual ions at all times. This is due to insufficient time for the ions to decay or to be removed between two succeeding half waves.

3) In most DBD applications, the figure is close to a parallelogram.

Figure 6-1  Voltage - Charge Lissajous figure of a dielectric barrier discharge cycle. U here stands for voltage, and Q is the charge. The figure was reproduced from [187]. For copyright issue, the figure is removed here.
For a discharge cycle, as shown in Fig. 6-1, \( \textcircled{1} \rightarrow \textcircled{2} \) and \( \textcircled{3} \rightarrow \textcircled{4} \) represent stages with discharge; and \( \textcircled{2} \rightarrow \textcircled{3} \) and \( \textcircled{4} \rightarrow \textcircled{1} \) are stages when discharge is off [187]. \( \bar{U} \) is the peak voltage in a discharge cycle. For the discharge to occur, the peak to peak voltage, \( 2\bar{U} \), needs to be equal or higher than \( 2U_{min} \) (the minimum voltage required for discharge to start). The capacitances can be estimated from the slopes of the Lissajous figure. In Fig. 6-1, the total capacitance of the electrode configuration, \( C_{Total} \), can be calculated from the slope of the discharge stages:

\[
C_{Total} = \frac{1}{\tan \alpha}.
\]

The capacitance of the dielectric for a fully bridged gap, \( C_D \), can be obtained via the slope of the discharge-off stages:

\[
C_D = \frac{1}{\tan \gamma}.
\]

The value of \( C_D \) should be a constant for a particular reactor set-up. However, in many cases, the gap is not fully bridged when in discharge [188,189], in which case the measured gradient is lower than \( C_D \), and is termed as the effective dielectric capacitance \( C_d \).

The capacitances follow the correlation below:

\[
\frac{1}{C_{Total}} = \frac{1}{C_{gap}} + \frac{1}{C_d}.
\]

Where \( C_{gap} \) is the overall capacitance of the gap. The electrical pathway of the plasma system, which is supplied with ac power, can be illustrated by a simple equivalent circuit, as shown in Fig. 6-2. The switch turns on or off when the magnitude of the voltage is above or below the breakdown threshold.
6.1.2 Estimation of the mean electron energy

The mean electron energy can indicate how much energy input is supplied to the system. In this study, it will be estimated from Einstein’s equation,

\[
\frac{k_B T_e}{e} = \frac{D_e}{\mu_e},
\]

where \(k_B\), \(D_e\) and \(\mu_e\) are the Boltzmann constant \((1.38 \times 10^{-23} \text{ J/K})\), diffusion constant, and drift mobility respectively. \(e\) is the elementary electron charge \((1.60 \times 10^{-19} \text{ C})\). \(T_e\) is the electron temperature. The mean electron energy, \(<\varepsilon>\), can be calculated from the electron temperature: \(<\varepsilon> = \frac{3}{2} k_B T_e\) [101]. The electron temperature, the mean electron energy and the value of \(\frac{D_e}{\mu_e}\), is typically a function of the reduced electric field, \(\frac{E}{N}\) \((E\) is the electric field and \(N\) is the density of neutral gas particles) [190]. Given the experimental values of \(\frac{E}{N}\), empirical values of \(\frac{D_e}{\mu_e}\) reported in literature can be used to estimate the mean electron energy. Figure 6-3 presents the experimentally measured \(\frac{D_e}{\mu}\) over a wide range of \(\frac{E}{N}\) by Al-Amin [191].

![Figure 6-2 Equivalent circuit of the DBD system applied with ac voltage.](image)
Figure 6-3 Ratio of diffusion coefficient to mobility over E/N for in methane (99.2% with impurities of 0.7% for N₂, BOC), where 1 Td = $10^8$ V · m. Note that the data are cited from Ref. [191].

6.2 Experiments and calculation of the parameters

6.2.1 Development of a plasma-assisted chemical reactor

A DBD reactor consists of two electrodes (planar, co-axial, or adjacent cylinders, refer to Fig. 1-4) made of metals, covered or separated by a dielectric material (s). Recent research on the conversion of fuels employing non-thermal plasma, largely used cylindrical configurations [123,179,189,192–194]. This is mainly because it is easier to directly couple such a plasma system configuration to the existing chemical reactors, such as plug flow reactors and packed bed reactors. In this chapter, a plasma-assisted chemical reactor is first developed. The design is based on a cylindrical quartz tube, as described in 2.3.4, with a distributor plate and allowing gas flowing in from the bottom of the tube. Stainless-steel mesh is used to cover the quartz tube, acting as the ground electrode; the high voltage electrode is a stainless-steel rod, sitting on the distributor with the other end supported by a cap on top of the quartz tube. The initial idea was to apply non-thermal plasma to a fluidised bed system. However, de-fluidisation inside the bed was observed when subjected to plasma discharge. This phenomenon did not improve regardless of varying the particle size (from 180 – 250 $\mu$m to 800 – 1000 $\mu$m), and flow rate through the bed (from just on fluidisation to $U/U_m > 10$). It is suspected with the supply of plasma
discharge, the particles inside the fluidised bed quickly become charged and the intra-particle forces between the charging particles led to the de-fluidisation of the bed. Understanding of the effect of plasma on fluidisation and development of a stable fluidised bed in the presence of plasma discharge would be necessary prior to the investigation of the chemical reactions in such systems. However, systems involving plasma in a fluidised bed have received little attention in the literature [195–198] have not been well understood. The main interest of this study (Chapters 6, 7 and 8) is on the reaction side, and a plasma-assisted packed bed reactor is investigated. For a packed bed reactor, the gas inflow is also introduced from the bottom of the reactor, whilst the flow rate is controlled to be low enough to avoid fluidisation. The details are described in 2.3.4.

### 6.2.2 Experiments

Characterisation of the electrical signals and the investigation of their effect on the conversion of CH, in the developed plasma-assisted packed bed, as described in 2.3.4, was carried out here. The experiments were conducted at temperatures from 293 to 723 K, with 100% CH as the feeding gas at a flow rate of 0.5 L/min. The gas from the packed bed was sampled at 0.2 L/min and mixed with a N\textsubscript{2} dilution stream at 0.8 L/min, giving a total flow rate of 1 L/min entering the analysers. The effect of applied voltage from 7 to 19 kV, and frequency from 20 to 29 kHz on the electrical signals and conversion of CH, were studied. For a typical experiment, when the gas flow through the DBD reactor stabilised, the plasma was then applied for 2.5 ± 0.2 min. SrFeO\textsubscript{δ}, with a particle size fraction of 600 - 850 μm, prepared from solid mixing (as presented in 2.2.2) was used as the bed material packing the DBD reactor, giving a height of the plasma discharge region of ~ 20 mm. The non-stoichiometry of SrFeO\textsubscript{δ} was found to be SrFeO\textsubscript{2-x}, which is presented in 7.3.1. As a control, alumina sand (600 - 850 μm), which was considered chemically inert, was also studied. In addition to the difference in chemical reactivity of the two materials, SrFeO\textsubscript{δ} has a much higher dielectric constant (between 200 – 400 in the applied AC frequency of 20 - 30 kHz [199]) than alumina sand (8 - 11, [200]).
6.2.3 Estimation of the parameters

- Capacitance of the dielectric \( C_D \)

The capacitance of the dielectric (quartz reactor), which is independent of the experimental conditions, can be calculated based on the geometry of the reactor set-up. The following equation [201] is used:

\[
C_D = \frac{2\pi \varepsilon_{\text{vacuum}} \varepsilon_D}{\ln(l+x)/l},
\]

where \( \varepsilon_{\text{vacuum}} \) is the dielectric constant of the vacuum \((8.854 \times 10^{-12} \ F/m)\); \( \varepsilon_D \) is the relative dielectric constant of quartz tube \((i.e. \sim 4.7)\); \( l \) is the discharge length, which is 25 mm. \( r \) is the inner diameter of the quartz tube, and \( x \) is thickness of the quartz tube. Based on the above values, \( C_D \) of the reactor is \( 9.0 \times 10^{-11} \ F \).

- Conversion of CH

The term, conversion of CH, studied here refers to the averaged conversion of CH, over the plasma discharge time \((e.g. \sim 2.5 \text{ min in this case})\), and was obtained from

\[
X_{\text{CH}_4, t} = \frac{\int_{t_0}^{t_{\text{end}}} (F_{\text{total}, 0} x_{\text{CH}_4, 0} - F_{\text{total}} x_{\text{CH}_4}) dt}{F_{\text{total}, 0} x_{\text{CH}_4, 0}},
\]

where \( x_{\text{CH}_4, 0} \) and \( x_{\text{CH}_4} \) are CH mole fractions measured at the reactor inlet and outlet, respectively. \( F_{\text{total}, 0} \) and \( F_{\text{total}} \) are the corresponding total flow rates. The converted CH, was averaged for the period with plasma discharge from \( t_0 \) to \( t_{\text{end}} \).

The methods for obtaining other electrical properties including the dissipated power and the estimated mean electron energy, can be found in 2.3.3 and 6.1.2, respectively.

6.3 Results and discussion

6.3.1 Understanding the electrical signals

- Discharge behaviour

Figure 6-4 presents the electrical signals of CH, plasma discharge with the DBD reactor packed with alumina sand at 293 K under two supplied plasma conditions. The electrical signals were captured when voltage and current signals were stable. The current
waveforms were obtained by differentiation of the measured charge waveforms, followed by smoothing using a moving average filter with a window size of 5% of the total data points. According to Fig. 6-4a, with the alumina sand-packed DBD reactor operated with a dissipated power of 22 W, some current pulses were observed. The plasma power was gradually increased to 22 W until conversion of CH, was observed. The number and the intensity of current pulses clearly increased when the plasma power increased to 32 W, as shown in Fig. 6-4b. A similar effect of plasma power on the discharge performance was also found at higher temperatures. In addition, a noisy sound was heard from the DBD reactor during plasma discharge. The presence of these current pulses and the noise indicate the presence of filamentary discharge in CH, plasma in the alumina sand bed, meaning the plasma formed cannot be homogeneously distributed. Ionised species and electrons in some areas can be very concentrated, which would result in sparks locally. Filamentary discharge like this is usually not favoured due to the significant noise level, and the waste of energy in the concentrated zone. In terms of the conversion of CH, in such bed at 293 K, when the voltage was only gradually increased to 15.4 kV (resulting a plasma power of 22 W and the frequency of 26.4 kHz), the conversion of CH, in the DBD reactor was observed. From this point, further increase in the voltage to 19 kV (resulting a plasma power of 32 W and the frequency of 23.8 kHz) led to an increase in the conversion of CH, (i.e. 0.051).
Figure 6-4 Voltage and current waveforms of plasma running in the alumina sand-packed DBD reactor at 293 K purged with 100% CH$_4$. (a) under the voltage of 15.4 kV at 26.8 kHz with a dissipated power of 22 W, giving an averaged conversion of CH$_4$ of 0.001; and (b) under the voltage of 19 kV at 23.8 kHz with a dissipated power of 32 W, giving an averaged conversion of CH$_4$ of 0.051.

The representative electrical signals in a SrFeO$_3$-packed bed are shown in Fig. 6-5. Similarly, the voltage was first gradually increased to the point where the conversion of CH$_4$ can just be observed. In the SrFeO$_3$-packed bed operated at 293 K, this value found was 11 kV (resulting a plasma power of 7 W and the frequency of 21.9 kHz). Compared to the case in the alumina sand bed, the voltage and power threshold required for starting CH$_4$ conversion in SrFeO$_3$-packed bed were significantly decreased. The amplitude (peak to peak value, ~ 0.06 A) of current in SrFeO$_3$, as shown in Fig. 6-5a, also increased.
significantly (compared to the value of ~ 0.02 in Fig. 6-4a; however, the current pulses were not clearly observed in Fig. 6-5a. The increase in the voltage to 13.3 kV (resulting a plasma power of 16 W and the frequency of 20.5 kHz) also did not generate clear current pulses, as shown in Figure 6-5b. These observations suggest that the it is easier to generate CH₄ plasma in the bed of SrFeO₃, and the plasma formed in such case did not have much filaments. This is further supported by the fact that no sound was heard from the plasma in the SrFeO₃ bed. The silent discharge mode, known as diffuse plasma, was also found in SrFeO₃ at higher temperatures. The difference in the results from Figs. 6-4 and 6-5 is mainly due to the variation in the dielectric constant of the two materials. High dielectric constant materials could improve the stabilisation of plasma and reduce the number of filaments [93]. This is also supported by the Lissajous figures, as presented in Fig. 6-6. It shows a typical comparison of the Charge-Voltage Lissajous plots in the two bed materials at 293 K, where the conversion of CH₄ just initiated under the corresponding voltages. To achieve the same chemical conversions of CH₄ in the DBD reactor, the Lissajous figure changes from ellipse-shaped in alumina sand bed to parallelogram-shaped in the SrFeO₃ bed. It is reported [202] that during plasma discharge, some charges are not spread out uniformly over the surface of the dielectric (the quartz tube and alumina sand in this case) and accumulate at some points. When the applied voltage is reversed, these residual charges memorise the previous polarity and generate filamentary channels, leading to less sharp edges in the Lissajous figures. The observed sharp edges at the reversal points in the SrFeO₃ loop in Fig. 6-6, indicates few residual ions present between two succeeding half waves, which is ideal for DBD reactors.
Figure 6-5 Voltage and current waveforms of plasma discharge in the SrFeO$_{0.8}$-packed DBD reactor at 293 K purged with 100% CH. (a). under voltage of 11 kV at 21.9 kHz with a dissipated plasma power of 7 W, giving an averaged conversion of CH of 0.001; and (b). under voltage of 13.3 kV at 20.5 kHz with a dissipated plasma power of 16 W, giving an averaged conversion of CH of 0.0210.
Figure 6-6 Lissajous figures of CH, plasma with the DBD reactor packed with the two bed materials at 293 K, both giving the conversion of CH, of 0.001. In the alumina sand bed, the electrical conditions were voltage of 15.4 kV, frequency of 26.8 kHz and plasma power of 22 W; in the strontium ferrite (SrFeO$_3$-$d$) bed, the voltage, the frequency and the plasma power were 13.3 kV, 20.5 kHz, and 16 W, respectively.

- **Correlation between voltage, plasma power and frequency**

The correlation between the applied voltage, power, and frequency to the DBD reactor are investigated. Figure 6-7 illustrates the plots of voltage versus plasmas power, and voltage versus frequency in SrFeO$_3$-$d$-packed DBD reactor at 293, 623 and 723 K. According to Fig. 6-7a, higher applied voltage to the plasma reactor results in higher dissipated plasma power at each temperature. In addition, based on the trendline of the data points collected, it seems that under the same applied voltage, higher temperature led to higher plasma power. For the relation between frequency and applied voltage, as shown in Fig. 6-7b, it seems that the increase in the applied voltage resulted in a decrease in frequency. This correlation may only apply to this particular plasma system, and the understanding of the system was only for the purpose of controlling the operating conditions for experiments in Chapters 7 and 8. The plasma generator used here was designed in a way that only the applied voltage can be manually controlled, and the
generator itself has a built-in tuning function to adjust the corresponding frequency in order to achieve stabilization of the system. At a same applied voltage, the increase in temperature seems to result in lower frequency; however, this trend is not decisive due to lack of data points available. In summary, from Fig. 6-7, low frequency appears together with high applied voltage and plasma power.

Figure 6-7 The correlations between voltage, frequency, and plasma power at different operating temperatures in the SrFeO$_{3.8}$-packed DBD reactor, (a) voltage versus plasma power, (b) voltage versus frequency.

Figure 6-8 shows the effect of plasma power on the effective capacitance of the quartz reactor at different temperatures. In the temperature range studied, the effective capacitance measured was from $3.6 \times 10^{-11}$ to $8.3 \times 10^{-11}$ F, which are below the
capacitance of the quartz $C_c (9.0 \times 10^{-11} \text{ F})$, indicating non-fully bridged gap in plasma discharge. On the other hand, the increase in the plasma power improved the effective capacitance, suggesting an increased bridging in the gaps. It is also found that, from 293 to 623 K, the increase in the temperature improved the effective capacitance; whilst from 623 to 723 K, there was no clear improvement.

Figure 6-8 The correlation between effective capacitance of the dielectric $C_c$ and the plasma power under different operating temperatures in a SrFeO$_{0.5}$-packed DBD reactor.

