STUDY OF DIRECT UTILIZATION OF SOLID CARBON AND CH\textsubscript{4}/CO\textsubscript{2} REFORMING ON SOLID OXIDE FUEL CELL

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STUDY OF DIRECT UTILIZATION OF SOLID CARBON AND CH$_4$/CO$_2$ REFORMING ON SOLID OXIDE FUEL CELL

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ABSTRACT

This study demonstrates the feasibility and optimization of utilizing carbon and CH₄ to generate electricity with solid oxide fuel cell (SOFC). Carbon sources including coconut shell biomass, coal, coke injecting into the anode compartment of the SOFC were heated rapidly. The detail reactions that occur on the carbon during this process were studied in the Chapter 4, fast pyrolysis of coconut biomass. The products of biomass fast pyrolysis consist of char, liquid and gases. The utilization of CH₄ and CO₂, which are the major pyrolysis products, was investigated in Chapter 5 with Rh-modification of the SOFC anode. The purpose of Rh-modification is to avoid carbon deposition in the anode matrix by promoting the dissociation of CO₂, as a result, increasing the rate of carbon oxidation. The importance of the rate of carbon electrochemical oxidation has been highlighted in the study of carbon-based SOFC in Chapter 3. The rate of carbon oxidation and CO oxidation was studied as a function of operating current density of carbon-based SOFC with Ag impregnated Ni/YSZ anode.

Chapter 3 reports the study of evolution of gases from direct utilization of carbon in a solid oxide fuel cell (C-SOFC) with coconut carbon, a carbonaceous material with low ash and sulfur content. The addition of CO₂ to the anode chamber increased CO formation and maximum power density from 0.09 Wcm⁻² to 0.13 Wcm⁻², indicating the occurrence of Boudouard reaction coupling with CO electrochemical oxidation on the C-SOFC. Analysis of CO and CO₂ concentration as a function of current and voltage revealed that electricity was mainly produced from the electrochemical oxidation of
carbon at low current density and produced from the electrochemical oxidation of CO at high current density.

The operating efficiencies of SOFC operated with coconut carbon and Ohio coal was evaluated to be less than 2% in Chapter 4. This low efficiency was mainly due to gaseous product of carbon pyrolysis leaving the anode chamber unreacted, which lead to the study of fast pyrolysis. The fast pyrolysis reactions occur on the carbon fuel during the feeding step into the SOFC at high temperature. The reaction pathway of coconut shell fast pyrolysis was studied by analysis of the transient evolution product profiles as a function of temperature, measured directly in the sample bed. Fast pyrolysis of coconut shell produced (i) pyrolysis liquid containing C-H, C=O, and C-O-C bands, (ii) char with the absence of C-OH and C=O suggesting that ether and carbonyl compounds were decomposed below 600 °C, and (iii) gaseous product majorly consisting of CO$_2$. The results of this study suggest the importance of utilization of gaseous species of fast pyrolysis, i.e., CH$_4$, CO, CO$_2$, and H$_2$.

The utilization of CH$_4$ and CO$_2$ to produce electricity was studied in SOFC comprising a Ni/YSZ anode impregnation of Rh. The Rh-Ni/YSZ anode SOFC and Ni/YSZ anode SOFC were tested simultaneously in the multiple SOFC reactor under flowing CH$_4$/CO$_2$. Exposure of the Ni/YSZ anode SOFC to CH$_4$/CO$_2$ produced a maximum power density that degraded from 0.06 to 0.01 W/cm$^2$ after 41 h. Impregnation of Rh at 0.01 and 0.03 wt.% onto the Ni/YSZ anode produced the Rh-Ni/YSZ anode that exhibited a maximum power density of 0.06 and 0.08 W/cm$^2$, respectively, for more than 185 h. Extensive testing of SOFC with various concentration of Rh in H$_2$/Ar and CH$_4$/CO$_2$ suggests the optimum Rh concentration of 0.07 – 0.10 wt%.
ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my research advisor Professor Steven S.C. Chuang for this continuous guidance and strong encouragement during the course of my research. I would also like to thank my committee members, Dr. Jie Zheng, Dr. Nic D. Leipzig, Dr. Guo-Xiang Wang, and Dr. Stephen Z. Cheng for supervision and guidance.

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I would like to dedicate this work to my family and those who have always unconditionally supported me. Thank you.
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CHAPTER I
INTRODUCTION

1.1 Carbon-based fuel cell

The direct utilization of solid carbon in a fuel cell (i.e., carbon fuel cell) is an attractive approach for electric power generation. The carbon fuel cell could offer significant advantages including: (i) high energy conversion efficiency, (ii) minimization of NO\textsubscript{x} emission due to its operating temperature range of 700 – 1000 °C, and (iii) the production of a nearly pure CO\textsubscript{2} exhaust stream for the direct CO\textsubscript{2} sequestration. The high energy conversion efficiency of the carbon fuel cell is a result of the electrochemical oxidation of carbon producing CO\textsubscript{2} \((C + 2O^2- \leftrightarrow CO_2)\), which could achieve an thermodynamic efficiency \((\eta = \Delta G_T / \Delta H_{298})\) exceeding 100 %.\cite{1} Table 1.1 shows the list of definition of efficiency used to describe a performance of the fuel cells. Thermodynamic efficiency is the amount of useful energy that can be exploited relative to the maximum work by the enthalpy input. The load efficiency represents the losses due to irreversible reaction in the fuel cell, which incorporates the actual cell voltage, \(E(i)\), and the thermal cell voltage or Nernst potential, \(E^0_H\). The fuel efficiency or fuel utilization accounts for the amount of fuel that is actually consumed in the fuel cell producing electricity relative to the amount of fuel input, \(v_{\text{fuel}}\). The effective efficiency considers the above losses, representing the practical amount of energy that the fuel cell system can produce in comparison to the amount of fuel used.
Table 1.1 Summary for fuel cell efficiency types and definitions

<table>
<thead>
<tr>
<th>Efficiency</th>
<th>Definition</th>
<th>Alternate name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermodynamic</td>
<td>$\xi_{ideal} = \Delta G/\Delta H$</td>
<td>Ideal efficiency</td>
</tr>
<tr>
<td>Load efficiency</td>
<td>$\xi_{load} = E(i)/E^{0}_{H}$</td>
<td>Voltage efficiency</td>
</tr>
<tr>
<td>Fuel efficiency</td>
<td>$\xi_{fuel} = (i/nF)/v_{fuel}$</td>
<td>Fuel utilization</td>
</tr>
<tr>
<td>Effective efficiency</td>
<td>$\xi_{eff} = \xi_{ideal} \times \xi_{load} \times \xi_{fuel}$</td>
<td>Real efficiency, practical efficiency</td>
</tr>
</tbody>
</table>

The use of carbon as fuel for the fuel cell has been studied with molten salt electrolyte fuel cell and solid oxide fuel cell.[2] The major drawbacks of the molten salt electrolyte fuel cell include corrosion from liquid electrolyte and degradation of the electrolyte from formation of carbonates during electrochemical oxidation of carbon. In contrast to molten salt electrolyte fuel cell, the solid oxide fuel cell provides the advantages of a ceramic solid electrolyte which does not suffer from corrosion or degradation and facilitates integration into stack assemblies. The operating principle of carbon-based solid oxide fuel cell (carbon fuel cell) is the electrochemical oxidation of solid carbon with oxygen anions ($O^{2-}$) on the surface of the anode electrode, producing CO and CO$_2$. Secondary reactions can also take place on the carbon fuel cell anode, including reversed Boudouard reaction ($C + CO_2 \leftrightarrow 2CO$) and electrochemical oxidation of CO producing CO$_2$. The diagram in Figure 1.1 shows the network of reactions between carbon, CO, and CO$_2$ on anode of the carbon fuel cell.
Our previous study showed that the production of CO from the reversed Boudouard reaction decreased with increasing the carrier gas flow rate and the presence of CO led to an increase in carbon fuel cell power density. Recent research studies have explored the use of secondary reactions to improve the carbon fuel cell performance by integrating a fluidized bed reactor for the Boudouard reaction of carbon to CO, and a SOFC for the electrochemical oxidation of the resulted CO. Results from these studies have shown power densities as high as 0.14 W/cm$^2$ at 0.5 V and 950 °C can be achieved. Despite the attractive power density, the electrochemical oxidation of CO ($CO + O^{2-} \rightarrow CO_2 + 2e^-$) could lead to the reduction of the thermodynamic efficiency of the carbon fuel cell as the electrochemical oxidation of carbon producing $CO_2$ ($C + 2O^{2-} \rightarrow CO_2 + 4e^-$) is a four-electron process and that of CO is a two-electron process. Our previous studies reported the feasibility of direct power generation from solid carbon with carbon fuel cell which could give an effective efficiency as high as 52.9 %. Table 1.2 shows the efficiency of the solid oxide fuel cells that are commercially available. The efficiencies of the SOFC are higher than 60 % which is significantly higher than that of coal-fired power plant. The scale of those fuel cell stacks are less than
200 kW that can replace power grid (100 – 200 kW) or serve for household power consumption (1 – 2 kW)

Table 1.2 Efficiency of commercial fuel cell

<table>
<thead>
<tr>
<th>Company</th>
<th>Fuel</th>
<th>Scale</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bloomenergy</td>
<td>Natural gas</td>
<td>100 – 200 kW</td>
<td>&gt;60%</td>
</tr>
<tr>
<td>Ceres Power</td>
<td>LPG</td>
<td>1 – 100 kW</td>
<td>60%</td>
</tr>
<tr>
<td>Ceramic Fuel Cell</td>
<td>Natural gas, LPG, H₂</td>
<td>1.5 kW</td>
<td>60%</td>
</tr>
<tr>
<td>Coal-fired power plant</td>
<td>Coal</td>
<td>&gt;1 MW</td>
<td>33 – 47%</td>
</tr>
</tbody>
</table>
Table 1.3 Literature review of the performance of SOFC operated in CH$_4$ fuel.

<table>
<thead>
<tr>
<th>Anode</th>
<th>Fuel</th>
<th>Temperature (°C)</th>
<th>Max P</th>
<th>Comment</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>GDC/LSCM</td>
<td>H$_2$</td>
<td>750</td>
<td>0.182</td>
<td>Cathode support</td>
<td>[8]</td>
</tr>
<tr>
<td>GDC/LSCM</td>
<td>CH$_4$</td>
<td>750</td>
<td>0.060</td>
<td>Cathode support</td>
<td>[8]</td>
</tr>
<tr>
<td>GDC/LSCM</td>
<td>H$_2$</td>
<td>800</td>
<td>0.419</td>
<td>Cathode support</td>
<td>[8]</td>
</tr>
<tr>
<td>GDC/LSCM</td>
<td>CH$_4$</td>
<td>800</td>
<td>0.158</td>
<td>Cathode support</td>
<td>[8]</td>
</tr>
<tr>
<td>LSCF/YSZ</td>
<td>CH$_4$</td>
<td>900</td>
<td>0.186</td>
<td>Electrolyte support</td>
<td>[9]</td>
</tr>
<tr>
<td>Ni/YSZ</td>
<td>CH$_4$/CO$_2$</td>
<td>800</td>
<td>0.245</td>
<td>Anode support, 50 % CH$_4$</td>
<td>[10]</td>
</tr>
<tr>
<td>Ni/YSZ</td>
<td>CH$_4$/CO$_2$</td>
<td>875</td>
<td>0.052</td>
<td>50 % CH$_4$</td>
<td>[11]</td>
</tr>
<tr>
<td>Ni/YSZ</td>
<td>CH$_4$/CO$_2$</td>
<td>850</td>
<td>0.046</td>
<td>37 % CH$_4$</td>
<td>[11]</td>
</tr>
<tr>
<td>Ir-Ce/Ni/YSZ</td>
<td>CH$_4$/H$_2$O</td>
<td>900</td>
<td>0.055</td>
<td>Electrolyte support 5% H$_2$O</td>
<td>[12]</td>
</tr>
<tr>
<td>Ni/Mg</td>
<td>CH$_4$/CO$_2$</td>
<td>800</td>
<td>0.017</td>
<td>12.5 % CH$_4$</td>
<td>[13]</td>
</tr>
<tr>
<td>Ni/YSZ</td>
<td>CH$_4$/H$_2$O</td>
<td>700</td>
<td>0.5</td>
<td>3 % H$_2$O</td>
<td>[14]</td>
</tr>
<tr>
<td>Ni/YSZ</td>
<td>CH$_4$/H$_2$O</td>
<td>750</td>
<td>0.8</td>
<td>3 % H$_2$O</td>
<td>[14]</td>
</tr>
<tr>
<td>Ni/YSZ</td>
<td>CH$_4$/H$_2$O</td>
<td>800</td>
<td>1.3</td>
<td>3 % H$_2$O</td>
<td>[14]</td>
</tr>
<tr>
<td>Ni/YSZ</td>
<td>CH$_4$/CO$_2$</td>
<td>700</td>
<td>0.65</td>
<td>75 % CH$_4$</td>
<td>[14]</td>
</tr>
<tr>
<td>Ni/YSZ</td>
<td>CH$_4$/CO$_2$</td>
<td>750</td>
<td>1.0</td>
<td>75 % CH$_4$</td>
<td>[14]</td>
</tr>
<tr>
<td>Ni/YSZ</td>
<td>CH$_4$/CO$_2$</td>
<td>800</td>
<td>1.3</td>
<td>75 % CH$_4$</td>
<td>[14]</td>
</tr>
<tr>
<td>Ni/GDC</td>
<td>CH$_4$/H$_2$</td>
<td>550</td>
<td>0.072</td>
<td>Tubular, 50 % CH$_4$</td>
<td>[15]</td>
</tr>
<tr>
<td>Sr$_2$CoMoO$_6$</td>
<td>H$_2$</td>
<td>800</td>
<td>1.0</td>
<td></td>
<td>[16]</td>
</tr>
<tr>
<td>Sr$_2$CoMoO$_6$</td>
<td>CH$_4$/H$_2$O</td>
<td>800</td>
<td>0.6</td>
<td>5% H$_2$O</td>
<td>[16]</td>
</tr>
<tr>
<td>Sr$_2$CoMoO$_6$</td>
<td>CH$_4$</td>
<td>800</td>
<td>0.4</td>
<td></td>
<td>[16]</td>
</tr>
<tr>
<td>GDC-SrMoO$_3$/YSZ</td>
<td>CH$_4$/H$_2$O</td>
<td>900</td>
<td>0.15</td>
<td>3% H$_2$O</td>
<td>[17]</td>
</tr>
<tr>
<td>GDC-SrMoO$_3$/YSZ</td>
<td>CH$_4$/H$_2$O</td>
<td>850</td>
<td>0.07</td>
<td>3% H$_2$O</td>
<td>[17]</td>
</tr>
<tr>
<td>Ni/YSZ</td>
<td>CH$_4$</td>
<td>800</td>
<td>0.06</td>
<td>YSZ electrolyte support</td>
<td>[18]</td>
</tr>
<tr>
<td>Ni(Au)/GDC</td>
<td>CH$_4$/CO$_2$</td>
<td>600</td>
<td>0.035</td>
<td>120 hr test, 50% CO$_2$</td>
<td>[19]</td>
</tr>
<tr>
<td>Ni(Au)/GDC</td>
<td>CH$_4$/CO$_2$</td>
<td>640</td>
<td>0.060</td>
<td>120 hr test, 50% CO$_2$</td>
<td>[19]</td>
</tr>
<tr>
<td>Ni/SDC</td>
<td>CH$_4$</td>
<td>700</td>
<td>0.027</td>
<td>Vary calcine temp.</td>
<td>[20]</td>
</tr>
<tr>
<td>Ni/YSZ</td>
<td>CH$_4$/H$_2$O</td>
<td>1000</td>
<td>0.18</td>
<td>S/C=3, 45% CH$_4$</td>
<td>[21]</td>
</tr>
<tr>
<td>Ru-Ni/YSZ</td>
<td>CH$_4$/H$_2$O</td>
<td>1000</td>
<td>0.28</td>
<td>S/C=3, 45% CH$_4$</td>
<td>[21]</td>
</tr>
<tr>
<td>Rh-Ni/YSZ</td>
<td>CH$_4$/H$_2$O</td>
<td>1000</td>
<td>0.24</td>
<td>S/C=3, 45% CH$_4$</td>
<td>[21]</td>
</tr>
<tr>
<td>Pd-Ni/YSZ</td>
<td>CH$_4$/H$_2$O</td>
<td>1000</td>
<td>0.265</td>
<td>S/C=3, 45% CH$_4$</td>
<td>[21]</td>
</tr>
<tr>
<td>Pt-Ni/YSZ</td>
<td>CH$_4$/H$_2$O</td>
<td>1000</td>
<td>0.265</td>
<td>S/C=3, 45% CH$_4$</td>
<td>[21]</td>
</tr>
</tbody>
</table>

Where
GDC: Gd-doped Ce
LSCM: La, Sr, Cr, Mn oxide
LSCF: La, Sr, Co, Fe oxide
YSZ: Y-stabilized Zr
LSM: La, Sr, Mn oxide
ScSZ: Sc-stabilized Zr
SDC: Sm-doped Ce

1.2 Hypothesis

The operation of the solid oxide fuel cell with solid carbon has been demonstrated with the current density of 150 mA/cm$^2$ at 0.56 V.[7] Despite the high predicted thermodynamic efficiency ($\eta = \Delta G_T / \Delta H_{298}$), the effective efficiency of only 52.9 % was achieved from the carbon fuel cell. This low effective efficiency was caused by (i) overpotential losses resulting in low load efficiency, which can be expressed by operating voltage/ ideal Nernst potential and (ii) the electrochemical oxidation of by-product such as CO, which offers lower thermodynamic efficiency than electrochemical oxidation of carbon.

The rate of electrochemical oxidation of carbon and CO fuel during the operation of the carbon fuel cell is governed by the rate of electrochemical oxidation of each fuel per reaction site on the anode and the three-phase boundary (TPB) length available for reactions. Guzman et al. reported that the rate of the carbon reaction is higher than that of the gas phase fuel reaction on per site basis; however, due to the TPB length available for the carbon reaction was found to be 100 times smaller than that available for gas
phase reaction, the mass transportation limitation can occur on the fuel cell with solid carbon fuel.

**Hypothesis 1: The utilization of carbon should be increased by operating the fuel cell at low current density. The increase in carbon utilization would result in an increase in the effective efficiency of the carbon fuel cell.**

The effect of the fast pyrolysis of carbon which occurred during rapidly loading into the fuel cell chamber was studied with coconut shell and coal at various heating rate. The results show CO, CO$_2$, CH$_4$, and H$_2$ as major gases products. The reaction pathway of coconut was studied with in situ IR study with high temperature DRIFT, showing that CO and CO$_2$ were mainly produced from cracking of C-H and C=O bonds. This results support the feasibility of operating the fuel cell with direct injecting of fresh biomass, since CO, CH$_4$, and H$_2$ can be consumed and increase the power density of the fuel cell.

In addition to the study of the carbon fuel cell, the research will be attempted to develop the use of CH$_4$ or natural gas as a fuel for solid oxide fuel cell. The major challenge of CH$_4$ fuel cell is the carbon deposition, (coking) on the Ni/YSZ matrix leading to the degradation in the power density and mechanical failure of the fuel cell. The coking occurs when the rate of CH$_4$ cracking is higher than the rate of carbon oxidation. The approach to avoid the coking includes modification of the fuel cell anode to reduce the rate of CH$_4$ cracking or reforming of the CH$_4$ to increase the rate of carbon oxidation. CH$_4$ Steam reforming has been widely used to produce CO and H$_2$ over Ni catalyst. The coking on the catalyst can be prevented by introduction of high ratio of steam/CH$_4$. The drawback of this process for the operation of a solid oxide fuel cell is the energy required for heating steam and CH$_4$ to the operating temperature at 700 – 900
°C. Dry reforming of CH₄ with CO₂, (CO₂/CH₄ reforming) offers an alternative method for steam reforming, which can produce CO and H₂O and prevent carbon deposition on the catalyst. The CO₂/CH₄ reforming reactions were reported to occur as the following mechanism.

\[
\begin{align*}
\text{CH}_4 + 5\leftrightarrow \text{*C} + 4\text{*H} \\
\text{CO}_2 + 2\leftrightarrow \text{*CO} + \text{*O} \\
\text{*C} + \text{*O} \leftrightarrow \text{*CO} + \text{*} \\
\text{*CO} \leftrightarrow \text{CO} + \text{*} \\
\text{*H} + \text{*O} \leftrightarrow \text{*OH} \\
\text{*OH} + \text{*H} \leftrightarrow \text{H}_2\text{O} + 2\text{*}
\end{align*}
\]

Where “*” indicates an adsorption site. Our prior studies also demonstrate that reversed Boudouard reaction (CO₂ + C \rightarrow 2CO) occur at appreciable rate on the carbon fuel cell operated at 750 °C. Modification of the fuel cell anode can be implemented to increase the rate of CO₂ dissociation and carbon oxidation. Rh has been selected as a good catalyst for CO₂/CH₄ reforming, which could be incorporated to the solid oxide fuel cell.

**Hypothesis 2: Impregnation of Rh onto Ni/YSZ anode could create dispersed Rh sites in the vicinity of three phase boundary.** The deposited Rh should promote the rate of CO₂/CH₄ reforming by offering additional absorption sites for CO₂ + 2* \leftrightarrow *CO + *O, which in turn increases the rate of *C + *O \leftrightarrow *CO + * reaction.

Figure 1.2 shows the schematic of the proposed role of impregnated Rh on Ni/YSZ fuel cell anode on the dissociation of CO₂ and oxidation of carbon.
1.3 Scope of work

Figure 1.3 show the schematic of the scope of work presented in the dissertation. Carbon sources including coconut shell biomass, coal, coke injecting into the anode compartment of the SOFC were heated rapidly. The detail reactions that occur on the carbon during this process were studied in the Chapter 4, fast pyrolysis of coconut biomass. The products of biomass fast pyrolysis consist of char, liquid and gases. The utilization of CH$_4$ and CO$_2$, which are the major pyrolysis products, was investigated in Chapter 5 with Rh-modification of the SOFC anode. The purpose of Rh-modification is to avoid carbon deposition in the anode matrix by promoting the dissociation of CO$_2$, as a result, increasing the rate of carbon oxidation. The importance of the rate of carbon electrochemical oxidation has been highlighted in the study of carbon-based SOFC in Chapter 3. The rate of carbon oxidation and CO oxidation was studied as a function of operating current density of carbon-based SOFC with Ag impregnated Ni/YSZ anode.
The experiments proposed to verify the hypotheses are divided into 3 chapters. Studies in Chapter 3 focus on the quantification analysis of the effect of the fuel cell load on the evolution of CO and CO$_2$ and the extent of the carbon and CO electrochemical oxidation from the fuel cell operated with coconut coke. The key findings of this study will include (i) occurrence of Boudouard reaction coupling with CO electrochemical oxidation in the solid oxide fuel cell operated with carbon and (ii) the quantification of the contribution of carbon and CO to the electrical power generation at different operating current. The quantification result of gaseous products of the carbon fuel cell operation at different current load will reveal the utilization of the coke and CO. The first hypothesis will be verified when the CO concentration increase or stable at low current operation and rapidly decrease at high current operation.
Chapter 4 discusses the reaction pathway of the coconut shell fast pyrolysis studied by analysis of the transient evolution product profiles as a function of temperature, measured directly in the sample bed. Coconut shell samples were pyrolyzed in a tubular reactor and an in situ high temperature DRIFT (Diffuse Reflectance Infrared Fourier Transform) cell. The use of high temperature DRIFT allows the examination of the surface structure of the biomass throughout the fast pyrolysis process. The tubular reactor with 1.2 g sample was employed for analysis of the reaction products. The fast pyrolysis in the tubular reactor produces sufficient amounts of products for IR analysis and allows the tuning of the pyrolysis conditions i.e., heating rate and maximum pyrolysis temperature. The results from this study show that CO$_2$ is the major gaseous product followed by CO, CH$_4$, and H$_2$. In situ IR study showed that the major liquid products change from vinyl-containing species to carbonyl-containing species when the pyrolysis temperature reached 615 °C. The effect of moisture on H$_2$ production was studied by addition of D$_2$O to the dry coconut shell followed by fast pyrolysis in the tubular reactor. The moisture content in biomass was found to have no effect on H$_2$ yield. The efficiencies of the fuel cell operated with coconut shell, coconut coke, and coal are included in this chapter.

