Declaration

To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgement has been made.

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university.

Signature: Zhenhua Min

Date: 22/11/2010
Abstract

Biomass has become an increasingly important renewable source of energy for enhanced energy security and reduced CO₂ emissions. Gasification is at the core of many biomass utilisation technologies for such purposes as the generation of electricity and the production of hydrogen, liquid fuels and chemicals. However, gasification faces a number of technical challenges to become a commercially feasible renewable energy technology. The most important one is the presence of tar in the gasification product gas. The ultimate purpose of this thesis was to investigate the catalytic reforming of tar using cheap catalysts as an effective means of tar destruction.

In this thesis, natural ilmenite ore and novel char-supported catalysts were studied as catalysts for the steam reforming of biomass tar derived from the pyrolysis of mallee biomass in situ in two-stage fluidised-bed/fixed-bed quartz reactors. In addition to the quantification of tar conversion, the residual tar samples were also characterised with UV-fluorescence spectroscopy. Both fresh and spent catalysts were characterised with X-ray diffraction spectroscopy, FT-Raman spectroscopy and thermogravimetric analysis.

The results indicate that ilmenite has activity for the reforming of tar due to its highly dispersed iron-containing species. Both the externally added steam and low concentration oxygen affect the tar reforming on ilmenite significantly. The properties of biomass affect the chemical composition of its volatiles and therefore their reforming with the ilmenite catalyst. Compared with sintering, coke deposited on ilmenite is the predominant factor for its deactivation.

During the steam reforming process, the char-supported iron/nickel catalysts exhibit very high activity for the reforming of tar. In addition, NOₓ precursors could be decomposed effectively on the char-supported iron catalyst during the steam reforming process. The hydrolysis of HCN and the decomposition of NH₃ on the catalyst are the key reactions for the catalytic destruction of NOₓ precursors.

The kinetic compensation effects demonstrate that the reaction pathways on the char-supported catalysts are similar but different from those on ilmenite. The properties of catalyst support could play important roles for the activities of the catalysts and the reaction pathways on the catalysts. The char support as part of the char-supported catalysts can undergo significant structural changes during the catalytic reforming of biomass volatiles.
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Lastly, I would like to dedicate this thesis to my parents and wife for all of their love, support and encouragement in all that I set out to achieve.

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Zhenhua Min
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Chapter 1

Introduction
1.1 Background

With increasing world population and gross domestic product, energy demand and global warming have become the most important issues in the world. According to World Energy Outlook, world primary energy demand would increase by 45% between 2006 and 2030 at an average annual growth rate of 1.6% (Table 1-1) [1]. The traditional fossil fuels can neither satisfy the increasing energy demand nor decrease the CO$_2$ emissions. For instance, CO$_2$ emissions from coal use totaled 11.7 Gt, equal to 42% of the global energy-related CO$_2$ emissions in 2006 and it is projected to rise by 2% per year, reaching 18.6 Gt in 2030 (Figure 1-1) [1].

Table 1-1. World primary energy demand by fuel (Mtoe) [1].

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</tr>
<tr>
<td>Biomass and waste**</td>
<td>748</td>
<td>1045</td>
<td>1186</td>
<td>1375</td>
<td>1662</td>
<td>1.4%</td>
</tr>
<tr>
<td>Other renewables</td>
<td>12</td>
<td>55</td>
<td>66</td>
<td>158</td>
<td>350</td>
<td>7.2%</td>
</tr>
<tr>
<td>Total</td>
<td>7223</td>
<td>10034</td>
<td>11730</td>
<td>14121</td>
<td>17014</td>
<td>1.6%</td>
</tr>
</tbody>
</table>

* Average annual rate of growth.
** Includes traditional and modern uses.

In addition, the utilization of coal can also generate other toxic and pollutant gases, which can seriously affect the local environment and human health. Biomass is becoming an increasingly popular renewable energy source because of its potential roles in overcoming the challenges of energy shortage and environmental issues [2-5]. Compared with fossil fuels such as coal, oil and natural gas, biomass has significant environmental advantages. CO$_2$ produced from biomass utilization can be counteracted by the removal of carbon dioxide during the growth of biomass. Moreover, the utilization of biomass can produce less N-/S-containing pollutants
than those of fossil fuels at least partly due to the lower contents of sulfur and nitrogen in biomass. Biomass is therefore considered as a clean renewable energy source [6-11].

![Graph showing CO₂ emissions by fuel from 1990 to 2030.](image)

**Figure 1-1.** World energy-related CO₂ emissions by fuel [1].

Among all renewable energy sources, biomass is the largest contributor to global primary energy supply. Total world demand for biomass would rise from 1186 Mtoe in 2006 to about 1660 Mtoe by 2030 at an average annual rate of growth of 1.4% (Table 1-1) [1]. Compared with other renewable energy resources, biomass can be a substitute for all fossil-fuel-based products by a wide range of technologies to convert the biomass into heat, electricity and liquid fuels (Figure 1-2) [1]. Biomass can be used directly in traditional ways for heating and cooking, or indirectly using modern conversion technologies. It was traditionally used as firewood for domestic use, which is an inefficient method and would cause air pollution [12, 13]. Nowadays, oil, syngas and other chemicals can be obtained from renewable biomass. The main methods of producing fuels from biomass include hydrolysis to obtain aqueous phase sugar or lignin, liquefaction and pyrolysis to generate bio-oil and biodiesel, and
gasification to produce syngas [6, 9]. Fermentation of waste biomass has been studied widely to obtain biogas, especially methane [14, 15]. Meanwhile, the production of ethanol and hydrogen from biomass has been investigated [16, 17]. Bio-diesel and bio-oil have also been obtained from the pyrolysis of biomass [18-22]. Furthermore, the gasification of biomass represents a potentially efficient way to obtain hydrogen or syngas from biomass [23-29], which can be used in fuel cells, gas engines and turbines to generate power with high efficiency and low environmental impacts.

Figure 1-2. Contribution of biomass to world primary energy demand, 2006. [1]

Biomass is particularly suitable for gasification due to its high moisture content, high volatile matter yields and low aromatic contents. Gasification is used to thermochemically convert solid biomass into a combustible gas-phase mixture in a gasification agent such as air, oxygen or steam. Biomass gasification has attracted high interest in the thermochemical conversion technologies due to its high efficiencies compared with combustion [6]. Syngas can be used to generate heat and electricity, synthesize liquid fuels and chemicals and produce fuel cells [6]. However, it has to be cleaned before its utilization to remove impurities such as tar, H₂S, NH₃, HCN, ash, etc. Table 1-2 shows gas quality for power generation [30]. Therefore, the purification of the product gas is one of the major issues of biomass gasification.
Table 1-2. Gas quality for power generation [30]:

<table>
<thead>
<tr>
<th></th>
<th>IC engine</th>
<th>gas turbine</th>
</tr>
</thead>
<tbody>
<tr>
<td>particle concentration, mg/Nm³</td>
<td>&lt;50</td>
<td>&lt;30</td>
</tr>
<tr>
<td>particle size, μm</td>
<td>&lt;10</td>
<td>&lt;5</td>
</tr>
<tr>
<td>tar, mg/Nm³</td>
<td>&lt;100</td>
<td>-</td>
</tr>
<tr>
<td>alkali metals, mg/Nm³</td>
<td>-</td>
<td>0.24</td>
</tr>
</tbody>
</table>

Biomass gasification faces a number of technical challenges to become a commercial renewable energy technology. The most important one is the presence of tar in the gasification product gas [31, 32]. Tar is an undesirable product of biomass gasification that has various definitions. It usually contains the condensable fraction of organic gasification products, largely consisting of aromatic compounds, such as naphthalene. The compositions of tar vary depending on the type of biomass and gasification temperatures. Tar can be classified into five groups based on its chemical, consideration and solubility properties (Table 1-3) [33-35]. Tar could cause the plugging of downstream equipments and the poisoning of catalysts, resulting in a drop in efficiency as well as a rise in maintenance cost. Hence, the removal of tar or the reforming of tar has become an important consideration in the development of a biomass gasification technology.

Generally, tar can potentially be removed from the gaseous products by physical separations (e.g. filtrations and scrubbing), thermal reforming and catalytic reforming processes [8, 36]. Physical separations require a cooling step until the gas reaches ambient temperature, which would causes large amounts of heat loss in the overall process. Moreover, scrubbing process produces large amounts of wastewater, resulting in an additional treatment or recycle system at downstream. Thermal cracking has low efficiency for tar removal unless the temperature reaches 1100 °C that is much higher than gasification temperature. It decreases the heat efficiency of the whole process. Catalytic reforming is the commonly accepted best option, because it does not have heat loss and can convert tar into syngas at the same temperature as gasifier efficiently. The investigation of catalytic reforming involves two approaches [10, 37]. One is catalytic gasification where the catalyst is used...
inside the main gasifier (e.g. being mixed with biomass) for the in situ reforming of tar within the gasifier. The other approach uses two reactors, a gasifier and a catalytic reformer. The tar is reformed in the catalytic reactor located at the downstream of the gasifier.

**Table 1-3. Classification of tar [33-35]**

<table>
<thead>
<tr>
<th>Class name</th>
<th>Tar components</th>
<th>Representative compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>GC Undetectable</td>
<td>The heaviest tars, cannot be detected by GC</td>
<td>Unidentified species (Determined by subtracting the GC- detectable tar fraction from the total gravimetric tar)</td>
</tr>
<tr>
<td>Tars</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heterocyclic</td>
<td>Tars containing hetero atoms; highly water-soluble compounds</td>
<td>Pyridine, phenol, cresols, quinoline, soquinoline, dibenzophenol</td>
</tr>
<tr>
<td>Light Aromatic</td>
<td>Aromatic components. Light hydrocarbons with single ring.</td>
<td>Toluene, ethylbenzene, xylenes, styrene</td>
</tr>
<tr>
<td>Hydrocarbons (LAH)</td>
<td>Important from the point view of tar reaction pathways, do not pose a problem on condensability and solubility</td>
<td></td>
</tr>
<tr>
<td>Light Poly Aromatic Hydrocarbons (LPAHs)</td>
<td>Two and three rings compounds; condense at low temperature even at very low concentration</td>
<td>Indene, naphthalene, methylnaphthalene, biphenyl, acenaphthalene, fluorine, phenanthrene, anthracene</td>
</tr>
<tr>
<td>Heavy Poly Aromatic Hydrocarbons (HPAHs)</td>
<td>Larger than three-rings, condense at high temperatures at low concentrations</td>
<td>Fluoranthe ne, pyrene, chrysene, perylene, coronene</td>
</tr>
</tbody>
</table>
1.2 A brief review of catalysts for tar reforming

According to Bridgwater et al. [36], the catalysts for tar elimination can be classified into three groups: dolomites, fluid catalytic reforming catalysts and precious metals. Sutton et al. divided catalysts for biomass gasification into dolomites, alkali metals and nickel [38]. The catalysts are categorised into two types, mineral and synthetic catalysts, based on their preparation methods in the thesis.

1.2.1 Mineral catalysts

Dolomites are considered as an attractive catalyst for tar elimination due to their low cost and high activity. Compared with calcite and magnesite, the calcined dolomite shows higher activity for tar removal. They, however, are soft and easily crushed in the fluidised bed [39]. Dolomites used in a secondary bed display better activity than those used \textit{in situ} because of its frangibility in gasifier [40]. Furthermore, ash that contains AAEM produced in the gasifier can become a catalyst to enhance the gasification rate and decrease the tar content in the gasification product gas. Ash, however, can be deactivated easily through particle agglomeration. These catalysts show high activity for tar removal and are cheap, especially dolomite. However, they lose their activities easily because of crushing and agglomerating during gasification.

Aluminosilicate minerals mainly consisting of SiO$_2$ and Al$_2$O$_3$ such as zeolites, kaolinites, montmorillonites and illites [10, 41] have been reported as catalysts for reforming tar. Zeolites, crystalline aluminosilicate minerals, can be used to break large hydrocarbon molecules into small hydrocarbon molecules without external hydrogen. The activity of zeolites is controlled by their structure, Si/Al ratio, particle size and the nature of the cation on the internal surface of zeolites [41]. The activity of zeolites can be improved by enhancing their acidic properties that are affected by the preparation processes and the Si/Al ratio. Zeolite, however, is easily deactivated due to coke deposition [41]. Coke deposited on the surface of zeolites would block its channels, reducing the pore size and the surface area. Also, some substances such as steam, nitrogen compounds and AAEM in volatiles would react with the acidic sites and cause catalyst poisoning. On the other hand, the activity of noncrystalline
aluminosilicate minerals is affected by their pore size, surface area and acidic sites [10]. These catalysts have lower price, but the activities of them are lower than that of dolomite and they are deactivated rapidly by coke formation. In addition, they are not suitable for operating at high temperatures due to the loss of pore structure and acidic sites.

Olivine, another inexpensive catalyst, mainly containing Fe and Mg with other metals (e.g., Mn, Cr, Co, and Ni), is more suitable for fluidized-bed operations than dolomite due to its attrition resistance [10]. It has been studied for removing tar during biomass gasification and for hydrocarbon steam reforming or dry reforming [42-48]. A variety of natural origins and pre-treatments of olivine showed strong influence on its reforming activity. Devi et al showed that the calcination at 900 °C caused the segregation of iron and the appearance of iron (III) phases at the surface of olivine, which exhibited the relationship with its catalytic activity [49-52]. The iron content at the surface and the catalytic activity of olivine enhanced with prolonging calcination time. Kuhn et al claimed that the phase and location of iron in olivine play important roles in its catalytic activity for the steam reforming of methane and tar [53, 54]. The decomposition of a Fe-bearing serpentine phase would form and deposit free Fe phase on or near the surface, resulting in its high activity. The iron in the olivine structure was dispersed as \( \alpha\text{-Fe}_2\text{O}_3 \) and Fe after initial calcination. The metallic Fe was formed and agglomerated under simulated syngas condition. Metallic Fe is considered as a site with high activity and would be more active for making and breaking C-C and C-H bond than iron oxide phase. However, it is easy to be deactivated due to carbon deposition and loss of Fe dispersion.

Various forms of iron have been reported as the catalysts for coal gasification reactions, pyrolysis and tar decomposition [55-65]. According to Tamhankar et al, metallic iron (reduced form) catalysts have higher activity for benzene decomposition and selectivity for methane formation than iron oxides [59]. Iron can be deactivated rapidly in the absence of hydrogen due to coke deposition. Nordgreen used metallic iron as a catalyst for tar elimination during the atmospheric gasification of biomass [63, 64]. It was claimed that elemental iron had high activity for tar removal. The yields of CO, CO\(_2\) and H\(_2\) increased, whereas the yield of CH\(_4\) and tar decreased. The activity of metallic iron is enhanced with increasing temperature.
Compared with iron oxides, the capability of metallic iron to break tar is extremely high. Furthermore, Matsuoka et al studied the effects of nonporous silica sand, porous $\gamma$-alumina and iron oxide-impregnated porous $\gamma$-alumina on the gas products during the steam reforming of woody biomass [65]. It was detected that iron oxide promoted the yield of $\text{H}_2$, especially at higher temperatures. They claimed that the effect of iron oxide on the yield of $\text{H}_2$ from coke reforming was insignificant [65]. A redox reaction of iron oxide is the predominant pathway for forming $\text{H}_2$. The iron oxide was reduced by CO produced during the steam reforming process. Then, the reduced iron oxide reacted with steam to produce H$_2$ [65].

1.2.2 Synthetic catalysts

Char, one of the partial gasification products, is another inexpensive catalyst. The activity of char for breaking tar is influenced by pore size, surface area and inorganic content (i.e. AAEM) of char [66-71]. The coke deposited on the char can block the pores and reduce the surface area to decrease its activity. Also, the char can be consumed by gasification/reforming agents and gaseous products, such as steam, $\text{O}_2$, and $\text{CO}_2$. Zanzi et al investigated the effects of the rapid pyrolysis conditions on the reactivity of char in a free-fall reactor [66]. It was found that high heating rate, small particle size and short residence time can be used to produce high reactivity char for breaking tar. Hayashi et al claimed that almost all nascent tars from the rapid pyrolysis of brown coal would be reformed into gases if the temperature is higher than 900 °C [68]. It was found that the activity of the char for the steam reforming of tar is ascribed to inherent AAEM highly dispersed on char surface. Recently, Hosokai et al claimed that coke would act as a promoter for tar elimination, if the K and/or Ca were supported on it [69]. The activity of charcoal for reforming tar and decomposing aromatics indicated that the aromatics were decomposed mainly by the coking because they were broken in the absence of steam as fast as in its presence [70, 71]. Compared with dolomite, the activity of char is lower. In addition, it is consumed due to gasification. The consumption of char would maintain its activity for tar removal by forming and regenerating micropores while the progress of gasification was greater than the carbon deposition [70, 71].
Ni-based catalysts are widely used in the petrochemical industry for reforming processes. The components of normal Ni-based catalysts are Ni element, support materials and prompters, controlling the activities of Ni-based catalysts [10]. Alumina is usually used as the support material to enhance the mechanical strength of the catalysts and AAEM are used as promoters [72-75]. Ni-based catalysts have high activity for tar removal and increase syngas yield. They are however expensive and easily deactivated because of coke deposition and poisoning. Coke deposition and poisoning on catalyst active sites are the main drawbacks of Ni-based catalysts. Zhang et al investigated the effects of three Ni-based catalysts (ICI46-1, Z409 and RZ409) on tar breakdown [76]. It was found that the conversion of heavy tars was higher than 99%. The yield of H\textsubscript{2} increased by 6-11 vol%(db). With elevating temperature, the yield of H\textsubscript{2} enhanced and the yield of light hydrocarbons dropped.