### 6.3.2 CH$_4$ conversion and mean electron energy

Table 6-1 Summary of the averaged conversion under different operating conditions in the alumina sand-packed DBD reactor.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Frequency (kHz)</th>
<th>Power dissipation (W)</th>
<th>Voltage (kV)</th>
<th>Averaged conversion of CH$_4$</th>
<th>Mean electron energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>26.8</td>
<td>22</td>
<td>15.4</td>
<td>0.001</td>
<td>4.60</td>
</tr>
<tr>
<td></td>
<td>23.8</td>
<td>32</td>
<td>19.0</td>
<td>0.035</td>
<td>4.61</td>
</tr>
<tr>
<td>473</td>
<td>25.6</td>
<td>23</td>
<td>16.0</td>
<td>0.020</td>
<td>4.60</td>
</tr>
<tr>
<td></td>
<td>23.1</td>
<td>40</td>
<td>16.2</td>
<td>0.039</td>
<td>4.60</td>
</tr>
<tr>
<td>573</td>
<td>26.3</td>
<td>21</td>
<td>14.0</td>
<td>0.007</td>
<td>4.59</td>
</tr>
<tr>
<td></td>
<td>23.1</td>
<td>25</td>
<td>15.0</td>
<td>0.041</td>
<td>4.60</td>
</tr>
<tr>
<td></td>
<td>20.4</td>
<td>92</td>
<td>16.0</td>
<td>0.053</td>
<td>4.60</td>
</tr>
<tr>
<td>723</td>
<td>28.6</td>
<td>33</td>
<td>12.6</td>
<td>0.001</td>
<td>4.59</td>
</tr>
<tr>
<td></td>
<td>25.5</td>
<td>43</td>
<td>13.8</td>
<td>0.019</td>
<td>4.59</td>
</tr>
<tr>
<td></td>
<td>21.2</td>
<td>77</td>
<td>14.0</td>
<td>0.029</td>
<td>4.59</td>
</tr>
</tbody>
</table>
Table 6-2 Summary of the averaged conversion under different operating conditions in the SrFeO₃-d-packed DBD reactor.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Frequency (kHz)</th>
<th>Power dissipation (W)</th>
<th>Voltage (kV)</th>
<th>Averaged conversion of CH₄</th>
<th>Mean electron energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>21.9</td>
<td>7</td>
<td>11</td>
<td>0</td>
<td>4.58</td>
</tr>
<tr>
<td></td>
<td>20.7</td>
<td>15</td>
<td>12</td>
<td>0.021</td>
<td>4.59</td>
</tr>
<tr>
<td></td>
<td>20.5</td>
<td>16</td>
<td>13.3</td>
<td>0.022</td>
<td>4.59</td>
</tr>
<tr>
<td>473</td>
<td>21.5</td>
<td>7</td>
<td>10.2</td>
<td>0</td>
<td>4.58</td>
</tr>
<tr>
<td></td>
<td>20.4</td>
<td>17</td>
<td>12</td>
<td>0.015</td>
<td>4.59</td>
</tr>
<tr>
<td>573</td>
<td>21.3</td>
<td>16</td>
<td>11.5</td>
<td>0.010</td>
<td>4.58</td>
</tr>
<tr>
<td></td>
<td>20.2</td>
<td>24</td>
<td>12.7</td>
<td>0.016</td>
<td>4.59</td>
</tr>
<tr>
<td>623</td>
<td>26.1</td>
<td>9</td>
<td>7</td>
<td>0.002</td>
<td>4.58</td>
</tr>
<tr>
<td></td>
<td>20.2</td>
<td>28</td>
<td>12</td>
<td>0.075</td>
<td>4.59</td>
</tr>
<tr>
<td></td>
<td>22.1</td>
<td>13</td>
<td>10</td>
<td>0.025</td>
<td>4.58</td>
</tr>
<tr>
<td>673</td>
<td>25.7</td>
<td>7</td>
<td>7.6</td>
<td>0</td>
<td>4.58</td>
</tr>
<tr>
<td></td>
<td>20.0</td>
<td>54</td>
<td>10.4</td>
<td>0.093</td>
<td>4.58</td>
</tr>
<tr>
<td></td>
<td>21.0</td>
<td>49</td>
<td>12</td>
<td>0.083</td>
<td>4.59</td>
</tr>
<tr>
<td>723</td>
<td>24.8</td>
<td>7</td>
<td>7.5</td>
<td>0.009</td>
<td>4.58</td>
</tr>
<tr>
<td></td>
<td>20.2</td>
<td>48</td>
<td>11</td>
<td>0.100</td>
<td>4.58</td>
</tr>
<tr>
<td></td>
<td>21.7</td>
<td>22</td>
<td>10</td>
<td>0.048</td>
<td>4.58</td>
</tr>
</tbody>
</table>

The conversions of CH₄ in the two different packing materials under each operating condition are presented in Tables 6-1 and 6-2, respectively. The conversion was averaged over the ~ 2.5 min plasma discharge. The mean electron energy was also estimated by calculating the reduced electric field, $\frac{E}{\mu_e}$, and referring to Fig. 6-3 to find corresponding values of $\frac{D_e}{\mu_e}$. For applied voltages below 12 kV (corresponding to 80 Td, or $8 \times 10^{-5}$ V · m), the mean electron energy values were estimated by extrapolating the curve in Fig. 6-3 on the low side. As seen in the two tables, for both in the alumina sand and SrFeO₃ beds, higher conversion of CH₄ at each temperature was always achieved at higher plasma power (lower frequency and applied voltage). According to Fig. 6-3, the values of $\frac{D_e}{\mu_e}$ are stable over a wide range of $\frac{E}{\mu_e}$, thus the mean electron energy values obtained here do not vary significantly, from 4.58 to 4.61 eV. It has been found that in non-thermal plasma, the reactions stimulated by vibrational excitation are responsible for the major part of energy exchange, in which the electron energies required to initiate reactions are usually between 1 - 3 eV [101]. For CH₄ cracking to C and H₂, $\text{CH}_4 \rightarrow \text{C} + \text{H}_2$, the electron energy needed is about 0.9 eV [101]. Therefore, the energy supplied here should be sufficient to
initiate the cracking of CH₄. The fact that the conversion of CH₄ was observed also supports this.

In the alumina sand bed, as shown in Table 6-1, the conversion of CH₄ was between 0.001 to 0.053. For most of the experimental results, both increasing the temperature of the DBD reactor and the plasma power can lead to higher conversion of CH₄. However, this is not always true. The conversion of CH₄ at 723 K, with a plasma power of 77 W was 0.029; whilst this is lower than the conversion (0.035) at 293 K with a plasma power of 32 W. The higher plasma power would indicate higher degree of ionisation occurred in the plasma reactor, while this does not necessarily mean higher conversion of CH₄. As introduced in 1.4.2 (Chapter 1), DIEI (where the ionisation happens by collisions between neutrals and previously un-excited species by collisions with electrons) is a significant route for ionisation in the non-thermal plasma. Alternatively, SIEI, where some electron species needs to be excited and the excitation can include vibrational and rotational excitation, can also be a route to reaction. In order to have SIEI, some supplied energy needs to be used for excitation only. In addition to ionisation, chemical reactions can also be initiated by routes other than ionisation, for instance, vibration without going through ionisation. The mean electrode energy, which is dependent on the applied voltage, was found to have a slightly higher value at 293 K than that at 723 K (i.e. 4.61 > 4.59 eV) However, the applied voltage at 293 K was significantly higher. It suggests that in this case the applied voltage, and thus the electric field strength plays an important role in converting CH₄. According to Ref. [101], similar mean electron energy values do not always guarantee better overall performance in a system. The distribution of the electron energy is a complicated function of multiple parameters. Depending on the actual situation, different electron energy distribution functions can be obtained for the same value of mean electron energy (refer to Fig. 6-9), for instance Maxwell distribution for elastic collisions dominated cases and Druyvesteyn distribution for the situations where the electron mean free path can be treated as constant [101]. To initiate the conversion of CH₄, the electron energy needs to go beyond a threshold value for the reaction, and thus the not only the mean electron energy is important, the overall distribution of the electron energy in a system also matters. Here, it seems that the applied voltage might have led to a clear difference in the distribution of electron energy distribution at 723 and 293 K, which could then be responsible for the difference in the conversions. In summary, higher plasma power can be used as a first guide for achieving higher conversion, whilst it is not
the only influencing factor. High mean electron energy and applied voltage, which would give indication of the electron energy distribution, should also be considered.

Figure 6-9 Comparison of Maxwell and Druyvesteyn electron energy distribution functions for the same electron mean energy value. Note that the figure was reproduced from Ref. [101]). For copyright issue, the figure is removed here.

In a bed of SrFeO₃, according to Table 6-2, the electron energies are rather stable, between 4.58 and 4.59 eV. The conversion of CH₄ in SrFeO₃ is very low from 293 to 573 K. However, when increasing the temperature above 623 K, there is a significant increase in the conversion. At 623 K, with a plasma power of 28 W and electron energy of 4.58 eV, the conversion reached 0.075. Under similar conditions at 573 K (i.e. 24 W and 4.58 eV), the conversion was 0.016. This big difference seems less likely due to the small temperature difference (573 and 623 K) in the gas phase, but more reasonably from the activation of SrFeO₃. Alumina sand was considered inert and does not chemically involve in the conversion of CH₄. In this case, the conversion of CH₄ only would be ascribed to the decomposition of CH₄. SrFeO₃ can be chemically reactive at sufficiently high temperatures and participate in the conversion of CH₄, i.e. the oxygen in SrFeO₃ can react with CH₄. Therefore, compared to the CH₄ conversion trend in the alumina sand bed, the sharp increase in the CH₄ from 623 to 723 K should be mainly due to the reaction between CH₄ and SrFeO₃. Further investigation of this is presented in Chapter 7.
6.4 Conclusions

A packed-bed DBD reactor for CH₄ conversion was developed, and the electrical behavior with two packing materials: alumina sand and SrFeO₃, were studied. The main observations from the preliminary study are:

(a) Filamentary discharge was found in the alumina sand; whilst in the SrFeO₃, the discharge mode was close to silent discharge (diffuse plasma).

(b) Based on the current plasma generator, at each operating temperature of the DBD reactor, higher plasma voltage always resulted in higher plasma power and lower frequency, e.g. at 723 K, an increase in the voltage from 7.5 to 11 W resulted in a power increase from 7 to 48 W and a decrease in frequency from 24.8 kHz to 20.2 kHz.

(c) Higher plasma power and temperature led to higher discharge performance, i.e. closer to fully-bridged gap in the discharge zone with an effective capacitance from $3.6 \times 10^{-11}$ to $8.3 \times 10^{-11}$ F.

(d) For most cases, higher plasma power always led to higher conversion of CH₄, while it is not the only criteria. Higher mean electron energy and applied voltage that affect the electron energy distribution should also be considered.
7.0 H₂ production in a plasma-assisted chemical looping system in the presence of SrFeO₃₋δ

7.1 Introduction

A plasma-assisted packed bed reactor for the conversion of CH₄ was successfully developed in Chapter 6. In this chapter, the developed set-up was used for the investigation of H₂ production from the conversion of CH₄. The aim of this study is to achieve high yield of H₂ at mild temperatures (from 293 to 773 K). SrFeO₃₋δ, as an active oxygen-donating material and also a promising material for the stabilisation of plasma, is studied here. To fully understand the chemical reactions taking place inside the DBD reactor, the process is studied in pure Ar, which provides an inert environment even in the plasma discharge condition, and ~ 8.5% CH₄/Ar respectively, instead of 100% CH₄.

7.1.1 SrFeO₃₋δ

Strontium ferrite, SrFeO₃₋δ, belongs to the family of perovskite materials, which possess a general formula of ABO₃ (i.e. A is usually an alkaline earth or rare earth cation, and B is a transitional metal cation). Perovskites have become increasingly attractive for chemical looping combustion, due to their high redox capability [203]. Particularly, SrFeO₃₋δ, was found promising from a recent study [42] of large scale in silico screening of materials. SrFeO₃₋δ, was able to release gaseous oxygen over multiple redox cycles (decomposition in N₂ or CO₂ followed by re-oxidation in air) at mild temperatures (~ 823 K), showing its promising chemical potential of oxygen for combustion and fast kinetics in redox. The material also showed good resistance to carbonation. To fit the aim of converting CH₄ at low temperatures in this study, SrFeO₃₋δ is adopted as a first trial in the developed DBD reactor for H₂ production.

7.1.2 H₂ production from chemical looping

As described in 1.5.1 in Chapter 1, steam reforming of natural gas is a main approach used industrially for the production of H₂-rich gas and normally carried out at temperatures above 1073 K. A water-gas shift stage, operated at much lower temperatures (~ 673 K), is usually employed for higher yield and selectivity for H₂. Overall, the process is endothermic, meaning the need for external heating. Non-thermal plasma-assisted reforming of CH₄, particularly DBD configuration, has been widely investigated as an
alternative process for H-rich gas production [123]. The feasibility of using a DBD reactor for H production from CH, reforming, either in the presence of CO, or H2O, has been demonstrated in recent studies [123,124]; whilst its possibility for employing active chemical looping materials for the conversion of fuels for H production has never been studied. In contrast to conventional plasma-assisted systems, an active oxygen carrier, SrFeO₃, is employed to provide a source of oxygen for CH₄ (ideally partial oxidation of CH₄) and suppress carbon deposition, without introducing a separate oxygen stream. Once depleted of oxygen, the oxygen carrier can be regenerated using air, allowing the cycle to be repeated. Thus, this plasma-assisted chemical looping H₂ production (PCLH) from CH₄, which is first proposed here, is similar to conventional chemical looping reforming [13] but can operate at much lower temperatures, where the water-gas shift equilibrium favours H₂.

7.2 Experimental methods

Around 7.5 ml of SrFeO₃, with a size fraction of 600 - 850 μm, prepared from solid mixing (as presented in 2.2.2) and calcination in air at 1273 K for 19 h, was used to pack the plasma-assisted quartz tube reactor. The experiments were carried out either in pure Ar or a mixed stream of CH₄ and Ar. Ar is considered relatively more chemically inert than other gases (such as N₂) both for conventional thermal conditions and in plasma. The investigation in Ar helps to understand the effect of plasma on the SrFeO₃, provided as a reference condition. The temperatures studied were from 293 K to 773 K. For a typical experiment, the gas inflow, either pure Ar or ~ 8.5% CH₄ (balance Ar) entered the packed bed at a flow rate of 0.72 L/min, equivalent to an hourly space velocity of 4670 h⁻¹. The gas from the packed bed was sampled at 0.5 L/min to the analysers. For a typical experiment with the feed gas being 8.5% ± 0.5% CH₄, the reactor was flowing in Ar to purge the system before the start of the experiment. Later, Ar was switched to the mixed stream of CH₄ and Ar. Plasma was then introduced for 2.5 ± 0.2 min. After CH/Ar plasma discharge, the gas was switched to air to burn off any deposited carbon as well as re-oxidise the bed materials. Plasma discharge was later introduced to assist the process of de-coking and re-oxidation of the bed material. For the experiment with the bed material treated in Ar plasma only, the plasma on and off operation kept the same, with only that the gas medium flowing through the DBD reactor being different. The applied voltage was controlled at 8.5 ± 0.5 kV, resulting a plasma power at 16.0 ± 1.5 W. More detailed description of the experimental set-up and the process was presented in 2.3.3.
For data analysis (refer to 6.2), the change in the total flow (as a result of conversion of CH\textsubscript{4}) at the reactor inlet and outlet, \( F_{\text{total},0} \) and \( F_{\text{total}} \), was corrected based on the assumption that Ar did not change over time, only CO, CO\textsubscript{2}, H\textsubscript{2}, C\textsubscript{2}H\textsubscript{6}, C\textsubscript{2}H\textsubscript{4} and Ar were present in the measured flow at the outlet, the total flow rate at the outlet (dry basis), \( F_{\text{total}} \), can be obtained from the Ar balance:

\[
F_{\text{total},0} \cdot (1 - x_{\text{CH}_{4},0}) = F_{\text{total}} \cdot (1 - x_{\text{CO}} - x_{\text{CO}_{2}} - x_{\text{C}_{2}\text{H}_{6}} - x_{\text{C}_{2}\text{H}_{4}} - x_{\text{H}_{2}}).
\]

### 7.3 Results

#### 7.3.1 Identification of the non-stoichiometry of SrFeO\textsubscript{3-\delta}

The non-stoichiometry, 3-\( \delta \), was determined by performing reduction of the prepared fresh SrFeO\textsubscript{3-\delta} (600 - 850 \( \mu \)m), in H\textsubscript{2} in Thermogravimetric analysis (TGA), as described in Ref. [40]. The non-stoichiometry was found to be 2.820, giving SrFeO\textsubscript{3-\delta}. The fresh SrFeO\textsubscript{3-\delta} (600 - 850 \( \mu \)m) was also XRD scanned, where the particles were first crushed to a particle size below 50 \( \mu \)m before scanning. The running parameters of the XRD scanning was presented in 2.4.1. Figure 7-1 shows the spectrum of the SrFeO\textsubscript{3-\delta} sample. The reference data of SrFeO\textsubscript{3.8064} with an angle range from 10\textdegree{} to 60\textdegree{}, was found to fit the sample spectrum well, not far from the results determined by TGA.

![Figure 7-1 XRD spectrum of the prepared SrFeO\textsubscript{3-\delta}, in comparison to the reference spectra of SrFeO\textsubscript{3.8064} (with a collection code of 154928, from ICSD).](image)

#### 7.3.2 Identification of the gaseous products

The product species in UV-Vis and IR regions in the gas phase was identified. The investigation of CH\textsubscript{4} conversion in a plasma environment was initially carried out in the
mixed gas of CH₄ and N₂. However, N₂, which is generally considered inert for traditional chemical processes in the temperature range studied, was found to chemically react with the bed material to generate species such as N₂O in the presence of plasma here. Therefore, the background gas changed to Ar, a chemically inert gas in plasma discharge.

- **Identification of products in the UV-Vis region**

Figure 7-2 UV-Vis spectrum results in the SrFeO₃d-packed DBD reactor at 293 K in the two gases: pure Ar, and ~ 8.5% CH₄ (balance Ar).

Figure 7-2 shows the uv-vis spectrums (from 200 to 800 nm) in the two gas mediums with the bed packed with SrFeO₃d and operated at 293 K. For the wavelength region below 275 nm, the peaks have not been assigned and identified, as they are not strong peaks of any species of interest here. Most of the peaks of interest fell into the range from 275 to 800 nm. Data from National Institute of Standard and Technology (NIST) Atomic Spectra Database Lines Form [204] were used for identification. According to Fig. 7-1, in pure Ar, the species detected were mainly Ar-based species (mostly > 650 nm), N₂-based species (mainly between 300 to 450 nm), and OH· radicals. The presence of N₂-based species and OH· radicals should mainly come from the excitation of the trace amounts of N₂ and moisture that entered the DBD reactor. Especially for the spectrum of OH· at 309.3 nm, which is generally found in plasma systems when there is moisture present [205]. In Fig. 7-1, however, it cannot show a complete OH· spectrum at ~ 309.3 nm, as it overlapped with the spectrum of a N₂-based excited species at ~ 313.0 nm. When a proportion of CH₄ (resulting 8.5% CH₄ in N₂) was introduced into the DBD reactor, the
intensity of most spectrums significantly decreased. One of the OH· radical spectrums (i.e. at ~ 295 nm) even became too weak to be detected in the presence of CH₄. On the other hand, there were two extra peaks found: ~ 430.1 nm, and ~ 517.0 nm. They match the spectrums of CH· radical, and C. swan band (with the peak at close to 517.0 nm) respectively. In general, the results are in agreement with the spectrum of CH₄ plasma; however, no strong H-based spectrum lines/peaks were observed here. The difference in the intensity of the Ar- and N₂-based spectrums in the two gas medium might be due to the difference in the plasma stability in pure Ar and 8.5% CH₄/Ar (see detailed discussion in 7.4.1).