Chapter 5 study operation of Ni/YSZ and Rh impregnated Ni/YSZ fuel cell with CO$_2$/CH$_4$. The effect of Rh on the CO$_2$ reforming reaction over Rh-Ni/YSZ catalyst is determined by temperature-programmed reaction (TPR) with CO$_2$/CH$_4$ in high temperature DRIFT. The distribution of Rh on Ni/YSZ anode will be characterized by SEM (scanning electron microscope), and TEM. Exposure of the Ni/YZ anode SOFC to CH$_4$/CO$_2$ produced a maximum power density that degraded from 0.06 to 0.01 W/cm$^2$. 
after 41 h due to formation of carbon. Impregnation of Rh at 0.01 and 0.03 wt.% onto the Ni/YSZ anode produced the Rh-Ni/YSZ anode that exhibited a maximum power density of 0.06 and 0.08 W/cm$^2$, respectively, for more than 160 h. Characterization of the anode microstructure by transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS) revealed that the impregnation of Rh to the Ni/YSZ anode results in the deposition of Rh nano particles on Ni and an improved resistance to the formation of carbon in the anode matrix.
1.4 References


2.1 Solid oxide fuel cell fabrication and characterization

The anode-supported SOFCs used in this study were fabricated by a tape casting and screen-printing technique. A Ni/YSZ anode-supported layer (650 µm, 70 wt % Ni), a Ni/YSZ anode interlayer (25 µm, 50 wt % Ni), and a 15 µm YSZ electrolyte were fabricated by tape casting slips containing NiO, YSZ (TZ-8Y, Tosoh), binder, dispersants, and ethanol. The slips were casted on top of each other and dried at 50 °C for 3 days, cut in the shape of 12.5 mm discs, and sintered at 1400 °C for 4 h at the heating rate of 3 °C/min. The YSZ/LSM (Strontium Manganite) cathode interlayer (50 wt.% LSM, CL86-8706A, Heraeus) and LSM layer (CL8706, Heraeus) were subsequently screen-printed onto the sintered cells and heated at 1150 °C for 2 h, resulted in a 10 µm thickness of cathode interlayer and cathode layer. The anode of the fuel cell was reduced in flowing H₂/Ar (100 sccm, 50 vol% H₂) at 700 °C for 4 h. The modification of the anode catalyst in Chapter 3 was performed by impregnation with AgNO₃ solution (15 wt % AgNO₃ in aqueous solution) and dried at 85°C for 2 hr. The modification performed in Chapter 5 involved impregnation with an aqueous RhCl₃•2H₂O solution (0.5 wt.% RhCl₃•2H₂O, Alfa Chemicals) producing 0.01 and 0.03 wt.% Rh in the anode weight. Rh was added to the anode with the purpose of increasing the rate of CH₄/CO₂ reforming. The microstructure of the SOFCs was characterized by
Scanning Electron Microscope (SEM, Quanta 200 FEI) and Energy Dispersive X-Ray Spectroscopy (EDX).

2.2 Carbon-based fuel cell testing

The experimental apparatus used included (i) a gas manifold with flow controllers (5850E, Brooks), (ii) the fuel cell attached on a steel tube placing in a furnace, (iii) an impedance spectrometer (Solatron 1470E CellTest System), (iv) a gas chromatographer (GC, SRI8610C, SRIGC), and (v) a mass spectrometer (MS, GSD-301 Pfeiffer), as shown in Figure 2.3 Experimental apparatus for gasification and in situ CO/CH4 oxidation reaction studies. The anode side of carbon fuel cell was attached with an alumina-based seal to the end of the steel tube, which served as anode current collector and anode compartment. The anode compartment was loaded with solid carbon (i.e., coconut coke, Petcoke) in a direct contact with the anode surface. The cathode side of carbon fuel cell was attached to an Ag strip (99.9 % purity, C.C. Silver and Gold Inc.) using an Ag conductive paste (#24469, Alfa-Aesar). The voltage-current density characteristics (V-I curves) and electrochemical impedance spectra of the fuel cell were recorded by the Solatron CellTest. A 4-port valve in the gas manifold allows switching the inlet flow between H\textsubscript{2}, He, or CO. The effluent composition of the anode compartment was constantly monitored by GC and MS. The MS response of the species produced in the carbon fuel cell was converted into concentration profiles by means of a calibration curve, obtained by flowing known concentrations of H\textsubscript{2}, He, CO, and CO\textsubscript{2} mixtures (i.e., calibration gas).
The calibration of GC was performed prior to the experiment on CO and CO$_2$ which are the main products of the carbon fuel cell. The calibration gas with various concentrations of CO, CO$_2$ and He were injected to GC via 1-cc auto sampling valve. The calibration curve was achieved by plotting the area under the chromatograph at 6.1 and 11.9 min versus the CO and CO$_2$ concentration in the calibration gas, as shown in Figure 2.2(a). The concentration of CO and CO$_2$ was calibrated over the range of 3.5 – 5.5 % and 0.2 – 2.7 % which were the range of CO and CO$_2$ concentrations observed during the operation of carbon fuel cell. The coefficient of determination ($R^2$) of the calibration curve were 0.963 and 0.998 for CO and CO$_2$, indicating the high reliability of
the calibration curves. This calibration curve was then used to determine the concentration of CO and CO₂ during the carbon fuel cell experiment.

The gaseous species from the outlet of carbon fuel cell was continuously monitored by MS and GC analysis was performed every 20 min during the experimental campaign. The conversion of MS intensity to CO and CO₂ concentration was achieved through the linear regression of MS intensity versus concentration obtained from GC analysis, as shown in Figure 2.2(b). The R² of the linear regression were 0.986 and 0.996 for CO and CO₂, evidencing the reliable calculation of the CO and CO₂ concentration from MS intensity.
Figure 2.2 (a) GC calibration curve of CO and CO$_2$ and (b) linear regression of MS intensity versus the concentration of CO and CO$_2$.

2.3 In situ IR study of carbon gasification with DRIFT

Figure 2.3 shows the experimental apparatus which consists of (i) a gas manifold with mass flow controllers, a 4-port valve, and a 6-port valve, (ii) a Harrick Diffuse Reflectance Infrared Fourier Transform (DRIFT) reactor with a sample situated in a Nicolet 5600 FT-IR bench (IR), and (iii) a Pfeiffer QMS 200 quadrupole mass spectrometer (MS). The gaseous stream from 6-port valve flows through the sample bed in the DRIFT reactor from the top to the bottom.
The gasification experiment was performed on Petcoke and coconut coke to determine functional groups that contribute to the production CO and CO$_2$ at the fuel cell operating condition and the reactivity of those solid carbons toward gasification reaction with CO$_2$. Mixtures of coke and KBr (120 mg, 5 wt% coke) was loaded in the DRIFT reactor and preheated to 150 ºC for 10 min to reduce moisture in the coke mixture. The coke gasification experiment consisted of the following steps: (i) heating from 50 to 600 ºC with the heating rate of 15 - 60 ºC/min and maintained for 10 min, under 50 sccm of flowing H$_2$, (ii) switching from H$_2$ to 40 sccm He, (iii) pulsing 3 cc CO$_2$ and 3 cc O$_2$ onto the sample bed with 6-port valve respectively, and (iv) the gaseous products of the reaction was monitored with MS and quantified with calibration curve obtain from GC.

Figure 2.3 Experimental apparatus for gasification and in situ CO/CH$_4$ oxidation reaction studies
CHAPTER III
ANALYSIS OF GAS PRODUCTS FROM DIRECT UTILIZATION OF CARBON IN A
SOLID OXIDE FUEL CELL

This study demonstrates the effect of the fuel cell load on the evolution of CO and
CO₂ and the extent of the carbon and CO electrochemical oxidation from a carbon fuel
cell operated with coconut coke, which contains low ash and processes high electrical
conductivity. Preliminary results from this study showed the increase in the formation of
CO and CO₂ with increasing fuel cell load when operated under carbon. The analysis of
the CO and CO₂ produced at difference current densities reveals that at low current
density, electricity was produced from an electrochemical oxidation of carbon while CO
is consumed to produce electricity at higher current density.

3.1 Abstract

The evolution of gases from direct utilization of carbon in a solid oxide fuel cell
(C-SOFC) was studied by potentiostatic/galvanostatic discharge of a fuel cell with
cocoanut carbon, a carbonaceous material with low ash and sulfur content. Operation of
C-SOFC at 750 ºC produced less CO and more CO₂ than those predicted by
thermodynamic calculation using total Gibbs free energy minimization method. The
addition of CO₂ to the anode chamber increased CO formation and maximum power
density from 0.09 Wcm⁻² to 0.13 Wcm⁻², indicating the occurrence of Boudouard reaction
(CO₂ + C △ 2CO) coupling with CO electrochemical oxidation on the C-SOFC.
Analysis of CO and CO$_2$ concentration as a function of current and voltage revealed that electricity was mainly produced from the electrochemical oxidation of carbon at low current density and produced from the electrochemical oxidation of CO at high current density. The results suggest the electrochemical oxidation of solid carbon is more mass transfer limited than electrochemical oxidation of CO.

3.2 Introduction

The direct utilization of solid carbon in a fuel cell (i.e., carbon fuel cell) is an attractive approach for electric power generation. The carbon fuel cell could offer significant advantages including: (i) high energy conversion efficiency, (ii) minimization of NO$_x$ emission due to its operating temperature range of 700 – 1000 °C, and (iii) the production of a nearly pure CO$_2$ exhaust stream for the direct CO$_2$ sequestration. The high energy conversion efficiency of the carbon fuel cell is a result of the electrochemical oxidation of carbon producing CO$_2$ (C + O$_2$ → CO$_2$), which could achieve an efficiency ($\eta = \Delta G_T / \Delta H_{298}$) exceeding 100 % [1].

The use of carbon as fuel for the fuel cell has been studied with molten salt electrolyte and solid oxide electrolyte fuel cells [2]. The major drawbacks of the molten salt electrolyte fuel cell include equipment corrosion from liquid electrolyte and degradation of the electrolyte due to formation of carbonates during electrochemical oxidation of carbon. In contrast to molten salt electrolyte fuel cell, solid electrolyte fuel cells provide the advantages of using a ceramic solid electrolyte which does not suffer from corrosion or degradation and facilitates integration into stack assemblies. The operating principle of the carbon solid oxide fuel cell (C-SOFC) is the electrochemical oxidation of carbon by oxygen anions (O$^{2-}$) diffused from cathode through the solid
electrolyte to the anode electrode, producing CO\(_2\) (reaction 1) and CO (reaction 2). Secondary reactions can also take place on the C-SOFC anode, including the Boudouard reaction [3] (reaction 3) and electrochemical oxidation of CO producing CO\(_2\) (reaction 4).

\[
\begin{align*}
C + 2O^2- & \rightarrow CO_2 + 4e^- \quad (1) \\
C + O^2- & \rightarrow CO + 2e^- \quad (2) \\
CO_2 + C & \rightleftharpoons 2CO \quad (3) \\
CO + O^2- & \rightarrow CO_2 + 2e^- \quad (4)
\end{align*}
\]

Recently, researchers have explored the use of secondary reactions to improve the C-SOFC performance by integrating a fluidized bed reactor for the Boudouard reaction of carbon to CO (reaction 3), and a solid oxide fuel cell for the electrochemical oxidation of the resulted CO [4]. Results from these studies have shown power densities as high as 0.14 Wcm\(^{-2}\) at 0.5 V and 950 °C can be achieved [5-6]. Despite the attractive power density, the electrochemical oxidation of CO could lead to the reduction of the overall energy conversion efficiency of the C-SOFC as the electrochemical oxidation of carbon producing CO\(_2\) is a four-electron process and that of CO is a two-electron process. Our previous studies reported the feasibility of direct power generation from a carbon solid oxide fuel cell (C-SOFC) which could give energy efficiencies as high as 52.9 % [7].

This study demonstrates the effect of fuel cell load on the evolution of CO and CO\(_2\) on the C-SOFC operated with coconut carbon, a solid fuel selected because of its low content of ash [8-9] and high electronic conductivity. Results from this study showed the rate of formation of CO and CO\(_2\) increase with decreasing the fuel cell load (i.e., increasing current densities). Analysis of the CO and CO\(_2\) produced at different current densities reveals that at low current density, electricity was produced from the
electrochemical oxidation of carbon while CO is consumed to produce electricity at higher current density.

3.3 Experimental

Figure 3.1 shows the flow chart of the plan for the experiment of this chapter. The experimental plan includes the testing of the carbon fuel cell with coconut coke by potentiostatic/galvanostatic discharge of the fuel cell in flowing He, CO, or CO$_2$. Quantification of the gaseous products from the fuel cell outlet will be further studied for the utilization of solid carbon and CO at different fuel cell load. The quantification result of gaseous products of the carbon fuel cell operation at different current load will reveal the utilization of the coke and CO and the effective efficiency of the fuel cell. The first hypothesis will be verified when the CO concentration increase or stable at low current operation and rapidly decrease at high current operation. The detail experimental set up and procedure are discussed in this section.
Verification of Hypothesis 1

Hypothesis 1: The utilization of carbon should be increased by operating the fuel cell at low current density. The increase in carbon utilization would result in an increase in the effective efficiency of the carbon fuel cell.

3.3.1 Fuel cell fabrication and characterization

Anode-supported fuel cells used in this study consisted of a Ni/YSZ (Yttria-stabilized zirconia) support layer (520 µm, 70 wt % Ni), a Ni/YSZ anode interlayer (21 µm, 50 wt %), a 32 µm YSZ electrolyte, a 21 µm YSZ/LSM cathode interlayer (50 % wt LSM), and a 15 µm LSM cathode layer. The Ni/YSZ anode support, Ni/YSZ anode interlayer, and YSZ electrolyte were fabricated by tape casting slips containing NiO, YSZ (TZ-8Y, Tosoh), binder, dispersants and ethanol. The slips were casted and dried at room temperature for 3 days, laminated, cut into 3.1 cm diameter cells, and sintered at 1000 °C for 4 hr and at 1450 °C for 4 hr. The YSZ/LSM cathode interlayer (Heraeus CL86-8706A) and LSM layer (Heraeus CL8706) were subsequently screen-printed onto the sintered cells and fired at 1200 °C and 1100 °C, respectively, for 2 hr. The anode was
further impregnated with an aqueous AgNO$_3$ solution (15 wt% AgNO$_3$) and dried at 85 °C for 2 hr. Ag was added to the anode with the purpose of increasing the conversion of CO, as reported in previous studies [10]. The microstructure of the solid oxide fuel cell was characterized by Scanning Electron Microscope (SEM, Quanta 200 FEI) and Energy Dispersive X-Ray Spectroscopy (EDX).

### 3.3.2 Fuel cell testing and characterization

The experimental apparatus for fuel cell testing, shown in Fig.1, consisted of (i) a gas manifold with flow controllers (5850E, Brooks), (ii) the fuel cell placed in a high temperature furnace, (iii) an impedance spectrometer (Solatron 1470E CellTest System), (iv) a gas chromatographer (GC, SRI8610C, SRIGC), and (v) a mass spectrometer (MS, GSD-301 Pfeiffer). The anode side of the fuel cell was attached to one end of a Fe-based steel tube serving both as anode compartment and anode current collector. The fuel cell was sealed to the steel tube with an alumina-based sealant, and loaded with 7 g of coconut carbon in direct contact with the Ni/YSZ anode surface. The cathode side of the cell was coated with an Ag conductive paste (#24469, Alfa-Aesar) and was attached to an Ag strip cathode current collector (99.9 % purity, C.C. Silver and Gold Inc.). The area coated with the Ag conductive paste (1cm$^2$) was used as the fuel cell active area. The voltage-current density characteristics (V-I curves) of the fuel cell were recorded by the Solatron CellTest System. A 4-port valve in the gas manifold was used to switch the inlet flow between H$_2$, He, CO or CO$_2$. The effluent composition of the anode compartment was constantly monitored by GC and MS. The MS response of the gaseous species produced from the fuel cell was converted into concentration profiles by means of
a calibration curve, obtained by flowing a calibration gas with known concentrations of 
H₂, He, CO, and CO₂.

The fuel cell containing the coconut carbon was heated from room temperature to 
750 °C at heating rate of 3 °Cmin⁻¹ and reduced at 750 °C for 12 hr in flowing H₂/He 
(265 sccm, 27.2 vol% H₂). The fuel cell was operated at 750 °C with the purpose of 
ensuring high conductivity of the Fe-based steel anode current collectors. Operating the 
fuel cell at temperatures higher than 750 °C promotes oxidation of the Fe-based steel, 
leading to increased Ohmic resistance and low fuel cell performance. The amount of 
coconut carbon depleted during the fuel cell heating and anode reduction was estimated 
to be 1 g (0.09 g hr⁻¹) from the CO and CO₂ outlet molar flow rates, indicating that 
sufficient amount of carbon remained in the anode compartment for the carbon fuel cell 
(C-SOFC) experiments. The effect of the C-SOFC load on the evolution of CO₂ and CO 
was studied by operating the fuel cell in coconut carbon and pure He (200 sccm), as well 
as in CO₂/He (210 sccm, 8.6 vol% CO₂) and CO/He (210 sccm, 7.4 vol% CO), recording 
the V-I curves.

Coconut carbon was produced by pyrolyzing a sample of coconut husks and shell 
in flowing He at 950 °C. The composition of the coconut carbon was characterized by X-
ray Fluorescence (XRF, µEDX 1300, Shimadzu), and Diffuse Reflectance Infrared 
Fourier Transform spectroscopy (DRIFT). Coconut carbon samples were pyrolyzed in a 
DRIFT cell to determine surface functional groups on the coconut carbon that produced 
CO and CO₂. Mixtures of coconut carbon and KBr (120 mg, 5 wt.% coconut carbon) 
were loaded in the DRIFT cell and preheated to 150 °C for 10 min to reduce moisture.
The samples were then heated from 50 to 680 °C at a heating rate of 15 °C/min, and maintained at 680 °C for 10 min in flowing He (10 sccm).

3.3.3 Equilibrium molar flow rate calculation

The equilibrium molar flow rates at the exhaust of the fuel cell were calculated as a function of current density. The equilibrium molar flow rate of the specie $i$, $(F_i)$, is the product of the volumetric flow rate and the concentration of specie $i$, derived from molar volume of ideal gas and the corresponding mole fraction ($y_j$). The mole fraction of the gaseous products was obtained through the total Gibbs free energy minimization method – an approach for determining the equilibrium composition of a simultaneous multi-reaction system [11-13].

$$G_{\text{system}} = \left( \sum n_j \left( \Delta G^0_{f,j} + RT \ln(y_j \cdot P) \right) \right)_{\text{gas}} + \left( \sum n_j \Delta G^0_{f,j} \right)_{\text{condensed}}$$

where

$G_{\text{system}}$ = total Gibbs free energy of the system (J)

$n_j$ = amount of species “$j$” (mol)

$y_j$ = $n_j / \sum n_{j, \text{gas}}$

The components considered in the C-SOFC anode compartment were CO, CO$_2$, carbon and O$_2$ transferred from the cathode. The amount of carbon available for the reactions on the anode of the C-SOFC was assumed to be 1 mg/sec (83.3 µmols$^{-1}$) representing the excess amount of carbon required by other reactants. The amount of O$_2$ transferred from the cathode $n_{O2}$ at the specific current density can be determined from Faraday’s law

$$n_{O2} \text{ (mol/s cm}^2\text{)} = i / Z_{O2}F$$
where \( i \) and \( F \) represent current density (Acm\(^{-2}\)) and Faraday's constant (96487 C mol\(^{-1}\)), respectively. The initial condition for the Gibbs free energy minimization calculation was \( n_{O_2} = 0 \) where \( O_2 \) is not transferred from the cathode under open circuit voltage conditions (OCV).

3.4 Results and Discussion

Figure 3.2 shows the current density and MS profiles of effluents of the C-SOFC recorded at 750 °C and a load of 0.4 V in coconut carbon and the H\(_2\)/He, pure He, CO\(_2\)/He, and CO/He gas feed. Operating the fuel cell in coconut carbon and the H\(_2\)/He gas feed produced a stable current density output of 0.47 Acm\(^{-2}\), consistent with the fuel cell performance reported in previous studies for Ni/YSZ anodes.[7] Changing the gas feed from He/H\(_2\) to pure He allowed operating the fuel cell exclusively in coconut carbon, causing a rapid decrease in current density output to 0.095 Acm\(^{-2}\), and the simultaneous increase in the MS profiles for CO (m/e=28) and CO\(_2\) (m/e=44). This increase in the MS profiles indicates that CO and CO\(_2\) are the main products of the C-SOFC.
Figure 3.2 MS profiles of the effluents from the fuel cell anode compartment during testing in coke at 750 °C, a load of 400 mV, and a gas feed of (a) H₂/He (265 sccm, 27.2 vol% H₂), and (b) pure He (200 sccm).

Figure 3.3 shows the fuel cell V-I curves in coconut carbon recorded after the continuous operation at 0.4 V for 39 min shown in Figure 3.2, displaying a maximum power density of 0.09 Wcm⁻² and a maximum current density of 0.27 Acm⁻². The C-SOFC power density in this study exceeded those previously reported in the 0.005 – 0.04 Wcm⁻² range [6-7, 14-17]. The rapid decline in the voltage of the V-I curve at current densities above 0.20 Acm⁻² indicates the occurrence of the mass transfer limitation. The feeding CO₂/He and CO/He to the C-SOFC extend the current density to 0.47 and 0.49 Acm⁻². Feeding H₂/He feed (265 sccm, 27% H₂) further increase the maximum current density to 0.86 Acm⁻² which is smaller than those reported for state of the art Ni/YSZ
anode supported fuel cells[18]. The low fuel cell current density can attributed to the use of Fe-based steel current collectors with an area specific resistance of 0.6 $\square \text{cm}^2$, which contributes a higher resistance than those of high cost precious metal current collectors (i.e., Au, Pt and Pd). The use of Pt current collector with an area specific resistance of 0.1 – 0.2 $\square \text{cm}^2$ is expected to increase the maximum power density of our fuel cell by approximately 30 %[4, 19].

Changing the gas feed from He to CO$_2$/He increased (i) the OCV from 0.79 to 1.06 V, (ii) the maximum power density from 0.09 to 0.13 Wcm$^{-2}$, and the maximum current density from 0.27 to 0.47 Acm$^{-2}$. The increase in electric power generation was accompanied by an increase in CO formation, shown by the MS profiles of Figure 3.2, suggesting the occurrence of the Boudouard reaction (reaction 3), and the power generating electrochemical oxidation of CO (reaction 4). Changing the gas feed from CO$_2$/He to CO/He resulted in a little variation in the performance of the C-SOFC in Figure 3.3, and the CO/CO$_2$ concentration in Figure 3.2, indicating that the rate of reaction 3 is significantly higher than that of reaction 4.

Figure 3.3(b) shows the impedance spectra corresponding to the V-I curves taken under the carbon fuel cell mode and with CO feed at OCV. The high frequency intercept on the left side of the impedance circle gives the ohmic resistance ($R_\Omega$); the low frequency intercept on the right side gives the total cell resistance, while the difference of the two values gives the polarization resistance ($R_p$).[20]
Table 3.1 summarizes the ohmic resistances and polarization resistances of the carbon fuel cell from the impedance spectra in Figure 3.3(b). The ohmic resistances of the carbon fuel cell mode and with CO feed were consistent at 0.9 - 1.0 $\Omega \text{ cm}^2$ suggesting that degradation of the current collectors and increase of the electrolyte resistance were negligible during the experimental campaign. The use of Fe-based current collector contributed to the high ohmic resistance of the carbon fuel cell in this study in comparison the other YSZ electrolyte-SOFCs with Pt current collector which was reported to be around 0.2 – 0.4 $\Omega \text{ cm}^2$.[21][22]

Figure 3.3 Plot of (a) V-I curves, (b) electrochemical impedance spectra of carbon fuel cell operated in flowing He, 7.4 vol% and 14.6 vol% CO taken at OCV and 750 °C
Table 3.1 Summary of the carbon fuel cell ohmic and polarization resistances

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Pmax (W/cm$^2$)</th>
<th>$R_\Omega$ (Ωcm$^2$)</th>
<th>Rp (Ωcm$^2$)</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>0.09</td>
<td>0.9</td>
<td>1.6</td>
<td>C 40 min Figure 3.3</td>
</tr>
<tr>
<td>Carbon</td>
<td>0.07</td>
<td>1.0</td>
<td>1.2</td>
<td>C 120 min Figure 3.3</td>
</tr>
<tr>
<td>Carbon</td>
<td>0.15</td>
<td>0.17</td>
<td>1.0</td>
<td>[4]</td>
</tr>
<tr>
<td>Carbon</td>
<td>0.047</td>
<td>0.82</td>
<td>2.23</td>
<td>[17]</td>
</tr>
<tr>
<td>CO</td>
<td>0.12</td>
<td>1.0</td>
<td>3.1</td>
<td>7.4% CO Figure 3.3</td>
</tr>
<tr>
<td>CO</td>
<td>0.14</td>
<td>1.0</td>
<td>2.6</td>
<td>14.6% CO Figure 3.3</td>
</tr>
<tr>
<td>CO</td>
<td></td>
<td></td>
<td></td>
<td>[23]</td>
</tr>
<tr>
<td>Butane</td>
<td>0.032</td>
<td>2.3</td>
<td>5.2</td>
<td>[20]</td>
</tr>
<tr>
<td>Syngas</td>
<td>0.09</td>
<td>1.2</td>
<td>10.8</td>
<td>[23]</td>
</tr>
<tr>
<td>H$_2$</td>
<td>0.22</td>
<td>0.9</td>
<td>1.1</td>
<td>This work</td>
</tr>
<tr>
<td>H$_2$</td>
<td>0.08</td>
<td>2.5</td>
<td>1.5</td>
<td>[20]</td>
</tr>
<tr>
<td>H$_2$</td>
<td></td>
<td>0.2</td>
<td>0.4</td>
<td>[22]</td>
</tr>
<tr>
<td>H$_2$</td>
<td>0.9</td>
<td>0.2</td>
<td>0.2</td>
<td>[21]</td>
</tr>
<tr>
<td>H$_2$</td>
<td>0.08</td>
<td>0.9</td>
<td>1.6</td>
<td>[24]</td>
</tr>
<tr>
<td>H$_2$</td>
<td>0.14</td>
<td>1.2</td>
<td>0.5</td>
<td>[25]</td>
</tr>
<tr>
<td>H$_2$</td>
<td></td>
<td>1.2</td>
<td>6.8</td>
<td>[23]</td>
</tr>
</tbody>
</table>

The loss caused by electrochemical reactions at the electrode surfaces is related to the polarization resistance. The polarization resistances of the carbon fuel cell operated in carbon and added CO mode were in the range of 1.5 – 2.3 and 2.6 – 3.1 Ω cm$^2$. This result was further investigated by estimating the current exchange density of the carbon fuel cell. The current exchange densities were obtained by the reduced Butler-Volmer equation at the condition near equilibrium potential.[26][27][28]

\[
l = i_0 \frac{nF\eta}{RT}
\]
where $I$ is the current density, $i_0$ is the current exchange density, $n$ is the number of electrons participated in the reaction, $\eta$ is the overpotential and $F, R, T$ are the Faraday constant, ideal gas constant and temperature, respectively. The current exchange density of carbon fuel cell in carbon at 40 min was 0.032 A/cm$^2$ and that of 7.4 % and 14.6 % CO were 0.014 and 0.021 A/cm$^2$. Considering the activation loss on the cathode electrode was consistent, this result suggests that the rate of carbon electrochemical oxidation was higher than the rate of CO electrochemical oxidation at low current density.