Additionally, dolomite and olivine can also act as supported materials for Ni-based catalysts. Srinakruang et al measured the activities and coke resistance of Ni/dolomite, Ni/Al\textsubscript{2}O\textsubscript{3} and Ni/SiO\textsubscript{2} catalysts during the reforming of a mixture of toluene and naphthalene [77]. The results showed that the support of the catalyst did not affect the activity when H\textsubscript{2}S was not fed in the process. However, Ni/dolomite exhibited better resistance of coke and poisoning than Ni/Al\textsubscript{2}O\textsubscript{3} and Ni/SiO\textsubscript{2} in present of H\textsubscript{2}S. Pfeifer et al investigated effects of Ni/olivine on the gasification of wood pellets [78]. The results demonstrated that the Ni/olivine catalyst had much higher activity for tar removal than unloaded olivine and it can keep its activity during the reaction testing. Heating value of the produced syngas dropped with increasing the mass of catalysts.

Some researchers have also used other novel metal catalysts for tar removal to improve their activities and lifetime. Tomishige et al compared the activities of the M/CeO\textsubscript{2}/SiO\textsubscript{2} (M=Rh, Pd, Pt, Ru, Ni) catalysts on tar removal during the cedar wood gasification [79]. The order of catalyst activity at 550 °C was the following: Rh>Pd>Pt>Ni>Ru. The tar conversion of the Rh/CeO\textsubscript{2}/SiO\textsubscript{2} catalyst was about 88% at 550 °C and jumped to 97% at 600 °C. In addition, Asadullah et al investigated the performance of the Rh/CeO\textsubscript{2}/M (M=SiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, and ZrO\textsubscript{2}) catalysts for the gasification in a continuous feeding fluidised-bed reactor [80-82]. The authors found that the Rh/CeO\textsubscript{2}/SiO\textsubscript{2} exhibited the best performance for producing syngas or
hydrogen. The Rh/CeO$_2$ catalyst was deactivated as its surface area dropped from 60 to 13 m$^2$/g in the continuous feeding system. Its activity can be maintained by loading CeO$_2$ on the high-surface-area SiO$_2$. Furusawa et al reported a Co catalyst that has potential to reforming naphthalene derived from biomass gasification \[83, \ 84\]. It was noticed that the large-sized Co metal particles were formed in the pre-calcined catalysts. Compared with the performance of Co/MgO catalyst and Ni/MgO catalyst on the reforming of naphthalene, the authors claimed that 12 wt% Co/MgO catalysts pre-calcined at 600 $^\circ$C showed a higher catalytic performance for the steam reforming of naphthalene than other Ni catalysts tested in the study. The conversion of naphthalene can reach 23%.

These catalysts show high activity, but they are expensive and have regeneration problems. Therefore, they are not suitable for industrial application.

### 1.3 The purpose of this study

From what has been discussed above, many catalysts examined so far for tar reforming still have lots of problems: low activity, high cost, easy poisoning and deactivation, and difficult regeneration. Therefore, investigating catalysts with low cost and high activity for tar reforming is significant for commercializing biomass gasification.

The purpose of the study is to investigate iron-based catalysts with low cost and high activity for the steam reforming of biomass tar. In Western Australia (WA), abundant mallee eucalypts are being developed to help control dryland salinity \[85, \ 86\]. Since the early 1990s, farmers have established about 30 million trees across the WA wheatbelt \[85\]. Besides environmental benefits, mallee biomass and mallee-derived bioenergy production can also play significant roles in meeting the needs of economic diversification for farmers in WA \[85\]. Therefore, mallee will be chosen as feedstock in the study.

Ilmenite, an abundant mineral in WA, is cheap and mainly consists of iron oxides and titanium dioxide. Iron-containing species in ilmenite could be dispersed well by
titanium dioxides, which may result in its high possibilities to become the catalyst for tar reforming during biomass gasification. Hence, ilmenite will be examined in the research.

On the basis of previous results [60-62], the catalytically active species could be ion-exchanged or impregnated for dispersion at molecular/atomic scales in the brown coal matrix. After the pyrolysis or partial gasification of the brown coal, the finely dispersed species would agglomerate into nano particles depending upon reaction conditions and loading level/ratio [60-62]. The catalyst would have high activity due to nano particle size and high dispersion in carbon [60-62]. In addition, the catalyst would have low price and be simply burned/gasified to reuse the energy of the char rather than be regenerated after it was deactivated [60-62]. Therefore, it is worthy to test the activity of the char-supported catalysts on the reforming of tar and the decomposition of NO\textsubscript{x} precursors in the study.

Furthermore, new and spent catalysts will be characterised. The function of support, the key parameters and the possible mechanisms and pathways of tar reforming on the catalysts will also be discussed.

1.4 Scope of thesis

Chapter 2 describes details of the design of reactors and the set-up of the reactor systems. The procedures of the catalyst preparation and the steam reforming of biomass tar are depicted, as will be the various analytical procedures of the catalysts and the properties of the products.

Chapters 3-7 illustrate the results and discussion of experimental results. Each of these chapters contains a review of relevant literature as an introduction to the chapter. Chapter 3 presents the results of ilmenite ore as a catalyst for the steam reforming of biomass tar derived from the pyrolysis of mallee wood \textit{in situ}. The \textit{in situ} activity of ilmenite on the steam reforming of tar is investigated under different operational conditions. The functions of iron oxides and titanium dioxides in ilmenite and the possible reaction pathways on ilmenite are also discussed. Novel nano
char-supported iron/nickel catalysts are prepared and tested for the steam reforming of biomass tar. The performance of the catalysts on the steam reforming of biomass tar is studied under different operational conditions. Effects of support on the reforming of tar are investigated. The kinetic parameters are calculated using a first order kinetic equation and the potential reaction pathways are discussed in Chapter 4. Then, effects of feedstock on the performance of ilmenite ore are discussed in Chapter 5. Except tar, NO\textsubscript{x} precursors are other drawbacks of the biomass gasification. Chapter 6 details the effects of the char-supported iron catalyst on the decomposition of NO\textsubscript{x} precursors during the steam reforming process. Effects of iron-containing species, feedstock and residence time on the activities of the catalyst are described in the Chapter. Furthermore, the changes in char properties and specific reactivity of spent char-supported iron catalyst are investigated for the disposal of catalysts and are detailed in Chapter 7.

Finally, the conclusions of the study and the recommendations for future work are summarized in Chapter 8.
1.5 References


Chapter 1 Introduction


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Chapter 2

Experimental methods
2.1 Introduction

The general experimental procedures in this study are detailed. The preparation of catalysts and biomass samples are also described. In addition, the methods of tar sample analysis and the characterization of new and spent catalysts are also detailed in this chapter.

2.2 Preparation of biomass and coal samples

2.2.1 Preparation of biomass samples

Australian mallee wood, bark and leaves were pulverised and sieved into different size fractions. The size ranging from 90 to 180 μm was used for this study. All biomass samples were kept in airtight containers in a freezer to avoid oxidation. The biomass samples were taken out freezer before experiment to make sure that the moisture content in biomass reached the balance with ambient atmosphere. Sampling of biomass for each experiment was done by mixing samples gently with a spatula to maximize homogeneity of samples. In order to minimize the agglomeration of biomass during feeding process, the wood and bark was dried at 105 °C overnight in a nitrogen atmosphere before the experiment, and the leaf was dried at 55 °C overnight because its colour changed (indication of possible chemical reactions) after drying at 105 °C.

The raw biomass samples were analysed by Herman Research Laboratories (HRL), located in Mulgrave, Victoria. The results obtained for the proximate and ultimate analyse of raw biomass samples are given in Table 2-1.
Table 2-1. Proximate and ultimate analyse of biomass.

<table>
<thead>
<tr>
<th>Biomass sample</th>
<th>Mallee Wood</th>
<th>Mallee Bark</th>
<th>Mallee Leaf</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash yield&lt;sup&gt;a&lt;/sup&gt;, wt% (db)</td>
<td>0.9</td>
<td>6.4</td>
<td>3.7</td>
</tr>
<tr>
<td>Volatile matter&lt;sup&gt;b&lt;/sup&gt;, wt% (db)</td>
<td>80.9</td>
<td>69.5</td>
<td>74.6</td>
</tr>
<tr>
<td>Fixed carbon, wt% (db)</td>
<td>18.2</td>
<td>24.1</td>
<td>21.7</td>
</tr>
<tr>
<td>C&lt;sup&gt;c&lt;/sup&gt;, wt %(daf)</td>
<td>48.2</td>
<td>48.5</td>
<td>59.3</td>
</tr>
<tr>
<td>H&lt;sup&gt;c&lt;/sup&gt;, wt %(daf)</td>
<td>6.1</td>
<td>5.5</td>
<td>6.8</td>
</tr>
<tr>
<td>N&lt;sup&gt;c&lt;/sup&gt;, wt %(daf)</td>
<td>0.15</td>
<td>0.3</td>
<td>1.3</td>
</tr>
<tr>
<td>S&lt;sup&gt;d&lt;/sup&gt;, wt %(daf)</td>
<td>0.01</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>Cl&lt;sup&gt;d&lt;/sup&gt;, wt %(daf)</td>
<td>0.04</td>
<td>0.2</td>
<td>0.0</td>
</tr>
<tr>
<td>O&lt;sup&gt;e&lt;/sup&gt;, wt %(daf)</td>
<td>45.5</td>
<td>45.4</td>
<td>32.4</td>
</tr>
<tr>
<td>Gross calorific value&lt;sup&gt;f&lt;/sup&gt;, MJ/kg (dry)</td>
<td>19.2</td>
<td>17.6</td>
<td>23.3</td>
</tr>
</tbody>
</table>

<sup>a</sup> measured using Leco MAC analyser, according to HRL Method 1.6  
<sup>b</sup> determined according to AS 2434.9  
<sup>c</sup> measured using Leco CHN 1000 analyser, according to HRL Method 1.4  
<sup>d</sup> determined according to AS 1038.6.3.3 and AS 1038.8.2  
<sup>e</sup> calculated by difference  
<sup>f</sup> measured using Leco AC 350 calorimeter, according to AS 1038.5
2.2.2 Preparation of coal samples

Loy Yang brown coal (Victoria, Australia) was pulverised and sieved into different size particles. The size ranging from 53 to 150 μm was chosen as the precursor of the catalyst.

The procedures for treating brown coal are mainly acid washing and ion-exchanging [1-3]. The raw coal was mixed in 0.2 M H₂SO₄ aqueous solution with a ratio of the acid solution to coal of 30:1 by mass and stirred in an argon atmosphere for 24 hours to remove the metallic species in the coal. The slurry was then filtered and washed with de-ionized water until the pH value of the filtrates was constant (4.5-5.0). The air-dried acid-washed coal that contains a negligible amount of inorganic species is termed as the H-form coal because all carboxylates (-COOM) have been turned into acids (-COOH).

The proximate and ultimate analyse of raw coal and H-form coal samples (Table 2-2) were determined by Herman Research Laboratories (HRL), located in Mulgrave, Victoria. The H-form coal was ion-exchanged with 0.2 M FeCl₃ or Ni(NO₃)₂ aqueous solution by stirring in an argon atmosphere for 24 hours in order to load iron or nickel into the H-form coal. The ratio of FeCl₃ or Ni(NO₃)₂ aqueous solution to H-form coal was also 30:1 by mass. The slurry was then filtered and washed using de-ionized water until the pH value of the filtrates was constant (4.5-5.0). Finally, the sample was dried in a nitrogen atmosphere. The treated coal is thus termed as the iron-loaded or nickel-loaded coal. The iron content of the iron-loaded coal and the nickel content of the nickel-loaded coal, measured by HRL method 1.12 and using fusion/ICP, were 1.06 wt% and 0.41 wt% on dry basis, respectively.

Similar to the preparation of biomass samples, all coal samples were stored in airtight containers in a freezer to minimize oxidation. The air-dried coal samples were taken out freezer to make sure that the moisture content in coal reached the balance with ambient atmosphere and were mixed slowly using a spatula to homogenize samples before experiment.
Table 2-2. Proximate and ultimate analayse of Loy Yang brown coal.

<table>
<thead>
<tr>
<th>Coal sample</th>
<th>Raw coal</th>
<th>H-form coal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash yield(^a), wt% (db)</td>
<td>3.2</td>
<td>2.1</td>
</tr>
<tr>
<td>Volatile matter(^b), wt% (db)</td>
<td>50.2</td>
<td>50.6</td>
</tr>
<tr>
<td>Fixed carbon, wt% (db)</td>
<td>46.6</td>
<td>47.3</td>
</tr>
<tr>
<td>C (^c), wt% (daf)</td>
<td>68.1</td>
<td>66.9</td>
</tr>
<tr>
<td>H (^c), wt% (daf)</td>
<td>4.9</td>
<td>5.0</td>
</tr>
<tr>
<td>N (^c), wt% (daf)</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>S (^d), wt% (daf)</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>Cl (^d), wt% (daf)</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>O (^e), wt% (daf)</td>
<td>25.7</td>
<td>26.8</td>
</tr>
<tr>
<td>Gross calorific value(^f), MJ/kg (dry)</td>
<td>26.4</td>
<td>23.9</td>
</tr>
</tbody>
</table>

\(^a\) measured using Leco MAC analyser, according to HRL Method 1.6  
\(^b\) determined according to AS 2434.9  
\(^c\) measured using Leco CHN 1000 analyser, according to HRL Method 1.4  
\(^d\) determined according to AS 1038.6.3.3 and AS 1038.8.2  
\(^e\) calculated by difference  
\(^f\) measured using Leco AC 350 calorimeter, according to AS 1038.5
2.3 Preparation of catalysts

2.3.1 Ilmenite catalysts

Natural ilmenite ore from Tiwest Joint Venture (Western Australia) was pulverised and sieved into different size particles. The size ranging from 106 to 150 μm was used in the study. The metal elemental analyse and the proximate and ultimate analyse of ilmenite samples (Tables 2-3 and 2-4) were also measured by Herman Research Laboratories (HRL).

*Table 2-3. Proximate and ultimate analyse of ilmenite.*

<table>
<thead>
<tr>
<th></th>
<th>ilmenite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash yield(^a), wt% (db)</td>
<td>98.4</td>
</tr>
<tr>
<td>Volatile matter(^b), wt% (db)</td>
<td>1.8</td>
</tr>
<tr>
<td>C (^c), wt% (db)</td>
<td>0.1</td>
</tr>
<tr>
<td>H (^c), wt% (db)</td>
<td>0.2</td>
</tr>
<tr>
<td>N (^c), wt% (db)</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>S (^d), wt% (db)</td>
<td>0.01</td>
</tr>
<tr>
<td>Cl (^d), wt% (db)</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>

\(^a\), measured using Leco MAC analyser, according to HRL Method 1.6
\(^b\), determined according to AS 2434.9
\(^c\), measured using Leco CHN 1000 analyser, according to HRL Method 1.4
\(^d\), determined according to AS 1038.6.3.3 and AS 1038.8.2

Similarly, ilmenite was stored in a freezer. The samples were taken out freezer to reach a moisture balance with ambient atmosphere and were mixed to homogenize samples before experiment.
Ilmenite was used as catalysts for the steam reforming of biomass volatiles directly. In some experiment, Ultra High Purity (>99.999 %) hydrogen controlled by a mass flow controller (0.3 L/min) was injected into the top stage to reduce ilmenite at 600 °C *in situ* for 1 hour before the steam reforming process (Section 2.4). Then, the hydrogen flow ceased and the reactor was heated up to the target temperature for the steam reforming experiments.