![Figure 7-3](image1.png)

**Figure 7-3** UV-Vis spectrum results in the SrFeO₃-d packed DBD reactor in pure Ar at different temperatures of 293, 673, 713 and 773 K.

![Figure 7-4](image2.png)

**Figure 7-4** UV-Vis spectrum results in the SrFeO₃-d packed DBD reactor in ~ 8.5% CH₄ (balance Ar) at different temperatures of 293, 673, 713 and 773 K.
Figures 7-3 and 7-4 present the emission spectrums from the SrFeO$_{0.8}$-packed DBD reactor from 293 K to 773 K in pure Ar (Fig. 7-2) and ~8.5% CH$_4$ (Fig. 7-3). According to Fig. 7-3, at 293 K, no strong peak was observed at 590 nm in pure Ar; whilst as the temperature increased to beyond 673 K, the peak at 590 nm was observed and most likely to be a N$_2$-based excited species. Ar-based excited species are relatively inert to other components. For other species including N$_2$-based species, OH$^\cdot$ radicals and C-based excited species, whether they would influence any chemical reactions inside the DBD reactor is unknown. For instance, OH$^\cdot$ radicals, is an oxygen source, understanding of its contribution to the conversion of CH$_4$ would be interesting. However, as the N$_2$-based excited species and OH$^\cdot$ radicals are only from the trace amounts of N$_2$ and H$_2$O, their effect is assumed to be negligible in this study. When a portion of CH$_4$ joined the Ar to enter the DBD reactor, the spectrums were shown in Fig. 7-4. In general, the intensity of the spectrums at different temperatures were comparable. C$_2$ and CH$^\cdot$ peaks in the spectrum were found at the 293 and 673 K; whilst when the temperature increased further, C$_2$ spectrum became invisible and CH$^\cdot$ radical was the only C-containing species found in the UV-Vis region.

![UV-Vis spectrum](image)

Figure 7-5 Full scale of the UV-Vis spectrum results in pure Ar at 293, 673, 713 and 773 K.

Figure 7-5 shows the full scale of spectrum in Fig. 7-2. It can be seen that unlike the conditions in ~8.5% CH$_4$ (where the intensities of the spectrums at different temperatures are similar), the intensity of the spectrums in the pure Ar vary significantly as a change
of temperature. The intensity of the spectrums of most excited species reached maximum at 673 K, much higher than those at 713 and 773 K (refer to the N₂- and Ar-based species in Fig. 7-5). In the meantime, gaseous oxygen from the DBD reactor was detected at 713 and 773 K, and the decreased intensity might be linked with the presence of these gaseous oxygen (refer to further discussion in 7.4.1).

- Identification of products in the IR region

![IR spectrums](image)

Figure 7-6 IR spectrums by FTIR from SrFeO₃-packed DBD reactor in ~ 8.5% CH₄ with/without plasma discharge, at a bed temperature of (a) 293 K, (b) 773 K.

Product species in the range of IR (with a wavenumber from 500 cm⁻¹ to 4000 cm⁻¹) were identified from the measurement in the FTIR. No product was detected in pure Ar during
plasma discharge. Figure 7-6 presents the FTIR results of with/without plasma discharge in 8.5% CH₄ (balance Ar) at 293 and 773 K, respectively. According to Fig. 7-6a, without plasma discharge in 8.5% CH₄, in addition to CH₄ peaks, only some fluctuation in the moisture level was observed. When plasma was introduced to the DBD reactor, some extra peaks were seen. The peaks at 650 - 800 cm⁻¹ and 3200 - 3360 cm⁻¹ are assigned with C₂H₂ peaks (with another peak in the range of 1300-1400 cm⁻¹ overlapped one of the CH₄ peaks), and the peak at 900 - 1000 cm⁻¹ is assigned with C₂H₂ (with its other peaks overlapped the CH₄ peaks). At 773 K, according to Fig. 7-6b, some CO₂ was observed even without plasma discharging the bed, suggesting the direct reaction between CH₄ and SrFeO₃·d to generate CO₂ at this temperature. The C₂H₂ peaks, seen at 293 K, were not found at 773 K. It is most likely that the reactivity of SrFeO₃·d at 773 K does not allow the existence of C₂H₂. C₂H₂ peaks were only observed at temperatures below 673 K. Combining the results in Fig. 7-4, it seems that C₂H₂ and C₃ always appeared simultaneously here. C₂H₂ was reported to be an important intermediate species in the combustion of hydrocarbons and a key species for soot formation and growth, and C₃ always appears together with the generation of C₂H₂ [206]. The fact that C₂H₂ and C₃ were only found at the low temperature is consistent with the very low carbon balance at ambient temperature (refer to Table 7-1 in discussion), indicating higher amount of solid phase carbon formed inside the DBD reactor.

7.3.3 H₂ production from plasma-assisted redox cycle

According to 7.3.2, the main gas species involved in the conversion of CH₄ in the UV-Vis and IR regions include CH₄, CO, CO₂, CH₂, CH₃, and O₃. CH₂, CH₃ and O₃ were only found at trace amounts, thus not considered in the following analysis. The generated H₂ from the system was measured by a separate conductivity analyser. In addition, O₂ was also produced under some conditions and was measured by a paramagnetic analyser. The results of the mole fractions with the SrFeO₃·d-packed DBD reactor in Ar and 8.5% CH₄/Ar were shown as follow.
- Results with the DBD reactor in pure Ar

Figure 7-7 Mole fraction of oxygen released from SrFeO₃-d-packed DBD reactor in pure Ar at 293 K. The plasma discharge time span was about 2.5 min.

Figure 7-7 shows the amount of gaseous oxygen, which was the only product detected in the gas phase, released from SrFeO₃-d bed in Ar plasma discharge at temperatures from 293 to 773 K. At ambient temperature, there was no significant release of gaseous oxygen for both with and without plasma discharge periods. When the bed temperature increased to 473 and 713 K, gaseous oxygen was observed when subjected to plasma discharge. At the highest temperature 773 K, some gaseous oxygen (~ 0.0015) was observed even without plasma; more oxygen was produced when plasma was applied. More interestingly, at 473 and 713 K, the released gaseous oxygen quickly dropped to zero; whilst at 773 K, the level of released gaseous oxygen was maintained at 0.006 for 0.7 min, followed by a decrease to zero (i.e. below its initial equilibrium level). It suggests that plasma might have led to some heating effect on the solids, resulting in release of oxygen. The surface temperature in non-equilibrium discharges can be much higher than the bulk gas temperature by having the species such as charge carriers, photons, metastable and excited neutrals hitting the surface of the materials [207]. The heating effect depends on the power coupled into the plasma and could have led to an increase in the bulk temperature of the solid bed, or/and formation of “hot spots”. Owing to this effect, the surface oxide reduction processes can be stimulated. When the plasma discharge was off, the solid beds require some time to fall back to its equilibrium temperature, as a result, ‘post-plasma’ effect of releasing oxygen at 773 K was observed. Additionally, according
to Fig. 7-7, after plasma discharge, SrFeO$_3$ has been reduced to a state that no longer released significant amount of gaseous oxygen.

- **Results with the DBD reactor in 8.5\% \pm 0.5\% CH, (balance Ar)**

\begin{itemize}
  \item \textbf{a. 293 K in SrFeO$_3$}
  \item \textbf{b. 293 K in AlO.}
  \item \textbf{c. 673 K in SrFeO$_3$}
\end{itemize}
Figure 7-8 Mole fractions of different gaseous species from the DBD reactor with the conditions being a. at 293 K in SrFeO$_{0.8}$; b. at 293 K in AlO$_{3}$; c. at 673 K in SrFeO$_{0.8}$; d. at 713 K in SrFeO$_{0.8}$; e. at 773 K in SrFeO$_{0.8}$. The plasma discharge time span in ~ 8.5% CH$_{4}$ was about 2.5 min.

Figure 7-8 presents the results of the gases observed from the DBD reactor including CO, CO$_{2}$, CH$_{4}$, O$_{2}$ and H$_{2}$, from 293 to 773 K in ~ 8.5% CH$_{4}$. A complete cycle of the bed first experiencing the reduction in ~ 8.5% CH$_{4}$, followed by the re-oxidation or regeneration in air at temperatures above 673 K is shown. According to Fig. 7-8a, when the packed
bed was purged with \(~8.5\%\) CH\textsubscript{4}, at 293 K, there was a constant conversion of CH\textsubscript{4} when subjected to plasma discharge. Uniform generation of H\textsubscript{2} was observed over the entire plasma discharge period in \(~8.5\%\) CH\textsubscript{4}. Other gaseous products formed include C.H and C.H\textsubscript{2}, but at trace amounts. The extreme low carbon balance (Table 7-1), which is defined as the ratio of the amount of carbon in the carbon-containing gaseous products over a complete redox cycle to the amount of converted CH\textsubscript{4} in the reduction stage, and the uniform generation of H\textsubscript{2} during plasma discharge suggest the formation of solid carbon inside the DBD reactor from direct CH\textsubscript{4} cracking by plasma. The results were compared to the condition when the DBD reactor was loaded with Al\textsubscript{2}O\textsubscript{3}, where Al\textsubscript{2}O\textsubscript{3} is considered chemically inert. According to Fig. 7-8a and 7-8b, similar levels of CH\textsubscript{4} conversion and H\textsubscript{2} production were observed, implying that at this temperature, SrFeO\textsubscript{3} was chemically inactive. When the operating temperature of the DBD reactor increased to 673 K, according to Fig. 7-8c, CH\textsubscript{4} was converted when plasma was active. Together with the conversion of CH\textsubscript{4}, the production of CO\textsubscript{2} (\(~0.0025\)), CO (\(~0.0009\)) and H\textsubscript{2} (\(~0.007\)) were observed. The generation of CO and CO\textsubscript{2} means that SrFeO\textsubscript{3} was activated by plasma and stimulated the conversion of CH\textsubscript{4}. This can either be \textit{via} a gas-gas reaction between CH\textsubscript{4} and gaseous oxygen (released from SrFeO\textsubscript{3}, as shown in Fig.7-7 in Ar), or direct gas-solid reaction between CH\textsubscript{4} and SrFeO\textsubscript{3}. It was noticed that there was some amount of gaseous oxygen detected in CH\textsubscript{4}/Ar before plasma discharge, whilst the oxygen level dropped to zero when the plasma was active; some oxygen was detected again as soon as plasma was tuned off. SrFeO\textsubscript{3} seems to have become active in donating oxygen at 673 K, and it suggests that at least gas-gas reaction between CH\textsubscript{4} and gaseous oxygen exist in this system. Comparing the amounts of H\textsubscript{2} produced at 293 and 673 K, lower amounts of H\textsubscript{2} were seen at 673 K, suggesting that some H\textsubscript{2} might have been oxidised to other species by SrFeO\textsubscript{3}, most probably H\textsubscript{2}O. In the air regeneration stage, no species other than O\textsubscript{2} were observed before plasma discharge; and higher [O\textsubscript{2}] than that in air was detected during air plasma discharge, indicating a release of gaseous oxygen from the solid bed.

When the bed temperature increased to 713 K, according to Fig. 7-8d, similarly, CO\textsubscript{2}, CO, and H\textsubscript{2} were observed during plasma discharge. A decrease in the [O\textsubscript{2}] over the discharge period in \(~8.5\%\) CH\textsubscript{4} was also found. The generation of CO and H\textsubscript{2} were not as uniform as those at lower temperatures (Fig. 7-8a and 7-8c), the amount of H\textsubscript{2} was gradually
As the cracking of CH, (by plasma) always takes place, regardless of the interaction between CH, and SrFeO₃δ, the gradually reduced [H₃] seems to suggest an increasing consumption of the generated H, due to an increase in the activity of the solid bed. In the meantime, the CO, CO and O₃ concentrations gradually increased to ~ 0.006, 0.0015, and 0.0002, respectively. Referring to the oxygen level with that (gradually increased to ~ 0.0035) in pure Ar at 713 K (Fig. 7-7), the sum of the oxygen amount from CO and CO was higher than in the gaseous O, released in Ar, suggesting that either more gaseous oxygen was pulled off from SrFeO₃δ in CH/Ar in the presence of plasma, or there is direct gas-solid reaction between CH, and SrFeO₃δ. More oxygen was detected when plasma was turned off (with the bed still in 8.5% CH₃) than that before plasma discharge. This indicates 1) the presence of post plasma heating effect; 2) the SrFeO₃δ contributes to the conversion of CH, and gas-gas reaction between CH, and gaseous O, was present. Whether gas-gas combustion will be dominant, however, is still not clear. In terms of the air regeneration of the bed material, similar to the results from lower temperatures, oxygen was pulled out from SrFeO₃δ during plasma discharge; interestingly, while plasma was stopped, [O₂] dropped to a level slightly lower than the air O₂ level, followed by a gradual increase to the expected [O₂] in air. Further discussion on this is presented in 7.4.4.

When the bed temperature increased to 773 K, as seen in Fig. 7-8e, some CO₃ (mole fraction of ~ 0.0028) was generated even without plasma. Meanwhile, an oxygen mole fraction of ~ 0.001 was detected. In Fig. 7-7, without plasma discharge in Ar, there was a mole fraction of around 0.0015 oxygen released from the solid bed. As it is expected that even more gaseous oxygen should be released from SrFeO₃δ in 8.5% CH₃, due to much lower partial pressure of oxygen (i.e. pure CH₃ is with pᵣ ~ 10⁻³⁵ bar) in the reducing environment, the lower detected amount of oxygen level in 8.5% CH₃ than that in Ar at least suggests the presence of direct combustion of CH₃ by the released O₂. The auto-ignition temperature of CH₃ is about 810 K [208], indicating a catalytic effect of SrFeO₃δ on the combustion of CH₃. Falcon et al. [209] observed similar catalytic effect of SrFeO₃δ for the combustion of CH₃. Whether there was direct gas-solid reaction between CH₃ and SrFeO₃δ is still unknown. When plasma was applied to the DBD reactor at t = 1.3 min, CO was found to be the primary product from the conversion of CH₃. The generation of CO started at about the same time with the generation of CO. [H₃] firstly
reached a maximum with a peak value of around 0.009, followed by its quick decrease, whilst CO, and CO concentrations kept rising. [O.] first dropped in the presence of plasma discharge, however, it quickly increased, and this might suggest some phase change of SrFeO$_{0.5}$, where SrFeO$_{0.5}$ became more reactive for releasing oxygen or the oxygen decoupling rate has become faster. In the air regeneration stage, similar to the conditions at 713 K (Fig. 7-7d), a quick drop to lower than air level [O.] after plasma discharge was observed at 773 K.

### 7.3.4 Results of conversion, selectivity and material balance

Table 7-1 shows the summarised results including the averaged conversion of CH$_4$, selectivity for different gaseous products, and hydrogen and carbon balances at different operating temperatures of the DBD reactor. The equation for obtaining the averaged conversion of CH$_4$, $X_{CH_4}$, has been described in 6.5.3. Other parameters were calculated based on the equations as follow.

The averaged selectivities, $S_a=CO$ or $CO_2$ for CO or CO$_2$, and $S_{H_2}$ for H$_2$, are given as:

$$S_a = \frac{\int_{t_0}^{t_{\text{end}}} F_{\text{total}} x_a dt}{\int_{t_0}^{t_{\text{end}}} (F_{\text{total,0}} x_{CH_4,0} - F_{\text{total}} x_{CH_4}) dt}$$

$$S_{H_2} = \frac{\int_{t_0}^{t_{\text{end}}} F_{\text{total}} x_{H_2} dt}{2 \int_{t_0}^{t_{\text{end}}} (F_{\text{total,0}} x_{CH_4,0} - F_{\text{total}} x_{CH_4}) dt},$$

where $S_a$ is based on C in CH$_4$, and $S_{H_2}$ is based on H in CH$_4$. The average yield for each product, $Y_i$, was defined as the amount of component $i$ produced for every mole of CH$_4$ introduced into the DBD reactor:

$$Y_i = \frac{\int_{t_0}^{t_{\text{end}}} F_{\text{total}} x_i dt}{F_{\text{total,0}} x_{CH_4,0}}.$$

The fraction of carbon deposited was estimated from the difference between the carbon input and that detected at the outlet during the reduction period:
\[
d_c = 1 - \frac{\int_{t_0}^{t_{\text{end}}} F_{\text{total}}(x_{CO} + x_{CO_2} + 2x_{C_2H_4} + 2x_{C_2H_2}) \, dt}{\int_{t_0}^{t_{\text{end}}} (F_{\text{total},0} x_{CH_4,0} - F_{\text{total}} x_{CH_4}) \, dt}.
\]