The V-I curve observed in coconut carbon and He feed in Figure 3.3 was replotted in Figure 3.4 along with the CO and CO$_2$ molar flow rates resulted from calibration of the C-SOFC MS profiles, and the equilibrium CO and CO$_2$ molar flow rates from the thermodynamic calculation. The CO and CO$_2$ molar flow rates obtained from the fuel cell MS profiles under OCV conditions, shown in Figure 3.4(b), were produced from pyrolysis of coconut carbon. The coconut carbon reacted with –OH functional group on its surface producing CO and CO$_2$, as evidenced by IR studies discussed later in a later section. Withdrawing current by applying a load to the C-SOFC initiated the electrochemical oxidation, resulting in increased formation of CO and CO$_2$. Drawing 0.27 Acm$^{-2}$ increased the CO and CO$_2$ molar flow rates to 2.56 and 0.75 $\mu$mol s$^{-1}$, respectively, evidencing these species constitute the main byproducts of the C-SOFC.
Figure 3.4 Plots of (a) voltage, (b) CO and CO$_2$ effluent molar flow rates, and (c) equilibrium molar flow rates as a function of current density for the C-SOFC operated on coconut carbon and He feed (200 sccm) at 750 °C.
The equilibrium molar flow rates of carbon, CO and CO$_2$ as a function of current density, shown in Figure 3.4(c), were obtained through minimization of Gibbs free energy considering a stoichiometric C/O$_2^-$ ratio. The absence of CO and CO$_2$ molar flow rates at 0 Acm$^{-2}$ reflects the lack of O$_2^-$ crossing the YSZ electrolyte under OCV conditions. In contrast to the thermodynamic calculation, the experimental data showed that CO and CO$_2$ were produced at OCV from oxidation of coconut carbon. Hence, it is appropriate to compare the relative increase in the CO and CO$_2$ flow rates ($\Delta F_{\text{CO}}$ and $\Delta F_{\text{CO}_2}$) obtained when drawing current from the C-SOFC to the equilibrium CO and CO$_2$ flow rates from the thermodynamic calculation. Figure 3.4(b) shows $\Delta F_{\text{CO}}$ and $\Delta F_{\text{CO}_2}$ at a current density of 0.27 Acm$^{-2}$ were 0.61 and 0.68 µmols$^{-1}$ while the predicted equilibrium CO and CO$_2$ flow rates, shown in Figure 3.4(c), were close to 1.40 and 0.01 µmols$^{-1}$. The thermodynamic calculation showed CO to be the main product under the fuel cell operating conditions with negligible amounts of CO$_2$, in agreement with previous research work [11].

The absence of CO$_2$ at equilibrium can be attributed to the high forward reaction rate of CO$_2$ + C $\rightarrow$ 2CO at elevated temperatures which can convert majority of CO$_2$ to CO in the presence of carbon [29]. The high CO$_2$ molar flow rates observed during the experiment suggest that the C-SOFC did not operate close to equilibrium conditions. Operation of the C-SOFC close to equilibrium conditions (i.e., producing high CO concentrations and negligible CO$_2$ formation) could be obtained by decreasing the carrier gas flow rate, as reported in our previous work [3]. The increased evolution of CO$_2$ during the experiment could result from electrochemical oxidation of carbon (reaction 1) and/or CO (reaction 4). The contribution of reactions 1 and reaction 4 to the evolution of
CO\textsubscript{2} was further investigated by analyzing the C-SOFC performance in CO\textsubscript{2}/He and CO/He gas feeds.

Figure 3.5 Plots of (a) voltage, (b) CO and CO\textsubscript{2} effluent molar flow rates, and (c) equilibrium flow rates as a function of current density for the C-SOFC operated on coconut carbon and CO\textsubscript{2}/He feed (210sccm, 8.6 vol\% CO\textsubscript{2}) at 750 °C.
Figure 3.5 shows the fuel cell V-I curve observed in coconut carbon and the CO₂/He feed as well as the CO and CO₂ molar flow rates resulted from calibration of the C-SOFC MS profiles, and the equilibrium CO and CO₂ molar flow rates from the thermodynamic calculation. Despite the presence of the CO₂/He feed (8.6 vol% CO₂, 2.4 µmols⁻¹), CO was the major product from the C-SOFC under OCV conditions with 6.63 µmols⁻¹ of CO and 4.87 µmol s⁻¹ of CO₂. This result shows that majority of CO₂ reacted with carbon producing CO at 750 °C, in agreement with the thermodynamic calculation of the equilibrium molar flow rates shown in Figure 3.5(c). Drawing current from the C-SOFC decreased the CO and increased the CO₂ molar flow rate. This observation suggests that the rate of CO₂ formation from electrochemical oxidation of carbon and CO (reaction 1 and 4) is higher than that of CO formation from Boudouard reaction and electrochemical oxidation of carbon to CO (reaction 2 and 3).
Figure 3.6 Plots of (a) voltage, (b) CO and CO\(_2\) effluent molar flow rates, and (c) equilibrium flow rates as a function of current density of the C-SOFC operated on coconut carbon and CO/He feed (210 sccm, 7.4 vol% CO) at 750 °C.
Figure 3.6 shows the fuel cell V-I curves in coconut carbon and the CO/He feed, as well as the CO and CO$_2$ molar flow rates obtained from calibration of the C-SOFC MS profiles, and the equilibrium CO and CO$_2$ molar flow rates from the thermodynamic calculation. Exposure of the fuel cell to the CO/He feed (7.4 vol% CO, 10.5 µmol$^{-1}$) under OCV conditions produced a molar flow rate of 8.01 and 1.77 µmol/sec for CO and CO$_2$, respectively. Drawing 0.27 Acm$^{-2}$ resulted in $\Delta F_{CO}$ of 0.41 µmol$^{-1}$, while the outlet CO molar flow rate decreased by 0.06 µmol$^{-1}$ ($\Delta F_{CO} = -0.06$ µmol/sec). Pursuing mole balance on carbon at 0.27 Acm$^{-2}$ revealed that the amount of consumed CO could only account for 14% of the increase CO$_2$. This result suggests that at current densities less than 0.27 Acm$^{-2}$, more than 80% of the electricity was produced from electrochemical oxidation of carbon to CO$_2$ (reaction 1). Drawing 0.51 Acm$^{-2}$ caused a rapid decrease in CO ($\Delta F_{CO} = -1.79$ µmol$^{-1}$) and an increase in CO$_2$ ($\Delta F_{CO2} = 1.74$ µmol$^{-1}$) molar flow rates, indicating that at high current densities the C-SOFC produces electricity by electrochemical oxidation of CO. These results are consistent with those of the C-SOFC with CO$_2$/He feed, showing that the rate of reaction 1 and 4 was higher than those of reaction (2) and (3). Considering that the rate of Boudouard reaction (reaction 3) was not affected by the applied current, the formation of CO$_2$ was promoted with increasing current density, a phenomena previously reported during the electrochemical oxidation of CH$_4$ on Ag catalyst [30-31]. The equilibrium diagram of carbon, CO, and CO$_2$ as a function of current density in the CO/He feed is shown in Figure 3.6(c). Similarly to the equilibrium diagram of C-SOFC in He feed, CO is suggested to be the major product with negligible amounts of CO$_2$ produced. In contrast to this equilibrium diagrams, the experiment showed evolution of CO$_2$ and consumption of CO at high
current densities, showing that the C-SOFC with CO/He feed was not operated near equilibrium conditions.

Figure 3.7 Plot of (a) CO and CO\textsubscript{2} equilibrium molar flow rates and (b) ratio of the equilibrium CO\textsubscript{2}/CO flow rates as a function of temperature for the C-SOFC operated at 0.5 and 1 A/cm\textsuperscript{2} on carbon with He feed (200 sccm).

Figure 3.7(a) shows the CO and CO\textsubscript{2} equilibrium molar flow rates as a function of temperature for the C-SOFC with He feed at a current density of 0.50 and 1 A/cm\textsuperscript{2} on carbon with He feed (200 sccm).

The equilibrium calculation indicates that elevating the C-SOFC operating temperature from 500 to 750 °C increases the CO flow rate. At temperatures above 750 °C, CO
becomes the dominant product while CO$_2$ flow rates reaches close to 0.01 µmols$^{-1}$. As a result operation of the C-SOFC at lower temperatures can increase the CO$_2$/CO molar flow rate ratio. Operation at high current densities (i.e., 1 Acm$^{-2}$) can also result in higher CO$_2$/CO ratio as shown in Figure 3.7(b), as suggested by previous thermodynamic studies of carbon fuel cells [11]. Evolution of high CO$_2$/CO molar flow rate ratios benefits the C-SOFC energy conversion efficiency, since electrochemical oxidation of carbon producing CO$_2$ is a four-electron process and that of CO is a two-electron process [16].

Figure 3.8 Images of (a) SEM image of the surface of carbon fuel cell anode and the corresponding EDX mapping of (b) Ag, (c) Ni, and (d) Zr

The SEM micrograph in Figure 3.8 displays a low porosity surface of the Ni/YSZ anode, which was estimated to be 20.7 % by Archimedes method [32]. The relatively
low porosity of the fuel cell anode relative to typical porosities of anode supported Ni/YSZ fuel cell (i.e., 35%) was intentionally set during the fabrication procedure with the purpose of enhancing the rigidity of the C-SOFC assembly, as discussed elsewhere [33]. EDX analysis of the Ni/YSZ anode surface shows that Ag particles (0.8 – 1.2 µm in diameter) were deposited on the Ni particles (2 – 3 µm in diameter) [24] with a molar ratio of Ag to Ni of 0.1. The composition of the coconut carbon was determined by X-Ray Fluorescence (XRF) prior to the fuel cell experiments, revealing a content of 1.5% of potassium (K) and 0.8% calcium (Ca) considering 3% of ash in coconut carbon. The presence of these alkaline metals in coconut carbon can catalyze formation of CO and CO$_2$ at elevated temperatures [34], explaining the molar CO and CO$_2$ flow rates observed during the C-SOFC testing in He feed at OCV conditions (Figure 3.4). The evolution of CO and CO$_2$ from coconut carbon at high temperature was further studied by infrared (IR) spectroscopy. Figure 3.9(a) shows the IR absorbance spectra of a sample of coconut carbon recorded at room temperature, displaying the presence of surface C-O, C-H, and O-H functional groups. The presence of these functional groups in coconut carbon is consistent with those reported in previous IR studies of carbon samples [35-36]. Heating the coconut carbon samples in inert He environment to 400, 500, 600 and 680 °C, as the IR absorbance shown in Figure 3.9(b), caused the progressive decrease in the intensity of the C-O-H and O-H bands at 1390 and 3160 cm$^{-1}$, and the simultaneous evolution of CO$_2$ at 2350 cm$^{-1}$. These results suggest that O-H functional group on the surface of coconut coke may react with carbon producing CO and CO$_2$ which was observed during the operation of C-SOFC at OCV conditions. In addition to the production of CO and CO$_2$, dissociation of C-O in C-O-H functional group could produce graphite structure and
increase the conductivity of the carbon [37]. The electrical conductivity of the coconut carbon was determined to be 0.21 S cm\(^{-1}\), which is comparable to that of highly conductive carbon black [38]. The high conductivity of the coconut carbon could facilitate the transportation of electrons and the electrochemical oxidation of the carbon on the anode.

![Figure 3.9 IR Absorbance spectra of coconut carbon (5% in KBr) (a) at room temperature, and (b) during heating to 400, 500, 600 and 680 °C in He environment. Absorbance was obtained by Abs. = \log(I_0/I) where I is single beam spectra taken during the heating and I_0 is single beam taken during the cooling at the corresponding temperature.](image-url)
3.5 Conclusion

The operation of a solid oxide fuel cell with coconut carbon (C-SOFC) at 750 °C produced a maximum current density of 0.27 Acm\(^{-2}\) and produced less CO and more CO\(_2\) from those predicted by thermodynamic calculation. The impact of CO and CO\(_2\) concentration in the anode chamber on the electricity generation was studied by addition of a CO and CO\(_2\) stream. The addition of the CO\(_2\) stream increased CO formation and maximum power density from 0.09 Wcm\(^{-2}\) to 0.13 Wcm\(^{-2}\), indicating the occurrence of Boudouard reaction (CO\(_2\) + C \rightarrow 2CO) coupling with CO electrochemical oxidation on the C-SOFC. The contribution of C and CO to the electrical power generation was investigated by analysis of CO and CO\(_2\) concentration at different operating voltage. Reducing the operating voltage shows an increase in CO\(_2\) formation at low current density and rapid consumption of CO at high current density, revealing that at low current density, electricity was produced from an electrochemical oxidation of carbon, while more CO was consumed to produce electricity at higher current density.
3.6 References


CHAPTER IV
FAST PYROLYSIS OF BIOMASS AND COAL: AN IN SITU FTIR

Research performed in this chapter focused on operation of the fuel cell with fresh biomass. Biomass was used instead of coal because the coke produced from biomass contains significant amount of ash, allowing measurement of carbon-based fuel cell performance without ash interference. The study includes analysis of the coconut shell fast pyrolysis product, reaction pathway and the operation of the fuel cell with coconut shell. This work contributes to the fuel cell research topic by (i) emulating the environment of solid biomass/coal during their injection to the high temperature anode chamber of the fuel cell, (ii) providing the feasibility of utilizing biomass as a fuel for the fuel cell and (iii) evaluating fuel cell performance without ash interference.

4.1 Abstract

The reaction pathway of coconut shell fast pyrolysis was studied by analysis of the transient evolution product profiles as a function of temperature, measured directly in the sample bed. Fast pyrolysis of coconut shell produced (i) pyrolysis liquid containing C-H, C=O, and C-O-C bands, (ii) char with the absence of C-OH and C=O suggesting that ether and carbonyl compounds were decomposed below 600 °C, and (ii) gaseous product majorly consisting of CO₂. Increase the heating rate has a greater effect on increasing the yield of aliphatic and carbonyl compounds compared to that of aromatic compounds. The selectivity of the fast pyrolysis liquid was shifted from vinyl species to
carbonyl species 500 and 615 °C. In situ IR study suggests that CO and CO₂ were mainly produced from cracking of C-H and C=O bonds. Fast pyrolysis of D₂O-saturated coconut shell showed that moisture in the biomass does not increase the H₂ yield at high temperature and H₂ is mainly produced from breaking of C-H bonds.

4.2 Introduction

Biomass is considered an environmentally friendly alternative to fossil fuels because it is naturally produced by photosynthesis from CO₂ and H₂O.[1-2] Production of gas and liquid fuels from biomass can be achieved through thermal conversion processes. These processes can be categorized into combustion, gasification, and pyrolysis according to the operating conditions. Pyrolysis operates in the absence of O₂ producing high liquid yields at elevated temperatures (400-500 °C), vapor residence times less than 5 s, and an apparent heating rate of 10 - 200 °C/s[3-5]. Apparent heating rates are usually determined by the temperature of the heating unit; i.e., oven or furnace.

Various kinds of biomass has been extensively investigated for fast pyrolysis, including corn stover, switchgrass, logging residue, and coconut shell. Coconut is one of the most abundant biomass, with a global production of 62.5 million tons per year[6]. Coconut shell, accounting for approximately 25 wt.% of a coconut, offers uniqueness of low ash and high alkaline contents. Because of the catalytic activity of alkali for gasification, coconut has been used as an activated carbon precursor. The low ash content allows coconut char to serve as an excellent fuel for carbon fuel cells[7].

Many studies have reported evolution profiles of gaseous products from conventional and fast pyrolysis.[8-10] The highly transient nature of fast pyrolysis presents a challenge for investigating the reaction process. Fast pyrolysis is typically
studied by analysis of accumulated gaseous and liquid products from heated biomass without a direct temperature measurement. An indirect temperature measurement, i.e., measurement of the oven temperature instead of the biomass temperature, leads to an overestimation of the actual biomass heating rate and neglects the effect of temperature gradients across the biomass sample on the overall pyrolysis process. The temperature gradients across the sample are usually large due to biomass poor thermal conductivity. Multiple temperature measurements, in the sample bed and at the surface, are needed for an accurate analysis of the transient reactions and the products evolved at different pyrolysis temperatures.

This study reports results of a fast pyrolysis study with emphasis on the analysis of the transient evolution product profiles as a function of temperature, measured directly in the biomass reactant. Coconut shell samples were pyrolyzed in a tubular reactor and an in situ high temperature DRIFT (Diffuse Reflectance Infrared Fourier Transform) cell. The use of high temperature DRIFT allows the examination of the surface structure of the biomass throughout the fast pyrolysis process. The fast pyrolysis of 15 mg sample in the DRIFT cell generates very small amounts of gaseous and liquid products, limiting the study of their properties. The tubular reactor with 1.2 g sample was employed for analysis of the reaction products. The fast pyrolysis in the tubular reactor produces sufficient amounts of products for IR analysis and allows the tuning of the pyrolysis conditions i.e., heating rate and maximum pyrolysis temperature. The results from this study show that CO₂ is the major gaseous product followed by CO, CH₄, and H₂. In situ IR study showed that the major liquid products change from vinyl-containing species to carbonyl-containing species when the pyrolysis temperature reached 615 °C. The effect
of moisture on H$_2$ production was studied by addition of D$_2$O to the dry coconut shell followed by fast pyrolysis in the tubular reactor. The moisture content in biomass was found to have no effect on H$_2$ yield.

4.3 Experimental

This section describes the fast pyrolysis experiment, an in situ FTIR study, and the fuel cell testing with coconut shell.

4.3.1 Fast pyrolysis experiments

The fast pyrolysis experimental apparatus, illustrated in Figure 4.1, consists of a high temperature furnace and an in-house built tubular reactor (5”L x 0.25” ID). The tubular reactor effluent line is connected to a cold trap to collect condensable volatiles. The composition of the gaseous effluent is analyzed by a Pfeiffer GSD-301 quadruple mass spectrometer (MS). The coconut shell for fast pyrolysis was dried in an oven at 120 °C for 12 hours. The dried coconut shell was ground with a rotary grinder to a particle size between 3 and 5 mm diameter. The tubular reactor was loaded with 1.1 – 1.2 g of the ground coconut shell and purged with He prior to the fast pyrolysis. The fast pyrolysis was initiated by inserting the tubular reactor into a preheated furnace at the temperature of interest, (i.e., 400-650 °C) and held for 20 minutes. The temperature of the biomass was monitored by two thermocouples, one on the sample holder wall ($T_w$) and one in the biomass sample bed ($T_s$). The multiple temperature measurements allow determination of the temperature gradient and the water evaporation process. Heating rates were controlled by adjusting the sample position in the tubular reactor with a mobile plunger. Flowing He at 50 cm$^3$/min was used as a carrier gas to ensure inert environment and to remove gas and vapor products from the reacting biomass. The vapor products
were condensed and collected on a cotton cloth filter housed within the cold trap. The effluent from the cold trap was monitored by MS to analyze the composition of the gaseous products of the fast pyrolysis as a function of $T_w$ and $T_s$. The MS response of the each gas specie was converted to volumetric flow rate (i.e., mole fraction x total volumetric flow rate) profiles by means of a calibration factor. The calibration factors were obtained by analyzing a calibration gas sample with known concentrations of $H_2$, He, CO, CO$_2$, and CH$_4$. Coconut char and pyrolysis liquid obtained from the experiment were characterized by a DRIFT cell situated in a Nicolet 560 FT-IR bench and XRF (X-ray fluorescence spectrometer, micro EDX1300, Shimadzu).

4.3.2 In situ FTIR study

Coconut shell fast pyrolysis was performed in a high temperature DRIFT cell situated in an IR bench. The ground coconut shell sample was pulverized and mixed with KBr to dilute the coconut sample down to 10 wt.%. The DRIFT cell was loaded with 150 mg of the coconut shell/KBr sample and heated from room temperature to 580 °C at a heating rate of 83 °C/min under flowing He at 50 cm$^3$/min. The temperature of sample was monitored from the thermocouple located at the center of the sample bed. The DRIFT cell was held at 580 °C for 15 minutes and cooled to room temperature. IR spectra of the coconut shell/KBr were collected throughout the experiment.
4.3.3 Fuel cell testing with coconut shell

Coconut shell was used as a fuel for a carbon fuel cell. Fabrication of the anode-supported cell and procedure of attaching the current collectors were described in the previous quarterly report. The anode of the fuel cell was attached to the steel tube and place in a furnace. Prior to the operation in coconut shell, the fuel cell was heated under flowing H$_2$/He (100 cm$^3$/min, 50 vol.% H$_2$) at 750 °C for 12 h. The operation of the fuel cell in coconut shell was performed by (i) switching the gas feed from H$_2$/He to 10 cm$^3$/min He, (ii) operating the fuel cell at 0.4 V, (iii) injecting 1.03 g of coconut shell on to the fuel cell anode, and (iv) monitoring the composition of the gaseous species from the effluent. The injection procedure of the coconut shell on the fuel cell anode involved
purging and pressurizing the injecting chamber with He for 30 min to minimize disturbance of O₂ during the injection. The operating efficiency and the effective efficiency of the fuel cell operated in coconut shell were determined via the formulation shown in Table 4.1.

Table 4.1 Fuel cell efficiency types and definitions

<table>
<thead>
<tr>
<th>Efficiency</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating efficiency</td>
<td>$\xi_{\text{operating}} = \frac{W_e}{\text{energy input}}$</td>
</tr>
<tr>
<td>Thermodynamic efficiency</td>
<td>$\xi_{\text{thermo}} = \frac{\Delta G}{\Delta H}$</td>
</tr>
<tr>
<td>Load efficiency</td>
<td>$\xi_{\text{load}} = \frac{E(i)}{E^0_H}$</td>
</tr>
<tr>
<td>Fuel efficiency</td>
<td>$\xi_{\text{fuel}} = \frac{(i/nF)}{v_{\text{fuel}}}, \frac{\text{mass}<em>{\text{reacted}}}{\text{mass}</em>{\text{feed}}}$</td>
</tr>
<tr>
<td>Effective efficiency</td>
<td>$\xi_{\text{eff}} = \xi_{\text{ideal}} \times \xi_{\text{load}} \times \xi_{\text{fuel}}$</td>
</tr>
</tbody>
</table>

Table 4.1 shows the definition of efficiencies describing a performance of the fuel cells. Operating efficiency is determined by the amount of actual electric energy generated from the fuel cell vs. the amount of energy input. Thermodynamic efficiency is the amount of useful energy that can be exploited relative to the maximum work by the enthalpy input. The load efficiency represents the losses due to irreversible reaction in the fuel cell, which incorporates the actual cell voltage, $E(i)$, and the thermal cell voltage or Nernst potential, $E^0_H$. The fuel efficiency or gaseous fuel utilization is the ratio of molar flow rate of fuel that is actually consumed in the fuel cell for producing electricity to the molar flow rate of fuel entering the fuel cell, $v_{\text{fuel}}$; the fuel efficiency of solid fuel utilization is the ratio of mass of the fuel reacted in the operation to the mass of the fuel fed to the fuel cell. The effective efficiency considers the above losses, representing the
theoretical amount of energy that the fuel cell system can produce in comparison to the amount of fuel used.

4.4 Results and Discussion

This section describes the result of study of biomass fast pyrolysis pathway and efficiency of carbon fuel cell operated with biomass and coal.