**Table 2-4. Metal elemental analyse of ilmenite**

<table>
<thead>
<tr>
<th></th>
<th>Fea</th>
<th>Ti</th>
<th>Ka</th>
<th>Mg</th>
<th>Na</th>
<th>Ca</th>
<th>Ala</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ilmenite</td>
<td>23</td>
<td>36</td>
<td>&lt;0.01</td>
<td>0.2</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>0.5</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>

*a*, wt%, dry basis, determined by ICP-AES, following borate fusion and acid dissolution of the ashed samples, according to AS 1038.14.1

**2.3.2 Iron oxide and titanium dioxide catalysts**

Powder of iron (III) oxide (Sigma-Aldrich, Fe₂O₃, particle size < 50 nm, >99%), powder of iron (II, III) oxide (Sigma-Aldrich, Fe₃O₄, particle size < 5 µm, >98%) were used as catalysts for the steam reforming of biomass volatiles.

**2.3.3 Char-supported catalysts**

The catalysts were prepared by pyrolyzing and subsequently gasifying the H-form coal, the iron-loaded coal and the nickel-loaded coal in an one-stage fluidized-bed/fixed-bed quartz reactor heated in a two-zone electrical furnace (Figure 2-1) [4].
Figure 2-1. A schematic diagram of the experimental set-up for catalyst preparation [modified from Ref 4]. 1, two-zone electrical furnace; 2, water-cooled probe; 3, thermocouples; 4, coal particles and argon; 5, argon and steam; 6, reactor outlet (to vent).
The reactor has some features of a fluidized-bed reactor and of a fixed-bed reactor. A sand bed was fluidized with a stream of argon. The whole reactor assembly was heated using an external electrical furnace. A water-cooled probe was used to prohibit pyrolysis/gasification of the sample particles until they get into the fluidized bed. In order to prevent the elutriation of char particles, another quartz frit (top) was installed inside the reactor. Therefore, the reactor can act as a fixed-bed reactor in terms of the formation of a char bed inside the reactor. *In situ* gasification of char can be achieved under the frit. A thin quartz tube (not shown) was connected to the reactor wall below the top frit, which was used for charging/discharging the sand and collecting the catalysts. It was also used to measure the temperature of the reactor in blank experiment.

Silica sand was used as the bed material. The sizes of sand particles were in the range of 212-300 μm. Two thermocouples were inserted into the reactor to monitor the temperature of the top frit and the temperature distribution along the reactor before the real experiment. The temperature distribution of the reactor ranged from 796 °C to 805 °C, when the temperature of the top frit reached 800 °C.

Ultra High Purity (>99.999 %) argon gas was divided and passed through three Aalborg mass flow controllers. The MFCs were calibrated frequently using a digital bubble flow meter and the flow rates were checked daily before an experiment. The flow rates of feeding gas and fluidizing gas were 1 L/min each, respectively. A HPLC pump (Alltech 426) was used to deliver water at a rate defined by the temperature of the experiment. The water passed through a coil of 1/16” ID tubing and water liquid would be converted into steam at reaction temperature and entrained into the reactor. The flow rate of steam was 15 vol% of the total gas flow rate.

The coal samples were fed into the reactor at a rate of around 300 mg/min through a water-cooled probe with 1 L/min cooling water after the reactor had reached and stabilized at the target temperature. After the feeding process, the coal gasification started and continued for 10 minutes. Immediately after gasification, the temperature of the reactor was quenched by being lifted out of the furnace. The fluidizing gas was continuously passed through the reactor in order to prevent any oxidation during quenching.
The char yield was determined by weighing the reactor before and after the experiment. The moisture contents of the coal sample and the char were considered in the calculation of the char yield. Finally, the char samples were collected via a cellulose thimble and used as catalysts for the reforming of biomass tar with steam in subsequent experiments.

The proximate and ultimate analysis of H-form char (Table 2-5) were determined by Herman Research Laboratories (HRL), located in Mulgrave, Victoria. The iron content of the char-supported iron catalyst and the nickel content of the char-supported nickel catalyst, measured by HRL method 1.12 and using fusion/ICP, were 2.34 wt% and 0.88 wt% on dry basis, respectively.
### Table 2-5. Proximate and ultimate analyse of H-form char.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash yield&lt;sup&gt;a&lt;/sup&gt;, wt% (db)</td>
<td>4.2</td>
</tr>
<tr>
<td>Volatile matter&lt;sup&gt;b&lt;/sup&gt;, wt% (db)</td>
<td>3.0</td>
</tr>
<tr>
<td>Fixed carbon, wt% (db)</td>
<td>92.8</td>
</tr>
<tr>
<td>C&lt;sup&gt;c&lt;/sup&gt;, wt % (daf)</td>
<td>95.0</td>
</tr>
<tr>
<td>H&lt;sup&gt;c&lt;/sup&gt;, wt % (daf)</td>
<td>0.8</td>
</tr>
<tr>
<td>N&lt;sup&gt;c&lt;/sup&gt;, wt % (daf)</td>
<td>1.2</td>
</tr>
<tr>
<td>S&lt;sup&gt;d&lt;/sup&gt;, wt % (daf)</td>
<td>-</td>
</tr>
<tr>
<td>Cl&lt;sup&gt;d&lt;/sup&gt;, wt % (daf)</td>
<td>-</td>
</tr>
<tr>
<td>O&lt;sup&gt;e&lt;/sup&gt;, wt % (daf)</td>
<td>3.0</td>
</tr>
<tr>
<td>Gross calorific value&lt;sup&gt;f&lt;/sup&gt;, MJ/kg (dry)</td>
<td>32.2</td>
</tr>
</tbody>
</table>

<sup>a</sup>, measured using Leco MAC analyser, according to HRL Method 1.6
<sup>b</sup>, determined according to AS 2434.9
<sup>c</sup>, measured using Leco CHN 1000 analyser, according to HRL Method 1.4
<sup>d</sup>, determined according to AS 1038.6.3.3 and AS 1038.8.2
<sup>e</sup>, calculated by difference
<sup>f</sup>, measured using Leco AC 350 calorimeter, according to AS 1038.5
2.4 Steam reforming of biomass tar

A two-stage fluidized-bed/fixed-bed quartz reactor with 3 frits was used in catalytic steam reforming of biomass tar \textit{in situ} (Figure 2-2). The difference between the two-stage reactor and the one-stage reactor shown in Figure 2-1 was the presence of an extra operating zone on the top of the one-stage reactor. Biomass was pyrolyzed in the bottom stage to release volatiles that were reformed with steam and the catalysts in the top stage.

In order to ensure the complete mixing of steam and volatiles before contacting the catalyst bed, another two-stage fluidized-bed/fixed-bed quartz reactor with 4 frits was used for the steam reforming of tar with heavy catalysts (e.g. ilmenite, Fe$_2$O$_3$, and Fe$_3$O$_4$) because of their high density (Figure 2-3). The distance between the catalyst bed and the steam injection position of two reactors (Figures 2-2 and 2-3) were constant (30 mm) and the heights of the static catalyst bed were similar (1.0-1.5 mm), which can minimize experimental errors. The design and dimension of the reactors were in general similar to minimize experimental errors (i.e. ID and OD of the quartz chambers, tubings and frits).

Silica sand with a particle size range of 212 to 300 µm was chosen as the bed material. Two thermocouples were inserted into the reactor to measure the temperature of the top frit and the temperature distribution of the bottom stage before the real experiment.

The catalysts were loaded in the top stage before heating up the reactor. The light powders, char-supported catalysts (1-2 g), were pre-loaded in the reactor (Figure 2-2) and formed a fixed bed under the top frit (1.0-2.0 mm). The heavy powders, ilmenite (5-20 g) and iron oxides (1-5 g), were pre-existing in the reactor (Figure 2-3) and became a fluidized bed in the top stage.
Figure 2-2. A schematic diagram of the experimental set-up for isothermal steam reforming process (3-frit reactor) [modified from Ref 1]. 1, two-zone electrical furnace; 2, water-cooled probe; 3, thermocouples; 4, biomass particles and argon; 5, steam; 6, argon; 7, gas outlet (to condenser).
Figure 2.3. A schematic diagram of the experimental set-up for isothermal steam reforming process (4-frit reactor). 1, two-zone electrical furnace; 2, water-cooled probe; 3, thermocouples; 4, biomass particles and argon; 5, steam or H$_2$/and O$_2$; 6, argon; 7, gas outlet (to condenser).
The flow rates of feeding gas and fluidizing gas, both being Ultra High Purity (>99.999 %) argon, were controlled by mass flow controllers, respectively (Table 2-6). The steam was generated by the water fed into the reactor. The flow rate of steam/water was 15 vol% of the total gas flow rate and controlled by a HPLC pump (Alltech 426). The steam was injected into the second stage. The configuration of the reactor meant that the steam did not contact the biomass char in the bottom stage during an experiment to prohibit biomass char gasification. In the reduction experiments, Ultra High Purity (>99.999 %) hydrogen controlled by a mass flow controller (0.3 L/min) was used to reduce ilmenite at 600 °C in situ for 1 hour before the steam reforming process (Figure 2-3). In some experiments, oxygen (1000 ppm and 3000 ppm of the total gas) was injected into reactor with steam during the steam reforming process (Figure 2-3).

Table 2-6. Gas flow rates for the steam reforming at different temperature

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>500</th>
<th>600</th>
<th>700</th>
<th>800</th>
<th>850</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feeding gas flow rate, L/min</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Fluidizing gas flow rate, L/min</td>
<td>1.50</td>
<td>1.21</td>
<td>0.98</td>
<td>0.80</td>
<td>0.72</td>
</tr>
<tr>
<td>Water (steam generation), ml/min</td>
<td>0.33</td>
<td>0.29</td>
<td>0.26</td>
<td>0.24</td>
<td>0.23</td>
</tr>
</tbody>
</table>

The biomass feeder was based on that used in a previous study [4]. Briefly, the feeder consists of a glass tube containing the biomass. Two concentric stainless steel tubes, of 1/4” and 1/8” OD, were positioned on the surface of the biomass bed. The glass tube was sealed by a screw connection at the top of the feeder. The glass tube was placed on a holder which could be moved upwards by a stepper motor. The 1/8” stainless steel tube at the exit of the feeder was connected to the reactor via a flexible silicone tube. The feeder gas entered the feeding system through the 1/4” stainless steel tube to entrain the biomass particles. The entrained biomass was then carried out of the feeder through a straight length of 1/8” stainless steel tubing into the reactor. The feeding rate was controlled by both feeding gas flow rate and the frequency of the stepper motor.
The biomass samples were fed into the reactor at 100 mg/min through a water-cooled probe with 1 L/min cooling water when the reactor reached and stabilized at the target temperature (500-850 °C). Immediately after the steam reforming process, the temperature of the reactor was quenched by being lifted out of the furnace. The fluidizing gas continuously passed through the reactor in order to prevent any oxidation during the quenching.

The char yield and the coke yield were measured by weighing the reactor before and after the experiment with the moisture content taken into consideration in the calculation of the char and coke yield. The coke yield was calculated by Equation 2-1.

\[
\text{Coke yield } \% = \frac{\Delta M_{\text{reactor}} - M_{\text{char}}}{M_{\text{biomass}}} \times 100 \%
\]  

(2-1)

\(\Delta M_{\text{reactor}}\): the mass difference of the reactor before and after the experiment;

\(M_{\text{char}}\): the mass of biomass char;

\(M_{\text{biomass}}\): the mass of biomass fed into the reactor.

Experiments without the catalyst (blank experiments) were carried out to determine the char yield of biomass (and thus \(m_{\text{char}}\) in Equation 2-1) during pyrolysis under otherwise identical conditions.

2.5 Sampling and analysis of products

2.5.1 Sampling and analysis of tar

Tar was captured with three tar traps connected in series (Figure 2-4). A mixture of HPLC-grade chloroform and methanol (80:20 by vol) was used in the traps to catch the tar. The volumes of solvents used in these three traps were about 50 ml, 40 ml and 30 ml, respectively. The solvents in the traps enhanced heat transfer and dissolved the tar immediately, which was favorable for condensing the tar and avoiding the blockage of the thimble filters.
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Figure 2-4. A schematic diagram of condensers. 1, 1st trap with a frit and 50 ml solvent; 2, 2nd trap with a thimble filter, wire mesh and 40 ml solvent; 3, 3rd trap with a frit and 30 ml solvent; 4, gas outlet (to vent).

The first trap with a frit was placed in an ice-water-cooled cold bath (0 °C) to condense the steam in the gas. The majority of steam would have been condensed in this trap. The condensation of steam in this trap avoids the blockage of the next trap that had a thimble filter surrounded by wire mesh and was set in a dry ice bath (-78 °C) to capture the tar. The thimble filter and wire mesh were used to enhance the absorption area and heat transfer.

Under our experimental conditions, the second trap was very efficient in capturing the tar because negligible amounts of heavy tar (i.e. no colour, Figure 2-5) were found in the third trap that was also maintained in a dry ice bath (-78 °C). Examination of the solution in the third trap with UV-fluorescence spectroscopy showed that it had a little (<10% of the intensity for the second trap) small aromatic rings (colourless tar, Figure 2-5). Hence, the solution in the third trap was used to wash other traps and the outlet of the reactor after the experiment. The recovered tar solutions from all three traps were mixed well and weighed accurately before the mixture was put into a refrigerator for storage.
Figure 2-5. Constant energy synchronous spectra of solution (4 ppm) in different tar traps after steam reforming of mallee wood without catalysts at 500 °C. (a) -2800 cm\(^{-1}\); (b) -1400 cm\(^{-1}\).
The tar yield was determined by quantifying the tar concentration in the solution. The aluminium tray was dried in oven at 35 °C before experiments. It was taken out for 20 minutes to equilibrate with atmospheric conditions and weighed accurately using a 5-digital balance. A certain amount of tar solution (1-2 ml) was put onto a weighed aluminium tray and dried at 35 °C for 4 hours to evaporate all solvents and water. The time of drying process was determined by the experiments of evaporating tar solution at 35 °C from 2 to 24 hours. No visible liquor can be found in the aluminium tray after 4 hours. Also, the weight loss was similar to the results after drying for 5 hours (Table 2-7). Hence, 4 hours was chosen to measure the tar yield.

**Table 2-7. Evaporation of tar at 35 °C as a function of time.**

<table>
<thead>
<tr>
<th>Temperature °C, Pyrolysis</th>
<th>2 hours</th>
<th>3 hours</th>
<th>4 hours</th>
<th>5 hours</th>
<th>24 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>500 °C, pyrolysis</td>
<td>34.2</td>
<td>34.1</td>
<td>32.7</td>
<td>32.3</td>
<td>29.4</td>
</tr>
<tr>
<td>600 °C, pyrolysis</td>
<td>18.1</td>
<td>18.0</td>
<td>16.1</td>
<td>16.5</td>
<td>15.7</td>
</tr>
<tr>
<td>700 °C, pyrolysis</td>
<td>7.7</td>
<td>7.4</td>
<td>6.8</td>
<td>6.4</td>
<td>5.5</td>
</tr>
<tr>
<td>800 °C, pyrolysis</td>
<td>3.4</td>
<td>3.1</td>
<td>2.9</td>
<td>2.8</td>
<td>1.6</td>
</tr>
</tbody>
</table>

The amount of tar solution was calculated accurately by weighing the vial before and after removing tar solution due to the evaporation of the solution. After drying process, the aluminium tray was taken out for another 20 minutes to equilibrate with atmospheric conditions and weighed accurately using a 5-digital balance. The residues in the solvents themselves were determined in blank experiments and considered in the calculation of the tar concentration (Equation 2-2).

\[
C = \frac{C_2 - C_1}{1 - C_1} \times 100 \%
\]

(2-2)

$C_1$: the residues concentration in the solvent, blank experiment;

$C_2$: the residues concentration in the tar solution.
The moisture content of the biomass substrate was also considered in the calculation of the tar yield. The tar yield was calculated by Equation 2-3.

\[
\text{Tar yield} \, \% = \frac{C \times M_{\text{solution}}}{M_{\text{biomass}}} \times 100 \, \%
\]  

(2-3)

\(C\): the tar concentration in the tar solution, calculated by Equation 2-2;

\(M_{\text{solution}}\): the mass of the total tar solution after the experiment;

\(M_{\text{biomass}}\): the mass of biomass fed into the reactor.

UV-fluorescence spectroscopy has been widely used for the identification and quantification of individual simple aromatic compounds (or aromatic ring systems) [5]. When the fluorescent component is excited at a fixed excitation wavelength, an emission spectrum can be obtained. Similarly, an excitation spectrum can be recorded by scanning the available range of excitation wavelengths while the emission wavelength is fixed. The third is synchronous spectrum that simultaneously varies both the excitation and emission wavelengths by keeping a constant wavelength interval between them. The wavelength difference between excitation and emission monochromators changes continuously whilst their energy difference remains constant. The effects of self-absorption, intermolecular energy transfer and/or excimer formation are important in interpreting the UV-fluorescence spectroscopy of tar samples. It would be impossible to separate the different aromatic ring systems in the large molecule into individual ones, unless they are chemically degraded by bond breakage. Therefore, UV-fluorescence spectroscopy is an efficient semi-quantitative measurement to tar samples.