The carbon and hydrogen balances, defined as the ratio of carbon/hydrogen-containing species measured to the carbon/hydrogen in the converted CH\textsubscript{4} in a complete redox looping cycle (\textit{i.e.} CH\textsubscript{4}/Ar plasma discharge followed by air plasma discharge stage), were also estimated. According to Table 7-1, the increase in the temperature leads to an increase in the conversion of CH\textsubscript{4}; however, the production of H\textsubscript{2} does not benefit from the increase in temperature. This might be due to the too high activity of SrFeO\textsubscript{3} at high temperatures that resulted in the oxidation of the produced H\textsubscript{2}. In the meantime, higher selectivity towards CO, was observed with an increase in temperature; whereas for CO\textsubscript{2}, the selectivity from 673 to 773 K seems to be stable. Similar to H\textsubscript{2}, both the selectivity towards C\textsubscript{2}H\textsubscript{4} and C\textsubscript{2}H\textsubscript{2} decreased. Due to the increased oxidising activity of SrFeO\textsubscript{3} with an increase in temperature, the carbon balance over a complete plasma-assisted redox cycle increased significantly. If the poor carbon balance was mainly due to deposited carbon in the DBD reactor, it seems that the even with the assistance of plasma discharge in the regeneration stage, not all the deposited carbon was removed, as no significant amount of CO or CO\textsubscript{2} was detected, as shown in Fig. 7-8.
Table 7-1 Summarised results of conversion of CH₄, product selectivity and material balances.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>293</td>
</tr>
<tr>
<td>Gas medium</td>
<td>CH/Ar</td>
</tr>
<tr>
<td>X_CCH₄</td>
<td>0.075</td>
</tr>
<tr>
<td>S_O₂</td>
<td>0</td>
</tr>
<tr>
<td>S_CO</td>
<td>0</td>
</tr>
<tr>
<td>S_CO₂</td>
<td>0.782</td>
</tr>
<tr>
<td>S_H₂</td>
<td>0.181</td>
</tr>
<tr>
<td>S_C₂H₄</td>
<td>0.191</td>
</tr>
<tr>
<td>Y_CO ×10</td>
<td>0</td>
</tr>
<tr>
<td>Y_CO₂ ×10</td>
<td>0</td>
</tr>
<tr>
<td>Y_H₂ ×10</td>
<td>115</td>
</tr>
<tr>
<td>H balance</td>
<td>0.918</td>
</tr>
<tr>
<td>C balance</td>
<td>0.311</td>
</tr>
</tbody>
</table>

7.4 Discussion

7.4.1 The effect of Ar on plasma intensity and conversion of CH₄

As described in Fig. 7-2, significantly higher intensity of the UV-Vis spectrum was observed in pure Ar plasma than that in CH/Ar, indicating that it was easier to form plasma species in pure Ar. The first ionisation energy of Ar is about 1520 kJ/mol, higher than that for CH₄ (~ 1220 kJ/mol) [210,211]. However, this does not mean it is easier to generate plasma in CH₄. CH₄ is more chemically active compared to Ar, and this would mean that some of the applied energy has been used for other routes besides ionisation, such as vibrational and rotational excitation. While in Ar, the routes to spread the energy of electrons are very limited, suggesting that the energy efficiency for ionisation in Ar would be higher than that in CH₄. Additionally, because there are many possible routes to spread the energy of electrons in CH₄ plasma, the mean free path of the electrons, the average distance traveled between successive collisions [212], in Ar plasma is estimated to be around 1.3 times that in CH₄ plasma (based on λ = 1/(nσ), where n is the number density of the particles, σ is the cross section of a two-particle collision, and λ is the mean free path between collisions) [213]. Given identical electric field, the electrons are accelerated by electric field to higher velocities, and therefore energies, in Ar compared
to CH, before they experience a collision. As a result, the energy density of the electrons in Ar would be higher, giving a more stable plasma in Ar. The addition of CH to the Ar gas is actually contaminating the Ar plasma environment, leading to a decrease in the plasma intensity. This is consistent with what has been reported by Matsumoto et al. [214] that only the addition of 2% CH into pure Ar in a DBD reactor dramatically decreased the degree of Ar excitation.

The effect of the purity of Ar on plasma can also be responsible for the difference in the spectra intensity in Fig. 7-5. The Ar spectra at 293 and 673 K were much higher than those at 713 and 773 K. At 293 and 673 K, during plasma discharge, no gaseous oxygen was produced to ‘contaminate’ the pure Ar environment; therefore, the intensity would be high. When the bed was increased to between 713 and 773 K, oxygen started to be released from SrFeO₈, especially at 773 K, where the oxygen mole fraction reached close to 0.015 (at its peak). This significantly affected the plasma intensity. This is because, compared to Ar, oxygen molecule is also much more chemically active. With its first ionisation energy (~ 1314 kJ/mol. [210,211]) being similar to that of Ar, the energy density of electrons in the presence of gas phase oxygen would also be much lower.

### 7.4.2 Investigation of the effects of plasma catalysis and plasma heating

The dissipated plasma power was determined by taking the integration of the parallelograms of the voltage-charge figures, as described in 2.3.3. To understand whether the plasma energy input is a significant amount, the thermal energy required for heating the DBD reactor was estimated for comparison. It was assumed that the thermal energy was only used for heating the bed of SrFeO₈ and the flowing gas through the DBD reactor. Heat capacities of each medium in each temperature range was estimated by taking the average of the values of the starting and end temperatures. The values of the heat capacity used are presented in Table 7-2:
Table 7-2 Heat capacities.

<table>
<thead>
<tr>
<th>Medium</th>
<th>Heat capacity (J/mol/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>from 293 to 773 K</td>
</tr>
<tr>
<td>SrFeO₃ (data based on [215])</td>
<td>106</td>
</tr>
<tr>
<td>CH₄ (data from NIST [131])</td>
<td>48.4</td>
</tr>
<tr>
<td>Ar (data from NIST [131])</td>
<td>20.8</td>
</tr>
</tbody>
</table>

Table 7-3 Estimated thermal energy input (assuming negligible heat loss from the bed).

<table>
<thead>
<tr>
<th>Temperature increase (K)</th>
<th>Heat for heating SrFeO₃ (J)</th>
<th>Heating power for the flowing gas (W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>585</td>
<td>1.67</td>
</tr>
<tr>
<td>420</td>
<td>2346</td>
<td>6.67</td>
</tr>
<tr>
<td>480</td>
<td>2682</td>
<td>7.99</td>
</tr>
</tbody>
</table>

According to Fig. 7-8, in the absence of plasma discharge, up to 713 K, no significant conversion of CH₄ was observed. The thermal energy required to heat the bed from 293 to 713 K was about 2346 J, and heating power for the flowing gas was about 6.67 W. The effects of plasma power and thermal energy input were compared. For a bed of SrFeO₃ at 293 K, plasma power supplied to the DBD reactor was gradually increased to the point where the conversion of CH₄ was just observable (converted mole fraction of CH₄ of ~ 0.001). The corresponding supplied power was 4.13 W and it took about 0.5 min to reach a stable conversion of CH₄, resulting in a plasma energy of about 123.9 J. This plasma input was much lower than the thermal heat input required to initiate the conversion of CH₄. Based on the observation that SrFeO₃ was chemically inert at 293 K, the conversion of CH₄ at such low temperature should be mainly due to the plasma catalysis, rather than plasma heating effect. A comparison of conversion of CH₄ between thermal approach and the plasma-assisted one was carried out in [101], as presented in Fig. 7-9. Line 1 is the thermodynamic equilibrium conversion of methane as a function
of specific energy input. Line 2 represents experimental results achieved by thermal preheating without plasma discharge, where the growth of methane conversion and increase of temperature happen at the same time. Lines 4, 5, and others represent the isotherms in the range between 250 and 650°C. Curves 3, 6, and 7 mean preheating the temperatures to 550, 500, and 600°C, followed by plasma discharge (generated from microwave) at different powers. According to curves 3, 6, and 7, non-equilibrium plasma drives the conversion curves closer to thermodynamic equilibrium. A small amount of plasma energy input can lead to significant decrease in the thermal energy, suggesting the effect of plasma catalysis.

Figure 7-9 Plasma conversion of methane (from steam methane reforming, where the methane to steam ratio varies from 1:1 to 1:2): results of experiments and simulations presented as the methane conversion dependence on specific energy input: (1) thermodynamic calculations of the quasi-equilibrium states; (2) experiments with purely thermal energy input; (3, 6, 7) experiments with a discharge; (4, 5) theoretical lines representing isotherms (fixed temperature T). The figure was cited from [101]. For copyright issue, the figure is removed here.

The plasma effect on the gas phase, CH₄, has now been understood as plasma catalysis. The plasma effect on the solid bed, SrFeO₃, is also studied here. The comparison of the electrical and thermal energy input to activate SrFeO₃ for donating gaseous oxygen was
conducted. According to Fig. 7-7, at 673 K, it took about 0.8 min to reach an O\(_2\)(g) mole fraction of 0.0018 during plasma discharge. A similar release of gaseous oxygen (~0.0018) was found when the bed was increased to temperature 773 K without plasma discharge. The thermal energy input (585 J to heat the SrFeO\(_\delta\) bed, and 1.67 W to heat the flowing gas, as shown in Table 7-3) to raise the whole DBD reactor from 673 to 773 K was compared with the plasma energy input with the DBD reactor at 673 K. Taking out the plasma power needed to heating the gas flow (1.67W), the actual plasma power supplied to the SrFeO\(_\delta\) bed would be 13.33 W (= 15 W - 1.67 W), resulting a total energy of 640 J to reach the oxygen concentration of 0.0018 at 673 K. This was comparable to the thermal heat required to drive SrFeO\(_\delta\) to release the same amount of oxygen. Therefore, the activation of SrFeO\(_\delta\) might be more of a thermal effect caused by plasma. The results and discussion in the current study agree with the findings reported in literature [101] that for heterogeneous non-thermal plasma processes, the production of actives species in plasma was usually controlled by the temperature of the electrons; whilst the surface reactions are usually controlled by the surface temperature and limiting the total kinetics.

### 7.4.3 Investigation of longer plasma discharge period in the SrFeO\(_\delta\)-packed DBD reactor

It has been found that when SrFeO\(_\delta\) became chemically reactive during plasma discharge, the production of CO\(_2\) became significant. It seems that the produced H\(_2\) can be oxidised by the activated SrFeO\(_\delta\) so that [H\(_2\)] dropped. The over-expected activity of SrFeO\(_\delta\) for the suppression of coking, is not an advantage here as it lowered the productivity of H\(_2\), though the conversion of CH\(_4\) improved. SrFeO\(_\delta\) has non-stoichiometry of oxygen and goes through phase transitions in a reducing environment, from perovskite (2.5 < 3-\(\delta\) < 3) to brownmillerite structure (3-\(\delta\) < 2.5) [39]. It would be interesting to know if there is a state of SrFeO\(_\delta\) that helps promote the oxidation of CH\(_4\), whilst still maintain a high selectivity for H\(_2\), as a product. Therefore, an experiment with a much longer plasma discharge period inside the DBD reactor at 773 K, as shown in Fig. 7-10, was carried out.
According to Fig. 7-10, plasma was introduced at \( t = 2.3 \) min, and the results in the first 2.5 min of the plasma discharge period appeared similar to those from Fig. 7-8e: \([H_2]\) firstly increased to a peak value and then dropped, this was then followed by an increase in the CO and CO. If the drop in the H\(_2\) concentration as plasma was introduced, was believed due to its oxidation to H\(_2\)O by SrFeO\(_{0.8}\), it seems the sequence for oxidation is H\(_2\) > CO. After the first 2.5 min of plasma discharge, \([CO]\) and \([CO_2]\) gradually dropped to zero, whilst \([H_2]\) dropped and seemed to finally stabilise at 0.002. A proposed reaction sequence which might have happened here is: at 773 K, before plasma discharge, a low amount of CH\(_4\) was oxidised by the SrFeO\(_{0.8}\), either directly with the solid SrFeO\(_{0.8}\) or with gaseous oxygen released from SrFeO\(_{0.8}\). As plasma was introduced, H\(_2\) was generated, mainly through the cracking of CH\(_4\). As the plasma acted on the SrFeO\(_{0.8}\) bed, the bed became active and started to oxidise the H\(_2\) produced to H\(_2\)O, and also CO and CO\(_2\). In the meantime, SrFeO\(_{0.8}\) also improved overall conversion of CH\(_4\), mostly to CO and CO\(_2\) (very likely via the route of direct combustion of CH\(_4\) by SrFeO\(_{0.8}\) to CO, CO\(_2\) and H\(_2\)O). Later on, SrFeO\(_{0.8}\) seemed less reactive, \([CO]\) and \([CO_2]\) was gradually dropped to zero, and some H\(_2\) was observed. The conversion of CH\(_4\) also dropped and gradually reached a stable value. The measured low level of H\(_2\) after \( t = 15 \) min should be a combined effect of the cracking of CH\(_4\) to H\(_2\), and some oxidation of H\(_2\) to H\(_2\)O by the less reactive SrFeO\(_{0.8}\), where SrFeO\(_{0.8}\) no longer react with CH\(_4\). The hypothesis is supported by that the conversion of CH\(_4\), when \([H_2]\) became stabilised (from \( t = 15 \) to 27.5 min), 0.078, similar to the conversion of CH\(_4\), at 293 K, 0.075 (refer to Table 7-1 and Fig.7-8a) where only cracking of CH\(_4\) by plasma was believed to dominate in the DBD reactor.
Overall, in a 26 min’s long plasma-assisted reduction period, SrFeO$_{\delta}$ did not help promote H$_2$ production in such systems, in different stages of the reduction process: (1) high [H$_2$] was detected when subjected to plasma discharge; (2) [H$_2$] quickly dropped, in the meantime, [CO$_2$] increased substantially and the conversion of CH$_4$ also improved; (3) [H$_2$] was maintained at a relatively constant level, whilst CO and CO$_2$ was no longer produced in a large amount and the conversion of CH$_4$ dropped. It was not clear what led to the change in the apparent activity of SrFeO$_{\delta}$, but the corresponding amounts of oxygen consumption from SrFeO$_{\delta}$ in each stage was estimated. Assuming that the cracking process of CH$_4$ by plasma catalysis was not affected by the change of SrFeO$_{\delta}$, and that the expected amounts of H$_2$ produced at 773 K was the same as those produced at 293 K, the lowered amount of H$_2$ in this case is believed due to oxidation from H$_2$ to H$_2$O by SrFeO$_{\delta}$. If the solid bed was converted uniformly over the plasma discharge period, and by calculating the amounts of oxygen in the products (i.e. CO, CO$_2$, O and estimated H$_2$O) at stages (1), (2) and (3), the corresponding phase transformation or change in the non-stoichiometry in SrFeO$_{\delta}$ in each stage can be estimated. According to Fig.7-1, the prepared fresh SrFeO$_{\delta}$ was with an oxygen non-stoichiometry of 2.820. Stages (1), (2) and (3) correspond to a change in SrFeO$_{\delta}$ from SrFeO$_{2.820}\rightarrow$ SrFeO$_{2.808}\rightarrow$ SrFeO$_{2.755}\rightarrow$ SrFeO$_{2.648}$. A recent study on the determination of ‘$\delta - p_{\delta} - T$’ diagrams for perovskite related oxides including SrFeO$_{\delta}$ carried out by Starkov et al. [39] showed that
the sequence of equilibrium phase transformation in a reducing environment for 
\( SrFeO_{3-\delta} \) at 773 K was \( SrFeO_{3.8} \rightarrow SrFeO_{3.7} \rightarrow SrFeO_{3.6} \), where \( SrFeO_{3.8} \rightarrow SrFeO_{3.7} \) corresponded to the change in oxygen vacancy in the perovskite phase and \( SrFeO_{3.7} \rightarrow SrFeO_{3.6} \) was the phase transition from perovskite to brownmillerite phase. Based on non-stoichiometry, it appears that here, \( SrFeO_{3.8} \) was still in perovskite phase in stages (1) and (2). The reduced particles (after stages (1) and (2)) were collected (with the bed quench in ~ 8.5% CH\(_4\)) and carefully observed. Some brown particles, indicating brownmillerite structure, were found randomly distributed. This implies inhomogeneous effect of plasma on the solid bed. In stage (3), some part of the bed (based on the non-stoichiometry) were in brownmillerate phase, whilst it still did not help H\(_2\) production. In summary, the results suggest that \( SrFeO_{3.8} \) might not be a good candidate for hydrogen production.

### 7.4.4 Investigation of O\(_2\) release from \( SrFeO_{3.8} \) in air regeneration stage

In the air regeneration stage at 713 and 773 K (Fig. 7-8d and 7-8e), gaseous oxygen from \( SrFeO_{3.8} \) was released during plasma discharge, resulting in a higher \([O_2]\) than that in the air. Interestingly, after the plasma was stopped, a decrease in \([O_2]\) to lower than that in air was observed, indicating a transport of oxygen from the air to \( SrFeO_{3.8} \). Extrapolating the results from Starkov et al. [39], at temperatures \( \leq 773 \) K, \( SrFeO_{3.8} \) with \((3-\delta) \geq 2.81\) would be the expected forms in thermodynamic equilibrium with air \([O_2] = 0.21\). In the results shown here, for CH/Ar plasma treated \( SrFeO_{3.8} \), where \((3-\delta)\) is usually below 2.81 \((e.g. 2.76 \text{ at } 773 \text{ K, as shown in Fig. 7-8})\), a significant release of gaseous oxygen from \( SrFeO_{3.8} \) to air was not expected. The observed increase in gaseous oxygen in plasma discharge, together with the transporting of oxygen to the solid bed after plasma stopped, means that plasma has forced \( SrFeO_{3.8} \) to release more gaseous oxygen than that from the bulk thermal equilibrium. This is very likely due to plasma local or surface heating on the solids. On the other hand, even with the improved oxygen-donating ability of \( SrFeO_{3.8} \) in plasma, it did not result in the burn off any of the deposited carbon on the solids in the air regeneration stage. This implies that the deposited carbon formed in the reduction stage was hard to be removed by the presence of (\( SrFeO_{3.8} \) + gaseous O\(_2\) + plasma), the significant generation of CO\(_2\) (and some CO) during reduction period should mainly come from the direct combustion of CH\(_4\), rather than experiencing an intermediate step via solid carbon.
7.4.5 Comparison of the system for H₂ generation and other industrial means of H₂ generation

The results from the current study suggest a SrFeO₅-doped DBD reactor is not promising for H₂-rich gas production due to its over-reactivity. An estimation of the energy cost for this process was compared with some processes for H₂ production. There are many ways to categorise the energy cost. Two definitions of energy cost were used here for comparison with other processes reported, EC₁ and EC₂.

$$EC_a = \frac{\left(\frac{W}{B_{CH_4}}+n_{CH_4}\right)HHV_{CH_4}}{n_{H_2}}$$

$$EC_b = \frac{W}{n_{H_2}}$$

W is the applied plasma power, measured from the Lissajous figure; n₁₂ is the amount of H₂ produced over time. B₁₄ is the chemical exergy of CH₄, which is ~ 52 MJ/kg [216]. η is the efficiency from thermal to electricity energy and a value of 60% is assumed here. n₁₄ is the converted amount of CH₄. HHV₁₄ is the high heating value of CH₄, 55.5 MJ/kg. EC₂ only takes into account the energy from the applied plasma for the production of H₂, whereas EC₁ converts the plasma energy back to the thermal energy equivalent to that from the combustion of CH₄, and also considers the chemical energy of converted CH₄. The definition of EC₁ here tries to normalise the energy cost from different approaches based on the exergy in CH₄, allowing easy comparison between various H₂ production techniques. It should be noted that for both EC₁ and EC₂, the energy of maintaining the reactor at the operating temperature has not been taken into account. For industrial H₂ production techniques such as steam reforming of CH₄, electricity input only accounts for a small amount of total energy input. In this study, the adoption of plasma generates heat inside the reactor, and this might account for the energy required to maintain the operating temperature; however, for simplicity, this reactor heating energy is not included in the estimation of the energy cost here.