4.4.1 Study of biomass fast pyrolysis pathway

Figure 4.2 shows the effluent volumetric flow rate from coconut shell fast pyrolysis in the tubular reactor with heating rates of 175 and 75 °C/min. The effluent volumetric flow rate was obtained by multiplying mole fraction of each species with the total volumetric flow rate. Figure 4.2 (a), (c), and (e) are plotted as a function of T_w, the sample holder wall temperature, representing the temperature of the outer surface of the biomass sample. Figure 4.2 (b), (d), and (e) are plotted as a function of T_s, the biomass sample bed temperature. Heavy hydrocarbons were condensed in the cold trap for the IR analysis. Heavy hydrocarbons, often plugging the MS sampling line, were not allowed to enter MS and are excluded from the analysis in Figure 4.2. CO₂ was produced as T_s reached 150 °C for the heating rate of 75 and 175 °C/min. The formation of CO, CH₄, and H₂ followed that of CO₂ as the temperature continued to increase. The temperature at which the formation of CO₂ and CO reached the maximum was at T_s equal to 300 °C. It has been reported that the pyrolysis of cellulose produces CO₂ and CO between 300 and 400 °C in a TGA experiment[11-12]. Comparison of our results with these reported results reveal the possibility of a significant temperature gradient across the bulk of the biomass samples in many reported data. This is not surprising due to the low thermal conductivity of biomass.
Figure 4.2. Effluent volumetric flow rate vs. sample holder wall temperature and sample bed temperature for coconut shell pyrolysis at heating rates of 175 °C/min and 75 °C/min.

CO₂ was proposed to be produced by cracking and reforming of C=O bonds, and CO was purposed to be generated from cracking of C-O-C and C=O bonds.[13] This pathway, shown in Figure 4.1(b), was further verified from the results of our in situ IR study, which will be discussed in Figure 4.5. The formation of CH₄, an indicative of C-C bond breaking, started at T_w of 400 °C. Continuing increasing the temperature to 500 °C resulted in release of H₂, suggesting the breaking of C-H bond and the formation of H-H bond. The formation of CH₄ and the evolution of H₂ at T_w = 400 and 500 °C are consistent with literature showing the H₂ was produced from pyrolysis of cellulose,
hemicellulose and lignin at the temperature above at temperatures above 400 °C[11]. These results are also consistent with the fact that the bond energy of C-C bond (348 kJ/mol) is less than that of C-H bond (413 kJ/mol).

Examining the effect of the heating rate on the gas evolution by comparing the gas profiles from Figure 4.2(a) to (c) revealed that fast pyrolysis at a high heating rate produced gaseous products in a wider temperature range than fast pyrolysis at a low heating rate. We can attribute this observation to the high temperature gradient between the surface and the bulk of the sample bed. Higher heating rate generated a greater gradient between $T_w$ and $T_s$. As a result, the coconut shell experienced a wider range of temperatures across the sample bed. Coconut shell fast pyrolysis at 75 °C/min shows two peaks for CO evolution. The first CO peak may be produced from pyrolysis, while the second CO peak at high temperature might be caused by secondary reaction between CO$_2$ and carbon. This behavior of two main CO generation peaks was also reported in literature for the pyrolysis of hemicellulose.[11] The amount of each gaseous product was quantified and summarized in Table 4.2.
Table 4.2 Product yields and experimental conditions for coconut shell fast pyrolysis.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(a),(b)</td>
</tr>
<tr>
<td>Maximum $T_w$ ($^\circ$C)</td>
<td>630</td>
</tr>
<tr>
<td>Heating rate ($^\circ$C/min)</td>
<td>175</td>
</tr>
<tr>
<td>Dry weight (g)</td>
<td>1.13</td>
</tr>
<tr>
<td>Coconut char yield (wt. %)</td>
<td>25.4</td>
</tr>
<tr>
<td>Gas yield$^a$ (wt. %)</td>
<td>5.8</td>
</tr>
<tr>
<td>Liquid yield$^b$ (wt. %)</td>
<td>68.9</td>
</tr>
</tbody>
</table>

Gas products (mmol/g biomass)

<table>
<thead>
<tr>
<th></th>
<th>(a),(b)</th>
<th>(c),(d)</th>
<th>(e),(f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>0.97</td>
<td>0.99</td>
<td>0.48</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>2.04</td>
<td>2.73</td>
<td>3.06</td>
</tr>
<tr>
<td>CO</td>
<td>0.26</td>
<td>0.36</td>
<td>0.33</td>
</tr>
<tr>
<td>H$_2$</td>
<td>0.58</td>
<td>0.34</td>
<td>0.04</td>
</tr>
</tbody>
</table>

$^a$ Determined by MS.

$^b$ Determined by mass balance.
Table 4.2 shows the product yields and fast pyrolysis conditions for the experiments shown in Figure 4.2. Decreasing the pyrolysis temperature caused reduction in the yield of gaseous products and increased the yield of coconut char observed in experiments (c) and (e). A reduction in the heating rate increased the yield of coconut char and gaseous products, as observed in experiments (a) and (c). These results validate the characteristic of the fast pyrolysis process, which is known for producing high liquid yields.[14] The production of higher liquid yields from higher heating rates is expected because the volatiles produced from the fast pyrolysis are allowed to further react at high temperature for short residence time producing more liquid products and leaving the high temperature before cracking or coking.[3, 15-16] The liquid yield for coconut shell fast pyrolysis reported in this work is comparable to those reported for other biomass sources. Table 4.3 provides a literature review of oil yield from various sources of biomass and different fast pyrolysis conditions.

The ratio of CO to CO$_2$ produced from fast pyrolysis was independent of the heating rate, which CO$_2$ was the major gaseous product. This result suggests that coconut shell contains a high amount of hemicelluloses which have been reported to produce more CO$_2$ than CO[11] via a pathway illustrated in Figure 4.1(b) that gaseous products was generated from cracking of intermediate species. The formation pathway of CO$_2$ and CO was proposed that saturation of aromatic rings and the breaking of C-C bond in lignin lead to the formation of CO$_2$ CO and water[13]. XRF was used to determine the composition of coconut char ash obtained from fast pyrolysis revealing a content of 82.7 mol% of K, 8.1 mol% of Cl, 6.5 mol% of Ni, and trace amounts of Fe and Cr. XRF only
measures the elements which have an atomic number greater than 23, as a result carbon, oxygen and hydrogen are not included in this analysis. The alkali content of the coconut char is similar to the alkali content in the coconut shell ash reported elsewhere, considering less than 3% of ash in coconut shell[17-20]. The heavy metal content (i.e., Ni, Cr, Fe) could be contaminants from the tubular reactor, indicating the corrosive nature of the fast pyrolysis process.
Table 4.3 Review of oil yield and operation conditions of biomass fast pyrolysis.

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Reactor</th>
<th>Temp (°C)</th>
<th>Oil yield (wt.%)</th>
<th>Residence time</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coconut shell</td>
<td>Fixed bed</td>
<td>615</td>
<td>61.0</td>
<td>20</td>
<td>4.8</td>
</tr>
<tr>
<td>Cotton seed</td>
<td>Fixed bed</td>
<td>550</td>
<td>48.3</td>
<td>30</td>
<td>88</td>
</tr>
<tr>
<td>Cotton seed</td>
<td>Fixed bed</td>
<td>550</td>
<td>42</td>
<td>30</td>
<td>88</td>
</tr>
<tr>
<td>Aspen wood</td>
<td>Batch</td>
<td>600</td>
<td>16</td>
<td>25</td>
<td>0.9</td>
</tr>
<tr>
<td>Sawdust</td>
<td>Cyclone</td>
<td>700</td>
<td>74</td>
<td>20</td>
<td>0.6</td>
</tr>
<tr>
<td>Tire rubber</td>
<td>PFR</td>
<td>500</td>
<td>54</td>
<td>20</td>
<td>0.6</td>
</tr>
<tr>
<td>Corn cob</td>
<td>Fluidized bed</td>
<td>400</td>
<td>57.1</td>
<td>10</td>
<td>4.8</td>
</tr>
<tr>
<td>Cassava plant</td>
<td>Fluidized bed</td>
<td>500</td>
<td>65</td>
<td>3.4</td>
<td></td>
</tr>
<tr>
<td>Mallee wood</td>
<td>Fluidized bed</td>
<td>500</td>
<td>52</td>
<td>120</td>
<td>4.1</td>
</tr>
<tr>
<td>Crop stems</td>
<td>Batch</td>
<td>450</td>
<td>52</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rice husk</td>
<td>Fixed bed</td>
<td>800</td>
<td>42</td>
<td>8</td>
<td>38</td>
</tr>
<tr>
<td>Rice husk</td>
<td>Fluidized bed</td>
<td>400</td>
<td>46.5</td>
<td>20</td>
<td>5</td>
</tr>
<tr>
<td>Rice husk</td>
<td>Fluidized bed</td>
<td>400</td>
<td>7.2</td>
<td>20</td>
<td>5</td>
</tr>
</tbody>
</table>
Figure 4.3 IR analysis of 5 wt.% coconut shell and coconut chars in KBr.

Figure 4.3 shows the IR absorbance spectra of coconut shell and coconut char obtained from fast pyrolysis. Absorbance was obtained by Abs. = \log(I_0/I) where I is single beam spectra of the coconut char sample and I_0 is single beam spectra of KBr. The absorbance spectrum of coconut shell exhibits distinct C=O band from carbonyl species (i.e., esters, carboxylic acid) at 1740 cm\(^{-1}\), aromatic ethers and aryl-alkyl ethers at 1238 cm\(^{-1}\), and C-OH band at 1112 cm\(^{-1}\). The predominance of these features and the broad adsorptions between 900 and 1400 cm\(^{-1}\) suggest that coconut shell is comprised mainly of lignin. The contribution of hemicellulose broadens the O-H stretching band between 3100 and 3600 cm\(^{-1}\) and C-H stretching bands between 2860 and 2927 cm\(^{-1}\). The absence of an intense absorption band at 1060 cm\(^{-1}\) for C-O stretching band and C-C stretching band between 400 and 700 cm\(^{-1}\) is characteristic of a low cellulose composition. The
relative composition estimated from IR analysis is in agreement with the literature value of 46 wt.% lignin, 32 wt.% hemicellulose, 14 wt.% cellulose, and 8 wt% residues[12].

The coconut char obtained from the fast pyrolysis at $T_w = 500 \, ^\circ C$ shows a few remaining C-H stretching bands accompanied by a reduction in the intensity of broad O-H stretching due to partial dehydration. The C-H bands intensity were further decreased with increasing fast pyrolysis temperatures, with a complete disappearance on coconut char obtained from fast pyrolysis at $T_w$ above 600 °C. Complete coconut shell dehydration occurred for during $T_w = 500$ to 615 °C, as shown in Figure 4.1(b), evidenced by the disappearance of the O-H stretching band. The C-OH, C=O from carbonyl species and the aromatic ether and aryl-alkyl ether absorption bands are absent in the coconut char spectrum produced at these temperatures. The absence of those absorption bands suggests that carbonyl and ether compounds in the coconut shell were decomposed at $T_w$ below 600 °C. A broad absorption bands between 1400 -1750 cm$^{-1}$ of coconut char pyrolyzed at $T_w$ = 615 and 630 °C is also reported from other biomass char obtained from the temperature range of 600 – 1000 °C[32]. The effect of the heating rate on the coconut char surface could not be clearly observed by the IR analysis.
Figure 4.4 IR analysis of liquid products from fast pyrolysis of coconut shell.

Figure 4.4 shows the IR absorbance spectra of the liquid obtained from fast pyrolysis. The measurement was performed by scanning a thin film of liquid applied on aluminum foil. Absorbance was obtained by Abs. = log(I/Isample) where I is single beam spectra of the liquid film sample and Isample is single beam spectra of the aluminum foil. The spectrum of liquids produced at 500 °C shows the presence of vinyl groups at 1660 cm⁻¹, C-H stretching bands at 2827 and 2650 cm⁻¹, and the absence of aromatic compounds. These results reveal that the liquid product of the fast pyrolysis of coconut shell at 500 °C consists of small hydrocarbons, suggested to be from the intermediate species shown in Figure 4.1(b). Increasing the pyrolysis temperature to 615 °C with the same heating rate of 75 °C/min increases the intensity of the C-H and C-OH bands, suggesting that oxygenated hydrocarbons are present in the liquid product. Disappearance of the vinyl
group from the spectrum of the liquid produced at 615 °C was accompanied by an increase in intensity of C=O at 1709 cm$^{-1}$ and 1740 cm$^{-1}$. This result shows that the selectivity of the fast pyrolysis liquid products was shifted from vinyl species to carbonyl species (ester, ketone, and carboxylic acid) at temperatures between 500 and 615 °C. Aromatic bands are observed on the spectrum of the pyrolysis liquid produced at 615 °C corresponding to the decrease in the aromatic bands observed on the coconut char surface when the pyrolysis temperature increased from 500 °C to 615 °C. The effect of heating rate on the pyrolysis liquid properties was investigated by comparing the absorbance spectra of the pyrolysis liquids produced at 615 and 630 °C. Raising the heating rate from 75 to 175 °C/min predominantly increased in the intensities of C-H and C=O absorption bands. These results suggest that the higher heating rate has a greater effect on increasing the yield of aliphatic and carbonyl compounds compared to that of aromatic compounds.
Figure 4.5 In situ IR study of 10 wt.% coconut shell in KBr fast pyrolysis in DRIFT cell with heating rate of 83 °C/min. The spectra were collected for the heating (h) and cooling (c) stages. The difference spectra between heating and cooling are labeled as c-h.

Figure 4.5 shows the coconut shell absorbance spectra at various temperatures throughout the in situ IR study of fast pyrolysis in DRIFT cell. The absorbance during heating and cooling (denoted as h-temperature and c-temperature, respectively) were obtained by Abs. = log(1/I) where I is the single beam spectra of the sample during the heating or cooling stages. The difference spectra comparing cooling and heating (denoted as c - h) was obtained by Abs = log(1/I_{cooling}) - log(1/I_{heating}). The difference between heating and cooling absorbance spectra represents the changes in the
concentration of the specific functional group on the sample surface at the given temperature, indicating the progress of the reactions. Decomposition of aromatic compounds is indicated by the decrease in the aromatic band at 1607 cm\(^{-1}\) for pyrolysis at 200 to 400 °C. Increase in the peak intensity of O-H, C-OH, C-H, and C=O bands from h-c-200 °C to h-c-400 °C indicates the formation of intermediate species[15, 33], proposed in the pathway shown in Figure 4.1(b). Continue heating to 500 °C resulted in (i) partial dehydration evidenced by the decrease in intensity of O-H and C-OH bands, which is in agreement with the change on the surface of coconut char shown in Figure 4.3, (ii) decreased the C-H and C=O bands, suggesting conversion of these intermediate species to gaseous and vapor products via cracking of carbonyl compounds. This temperature range corresponds to the maximum flow rate of CO and CO\(_2\) from the fast pyrolysis experiment in the tubular reactor, suggesting that CO and CO\(_2\) were mainly produced from cracking of C-H and C=O bonds. Formation of liquid products was a result of rapid cooling of the intermediate species and vapor product forming small hydrocarbon and aromatics. Increasing the pyrolysis temperature to 580 °C completely dehydrates the coconut shell, evidenced by the absence of O-H and C-OH bands. Crossing-linking of aromatic and cracking aromatic ether and aryl-alkyl ether was observed from the decrease in the C-O-C above 500 °C. This cross-linking is proposed to produce coconut char. Further cracking of C-H bonds was also observed between 500 – 580 °C, matching the production of H\(_2\) from the fast pyrolysis in the tubular reactor. This result evidences that H\(_2\) was produced from cracking of C-H bonds present in the biomass.
Figure 4.6 Effluent volumetric flow rate vs. sample holder wall temperature and sample bed temperature for the fast pyrolysis of 19 wt.% D$_2$O coconut shell with heating rate of 120 °C/min.

The effect of moisture was studied on coconut shell saturated with D$_2$O (19 wt.% D$_2$O). The fast pyrolysis experiment in the tubular reactor was performed with a heating rate of 120 °C/min. The gas evolution profile as a function of $T_w$ and $T_s$ is shown in Figure 4.6. This profile is similar to that of the gas evolution for dry coconut shell pyrolysis with heating rate of 175 °C shown in Figure 4.2(a) and (b). Production of D$_2$ started at $T_w = 300$ °C and the maximum D$_2$ formation was observed at 450 °C. D$_2$ generation could result from the reaction of D$_2$O with CO via water-gas shift reaction (D$_2$O + CO $\leftrightarrow$ D$_2$ + CO$_2$). The low concentration of HD in the gaseous products results in a low intensity MS signal and the fluctuation was caused by multiplication of the signal. According to the detection limit of the MS toward D$_2$ and HD of less than 20
ppm, the result suggests that these products were formed only in trace amounts at the H₂ evolution region (> 500 °C)[34] and the moisture content in the biomass does not increase the H₂ yield for high temperature fast pyrolysis. In contrast, the effluent volumetric flow rate as a function of T_s exhibits a different trend than that observed for the other pyrolysis experiments (i.e, using dry coconut shell). The addition of D₂O caused the sample temperature to remain steady at 100 °C for approximately 15 s due to evaporation, while the temperature at the wall continued to rise generating the step-like increase in gas production observed at 100 °C.

4.4.2 Efficiency of fuel cell operated with biomass and coal

Figure 4.7 shows the MS profiles of the fuel cell effluent and the current generated by the fuel cell operated in coconut shell under 50 sccm He at a voltage of 0.4 V at 750 °C. The active cathode area of the fuel cell used in this study was 1 cm². Injection of coconut shell in the anode chamber at 750 °C produced rapid increase in the MS intensities of CO, CO₂, CH₄, and H₂ (m/e = 28, 44, 15, and 2 respectively). This increase was the result of pyrolysis of coconut shell which the production of gaseous species is in agreement with the result of the fast pyrolysis study. Injection of the coconut shell accompanied with the production of CO, CH₄, and H₂ increased the current produced by the fuel cell to the maximum of 0.14 A at 2 min after the injection. Operation of the fuel cell in coconut shell gradually decreased the current to 0.08 A in 37 min and the operation was stopped to determine the effective efficiency. The fuel cell was removed from the furnace immediately to prevent further pyrolysis reaction of the coconut shell in the anode chamber for accurate measurement of the fuel consumption.
Figure 4.7 MS profiles of the fuel cell effluent and the current generated by the fuel cell operated in coconut shell under 50 sccm He at 750 °C.

The operating efficiency was calculated by relating the electric power produced by the fuel cell at the operating voltage, $W_e$, and the energy provided from the consumption of the coconut shell.

$$ W_e = V \int I dt $$

where

$I = current (A)$

$V = voltage (V)$

$t = time (sec)$

Resulting in $W_e$ of 90.0 J.

The energy provided from coconut shell consumption is calculated as

$$ Energy = \left[ \text{LHV} \right]_{shell} \times \text{coconut shell injected} $$

Where
\[ LHV = \text{lower heating value (coconut shell} = 23.01 \text{ kJ/g, coconut char} = 30.12 \text{ kJ/g)} \]

Coconut shell injected = 1.03 g.

Coconut char remain on the fuel cell = 0.16 g.

Resulting in the energy input of 18.88 kJ

The operating efficiency of the fuel cell is calculated as

\[ \xi_{\text{operating}} = \frac{W_e}{\text{energy input}} = \frac{90.0 \text{ J}}{18.88 \text{ kJ}} = 0.48 \% \]

The effective efficiency, \( \xi_{\text{eff}} \), representing the theoretical limiting efficiency of the fuel cell at 0.4 V and 750 °C was calculated as

\[ \xi_{\text{net}} = \frac{\Delta G}{\Delta H_{298}} \times \frac{E(i)}{E^\theta_H} \times \frac{\text{fuel consumed}}{\text{fuel input}} = 1.18 \times \frac{0.40}{0.94} \times \frac{0.87}{1.03} = 44.6\% \]

Where \( \frac{\Delta G}{\Delta H_{298}} \) was estimated from the operation of carbon fuel cell producing equimolar of CO and CO\(_2\).

The low operating efficiency of the fuel cell operated in coconut shell can be attributed to the majority of the gaseous product produced from the fast pyrolysis leaving the anode chamber prior to the electrochemical oxidation due to the use of high carrier gas flow rate. The next experiment addressed this issue by reducing the carrier gas flow rate from 50 sccm to 6 sccm.

Figure 4.10 shows the effluent molar concentration and the current generated by the SOFC operated in coconut shell under 6 sccm Ar at a voltage of 0.3 V and 750 °C. Injection of coconut shell in the anode chamber at 750 °C produced rapid increase in the
molar concentration of CO, CO₂, CH₄, and H₂. This increase was the result of the fast pyrolysis of coconut shell, which produced majority of CO at 45 vol%. Injection of the coconut shell accompanied with the production of CO, CH₄, and H₂ increased the current produced by the fuel cell to the maximum of 0.19 A. Operation of the fuel cell in coconut shell gradually decreased the current to 0.05 A in 130 min and the operation was stopped. The fuel cell was removed from the furnace immediately to prevent further pyrolysis reaction of the coconut shell in the anode chamber for accurate measurement of the fuel consumption.

![Diagram](image.png)

Figure 4.8 Effluent molar concentration and the current generated by fuel cells operated with coconut shell under 6 sccm Ar at 0.3 V and 750 °C

The operating efficiency was calculated by relating the electric power produced by the fuel cell at the operating voltage, $W_e$, and the energy provided from the consumption of the coke.
\[ W_e = V \int I \, dt \]

where

\[ I = \text{current (A)} \]
\[ V = \text{voltage (V)} \]
\[ t = \text{time (sec)} \]

Resulting in \( W_e \) of 198.1 J.

The energy provided from coconut shell consumption is calculated as

\[ \text{Energy} = \frac{\text{LHV}}{\text{_shell}} \times \text{coconut shell injected} \]

Where

\[ \text{LHV} = \text{lower heating value (coconut shell = 23.01 kJ/g, coconut char = 30.12 kJ/g)} \]

Coconut shell injected = 0.5 g.

Coconut char remain on the fuel cell = 0.11 g.

Resulting in the energy input of 11.5 kJ

The operating efficiency of the fuel cell is calculated as

\[ \xi_{\text{operating}} = \frac{W_e}{\text{energy input}} = \frac{198.1 \text{ J}}{11.5 \text{ kJ}} = 1.7 \% \]

The effective efficiency, \( \xi_{\text{eff}} \), representing the theoretical limiting efficiency of the fuel cell at 0.4 V and 750 °C was calculated as

\[ \xi_{\text{net}} = \frac{\Delta G}{\Delta H_{298}} \times \frac{E(i)}{E_H} \times \frac{\text{fuel consumed}}{\text{fuel input}} = 1.18 \times 0.40 \times 0.94 \times 0.49 = 39.2\% \]

Where

\[ \frac{\Delta G}{\Delta H_{298}} \] was estimated from the operation of carbon fuel cell producing equimolar of CO and CO\(_2\).
Figure 4.9 Schematic diagram of material and energy balance of carbon fuel cell operated with coconut shell at 750 °C.

Figure 4.9 shows the schematic of the energy and material balance of the operation of carbon fuel cell with 0.5 g of coconut shell at 750 °C. The electric energy produced from fuel cell account for only 1.7% of the fuel energy, while the major loss was gases product (i.e., CO, H$_2$, CH$_4$). The study was repeated at elevated temperature of 800 °C to observe the change in fuel cell efficiency.

Figure 4.10 shows the effluent molar concentration and the current generated by the SOFC operated in coconut shell under 6 sccm Ar at a voltage of 0.3 V and 800 °C. Injection of coconut shell in the anode chamber at 800 °C produced rapid increase in the molar concentration of CO, CO$_2$, CH$_4$, and H$_2$. This increase was the result of the fast pyrolysis of coconut shell, which produced majority of CO at 40 vol%. H$_2$ yield increased from the operation at 750 °C which is in agreement with the fast pyrolysis result that H$_2$ was produced at high temperature. Injection of the coconut shell accompanied with the production of CO, CH$_4$, and H$_2$ increased the current produced by the fuel cell to the maximum of 0.15 A. Operation of the fuel cell in coconut shell gradually decreased the current to 0.05 A in 50 min and produce a stable current of 0.05 A for 3 h. The operation was stopped at 240 min due to the rapid decline in the SOFC.
current, suggesting the depletion of the coconut shell. The fuel cell was removed from the furnace immediately to prevent further pyrolysis reaction of the coconut shell in the anode chamber for accurate measurement of the fuel consumption.

![Figure 4.10 Effluent molar concentration and the current generated by 3 SOFCs operated with coconut shell under 6 sccm Ar at 0.3 V and 800 °C](image)

The operating efficiency was calculated by relating the electric power produced by the fuel cell at the operating voltage, $W_e$, and the energy provided from the consumption of the coke.

$$ W_e = V \int I dt $$

where

$I = current(A)$

$V = voltage(V)$

$t = time(sec)$

Resulting in $W_e$ of 262.1 J.

The energy provided from coconut shell consumption is calculated as
Energy = \[\text{LHV}_{\text{shell}} \times \text{coconut shell injected}\]

Where

\[\text{LHV} = \text{lower heating value (coconut shell = 23.01 kJ/g, coconut char = 30.12 kJ/g)}\]

Coconut shell injected = 0.5 g.

Coconut char remain on the fuel cell = 0 g.