A Perkin–Elmer LS50B luminescence spectrometer with a 1 cm light path length was used to record the UV-fluorescence spectra of the tars. The tar solution obtained from experiment was diluted with methanol (Uvasol for spectroscopy; purity (GC): \(\geq 99.9\%\)) to 2 ppm and 4 ppm (wt). The synchronous spectra were recorded with constant energy differences of -1400 cm\(^{-1}\) and -2800 cm\(^{-1}\). The slit width was 2.5 nm and the scan speed was 200 nm/min. Each spectrum shown represents the average of four scans. At the same concentration, the fluorescence intensity was multiplied by the tar yield to show the fluorescence intensity on the basis of ‘per gram of biomass (db)’ [5].
2.5.2 Sampling and analysis of NO\textsubscript{x} precursors

Gas products from the reactor passed through a bubbler containing an absorption solution. NH\textsubscript{3} was absorbed into a 0.02 M CH\textsubscript{3}SO\textsubscript{3}H solution, and HCN was absorbed into a 0.1 M NaOH solution in separate experiments. Separate experiments were run for the collection of HCN and NH\textsubscript{3} due to their non-negligible solubility in tar solution or MSA and NaOH. After each experiment, the solution containing some light tars was weighed accurately. Then, the sample was poured into a clear plastic vial by passing a syringe filter to remove tars in the solution. Dionex 500 ion chromatograph was used to quantify NH\textsubscript{3} and HCN with two separate analytical methods [6-8].

Briefly, the concentration of HCN in the solution has to be measured using amperometric detection with a silver electrode immediately after each experiment because of its easy decomposition at room temperature. A Dionex AS7 column was used for the separation of CN\textsuperscript{-} with an eluent, aqueous solution of 0.1 M NaOH, 0.7 M CH\textsubscript{3}COONa and 0.5% H\textsubscript{2}NCH\textsubscript{2}CH\textsubscript{2}NH\textsubscript{2}. The calibration of CN\textsuperscript{-} was done before injecting samples using standard solutions (NaCN, Alltech) with four different concentrations that cover the concentration of samples. In contrast, the quantification of NH\textsubscript{3} was carried out using electrical conductivity detection every week to minimize experimental errors. A CS12A column and a CG12A guard column were used for the separation of NH\textsubscript{4}\textsuperscript{+} with an eluent, 0.02 M CH\textsubscript{3}SO\textsubscript{3}H aqueous solution. The concentration of NH\textsubscript{4}\textsuperscript{+} was calibrated before injecting samples using standard solutions with seven different concentrations that cover the concentration of samples.

The HCN/NH\textsubscript{3} yields of reforming with the catalyst were calculated by Equation 2-4.

\[
\text{HCN(NH}_3\text{)}\text{f}_{\%} = \frac{\text{HCN(NH}_3\text{)}_{\text{catalyst+biomass}} - \text{HCN(NH}_3\text{)}_{\text{catalyst}}}{N_{\text{biomass}}} \times 100\% 
\]  

(2-4)

HCN(NH\textsubscript{3})\text{catalyst+biomass}: the amount of HCN(NH\textsubscript{3}) from reforming with the catalyst;
HCN(NH\textsubscript{3})\text{catalyst}: the amount of HCN(NH\textsubscript{3}) from gasifying the catalyst without feeding biomass (blank);

N\text{biomass}: the amount of N in biomass fed into the reactor.
Experiments of gasifying the H-form char catalyst and the char-supported iron catalyst without feeding biomass (blank experiments) were carried out to determine the amounts of HCN and NH$_3$ generated (and thus HCN(NH$_3$)$_{\text{catalyst}}$ in Equation 2-4) under otherwise identical conditions.

2.6 Characterisation of catalysts

2.6.1 Crystal phases in the catalysts

The fresh and spent catalysts were characterized by X-ray diffraction (XRD). They were scanned on a Philips PW1140/90 diffractometer with Cu K$_\alpha$ radiation (25 mA and 40 kV) or a D8 advance diffractometer with a lynxeye detector (40 mA and 40 kV) at a scan rate of 2°/min with a step size of 0.02°.

2.6.2 Char structure in the char-supported iron catalysts

The structural features of fresh and spent char-supported iron catalysts were characterized using a Perkin–Elmer Spectrum GX FT-Raman spectrometer [9-11]. FT-Raman spectra were acquired at room temperature in air. An InGaAs detector in liquid nitrogen was used to collect Raman scattering using a back scattering configuration.

The sample was diluted with IR grade KBr to a concentration of 0.25 wt% (Figure 2-6) and ground for 15 minutes to minimize the effects of concentration and particle size of char on the Raman intensity [11-13], because char particles can be heated up easily in the laser beam which would cause the emission of Planck radiation [14] and the damage of char structure.

The excitation laser wavelength was 1064 nm, the laser power was 150 mW and the spectral resolution was 4 cm$^{-1}$ for Raman spectra reported here. The diameter of the incidental laser spot was about 1 µm, much larger than the micro-crystallites in the samples.
The Raman spectra ranged from 800 to 1800 cm\(^{-1}\) were deconvoluted into 10 Gaussian bands (Table 2-8) using the GRAMS/32 AI software [9] and a detailed discussion of Raman band assignments can be found elsewhere [10]. Briefly, the D band mainly represents the large aromatic ring systems (not less than 6 fused rings) in chars, while G\(_r\), V\(_l\) and V\(_r\) bands mainly represent the 3-5 fused rings, methylene or methyl semicircle breathing of aromatic rings and methyl semicircle breathing of aromatic rings in chars, respectively. Therefore, the ratio of \(I_D/I_{Gr+Vl+Vr}\) was used to express the ratio between large and small aromatic ring systems in chars.

**Figure 2-6.** Effects of char concentration in char-KBr mixture on the total Raman peak area ranged from 800 to 1800 cm\(^{-1}\).
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Table 2-8. A summary of peak/band assignments [9]

<table>
<thead>
<tr>
<th>Band name</th>
<th>Band position cm(^{-1})</th>
<th>Description</th>
<th>Bond type</th>
</tr>
</thead>
<tbody>
<tr>
<td>G(_1)</td>
<td>1700</td>
<td>Carbonyl group C=O</td>
<td>sp(^2)</td>
</tr>
<tr>
<td>G</td>
<td>1590</td>
<td>Graphite (E_{2g}); aromatic ring quadrant breathing; alkene C=C</td>
<td>sp(^2)</td>
</tr>
<tr>
<td>G(_r)</td>
<td>1540</td>
<td>Aromatics with 3~5 rings; amorphous carbon structures</td>
<td>sp(^2)</td>
</tr>
<tr>
<td>V(_1)</td>
<td>1465</td>
<td>Methylene or methyl; semicircle breathing of aromatic rings; amorphous carbon structures</td>
<td>sp(^2), sp(^3)</td>
</tr>
<tr>
<td>V(_r)</td>
<td>1380</td>
<td>Methyl group; semicircle breathing of aromatic rings; amorphous carbon structures</td>
<td>sp(^2), sp(^3)</td>
</tr>
<tr>
<td>D</td>
<td>1300</td>
<td>D band on highly ordered carbonaceous materials; C-C between aromatic rings and aromatics with not less than 6 rings</td>
<td>sp(^2)</td>
</tr>
<tr>
<td>S(_l)</td>
<td>1230</td>
<td>Aryl-alkyl ether; para-aromatics</td>
<td>sp(^2), sp(^3)</td>
</tr>
<tr>
<td>S</td>
<td>1185</td>
<td>C(<em>{\text{aromatic}})-C(</em>{\text{alkyl}}); aromatic (aliphatic) ethers; C-C on hydroaromatic rings; hexagonal diamond carbon sp(^3); C-H on aromatic rings</td>
<td>sp(^2), sp(^3)</td>
</tr>
<tr>
<td>S(_r)</td>
<td>1060</td>
<td>C-H on aromatic rings; benzene (ortho-di-substituted) ring</td>
<td>sp(^2)</td>
</tr>
<tr>
<td>R</td>
<td>960-800</td>
<td>C-C on alkanes and cyclic alkanes; C-H on aromatic rings</td>
<td>sp(^2), sp(^3)</td>
</tr>
</tbody>
</table>
2.6.3 Specific reactivity of the char-supported iron catalysts

In order to investigate effects of the coke deposits and the iron-containing species on the disposal of spent catalysts (i.e. combustion), the reactivity of fresh and spent char-supported iron catalyst was measured in air at 400°C using a Perkin-Elmer Pyris thermogravimetric analyser (TGA) following the procedure described in detail previously [4, 11].

Briefly, an empty platinum crucible was placed on the holder and heated to 110 °C under N₂ flow followed by holding for 30 minutes until the balance reading was stabilized and teared to zero. Approximately 4 mg of char sample was loaded into the crucible and heated again to 110 °C under N₂ flow with holding for another 30 minutes to completely evaporate the moisture from the char. The sample temperature was then increased to 400 °C at a rate of 50 °C/min. After holding for ~2 minutes, the atmosphere for the sample was switched to instrument air. After enough time for char conversion at 400 °C, the temperature was increased to 600 °C and held 30 minutes to remove residual carbon completely. The final mass was then taken as the mass of ash. The specific reactivity (R) of char was calculated using the following Equation 2-5:

\[
R = -\frac{1}{W} \frac{dW}{dt}
\]

(2-5)

where W is the mass (daf basis) of the char at any given time.
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Chapter 3

Catalytic steam reforming of tar on ilmenite ore during biomass gasification
3.1 Introduction

Biomass gasification is considered as an important option for converting biomass to fuel or chemicals [1-4]. Tar reforming is one of the most important aspects of biomass gasification because tar can cause damage to downstream equipments, poisoning of catalyst and high cost of maintenance [2, 3]. Compared with physical removal methods, tar reforming, especially catalytic reforming, is an attractive method for reforming tar because physical methods usually require the cooling down of the gas products, leading to the loss of thermal efficiency in the overall process.

Natural minerals, such as dolomites and olivine, are inexpensive and can be used to reform tar. Although dolomites show good activity for tar reforming, they are fragile resulting in the need of frequent catalyst replacement [5-12]. Olivine, another inexpensive catalyst with high attrition resistibility, has been examined for tar reforming during biomass gasification and for the steam reforming or the dry reforming of hydrocarbon [13-27]. However, the catalysts need to be pretreated to obtain high activity for tar reforming and they are easy to be deactivated due to carbon deposition and the loss of Fe dispersion [22-24, 28].

Ilmenite ore, mainly consisting of iron oxides and titanium dioxides, has high attrition resistibility and is widely present in Western Australia. In this Chapter, it is employed as catalysts for the steam reforming of biomass tar derived from the pyrolysis of mallee wood in situ. The in situ activity of ilmenite on the steam reforming of tar was investigated under different operating conditions. Furthermore, previous studies mainly focused on the activities of iron oxides [23-28]. The functions of support in the catalysts and the reaction pathways on the catalysts are not clear. The functions of iron oxides and titanium dioxides in ilmenite and the possible reaction pathways on ilmenite are also discussed in this Chapter.
3.2 Results and discussion

3.2.1 Effects of temperature on tar reforming

![Graph](image)

**Figure 3-1.** The tar yields of mallee wood after reforming without/with ilmenite (10 g) at different temperatures.

Figures 3-1 shows the tar yields of mallee wood after reforming without/with ilmenite at different temperatures. The tar is defined experimentally as the material soluble in the mixture solvents (methanol and chloroform, 1:4) and did not evaporate at 35 °C within 4 hours. It was found that all tar yields decreased with increasing temperature due to enhanced thermal cracking and reforming. The tar yields after pyrolysis were similar to the results after reforming without catalyst, indicating that the external steam has little effects on thermal cracking of tar in the gas phase, which is in agreement with literatures [29, 30]. Large amounts of steam and carbon dioxide produced in the bottom stage of the reactor during pyrolysis would have already reformed some light compounds of volatiles (e.g. aliphatics and O-containing groups) in the gas phase in the absence of the external steam. In fact, pyrolysis experiment is actually a self-reforming process. Moreover, the external steam may reform some
light compounds of tar, but the tar yields (the mass of heavy compounds) did not change because of the low reactivity of heavy tar especially at low temperature. Therefore, the tar yields after pyrolysis were similar to the results after the steam reforming without catalyst. Obviously, the tar yields dropped when ilmenite was employed in the top stage of reactor. Adsorption of tar on the catalyst would extend the resident time and result in the enhancement of thermal cracking and reforming. Most importantly, the reduction of tar on ilmenite is not only due to the extension of the resident time but also the active phase in ilmenite.

Figure 3-2. The coke yields of mallee wood after reforming with ilmenite (10 g) at different temperatures.

The volatiles produced from the pyrolysis of biomass contained abundant radicals which would react with tar molecules to form activated tar fragments by H- and CH$_3$- abstraction in the gas phase or/and on the surface of the catalyst. These activated tar fragments would be reformed into gas by two pathways on the surface of the catalyst, i.e. steam reforming into gas or/and coke formation and subsequent gasification. At low temperature, the high coke yields indicated that the coke formation was more significant than the steam reforming on ilmenite (Figure 3-2). On the one hand, the molecules in the tar were large and the reactivity of steam was
low at low temperature. The activated tar fragments would combine together easily on the surface of the catalyst, resulting in high coke deposits. On the other hand, the reaction rate of coke gasification was still weak at low temperature. Hence, a significant portion of the tar was converted into coke at low temperature. With increasing temperature, the size of the molecules in the tar decreased due to the enhancement of thermal cracking, the reactivity of steam enhanced, the activity of ilmenite improved and the reaction rate increased. All of these combined to cause low tar yields.

![Figure 3-3](image-url).

**Figure 3-3.** Constant energy synchronous spectra of mallee wood tar solutions produced at different temperatures. (a) 850 °C, reforming with 5 g ilmenite, -2800cm\(^{-1}\) (b) 850 °C, reforming with 5 g ilmenite, -1400cm\(^{-1}\).

Aromatic ring systems in the tar that would cause the coke deposits easily in downstream equipments are the major concern of gas quality. The tar yields can not always reflect the changes in aromatic ring systems because aromatic ring systems are only a part of tar that has other structures such as aliphatics, O-containing functional groups. Therefore, UV-fluorescence spectroscopy was used to characterize aromatic ring systems in the tar. In order to minimize the self-absorption of fluorescence by the tar solution, 2 ppm and 4 ppm (wt) solutions were tested under the same conditions. The intensities of 2 ppm (Figure 3-3) were about half of those of 4 ppm, which illustrated that 4 ppm was low enough to minimize the self-absorption effects.

Figures 3-4 and 3-5 display the constant energy synchronous spectra of mallee wood tar solutions after the steam reforming with/without ilmenite (10 g) at different temperatures. In agreement with tar yields, the UV-fluorescence data after the steam
reforming without catalyst were similar to those after pyrolysis at low temperature and only slight lower at high temperature, which gave evidence that the external steam had slight improvement for the thermal cracking and reforming of the aromatic ring systems in the gas phase. Similarly, it is due to the low reactivity of steam and the high thermal stability of aromatic ring systems at low temperature. In contrast, large molecules were broken and large aromatic ring systems were reformed because of enhanced thermal cracking with increasing temperature. The reactivity of steam also improved. Consequently, all of these contributed to the slight drop of the aromatic ring systems after reforming in the gas phase at high temperature.