Table 7-4 presents EC₁ and EC₂ of this study, with the temperature from 293 to 773 K. EC₁ is first compared with other conventional H₂ production processes such as steam reforming of CH₄, and water electrolysis. According to Table 7-4, EC₁ varies from 2680 to 4070 MJ/kg, depending on the temperature. For conventional steam reforming of CH₄, the energy cost (EC₁) is reported to be less than 160 MJ/kg [104], significantly lower
than the values obtained here. However, steam reforming, which requires multiple stages to achieve high H\textsubscript{2} yield, is more suited for large-scale H\textsubscript{2} production. For small scales or point-of-use, water electrolysis (water splitting) is one of the popular approaches, with its energy cost for was reported to be from 320 to 510 MJ/kg [217] (estimated based on the original data of electricity consumption 50 kWh/kg to 79 kWh/kg). Still, the energy cost from the current study is too high. However, these are only preliminary results without optimization of the process and reactor set-up. The increase in the scale can usually lead to a decrease in the production cost. On the other hand, the biggest issue revealed from the preliminary results is that SrFeO\textsubscript{3.5} did not to show apparent advantage in improving the hydrogen production from such process. The lowest hydrogen production cost was found at 293 K, where SrFeO\textsubscript{3.5} was considered to be chemically inert. SrFeO\textsubscript{3.5} seems to be too reactive here. The positive side is that the presence of local oxygen source did help decrease the coking. Therefore, suitable oxygen carriers that are reactive enough to suppress coking but not too reactive to combust hydrogen are needed.

Table 7-4 Energy cost $E_C_b$ from 293 to 773 K.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$E_C_a$ (MJ/kg)</th>
<th>$E_C_b$ (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>2680 ± 80</td>
<td>1400 ± 40</td>
</tr>
<tr>
<td>673</td>
<td>4070 ± 70</td>
<td>2080 ± 60</td>
</tr>
<tr>
<td>713</td>
<td>4040 ± 110</td>
<td>1940 ± 60</td>
</tr>
<tr>
<td>773</td>
<td>3680 ± 90</td>
<td>2300 ± 70</td>
</tr>
</tbody>
</table>

Improving the energy cost by varying other parameters is also possible. Nozaki et al. [218] carried out extensive experimental work in a non-thermal plasma-assisted system and the results are summarised in Table 7-5. The energy cost, $E_C_b$, as shown in Table 7-4, can be compared with those obtained by Nozaki et al. Here $E_C_b$ is between 2680 to 4070 MJ/kg; compared with 136 to 8080 MJ/kg. According to Table 7-5, the use of Ni/SiO\textsubscript{2} and increase in temperature substantially improved hydrogen production by reducing the energy cost from 8080 to 1004 MJ/kg at 673 K when the DBD reactor was loaded with Ni/SiO\textsubscript{2}, and from 1330 to 136 MJ/kg when increasing the bed temperature from 673 to 873 K. In addition, the increase in operating frequency also contributed to the reduction of energy cost. From this perspective, though the current energy cost is
significantly higher than the conventional H₂ production techniques, especially for steam reforming of CH₄, there are opportunities for improvement, particularly by employing some catalyst such as Ni.

Table 7-5 Comparison of the energy cost. Data from [218].

<table>
<thead>
<tr>
<th>Reactor type</th>
<th>Operating temperature (K)</th>
<th>Operating frequency (kHz)</th>
<th>$EC_b$ (MJ/kg H₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DBD</td>
<td>473</td>
<td>10</td>
<td>5974</td>
</tr>
<tr>
<td>DBD</td>
<td>673</td>
<td>76</td>
<td>8080</td>
</tr>
<tr>
<td>DBD + Ni/SiO₂</td>
<td>673</td>
<td>10</td>
<td>1330</td>
</tr>
<tr>
<td>DBD + Ni/SiO₂</td>
<td>673</td>
<td>76</td>
<td>1004</td>
</tr>
<tr>
<td>DBD + Ni/SiO₂</td>
<td>873</td>
<td>10</td>
<td>136</td>
</tr>
</tbody>
</table>

7.4.6 Investigation of Ni on SrFeO₃ for hydrogen production

As shown in 7.4.5, the presence of Ni could significantly improve the production of H₂, and thus decrease the energy cost. Ni was found to be an efficient catalyst for H₂ production. However, the use of Ni usually results in severe coking. For a DBD system therefore, an optimum material is likely to be a catalyst such as Ni, coupled with an oxygen carrier such as SrFeO₃ to prevent coking. The concept is tested here. Ni was doped onto the previously prepared SrFeO₃ by dry-impregnation from nickel nitrate hexahydrate. The resulting particles, with a particle size fraction of 600 – 850 µm, had a molar ratio of Ni to total metals (i.e. Ni + Sr + Fe) of 1:10. The detailed preparation protocol was presented in 2.2.2. The fresh Ni-doped SrFeO₃ sample was XRD performed to identify the phases formed, and the spectra is shown in Fig. 7-11. As seen in Fig. 7-11, in the fresh sample, the peaks were assigned to NiO and SrFeO₃ (the XRD patterns of the recovered samples are discussed below in appropriate section).
Figure 7-11 XRD spectra of fresh NiO/SrFeO$_{3-d}$, NiO/SrFeO$_{3-d}$ regenerated at 773 K and NiO/SrFeO$_{3-d}$ regenerated at 1273 K.

Figure 7-12 Plasma-assisted cracking/partial oxidation of CH$_4$ at 773 K in fresh NiO/SrFeO$_{3-d}$.

The result of converting CH$_4$ in the fresh NiO/SrFeO$_{3-d}$-packed DBD reactor is shown in Fig. 7-12. In the bed of fresh NiO/SrFeO$_{3-d}$, similar to the bed of SrFeO$_{3-d}$, gaseous O$_2$ was detected before introducing plasma; however, CO$_2$ was not observed here. From $t = 2.0$
to \( t = 22.4 \) min, the packed bed was subjected to plasma, where periods a and b correspond to plasma power of 13.1 W and 16.2 W, respectively. A decrease in \([\text{CH}_4]\), and an increase in \([\text{CO}]\) were clearly seen as soon as the plasma was applied, suggesting that \( \text{CH}_4 \) was largely converted to \( \text{CO} \) as a result of plasma discharge. The \([\text{H}_2]\) and \([\text{O}_2]\) also dropped from \( t = 2 \) to \( t = 8 \) min, indicating the consumption of gaseous oxygen (released from \( \text{SrFeO}_x \)) and \( \text{H}_2 \) during this period. An increase in the plasma power from 13.1 to 16.2 W from \( t = 8 \) min led to subsequent increase in \( \text{CH}_4 \), conversion and \( \text{CO} \), production. No \( \text{H}_2 \) was detected from \( t = 8 \) min to \( t = 11 \) min. However, from \( t = 11 \) min, \( [\text{H}_2] \) started to sharply increase; in the meantime, production of \( \text{CO} \) was observed; whilst [CO] dropped and the conversion of \( \text{CH}_4 \) started to decrease. Both the concentrations of \( \text{H}_2 \) and \( \text{CO} \) reached a maximum first, followed by their gradual drop. After the plasma was stopped at \( t = 22.5 \) min, the bed still showed a relatively high activity for \( \text{H}_2 \) production. What happens in the \( \text{NiO/SrFeO}_x \) in the initial period seems very similar to that in the \( \text{SrFeO}_x \) bed: the solid oxygen carrier seems to be too reactive to maintain the \( \text{H}_2 \) produced from \( \text{CH}_4 \), cracking, the \( \text{H}_2 \) was oxidised probably to \( \text{H}_2\text{O} \). However, when the reduction of the oxygen carrier reached a certain stage, the bed seemed to be less oxidising and exhibited very high selectivity for \( \text{H}_2 \) and \( \text{CO} \), though \( \text{CH}_4 \) was converted less due to lower reactive of the bed. That fact that both high \([\text{H}_2]\) and \([\text{CO}]\) were observed in the second half of the reduction stage suggests that during this period, the system seems to be in the state where the overall process was very likely controlled by thermodynamics of \( \text{SrFeO}_x \). The mechanism giving the much-increased production of \( \text{H}_2 \) is unclear, whether it is \( \text{NiO} \) or the reduced metal phase, \( \text{Ni} \), or some other phase responsible for \( \text{H}_2 \) production is uncertain here.

According to Fig. 7-12, \( \text{NiO/SrFeO}_x \), denoted as NSFO1 in the following text, showed great potential (when sufficiently reduced) for \( \text{H}_2 \)-rich gas production in a plasma-assisted system. To test its cyclability, the material was regenerated in air plasma at 773 K, as shown from \( t = 31 \) min in Fig. 7-12. During regeneration, substantial amounts of \( \text{CO}_2 \) and \( \text{CO} \) were observed as soon as the bed was switched from \( \text{Ar} \) to air, indicating a large amount of solid carbon deposited in the bed; this carbon was easily removed. Plasma was later applied to assist carbon removal, though no clear carbon-containing species were detected. The regenerated sample was denoted as NSFO2 and tested in the second reduction. Figure 7-13 shows the results of converting \( \text{CH}_4 \), in the NSFO2 with a plasma
power of 16.3 W. It was found that H₂ production was insignificant over the 17 min’s plasma-assisted reduction period. There was no period of the reduction that favored the generation of H₂ and CO over CO₂ (and H₂O). To understand what might have happened here, NSFO2 was XRD scanned and its spectra was presented in Fig. 7-11. In addition to NiO and the perovskite structure (SrFeO₃₋ₓ), SrCO₃ was detected.

The perovskite structure peaks, SrFeO₃₋ₓ, in NSFO2 shifted towards lower angle (e.g. the peaks between 65° and 80° shifted towards left by ~ 0.1°). On the other hand, the NiO peaks in NSFO2 shifted towards higher angle by 0.1°. In combination with the fact that SrCO₃ phase was also detected, it suggests some Sr segregated from the perovskite structure, indicating the segregation of Fe from SrFeO₃₋ₓ. The segregated Fe might have diffused into the NiO crystal structure, leading to a shift of NiO (probably resulting in <$Ni, Fe, O$>, compounds containing Ni, Fe, and O, where the main crystal structure is still governed by NiO). The deactivation of NSFO2 might be very likely due to this segregation. To further investigate this, NSFO2 was calcined at 1273 K for 6 h, which was intended to regenerate perovskite from the segregated SrCO₃ and possibly segregated Fe. The re-calcined particles, denoted as NSFO3, was also tested for H₂ production at 773 K from CH₄. However, similar results to those of NSFO2 were obtained. The XRD spectra of NSFO3 was also presented in Fig. 7-11. In NSFO3, apart from the shifted perovskite phase and shifted NiO phase, peaks of SrO were observed, whereas the SrCO₃ disappeared. This implies that the segregation of Sr and probably Fe from NiO/SrFeO₃₋ₓ cannot be easily recovered.
Figure 7-13 Plasma-assisted cracking/partial oxidation of CH₄ at 773 K in the bed of regenerated NiO/SrFeO₃ (NSFO2).

7.5 Conclusions

Preliminary study of H₂ production from a SrFeO₃-d-packed DBD reactor at temperatures from 293 to 773 K was carried out in this chapter, and the main results are:

(a) The intensity of plasma-generated excited species in pure Ar was significantly higher than that in the mixed gas of CH₄ and Ar.

(b) To achieve similar level of CH₄ conversion (without the chemical interaction with the solid beds), the plasma and thermal energy input were compared. It was found that plasma input \((i.e. 123.9 \text{ J})\) was significantly lower than that of thermal input \((i.e. 2346 \text{ J})\), suggesting plasma catalysis effect for the cracking of CH₄. For the effect of plasma on SrFeO₃, the plasma energy input \((i.e. 640 \text{ J})\) was comparable to thermal input \((i.e. 585 \text{ J})\), indicating a heating effect by plasma on the solids.

(c) SrFeO₃ was found to have very low yield of H₂ \((< 0.12 \text{ mole for every mole of CH₄ introduced into the system})\) at all temperatures studied. The yield of H₂ decreased with an increase in temperature \((i.e. \text{ from 0.115 at 293 K to 0.032 at 773 K})\) due to its high oxidising property. Therefore, it is not a good candidate for H₂ production in such system.
(d) NiO/SrFeO$_3$ was found effective for H$_2$ production, whilst the bed lost activity after being regenerated.

8 H$_2$ production from partial oxidation of CH$_4$ by Fe$_2$O$_3$-supported Ni-based catalysts in a plasma-assisted packed bed reactor

8.1 Introduction
SrFeO$_3$ and NiO/SrFeO$_3$ proved over-oxidising for hydrogen production, when used in the DBD reactor for chemical looping H$_2$ production. In the current chapter, a conventional and less oxidative oxygen carrier, Fe$_2$O$_3$, is studied as the support, and NiO was doped onto Fe$_2$O$_3$ to hopefully promote the production of H$_2$, with the DBD reactor operated at 673 K.

8.2 Experimental methods and data analysis
8.2.1 Experiments
Two Fe$_2$O$_3$-supported catalysts were prepared: NiO/Fe$_2$O$_3$ and NiFe$_2$O$_4$/Fe$_2$O$_3$, where NiFe$_2$O$_4$ is the stable equilibrium phase to be formed in a Ni-Fe-O system under the experimental conditions. Pure Fe$_2$O$_3$ was also studied for comparison. Fe$_2$O$_3$ particles were prepared from iron oxide powders, followed by calcination. The Ni-based Fe$_2$O$_3$-supported materials were then prepared by dry-impregnating with Nickel nitrate hexahydrate onto the Fe$_2$O$_3$. NiO/Fe$_2$O$_3$ was first obtained by calcination at 823 K for 5 h, and to obtain NiFe$_2$O$_4$/Fe$_2$O$_3$, further calcination of NiO/Fe$_2$O$_3$ in air at 1123 K was required. As a control, materials were also prepared with Al$_2$O$_3$ instead of Fe$_2$O$_3$, giving Ni/Al$_2$O$_3$ and NiO/Al$_2$O$_3$. The detailed preparation procedures for the materials were described in 2.2.2. The experiments were carried out in the same set-up as that in Chapters 6 and 7, which was illustrated in 2.3.4. The gas stream entered the DBD reactor from the bottom at a flow rate of 0.75 L/min. The product gas was sampled at 0.5 L/min. For a typical experiment, the reactor was heated to 673 K in flowing air, followed by Ar to purge the system before the start of the experiment. During an experiment, a stream of CH$_4$ was mixed with Ar to give 8.5% ± 0.5% CH$_4$. After the mixed gas flow stabilised, the plasma was applied. For each experiment, the plasma discharge period was about 5.6 ± 0.5 min. After CH$_4$/Ar plasma discharge, the gas was switched to air to burn off any deposited carbon as well as re-oxidise the bed materials. Plasma discharge was later introduced to assist the process of de-coking and re-oxidation. The reduction-oxidation cycle was
repeated 2 more times. Ac power (primary) supplied to the DBD reactor was with a voltage of $10.5 \pm 1.0$ kV and frequency $26.0 \pm 3.0$ kHz. The dissipated plasma power (determined by Q-V Lissajous plot) was controlled at $7.2 \pm 0.7$ W.

### 8.2.2 Data analysis

Similar to the results shown in Chapter 7 that the main gaseous products observed were H$_2$, CO, CO$_2$, and traces of C$_2$H$_4$, and C$_2$H$_2$ (< 150 ppm). The study mainly focuses on parameters including averaged conversion of CH$_4$, selectivity and yield for different products, and material balances, where the equations for obtaining the values were presented in 7.3.4. Due to the low amounts of C$_2$H$_4$ and C$_2$H$_2$, the selectivity for the two were out of the interest here.