Resulting in the energy input of 11.5 kJ

The operating efficiency of the fuel cell is calculated as

\[\xi_{\text{operating}} = \frac{W_e}{\text{energy input}} = \frac{262.1 J}{11.5 kJ} = 2.3 \%\]

The effective efficiency, \(\xi_{\text{eff}}\), representing the theoretical limiting efficiency of the fuel cell at 0.4 V and 750 °C was calculated as

\[\xi_{\text{net}} = \frac{\Delta G}{\Delta H_{298}} \times \frac{E(i)}{E_H^0} \times \frac{\text{fuel consumed}}{\text{fuel input}} = 1.19 \times \frac{0.40}{0.94} \times 1 = 50.9\%\]

Where

\[\frac{\Delta G}{\Delta H_{298}}\] was estimated from the operation of carbon fuel cell producing equimolar of CO and CO₂.
Figure 4.11 shows the schematic of the energy and material balance of the operation of carbon fuel cell with 0.5 g of coconut shell at 750 °C. The electric energy produced from fuel cell account for only 2.3% of the fuel energy, while the major loss was gases product (i.e., CO, H₂, CH₄). This improve in the efficiency can be attributed to the higher rate of carbon electrochemical oxidation at higher temperature. The study was repeated with coal as a fuel.

Figure 4.12 shows the current generated by the SOFC operated in coal under 6 sccm Ar at a voltage of 0.3 V and 800 °C. Injection of coconut shell in the anode chamber at 800 °C increased the current produced by the fuel cell to the maximum of 0.18 A. Operation of the fuel cell in coal gradually decreased the current to 0.0 A in 53.
Figure 4.12 The current generated by SOFCs operated with coal under 6 sccm Ar at 0.3 V and 800 °C.

The operating efficiency was calculated by relating the electric power produced by the fuel cell at the operating voltage, $W_e$, and the energy provided from the consumption of the coke.

$$ W_e = V \int I dt $$

where

$I = current (A)$

$V = voltage (V)$

$t = time (sec)$

Resulting in $W_e$ of 66.4 J.

The energy provided from coconut shell consumption is calculated as

$$ Energy = \frac{\text{LHV}_{coal}}{\text{coal}} \times \text{coal} $$

Where

$LHV =$ lower heating value (coal = 19.77 kJ/g)
Coconut shell injected = 0.58 g.

Resulting in the energy input of 11.5 kJ

The operating efficiency of the fuel cell is calculated as

\[
\xi_{\text{operating}} = \frac{W_e}{\text{energy input}} = \frac{66.4 \text{ J}}{11.5 \text{ kJ}} = 0.58 \%
\]

The low operating efficiency of the fuel cell operated in coal can be attributed to the majority of the gaseous product produced from the fast pyrolysis leaving the anode chamber prior to the electrochemical oxidation. Operation in the batch-mode will allow the pyrolysis gas to react on the fuel cell anode and increase the operating efficiency.

Figure 4.13 shows the current generated by the SOFC operated in coal with recycled gas stream of 200 sccm at a voltage of 0.3 V and 800 °C. Injection of coconut shell in the anode chamber at 800 °C increased the current produced by the fuel cell to the maximum of 0.20 A. Operation of the fuel cell in coal gradually decreased the current to 0.0 A in 60.
Figure 4.13 The current generated by 3 SOFCs operated with coal and recycle gas at 0.4 V and 800 °C

The operating efficiency was calculated by relating the electric power produced by the fuel cell at the operating voltage, $W_e$, and the energy provided from the consumption of the coke.

$$W_e = V \int I dt$$

where

$I = \text{current (A)}$

$V = \text{voltage (V)}$

$t = \text{time (sec)}$

Resulting in $W_e$ of 66.4 J.

The energy provided from coconut shell consumption is calculated as

$$\text{Energy} = [LHV]_{\text{coal}} \times \text{coal}$$

Where

$LHV = \text{lower heating value (coal = 19.77 kJ/g)}$
Coconut shell injected = 0.90 g.

Resulting in the energy input of 17.8 kJ

The operating efficiency of the fuel cell is calculated as

\[
\xi_{operating} = \frac{W_e}{\text{energy input}} = \frac{110.1 J}{17.8 \text{ kJ}} = 0.62 \%
\]

The operating efficiency of the fuel cell operated in coal with recycle gas show slight improvement over that without recycle gases. This improvement was not significant due to the leakage in the vacuum pump used for recycling the gases. The product of coal fast pyrolysis was studied separately in the next experiment.

Figure 4.14 shows the MS profiles from the effluent from coal fast pyrolysis in the tubular reactor with heating rates of 240 °C/min. Heavy hydrocarbons were condensed in the cold trap. Heavy hydrocarbons, often plugging the MS sampling line, were not allowed to enter MS and are excluded from the analysis in Figure 4.14. CO\textsubscript{2} was produced since T\textsubscript{s} was below 100 °C. The formation of CO, CH\textsubscript{4}, and H\textsubscript{2} followed that of CO\textsubscript{2} as the temperature continued to increase. The formation of CO\textsubscript{2}, CO, and CH\textsubscript{4} reached the maximum at T\textsubscript{s} equal to 400 °C. The majority of H\textsubscript{2} was produced at 400 – 700 °C.
Figure 4.14 Effluent MS profiles vs. sample holder wall temperature (T\textsubscript{w}) and sample bed temperature (T\textsubscript{s}) for the fast pyrolysis of coal in Ar (100 sccm)
Table 4.4 Summary of carbon fuel cell efficiencies

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Temp. (°C)</th>
<th>Carrier gas flow rate (sccm)</th>
<th>Energy produced (J)</th>
<th>( \xi_{operating} )</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coconut shell</td>
<td>750</td>
<td>50</td>
<td>90.0</td>
<td>0.45</td>
<td>The flow rate was too high</td>
</tr>
<tr>
<td>Coconut shell</td>
<td>750</td>
<td>6</td>
<td>198.1</td>
<td>1.32</td>
<td>The temperature was too low</td>
</tr>
<tr>
<td>Coconut shell</td>
<td>800</td>
<td>6</td>
<td>262.1</td>
<td>1.74</td>
<td>Energy lost in gas product</td>
</tr>
<tr>
<td>Coal</td>
<td>800</td>
<td>6</td>
<td>66.4</td>
<td>0.58</td>
<td></td>
</tr>
<tr>
<td>Coal</td>
<td>800</td>
<td>200*</td>
<td>110.1</td>
<td>0.62</td>
<td>Leakage problem</td>
</tr>
</tbody>
</table>

* recycled gas flow rate

4.5 Conclusion

\( \text{CO}_2 \) is the main gaseous product released from coconut shell fast pyrolysis at temperatures between 500 and 630 °C. Increasing the heating rate from 75 to 175 °C/min increased the temperature range of gaseous production due to high temperature gradient across the biomass sample. Higher heating rate decreases the gas and coconut char yield.

The IR analysis of coconut char and pyrolysis liquid indicates that higher heating rate increases the amount of aliphatic and carbonyl compounds and slightly increases the amount of aromatic compounds. In situ IR study reveals carbonyl intermediate species were formed between 200 and 400 °C, followed by breaking of \( \text{C}=\text{O} \) and \( \text{C}-\text{O}-\text{C} \) bonds occurred between 400 and 500 °C where \( \text{CO} \) and \( \text{CO}_2 \) are formed. Production of \( \text{CH}_4 \) was observed between 500 and 580 °C caused by breaking of \( \text{C}-\text{H} \) bond. Fast pyrolysis of \( \text{D}_2\text{O} \)-saturated coconut shell showed that moisture in the biomass does not increase the
H₂ yield at high temperature and that H₂ is mainly produced from breaking of the C-H bond.

Operation of the fuel cell in coconut shell produced the maximum current of 0.14 A at 0.4 V. Continuous operation for 37 min resulted in the electric power output of 225.1 J and the operating efficiency of 1.2 %. The low operating efficiency compared to the effective efficiency, which suggests the theoretical efficiency, of 44.6 % can be attributed to the majority of the gaseous product produced from the fast pyrolysis leaving the anode chamber prior to the electrochemical oxidation.

4.6 References


CHAPTER V

CH₄/CO₂ REFORMING IN SOLID OXIDE FUEL CELL WITH Rh-Ni/YSZ ANODE

5.1 Abstract

The utilization of CH₄ and CO₂ to produce electricity was studied in a solid oxide fuel cell (SOFC) comprising a Ni/YSZ anode prepared by the tape casting method followed by impregnation of Rh onto Ni/YSZ to obtain Rh-Ni/YSZ anode. The Rh-Ni/YSZ anode SOFC (0.01 and 0.03 wt.% Rh) and Ni/YSZ anode SOFC were tested simultaneously in the multiple SOFC reactor under flowing CH₄/CO₂ (100 sccm, 33 vol.% CH₄). The addition of CO₂ to CH₄ feed at the SOFC operating temperature of 700 °C over Ni or Rh catalyst initiates CH₄/CO₂ reforming reducing the rate of carbon deposition in the anode matrix. Exposure of the Ni/YSZ anode SOFC to CH₄/CO₂ produced a maximum power density that degraded from 0.06 to 0.01 W/cm² after 41 h. Impregnation of Rh at 0.01 and 0.03 wt.% onto the Ni/YSZ anode produced the Rh-Ni/YSZ anode that exhibited a maximum power density of 0.06 and 0.08 W/cm², respectively, for more than 185 h. Temperature-programmed reaction of CH₄/CO₂ reforming confirmed that impregnation of Rh onto Ni/YSZ increased the catalytic activity of CH₄ and CO₂ dissociation. Extensive testing of SOFC with various concentration of Rh in H₂/Ar and CH₄/CO₂ suggests the optimum Rh concentration of 0.07 – 0.10 wt%. 

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5.2 Experimental

This section describes the SOFC testing and temperature-programmed reaction experimental procedure.

5.2.1 SOFC fabrication

The anode-supported SOFCs used in this study were fabricated by a tape casting and screen-printing technique. A Ni/YSZ anode-supported layer (650 µm, 70 wt % Ni), a Ni/YSZ anode interlayer (25 µm, 50 wt % Ni), and a 15 µm YSZ electrolyte were fabricated by tape casting slips containing NiO, YSZ (TZ-8Y, Tosoh), binder, dispersants, and ethanol. The slips were casted on top of each other and dried at 50 °C for 3 days, cut in the shape of 12.5 mm discs, and sintered at 1400 °C for 4 h at the heating rate of 3 °C/min. The YSZ/LSM (Strontium Manganite) cathode interlayer (50 wt.% LSM, CL86-8706A, Heraeus) and LSM layer (CL8706, Heraeus) were subsequently screen-printed onto the sintered cells and heated at 1150 °C for 2 h, resulted in a 10 µm thickness of cathode interlayer and cathode layer. The anode of the fuel cell was reduced in flowing H₂/Ar (100 sccm, 50 vol% H₂) at 700 °C for 4 h. Figure 5.1 shows a SEM image of cross section of the SOFC after the experiment. The reduced Ni/YSZ anode was impregnated with an aqueous RhCl₃•2H₂O solution (0.5 wt.% RhCl₃•2H₂O, Alfa Chemicals) producing 0.01 and 0.03 wt.% Rh in the anode weight by sequential impregnation. Rh was added to the anode with the purpose of increasing the rate of CH₄/CO₂ and the sequential impregnation of Rh onto Ni at 0.021 mol% was reported to produced a highly active catalyst for CH₄ reforming [1-2].
5.2.2 SOFC testing and characterization

The SOFC testing apparatus consisted of (i) a gas manifold with flow controllers (5850E, Brooks), (ii) the SOFC reactor placed in a high temperature furnace, (iii) an impedance spectrometer (Solatron 1470E CellTest System), (iv) a gas chromatographer (GC, SRI8610C, SRIGC), and (v) a mass spectrometer (MS, GSD-301 Pfeiffer). The SOFC reactor made of Fe-based steel tube serving as an anode compartment and anode current collectors of 3 SOFCs. The 3 SOFCs, including Ni/YSZ anode SOFC (Ni/YSZ cell), 0.01 and 0.03 wt.% Rh impregnated Ni/YSZ anode SOFC (0.01% Rh-Ni/YSZ and 0.03% Rh-Ni/YSZ) were sealed to the steel tube with an alumina-based sealant. The cathode of the SOFCs was attached to a metal alloy strip cathode current collector with the aid of Ag conductive paste. The performance of the SOFCs was studied at 700 °C in H₂/Ar (100 sccm, 50 vol% H₂) and CH₄/CO₂ (75 sccm, 33% CH₄) by recording the voltage – current polarization curves (V-I curves) and electrochemical impedance spectra with the Solatron CellTest System. The impedance spectra were obtained at the voltage bias of 0.80 V, 0.35 V, and 0.01 V with a voltage perturbation of 0.005 V. These
voltages biases of the impedance spectra measurement were selected close to the open
circuit voltage (OCV), maximum power, and maximum current of the SOFCs. The
operating voltage of the SOFCs was switched between 0.35 V and 0.01 V every 2 h
during the course of 186 h operation in CH₄/CO₂, prior to switching the inlet feed to
H₂/Ar. The SOFCs reactor effluent while operated in CH₄/CO₂ was continuously
monitored with GC and MS. The MS response of the effluent was converted into
concentration profiles by means of a calibration curved obtained by injecting a calibration
gas with known amount of H₂, CO, CO₂, and CH₄. The BET surface area of the SOFC
was measure from N₂ adsorption and desorption isotherm at liquid N₂ temperature. The
microstructure of the SOFC anode was characterized by scanning electron microscope
(SEM, TM3000, Hitachi) and transmittance electron microscope (TEM).

5.2.3 Temperature-programmed reaction in high temperature DRIFT

Temperature-programmed reaction of CH₄/CO₂ reforming over Rh-Ni/YSZ
catalyst was performed in high temperature DRIFT cell situated in a Nicolet 560 IR
bench couple with MS. Rh-Ni/YSZ catalysts were prepared by sequential impregnation
of RhCl₃•2H₂O aqueous solution onto pulverized SOFC anode. The DRIFT cell was
loaded with 190 - 220 mg of catalyst samples and heated from room temperature to 700
°C at a heating rate of 10 °C/min under flowing CH₄/CO₂ (45 sccm, 33 vol% CH₄). The
temperature of sample was monitored from the thermocouple located at the center of the
sample bed. The DRIFT cell was held at 700 °C for 5 min prior to cooling down at 60
°C/min. IR spectra of the samples were collected throughout the pulsing experiment at a
resolution of 4 cm⁻¹ with 100 co-added scan. The effluent of the DRIFT cell was
monitored with MS allowing the qualitative determination of the conversions.
5.3 Results and Discussion

Figure 5.2 (a) shows the V-I curves of Ni/YSZ, 0.01% and 0.03% Rh-Ni/YSZ operated in flowing H\textsubscript{2}/Ar at 700 °C prior to switching to CH\textsubscript{4}/CO\textsubscript{2}. The Ni/YSZ SOFC produced a maximum power density of 0.06 W cm\textsuperscript{-2} and a maximum current density of 0.32 A cm\textsuperscript{-2}. The SOFC maximum current density was found to be 30 - 40 % lower than those previously reported from the Ni/YSZ anode-supported SOFC [3-4]. The low SOFC current density can be attributed to the use of Fe-based anode and cathode current collectors. These Fe-based current collectors possess an area specific resistance (ASR) of 0.08 Ωcm\textsuperscript{2}, which is comparable to the ASR reported from Fe-based alloy developed for SOFC interconnector [5]. The SOFCs with Rh impregnation, 0.01 % and 0.03 % Rh-Ni/YSZ, produced the maximum current densities 10 % higher than that of the Ni/YSZ SOFC. This variation in the electric current generation could be the deviation in the SOFC performance from the same batch because Rh is not reported to catalyze the oxidation of H\textsubscript{2}. Figure 5.2 (b) shows the impedance spectra of SOFCs recorded at OCV in the frequency range of 0.1 Hz – 100 kHz with 10 mA excitation AC amplitude. The impedance spectra of the SOFCs display two arcs, which the high frequency intercept of the impedance arc gives the ohmic resistance, resulted from the resistance of electrolyte, anode, cathode and the wires connected to the measuring device. The low frequency arc interception gives the total fuel cell resistance, which includes the ohmic resistance and polarization loss. The impedance spectra of Ni/YSZ, 0.01 and 0.03 Rh-Ni/YSZ SOFC display an ohmic resistance of 1.2 Ωcm\textsuperscript{2} and the total resistance in the range of 4.5 – 5.5 Ωcm\textsuperscript{2} showing the consistency of these SOFCs performance in H\textsubscript{2} fuel. The use of Fe-
based current collector contributed a higher ohmic resistance than those of high cost precious metal current collector (i.e., Au, Pd, and Pt) which has been reported to produce the ohmic resistance to 0.1 – 0.2 $\Omega \text{cm}^2$.

Figure 5.2 V-I curve and EIS recorded at OCV of the fuel cells operated in H$_2$/Ar (100 sccm, 50 vol% H$_2$)

Figure 5.3 shows the current density of the SOFCs operated in flowing CH$_4$/CO$_2$ at the operating voltage of 0.35 and 0.01 V as a function of time exposed to CH$_4$/CO$_2$. Changing the gas feed from H$_2$/Ar to CH$_4$/CO$_2$ at 0 h caused a gradually decrease in current density output of Rh impregnated SOFCs up to 20 h, while continuous decrease in the current density was observed from Ni/YSZ SOFC without Rh impregnation. The current density at 0.35 V of the 0.03% and 0.01% Rh-Ni/YSZ SOFC was stable around
0.18 A/cm$^2$ and 0.10 A/cm$^2$ for 185 h, which were 72 % and 57 % of the respective current density measured at 0 hr. The current density at 0.01 V of the 0.03% and 0.01 % Rh-Ni cell decreased to 55 % and 53 % of the current density measured at 0 h. The larger decrease in current density at 0.01 than that at 0.35 V indicates the concentration polarization, which can be investigated in V-I curves.

Figure 5.3 Current density of the SOFCs operated in flowing CH$_4$/CO$_2$ (75 sccm, 33 vol% CH$_4$) at 0.35 V and 0.01 V

Figure 5.4 (a),(c), and (e) are V-I curves of Ni/YSZ, 0.01 and 0.03 % Rh-Ni/YSZ SOFC operated in CH$_4$/CO$_2$ from 1 hr to 185 hr. Changing the inlet stream from H$_2$/CH$_4$ to CH$_4$/CO$_2$ resulted in slight decrease in OCV due to low concentration of CH$_4$ (33 vol% vs. 50 vol% H$_2$) and increase in the equilibrium oxygen partial pressure in CH$_4$/CO$_2$ from H$_2$/Ar [6]. The maximum power density outputs show negligible change after 1 hr of continuous exposure. The area specific resistances (ASR) were in the range of 4.6 – 5.5 $\square$cm$^2$ consistent with the operation in H$_2$/Ar. Continuous exposure to CH$_4$/CO$_2$ for 41 hr
greatly decreased the OCV and maximum power density output of the Ni/YSZ SOFC. The decrease in OCV suggests the failure of the electrolyte which could be caused by carbon deposition and cracking. The V-I curves of 0.01 % and 0.03 % Rh-Ni/YSZ in Figure 5.4 (c) and (e) show significant concentration polarization indicated by rapid decline in the voltage at the current density higher than 0.2 A/cm², which has been reported from the operation of SOFC in CH₄/CO₂ [7]. The concentration polarization could be cause by the formation of carbon on the surface of porous catalyst leading to the decrease of porosity and limiting the diffusion of the fuel to the anode active sites [8-9].

![Graphs showing V-I curves and EIS recorded at OCV of the SOFCs operated in CH₄/CO₂ (75 sccm, 33 vol% CH₄).](image)

Figure 5.4 V-I curves and EIS recorded at OCV of the SOFCs operated in CH₄/CO₂ (75 sccm, 33 vol% CH₄).

The EIS of Ni/YSZ, 0.01 and 0.03 % Rh-Ni/YSZ SOFC operated in CH₄/CO₂, recorded at OCV are shown in Figure 5.4 (b), (d), and (e) respectively. The EIS of Ni/YSZ SOFC after 41 h of exposure to CH₄/CO₂ are fluctuated at low frequency region.
as a result of the SOFC degradation. The ohmic resistance of 0.01 % and 0.03 % Rh-Ni/YSZ decreased from 1.2 $\Omega \text{cm}^2$ when operated in H$_2$/Ar to 0.8 $\Omega \text{cm}^2$ after exposed to CH$_4$/CO$_2$ for more than 15 hr. This decrease in the resistance can be attributed to the formation of carbon on the surface of anode matrix and reduction of the porosity [10]. Continuous operation in CH$_4$/CO$_2$ results in depressed electrode arcs and decrease the total cell resistance, which also reported from the operation of SOFC in CH$_4$/CO$_2$ [7]. The decrease in total resistance of the SOFC operated in hydrocarbon is proposed to be the effect of carbon deposition that connects the isolated metal particles [10]. The total resistances of the SOFC with Rh-impregnation were in the range of 2 – 4 $\Omega \text{cm}^2$ after exposed to CH$_4$/CO$_2$ for more than 41 hr. The total resistances indicated from the EIS were less than the ASR evaluated from the V-I curves, suggesting the insufficient compressive stress applied on the current collectors [6].
Figure 5.5 V-I curve and EIS of the SOFCs after operated in CH$_4$/CO$_2$ and H$_2$/Ar after exposure to CH$_4$/CO$_2$ for 185 h at 700 °C.

The V-I curves and EIS of the SOFC recorded at 185 h in CH$_4$/CO$_2$ and in H$_2$/Ar after switching from CH$_4$/CO$_2$ were plotted side by side in Figure 5.5. The maximum power densities of SOFCs with Rh-impregnation operated in H$_2$/Ar at 185 h were as high as 0.11 W/cm$^2$, which improved from 0.07 W/cm$^2$ prior to the exposure to CH$_4$/CO$_2$. The Ni/YSZ SOFC was severely degraded by the exposure to CH$_4$/CO$_2$ and was not regenerated by switching the inlet feed to H$_2$/Ar. This results evidence the effect of Rh...
on increasing the durability of SOFC operated in CH$_4$/CO$_2$ long term operation. The diffusion limitation, which can be observed from V-I curves recorded in CH$_4$/CO$_2$, did not persist in the operation with H$_2$/Ar. This is in agreement with the EIS recorded at 0.01 V of SOFCs operated in CH$_4$/CO$_2$ and H$_2$/Ar; where the polarization loss was greater than 6 $\Omega \text{cm}^2$ in CH$_4$/CO$_2$ and decreased to 1.5 – 3 $\Omega \text{cm}^2$ in H$_2$/Ar. The decrease in the ohmic resistance by switching the inlet feed to H$_2$/Ar suggests that the SOFC anode was further reduced and catalyst oxidation also contributed to the degradation of SOFC.

Figure 5.6 shows the EDX analysis, SEM and TEM micrographs of the SOFCs anode after exposed to CH$_4$/CO$_2$ for 185 hr at 700 °C. SEM image reveals Ni particle size in the range of 3 – 5 µm. EDX analysis shows 0.2 wt% Rh on the anode surface of 0.03 % Rh-Ni/YSZ, while Rh was not detected in the cross-section image. This result suggests that Rh was not uniformly distributed across the anode matrix layer. EDX analysis of 0.01 % Rh-Ni/YSZ did not reveal the Rh, which may be due to the low concentration of Rh. Carbon was not detected by the EDX analysis of the 0.03 and 0.01 % Rh-Ni/YSZ, while the anode surface of Ni/YSZ show 7 wt% of carbon. The results evidence the enhancement of coking resistance of the Ni/YSZ anode by impregnation of Rh. The TEM image of 0.03 % Rh-Ni/YSZ shows the deposition of 4 – 6 nm Rh particles on both Ni and YSZ. Rh deposition on YSZ has been reported to have high catalytic activity toward CH$_4$/CO$_2$ reforming at 700 °C [11] and the particles size of metal less than 10 nm was shown to significantly reduce the formation of carbon [12].
Figure 5.6 Microscope images of 0.03 %, 0.01 % Rh-Ni/YSZ anode after 185 h exposure to CH₄/CO₂ obtained from (a) SEM and (b) TEM.