In addition, ilmenite showed activity for reforming the aromatic ring systems during the steam reforming process and the activity enhanced with increasing temperature. Compared with the data of non-catalytic reforming, the presence of catalyst caused the peak area of the synchronous spectra to decrease by 45% at 600 °C and by 76% at 850 °C. Similar to the tar yields, the loss of the aromatic ring systems was also at least partly due to coke deposits on the catalyst at low temperature. Higher amounts of ilmenite provided higher total surface area and more active sites. The adsorbed and activated aromatic ring systems would polymerise to form coke easily on the surface of the catalyst because of the low reactivity of steam and the high thermal stability of the aromatic ring systems at low temperature, finally resulting in the low activity of ilmenite for breaking down the aromatic ring systems and the high coke yields at low temperature. With increasing temperature, the reactivity of steam enhanced. More importantly, ilmenite showed high activity for the steam reforming of the aromatic ring systems at high temperature and thus the total aromatic ring systems in the tar decreased.
Figure 3-4. Constant energy (-2800 cm\(^{-1}\)) synchronous spectra of mallee wood tar solutions (4 ppm) produced using 10 g ilmenite as catalysts at different temperatures. (a) 600 °C; (b) 700 °C; (c) 800 °C; (d) 850 °C.
Figure 3-5. Constant energy (-1400 cm\(^{-1}\)) synchronous spectra of mallee wood tar solutions (4 ppm) produced using 10 g ilmenite as catalysts at different temperatures. (a) 600 °C; (b) 700 °C; (c) 800 °C; (d) 850 °C.
3.2.2 Effects of external steam and contact time on tar reforming

While the above mentioned results demonstrate that the externally added steam had little effects on the gas phase reforming of volatiles especially at low temperature, the roles of steam on the reforming reaction on the catalyst require further consideration. In particular, the roles of steam on the outcome of two competing reactions involving molecules/fragments adsorbed on catalyst, i.e. reforming into gas or polymerising into coke, need to be clarified. For this reason, two isothermal reactors (3-frit reactor, Figure 2-2 and 4-frit reactor Figure 2-3) and two steam injection methods (continuous and pulsing injections) were used here to investigate the catalytic reforming of biomass tar on ilmenite catalyst in the absence and presence of the external steam. With the figuration of the 3-frit reactor, the injecting position of the external steam is on the top of the second frit (i.e. below the ilmenite bed). Ilmenite formed a fluidized bed during the steam reforming process. The volatiles and external steam might not have been well mixed before contacting with ilmenite in the 3-frit reactor because of the short contact time. To minimize this influence on the performance of ilmenite, the 4-frit reactor whose external steam injecting position is 30 mm lower than the second frit was designed and used in the steam reforming process. In addition, continuous and pulsing injections of the external steam were employed to clarify the reaction pathways and the effects of the external steam during the reforming process.

Figure 3-6 shows the coke yields of mallee wood after reforming using different steam injection methods with 5 g ilmenite at 850 °C. During the initial 30 minutes, the coke yields were negative. Firstly, the moisture of ilmenite, approximately 0.5%, can be removed when the temperature reached 100 °C. Secondly, various crystal waters of ilmenite and possibly some volatiles were released during the heat up (Figure 3-7,100-600 °C). Thirdly, the reduction of ilmenite is another important reason for its weight loss because large amounts of syngas, good reductants, were produced during the steam reforming process. The XRD results also proved that the iron-containing species were reduced after the steam reforming. Therefore, all these combined to decrease the weight of ilmenite catalyst.
Figure 3-6. The coke yields of mallee wood after reforming using different steam injection methods with 5 g ilmenite at 850 °C.

Figure 3-7. The weight loss during the heat up of ilmenite ore using TGA.
The coke yields became constant during 30-50 minutes. Compared with the 3-frit reactor, steam was mixed well with volatiles before contacting with the catalyst in the 4-frit reactor, resulting in lower coke formation on the catalyst in the 4-frit reactor. When the steam was injected into reactor as pulses, the steam concentration in the reactor at the moment when the steam was not injected would have dropped. In this case, the tar tended to polymerise on catalyst surface, or the gasification of coke on the catalyst also slowed down. Hence, the coke yields after reforming with pulsed steam injection increased (Figure 3-6).

![Figure 3-8](image)

**Figure 3-8.** The tar yields of mallee wood after reforming using different steam injection methods with 5 g ilmenite at 850 °C.

Figure 3-8 reveals the tar yields of mallee wood after reforming with different steam injection methods with 5 g ilmenite at 850 °C. Tar would be reformed by two pathways on the surface of the catalyst, direct steam reforming into gas or/and coke formation and subsequent gasification. The results of the pulsing steam injection showed that the tar reduction decreased in the absence of the external steam, indicating that the external steam would change the reaction pathway on ilmenite during the catalytic reforming process. In the presence of the external steam, the activated tar fragments would continuously be reformed into gas on ilmenite at high temperature. Contrarily, the tar fragments activated on catalyst surface would
combine together to form coke rather than gas in the absence of the external steam because in the absence of sufficient reactant/oxidizer, polymerisation/condensation became an important reaction at high temperature. Also, the gasification rate of coke dropped in the absence of the external steam due to the lack of gasifying agent. With the accumulation and further condensation of coke on the catalyst, the activity for tar reforming decreased, finally resulting in high tar yields from the reforming with the pulsed steam injection.

It was observed that ilmenite had activity for reforming the aromatic ring systems (Figures 3-9). The reduction in the peak area of synchronous spectra, as a reflection of the conversion of the aromatic ring systems, with ilmenite in the 4-frit reactor was 71%. Compared with the results in the 3-frit reactor, the UV-fluorescence intensities of the tars produced in the 4-frit reactor with continuously steam injection were lower and stable, indicating that the catalyst in the 4-frit reactor showed stable activity for reforming the aromatic ring systems because of the good mixing of steam and volatiles. Coke deposit was a crucial factor to the activity of the catalyst.

As is shown in Figures 3-10, the activity of ilmenite for reforming the aromatic ring systems decreased when the external steam was injected discontinuously in the reactor. Additionally, the activity of ilmenite dropped with extending the time in the absence of the external steam. The results clearly showed that the requirements of reforming the small aromatic ring systems and large aromatic ring systems are different. Compared with the reforming of the small aromatic ring systems, the reforming of the large aromatic ring systems would need multiple vacant active sites to be adjacent to each other on the surface of the catalyst. This is because the reforming of a large tar molecule (or a large aromatic ring) is to follow a dual-site (multi-site) reaction mechanism. Alternatively, the reforming of large aromatic ring systems would require many sites due to steric hindrance. As was discussed above, the tar fragments activated on the catalyst would form coke easily on the catalyst surface in the absence of the external steam, which would cover the active sites on the catalyst. Once the coke deposit is formed on the catalyst, the reforming of the large aromatic ring systems became difficult due to the lack of continuously available active sites on the surface of the catalyst. Hence, the catalyst lost activity for reducing large aromatic rings firstly in the absence of the external steam. In contrast,
the reforming of the small aromatic ring systems would still have chance to be reformed on the catalyst because they needed less vacant sites to be adjacent to each other. With prolonged time in the absence of the external steam, the accumulated coke would continuously cover active sites on the surface of the catalyst, finally causing the loss of its activity for the steam reforming of all aromatic ring systems.
Figure 3-9. Constant energy synchronous spectra of mallee wood tar solution (4 ppm) produced with 5 g ilmenite in different reactors at 850 °C. (a) 3-frit reactor, -2800 cm\(^{-1}\); (b) 4-frit reactor, -2800 cm\(^{-1}\); (c) 3-frit reactor, -1400 cm\(^{-1}\); (b) 4-frit reactor, -1400 cm\(^{-1}\).
Figure 3-10. Peak area of constant energy synchronous spectra of mallee wood tar solutions (4 ppm) produced using different steam injection methods with 5 g ilmenite at 850 °C. (a), $\Delta \nu = -2800 \text{ cm}^{-1}$; (b), $\Delta \nu = -1400 \text{ cm}^{-1}$. 

Chapter 3 Catalytic steam reforming of tar on ilmenite ore
In order to improve the performance of ilmenite for tar reforming, the contact time was prolonged by increasing the mass of the catalyst while the properties of catalyst (e.g. density, particle size) and the gas flow rate remained unchanged. The contact times of different amounts catalysts were 0.012 s, 0.024 s and 0.048 s, respectively. From Figure 3-11, it was observed that the conversion of the tar on ilmenite was higher than 70%. However, it is difficult to compare the results after the steam reforming with different amounts of ilmenite here because all data were low and in the range of experimental errors. Therefore, the aromatic ring systems in tar produced with different amounts of ilmenite were compared by UV-fluorescence spectroscopy, which is more sensitive than the tar yield measurement. As are shown in Figures 3-12 and 3-13, the aromatic ring systems of the tar after reforming with ilmenite decreased with increasing catalyst weight, which demonstrated that the performance of ilmenite for reforming aromatic ring systems was improved with increasing catalyst weight. Increasing weight of ilmenite prolonged the contact time, increased the total surface area and total active sites of the catalyst, which improved the reforming of tar into gas on the catalyst.

![Figure 3-11. The tar yields of mallee wood after reforming with different amounts of ilmenite at 850 °C.](image-url)
Figure 3-12. Constant energy (-2800 cm\(^{-1}\)) synchronous spectra of mallee wood tar solutions (4 ppm) produced at 850 °C with different amounts of ilmenite. (a) 30 minutes; (b) 40 minutes; (c) 50 minutes; (d) 60 minutes; (e) 70 minutes; (f) 80 minutes.
Figure 3-13. Constant energy (-1400 cm\(^{-1}\)) synchronous spectra of mallee wood tar solutions (4 ppm) produced at 850 °C with different amounts of ilmenite. (a) 30 minutes; (b) 40 minutes; (c) 50 minutes; (d) 60 minutes; (e) 70 minutes; (f) 80 minutes.
3.2.3 Effects of additional oxygen on tar reforming

Oxygen or air is usually used in the industrial scale biomass gasification. Therefore, it is necessary to understand the effects of external oxygen on the performance of ilmenite. Table 3-1 and Figure 3-14 show the coke and tar yields of mallee wood after reforming with ilmenite and low concentration O$_2$. It was found that the coke and tar yields were similar and in the range of experimental error.

**Table 3-1.** The coke yields of mallee wood after reforming with 10 g ilmenite and low concentration O$_2$ at 800 °C and 850 °C.

<table>
<thead>
<tr>
<th></th>
<th>800 °C$^a$ (%)</th>
<th>850 °C$^a$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No O$_2$</td>
<td>1.0</td>
<td>0.6</td>
</tr>
<tr>
<td>1000 ppm O$_2$</td>
<td>1.8</td>
<td>1.4</td>
</tr>
<tr>
<td>3000 ppm O$_2$</td>
<td>0.7</td>
<td>1.0</td>
</tr>
</tbody>
</table>

$^a$, Dry basis.

**Figure 3-14.** The tar yields of mallee wood after reforming with 10 g ilmenite and low concentration O$_2$ at 800 °C and 850 °C.
Figures 3-15 and 3-16 are the constant energy synchronous spectra of mallee wood tar solutions produced using 10 g ilmenite as catalyst and with/without additional O\textsubscript{2} at 800 °C and 850 °C. It was observed that the tar produced with additional O\textsubscript{2} tended to include less small aromatic ring systems (wavelength < 360 nm) and more large aromatic ring systems (wavelength > 360 nm) than that produced without oxygen during the steam reforming without catalyst. The results demonstrated that the additional oxygen at low concentration can activate the small aromatic ring systems and polymerise them into new large aromatic ring systems in the gas phase. There are three potential effects by supplying external oxygen [31]. Firstly, it would enhance polycyclic aromatic hydrocarbons (PAH) production due to the increase in the radical pool concentration. Secondly, oxygen would change the formation pathway of PAH, causing selective production. Thirdly, it would decrease PAH yields due to oxidation. The outcomes of the competition among the conflicting effects of additional oxygen vary according to the concentration of oxygen [31]. In our experiments, the concentration of oxygen was low and insufficient for combustion. Therefore, it would enhance the free radicals in the gas phase, resulting in the improvement of the polymerisation rate and the formation of the large aromatic ring systems in the gas phase. As is suggested in the literature [32, 33], low concentration oxygen would enhance aryl radicals by H- and/or CH\textsubscript{3}- abstraction of the aromatic ring systems in the gas phase. These aryl radicals could combine easily to form the large aromatic ring systems rather than continuous reforming in the gas phase. The net result is the loss of the small aromatic ring systems (as the reactants) and the increase of the large aromatic ring systems (as the products) in the tar. The increase of the large aromatic ring systems would form coke on the surface of the catalyst.

During the steam reforming with ilmenite, the small aromatic ring systems in the tar after reforming with additional oxygen were lower, but the large aromatic ring systems in the tar were higher than those of the tar after reforming without oxygen (Figure 3-16). According to above discussion, low concentration oxygen was consumed and changed the aromatic ring systems in the gas phase before contacting with the catalyst. Consequentially, they contributed to the changes of the aromatic ring systems in tar during the steam reforming with low concentration oxygen.
Figure 3-15. Constant energy synchronous spectra of mallee wood tar solutions (4 ppm) produced using 10g ilmenite as catalysts and with/without 1000 ppm additional O\textsubscript{2} at 800 °C and 850 °C. (a) 800 °C, -2800 cm\textsuperscript{-1}; (b) 850 °C, -2800 cm\textsuperscript{-1}; (c) 800 °C, -1400 cm\textsuperscript{-1}; (d) 850 °C, -1400 cm\textsuperscript{-1}.
Figure 3-16. Constant energy synchronous spectra of mallee wood tar solution (4 ppm) produced using 10g ilmenite as catalysts and with additional O\textsubscript{2} at 800 °C and 850 °C. (a) 800 °C, -2800 cm\textsuperscript{-1}; (b) 850 °C, -2800 cm\textsuperscript{-1}; (c) 800 °C, -1400 cm\textsuperscript{-1}; (d) 850 °C, -1400 cm\textsuperscript{-1}.
3.2.4 Iron-containing species acting as an active phase

Fresh and spent ilmenites were analyzed using X-ray diffraction in order to understand the forms of the iron-containing species in the catalyst. Figures 3-17 and 3-18 illustrate the XRD patterns of the catalysts before and after experiments. In raw ilmenite ore (Figure 3-17a), only slight TiO$_2$ peak and some Fe$_2$O$_3$ peak were observed, indicating that the iron-containing species mainly existed in amorphous forms. In contrast, spent ilmenite showed strong TiO$_2$ peak, TiFeO$_3$ peak and slight metallic iron peak. These demonstrated that the crystal compounds existing in raw ilmenite ore were TiO$_2$ and Fe$_2$O$_3$ (Fe$^{3+}$). Fe$_2$O$_3$ and/or other amorphous iron-containing species would be crystallized and/or reduced during the steam reforming process. After the catalytic steam reforming of biomass volatiles, TiFeO$_3$ (Fe$^{2+}$) and some metallic iron (Fe$^0$) were formed and stably existed in spent ilmenite, implying that the reduction of iron oxide occurred during the steam reforming.

The crystal sizes of spent ilmenite were calculated by Scherrer equation (Table 3-2). The crystal size of spent ilmenite unchanged with increasing temperature because TiO$_2$ in ilmenite would primarily act as a support for the catalyst, which would prevent sintering and agglomeration of the iron-containing species during the steam reforming, and thus maintain the consistent crystal size of the iron-containing species.
Figure 3-17. XRD spectra of new and spent ilmenite after the catalytic steam reforming of mallee wood tar at 850 °C. (a) Raw ilmenite ore (b) 5g ilmenite after being used for 10 minutes; (c) 5g ilmenite after being used for 50 minutes; (d) 10g ilmenite after being used for 80 minutes; (e) 20g ilmenite after being used for 80 minutes (1. TiO$_2$ 2. FeTiO$_3$ 3. Fe$_2$O$_3$ 4. Fe).
Figure 3-18. XRD spectra of spent ilmenite after the catalytic steam reforming of mallee wood tar at different temperatures. (a) 600 °C, 80 minutes; (b) 700 °C, 80 minutes; (c) 800 °C, 80 minutes; (d) 850 °C, 80 minutes (1. TiO$_2$ 2. TiFeO$_3$ 3. Fe$_2$O$_3$ 4. Fe).
### Table 3-2. Crystal sizes of spent ilmenite catalysts after the catalytic steam reforming of mallee wood tar at different temperatures

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>FeTiO$_3$(^a) (nm)</th>
<th>TiO$_2$(^a) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>600, 10 g, 80 min</td>
<td>42.3</td>
<td>42.3</td>
</tr>
<tr>
<td>700, 10 g, 80 min</td>
<td>42.2</td>
<td>44.9</td>
</tr>
<tr>
<td>800, 10 g, 80 min</td>
<td>44.3</td>
<td>43.3</td>
</tr>
<tr>
<td>850, 10 g, 80 min</td>
<td>42.2</td>
<td>43.4</td>
</tr>
</tbody>
</table>

\(^a\) Crystal size calculated by Scherrer equation.
In order to understand the function of the iron-containing species in ilmenite, iron oxides were used as catalysts for tar reforming. As are shown in Figure 3-19, ilmenite and Fe$_2$O$_3$ exhibit higher activity for reforming the aromatic ring systems than Fe$_3$O$_4$. In the initial reforming process, Fe$_2$O$_3$ can be reduced by syngas to Fe$_3$O$_4$ (Figure 3-20) easily and supply some oxygen to the tar reforming process, resulting in high activity for tar reforming. Moreover, the activity of reduced ilmenite for breaking down the aromatic ring systems was slightly higher than that of ilmenite, which revealed that the reduced forms of the iron-containing species would have higher activity for reforming tar than iron oxides, and syngas in the reactor would reduce ilmenite to obtain its high activity for tar reforming during the steam reforming.