### 8.3 Results

#### 8.3.1 The results of Al$_2$O$_3$ and Fe$_2$O$_3$

The results of plasma-assisted cracking or/and partial oxidation of CH$_4$ in undoped Al$_2$O$_3$ and Fe$_2$O$_3$ beds are presented in Fig. 8-1. For both materials, CH$_4$ conversion was only observed when plasma discharge was applied. H$_2$ was found to be the main product and its generation over the discharge period in $8.5\% \pm 0.5\%$ CH$_4$ was relatively uniform. CO and CO$_2$ were observed only at trace levels (< 250 ppm). This suggests that H$_2$ was primarily generated from CH$_4$ cracking by the plasma, and the carbon from the converted CH$_4$ became the solid phase. This agrees with the fact that the ratio of generated H$_2$ to converted CH$_4$ was $1.7 \pm 0.1$ (based on three cycles) for both materials. Taking into account the C$_2$H$_4$ and C$_2$H$_2$ generated during discharge period (at ppm levels), over 80% hydrogen balance was obtained for both materials (refer to Table 8-1). The conversion of CH$_4$, as well as the generation of H$_2$, in the Al$_2$O$_3$ and Fe$_2$O$_3$ beds were similar, suggesting that neither material is a good catalyst for CH$_4$ cracking. In the air regeneration (and plasma discharge) period, trace levels (< 100 ppm) of CO and CO$_2$ were observed, suggesting the presence of deposited carbon from the cracking process in the bed. However, the deposited carbon could not be removed completely at such low temperatures even with the assistance of plasma discharge. Further regeneration of the bed was carried out by raising the temperature of the reactor to 823 K for over 30 min until no CO and CO$_2$ were detected.
8.3.2 The results of NiO/Al₂O₃, Ni/Al₂O₃, NiO/Fe₂O₃, and NiFe₂O₄/Fe₂O₃

The results for Ni-doped Al₂O₃ and Fe₂O₃-supported materials are presented in Fig. 8-2. CH₄ conversion in the NiO/Al₂O₃ bed, as shown in Fig. 8-2a, is similar to those in the Al₂O₃ and Fe₂O₃ beds, suggesting that this material also has little effect on CH₄ reforming or partial oxidation. For Ni/Al₂O₃ as seen in Fig. 8-2b, a significant rise in [H₂] was observed when CH₄ was introduced into the reactor, without plasma. This was mainly due to the catalytic effect of Ni, as reported in Ref. [219]. However, the catalytic effect did not last long and the H₂ level dropped and gradually reached a mole fraction of 0.01, whilst in the meantime, no significant production of CO and CO₂ was observed. This suggests that the presence of Ni mainly improved the cracking of CH₄ to H₂ and solid carbon, and the deactivation of Ni was likely due to the formed carbon. In addition, the formation of some nickel aluminate, which can be confirmed by post-reaction XRD results shown in Fig. 8-3, could also contribute to this deactivation. When plasma discharge was applied from \( t = 9.5 \) to \( t = 15.6 \) min, higher degrees of CH₄ conversion and H₂ production were achieved. At \( t = 22.0 \) min, CH₄ was stopped, leaving the bed purging in Ar. Then, as soon as the gas was switched from Ar to air, a significant CO₂ peak together with a small CO peak was observed and an overall carbon balance of 94% was obtained.
Figure 8-2 Plasma-assisted cracking/partial oxidation of CH₄ at 673 K with DBD reactor packed with (a) NiO/Al₂O₃; (b) Ni/Al₂O₃; (c) NiFe₂O₄/Fe₂O₃; (d) NiO/Fe₂O₃.

Figure 8-3 XRD spectra of CH₄/Ar plasma treated NiO/γ-Al₂O₃. Material was only reduced in 8.5% CH₄ plasma, and not regenerated with air (and plasma). The collection codes of the reference patterns from ICSD were presented in Table 8-2.

When the reactor was loaded with NiFe₂O₄/Fe₂O₃, according to Fig. 8-2c, no significant conversion of CH₄ was seen without plasma discharge. At t = 6.8 min, when plasma was
introduced, much improved generation of H₂ over the whole discharge period was observed; at the same time, there was a clear production of CO and CO₂, indicating that the reduction of the bed material, NiFe₂O₄/Fe₂O₃, occurred as it was the only source of oxygen in the system. The overall result was a partial oxidation of CH₄ by plasma discharge to H₂-rich gas that contains some CO and CO₂. When plasma discharge was stopped, H₂ was still produced from the NiFe₂O₄/Fe₂O₃ bed, though at lower levels. The fact that NiFe₂O₄ was not reactive for H₂ production before plasma discharge but was after, suggests the generation of some additional phase other than NiFe₂O₄ during plasma discharge, with this (probably reduced) phase having a catalytic effect even without plasma. In the air regeneration stage, CO₂ was only observed when plasma was applied.

In the NiO/Fe₂O₃ bed, according to Fig. 8-2d, no conversion of CH₄ was observed until the plasma was applied, at which point a significant amount of H₂ was generated. The CO and CO₂ productions were also much higher than those from other beds during plasma discharge. CH₄ conversion reached 32% in this case. Similar to the case in the NiFe₂O₄/Fe₂O₃ bed, when plasma was switched off, there was still post-plasma H₂ production. Most of the deposited carbon was recovered in air, without the presence of plasma.

Table 8-1 Summarised results in different bed materials (errors show the range of three repeats)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Al₂O₃</th>
<th>NiO/Al₂O₃</th>
<th>Ni/Al₂O₃</th>
<th>Fe₂O₃</th>
<th>NiO/Fe₂O₃</th>
<th>NiFe₂O₄/Fe₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>d_c</td>
<td>0.75 ± 0.04</td>
<td>0.75 ± 0.03</td>
<td>0.90 ± 0.07</td>
<td>0.71 ± 0.05</td>
<td>0.15 ± 0.03</td>
<td>0.47 ± 0.08</td>
</tr>
<tr>
<td>C balance</td>
<td>0.26 ± 0.02</td>
<td>0.25 ± 0.02</td>
<td>0.94 ± 0.02</td>
<td>0.38 ± 0.02</td>
<td>0.94 ± 0.03</td>
<td>0.63 ± 0.04</td>
</tr>
<tr>
<td>H balance</td>
<td>0.93 ± 0.04</td>
<td>0.94 ± 0.03</td>
<td>0.96 ± 0.04</td>
<td>0.82 ± 0.02</td>
<td>0.82 ± 0.03</td>
<td>0.99 ± 0.06</td>
</tr>
<tr>
<td>X_Cu₄</td>
<td>0.05 ± 0.01</td>
<td>0.05 ± 0.01</td>
<td>0.10 ± 0.02</td>
<td>0.04 ± 0.01</td>
<td>0.39 ± 0.07</td>
<td>0.19 ± 0.04</td>
</tr>
<tr>
<td>S_co</td>
<td>0.01 ± 0.01</td>
<td>0.01 ± 0.01</td>
<td>0.03 ± 0.01</td>
<td>0.01 ± 0.01</td>
<td>0.12 ± 0.01</td>
<td>0.25 ± 0.01</td>
</tr>
<tr>
<td>S_co₂</td>
<td>0.03 ± 0.01</td>
<td>0.06 ± 0.01</td>
<td>0.02 ± 0.01</td>
<td>0.08 ± 0.01</td>
<td>0.71 ± 0.02</td>
<td>0.27 ± 0.02</td>
</tr>
<tr>
<td>S_H₂</td>
<td>0.84 ± 0.01</td>
<td>0.85 ± 0.01</td>
<td>0.95 ± 0.01</td>
<td>0.74 ± 0.01</td>
<td>0.92 ± 0.01</td>
<td>0.98 ± 0.07</td>
</tr>
<tr>
<td>Y_co×10⁴</td>
<td>0.3 ± 0.1</td>
<td>0.3 ± 0.1</td>
<td>0.3 ± 0.1</td>
<td>0.2 ± 0.1</td>
<td>45.2 ± 4.9</td>
<td>38.4 ± 5.2</td>
</tr>
<tr>
<td>Y_co₂×10⁴</td>
<td>1.2 ± 0.3</td>
<td>2.7 ± 0.5</td>
<td>2.2 ± 0.6</td>
<td>3.2 ± 0.7</td>
<td>285.5 ± 15.1</td>
<td>45.4 ± 3.1</td>
</tr>
<tr>
<td>Y_H₂×10⁴</td>
<td>64.7 ± 1.4</td>
<td>81.3 ± 1.2</td>
<td>180.6 ± 11.2</td>
<td>58.9 ± 1.1</td>
<td>621.7 ± 32.3</td>
<td>319.0 ± 40.2</td>
</tr>
</tbody>
</table>

Table 8-1 presents the summarised results of degree of carbon deposition d_c (defined as in 7.3.4), conversion of CH₄, selectivity and yield for products, carbon and hydrogen balances. It should be noted that the results here show three redox looping
cycles of each material, starting from the fresh samples. No mechanical deterioration was observed for any of the tested materials in the repeated cycles. Overall, NiO/Fe₂O₃ seems to be the most promising material for H₂ production due to its low degree of carbon deposition, high carbon and hydrogen balances, and high selectivity and yield for H₂. The hydrogen balance in the case of NiO/Fe₂O₃ was slightly lower than those in other Ni-doped materials. This suggests that some H-containing products other than H₂ might have been generated, probably H₂O. NiFe₂O₄/Fe₂O₃ also exhibited very high selectivity towards the production of H₂, although its resistance to coking, carbon balance and the conversion of CH₄ were not as good as those of NiO/Fe₂O₃.

8.3.3 XRD characterization of NiO/Fe₂O₃ and NiFe₂O₄/Fe₂O₃.
Based on 8.3.1 and 8.3.2, NiO/Fe₂O₃ and NiFe₂O₄/Fe₂O₃ show promising properties for hydrogen production. The evaluation of any possible change in the material structure after the plasma-assisted CH₄ conversion was carried out. The samples of NiO/Fe₂O₃ and NiFe₂O₄/Fe₂O₃ in different stages were collected for XRD scanning. The phases in the samples were identified using the reference patterns from ICSD database, as shown in Table 8-2.

<table>
<thead>
<tr>
<th>Component</th>
<th>Fe₂O₃</th>
<th>Fe₃O₄</th>
<th>NiO</th>
<th>Ni</th>
<th>NiFe₂O₄</th>
<th>(Ni, Fe)</th>
<th>NiAl₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Collection Code from ICSD</td>
<td>15840</td>
<td>30860</td>
<td>9866</td>
<td>260169</td>
<td>40040</td>
<td>56386</td>
<td>9556</td>
</tr>
</tbody>
</table>

- NiO/Fe₂O₃.
Figure 8-4 shows the XRD patterns of NiO/Fe₂O₃ samples: freshly prepared, with CH₄/Ar plasma treatment and after regeneration in air plasma. Major peaks of each phase and an unknown peak (2θ = 26.7) are marked accordingly. For the freshly calcined NiO/Fe₂O₃, only patterns of NiO and Fe₂O₃ were detected. This suggests no chemical interaction between NiO and Fe₂O₃ during the initial preparation of NiO/Fe₂O₃. After CH₄/Ar plasma treatment, NiO was no longer detected; instead, other peaks, which were assigned with the patterns of metallic Ni and magnetite, Fe₃O₄, were detected. For the air regenerated NiO/Fe₂O₃, similar to the fresh sample, NiO and Fe₂O₃ were the only phases detected, suggesting that the NiO phase can remain separate during plasma discharge in air.
Figure 8-4 XRD spectra of fresh NiO/Fe\textsubscript{2}O\textsubscript{3}, CH/Ar plasma treated NiO/Fe\textsubscript{2}O\textsubscript{3} and air plasma regenerated NiO/Fe\textsubscript{2}O\textsubscript{3}.

- NiFe\textsubscript{2}O\textsubscript{4}/Fe\textsubscript{2}O\textsubscript{3}

XRD results of NiFe\textsubscript{2}O\textsubscript{4}/Fe\textsubscript{2}O\textsubscript{3} samples are presented in Fig. 8-5. Fe\textsubscript{2}O\textsubscript{3} and NiFe\textsubscript{2}O\textsubscript{4} phases were observed in the fresh sample. The formation of NiFe\textsubscript{2}O\textsubscript{4} indicates the diffusion of NiO into the Fe\textsubscript{2}O\textsubscript{3} crystal structure during calcination. In the XRD pattern of the CH/Ar plasma treated NiFe\textsubscript{2}O\textsubscript{4}/Fe\textsubscript{2}O\textsubscript{3}, there was a decrease in the intensity of the peaks for the NiFe\textsubscript{2}O\textsubscript{4} phase; additionally, peaks assigned with metallic alloy of Ni-Fe, expresses as (Ni, Fe), were observed. There was no clear evidence of the presence of Fe\textsubscript{2}O\textsubscript{4}, suggesting that the oxygen in the produced CO and CO\textsubscript{2} in the CH/Ar discharge period probably came from the reduction of NiFe\textsubscript{2}O\textsubscript{4} to the metallic (Ni, Fe). In the air regeneration stage, the (Ni, Fe) phase disappeared, but the intensity of NiFe\textsubscript{2}O\textsubscript{4} peaks did not return to the higher level as seen in the fresh NiFe\textsubscript{2}O\textsubscript{4}/Fe\textsubscript{2}O\textsubscript{3} sample.
Figure 8-5 XRD spectra of fresh NiFe₂O₄/Fe₂O₃, CH/Ar plasma treated NiFe₂O₄/Fe₂O₃, and air plasma regenerated NiFe₂O₄/Fe₂O₃.
8.4 Discussion

8.4.1 Catalytic effect

As shown in Figs. 8-1 and 8-2, NiO (when supported on inert Al₂O₃) and Fe₂O₃ alone did not show good catalytic activity for the conversion of CH₄, even in the presence of the plasma discharge. However, the combination of NiO and Fe₂O₃, which resulted in NiO/Fe₂O₃ or NiFe₂O₄/Fe₂O₃, demonstrated significantly improved performance in the plasma, especially for NiO/Fe₂O₃. The catalytic mechanism is attempted to understand as follow.

- **NiO/Fe₂O₃**

The results in Fig. 8-4 show the formation of Ni when NiO/Fe₂O₃ was subjected to CH₄/Ar plasma discharge. Unlike Ni/Al₂O₃ experiment (in Fig. 8-2b), with which the production of H₂ was high at the very beginning of the plasma discharge but decreased quickly, the bed of NiO/Fe₂O₃ was able to produce significant amounts of H₂ over the entire plasma discharge period. The superior performance of NiO/Fe₂O₃ might result from lattice oxygen source in NiO/Fe₂O₃, which seems to suppress the coking of the solid bed, so that the catalytic activity of Ni can be maintained. This is supported by the smaller amount of carbon deposited in the NiO/Fe₂O₃ bed. Owing to the presence of Fe₂O₃, it was difficult to determine if NiO was still present in the plasma treated reduced NiO/Fe₂O₃ sample from the XRD (NiO peaks overlap with those from Fe₂O₃). However, calculation of the oxygen balances would give some indication of the presence of NiO phase. It was found that the amount of oxygen in the produced CO, CO₂, and H₂O (estimated from the hydrogen balance) during CH₄/Ar plasma discharge period accounted for 3.2 wt.% ± 0.2 wt.% of the total mass of NiO/Fe₂O₃. The NiO oxygen capacity (NiO → Ni) in the fresh material was 2.0 wt%, whilst the amount of oxygen from Fe₂O₃ → Fe₃O₄ was 3.0 wt%. As most of the hematite was reduced (only low intensity of Fe₂O₃ peaks were detected), it is possible that some NiO might be still in the sample after being treated with CH₄/Ar plasma discharge.

Interestingly, the NiFe₂O₄ phase was not observed in the XRD patterns of the NiO/Fe₂O₃ (refer to Fig. 8-4), suggesting little interaction between NiO and Fe₂O₃, either during calcination or plasma treatment. The fact that NiO alone is inactive during plasma discharge, suggests the presence of some available oxygen in the NiO/Fe₂O₃ to suppress
coking. One of the two hypothesis might describe these conditions: 1) NiO itself is responsible for the partial oxidation of CH, via NiO + CH → CO + CO₂ + H₂ + Ni, and Fe₂O₃ helps the process to continue by transporting oxygen to the Ni sites; 2) metallic Ni is responsible for the catalytic effect of the generation of H₂ via CH₄ → C + H₂, and the presence of Fe₂O₃ helps to remove the solid carbon from the Ni sites. The carbon formed in 2) is not necessarily solid carbon, it can also be some transient carbon that has not deposited. An illustration of the two hypothesis is shown in Fig. 8-6. In hypothesis 2, Ni is believed to be generated as soon as the system is subjected to plasma discharge, and triple-phase intimate contact (CH₄, Ni, and the incoming oxygen to Ni site) in crucial.

![Hypothesis 1](image1)

![Hypothesis 2](image2)

Figure 8-6 Graphic presentation of the two hypothesis accounting for the catalytic effect of H₂ production in NiO/Fe₂O₃.

The results obtained in this study indicate that hypothesis 2 seems to dominate. This is because (1) the H₂ production rate in the NiO/Fe₂O₃ bed was comparable to that when Ni/Al₂O₃ was just exposed to 8.5% CH₄/Ar (i.e. the initial H₂ peak); (2) SEM/EDX analysis of NiO/Fe₂O₃ particles (as shown in Fig. 8-7 and Table 8-3), where the particles was collected after CH₄/Ar plasma-assisted reduction (no air regeneration), showed that the surface of NiO/Fe₂O₃ particles was predominantly covered by Ni; (3) the trace amounts
of CO and CO₂ produced from NiO/Al₂O₃ subjected to CH₄/Ar plasma discharge were similar to those from Al₂O₃ and Fe₃O₄ beds, showing that NiO in the absence of Fe₃O₄ cokes easily, or does not react with CH₄.

Figure 8-7 SEM micrograph combined with EDX analysis of NiO/Fe₃O₄ particle surface after experiment in the DBD reactor. The quantitative results from the EDX analysis are presented in Table 8-3.