The temperature-programmed reaction of CH₄/CO₂ reforming over Rh-Ni/YSZ catalyst was carried out in DRIFT cell. Various concentrations of Rh-Ni/YSZ sample were prepared by sequential impregnation separately from the SOFCs used in the prior experiment. Figure 5.7 shows the MS profiles of effluent from the CH₄/CO₂ reforming reaction in the DRIFT cell. The labels A to E notified the sample names which the properties were listed in Table 5.1. The concentration of CH₄ and CO₂ fed to the DRIFT cell was fixed at 33.3 vol% CH₄, which was the same concentration as the inlet stream used in the operation of the SOFC. The space velocities of these experiments were
controlled in the range of 1.8 – 2.0 gh/mol. CH₄ and CO₂ decomposition over Ni/YSZ catalyst without Rh-impregnation started at 550 °C and small amount of H₂O was produced. The consumption of CH₄ and CO₂ rapidly accelerated at 600 °C where CO and H₂ were observed. Addition of Rh as low as 0.015 wt% (sample B) reduced the decomposition temperature to 430 °C and increase the production of H₂, CO, and H₂O observed from the increase in MS intensities. Gradually increasing the concentration of Rh from 0.015 wt% to 0.139 wt% shows that (i) the decomposition temperature of remained at 430 °C, (ii) the conversion of CH₄ and CO₂ increased with increasing Rh loading, and (iii) the production of H₂, CO, and H₂O increased with increasing Rh loading. The increase in H₂O production cannot be clearly observed due to condensation in the line from DRIFT cell to MS. This result is in agreement with various studies that the addition of Rh promotes the CH₄/CO₂ reforming and steam reforming reactions [1, 11, 13].
Figure 5.7 MS profiles of the DRIFT effluent during temperature-programmed reaction of CH$_4$/CO$_2$ reforming over various concentration of Rh in Ni/YSZ. The heating rate used was 10 °C/min.
Table 5.1 List of Rh-Ni/YSZ sample used for TPR experiment (Figure 5.7), surface area, experimental parameter, and CH$_4$, CO$_2$ conversion at 700 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rh content (wt%)</th>
<th>Space velocity (gh/mol)</th>
<th>BET surface area (m$^2$/g)</th>
<th>Conversion at 700 °C</th>
<th>CH$_4$ (%)</th>
<th>CO$_2$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0</td>
<td>2.0</td>
<td>189.4</td>
<td>26.0</td>
<td>21.4</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>0.015</td>
<td>1.9</td>
<td>221.2</td>
<td>32.0</td>
<td>26.9</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.034</td>
<td>1.9</td>
<td>194.9</td>
<td>42.2</td>
<td>33.9</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>0.087</td>
<td>1.9</td>
<td>285.3</td>
<td>39.9</td>
<td>37.5</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>0.139</td>
<td>1.8</td>
<td>203.1</td>
<td>50.2</td>
<td>43.6</td>
<td></td>
</tr>
</tbody>
</table>

The conversion of CH$_4$ and CO$_2$ from the temperature-programmed reaction at 700 °C was summarized in Table 5.1. Addition of 0.139 wt% Rh in Ni/YSZ increased the conversion of CH$_4$ and CO$_2$ by 93 % and 104 %. The conversion of CH$_4$ was approximately 1.2 times higher than the conversion of CO$_2$ over Ni/YSZ and this ratio slightly decreased with the addition of Rh. This decrease in the ratio of CH$_4$ conversion over CO$_2$ conversion indicates that Rh promotes the dissociation of CO$_2$ slightly more than that of CH$_4$. This increase in CO$_2$ conversion could also be contributed from the adsorbed H from CH$_4$ dissociation, which has been reported [11, 13]. The effect of Rh on promoting CO$_2$ dissociation benefits the operation of SOFC in CH$_4$/CO$_2$ by reducing the carbon deposition via reversed Boudouard reaction (CO$_2$ + C $\rightarrow$ 2CO), which was found to occurred in the operation of SOFC in presence of carbon and steam/CO$_2$ reforming of CH$_4$ [4, 14]. The surface area of the catalyst determined by BET after the experiment does not show the linear relationship with the Rh loading. It should be noted that these samples were held at 700 °C for 5 min. The surface area of the SOFC anode after exposure to CH$_4$/CO$_2$ at 700 °C for 185 h was found to be as low as 10 m$^2$/g. This
decrease in surface area can be attributed to agglomeration of Ni particle and carbon deposition.

Figure 5.8 Absorbance spectra of temperature-programmed reaction over 0.139 wt% Rh-Ni/YSZ (sample E) in DRIFT cell with heating rate of 10 °C/min. The spectra were collected for the heating (h) and cooling (c) stages. The difference spectra between cooling and heating are labeled as c-h.

Figure 5.8 shows the 0.139 wt% Rh-Ni/YSZ absorbance spectra at various temperatures throughout the temperature-programmed reaction study in DRIFT cell. The absorbance spectra comparing cooling and heating (denoted as c - h) was obtained by

\[
\text{Abs} = \log\left(\frac{1}{I_{\text{cooling}}}\right) - \log\left(\frac{1}{I_{\text{heating}}}\right)
\]

The absorbance spectra between cooling and heating
represent the changes in the concentration of the specific functional group on the sample surface at the given temperature, indicating the progress of the reactions. The upward peak indicates that the concentration of that particular function group is higher during the cooling than that during heating, suggesting the formation of the species above that specific temperature and vice versa. The decrease in CO band at 2175 cm\(^{-1}\) indicates that production of CO was higher during the heating step than that during the cooling step, suggesting the degradation of the catalyst. The high conversion in the first hour of the reaction was also reported on CH\(_4\)/CO\(_2\) reforming over Pt/YSZ catalyst [15]. Increase in the peak intensity of CH\(_4\) gas at 1350 and 1290 cm\(^{-1}\) observed in c-h 500 °C to 600 °C spectra indicates that degradation of the catalyst occurred in this temperature range, which is in agreement with the peak intensity of CO gas. Decrease in C=O peak intensity at 1726 cm\(^{-1}\) observed from c-h 500 °C to 600 °C spectra suggests the formation of carbon with C=O functional group at the temperature between 500 – 600 °C. This temperature range corresponds to the catalyst degradation temperature, confirming that carbon formation degrade the catalyst. The C-OH peaks at 1121 and 1064 cm\(^{-1}\) and adsorbed CH\(_3\) peak at 1410 cm\(^{-1}\) evidence the participation of surface OH group with adsorbed CH\(_3\) specie in the CH\(_4\)/CO\(_2\) reforming reactions at the temperature above 400 °C. The surface reaction of OH groups with CH\(_3\) on Ni catalyst produces H\(_2\) and CO via deformation of formate species (CH\(_x\)O) [16-17].
Table 5.2 Summary of maximum current density of SOFC with various concentration of Rh operated in H₂/Ar and CH₄/CO₂ at 700, 750, and 800 °C.

<table>
<thead>
<tr>
<th>No.</th>
<th>Rh content (wt%)</th>
<th>Maximum current density (A/cm²)</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>700 °C H₂</td>
<td>700 °C CH₄/CO₂</td>
</tr>
<tr>
<td>1</td>
<td>0.11%</td>
<td>0.41</td>
<td>0.41</td>
</tr>
<tr>
<td>2</td>
<td>0.08%</td>
<td>0.24</td>
<td>0.29</td>
</tr>
<tr>
<td>3</td>
<td>0.00%</td>
<td>0.42</td>
<td>0.33</td>
</tr>
<tr>
<td>4</td>
<td>0.03%</td>
<td>0.17</td>
<td>0.10</td>
</tr>
<tr>
<td>5</td>
<td>0.16%</td>
<td>0.32</td>
<td>0.09</td>
</tr>
<tr>
<td>6</td>
<td>0.00%</td>
<td>0.28</td>
<td>0.21</td>
</tr>
<tr>
<td>7</td>
<td>0.18%</td>
<td>0.18</td>
<td>0.12</td>
</tr>
<tr>
<td>8</td>
<td>0.14%</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>0.05%</td>
<td>0.23</td>
<td>0.23</td>
</tr>
<tr>
<td>10</td>
<td>0.06%</td>
<td>0.43</td>
<td>0.23</td>
</tr>
<tr>
<td>11</td>
<td>0.21%</td>
<td>0.38</td>
<td>0.11</td>
</tr>
<tr>
<td>12</td>
<td>0.15%</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>13</td>
<td>0.00%</td>
<td>0.33</td>
<td>0.36</td>
</tr>
<tr>
<td>14</td>
<td>0.01%</td>
<td>0.35</td>
<td>0.34</td>
</tr>
<tr>
<td>15</td>
<td>0.03%</td>
<td>0.36</td>
<td>0.45</td>
</tr>
</tbody>
</table>

The effect of Rh on the activity of Ni/YSZ anode was further investigated by operation of 12 SOFCs with various concentrations of Rh, shown in Table 5.2. Table 5.2 reports the maximum current density produced in H₂/Ar (100 sccm, 50 vol% H₂) and CH₄/CO₂ (100 sccm, 50 vol% CH₄) at 700, 750, and 800 °C. The maximum current densities were used for analysis of the effect of Rh because the current density of SOFC is directly related to the rate of electrochemical oxidation via Faraday’s law:

\[ N_{\text{fuel}} (mol/s cm^2) = \frac{i}{Z_{\text{fuel}} F} \]
where $N_{\text{fuel}}$ is the rate of electrochemical oxidation of fuel (i.e., CH$_4$, C, and CO). $Z_{\text{fuel}}$ is the number of electron involving in the electrochemical oxidation reaction. $i$ and $F$ represent current density (Am$^{-2}$) and Faraday's constant (96487 C mol$^{-1}$), respectively.

The maximum current density of SOFCs operated in H$_2$ at 700 °C were in the range of 0.17 – 0.43 A/cm$^2$, consistent with the performance of SOFCs used for long term test, shown in Figure 5.2 and higher than previous reports by SOFC operated in CH$_4$/CO$_2$ [9, 18]. Failures of the SOFC from short circuit were observed from the SOFC with impregnation of Rh over 0.10 wt%. This short circuit could be due to the leakage of Rh solution through pinholes on electrolyte. Raising the operating temperature from 700 °C to 800 °C increased the maximum current density of the Ni/YSZ SOFC operated in H$_2$/Ar by 45% and as high as 86% for operation in CH$_4$/CO$_2$. The rate determining steps of CH$_4$/CO$_2$ reforming over Rh and Ni catalyst [2, 13] were proposed to be CH$_4$ and CO$_2$ decomposition (CH$_4$ $\rightarrow$ CH$_{x(a)}$ + y H$_2$, CO$_2$ $\rightarrow$ CO$_{(a)}$ + O$_{(a)}$). These reactions are promoted as the operating temperature increased, as a result, high operating temperature benefitted the SOFC with CH$_4$/CO$_2$ feed more than that with H$_2$/Ar feed. The effect of increase in operating temperature on the maximum current density of Rh-impregnated SOFC was mixed. Increase in the maximum current density was observed on concentration of Rh less than 0.05 wt% and decrease or slightly increase in maximum current density was observed on concentration of Rh higher than 0.10 wt%. The degradation at the temperature above 700 OC of high Rh concentration could be the result of (i) agglomeration of Rh nano particles, which lose surface area and catalytic activity, (ii) decrease in number of electrical conducting paths due to increase in Ni particle size [12, 19], and (iii) the degradation due to oxidation of anode catalyst [20],
which was also observed after exposure to CH$_4$/CO$_2$ for 185 h, shown in Figure 5.5. The maximum current density of SOFC at 700 °C decreased in the range of 20 – 50 % by operation at elevated temperature (i.e., 750, 800 °C) for 2 h. This degradation could be attributed mainly to the degradation of low cost Fe-based current collector, which was not design to be operated at high temperature and the growth of Ni particle size [21].

The effect of Rh on the maximum current density of SOFCs operated in CH$_4$/CO$_2$ was investigated by comparison between maximum current density in CH$_4$/CO$_2$ vs. maximum current density in H$_2$/Ar ($I_{\text{max}(\text{CH}_4/\text{CO}_2)} : I_{\text{max}(\text{H}_2)}$), shown in Figure 5.9. The SOFC without Rh-impregnation operated in CH$_4$/CO$_2$ produced the maximum current density of 0.75 % of that in operated H$_2$/Ar. The ratio $I_{\text{max}(\text{CH}_4/\text{CO}_2)} : I_{\text{max}(\text{H}_2)}$ as a function Rh content shows that impregnation of Rh increase the relative maximum current density of SOFC operated in CH$_4$/CO$_2$ and suggests the optimum Rh concentration in the range of 0.07 – 0.10 wt%. Rh concentration of higher than 0.10 wt% decreased the SOFC relative maximum current density of SOFC operated in CH$_4$/CO$_2$. This decrease could be attributed to reduction of porosity of the anode matrix and coverage of Ni particles, which is an excellent catalyst for CH$_4$ cracking.
Figure 5.9 Ratio of the maximum current density of SOFC operated in CH\(_4\)/CO\(_2\) over that in H\(_2\)/Ar at 700 °C as a function of current density.

5.4 Conclusion

The utilization of CH\(_4\) and CO\(_2\) to produce electricity was studied in a solid oxide fuel cell (SOFC) comprising a Ni/YSZ anode prepared by the tape casting method followed by impregnation of Rh onto Ni/YSZ to obtain Rh-Ni/YSZ anode. The Rh-Ni/YSZ anode SOFC (0.01 and 0.03 wt.% Rh) and Ni/YSZ anode SOFC were tested simultaneously in the multiple SOFC reactor under flowing CH\(_4\)/CO\(_2\) (100 sccm, 33 vol.% CH\(_4\)). The addition of CO\(_2\) to CH\(_4\) feed at the SOFC operating temperature of 700 °C over Ni or Rh catalyst initiates CH\(_4\)/CO\(_2\) reforming reducing the rate of carbon deposition in the anode matrix. Exposure of the Ni/YSZ anode SOFC to CH\(_4\)/CO\(_2\) produced a maximum power density that degraded from 0.06 to 0.01 W/cm\(^2\) after 41 h.
Impregnation of Rh at 0.01 and 0.03 wt.% onto the Ni/YSZ anode produced the Rh-Ni/YSZ anode that exhibited a maximum power density of 0.06 and 0.08 W/cm², respectively, for more than 185 h. Characterization of the anode microstructure by transmission electron microscopy (TEM) revealed that the impregnation of Rh to the Ni/YSZ anode results in the deposition of Rh nano particles on Ni. Temperature-programmed reaction of CH₄/CO₂ reforming confirmed that impregnation of Rh onto Ni/YSZ increased the catalytic activity of CH₄ and CO₂ dissociation. The experiment also revealed that Rh promotes the dissociation of CO₂ slightly more than that of CH₄, which could reduce carbon deposition in the SOFC anode. Extensive testing of SOFC with various concentration of Rh in H₂/Ar and CH₄/CO₂ suggests the optimum Rh concentration of 0.07 – 0.10 wt%.

5.5 References

2. Chen, Y.-g., et al., Promoting effect of Pt, Pd and Rh noble metals to the Ni0.03Mg0.97O solid solution catalysts for the reforming of CH4 with CO2. Applied Catalysis A: General, 1997. 165(1–2): p. 335-347.


CHAPTER VI
CONCLUSIONS

Chapter 3 demonstrates that the operation of a solid oxide fuel cell with coconut carbon (C-SOFC) at 750 °C produced a maximum current density of 0.27 A/cm$^2$ and produced less CO and more CO$_2$ from those predicted by thermodynamic calculation. The impact of CO and CO$_2$ concentration in the anode chamber on the electricity generation was studied by addition of a CO and CO$_2$ stream. The addition of the CO$_2$ stream increased CO formation and maximum power density from 0.09 W/cm$^2$ to 0.13 W/cm$^2$, indicating the occurrence of Boudouard reaction (CO$_2$ + C $\rightarrow$ 2CO) coupling with CO electrochemical oxidation on the C-SOFC. The contribution of C and CO to the electrical power generation was investigated by analysis of CO and CO$_2$ concentration at different operating voltage. Reducing the operating voltage shows an increase in CO$_2$ formation at low current density and rapid consumption of CO at high current density, revealing that at low current density, electricity was produced from an electrochemical oxidation of carbon, while more CO was consumed to produce electricity at higher current density. These results benefit the choosing of the operating condition of the C-SOFC to achieve high efficiency.

The operating efficiencies of SOFC operated with coconut carbon and Ohio coal was evaluated to be less than 2 % in chapter 4. This low efficiency was mainly due to gaseous product of carbon pyrolysis leaving the anode chamber unreacted, which lead to
the study of fast pyrolysis. Fast pyrolysis of coconut shell produced CO\textsubscript{2} as a major
gaseous product at temperatures between 500 and 630 °C, while the formation of CO, 
CH\textsubscript{4}, and H\textsubscript{2} followed as the temperature continued to increase. Increasing the heating 
rate from 75 to 175 °C/min increased the temperature range of gaseous production due to 
high temperature gradient across the biomass sample, while decreased the gas and 
coconut char yield. The IR analysis of coconut char and pyrolysis liquid indicates that 
higher heating rate increases the amount of aliphatic and carbonyl compounds and 
slightly increases the amount of aromatic compounds. In situ IR study reveals carbonyl 
intermediate species were formed between 200 and 400 °C, followed by breaking of C=O 
and C-O-C bonds occurred between 400 and 500 °C where CO and CO\textsubscript{2} are formed. 
CH\textsubscript{4}, observed between 500 and 580 °C, was produced from breaking of C-C bond. Fast 
pyrolysis of D\textsubscript{2}O-saturated coconut shell showed that moisture in the biomass does not 
increase the H\textsubscript{2} yield at high temperature and that H\textsubscript{2} is mainly produced from breaking 
of the C-H bond.

The utilization of CH\textsubscript{4} and CO\textsubscript{2} to produce electricity was studied in SOFC 
comprising a Ni/YSZ anode prepared by the tape casting method followed by 
impregnation of Rh onto Ni/YSZ to obtain Rh-Ni/YSZ anode. The Rh-Ni/YSZ anode 
SOFC (0.01 and 0.03 wt.% Rh) and Ni/YSZ anode SOFC were tested simultaneously in 
the multiple SOFC reactor under flowing CH\textsubscript{4}/CO\textsubscript{2} (100 sccm, 33 vol.% CH\textsubscript{4}). The 
addition of CO\textsubscript{2} to CH\textsubscript{4} feed at the SOFC operating temperature of 700 °C over Ni or Rh 
catalyst initiates CH\textsubscript{4}/CO\textsubscript{2} reforming reducing the rate of carbon deposition in the anode 
matrix. Exposure of the Ni/YSZ anode SOFC to CH\textsubscript{4}/CO\textsubscript{2} produced a maximum power density that degraded from 0.06 to 0.01 W/cm\textsuperscript{2} after 41 h. Impregnation of Rh at 0.01
and 0.03 wt.% onto the Ni/YSZ anode produced the Rh-Ni/YSZ anode that exhibited a maximum power density of 0.06 and 0.08 W/cm$^2$, respectively, for more than 185 h. Temperature-programmed reaction of CH$_4$/CO$_2$ reforming confirmed that impregnation of Rh onto Ni/YSZ increased the catalytic activity of CH$_4$ and CO$_2$ dissociation. Extensive testing of SOFC with various concentration of Rh in H$_2$/Ar and CH$_4$/CO$_2$ suggests the optimum Rh concentration of 0.07 – 0.10 wt%.
APPENDICES
APPENDIX A

IN SITU STUDY OF CATALYTIC UPGRADING OF PYROLYSIS VAPOR
OBTAINED FROM FAST PYROLYSIS AND CHAR CHARACTERIZATION BY RAMAN SPECTROSCOPY

Introduction

Biomass is a renewable resource, which has gained great interest because of the increasing energy demands. The sources of biomass include agricultural wastes, energy crop, forestry wastes, or solid wastes. Biofuel is derived from biomass and has the potential to be an environmental friendly alternative for the energy production. Unlike the petroleum-based fuels, biofuels can be considered an environmentally benign alternative because CO\textsubscript{2} produced during biofuel combustion can be taken to have been recently extracted by plants as they have grown.

This section presents the chemical aspect of biomass, biomass processing and bio-oil, which is the derivative of biomass.

Chemical structure and components of biomass

Biomass is hydrocarbon material that mainly composes of carbon, hydrogen, oxygen, nitrogen and small amount of sulfur. The chemical structure and the composition of the biomass are very important in the development of the production of biofuel and chemicals, as the product yield and properties can be greatly influenced. The
components of biomass include cellulose, hemicelluloses, lignin, extractive, and ash[1]. In general, hardwoods, which are the most common biomass, contain 43-47 wt.% cellulose, 25-35 wt.% hemicelluloses, 16-40 wt.% lignin, and 2-8 wt.% extractives.

Cellulose is a linear homopolysaccharide composed of 10,000 - 15,000 glucose units linked by glycosidic bonds, as shown in Figure A.1(a). Cellulose fibers provide wood strength and comprise approximately 50 wt.% of dry woods. Unlike cellulose, which is homopolymer, hemicelluloses are complex heteropolysaccharides that are mixtures of pentoses, arabinose, glucose, mannose, and galactose. Figure A.1(b) shows the schematic of some sugar units of hemicelluloses. The number of repeating saccharide monomers in hemicellulose is around 150 units, thus it exhibits lower molecular weight than that of cellulose. Hemicelluloses usually account up to 35 wt.% of dry wood[2].

Lignin is the final major constituent of biomass. Lignin is a heterogeneous polymer consisting of phenylpropane units. The chemical structure of phenylpropane units of lignin is shown in Figure A.1(c). Lignin acts as a binder of cellulose and hemicellulose in the biomass. Lignin contents on a dry wood range up to 40 wt.. Extractives are nonstructural compounds produced during a secondary metabolism of plants. Extractives contain lipophilic and hydrophilic organic. Ash is the mineral materials composed mainly of carbonates, sulfates and phosphates of Si, Ca, Mg, Na or K. These compounds can act as catalysts for polymerization leading to char formation during the pyrolysis.
Figure A.1 Schematic of (a) cellulose structure, (b) sugar units in hemicellulose, and (c) lignin monomeric units.

Thermal conversion of biomass

Biofuel that is derived from biomass can be used for transportation, heating, electricity generation as the fossil fuel substitute. The conversion of biomass to biofuel can be accomplished through several processes such as biochemical conversion and thermal conversion. Biofuels obtained from the conversion can be gaseous, liquid and solid fuels that contain high energy.
Thermal conversion offers an effective means to converse energy content of biomass to fuels. The products are greatly affected by the type of process and the operating condition. Figure A.2 shows the overview schematic of the thermal conversion of biomass and the products. The processes of thermal conversion can be generally categorized by the difference in an operating environment. Combustion, occurring in the excess oxygen environment, is the most direct process for energy conversion. In combustion, the hydrocarbon in biomass is completely oxidized. The resulting gas (flue gas) contains majority of CO$_2$ and small amount of water. The mean of recovering the energy is from the heat of combustion that can be used for steam generation producing electricity. Gasification takes place in partial air environment, where oxygen is present but not in excess. In gasification, steam or hydrogen may be introduced into the system. These reactants reacted with carbon at the gasification operating condition to produce gas yield. The gaseous product of gasification is a combustible gas such as synthesis gas containing CO and H$_2$. The synthesis gas is typically treated by stream-reforming and processed via Fischer-Tropsch synthesis to produce valuable hydrocarbon. Pyrolysis, the last thermal conversion process, occurs in the absence of oxygen or significantly less oxygen than required for complete combustion.
Pyrolysis of biomass produces gaseous (pyrolysis gas), liquid (bio-oil), and solid (char) product. Pyrolysis of biomass has been categorized by the residence time as shown in Table A.1.

Table A.1 The operation condition of pyrolysis process[3][2]

<table>
<thead>
<tr>
<th>Pyrolysis technique</th>
<th>Vapor residence time (s)</th>
<th>Heating rate (°C/s)</th>
<th>Temperature (°C)</th>
<th>Solid yield</th>
<th>Liquid yield</th>
<th>Gas yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional</td>
<td>10 - 30</td>
<td>0.1 - 1</td>
<td>200 - 650</td>
<td>25%</td>
<td>50%</td>
<td>25%</td>
</tr>
<tr>
<td>Fast</td>
<td>1 - 5</td>
<td>10 - 200</td>
<td>500 - 900</td>
<td>12%</td>
<td>75%</td>
<td>13%</td>
</tr>
<tr>
<td>Flash</td>
<td>&lt;0.5</td>
<td>&gt;1000</td>
<td>800 - 1150</td>
<td>17%</td>
<td>68%</td>
<td>15%</td>
</tr>
</tbody>
</table>

Slow pyrolysis or conventional pyrolysis is favorable for the char production.

Short residence time pyrolysis at the temperature around 500 °C produces high yield of bio-oil and at the high temperature around 800°C produces high yield of pyrolysis gas.

The mechanism of the pyrolysis of biomass was proposed as[4]

1. Heat transfer to increase the temperature inside biomass.
2. Primary pyrolysis releases volatiles and forms char.

3. Transportation of hot volatiles toward cooler solid biomass.

4. Condensation of some volatile and secondary reaction of the volatile producing tar.

5. Autocatalytic secondary pyrolysis reactions proceed simultaneously with the primary reaction.

6. Further thermal decomposition, reforming, or water gas shift reaction occur as a function of the residence time, temperature or catalyst.

The pyrolysis is attractive for biomass conversion because of the possibility of high bio-oil yield. This bio-oil has advantages in transportation, storage, combustion, reprocessing and flexibility in production.

Bio-oil

Bio-oil is dark brown in appearance and has elemental composition similar to that of biomass source. Wood-derived bio-oil typically contains around 56 wt.% of C, 6 wt.% of H, 38 wt.% of O and small trace of N. Bio-oil is a complex mixture of oxygenated hydrocarbons with a proportion of water both inherited from original moisture and reaction product[5][6]. The water content in bio-oil is approximately 25 wt.%.

The bio-oil is formed during the quenching of the intermediate product of pyrolysis with short residence time (fast pyrolysis), hence this bio-oil contains various reactive species. These active species increase the complexity of the bio-oil upgrading, handling and storage. Bio-oil cannot be vaporized once it has been condensed from gas phase. Heating bio-oil over 100 °C causes rapid reaction that eventually produces a solid residue up to around 50 wt.% Bio-oil properties gradually change with time, which
cause the storage problem. The most noticeable issue is a gradual increase in viscosity or aging, which is well known phenomena caused by slow secondary reactions in the liquid. Research suggests prevention methods, such as addition of ethanol or methanol. The upgrading of bio-oil is discussed in detail in section 3 of the report.