Previous studies claimed that olivine with more surface iron and greater reducibility would have higher activity [26, 27]. Similarly, it is speculated that Fe$^{3+}$ existing in raw ilmenite ore would be transformed into reduced forms, TiFeO$_3$ (Fe$^{2+}$) and/or metallic iron (Fe$^0$) during initial steam reforming process. The reduced irons on the surface of the catalyst would be maintained because of the large amounts of syngas in the reactor and would have high activity for reforming tar during the steam reforming process. Meanwhile, TiO$_2$ could act as a support, which can restrain sintering and agglomeration of the iron-containing species and keep its high dispersion during the steam reforming process. Finally the highly dispersed iron-containing species in ilmenite brought its high and consistent activity for tar reforming.
Figure 3-19. Peak area of constant energy synchronous spectra ($\Delta \nu = -2800 \text{ cm}^{-1}$) of mallee wood tar solution (4 ppm) produced using ilmenite and iron oxides as catalysts at 700 $^\circ$C and 850 $^\circ$C. (a) 700 $^\circ$C; (b) 850 $^\circ$C.
Figure 3-20. XRD spectra of new and spent Fe$_2$O$_3$ after being used for steam reforming of mallee wood tar at 700 °C and 850 °C. (a) new Fe$_2$O$_3$; (b) spent Fe$_2$O$_3$, 700 °C, 10 minutes; (c) spent Fe$_2$O$_3$, 850 °C, 10 minutes; (1. Fe$_2$O$_3$ 2. Fe$_3$O$_4$)
3.3 Conclusions

Ilmenite, a natural iron-containing mineral in Western Australia, exhibited activity for reforming tar during the steam reforming process. The highly dispersed iron-containing species in ilmenite contributed to its high and consistent activity and the function of TiO$_2$ is a support that could inhibit its sintering and agglomeration.

The external steam had little effect on the thermal cracking and reforming of tar in the gas phase. However, it played an important role in the steam reforming of tar on ilmenite. Tar was mainly converted into coke on the catalyst at low temperature, whereas it was primarily reformed into gas on ilmenite at high temperature in the presence of the external steam.

Low concentration oxygen significantly changed the compositions of volatiles during the thermal cracking in the gas phase. It activated the small aromatic ring systems and polymerise them into new large aromatic ring systems. Finally, it increased the reforming of the small aromatic ring systems but decreased the reforming of the large aromatic ring systems on ilmenite catalysts.
3.4 References


Chapter 3 Catalytic steam reforming of tar on ilmenite ore


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Chapter 4

Importance of support in iron-based catalysts during the steam reforming of biomass tar
4.1 Introduction

Catalytic reforming is the commonly accepted best option that can convert tar into syngas efficiently [1-3]. It has been reported that many catalysts such as minerals [4-10] and Ni-based catalysts [11-17] can be used as catalyst to reform tar. Inexpensive catalysts, such as natural minerals, show activities for tar reforming, but the activities are not high enough to remove tar to an acceptable level. In contrast, Ni-based catalysts have high activity for reforming tar and increasing syngas yield. They are however expensive, easily deactivated by coke deposition and poisoning during the steam reforming process. In addition, various forms of iron have been reported as the catalysts for reforming tar during biomass gasification [18-21]. Metallic iron has higher activity for the reforming of tar than iron oxides, but it can be deactivated rapidly in the absence of hydrogen due to coke deposition.

The functions of support are important for the activity of the catalyst. The support would be favourable for extending the life of catalyst by inhibiting the agglomeration of the active phases in the catalyst. Char, cheap and one of products in the gasifier, exhibits some activity for tar reforming and its activity is influenced by pore size, surface area and AAEM contents of char [22-24]. The coke deposited on the char can block the pores and reduce the surface area to decrease its activity. However, it can be consumed by gasification/reforming agents and gaseous products, such as steam, O$_2$, and CO$_2$, which would inhibit its deactivation by producing new pores [23, 24]. Furthermore, char can act as a good support that dispersed the active clusters at nano scale depending on reaction conditions and loading level/ratio after pyrolysis or partial gasification [25-28]. The char-supported catalyst would have low price and be simply burned/gasified to reuse the energy of the char rather than be regenerated after it was deactivated [28]. Hence, it is worthy to understand the effects of the char-supported catalyst on tar reforming and the functions of char during the catalytic steam reforming process.

In this study, char-supported iron/nickel and ilmenite catalysts are used for the steam reforming of biomass tar derived from the pyrolysis of mallee wood *in situ*. The performance of the catalysts on the steam reforming of biomass tar was studied under different operating conditions. Effects of support on the steam reforming of tar
were investigated. The kinetic parameters were calculated using a first order kinetic equation and the potential reaction pathways are discussed.

4.2 Results and discussion

4.2.1 Tar reforming on char-supported catalysts

4.2.1.1 Reduction of tar yields

Figure 4-1 shows the tar yields after the steam reforming of volatiles from mallee wood with/without char-supported catalysts at different temperatures. The tar is hereby defined experimentally as the material soluble in the mixture solvents (methanol and chloroform, 1:4), and is residues after the evaporation of solvents at 35 °C within 4 hour. The tar yields after pyrolysis were similar to these after the steam reforming without catalyst. In agreement with literature [29, 30], the external steam has weak influences on the thermal cracking and reforming of tar in the gas phase due to its low reactivity at low temperature. However, the tar yields decreased with elevating temperature due to the enhancement of thermal cracking and reforming.

The H-form char catalyst showed some activity for decreasing the tar yield at high temperature. Obviously, the tar yields after the steam reforming with char-supported catalysts dropped compared with those after the steam reforming without catalyst. According to our previous studies [25-28], the iron/nickel clusters were nano particles with high dispersion in the char, giving their high activities. Although the effects of the char-supported iron catalyst on the tar yields were inconspicuous at low temperature, its catalytic activity became very prominent at high temperature (≥ 800°C). Taking the tar yields after pyrolysis as the basis for comparison, the use of the char-supported iron catalyst brought about 84% and 96% reduction in the tar yield at 800 °C and 850 °C, respectively. In addition, the tar yields after the steam reforming with the char-supported nickel catalyst were even lower than those after the steam reforming with the char-supported iron catalyst,
especially at low temperature. Nickel clearly has higher activity for tar reforming than iron even at temperature as low as 500 °C. Moreover, it was observed that the yields of tar after reforming with the char-supported iron catalyst remained unchanged from 10 to 50 minutes (Figures 4-2), demonstrating that the catalyst can keep its high activity for tar removal within the time range investigated.

![Tar yield graph](image)

**Figure 4-1.** The tar yields of mallee wood after pyrolysis, reforming without the catalyst, reforming with the H-form char catalyst and the char-supported iron and nickel catalysts at different temperatures.
4.2.1.2 Reduction of aromatic ring systems

Tar is a very complex mixture of compounds having aromatic, aliphatic and oxygen structures. The presence of aromatic structures in tar is the major concern in terms of gasification product gas quality. The tar yields do not always reflect the changes in aromatic ring systems during the steam reforming process. Instead, UV-fluorescence spectroscopy was used to characterize the aromatic structural features of the tar so as to understand the performance of the catalyst on the steam reforming of the aromatic ring systems. 2 ppm and 4 ppm (wt) solutions were examined under the same conditions to confirm the minimal self-absorption of fluorescence by the tar solution. The intensities of 4 ppm (Figure 4-3) were about double of those of 2 ppm, demonstrating that 4 ppm was low enough to minimize the self-absorption effects and the UV-fluorescence intensity reflected the concentration of the aromatic ring systems in the tar solution.
It was noticed that the types of peaks were similar at the same temperature (Figures 4-4 and 4-5), indicating that the types of aromatic ring systems were similar in the tars produced under different steam reforming conditions. At low temperature, the intensities of the tar after pyrolysis and the steam reforming without the catalyst were similar. This implies that the aromatic ring systems can not be further broken down by the external steam to large extents without the catalyst at low temperature due to the low activity of steam and the high thermal stability of the aromatic ring systems at low temperature (Figures 4-4a and 4-4b). With increasing temperature to 700 °C, the intensity of the tar after the steam reforming without the catalyst became slightly lower than that after pyrolysis (Figures 4-4c, 4-4d and 4-4e). It demonstrated that some aromatic ring systems would be reformed by the external steam when the temperature was higher than 700 °C. With increasing temperature, large aromatic ring systems were reformed and the reactivity of steam improved, resulting in the decrease of the aromatic ring systems in the gas phase at high temperature.
Figure 4-4. Constant energy (-2800 cm$^{-1}$) synchronous spectra of mallee wood tar solutions (4 ppm) produced at different temperatures. (a) 500 °C; (b) 600 °C; (c) 700 °C, (d) 800 °C; (e) 850 °C.
Figure 4-5. Constant energy (-1400 cm$^{-1}$) synchronous spectra of mallee wood tar solutions (4 ppm) produced at different temperatures. (a) 500 °C; (b) 600 °C; (c) 700 °C, (d) 800 °C; (e) 850 °C.
The UV-fluorescence intensities changed drastically when the catalyst was pre-loaded in the reactor. The yields of the small aromatic ring systems (mainly 2-3 rings, 280 nm < wavelength < 360 nm) after catalytic steam reforming were higher than those after pyrolysis and the steam reforming without the catalyst while the yields of the larger aromatic ring systems (wavelength > 360 nm) were similar at 500 °C and 600 °C (Figures 4-4a and 4-4b). There are three possible reactions here. Firstly, small aliphatic hydrocarbons may combine together to form new aromatic ring systems through polymerisation [31]. However, the reaction seems impossible here because it only occurs at high temperature (> 1000 °C) [31]. Secondly, the additional small aromatic ring systems would come from the decomposition of large molecules. The energy transfer would take place from small aromatic ring systems to large aromatic ring systems if they are within the same tar molecule [32]. Meanwhile, the larger aromatic ring systems would be little affected by the presence of smaller aromatic ring systems in the same tar molecule [32]. Thirdly and importantly, it is due to the dehydration and dehydrogenation of aliphatics and/or O-functional groups, especially sugar compounds from the pyrolysis of cellulose and hemicelluloses. Sugar compounds in the volatiles contained larger amounts of -OH groups which could be dehydrated and dehydrogenated easily to form new heterocyclic and/or substitutional aromatic ring systems on the surface of the catalyst. The porous structures and the surface properties of char support would enhance the dehydration and dehydrogenation. Therefore, the dehydration and dehydrogenation of aliphatics and/or O-functional groups would be a predominant factor for generating new aromatic ring systems at low temperature.

The yields of the aromatic ring systems after the catalytic reforming were significantly lower than those after pyrolysis and the steam reforming without the catalyst at high temperature (Figures 4-4c, 4-4d and 4-4e). The char-supported iron catalyst showed higher activity for the reforming of the aromatic ring systems than the H-form char catalyst at high temperature and its function proliferated dramatically with increasing temperature, which were in agreement with the tar yield (Figure 4-1). At high temperature, the molecules in the tar were small, and the reactivity of steam, the reaction rate and the activity of iron-containing species enhanced. Therefore, the effects of the char-supported iron catalyst on reforming aromatic ring systems were extremely high at high temperature.
It was also observed that the fluorescence intensity of aromatic ring systems in the tar after the steam reforming with the char-supported iron catalyst at 500 °C was higher than that after the steam reforming with the H-form char catalyst, which demonstrated that the iron-containing species could enhance the formation of the small aromatic ring systems at low temperature. Oppositely, the intensity of the tar after the steam reforming with the char-supported iron catalyst was slight lower than that after the steam reforming with the H-form char catalyst at 600 °C (Figure 4-4b), indicating that some small aromatic ring systems started to be broken down at 600 °C due to the activity of the iron-containing species. In addition, it was found that the intensity of the tar after the steam reforming with the char-supported nickel catalyst was lower than that after the steam reforming with char-supported iron catalyst, even at 500 °C. The data implied that the char-supported nickel catalyst had much higher activity than the char-supported iron catalyst and can break down aromatic ring systems even at low temperature, but it became similar to that of the char-supported iron catalyst at 800 and 850 °C. Furthermore, the aromatic ring systems after reforming with the char-supported iron catalyst kept constant in the duration of 50 minutes (Figures 4-6 and 4-7), similar to tar yields, which implied the catalyst could have stable activity for reforming aromatic ring systems within the experimental time.
Figure 4-6. Constant energy (~2800 cm\(^{-1}\)) synchronous spectra of mallee wood tar solutions (4 ppm) produced by reforming without/with the char-supported iron catalyst at 800 °C and 850 °C for different feeding times. (a) Reforming without catalyst, 800 °C; (b) Reforming with the char-supported iron catalyst, 800 °C; (c) Reforming without catalyst, 850 °C; (d) Reforming with the char-supported iron catalyst, 850 °C.
Figure 4-7. Constant energy (-1400 cm\(^{-1}\)) synchronous spectra of mallee wood tar solutions (4 ppm) produced by reforming without/with the char-supported iron catalyst at 800 °C and 850 °C for different feeding times. (a) Reforming without catalyst, 800 °C; (b) Reforming with the char-supported iron catalyst, 800 °C; (c) Reforming without catalyst, 850 °C; (d) Reforming with the char-supported iron catalyst, 850 °C.
4.2.2 Active phases in char-supported iron catalysts

In order to understand the chemical forms of the iron-containing species in the catalyst, the fresh and spent char-supported iron catalysts were analyzed using X-ray diffraction. Figures 4-8 and 4-9 show the XRD patterns of the catalysts before and after experiments at different temperatures and different in-steam times. In the iron-loaded coal (Figure 4-8a), no other peaks can be observed except quartz that would be originated from raw coal (i.e. mineral matter in coal). Previous results showed that iron would exist in the form of FeOOH or be associated with certain functional groups (-COOH, -OH) [25-28]. Both forms of iron were well dispersed in the coal matrix and cannot be detected by XRD. As are shown in Figures 4-8 and 4-9, the XRD patterns of the char-supported iron catalysts indicated the presence of magnetite (Fe$_3$O$_4$) coexisting with the metallic irons ($\alpha$-Fe and $\gamma$-Fe). According to the Fe-C equilibrium phase diagram, $\alpha$-Fe is a stable species when the temperature is lower than 700 °C and $\gamma$-Fe become a stable species when the temperature is higher than 900 °C. The iron phases present in the char depend on the cooling rate of the sample [25]. $\gamma$-Fe (C) would be kept rather than transformed into $\alpha$-Fe/Fe$_3$C when cooling rapidly [25]. In addition, the results indicated the presence of magnetite (Fe$_3$O$_4$) coexisting with the metallic irons ($\alpha$-Fe and $\gamma$-Fe) even after being used for 50 minutes (Figure 4-9).

The crystal sizes of the iron-containing species were calculated using Scherrer equation (Tables 4-1 and 4-2). The crystal size of SiO$_2$ was calculated as a standard to verify the Scherrer equation. The crystal size of Fe$_3$O$_4$ in the catalyst was consentaneous because carbon would inhibit sintering and agglomeration of the iron-containing species during the steam reforming process.
Figure 4-8. XRD spectra of the char-supported iron catalysts. (a) raw Fe-loaded coal; (b) char-supported iron catalyst prepared at 800 °C, gasification for 10 minutes; (c) used catalyst after reforming at 500 °C for 10 minutes; (d) used catalyst after reforming at 600 °C for 10 minutes; (e) used catalyst after reforming at 700 °C for 10 minutes; (f) used catalyst after reforming at 800 °C for 10 minutes; (g) used catalyst after reforming at 850 °C for 10 minutes (‘M’: magnetite (Fe₃O₄); ‘α’: α-Fe; ‘γ’: γ-Fe; ‘Q’: quartz).
Figure 4-9. XRD spectra of the char-supported iron catalysts. (a) used catalyst after reforming at 800 °C for 10 minutes; (b) used catalyst after reforming at 800 °C for 20 minutes; (c) used catalyst after reforming at 800 °C for 30 minutes; (d) used catalyst after reforming at 800 °C for 40 minutes; (e) used catalyst after reforming at 800 °C for 50 minutes; (f) used catalyst after reforming at 850 °C for 10 minutes; (g) used catalyst after reforming at 850 °C for 20 minutes; (h) used catalyst after reforming at 850 °C for 30 minutes; (i) used catalyst after reforming at 850 °C for 40 minutes; (j) used catalyst after reforming at 850 °C for 50 minutes ('M': magnetite (Fe$_3$O$_4$); 'α': α-Fe; 'γ': γ-Fe; 'Q': quartz).
Table 4-1. Crystal sizes of iron-containing species in fresh and spent char-supported iron catalysts.