Table 8-3 Results from the EDX analysis of NiO/Fe₃O₄ particle surface after experiment in the DBD reactor.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight in wt%</th>
<th>σ in wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>6.59</td>
<td>0.06</td>
</tr>
<tr>
<td>O</td>
<td>10.84</td>
<td>0.03</td>
</tr>
<tr>
<td>Fe</td>
<td>20.28</td>
<td>0.05</td>
</tr>
<tr>
<td>Ni</td>
<td>62.20</td>
<td>0.07</td>
</tr>
</tbody>
</table>
Due to the relative inertness between NiO and FeO, it is reasonable to identify the sequence of phase transformation of NiO/FeO in the CH4 reducing environment by referring to the Ni-O and Fe-O phase diagrams, as shown in Figs. 8-8 and 8-9, where the diagrams were computed by MTDATA [139]. Thermodynamically, at 673 K, the partial pressure of O₂, \( P_{O_2} \), to cause a phase transition from NiO to Ni is lower than that for FeO to FeO₂, but higher than that for FeO₂ to Fe. This means that assuming negligible solubility of NiO into the FeO system, the sequence for reduction would be: FeO + NiO → NiO + FeO₂ → Ni + FeO₂. Therefore, thermodynamically, in a reducing environment, it is expected that if Ni was detected, FeO₂ would then also be present. However, at the relatively mild temperatures in this study, reaction kinetics are important and FeO₂ is unreactive towards CH₄. A high level of H₂ production in NiO/FeO was observed as soon as the plasma discharge was applied. If the catalytic effect for H₂ production was only due to the presence of metallic Ni, then the formation of Ni must have happened as soon as NiO/FeO was subjected to plasma discharge. This contrasts with the pure NiO/Al₂O₃ material, which could also have reduced to Ni locally, but for some reason remained inactive. Such a different behaviour of NiO/Al₂O₃ might have been caused by coking, where carbon immediately deposited on any newly created Ni-metallic site. Additionally, the formation of nickel aluminate after plasma treatment also means that less Ni is available for CH₄ cracking. If Ni immediately formed when plasma was applied in the NiO/FeO bed, the suppression of coking was most likely due to the presence of an oxygen source, i.e. FeO₂. The co-existence of Ni and FeO₂ is thermodynamically unstable, and the system tends to form NiO and FeO₂ at equilibrium. The transfer of oxygen to the Ni sites would then help remove any deposited carbon or prevent transiently formed absorbed carbon species from forming coke, and thus maintaining the catalytic activity of Ni. For NiO/FeO, not only was less coke formed, the remaining coke was also more easily burned off during the air regeneration stage, compared with other materials e.g. NiO/Al₂O₃ and FeO₂. The superior performance of the NiO/FeO for H₂ production and its easy regeneration demonstrate the proposed concept of having plasma-assisted chemical looping system for H₂ production at mild temperatures.
• NiFe₂O₄/FeO₃

In Fig. 8-5, the observed (Ni, Fe) phase together with the decreased intensity of NiFe₂O₄ peaks in the XRD spectra in the CH₄/Ar plasma treated sample, indicates the phase segregation of NiFe₂O₄ to (Ni,Fe). This seems to be consistent with study carried out by Raghavan [220]. At 1273 K and low \( P_{O_2} \) (\( P_{O_2} < 10^{-11} \) bar), NiFe₂O₄ tends to reach equilibrium with (Ni, Fe)O, and (Ni, Fe). Extrapolating to the low temperatures used
here, it is reasonable to expect that the reduction follows NiFe$_2$O$_4$ $\rightarrow$ (Ni, Fe)$_3$O$_4$ + (Ni, Fe). In our study, when the NiFe$_2$O$_4$ material was regenerated in air plasma at 673 K, the (Ni, Fe) peaks disappeared (refer to Fig. 8-5). The most likely route for the oxidation of Ni is to create NiO. However, the presence of NiO was difficult to confirm, due to significant overlap of the NiO and NiFe$_2$O$_4$ peaks in the XRD pattern. For Fe, no evidence of wustite or magnetite phase was observed. The most likely route would then be Fe $\rightarrow$ Fe$_2$O$_3$. In terms of the catalytic effect in the NiFe$_2$O$_4$ bed, it was found that the H$_2$ yield improved slightly in the second and third reduction cycles, especially in the initial plasma discharge period, as presented in Fig. 8-10. If NiO was indeed created in the regeneration stage, then it could have helped with the production of H$_2$ in subsequent reductions.

![Figure 8-10 H$_2$ concentration measured during three subsequent CH$_4$/Ar plasma discharge experiments, using NiFe$_2$O$_4$/Fe$_2$O$_3$ as the bed material.](image)

8.4.2 Comparison to water gas shift equilibrium

In the bed of NiO/Fe$_2$O$_3$, the products from CH$_4$/Ar plasma discharge were mainly H$_2$ and CO$_2$. A high yield of H$_2$ and CO$_2$ at such low temperature (673 K) could be linked with the water-gas shift reaction (WGSR: H$_2$O + CO $\rightarrow$ H$_2$ + CO$_2$). Assuming that water was also produced in the NiO/Fe$_2$O$_3$ bed (which would also account for the discrepancy in the hydrogen balance, Table 1), then the reaction quotient $\frac{[H_2][CO_2]}{[H_2O][CO]} = 64.6 \pm 19.1$, can be compared with the equilibrium constant of WGRS at 673 K, $K_e = 12.0$ [221]. This
suggests that the plasma-assisted process tends to push production of H₂ and CO₂, beyond the thermodynamic equilibrium of WGSR. To achieve a $K_e$, close to the reaction quotient achieved here, the conventional WGSR would need to operate at a much lower temperature, where slow reaction kinetics may be problematic (though it should be noted that excess water is usually used to shift the equilibrium). The fact that such high production of H₂ and CO₂ was achieved within such a small bed (~ 7.5 ml) and at a low temperature indicates very fast reaction rates. For the WGSR to achieve a high conversion to H₂ and maintain favourable kinetics, multiple reaction stages are often employed (e.g. moving from high to low temperatures), and thus complicating the process. Therefore, the alternative H₂ and CO₂ production method described here, offers a promising new route. The high value of $\frac{[H_2][CO_2]}{[H_2O][CO]}$ found here seems to suggest that H₂ and CO₂ might be directly produced from the partial oxidation of CH₄ by the oxygen carrier, without going through some intermediate step involving WGSR. The unusually high ratio is likely to be a result of H₂ and CO₂ not having sufficient time to reach a WGSR equilibrium.

The energy cost, $EC_a$, as described in 7.4.5, is also estimated here, to compare with H₂ production with those in SrFeO₅ and for conventional industrial processes. The results are presented in Table 8-4. Compared to the SrFeO₅ bed (refer to Table 7-4), the energy cost in NiO/Fe₂O₃ and NiFe₂O₄/Fe₂O₃ beds is significantly decreased. More excitingly, the current values are in the same magnitude with the industrial water electrolysis (from 320 to 510 MJ/kg). Given that the current experimental set-up can be further modified to improve the H₂ production such as varying the dimension of the plasma region, changing the flow rate and etc., the results exhibit its promising application in the industry of H₂ production.

Table 8-4 The energy cost, $EC_a$ for H₂ production in NiO/Fe₂O₃ and NiFe₂O₄/Fe₂O₃ (note: the error bar show the range of three repetitions), and in comparison to that from water electrolysis.

<table>
<thead>
<tr>
<th>NiO/Fe₂O₃ (MJ/kg)</th>
<th>NiFe₂O₄/Fe₂O₃ (MJ/kg)</th>
<th>Water electrolysis (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>440 ± 20</td>
<td>550 ± 40</td>
<td>320 - 510</td>
</tr>
</tbody>
</table>
8.4.3 Discussion of the H$_2$ production in Fe,O$_x$-based and SrFeO$_{3\delta}$-based materials in the plasma-assisted chemical looping system

- The catalytic effect in NiO/SrFeO$_{3\delta}$

In NiO/Fe,O$_x$, the catalytic effect was considered due to hypothesis 2, i.e. the instantly generated Ni subjected to plasma discharge is responsible for the high generation of H$_2$. In the SrFeO$_{3\delta}$-based system, as studied in Chapter 7, SrFeO$_{3\delta}$ itself did not promote the production of H$_2$; on the contrary, it directly combusted the H$_2$ generated (from direct CH$_4$ cracking by plasma catalysis). The addition of NiO seems significant improved the generation of H$_2$ in the first reduction. It seems that hypothesis 2 can also explain what have happened to the NiO/SrFeO$_{3\delta}$ system for H$_2$ production. The general idea is that for this plasma-assisted chemical looping H$_2$ production at low temperatures to work, an oxygen donor and a catalyst that promotes H$_2$ production, need both to be present. On the other hand, it was found that only the freshly prepared NiO/SrFeO$_{3\delta}$, NSFO1, was active for H$_2$ production. Based on the change in the XRD patterns in the re-used material, NSFO2, as shown in Fig. 7-11, the decreased activity of NSFO2 might have resulted from the segregation of the material and the possibly segregated Fe could have deactivated NiO. This can be further supported by that the results in a bed of NSFO2 (Fig.7-13) are very similar to those in SrFeO$_{3\delta}$ (Fig.7-10).

- Comparison between NiO/Fe,O$_x$ and NiO/SrFeO$_{3\delta}$

Regardless of the fact that NiO/SrFeO$_{3\delta}$ was only active for one cycle, understanding of H$_2$ production in the both NiO/SrFeO$_{3\delta}$ and NiO/Fe,O$_x$ would provide important information of the selection of proper materials for the plasma-assisted chemical looping system for H$_2$ production. This is because Fe,O$_x$ and SrFeO$_{3\delta}$ are two typical examples of showing how oxygen carriers with very different activity would react in such a system.

Though hypothesis 2 can be used to explain high yield of H$_2$ for both NiO/SrFeO$_{3\delta}$ and NiO/Fe,O$_x$, as shown in Figs. 7-12 and 8-2d, they behaved very differently when subjected to plasma discharge. In NiO/SrFeO$_{3\delta}$, a large amount of CO$_2$ was produced in the initial period of plasma discharge, and the catalytic effect of metallic Ni on H$_2$ production seems to be inhibited. H$_2$, together with some CO$_2$, was only observed when CO$_2$ was no longer generated, and this seems to be the stage that metallic Ni started to influence. The results
suggest that for NiO/SrFeO$_{3-d}$, in the initial period, the apparent reduction of NiO was not possible due to fast oxygen decoupling rate of SrFeO$_{3-d}$. Even if there was reduction of NiO to metallic Ni phase, the generated Ni can be quickly surrounded by the lattice oxygen from SrFeO$_{3-d}$, or the gaseous oxygen released from SrFeO$_{3-d}$ (due to high chemical potential of oxygen). The rate of CH$_4$ cracking for H$_2$ production over the catalytic Ni sites could have been much slower than the oxygen decoupling rate of SrFeO$_{3-d}$, and thus the oxidation rate of Ni (to NiO). Only when SrFeO$_{3-d}$ has been reduced to a state with lower chemical potential of oxygen, or/and lower oxygen decoupling rate, the presence of metallic Ni could be stable and exhibited its catalytic effect for H$_2$ production. As seen in Fig. 7-12d, after the initial period, [CO$_2$] dropped, CO and H$_2$ were significantly produced simultaneously, and this is where oxygen decoupling from SrFeO$_{3-d}$ became the rate-limiting step for the overall reaction.

In a NiO/FeO$_2$ bed, according to Fig.8-2d, H$_2$ was immediately generated when plasma was applied to the DBD reactor. In the meantime, some CO and CO were simultaneously generated. Based on hypothesis 2, NiO was immediately reduced to metallic Ni and promoted the H$_2$ production. This means that the oxygen decoupling rate, or the rate of oxygen transfer to the reduced Ni sites was just sufficient to suppress coking onto the Ni sites but not too fast to re-oxidise the Ni. The whole system seems to be in a perfect equilibrium of removal of any solid or transient carbon, and the transfer of lattice oxygen to the Ni sites, so that Ni can always be catalytic active.

The performance of NiO/FeO$_2$ in the DBD reactor is stable for at least three looping cycles; whilst in the bed of NiO/SrFeO$_{3-d}$, it was only active in the fresh cycle. A holistic understanding of the deactivation needs further investigation. But the important message from the investigation of doping Ni/NiO onto the SrFeO$_{3-d}$ is that though the freshly prepared NiO/SrFeO$_{3-d}$ is promising for H$_2$ production, it has poor cyclability and thus not applicable in such system.

To summarise, a suitable chemical looping material for H$_2$ production in such as DBD reactor should meet the following requirements:

1) Contain a catalytic material for production or promotion of H$_2$ production.
2) Contain an oxygen source to remove coke and keep the catalytic active. More importantly, the oxygen carrier should not be too active.

3) Have good looping performance.

Theoretically, this idea would work for other systems that employing catalysts and oxygen carriers for fuel synthesis or production, depending on the product of interest.

8.5 Conclusions

The main novelty of this work is to convert a CH₄ stream to H₂-rich gas at a low temperature (673 K), without the addition of gaseous oxygen (which comes from the chemical loop here). In addition, this process can work without any steam input. For Ni-doped Fe₂O₃-based looping materials for H₂ production, the results obtained are:

(a) The active nature of the supporting metal oxide, Fe₂O₃, positively influences the activity of the catalyst. Among the tested materials, NiO/Fe₂O₃ exhibited the best performance, resulting in the highest H₂ yield, whilst carbon deposition and the subsequent catalyst deactivation were significantly lower than those from NiO or Ni supported on alumina.

(b) The catalytic activity for H₂ production in the combined catalyst/oxygen carrier (NiO/Fe₂O₃) was attributed to the generation of metallic Ni, and the suppression of carbon deposition was connected to the presence of the active metal oxide, Fe₂O₃. The plasma-assisted CH₄ reforming and oxidation by the oxygen carrier significantly exceeded the theoretically expected performance if the water-gas shift equilibrium were applied.

(c) The energy cost estimated was found comparable to industrial water electrolysis, for instance, 440 +/- 20 MJ/kg of hydrogen in a NiO/Fe₂O₃ bed, compared to 320 - 510 MJ/kg for water electrolysis.

A comparison of SrFeO₃-based (studied in Chapter 7) and Fe₂O₃-based materials for H₂ production were carried out. It was found that oxygen carrier only with appropriate oxygen donating activity (not too active) works best for keeping the catalytic site active.


9.0 Conclusion

The dissertation was mainly concerned with investigating the effect of oxygen carriers on the conversion of fuels, for various processes including combustion of solid fuels (Polish coal-derived char and wood chips) as presented in Chapters 3 and 5, and hydrogen production from CH₄ in Chapters 6, 7 and 8.

In Chapter 3, to achieve effective overall combustion of Polish coal-derived char by Fe₂O₃ and ZrO₂-supported Fe₂O₃ in a fluidised bed from 1123 to 1248 K, gasification of Polish char by CO was carried out in situ, prior to the combustion by the oxygen carriers. Before investigating the interaction between oxygen carriers and the gasification products, the gasification of Polish char was studied first. Comparing the measured experimental gasification rate and the estimated external mass transfer rate, the gasification was believed to be free of external mass transfer limitation. The activation energy values, based on the Arrhenius plot, were found to be 196 to 216 kJ mol⁻¹, suggesting a kinetically controlled regime for gasification. The replacement of the fluidising bed from inert silica sand to Fe₂O₃ particles initiated the combustion of the CO produced from gasification, to CO₂. Whilst Fe₂O₃ did not affect the gasification step, and this is mostly because the gasification was not affected by external mass transfer. The effect of ZrO₂-supported Fe₂O₃, however, significantly decreased the measured apparent rate of gasification. By comparing the reduction of ZrO₂-supported Fe₂O₃ and Fe₂O₃ in 10% CO, it was found that the reduction reactivity of ZrO₂-supported Fe₂O₃ with CO was higher, implying less likelihood of an inhibition effect from this step. Results with ZrO₂ as the fluidising bed for gasification exhibited much lower measured gasification rate, indicating that the inhibition effect of ZrO₂-supported Fe₂O₃ mainly came from ZrO₂. It is suspected that the inhibition is due to the interaction between CO and ZrO₂, whilst this requires future work to be conducted.

In chapter 4, a numerical model based on Ergun’s two step mechanism was developed to describe the gasification of a Polish char particle. Using the kinetic data obtained from CO gasification of the char, with CO concentration varying from 0% to 100% (balance N₂), the modelled results fitted well of the experimental data. However, when CO was intentionally introduced into the system, the model did not give a good fit: the gasification rate was apparently over-estimated by the model. Two approaches were attempted to re-
fit the experimental data. In the first method, the kinetic data were re-calculated by including the experimental results of adding CO to the system. The new kinetic data showed higher inhibition effect of CO, and the re-substituted model exhibited good agreement of the experimental results at various conditions. The second approach modified the rate expression based on a three-step mechanism. The new model also amplified the effect of CO, and it described the gasification reasonably well. In summary, both the approaches showed that the inhibition effect of CO was more significant than previously expected. Referring to the modified Thiele modulus, as defined by Roberts and Satterfield [172], the added CO can suppress the rate gradient across the particle. This might be the main reason accounting for the gasification rate being more sensitive to the surface CO concentration than that locally.

Combustion of a biomass fuel, wood chips, at temperatures from 773 to 1173 K, was carried out in a fluidised bed reactor, by Fe₂O₃ and mayenite-supported CuO, respectively. The developed non-thermal plasma reactor, DBD reactor, was positioned in the downstream of the fluidised bed, for the continuous measurement of tar. It utilised the capability of the DBD reactor for cracking and converting heavy hydrocarbons into easily detectable gases (e.g. CO, CO₂), which allowed the quantification of the carbon content in the tar to be conducted. Based on the coupled system, both Fe₂O₃ and mayenite-supported CuO were effective in reducing tar in situ, and the tar was mostly converted to CO₂. Mayenite-supported CuO exhibited even higher reactivity due to its capability of releasing gaseous oxygen at temperatures above 1073 K, making it a promising candidate for the direct total combustion of biomass in the fluidised bed. The effect of the oxygen carriers on the distribution of the products from a pyrolysing environment was compared with that in the presence of CO₂. CO₂ was found to reform/gasify the biomass-derived products at temperatures above 973 K.

Oxygen carriers (SrFeO₃, Fe₂O₃, and NiO-doped SrFeO₃ and Fe₂O₃) were used to produce H₂ from CH₄ in Chapters 7 and 8. This was achieved using a plasma-assisted chemical reactor- that allowed H₂ production to occur at milder temperatures (~ 473 K) than those for conventional methane steam reforming for H₂ production. Oxygen carriers were packed in the DBD reactor in the plasma discharge zone, and enhanced the conversion of methane. The redox nature of the oxygen carriers provided the possibility of a chemical
loowing scheme for H₂ production. The electrical behaviors of the developed plasma-assisted packed bed reactor were firstly studied in Chapter 6. It was found that the dielectric constant of packing materials affected the type of the discharge: noisy and filamentary discharge dominated in the bed with lower dielectric constant (i.e. alumina sand), whilst silent and diffuse discharge occurred in the SrFeO₃δ bed with a significantly higher dielectric constant. Plasma power was observed to have the biggest influence on the conversion of CH₄; whereas the electron energy, a function of the applied voltage, also affected the conversion.