Biomass fast pyrolysis

Fast pyrolysis is a thermal conversion process in which biomass is rapidly heated in absence of oxygen. The heating rate is usually in the range of 10 - 200 °C/s and the pyrolysis temperature is between 500-950 °C. Fast pyrolysis has attracted much interest for high liquid yield, which can be up to 60 - 75 %. Maximizing the liquid yield of fast pyrolysis requires (i) very high heat transfer rates, (ii) accurate control of the pyrolysis temperature between 450 - 550 °C, (iii) short vapor residence time (< 2 s) and (iv) rapid cooling of the pyrolysis vapor resulting in bio-oil. Table A.2 shows the literature review of bio-oil yield from biomass fast pyrolysis process.
Table A.2 Literature review of bio-oil yield from biomass fast pyrolysis

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Catalyst</th>
<th>Reactor</th>
<th>Temp (°C)</th>
<th>Oil yield (%)</th>
<th>Carrier gas</th>
<th>Residence time</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cotton seed</td>
<td>Fixed bed</td>
<td>550</td>
<td>48.3</td>
<td>N₂</td>
<td>30</td>
<td>88</td>
<td>[7]</td>
</tr>
<tr>
<td>Cotton seed</td>
<td>5% MgO</td>
<td>Fixed bed</td>
<td>550</td>
<td>42</td>
<td>N₂</td>
<td>30 88</td>
<td>[7]</td>
</tr>
<tr>
<td>Aspen wood</td>
<td>Batch</td>
<td>600</td>
<td>16</td>
<td>He</td>
<td>25</td>
<td>0.9</td>
<td>[8]</td>
</tr>
<tr>
<td>Beech wood</td>
<td>Single pellet</td>
<td>70</td>
<td>70</td>
<td>N₂</td>
<td>0.4</td>
<td></td>
<td>[9]</td>
</tr>
<tr>
<td>Sawdust</td>
<td>Cyclone</td>
<td>700</td>
<td>74</td>
<td>N₂</td>
<td>20</td>
<td>0.6</td>
<td>[10]</td>
</tr>
<tr>
<td>Tire rubber</td>
<td>PFR</td>
<td>500</td>
<td>54</td>
<td>N₂</td>
<td>0.9</td>
<td></td>
<td>[11]</td>
</tr>
<tr>
<td>Corn cob</td>
<td>Fluidized bed</td>
<td>400</td>
<td>57.1</td>
<td>N₂</td>
<td>10</td>
<td>4.8</td>
<td>[12]</td>
</tr>
<tr>
<td>Cassava plant</td>
<td>Fluidized bed</td>
<td>500</td>
<td>65</td>
<td>N₂</td>
<td>3.4</td>
<td></td>
<td>[13]</td>
</tr>
<tr>
<td>Mallee wood</td>
<td>Fluidized bed</td>
<td>500</td>
<td>52</td>
<td>N₂</td>
<td>120</td>
<td>4.1</td>
<td>[14]</td>
</tr>
<tr>
<td>Crop stems</td>
<td>Batch</td>
<td>450</td>
<td>52</td>
<td>N₂</td>
<td>20</td>
<td></td>
<td>[15]</td>
</tr>
<tr>
<td>Rice husk</td>
<td>Fixed bed</td>
<td>800</td>
<td>42</td>
<td>N₂</td>
<td>8</td>
<td>38</td>
<td>[16]</td>
</tr>
<tr>
<td>Rice husk</td>
<td>Fluidized bed</td>
<td>400</td>
<td>46.5</td>
<td>N₂</td>
<td>20</td>
<td>5</td>
<td>[17]</td>
</tr>
<tr>
<td>Rice husk</td>
<td>ZSM-5</td>
<td>Fluidized bed</td>
<td>400</td>
<td>7.2</td>
<td>N₂</td>
<td>20 5</td>
<td>[17]</td>
</tr>
</tbody>
</table>

Various sources of biomass can be utilized by fast pyrolysis. Many types of biomass have been tested such as straw, woods, nut shells, bark, rice husk or crop stems. Biomass preparation for fast pyrolysis process includes drying to less than 10 wt.% water in order to reduce the water in bio-oil product and grinding the feed to ensure the rapid heat transfer rate. The remaining moisture can be utilized as a carrier gas when vaporized.

Figure A.3 shows the distribution of the product yield as a function of temperature reported by Putun[7]. Char yield reached the maximum at low temperature (400 °C) and increasing the pyrolysis temperature decreased the char yield. The pyrolysis gas yield
behaved in contradiction of the char yield that decreased as the pyrolysis temperature increased. The bio-oil yield was 44 % at 400 °C and reached a maximum of 50 % at the pyrolysis temperature of 550 °C. The yield of bio-oil decreased to 48 % at 700 °C. These results suggest that the secondary reaction of the liquid and char decomposition is proceeded with increasing temperature resulting in higher fraction of pyrolysis gas. These results are in agreement with various studies[18],[19],[17].

![Pyrolysis product yield as a function of temperature.](image)

Figure A.3 Pyrolysis product yield as a function of temperature.

Heat transfer is one of the most important challenges for the development of fast pyrolysis[20]. Pyrolysis is an endothermic process which requires substantial amount of heat to raise biomass to the reaction temperature. The heat flux of 50 W/cm² is needed to achieve fast pyrolysis condition[21]. The by-products of the pyrolysis process such as char and pyrolysis gas are typically used to generate heat for the pyrolysis reactor by combustion. The char contains about 25 % and pyrolysis gas contains about 5 % of the
energy of biomass feedstock. The methods of supplying heat to the biomass for pyrolysis include

1. heat transfer through the reactor surface and conducting to the biomass
2. heating the fluidization gas
3. removing and reheating the biomass bed as used in circulating fluidized bed reactor
4. addition of some air for combustion, although this can increase the cracking of bio-oil, and reduce the overall efficiency of the process.

The cracking of bio-oil product is majorly caused from char residue in the oil. Char acts as a vapor cracking catalyst, thus the rapid removal of the char and rapid quenching of the pyrolysis vapor are essential. Cyclones are the typical equipment used to separate char from the pyrolysis products in the pyrolysis industry. Researchers suggest hot vapor filtration, which still have the problems of the disengagement of the filter cake due to the sticky nature of fine char. The vapor product is needed to be cooled to prevent secondary reaction. Quenching in product bio-oil or an immiscible hydrocarbon solvent is widely practiced.

The direct use of catalyst in biomass fast pyrolysis to upgrade the quality of the pyrolysis vapor or oil has been studied by mixing the catalyst with the biomass. Although the quality of the pyrolysis products can be improved, the actual implementation of direct catalytic fast pyrolysis faces the problem of separation and degradation of catalysts. Most research effort has attempted to incorporate the catalytic upgrading process on the pyrolysis vapor or bio-oil resulting from the fast pyrolysis.
Bio-oil upgrading

Bio-oil can be upgraded in various methods which can be classified into two routes: physical upgrading and chemical upgrading. The physical upgrading includes hot gas filtration, emulsification, and solvent addition and the chemical upgrading includes hydrotreating (hydrodeoxyxygenation) and catalytic cracking. The objectives of the upgrading are to use pyrolysis products in fuel application or to produce valuable chemicals. The important properties that are in focus of the upgrading include oxygen content, water content, composition of bio-oil, solid content, viscosity and chemical stability. For effective use as a fuel, bio-oil should be soluble in hydrocarbon fuel and has low oxygen content to increase the heating value. To achieve the solubility in hydrocarbon, solvent fractionation and emulsification are typically used. Deoxygenation of bio-oil or pyrolysis vapor usually involves chemical upgrading with catalytic reactions.

Catalytic cracking of pyrolysis vapor is the catalytically decomposition of oxygen species resulting in light hydrocarbon. The removed species form H₂O, CO₂ or CO[22]. The catalytic upgrading can operate on the bio-oil or pyrolysis vapor and can be integrated to the pyrolysis process or decouple as a separate process. The composition of desired products, such as C₁-C₄ hydrocarbons or aromatic hydrocarbons can be greatly affected by the catalyst used in the process. Various types of catalyst have been studied including ZnO[22], Ni-Al₂O₃[23], Al-MCM-41, Cu/Al-MCM-41, and many zeolite-based catalysts[8]. Among the zeolite-based catalysts, HZSM-5 is the most effective for cracking or reforming of bio-oil as the zeolite promote high yields of liquid product, high hydrocarbon and aromatic formation, and the least coke formation. Reaction pathways were proposed that thermal effects and thermocatalytic effects involve in the conversion
process. The thermal effects separate bio-oil into light and heavy organics and polymerization of heavy bio-oil to char. Following the thermal effects, the thermocatalytic effect produced coke, tar, gas, water and organic fraction according to the operating condition. The catalytic cracking is regarded as a cheaper route to convert oxygenated bio-oil to light hydrocarbon; however, catalyst deactivation due to coking remains the most prominent problem.

The composition of bio-oil is generally divided into desirables including phenolics, alcohols, and hydrocarbons and undesirables including acids, carbonyls, polycyclic aromatic hydrocarbons (PAHs) and heavy oxygenates. The undesirable should be removed because it can initiate secondary reaction during storage and PAHs are toxic. However, mono aromatic compounds are considered valuable chemical due to their application. Previous studies show that upgrading bio-oil with strong acid zeolite significantly reduced the production of undesired oxygenates and produced various aromatic compounds [24][25][26][27]. The selectivity for the production of aromatic is governed by the facile accessibility of the zeolite used in the catalytic upgrading.

Hydrotreating process is performed in hydrogen environment under catalyst and removes oxygen as water by catalytic reaction. Hydrotreating is usually a separate process from the fast pyrolysis. The process condition is typically high pressure (2 - 20 MPa) and the temperature less than 400 °C. A substantial amount of H$_2$ is required for hydrotreating to hydrogenate the organic content in bio-oil and remove oxygen as water. This H$_2$ requirement can be supplied by processing an additional biomass to produce H$_2$ but the overall efficiency of the process can be suffered. The desired products of the hydrotreating usually include paraffins, olefins, alcohols, ketones, aromatic, and
naphthenes[28]. The expected yield of hydrocarbon is around 25 - 55 % of biomass energy. The conceptual reaction is[20]:

\[ C \text{_{1H_{1.33O_{0.43}}} + 0.77 H_{2} \rightarrow CH_{2} + 0.43 H_{2}O} \]

The catalysts used for hydrotreating are sulfided CoMo[29][28] or NiMo[30], Rh, Ni, NiCu and the supports are SiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, ZrO\textsubscript{2}, CeO\textsubscript{2} or aluminosilicate. The problem of these catalysts includes instability of the alumina or aluminosilicate support under high water content in the bio-oil and sulfur functional group can be stripped away. This operating condition and catalyst constrains increase the complexity of the hydrotreating; therefore, the hydrotreating needs complicated equipments and expensive operating cost.

Carbon footprint analysis

Carbon footprint expresses the quantity of greenhouse gas (GHG) emitted by a specific source or process. The GHG emission is reported as CO\textsubscript{2}-equivalent (CO\textsubscript{2}e) which was determined from CO\textsubscript{2}, CH\textsubscript{4}, and NO\textsubscript{2} emitted from combustion fuels. The carbon footprint of the process is evaluated from the amount of energy and the type of fuel used in the process. Bio-oil production by fast pyrolysis process usually composed of (i) fluidized bed reactor, (ii) cyclones for char separation, (iii) condenser for condensing pyrolysis gas resulting in bio-oil, and (iv) combustion chamber to generate heat for the process[1].
A part of the heat required by the process can be provided from combustion of the by-product char and pyrolysis gas. The char and pyrolysis gas typically contain about 25% and 5% of the energy of the biomass feedstock. Figure A.4 shows the conceptual mass and energy flow diagram of the bio-oil production on a basis of 1 kg of biomass, which has high heating value of 18 MJ/kg[1]. The by-products, char and pyrolysis gas, of the process contain 5.4 MJ/kg. Combustion of these by-products to recycle the heat to the process can recover approximately 4.6 MJ/kg of biomass feedstock, considering 15% heat loss in the process[31]. This combustion of char and pyrolysis gas generates GHG emission of 9.8 gCO$_2$e. The GHG emission of bio-oil production process could be as low as 9.8 gCO$_2$e, if the amount of energy provided by the by-product is sufficient. Another source of GHG emission of the process is the additional energy required.

The amount of additional energy required for the process is strongly depended on the type of equipments and the scale of the production. Current research effort has been focusing on logistic and ecological footprint of biomass to study the feasibility of
production of biofuel[32][33][34]. The total GHG emission of the additional energy is
governed by the fuel types used to generate the energy. Table A.3 summarizes the usage
of each fuel type and the associated GHG emission. The energy usage data of chemicals
sector is provided by the U.S Department of Energy (DOE) Energy Information
Administration’s (EIA’s) Manufacturing Energy consumption Survey[31]. The average
GHG emission of the fuels used for chemical process is 97 gCO$_2$e /MJ. The total GHG
emission of biomass combustion reported in Table A.3 does not include CO$_2$ emission
because the uptake of CO$_2$ during growth of plants result in zero emission over time, with
an assumption that the forest area will be preserved[31]. This concept of zero emission
of biofuel is still controversial[35]. This data suggests that the use of biofuel as
replacement of fossil fuels could result in lower GHG emission.

Table A.3 Fuel usage and fuel combustion emission

<table>
<thead>
<tr>
<th>Fuel type</th>
<th>Usage (%)</th>
<th>Combustion emission factor (gCO$_2$e per MJ)</th>
<th>CO$_2$</th>
<th>CH$_4$</th>
<th>N$_2$O</th>
<th>Total GHG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural gas</td>
<td>21</td>
<td>50.25</td>
<td>0.03</td>
<td>0.03</td>
<td>50.30</td>
<td></td>
</tr>
<tr>
<td>Coal</td>
<td>2</td>
<td>89.01</td>
<td>0.27</td>
<td>0.45</td>
<td>89.72</td>
<td></td>
</tr>
<tr>
<td>Other fuels</td>
<td>1</td>
<td>70.60</td>
<td>0.08</td>
<td>0.17</td>
<td>70.84</td>
<td></td>
</tr>
<tr>
<td>Electricity</td>
<td>25</td>
<td>167.50</td>
<td>0.09</td>
<td>0.76</td>
<td>168.34</td>
<td></td>
</tr>
<tr>
<td>Steam</td>
<td>52</td>
<td></td>
<td></td>
<td></td>
<td>82.32</td>
<td></td>
</tr>
<tr>
<td>Biomass (wood)</td>
<td>-</td>
<td>89.90</td>
<td>0.76</td>
<td>1.18</td>
<td>2.12</td>
<td></td>
</tr>
</tbody>
</table>
Hypothesis and Proposed experiment

Gaseous products of biomass pyrolysis mainly compose of carbon oxides and small hydrocarbons and hydrogen. Many studies have been focused on the production of H$_2$ from biomass pyrolysis, which can be achieved by several techniques.[36] Most of the technique involves introduction of water or high pressure that would have to encounter with the drawback of product separation and harsh operating condition. Recent research has suggested biological water gas shift reaction for conversion of biomass to hydrogen-rich product, while the rate of production was limited by the low rate of reaction. The operating temperature of biomass pyrolysis process could promote water gas shift reaction (CO + H$_2$O $\leftrightarrow$ CO$_2$ + H$_2$) which can occur at the temperature below 500 °C while the evolution of H$_2$ in biomass pyrolysis was reported to occur at 700 – 900 °C.[37] The hypothesis of this study is moisture in biomass should facilitate the evolution at the temperature below 500 °C. The experiment was set up to examine the effect of moisture contain in the biomass on the evolution of H$_2$ at different temperature.

Figure A.5 shows the experimental apparatus separated into 3 group: (i) fast pyrolysis study including a gas manifold with flow controller for He carrier gas, high temperature furnace, and a K type thermocouple place inside a stainless steel pyrolysis reactor, (ii) gaseous products analysis consisting of cold trap to collect bio-oil that condense before reaching IR and high temperature diffuse reflectance Fourier transform infrared (DRIFT) reactor and MS to monitor the pyrolysis gas.
Fast pyrolysis

Coconut shell was used in the fast pyrolysis because of its consistency and availability. The shell was grinded into the particle size around 0.2 mm. The sample was prepared into 2 level of moisture content. The first sample was dried at 100 °C for 2 hr (wet shell) and the second sample was dried for 20 hr (dry shell). The moisture content was then determined by the weigh different between the sample and dry weight. The sample was loaded into the middle of the pyrolysis reactor. Prior to the pyrolysis, the furnace was preheated to 650 and 800 °C to obtain the pyrolysis temperature in the sample of 450 and 650 °C respectively. The pyrolysis reactor was then inserted into the heating zone during the fast pyrolysis experiment in the He carrier gas flow rate of 50 sccm which resulted in the vapor residence time of 2 s. The heating rate and the temperature were monitored by the thermocouple placed inside the sample bed. The sample remained in the furnace for 30 min to complete the pyrolysis process.

Pyrolysis gas analysis and product characterization

DRIFT was used to characterize pyrolysis vapor, biooil collected in the cold trap, and char resulted from the pyrolysis. The effluent from the DRIFT reactor will be condensed in a cold trap leaving non-condensable pyrolysis gas. The composition of the pyrolysis gas will be constantly monitored by MS.
Preliminary results

Figure A.6 shows the MS and temperature profiles of the effluent of wet sample pyrolysis in flowing He 50 cc/min. The temperature of the sample was raised from 180 °C to 700 °C in 5 min when the pyrolysis reactor was placed in the furnace. The corresponding MS profiles show immediate increase in the intensity of CO and CO$_2$ (m/e = 28 and 44) following by the increase in CH$_4$ and H$_2$ (m/e = 15 and 2).

MS and temperature profiles of the pyrolysis of the dry sample were shown in Figure A.7. The pyrolysis temperature of 650 °C was obtained in 7 min after placing the reactor in the furnace. MS profiles of the effluent indicated that CO, CO$_2$ and CH$_4$ were produced similarly to the pyrolysis of wet sample while the evolution of H$_2$ was delay for around 5 min. These results suggest that moisture in the sample may facilitate the production of H$_2$ at lower temperature. The mechanism of the reaction will be further study by in-situ DRIFT experiment.
Figure A.6 MS and temperature profiles of the effluent of wet coconut shell pyrolysis in flowing He 50 cc/min.
Figure A.7 MS and temperature profiles of the effluent of dry coconut shell pyrolysis in flowing He 50 cc/min.

The IR absorbance spectra of the fresh coconut shell, char, and bio-oil obtained from pyrolysis of coconut shell at 700 °C is shown in Figure A.8. The O-H stretching band at 3231 cm\(^{-1}\) indicates the presence of water, phenols and alcohols; the C-H stretching bands at 2963, 2925, and 2853 cm\(^{-1}\) and C-H deformation bands at 1456 and 1376 cm\(^{-1}\) indicate the presence of alkanes. The C=O stretching bands at 1704 and 1654 cm\(^{-1}\) indicate the presence of carboxylic acids, ketones and aldehydes. The C=C stretching band at 1585 cm\(^{-1}\) indicates the presence of alkenes and aromatics. The O-H bending bands at 834, 745 and 700 cm\(^{-1}\) indicate the presence of phenols, esters, and aromatic\cite{38}\cite{39}\cite{40}. Analysis of these IR spectra obtained from in situ study will allow understanding of the progress of product formation as a function of temperature.
Figure A.8 Absorbance spectra of the coconut shell, pyrolyzed coconut shell and the oil produced from the fast pyrolysis. Absorbance was obtained by $\text{Abs.} = \log(I_0/I)$ where $I$ is single beam spectra of the sample and $I_0$ is single beam of KBr.

Study of char reactivity and structure by Raman spectroscopy

Char reactivity

Char gasification reactivity in CO$_2$, air, or inert gas is mainly studied by a thermogravimetric analysis (TGA). TGA measures weight loss during heating the sample in a specific environment. Figure A.9 shows the schematic of typical characteristic of the char weight loss as a function of temperature obtained with small amount of char and slow heating rate. The curves show several regions which represent different stages taking place during different ranges of temperature[41]. The first region of rapid weight loss at the temperature below 350 °C is devolatilization stage, which is governed by the presence of oxygen. The combustion of char occurs and completes at
around 500 °C in presence of oxygen. In the absence of oxygen, the pyrolysis arises instead of combustion. The gasification with CO$_2$ is significantly observed at the temperature above 750 °C.

Figure A.9 Schematic of the typical conversion (X) as a function of temperature obtained from TGA

The specific reactivity ($R_x$) can be calculated from the TGA result. The specific reactivity, which expresses the kinetic of char conversion is defined as

$$R_x = -\frac{1}{W} \frac{dW}{dt} = \frac{1}{1 - X} \frac{dX}{dt}; X = \frac{W - W_0}{W_0 - W_\infty}$$

where $W$ is the mass of the char sample, $W_\infty$ is the final weight (ash weight), and $X$ is the degree of conversion.
Raman spectra of char and correlation with reactivity

Char composes of highly disordered carbonaceous material that has short range order polycrystalline structure. The Raman spectroscopy technique is widely used to analyze the structure of char because it is sensitive to both the crystalline structure and the molecular structure. Table A.4 summarizes the manufacturers and the light sources of the Raman spectroscope used for studying characteristic of biomass char.
Table A.4 Manufacturers and light sources of Raman spectroscope

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Source</th>
<th>Sample</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perkin-Elmer GX FT-IR/Raman</td>
<td>Nd:YAG laser at 1064 nm</td>
<td>Char+KBr</td>
<td>[42]</td>
</tr>
<tr>
<td></td>
<td>100mW</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Perkin-Elmer GX FT-IR/Raman</td>
<td>Nd:YAG laser at 1064 nm</td>
<td>Char+KBr</td>
<td>[43]</td>
</tr>
<tr>
<td></td>
<td>100mW</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Perkin-Elmer GX FT-IR/Raman</td>
<td>Nd:YAG laser at 1064 nm</td>
<td>Char+KBr</td>
<td>[44]</td>
</tr>
<tr>
<td></td>
<td>100mW</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Perkin-Elmer GX FT-IR/Raman</td>
<td>Nd:YAG laser at 1064 nm</td>
<td>Char+KBr</td>
<td>[45]</td>
</tr>
<tr>
<td></td>
<td>100mW</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jobin Yvon Labram HR800</td>
<td>Ar-laser 514.5 nm 1mW</td>
<td>Char</td>
<td>[46]</td>
</tr>
<tr>
<td>Perkin-Elmer GX FT-IR/Raman</td>
<td>Nd:YAG laser at 1064 nm</td>
<td>Char+KBr</td>
<td>[47]</td>
</tr>
<tr>
<td></td>
<td>150mW</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Renishaw RM3000</td>
<td>Ar⁺ laser 514 nm</td>
<td>Char</td>
<td>[48]</td>
</tr>
<tr>
<td>XY Raman (Dilor Co., France)</td>
<td>Ar⁺ laser 514.53 nm</td>
<td>Char</td>
<td>[49]</td>
</tr>
<tr>
<td>XY double subtractive</td>
<td>514.5 nm Ar⁺ laser 1-4mW</td>
<td>Char</td>
<td>[50]</td>
</tr>
<tr>
<td>spectrograph with</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>premonochromator</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Renishaw, System 2000;</td>
<td>Ar⁺ laser (514 nm, 17 mW), a He–Ne laser (632.8 nm, 25 mW), and a NIR diode laser (780 nm, 26 mW)</td>
<td>Char</td>
<td>[51]</td>
</tr>
<tr>
<td>Yobin Yvon, LabRAM HR</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The analysis of Raman spectra of char is usually referred to the structure of highly ordered carbonaceous material of graphite. The perfect graphite band is noted as the G band at 1585 cm⁻¹, corresponding to the stretching vibration mode with $E_{2g}$ symmetry in the aromatic layer of the graphite. The disordered carbonaceous materials show the band
around 1350 cm$^{-1}$, which is commonly called the defect band (D band). Although the graphite gives narrow spectra, the spectra of biomass char show much broader peaks near the G and D bands. Analysis of the overlaps between the D and G bands as well as the shoulders at those two bands also reveals important information about the structure of the char. The Raman spectra between 800 and 1800 cm$^{-1}$ were curve fitted to analyze the area of each peak. Figure A.10 shows the schematic of a typical example of Raman spectra curve-fitting with 10 Gaussian bands generated from the computational software. The band names were assigned by Li et al. as shown in
Table A.5[43]. The molecular vibration of aromatic quadrant ring breathing is at the same position as the G band. The Raman signal at the G band in the biomass char study is mainly attributed to the aromatic ring breathing because the graphite has much lower Raman intensity than the char[45]. Similarly, the D band represents both defect graphite structure and, more importantly, aromatics with not less than 6 rings. The overlap between G and D bands was separated into three bands: $G_r$, characterized at 1540 cm$^{-1}$, $V_l$ at 1465 cm$^{-1}$, and $V_r$ at 1380 cm$^{-1}$. These bands represent structure in amorphous carbon with smaller aromatic ring as well as the semi-circle breathing of aromatic rings. The peaks to the right of D band represent $C_{\text{aromatic}}-C_{\text{alkyl}}$, aromatic ether, diamond carbon sp$^3$, and C-H on aromatic rings.