<table>
<thead>
<tr>
<th></th>
<th>SiO$_2$ (nm)$^a$</th>
<th>Fe$_3$O$_4$ (nm)$^a$</th>
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<tbody>
<tr>
<td>Fresh catalyst</td>
<td>34.1</td>
<td>16.2</td>
</tr>
<tr>
<td>After being used at 500 °C</td>
<td>33.4</td>
<td>17.9</td>
</tr>
<tr>
<td>After being used at 600 °C</td>
<td>33.9</td>
<td>18.7</td>
</tr>
<tr>
<td>After being used at 700 °C</td>
<td>33.8</td>
<td>21.5</td>
</tr>
<tr>
<td>After being used at 800 °C</td>
<td>34.6</td>
<td>15.4</td>
</tr>
<tr>
<td>After being used at 850 °C</td>
<td>34.6</td>
<td>15.3</td>
</tr>
</tbody>
</table>

$^a$, Crystal size calculated by Scherrer equation.

Table 4-2. Crystal sizes of iron-containing species in spent char-supported iron catalysts after the steam reforming at 800 °C and 850 °C.

<table>
<thead>
<tr>
<th></th>
<th>SiO$_2$ (nm)$^a$</th>
<th>Fe$_3$O$_4$ (nm)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>800°C</td>
<td>850°C</td>
</tr>
<tr>
<td>10 min</td>
<td>34.6</td>
<td>34.6</td>
</tr>
<tr>
<td>20 min</td>
<td>34.7</td>
<td>34.9</td>
</tr>
<tr>
<td>30 min</td>
<td>34.8</td>
<td>34.7</td>
</tr>
<tr>
<td>40 min</td>
<td>34.5</td>
<td>33.9</td>
</tr>
<tr>
<td>50 min</td>
<td>34.1</td>
<td>34.9</td>
</tr>
</tbody>
</table>

$^a$, Crystal size calculated by Scherrer equation.
Literatures claimed that the metallic iron in the catalyst would bring the high activity for tar reforming [18-20]. Therefore, it would have a prospective redox reaction cycle involving the iron-containing species during the steam reforming process. The magnetite would be reduced by carbon/syngas, which would bring high activity of the char-supported iron catalyst during the steam reforming process.

Further experiments were carried out using magnetite, reduced char-supported iron catalyst and the mixture of magnetite and H-form char as catalysts for the steam reforming of volatiles from mallee wood. The peak areas of UV-fluorescence spectra of tar produced with different catalysts at 800 °C are shown in Figure 4-10. All catalysts showed activity for aromatic ring systems reforming. Compared with the mixture of magnetite and the H-form char (Fe₃O₄ content, 10%), magnetite or the H-form char itself exhibited lower activity for breaking down aromatic ring systems. The H-form char in the mixture would improve the dispersion of magnetite. More importantly, the H-form char (carbon) would interact with magnetite to produce new forms of iron (i.e. metallic irons and/or other reduced forms) which would have high activity. As mentioned above, it would relate to a redox reaction since carbon and syngas are strong reductants. However, the activity of the mixture of magnetite and H-form char was lower than that of the char-supported iron catalyst because the physically mixing cannot disperse the iron-containing species in the char as well as ion-exchanging. Meanwhile, the results of the reduced char-supported iron catalyst were similar to those of the char-supported iron catalyst, implying that syngas and carbon in the catalyst were enough to reduce the iron-containing species during the steam reforming process, proving that the highly dispersed iron-containing species in the catalyst were the predominate factor for its high activity for tar reforming.
Figure 4-10. Peak area of constant energy synchronous spectra of mallee wood tar solutions (4 ppm) produced with different catalysts at 800 °C. (a) $\Delta\nu = -2800$ cm$^{-1}$; (b) $\Delta\nu = -1400$ cm$^{-1}$.
4.2.3 Kinetic aspects of steam reforming over iron-based catalysts

According to the tar yields, the kinetic parameters were calculated using a simple first order kinetic equation (Equations 4-1 and 4-2) for the overall tar reforming reactions [33-39].

\[- \frac{dX_{\text{tar}}}{dt} = A_{\text{app}} \exp(- \frac{E_{\text{app}}}{RT})(1 - X_{\text{tar}})\]  

(4-1)

\[\ln\left(- \frac{\ln(1 - X_{\text{tar}})}{\tau}\right) = \ln A_{\text{app}} - \frac{E_{\text{app}}}{RT}\]  

(4-2)

$X_{\text{tar}}$: Tar conversion after the steam reforming on the basis of tar yield after pyrolysis at 500 °C;

$A_{\text{app}}$: The apparent pre-exponential factor;

$E_{\text{app}}$: The apparent activation energy;

$\tau$: The space-time of gas the in the catalytic bed.

The space-time for the catalytic bed was defined as Equation 4-3.

\[\tau = \frac{\text{kg of catalyst in the bed}}{m^3/h \text{ (exit wet gas flow rate, reactor temperature)}}\]  

(4-3)

The Arrhenius plot and Cremer-Constable diagram of the catalytic steam reforming (500-850 °C) is shown in Figure 4-11. The slopes and intercepts were calculated by linear regression. Table 4-3 gives the apparent activation energies and pre-exponential factors of the H-form char catalyst, the char-supported iron catalyst, the char-supported nickel catalyst and ilmenite.
Figure 4-11. Arrhenius plot (a) and Cremer-Constable diagram (b) of the catalytic steam reforming of biomass tar.
Table 4-3. Apparent activation energies and pre-exponential factors for the overall tar removal reaction.

<table>
<thead>
<tr>
<th></th>
<th>$E_{app}$ (kJ/mol)</th>
<th>$A_{app}$ ($m^3/(kg/h)$)</th>
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</thead>
<tbody>
<tr>
<td>H-form char catalyst</td>
<td>82.1</td>
<td>5.4E+06</td>
</tr>
<tr>
<td>Char-supported iron catalyst</td>
<td>60.8</td>
<td>2.1E+06</td>
</tr>
<tr>
<td>Char-supported nickel catalyst</td>
<td>57.3</td>
<td>1.3E+06</td>
</tr>
<tr>
<td>Ilmenite</td>
<td>72.6</td>
<td>5.3E+05</td>
</tr>
</tbody>
</table>

The apparent activation energy and pre-exponential factor of the H-form char was higher than those of the char-supported catalysts, implying that the iron/nickel-containing species in the char supported catalysts extremely improved their activity for the reforming of tar under the current experimental conditions. The apparent activation energy of ilmenite was higher and the pre-exponential factor of ilmenite was lower than those of char-supported iron catalyst, which indicated that the char-supported iron catalyst had higher activity for the reforming of tar. Both of them were in agreement with above discussion.

4.2.4 Roles of support in tar reforming

The parameters of char-supported catalysts exhibited a genuine and precise compensation effect, closely following the Cremer-Constable relationship (Figure 4-11b), but the parameters of ilmenite was out of the relationship. Therefore, it would be concluded that the reaction mechanisms or pathways of the steam reforming process on the char-supported catalysts were similar, but the steam reforming reactions on ilmenite followed different pathways. The support proprieties played important roles on the reaction pathways on the catalysts because ilmenite and the char-supported iron catalyst showed different activities for reforming tar although they have similar active phase (i.e. iron-containing species). The structural properties
Chapter 4 Importance of support in iron-based catalysts

of char are propitious to the dehydration and dehydrogenation. Char would not only disperse the iron-containing species but also interact with the iron-containing species, which can improve its activity for tar reforming, especially at high temperature.

In order to further understand the importance of support in iron-based catalysts for the steam reforming of tar, the peak areas of UV-fluorescence spectra of aromatic ring systems in tar produced with ilmenite and the char-supported iron catalyst are compared in Figure 4-12. Their activities are different during the steam reforming of biomass tar. At low temperature, the aromatic ring systems increased after the steam reforming with the char-supported iron catalyst, whereas they decreased after the steam reforming with ilmenite. In contrast, the char-supported iron catalyst showed higher activity for reforming aromatic ring systems than ilmenite at high temperature.

The differences in the behaviour of these two catalysts must be mainly due to the differences in the properties of support. Firstly, the difference in the amount of oxygen on the surface of TiO$_2$ and char would affect the adsorption of volatiles on their surface, especially at low temperature. Compared with char, the surface of ilmenite contained large amounts of oxygen groups (e.g. TiO$_2$) which would be favourable to the stable adsorption of aromatic ring systems due to its polarity. These adsorbed molecules were combined together easily to form coke on the ilmenite at low temperature due to the low reactivity of steam and the high thermal stability of aromatic ring systems. Contrarily, the heavy compounds (tar) in volatiles were difficulty adsorbed on the char surface due to its less oxygen groups and steric hindrance. In addition, huge amounts of radicals would be formed on the char surface from the char gasification, which may be favourable for the stabilization of the tar molecules. Thus, the tar molecules would pass through the catalyst bed easily, which resulted in the constant tar yields at low temperature (Figure 4-1). Secondly and more significantly, the porous structure and the surface properties of char support enhanced the dehydration and dehydrogenation of sugar compounds and finally led to the increase of aromatic ring systems on the char-supported iron catalyst at low temperature (Figures 4-4 and 4-5).

With increasing temperature, the activity of the iron-containing species became an important factor. The iron-containing species in the char-supported iron catalyst
exhibited much smaller particle size and higher dispersion than those in ilmenite, resulting in the extremely high activity of the char-supported iron catalyst at high temperature. Char (carbon) acted as not only a support but also a reductant for the catalyst. On the one hand, char, mainly acting as a support of the catalyst, similar to TiO$_2$ in ilmenite could prohibit the agglomeration and stinting of the iron-containing species. On the other hand, it would interact with the iron-containing species to produce reduced forms of iron which would have high activity for the steam reforming of tar.
Figure 4-12. Peak area of constant energy (-2800 cm⁻¹) synchronous spectra of mallee wood tars solutions (4 ppm) produced with/without catalysts at different temperatures. (a) Small aromatic ring systems (wavelength<360 nm); (b) Large aromatic ring systems (wavelength>360 nm).
4.3 Conclusions

Tar was reformed efficiently on the char-supported catalysts during the steam reforming process. The H-form char catalyst showed some activity for tar reforming, when the operating temperature reached 800 °C. The char-supported iron/nickel catalysts exhibited much higher activity for the reforming of tar than the H-form char catalyst. Compared with the char-supported nickel catalyst, the inexpensive char-supported iron catalyst may have significant economical advantages in industrial applications. In addition, the char-supported iron catalyst can keep its activity within the time range investigated.

The support proprieties significantly influenced the activities of the catalysts and the reaction pathways on the catalysts. Ilmenite and the char-supported iron catalyst showed different activities although they included similar active phases. Meanwhile, kinetic parameters indicated that the reaction pathways of the steam reforming process on the char-supported catalysts were similar, but were different from the reactions on ilmenite. With increasing temperature, the char-supported iron catalyst exhibited higher activity for breaking down aromatic ring systems than ilmenite. Compared with TiO$_2$ in ilmenite, char would interact with the active phases in the catalyst to improve its activity.
4.4 References


[36] Corella J, Caballero MA, Aznar M, Brage C. Two advanced models for the kinetics of the variation of the tar composition in its catalytic elimination in...


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Chapter 5

Effects of feedstock on the performance of ilmenite ore during the steaming reforming of biomass tar
5.1 Introduction

Biomass fuels contributed 14% of the total energy consumption in the world [1]. Biomass is becoming an increasingly popular renewable energy source because of its potential roles in overcoming the challenges of energy shortage and global warming [2, 3]. Tar, usually defined as condensed organic compounds with a boiling point higher than benzene, is an undesirable product of biomass gasification, because tar causes the blocking and fouling in downstream equipments and the poisoning of catalysts. In order to convert tar into syngas efficiently, the catalytic reforming has been studied intensively [4]. Many catalysts were studied for reforming tar during biomass gasification, such as dolomites [5-10], olivine [4, 11, 12], and Ni-based catalysts [13-19]. Ni-based catalysts display high activity for tar reforming and increase syngas yield, but they are expensive and easily deactivated because of coke deposits and poisoning.

Biomass mainly consists of three major components, hemicellulose, cellulose, and lignin, together with some extractives and inorganic substances [20, 21]. Usually, cellulose, hemicellulose, and lignin cover 40-50 wt %, 25-35 wt % and 16-25 wt % of dry wood, respectively [1, 3]. The composition of biomass affects its behaviour and product yields during pyrolysis [22-24]. Inorganic substances also influence biomass pyrolysis significantly. They could enhance the formation of glycolaldehyde, hydroxyacetone and carbonized products with reduced formation of anhydrosugars [25-27]. Therefore, the differences in feedstock and pyrolysis temperature would change the composition and quantity of volatiles to affect the performance of the catalyst during the steam reforming process. Little is currently known in this area.

In this study, mallee wood, bark and leaf are used to produce volatiles for the catalytic steam reforming with ilmenite ore in situ. Influences of feedstock on the tar properties and their further effects on the performance of ilmenite are investigated under different operating conditions. In addition, the deactivation and regeneration of ilmenite are discussed.
5.2 Results and discussion

5.2.1 Effects of feedstock on the properties of biomass tar

The char yields of mallee wood, bark and leaf, which are not affected by steam due to the uniform configuration of reactor design, as a function of temperature are shown in Figure 5-1. Briefly, biomass was pyrolyzed in the bottom stage to release volatiles that were reformed with steam in the top stage of the 4-frit reactor (Figure 2-3). It was observed that all the char yields decreased with increasing temperature. The char yields of bark were the highest, followed by leaf and wood at low temperature and they became similar at high temperature. Compared with wood and leaf, bark contains more lignin that has large amounts of aromatic ring systems and \(-\text{OCH}_3\) groups [3, 28]. During pyrolysis, lignin is easy to undergo cross-linkage reactions to form char [28], explaining why bark produced more char than leaf and wood at low temperature. With elevating temperature, the nascent char would decompose, reducing their char yield.

![Figure 5-1. The char yields of mallee wood, bark and leaf after the steam reforming without catalysts at different temperatures.](image)
Figure 5-2. The tar yields of mallee wood, bark and leaf after the steam reforming without catalysts at different temperatures.

Figure 5-2 gives the tar yields of mallee wood, bark and leaf after the steam reforming without a catalyst at different temperatures. It is clear that bark produced the lowest tar yield, whereas leaf generated the highest tar yield. These are in good agreement with the data in Table 2-1 that bark had the lowest volatile matter yield (69.5 %) according to traditional standard test method. The high lignin content in bark is unfavourable to liquid yields. In addition, bark had a high ash yield and its inorganic matters would act as a catalyst for the conversion of tar to gas. Both of them caused the lowest tar yields from bark. Oppositely, wood and leaf had higher volatile matter yields than bark (80.9 % and 74.6 %, respectively), resulting in their high tar yields. Although its volatile matter yield was lower than that of wood, leaf generated higher tar yields than wood because it contained large amounts of eucalyptus oil [31] and phenolic extractives [30]. The condensation of these phenolic extractives would induce the high viscosity values of oil from leaf [30]. This implied that the volatiles of leaf would contain more heavy compounds (e.g. large aromatic ring systems) than those of wood, in agreement with its observed high tar yields.
The aromatic structural features of tar were characterized by UV-fluorescence spectroscopy (Figures 5-3 and 5-4). It was found that the shapes of UV-fluorescence spectra of wood, bark and leaf tars were different at low temperature but became similar at high temperature, indicating that the properties of biomass would affect the chemical composition of its volatiles and the influence dropped with increasing temperature. The concentration of aromatic ring systems in the leaf tar were higher than those in the bark and wood tars, especially large aromatic ring systems (wavelength > 360 nm), illustrating that the chemical structures in leaf such as eucalyptus oil and phenolic extractives would be favourable to release more large aromatic ring systems that contributed to its high tar yields during pyrolysis (Figure 5-2). The aromatic ring systems in bark tar were higher than those of wood tar at low temperature and became lower when the temperature was higher than 800 °C. Similar to above discussion, the volatiles of bark would contain more lignin-derived compounds than those of wood, which may lead to its high aromatic ring systems at low temperature. With increasing temperature, the lignin-derived compounds in bark volatiles may cross-link easily to form coke/soot on the surface/frit of the reactor, resulting in its low contents of aromatic ring systems in the tar.
Figure 5-3. Constant energy (-2800 cm\(^{-1}\)) synchronous spectra of tar solutions (4 ppm) produced from mallee wood, bark and leaf with ilmenite at different temperatures. (a) 500 °C; (b) 600 °C; (c) 800 °C; (d) 850 °C.
Figure 5-4. Constant energy (-1400 cm\(^{-1}\)) synchronous spectra of tar solutions (4 ppm) produced from mallee wood, bark and leaf with ilmenite at different temperatures. (a) 500 °C; (b) 600 °C; (c) 800 °C; (d) 850 °C.
5.2.2 Effects of feedstock on the performance of ilmenite

The coke yields of mallee wood, bark and leaf after the steam reforming with 10 g ilmenite at 800 and 850 °C are displayed in Figure 5-5. It was observed that the volatiles of bark deposited the highest amounts of coke on the catalyst, followed by leaf and wood. In agreement with the above discussion, bark contains more lignin than wood and leaf, which could release more aromatic ring systems and -OCH$_3$ groups in volatiles [28]. Hence, these molecules derived from lignin would be difficult to be reformed into gas, but be easy to be cross-linked together and form large molecules like soot/coke on the catalyst. Also, the volatiles of leaf had more aromatic ring systems than those of wood, which would form coke on the catalyst easily compared with aliphatics [32]. As are shown in Figure 5-6, the tar yields of bark and leaf can be reduced efficiently after the steam reforming with ilmenite. However, the activity of ilmenite for tar reforming decreased with prolonging feeding time due to their high coke deposits.