In Chapter 7, H₂ production from CH₄ was firstly investigated in a SrFeO₃δ-packed DBD reactor at temperatures from 293 to 773 K. The experiments were carried out in pure Ar and a mixed stream of CH₄ and Ar, where Ar can be treated as inert to other species in such a plasma system. The intensity of plasma-generated excited species in pure Ar was significantly higher than that in the mixed gas, due to the contamination effect of CH₄. Similarly, the presence of gaseous O₂ (released from SrFeO₃δ at high temperatures) was also found to decrease the intensity of the plasma excited species. Direct cracking of CH₄ by plasma catalysis was observed; however, the effect of plasma on SrFeO₃δ was mainly the surface heating. In general, SrFeO₃δ was not promising for H₂ production in such system due to its over-reactivity, leading to the total combustion to CO₂ and H₂O. Ni was doped onto the surface of SrFeO₃δ (resulting NiO/SrFeO₃δ). This significantly improved the yield of H₂; whilst the high reactivity towards H₂ production was observed in the fresh NiO/SrFeO₃δ bed only.

Chapter 7 suggests that less reactive oxygen carriers are more suited for plasma-assisted chemical looping H₂ production. In Chapter 8, Fe₂O₃, NiO/Fe₂O₃ and NiO/NiFe₂O₄ were investigated, and compared with those from alumina-based beds. The experiments were carried out at 673 K. Fe₂O₃, on its own, was found inert to CH₄, even with plasma discharge. In contrast, the presence of Ni stimulated the production of H₂ for both the two forms of Ni-Fe-O system. A high H₂ yield in the two beds was maintained for three chemical looping cycles. NiO/Fe₂O₃ exhibited better performance, with a higher H₂ yield and carbon balance. In an inert alumina bed, low production of H₂ and severe carbon deposition were found. The catalytic activity for H₂ production in the combined catalyst/oxygen carrier (NiO/Fe₂O₃) could be most likely attributed to the generation of metallic Ni, and the
suppression of carbon deposition was connected to the presence of the active metal oxide, FeO. The comparison between NiO/SrFeO₈ (studied in Chapter 7) and NiO/FeO₃ for H₂ production indicated that oxygen carrier only with appropriate oxygen donating activity (not too active) works best for keeping the catalytic site active and effective. The high and repeatable H₂ yield in multiple cycles in a bed of NiO/FeO₃ demonstrated the promising application of the proposed plasma system for H₂ production at mild temperatures. The estimated energy cost, 440 ± 20 MJ/kg of H₂, was also found comparable to that for water electrolysis.
10.0 Future Work

For Polish coal-derived char, the presence of ZrO$_2$-supported Fe$_2$O$_3$ was found to decrease the apparent gasification rate in a fluidised bed. The experimental results of much lower gasification rate in a bed of ZrO$_2$ than that in silica sand indicate that the ‘inhibition’ effect of ZrO$_2$-supported Fe$_2$O$_3$ on gasification mainly came from ZrO$_2$. This seems to be different from fact that ZrO$_2$ has been used as an inert support in many applications reported in literature. Further investigation on how ZrO$_2$ inhibited the gasification needs to be carried out in future. A most likely link to this might be to do with the surface of ZrO$_2$, for instance the surface interaction between ZrO$_2$ with CO, either chemically or physically.

In chapter 5, the developed tar measurement system allows an apparent rate profile of tar production to be obtained. Understanding the production of tar from the biomass over time, which is essentially the rate of devolatilisation, is of great importance for studying pyrolysis. To obtain a true tar production rate profile from the upstream, deconvolution of the system needs to be carried out further. This can be achieved by assuming a continuous stirred tank reactor coupled with a plug flow reactor.

The plasma-assisted packed bed reactor system for H$_2$ production from CH$_4$ partial oxidation by oxygen carriers exhibited its promising capability in chapters 7 and 8. Both NiO/SrFeO$_3$ and NiO/Fe$_2$O$_3$ showed high activity for producing H$_2$, but only the performance of NiO/Fe$_2$O$_3$ was maintained after multiple looping cycles. The deactivation of NiO/SrFeO$_3$ after the 1st (fresh) cycle should be further explored. So far, it seems that this might be due to the interaction between NiO and SrFeO$_3$ by plasma effect or reduction. Future work on the effect of Ni onto the SrFeO$_3$ perovskite structure on H$_2$ production would also be interesting. The current goal of chapters 7 and 8 was to introduce a new concept for H$_2$ production at mild temperatures. The focus has been on understanding the synergistic effect of NiO/Fe$_2$O$_3$ and NiO/SrFeO$_3$. In addition to these, process parameters can significantly influence the outcome of the investigated process. Further work, especially for NiO/Fe$_2$O$_3$, on exploring the effect such as of temperature, the flow rate, and the height of the packed bed is worth conducting. The results obtained here demonstrated the feasibility of PCLH. It is just the start of this exciting subject, and
this should be followed by investigation of other potential oxygen carriers and catalysts, to improve the H₂ yield further.
# List of abbreviations and symbols

## Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-CLR</td>
<td>Auto-thermal chemical looping reforming</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
</tr>
<tr>
<td>BJH</td>
<td>Barrett-Joyner-Halenda</td>
</tr>
<tr>
<td>CCS</td>
<td>Carbon capture and storage</td>
</tr>
<tr>
<td>CLC</td>
<td>Chemical looping combustion</td>
</tr>
<tr>
<td>CLOU</td>
<td>Chemical looping oxygen uncoupling</td>
</tr>
<tr>
<td>DBD</td>
<td>Dielectric barrier discharge</td>
</tr>
<tr>
<td>DI</td>
<td>De-ionised water</td>
</tr>
<tr>
<td>DIEI</td>
<td>Direct ionisation by electron impact</td>
</tr>
<tr>
<td>FeZr</td>
<td>ZrO$_2$-supported Fe$_2$O$_3$</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared</td>
</tr>
<tr>
<td>GHG</td>
<td>Greenhouse gas</td>
</tr>
<tr>
<td>ICSD</td>
<td>Inorganic Crystal Structure Database</td>
</tr>
<tr>
<td>ICHIP</td>
<td>Ionisation by collision of heavy particles</td>
</tr>
<tr>
<td>IEA</td>
<td>International Energy Agency (IEA)</td>
</tr>
<tr>
<td>IPCC</td>
<td>Intergovernmental Panel On Climate Change</td>
</tr>
<tr>
<td>NIST</td>
<td>National Institute of Standards of Technology, USA</td>
</tr>
<tr>
<td>NPL</td>
<td>National Physical Laboratory, UK</td>
</tr>
<tr>
<td>PCLH</td>
<td>Plasma-assisted chemical looping hydrogen production</td>
</tr>
<tr>
<td>PI</td>
<td>Photo-ionisation</td>
</tr>
<tr>
<td>SR-CLC</td>
<td>Stem reforming with chemical looping combustion</td>
</tr>
<tr>
<td>SED</td>
<td>Specific energy density</td>
</tr>
<tr>
<td>SEM-EDX</td>
<td>Scanning electron microscope with energy dispersive X-ray spectroscopy (SEM/EDX)</td>
</tr>
<tr>
<td>SI</td>
<td>Surface ionisation</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analyser</td>
</tr>
<tr>
<td>VOCs</td>
<td>Volatile organic compounds</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray (powder) diffraction</td>
</tr>
</tbody>
</table>
## Symbols

<table>
<thead>
<tr>
<th>Symbols</th>
<th>units</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A )</td>
<td>frequency factor</td>
</tr>
<tr>
<td>( c )</td>
<td>concentration of active sites per unit mass of carbon</td>
</tr>
<tr>
<td>( C_D )</td>
<td>capacitance of the dielectric</td>
</tr>
<tr>
<td>( C_d )</td>
<td>effective dielectric capacitance</td>
</tr>
<tr>
<td>( C_{gap} )</td>
<td>overall capacitance of the gap</td>
</tr>
<tr>
<td>( C_{Total} )</td>
<td>total capacitance of the electrode configuration</td>
</tr>
<tr>
<td>( D )</td>
<td>diffusion coefficient</td>
</tr>
<tr>
<td>( (D_A)_{ij} )</td>
<td>overall diffusivity</td>
</tr>
<tr>
<td>( (D_B)_{ij} )</td>
<td>molecular diffusivity of component i in j</td>
</tr>
<tr>
<td>( d_c )</td>
<td>degree of carbon deposition</td>
</tr>
<tr>
<td>( D_{CO_2} )</td>
<td>diffusivity of CO.</td>
</tr>
<tr>
<td>( (D_K)_i )</td>
<td>Knudsen diffusivity of component i</td>
</tr>
<tr>
<td>( d_p )</td>
<td>particle diameter</td>
</tr>
<tr>
<td>( d_{pore} )</td>
<td>pore diameter</td>
</tr>
<tr>
<td>( E, E_i )</td>
<td>activation energy</td>
</tr>
<tr>
<td>( EC_a, EC_b )</td>
<td>energy cost</td>
</tr>
<tr>
<td>( g )</td>
<td>acceleration due to gravity</td>
</tr>
<tr>
<td>( F_{air} )</td>
<td>air flow rate to mix with the sampled product flow from the fluidised bed</td>
</tr>
<tr>
<td>( F_{total} )</td>
<td>total flow rate in the sampling line</td>
</tr>
<tr>
<td>( F_{FB} )</td>
<td>total gas flow rate in the fluidised bed</td>
</tr>
<tr>
<td>( F_{sampling} )</td>
<td>flow rate of the sampling line from the fluidised bed</td>
</tr>
<tr>
<td>( J_a )</td>
<td>molar flux of component a</td>
</tr>
<tr>
<td>( k )</td>
<td>volumetric rate constant</td>
</tr>
<tr>
<td>( k' )</td>
<td>Effective shrinking core rate constant</td>
</tr>
<tr>
<td>( k_B )</td>
<td>Boltzmann constant ((1.38 \times 10^{-23} , \text{J/K}))</td>
</tr>
<tr>
<td>( k_i )</td>
<td>rate constant per active site</td>
</tr>
<tr>
<td>( K, K_p )</td>
<td>equilibrium constant</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>---------------</td>
<td>------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>$M_{\text{carbon}}$</td>
<td>molar mass of carbon</td>
</tr>
<tr>
<td>$m_{\text{C,tar}}$</td>
<td>mass of carbon in the tar entering the sampling system</td>
</tr>
<tr>
<td>$M_{\text{C,tar}}$</td>
<td>total mass of carbon in the tar produced in the fluidised bed</td>
</tr>
<tr>
<td>$M_{\text{C,total}}$</td>
<td>total carbon content in the wood fed</td>
</tr>
<tr>
<td>$m_i$</td>
<td>mass of carbon in the carbon-containing species $i$</td>
</tr>
<tr>
<td>$m_t$</td>
<td>accumulated increased amount of carbon in the gaseous phase</td>
</tr>
<tr>
<td>$m_o$</td>
<td>initial mass of char fed into the reactor</td>
</tr>
<tr>
<td>$M_{\text{wood,total}}$</td>
<td>total mass of wood fed into the FB</td>
</tr>
<tr>
<td>$m%$</td>
<td>mass balance of carbon</td>
</tr>
<tr>
<td>$N_{Ga}$</td>
<td>Galileo number</td>
</tr>
<tr>
<td>$n_{H_2}$</td>
<td>amount of H₂ produced</td>
</tr>
<tr>
<td>$P$</td>
<td>total pressure</td>
</tr>
<tr>
<td>$p_{CO}$</td>
<td>partial pressure of CO</td>
</tr>
<tr>
<td>$p_{CO_2}$</td>
<td>partial pressure of CO₂</td>
</tr>
<tr>
<td>$R$</td>
<td>sphere radius</td>
</tr>
<tr>
<td>$R^2$</td>
<td>R-squared values of fitting for kinetic parameters</td>
</tr>
<tr>
<td>$R_{\text{co,burn-off}}$</td>
<td>rate of production of CO during burn-off</td>
</tr>
<tr>
<td>$R_{\text{co₂,burn-off}}$</td>
<td>rate of production of CO₂ during burn-off</td>
</tr>
<tr>
<td>$R_{\text{CO,silica}}$</td>
<td>overall rate of production of CO in silica sand</td>
</tr>
<tr>
<td>$R_{\text{CO₂,silica}}$</td>
<td>overall rate of production of CO₂ in the presence of oxygen carriers</td>
</tr>
<tr>
<td>$R_{\text{CO,oc}}$</td>
<td>overall rate of production of CO in the presence of oxygen carriers</td>
</tr>
<tr>
<td>$R_{\text{CO₂,oc}}$</td>
<td>overall rate of production of CO₂ in silica sand</td>
</tr>
<tr>
<td>$r_g$</td>
<td>gasification rate per unit volume of carbon</td>
</tr>
<tr>
<td>$Re_{mf}$</td>
<td>Reynolds number at minimum fluidisation</td>
</tr>
<tr>
<td>$R'_g$</td>
<td>gasification rate over time</td>
</tr>
<tr>
<td>$R'_{g,0}$</td>
<td>initial gasification rate (at $t = 0$)</td>
</tr>
<tr>
<td>$R_i$</td>
<td>rate of production of carbon in the carbon-containing species $i$</td>
</tr>
<tr>
<td>$R_{\text{ideal}}$</td>
<td>ideal gas constant</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>$R_{max}$</td>
<td>maximum rate of gasification (external mass transfer rate)</td>
</tr>
<tr>
<td>$r_{obs}$</td>
<td>observed rate of reaction</td>
</tr>
<tr>
<td>$r_{oc}$</td>
<td>rate of production of CO$_2$ from the reaction between CO and oxygen carriers</td>
</tr>
<tr>
<td>$r_s$</td>
<td>rate of reaction at the particle surface</td>
</tr>
<tr>
<td>Sh</td>
<td>Sherwood number</td>
</tr>
<tr>
<td>$S_a$</td>
<td>averaged selectivity of species a</td>
</tr>
<tr>
<td>T</td>
<td>temperature</td>
</tr>
<tr>
<td>$t_0$</td>
<td>Initial pyrolysis time</td>
</tr>
<tr>
<td>$t_a$</td>
<td>processing at time a (pyrolysis)</td>
</tr>
<tr>
<td>$t_b$</td>
<td>processing time at time b (burn-off)</td>
</tr>
<tr>
<td>U</td>
<td>superficial velocity in a fluidised bed</td>
</tr>
<tr>
<td>$\bar{U}$</td>
<td>peak voltage in a discharge cycle</td>
</tr>
<tr>
<td>$U_{mf}$</td>
<td>minimum fluidisation velocity</td>
</tr>
<tr>
<td>$U_{min}$</td>
<td>minimum voltage required for discharge to start</td>
</tr>
<tr>
<td>$v$</td>
<td>kinematic viscosity of fluidising gas</td>
</tr>
<tr>
<td>$v_a$</td>
<td>stoichiometric coefficient for species a</td>
</tr>
<tr>
<td>$v'_a$</td>
<td>atomic diffusion volume</td>
</tr>
<tr>
<td>W</td>
<td>applied plasma power</td>
</tr>
<tr>
<td>X</td>
<td>conversion of carbon</td>
</tr>
<tr>
<td>$x_c$</td>
<td>weight fraction of elemental carbon in the wood</td>
</tr>
<tr>
<td>$x_i$</td>
<td>mole fraction of the product species $i$</td>
</tr>
<tr>
<td>$Y_i$</td>
<td>the yield of gaseous species $i$</td>
</tr>
</tbody>
</table>

**Greek symbols**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho_f$</td>
<td>the density of the fluidising gas</td>
<td>kg/m$^3$</td>
</tr>
<tr>
<td>$\rho_s$</td>
<td>the density of the solid particles</td>
<td>kg/m$^3$</td>
</tr>
<tr>
<td>$\mu$</td>
<td>dynamic viscosity</td>
<td>Pa s</td>
</tr>
<tr>
<td>$\mu_e$</td>
<td>drift mobility</td>
<td>m$^2$ V$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Thiele modulus</td>
<td>-</td>
</tr>
<tr>
<td>$\phi_m$</td>
<td>modified Thiele modulus</td>
<td>-</td>
</tr>
<tr>
<td>$\eta$</td>
<td>effectiveness factor</td>
<td>-</td>
</tr>
</tbody>
</table>
| \( \eta_{\text{with capture}} \) | power plant energy efficiency with carbon capture installed |  \\
| \( \eta_{\text{without capture}} \) | power plant energy efficiency without carbon capture installed |  \\
| \( \varepsilon \) | porosity or voidage of the particle |  \\
| \( \varepsilon_D \) | relative dielectric constant of quartz tube |  \\
| \( \varepsilon_{mf} \) | voidage at minimum fluidisation |  \\
| \( \varepsilon_{\text{vacuum}} \) | dielectric constant of the vacuum | Fm$^1$  \\
| \( \tau^2 \) | tortuosity factor of the particle |  \\
| \( \theta \) | surface active coverage |  \\
| \( \delta \) | oxygen vacancy in SrFeO,$\delta$ |  \\


Reference


[30] M. Rydén, A. Lyngfelt, T. Mattisson, Combined manganese/iron oxides as oxygen carrier for chemical looping combustion with oxygen uncoupling


H.B. Goyal, D. Seal, R.C. Saxena, Bio-fuels from thermochemical conversion of


[100] M. Keller, H. Leion, T. Mattisson, Chemical looping tar reforming using La/Sr/Fe-containing mixed oxides supported on ZrO2, Applied Catalysis B:


[121] Y. Zeng, X. Zhu, D. Mei, B. Ashford, X. Tu, Plasma-catalytic dry reforming of


https://books.google.co.uk/books/about/Blast_furnace_phenomena_and_modelling.html?id=YJxTAAAAMAAJ&pgis=1 (accessed June 18, 2015).


[141] A. Hayhurst, M. Parmar, Measurement of the mass transfer coefficient and sherwood number for carbon spheres burning in a bubbling fluidized bed,


[152] N.M. Laurendeau, Heterogeneous kinetics of coal char gasification and


doi:10.1615/AtoZ.m.mean_free_path.