Figure A.10 An example of Raman spectra curve-fitting with 10 bands.
Table A.5 Summary of Raman spectra band assignment

<table>
<thead>
<tr>
<th>Band name</th>
<th>Peak position (cm&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>Description</th>
<th>Bond type</th>
</tr>
</thead>
<tbody>
<tr>
<td>G&lt;sub&gt;i&lt;/sub&gt;</td>
<td>1700</td>
<td>Carbonyl group C=O</td>
<td>sp&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>G</td>
<td>1590</td>
<td>Graphite, aromatic ring, alkene, E&lt;sub&gt;2g&lt;/sub&gt;–symmetry</td>
<td>sp&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>G&lt;sub&gt;r&lt;/sub&gt;</td>
<td>1540</td>
<td>Aromatics with 3-5 rings</td>
<td>sp&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>V&lt;sub&gt;i&lt;/sub&gt;</td>
<td>1465</td>
<td>Methylene, methyl, aromatic rings</td>
<td>sp&lt;sup&gt;2&lt;/sup&gt;, sp&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
<tr>
<td>V&lt;sub&gt;r&lt;/sub&gt;</td>
<td>1380</td>
<td>Methylene, aromatic rings, amorphous carbon</td>
<td>sp&lt;sup&gt;2&lt;/sup&gt;, sp&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
<tr>
<td>D</td>
<td>1350</td>
<td>Disorder carbon, aromatics &gt;= 6 rings A&lt;sub&gt;1g&lt;/sub&gt;-symmetry</td>
<td>sp&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>S&lt;sub&gt;i&lt;/sub&gt;</td>
<td>1230</td>
<td>Aryl-alkyl ether, para-aromatics</td>
<td>sp&lt;sup&gt;2&lt;/sup&gt;, sp&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
<tr>
<td>S</td>
<td>1185</td>
<td>C&lt;sub&gt;aromatic&lt;/sub&gt;-C&lt;sub&gt;alkyl&lt;/sub&gt;, aromatic ethers, diamond carbon</td>
<td>sp&lt;sup&gt;2&lt;/sup&gt;, sp&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
<tr>
<td>S&lt;sub&gt;r&lt;/sub&gt;</td>
<td>1060</td>
<td>C-H on aromatic, benzene ring</td>
<td>sp&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>R</td>
<td>960-800</td>
<td>C-C on alkanes, C-H on aromatic</td>
<td>sp&lt;sup&gt;2&lt;/sup&gt;, sp&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

The effect of pyrolysis temperature on the Raman spectra of the char was studied by Asadullah et al.[42]. Increasing the pyrolysis temperature reduced the total Raman intensity area in the region 800 - 1800 cm<sup>-1</sup>. The reduction in Raman intensity suggests that the oxygenated compounds, which are more sensitive to Raman spectra, form aromatics and cross-linked network structure, which are less sensitive. The aromatic structure in char increases the light absorptivity and decreases the Raman sensitivity. The peaks position remains almost constant regardless the decrease in intensity from increasing pyrolysis temperature. This information allows rapid determining of the degree of cracking, cross-linking, and condensation of the ring systems in the char.
obtained from pyrolysis by correlating to the total intensity. The uniformity of the carbon structure can be evaluated by the Raman intensity ratio $I_D/I_{\left(G_r+V_l+V_g\right)}$. The large aromatic ring compounds in char increase with increasing the ratio $I_D/I_{\left(G_r+V_l+V_g\right)}$. The increase of char structural order with increasing pyrolysis temperature is in agreement with other studies[46][48][47].

The specific reactivity of the char determined by TGA shows the relationship with the Raman intensity ratio $I_D/I_{\left(G_r+V_l+V_g\right)}$. Generally, the reactivity of char decreases with increasing pyrolysis temperature. This phenomena can be explained by the increase of the Raman intensity ratio $I_D/I_{\left(G_r+V_l+V_g\right)}$, which indicates that large and condensed aromatic ring is the major component of char produced from high temperature pyrolysis. This large aromatic ring is not active for combustion and gasification reaction, thus the reactivity decreases. Another explanation is that the alkali species in the carbon structure of char, which are the catalysts for gasification, is difficult to participate in the reaction due to the condensed structure. This rapid Raman spectra analysis demonstrates the capability to determine the structural order, char reactivity, and rough estimation of the aromatic components, which could be a great benefit to the screening of the fuel for gasification or other research activities.

Conclusion

The principle of fast pyrolysis and the catalytic upgrading of bio-oil/ pyrolysis vapor are addressed in this candidacy report. Fast pyrolysis is a thermal conversion process in which biomass is rapidly heated in the absence of oxygen. The major advantage of fast pyrolysis is high bio-oil yield, which can be as high as 75%.
Maximizing the bio-oil yield requires (i) very high heating rate, which was reported around 50 W/cm², (ii) accurately control of the pyrolysis temperature between 450 - 550 °C, (iii) short vapor residence time (0.5 - 5 s), and (iv) rapid cooling of the pyrolysis vapor to prevent further cracking or coking.

Bio-oil obtained from the pyrolysis process contains water and oxygenated organic compounds. These oxygenated compounds can initiate the secondary reaction during the storage, hence the upgrading to remove the oxygen is needed. Deoxygenation of bio-oil by catalysis cracking of pyrolysis vapor is widely used for upgrading. Catalytic cracking is the decomposition of oxygenated compound resulting in light hydrocarbon and the removal forms H₂O, CO₂ and CO. HZSM-5 was reported to be the most effective catalyst for cracking or reforming bio-oil as the zeolite promotes high hydrocarbon and aromatic formation. The major challenge is the catalyst deactivation due to coking.

The proposed experiment is to examine the catalytic upgrading of pyrolysis vapor derived from biomass fast pyrolysis with in situ IR technique. The pyrolysis vapor will be upgraded through catalytic cracking on HZSM-5, GaZSM-5, and NiZSM-5, aiming to achieve high yield of valuable aromatic, such as benzene, toluene or xylene. The effect of catalyst and operating temperature on the pyrolysis vapor upgrading reaction and product distribution will be studied by analysis of data obtain from in situ IR. Various characterization techniques will be employed, including GC/MS for bio-oil and MS for pyrolysis gas.

The char characterization can be performed by Raman spectroscopy. The studies reveals that degree of cracking, cross-linking, and condensation of the aromatics in the char obtained from pyrolysis has a relationship with the total intensity of Raman spectra.
The reduction of the Raman spectra intensity indicates the higher degree of aromatic/cross-linking form in the char. The intensity ratio $I_D/I_{(G_r+V_l+V_f)}$ suggests the carbon structural order and char reactivity. The increase of $I_D/I_{(G_r+V_l+V_f)}$ ratio indicates large aromatic ring which is not active for combustion or gasification.

References


APPENDIX B

SUPPLEMENTALY INFORMATION OF THE STUDY OF CH$_4$/CO$_2$ REFORMING IN SOLID OXIDE FUEL CELL WITH Rh-Ni/YSZ ANODE

Figure B.1 Conversion of CH$_4$ and CO$_2$ at 700 °C as a function of Rh content in Ni/YSZ powder
Figure B.2 1/single beam of 0.139 wt% Rh-Ni/YSZ TPR
Figure B.3 Absorbance of 0.139 wt% Rh-Ni/YSZ TPR across 100 °C difference in temperature during heating and cooling.
Figure B.4 Absorbance of cooling – heating of 0.139 wt% Rh-Ni/YSZ TPR
Figure B.5 (a) CO and Ar MS profiles during the CO adsorption and TPD over 0.137 wt% Rh-Ni/YSZ anode powder, (b) IR single beam spectra, and (c) corresponding IR absorbance. Absorbance is obtained by Abs. = log(I/I₀), where I is single beam spectra taken at difference stage during the CO adsorption and TPD and I₀ is single beam taken prior to the CO adsorption.
Figure B.6 IR single beam spectra, and (c) corresponding IR absorbance of CO adsorption and TPD over 0.137 wt% Rh-Ni/YSZ diluted in KBr (10 wt%). CO adsorption step was performed by 3cc and 1 cc injection of pure CO into 30 sccm stream of Ar. Absorbance is obtained by $\text{Abs.} = \log\left(\frac{I}{I_0}\right)$, where $I$ is single beam spectra taken at difference stage during the CO adsorption and TPD and $I_0$ is single beam taken prior to the CO adsorption.
Figure B.7 SEM images of 0.03 % Rh-Ni/YSZ anode surface after the experiment.
Figure B.8 SEM images of 0.01 % Rh-Ni/YSZ anode surface after the experiment.

Figure B.9 SEM images of Ni/YSZ anode surface after the experiment.
Figure B.10 EDX analysis of 0.03 % Rh-Ni/YSZ anode surface after the experiment.
Figure B.11 EDX analysis of 0.01 % Rh-Ni/YSZ anode surface after the experiment.
Figure B.12 EDX analysis of Ni/YSZ anode surface after the experiment.
Figure B.13 TEM images of 0.03 % Rh-Ni/YSZ anode surface after the experiment.
Figure B.14 TEM images of 0.01 % Rh-Ni/YSZ anode surface after the experiment.
Figure B.15 TEM images of Ni/YSZ anode surface after the experiment.
Figure B.16 TEM images of 0.14 % Rh-Ni/YSZ powder after the TPR experiment.
APPENDIX C

EFFECT OF CARBON TYPE ON THE CARBON-BASED SOFC PERFORMANCE
AND GASIFICATION WITH CO$_2$

The objective of this chapter is to evaluate the performance of the C-SOFC with petroleum coke (Pet coke) and coconut coke in the presence of a CO$_2$ stream. The effect of the type of carbon fuel on the fuel cell performance was studied by operating the cell in Pet coke and coconut coke. The performance of the fuel cell was determined by the electric current and power generated.

Experiment

The preparation of the fuel cell and the fuel cell assemble was described in the section 2.1 and 2.2. The fuel cell was heated in a flowing He at a heating rate of 3 $^\circ$C/min and held at 750 $^\circ$C in open circuit voltage (OCV) for 12 h. A H$_2$/He stream (200 sccm, 50 vol.% H$_2$) was introduced to the anode compartment for 1 hr to reduce the anode prior to the operation in CO$_2$. The fuel cell was tested in Pet coke by switching the inlet gas stream from H$_2$/He to a pure He (200 sccm). The effect of CO$_2$ on the C-SOFC performance was studied by switching the inlet gas stream from pure He to a CO$_2$/He stream (20sccm, 50 vol% CO$_2$) and to a pure CO$_2$ stream (100, 200 and 500 sccm). The V-I curves and electrochemical impedance spectra of the fuel cell were recorded along with the effluent MS profiles.

Results and discussion
Figure C.1 shows the normalized MS profiles of the effluents and the corresponding current densities recorded during testing of the fuel cell at 0.40 V and 750 °C in Pet coke + H₂, Pet coke, and Pet coke + CO₂. Letters A to F noted in the Figure C.1 correspond to different operating conditions, as discussed in the following sections.

Exposure of the fuel cell to the H₂/He (section A) produced an electrical current of 0.60 A/cm² at 0.40 V. Switching the inlet stream from H₂/He to pure He (section B) allowed the operation in Pet coke (direct C-SOFC) producing a current density of 0.14 A/cm². Changing the inlet stream from He to CO₂/He (section C) decreased the current density to 0.08 A/cm² and increased CO and CO₂ MS intensities (m/e 28 and 44). The increase in the CO MS intensity with the introduction of the CO₂/He stream indicates formation of CO from Boudouard reaction (CO₂+C→2CO). Reducing the total inlet flow rate to 100 sccm pure CO₂ (section D) improved the fuel cell current density, which reached a maximum of 0.09 A/cm². The rapid drop in the MS intensities at t= 160 min in section D indicates the occurrence of a major leakage that prevented accurate monitoring of the effluent concentration. Increase CO₂ flow rate to 200 and 500 sccm decrease the current density to 0.06 and 0.04 A/cm².
Figure C.1 MS profiles of the outlet stream, voltage and current generated by the fuel cell at 750°C.

Figure C.2 shows the V-I curves and impedance spectra recorded during testing of the fuel cell at 750 °C in Pet coke at the beginning of the experimental campaign (section B in Figure C.1) and after exposure to the CO₂ streams (sections G in Figure C.1). The V-I curves exhibit a linear relationship comprising two sections with different slope. The initial V-I curve recorded in Pet coke (section B) shows a sudden change in the slope at a current density of 0.35 A/cm², marking the presence of mass transfer limitations. The
V-I curve recorded in Pet coke (section G) shows that the change of slope occurred at a much lower current density, indicating that fuel supplied to the anode was limited because Pet coke on the anode surface was consumed during the experiment.

The impedance spectra of Figure C.2(b) display a single frequency-dependant arch at 5 Hz. The intercept of the impedance arch with the real axis at high frequencies gives the fuel cell ohmic resistance $R_\Omega$; while the intercept of the impedance arch with the real axis at low frequencies gives the total cell resistance $R_T$, and the difference of the two intercepts marks the electrode polarization losses $R_E$. The total cell resistance $R_T$ comprises the ohmic contributions from the electrolyte layer, the anode and cathode electrodes as well as their interfaces with the electrolyte, and the current collectors. Initial testing of the fuel cell in Pet coke (section B in Figure C.1) produced a total cell resistance $R_E = 1.5 \ \Omega \text{cm}^2$, which increased to $2.6 \ \Omega \text{cm}^2$ after the exposure of the fuel cell to the CO$_2$ streams. The increase in $R_E$ upon exposure to CO$_2$ can be attributed to an increased electrode polarization $R_E$ given that the ohmic resistance $R_\Omega$ remained under $0.6 \ \Omega \text{cm}^2$ throughout the experiments. The result is in agreement with the performance of the C-SOFC determined from V-I curves in Figure C.2(a).
Figure C.2 V-I curve and impedance spectra of C-SOFC before exposure to flowing CO\textsubscript{2}, (section B), and after exposure, (section G), at 750\textdegree C

Figure C.3 shows V-I curve and impedance spectra of the C-SOFC during testing in flowing CO\textsubscript{2}/He (200 sccm, 50 vol\% CO\textsubscript{2}, marked as B in Figure C.1) and pure CO\textsubscript{2} (100, 200, and 500 sccm, marked in Figure C.1 as D, E and F respectively). The C-SOFC under flowing 50\% CO\textsubscript{2} produced an OCV of 0.63 V. The OCV increase to 0.73 V when pure CO\textsubscript{2} was used, which is in agreement with the Nernst potential equation. Flowing CO\textsubscript{2} at 100 sccm produced maximum current density of 0.21 A/cm\textsuperscript{2}. The maximum current density decreased to 0.14 and 0.07 A/cm\textsuperscript{2} when the CO\textsubscript{2} flow rate increased to 200 and 500 sccm. Flowing CO\textsubscript{2} at high flow rate decreased the residence
time of CO\(_2\) to react with coke producing CO. This produced CO and further
electrochemical oxidized on the anode generating electricity. Thus, increase the flow rate
of CO\(_2\) resulted in decrease of the CO concentration on the C-SOFC anode and decrease
of the electrical power generation. The total cell resistance of the C-SOFC under flowing
50\% CO\(_2\) was 2.3 \(\Omega\) cm\(^2\) and those of the pure CO\(_2\) at 100, 200 and 500 sccm were 2.4,
2.7 and 4.7 \(\Omega\) cm\(^2\). This increase of the total cell resistance was resulted from the higher
polarization losses.

![V-I curve and impedance spectra of C-SOFC](image)

Figure C.3 V-I curve and impedance spectra of C-SOFC in flowing 200 sccm of 50 \%
CO\(_2\) (section C), 100 sccm, 200 sccm, 500 sccm of pure CO\(_2\) (section D, E, and F) at
750\(^\circ\)C
Figure C.4 shows V-I curve and impedance spectra of the C-SOFC operated in Pet coke and coconut coke. Testing of the C-SOFC in Pet coke in flowing CO\textsubscript{2}/He (200sccm, 50 vol.% CO\textsubscript{2}) decrease the maximum current density from 0.40 to 0.21 A/cm\textsuperscript{2}. The detail analysis of the C-SOFC performance in coconut coke was reported in the Chapter 3. As oppose to the Pet coke, flowing CO\textsubscript{2} to the C-SOFC operated in coconut coke increase the maximum current density from 0.28 to 0.46 A/cm\textsuperscript{2} and the maximum power density from 0.09 to 0.13 W/cm\textsuperscript{2}. The opposing C-SOFC performance trends observed during testing in coconut fuel and Pet coke under CO\textsubscript{2} provides experimental evidence supporting the dependence of extent of the Boudouard reaction on the type of carbon fuel utilized. The power densities observed in Figure C.4 indicate that the coconut fuel is far more active than Pet coke towards Boudouard reaction under the fuel cell operating conditions.
Figure C.4 V-I curve and impedance spectra of C-SOFC in Pet coke (section B), Pet coke with flowing 200 sccm 50% CO$_2$ (section C), coconut coke, and coconut coke with flowing 200 sccm 8.6% CO$_2$, at 750°C.

The characteristic of the C-SOFC performance in presence of CO$_2$ was further investigated with coconut coke. Figure C.5 shows the V-I curves and impedance spectra recorded during the operation of the C-SOFC with coconut coke in flowing He and CO$_2$/He at 750, 800 and 850°C. The V-I curves exhibit a linear relationship and do not show a sudden change in the slope at high current densities. This result suggests that the coconut coke C-SOFC was not limited by mass transfer limitations of fuel to the anode surface, as previously observed with the C-SOFC with Pet coke. The absence of mass...
transfer limitations on the coconut coke C-SOFC may be attributed to the high electronic conductivity and low ash content of the coconut coke fuel.

Testing of the C-SOFC at 750 °C in He produced a maximum current density of 0.088 A/cm². Introducing CO₂ to the C-SOFC at 750 °C increased the maximum current density by 13.6 % (0.1 A/cm²). The improvement of the fuel cell maximum current density by addition of CO₂ was further evidenced by elevating the fuel cell operating temperature (i.e., 42 % at 800 °C and 33 % at 850 °C). The trend observed in Figure C.5 indicates that development of a high performance C-SOFC requires fine-tuning the operating temperature and CO₂ inlet concentration.

The impedance spectra recorded during the experiments are show in Figure C.5(b) and Figure C.5(d). The C-SOFC in flowing He at 750, 800 and 850 °C and in flowing CO₂/He at 750 and 800 °C display a frequency-dependant arch at high frequency regime and a linear relationship at low frequency regime. The fuel cell ohmic resistance was determined from the intercept of the impedance arch with the real axis at high frequencies. The ohmic resistances of the C-SOFC were found to decrease with increasing temperature. The decrease in the fuel cell ohmic resistance correlated well with the increase in ionic conductivity of the YSZ electrolyte.
Figure C.5 V-I curves and electrochemical impedance spectra of C-SOFC operated on coconut coke with flowing He and CO\textsubscript{2}/He at 750, 800, and 850 °C.

Figure C.6(a) shows the CO and CO\textsubscript{2} molar flow rates at the outlet of the fuel cell during testing at OCV conditions and He flow as a function of temperature. The amounts of CO and CO\textsubscript{2} observed at the fuel cell outlet under OCV and He flow evidence the occurrence of coconut coke gasification reactions. Elevating the operating temperature resulted in a significant reduction on the CO flow rate at the fuel cell outlet, suggesting depletion of the fraction of coconut coke that can be gasified. Although the amount of CO at the fuel cell outlet decreased at high temperatures during testing in He flow, the fuel cell maximum current density exhibited a 2.4 times improvement, as shown in Figure C.5(a). This observation suggests that the improvement in the fuel cell performance at high temperatures was the result of electrochemical oxidation of coconut coke.
Analysis of the molar flow rates at the outlet of the fuel cell during testing at OCV conditions and CO$_2$/He flow, shown in Figure C.6(b), evidenced nearly a threefold increase in CO formation at high temperatures (7.2 µmol/s at 750 °C and 21.5 µmol/s at 850 °C). The higher conversion of CO$_2$ to CO at high temperatures is in agreement with the predicted increase in the thermodynamic equilibrium constant for the endothermic reaction CO$_2$ + C $\rightarrow$ 2CO ($\Delta H = 172.54$ kJ/mol). Comparison of the fuel cell performance in He/CO$_2$, shown in Figure C.6(c), and the CO molar flow rates as a function of temperature indicates that addition of CO$_2$ to the C-SOFC facilitates gasification of coconut coke producing CO, which in turn can be electrochemically oxidized at the anode electrode.

Figure C.6 CO and CO$_2$ outlet flow rate as a function of temperature of the C-SOFC operated on coconut coke at OCV with (a) 56 sccm of He and (b) 56 sccm of He and 20 sccm of CO$_2$

The V-I curve produced from coconut coke at 850 °C in Figure C.5(a) was replotted in Figure C.7(a) along with the outlet molar flow rate of CO and CO$_2$ in Figure
C.7(b). At OCV conditions, the conditions at which electrochemical oxidation cannot take place, CO and CO\textsubscript{2} were produced from the gasification of coconut coke. The outlet flow rate of CO and CO\textsubscript{2} at OCV and 850 °C were 4.66 and 0.13 \textmu mol/sec.

Withdrawing the electric current with applying electrical load to the C-SOFC initiated the electrochemical oxidation on the anode, resulting in the formation of CO and CO\textsubscript{2}. Drawing 0.21 A/cm\textsuperscript{2} led to an increase in molar flow rate of CO and CO\textsubscript{2} to 5.95 and 0.25 \textmu mol/sec. The change in CO and CO\textsubscript{2} product may be caused by this oxygen ion induced from the current production or by the leakage of O\textsubscript{2} into the anode chamber. The MS profiles of O\textsubscript{2} and N\textsubscript{2}, shown in Figure C.7(c), indicate that the extent of the O\textsubscript{2} leakage is minimal. The increase in CO and CO\textsubscript{2} flow rate (\Delta F\textsubscript{CO} and \Delta F\textsubscript{CO\textsubscript{2}}) were 1.29 and 0.12 \textmu mol/sec, representing the amount of CO and CO\textsubscript{2} produced from oxygen transferred from cathode. This ratio of the CO\textsubscript{2}:CO produced at 0.21 A/cm\textsuperscript{2} was 0.093:1 which was higher than that at OCV. The ratio of outlet molar flow rate of CO\textsubscript{2}:CO at OCV, in Figure C.6a, was 0.028:1. This result suggests that operation of C-SOFC in coconut coke majorly produced CO\textsubscript{2} and further convert to CO following the equations

\[ C + O^{2-} \rightarrow CO_{2} + 4e^{-} \] \hspace{1cm} \textit{----- 1}

\[ CO_{2} + C \rightarrow 2CO \] \hspace{1cm} \textit{----- 2}
Figure C.7 Plots of (a) voltage and (b) CO and CO\textsubscript{2} outlet flow rate as a function of current density of the C-SOFC operated on coconut coke with 56 sccm of He at 850 °C, and (c) MS intensity of N\textsubscript{2} and O\textsubscript{2} during V-I measurement.
Conclusion

1. The C-SOFC operated in Pet coke produced the maximum current density of 0.40 A/cm$^2$ and decreased to 0.12 A/cm$^2$ after 6 hr of operation. The decrease was caused from the consumption of the coke on the anode surface. Flowing CO$_2$ at 100, 200 and 500 sccm to the C-SOFC anode decrease the maximum current density to 0.21, 0.14 and 0.07 A/cm$^2$. The residence time of CO$_2$ to react with coke producing CO was decreased by increasing the flow rate of CO$_2$ resulting in the low concentration of CO on the anode and decrease of C-SOFC performance. As oppose to the Pet coke, flowing 8.6% CO$_2$ to the C-SOFC operated in coconut coke increased the maximum current density from 0.28 to 0.46 A/cm$^2$. The result suggests that coconut coke is more active than PET coke towards Boudouard reaction under the fuel cell operating condition.

2. The amounts of CO and CO$_2$ observed at the fuel cell outlet under OCV and He flow evidence the occurrence of coconut coke gasification reactions. Elevating the operating temperature resulted in a significant reduction on the CO flow rate at the fuel cell outlet. Although the amount of CO at the fuel cell outlet decreased at high temperatures during testing in He flow, the fuel cell maximum current density exhibited a 2.4 times improvement. This observation suggests that the improvement in the fuel cell performance at high temperatures was the result of electrochemical oxidation of coconut coke.

3. Analysis of the molar flow rates at the outlet of the fuel cell during testing at OCV conditions and CO$_2$/He flow evidenced nearly a threefold increase in CO formation at high temperatures. Comparison of the fuel cell performance in CO$_2$/He and the CO molar flow rates as a function of temperature indicates that addition of CO$_2$ to the
C-SOFC facilitates gasification of coconut coke producing CO, which in turn can be electrochemically oxidized at the anode electrode.

4. The molar flow rates at the outlet of the fuel cell during testing at variable load (i.e., V-I curve testing) at 850 °C and He flow revealed that operation at high current densities results in higher formation of CO$_2$. 