The intensities of the aromatic ring systems after the steam reforming with ilmenite dropped obviously (Figures 5-3, 5-4, 5-7 and 5-8). The performance of ilmenite enhanced with increasing temperature. The UV-fluorescence intensities of bark tar after reforming with ilmenite, as a reflection of the concentration of the aromatic ring systems, were lower than those of leaf tar. On the one hand, the volatiles of bark tended to form more coke by cross-linking reactions (Figures 5-5), contributing to less aromatic ring systems in the tar after the steam reforming with ilmenite. On the other hand, leaf released more aromatic ring systems than bark and wood at the same pyrolysis temperature (Figures 5-3 and 5-4). Compared with the results of bark and leaf, it was found that the efficiency of ilmenite in breaking down aromatic ring systems of wood tar was the highest, probably because the volatiles of wood produced the lowest coke deposits on ilmenite which would be favourable to keep its high activity.
Figure 5-5. The coke yields of mallee wood, bark and leaf after the steam reforming with 10 g ilmenite. (a) 800 °C; (b) 850 °C.
Figure 5-6. The tar yields of mallee bark and leaf after the steam reforming with 10g ilmenite at 800 °C and 850 °C. (a) bark; (b) leaf.
Figure 5-7. Constant energy (-2800 cm\(^{-1}\)) synchronous spectra of tar solutions (4 ppm) produced from mallee wood, bark and leaf with ilmenite at different temperatures. (a) 500 °C; (b) 600 °C; (c) 800 °C; (d) 850 °C.
Figure 5-8. Constant energy (-1400 cm\(^{-1}\)) synchronous spectra of tar solutions (4 ppm) produced from mallee wood, bark and leaf with ilmenite at different temperatures. (a) 500 °C; (b) 600 °C; (c) 800 °C; (d) 850 °C.
5.2.3 Deactivation and regeneration of ilmenite

Spent ilmenite was regenerated via burning the coke deposits at 800 °C for 20 minutes. Figure 5-9 displays the UV-fluorescence spectra of tar from mallee leaf after the steam reforming with new and regenerated ilmenite. It is clear that ilmenite can be regenerated after burning the coke deposits, illustrating the coke deposits on ilmenite surface was one of reasons for the deactivation of ilmenite by continuously covering active sites on the surface of the catalyst. As the regeneration did not recover the catalytic activity completely, the deactivation of the catalyst was not only due to coke deposit on the surface but also due to sintering.

![UV-fluorescence spectra](image)

**Figure 5-9.** Constant energy synchronous spectra of tar solutions (4 ppm) produced from mallee leaf using regenerated 10 g ilmenite as catalysts at 800 °C (used 50 minutes and burn 20 minutes at 800 °C). (a) -2800 cm⁻¹; (b)-1400 cm⁻¹.

In order to further understand the roles of coke deposits and sintering on the deactivation of ilmenite, the spent ilmenite was regenerated three times and used in the steam reforming of biomass tar. From Figure 5-10, it was found that the UV-fluorescence intensities of aromatic ring systems after the steam reforming with regenerated ilmenite imply that ilmenite could keep its high activity for reforming aromatic ring systems after regeneration for three times, especially the third time (i.e. burning 60 minutes). The sintering of ilmenite thus was not completely detrimental.
in terms of catalyst deactivation. As has been discussed in Chapter 3, titanium dioxide in ilmenite acts as a support to inhibit the sintering of the catalyst. Therefore, the accumulated coke deposited on the active sites and/or surface of ilmenite was the primary factor for the deactivation of ilmenite.

**Figure 5-10.** Constant energy synchronous spectra of tar solutions (4 ppm) produced from mallee leaf using regenerated 10 g ilmenite as catalysts at 800 °C (1\textsuperscript{st}, used 50 minutes and burn 20 minutes at 800 °C; 2\textsuperscript{nd}, used another 20 minutes and burn 20 minutes at 800 °C; 3\textsuperscript{rd}, used another 20 minutes and burn 60 minutes at 800 °C). (a) -2800 cm\(^{-1}\); (b)-1400 cm\(^{-1}\).
5.3 Conclusions

During pyrolysis, bark produced more solid products (e.g. char, coke or soot) than wood. By contrary, leaf released more liquid products than wood. The properties of biomass affected the chemical composition of its volatiles with the differences to decrease with increasing temperature.

Tar derived from wood, bark and leaf can be reduced efficiently by ilmenite. The activity of ilmenite for reforming tar from bark and leaf dropped with prolonging feeding time due to their high coke deposits.

Ilmenite can be regenerated by burning coke. The accumulated coke deposited on the surface of ilmenite was a more important factor than sintering for the deactivation of ilmenite.
5.4 References


Chapter 5 Effects of feedstock on the performance of ilmenite ore


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Chapter 6

Decomposition of NO$_x$ precursors on the char-supported iron catalyst during the steam reforming of biomass tar
6.1 Introduction

Nitrogen exists in various structures of biomass, such as amino acids, chlorophyll, DNA, RNA and alkaloids [1]. These N-containing structures can be converted into NO$_x$ precursors in the gas products of biomass gasification. HCN and NH$_3$ have been identified as two major precursors of NO$_x$/N$_2$O [1-11]. HCN is mainly formed from the thermal decomposition of the volatile-N, whereas NH$_3$ is mainly generated from the primary pyrolysis of coal/biomass and/or the hydrogenation of char-N [2-9]. During the gasification in steam, the steam provides external H radicals for enhanced NH$_3$ formation [2, 3, 8, 9]. The inherent mineral in coal, AAEM and iron species showed some activities for decomposing NO$_x$ precursors [12-23]. During pyrolysis and gasification in CO$_2$, they can enhance the formation of N$_2$ and reduce the formation of HCN/NH$_3$. By contrary, during the steam gasification, the interaction of ash/externally loaded sodium catalyst with char and volatiles can increase the NH$_3$ yield and decrease the HCN yield [3].

The NO$_x$ precursors would be converted into NO$_x$ when the fuel gas of gasification is burnt in a gas turbine/engine. There are two approaches to minimize the NO$_x$ emission from a gasification-based power plant [24]. The first approach is to reduce the formation of the NO$_x$ precursors (especially HCN and NH$_3$) during gasification by optimising reaction conditions. The second approach is the cleaning of the gasification product gas prior to combustion to remove the NO$_x$ precursors. For example, the NO$_x$ precursors can be removed by some catalysts before combustion.

The purpose of the study is to investigate the effects of the char-supported iron catalyst on the formation and destruction of NO$_x$ precursors during the steam reforming of volatiles from the pyrolysis of mallee bark and leaf. Effects of iron-containing species, feedstock and resident time on the activities of the catalyst are investigated in the Chapter. The results have significant implications to decompose NO$_x$ precursors in a reformer in industry.
6.2 Results and discussion

6.2.1 Effects of iron-containing species

Figures 6-1 and 6-2 are the HCN and NH$_3$ yields of leaf after reforming without/with the catalyst. The HCN/NH$_3$ yields were calculated by Equation 2-4 that N from catalyst (blank) has been deducted in the calculation. During the steam reforming without the catalyst at 700 °C, approximately 16% and 14% of leaf-N were converted into HCN and NH$_3$, respectively. Both HCN and NH$_3$ yields of leaf increased with increasing temperature during feeding for 10 min (Figures 6-1a and 6-2a). Compared with the HCN and NH$_3$ yields of leaf after reforming without the catalyst, it was found that the HCN yields after reforming with the catalyst were lower and the NH$_3$ yields after reforming with the catalyst were higher. Moreover, the HCN and NH$_3$ yields of leaf were tiny during the holding period (Figures 6-1b and 6-2b), when the feedings of steam and biomass were stopped.

When the H-form char was used as catalysts in the reactor, the HCN yields decreased slightly (1-3%) and the NH$_3$ yields remained almost unchanged compared with the case of no catalyst. It appears that the H-form char catalyst had a very low activity in decomposing NO$_x$ precursors. All metallic species that can act as catalysts (AAEM) in the coal (ash) and display selective activity for the formation of NH$_3$ during the steam gasification [3] were removed during the preparation of the catalyst.

On the contrary, the HCN yield dropped and the NH$_3$ yield enhanced dramatically when the char-supported iron catalyst was used in the top stage of the reactor. The HCN conversion reached approximate 88% at 850 °C (Figure 6-1a) and the decrease of the HCN yield was a little higher than the increase of the NH$_3$ yield (3-4%). Considering the decomposition of small amounts of NH$_3$ on the surface and the frits of the quartz reactor [1-3, 25] and the possible experimental errors in the quantification of HCN and NH$_3$, the decrease in the HCN yield would appear to match the increase in the NH$_3$ yield. Almost all of HCN can be hydrolyzed and converted into NH$_3$ when it was in contact with the char-supported iron catalyst during the steam reforming, even at low temperature (700 °C).
Figure 6-1. The HCN yields of leaf after reforming without the catalyst, with the H-form char catalyst and the char-supported iron catalyst. (a, feeding 10 minutes; b, holding 30 minutes)
Figure 6-2. The NH$_3$ yields of leaf after reforming without the catalyst, with the H-form char catalyst and the char-supported iron catalyst. (a, feeding 10 minutes; b, holding 30 minutes)
Chapter 6 Decomposition of NO\textsubscript{x} precursors on the char-supported iron catalyst

Previous study has shown that the metallic iron presents the activity to decompose ammonia to N\textsubscript{2} under pyrolysis/CO\textsubscript{2} gasification [23]. A cycle mechanism involving \(\alpha\)-Fe and Fe\textsubscript{4}N in the catalysts would promote NH\textsubscript{3} decomposition (Equations 6-1 and 6-2) [23].

\[2\text{NH}_3 + 8\text{Fe} \rightarrow 2\text{Fe}_4\text{N} + 3\text{H}_2 \] (6-1)

\[2\text{Fe}_4\text{N} \rightarrow 4\text{Fe} + \text{N}_2 \] (6-2)

However, the char-supported iron catalyst did not show any activity for NH\textsubscript{3} decomposition during the steaming reforming process shown in Figure 6-2a. Two possible factors would contribute to the observation. On the one hand, the char-supported iron catalyst can improve the water-gas-shift reaction [26-28] that would produce large amount of H\textsubscript{2} during the steam reforming process. Although the presence of H\textsubscript{2} protected metallic iron and kept the activity of the catalyst under pyrolysis, the NH\textsubscript{3} conversion dropped rapidly when syngas was added into the reaction [23]. Hence, syngas would result in rapidly reducing the activity of the catalyst for NH\textsubscript{3} decomposition during the steam reforming process. On the other hand, the formation and destruction of NH\textsubscript{3} are affected by H radicals and the steam acts as an external source of H radicals during the steam gasification [2, 3, 8, 9]. The gasification of the char-supported iron catalyst would release abundant H radicals because the iron-containing species in the char can enhance the gasification of the char. The existing of H radicals in the gas would be adsorbed and saturated on the surface of the char-supported iron catalyst and inhibit the decomposition of NH\textsubscript{3}. Therefore, N radicals mainly produced from the hydrolysis of HCN would easily combine with the H radicals to form NH\textsubscript{3} in the short residence time (<0.01 s) during the steam reforming process.
6.2.2 Effects of feedstock

In order to understand the influences of feedstock on the performance of the char-supported iron catalyst, bark and leaf were used to generate volatiles for the steam reforming. The HCN and NH₃ yields of bark and leaf after reforming without/with the char-supported iron catalyst at 800 °C and 850 °C are shown in Figures 6-3 and 6-4. It was found that both HCN and NH₃ yields of bark and leaf increased when the temperature reached 850 °C. In addition, the HCN yields of bark were slightly higher and its NH₃ yields were slightly lower than those of leaf. The data could be attributed to different N-containing compounds in bark and leaf. Leaf contains large amount of nitrogen compounds that are favourable for NH₃ formation during pyrolysis process, such as amino acids and chlorophyll [24, 29]. Thereby, leaf-N preferred to form NH₃ compared with bark-N. However, the difference of bark and leaf were very small. The experimental errors in analysing the N contents of these samples would caution against a detailed comparison.

Similar to above results, the HCN yields of bark and leaf decreased and the NH₃ yields of bark and leaf increased drastically after reforming with the char-supported iron catalyst (Figures 6-3a and 6-4a). The decrease in of the HCN yields was similar to the increase in the NH₃ yields considering possible experimental errors. It appeared that the char-supported iron catalyst could promote the hydrolysis of HCN in volatiles, no matter what kinds of feedstock were used to generate volatiles. Furthermore, it was observed that the HCN conversions of bark and leaf were similar (88% and 86% at 800 °C, 89% and 88% at 850 °C, respectively), which further demonstrated that the effects of feedstock on the performance of the catalyst were small.
Figure 6-3. The HCN yields of bark and leaf after reforming without/with the char-supported iron catalyst at 800°C and 850°C. (a, feeding 10 minutes; b, holding 30 minutes)
Figure 6-4. The NH$_3$ yields of bark and leaf after reforming without/with the char-supported iron catalyst at 800 °C and 850 °C. (a, feeding 10 minutes; b, holding 30 minutes)
6.2.3 Consecutive reactions on the catalyst

The experimental results presented so far indicate that HCN can be efficiently hydrolyzed and converted into NH$_3$ under the steam reforming in the presence of the char-supported iron catalyst. In order to test if the char-supported iron catalyst can catalyse the decomposition of NH$_3$, the contact time was extended using two methods, decreasing total gas flow rate (Figures 6-5 and 6-6) and increasing the mass of catalyst (Figures 6-7 and 6-8).

As are shown in Figure 6-5a, the HCN yields by halving the gas flow rate with the char-supported iron catalyst were similar to the initial results at 800 °C and 850 °C. Similarly, doubling the amount of catalyst did not cause any major change in the yield of HCN (Figure 6-7a). It thus appeared that increasing contact time had little effect on the observed HCN yield. One possible explanation is that hydrolysis is a rapid reaction. The contact time under the ‘normal’ condition would be long enough and any increase does not greatly change the conversion achieved. Oppositely, the NH$_3$ yields of bark and leaf after reforming with the char-supported iron catalyst dropped when the contact time was doubled (Figures 6-6a and 6-8a). All these data (Figures 6-5, 6-6, 6-7 and 6-8) confirmed that the char-supported iron catalyst showed high activity for decomposing NH$_3$ during the steam reforming process when the contact time was extended.

On the basis of above data, the NO$_x$ precursors, HCN and NH$_3$, would be decomposed to N$_2$ in a series of reactions during the steam reforming process (Equation 6-3).

$$H_2O + HCN \rightarrow NH_3 \rightarrow Fe-H \rightarrow N_2$$  \hspace{1cm} (6-3)

Firstly, HCN would be hydrolyzed into NH$_3$, which were highly catalyzed by the iron-containing species in the catalyst (Figures 6-1 and 6-2) and would not be affected by feedstock and contact time. NH$_3$ would then be converted into N$_2$ when the contact time was long enough (Figures 6-7 and 6-8). Therefore, the char-supported iron catalyst would have high activity for decomposing NO$_x$ precursors during the steam reforming process if the volatiles have enough time to be in contact with the catalyst.
Figure 6-5. The HCN yields of leaf after reforming with the char-supported iron catalyst for doubled contact time at 800°C and 850 °C. (a, feeding 10 minutes; b, holding 30 minutes)
Figure 6-6. The NH$_3$ yields of leaf after reforming with the char-supported iron catalyst for doubled contact time at 800 °C and 850 °C. (a, feeding 10 minutes; b, holding 30 minutes)
Figure 6-7. The HCN yields of bark and leaf after reforming without/with the char-supported iron catalyst for doubled contact time at 850 °C. (a, feeding 10 minutes; b, holding 30 minutes)
Figure 6-8. The NH$_3$ yields of bark and leaf after reforming without/with the char-supported iron catalyst for doubled contact time at 850 °C. (a, feeding 10 minutes; b, holding 30 minutes)
6.3 Conclusions

In summary, the H-form char catalyst showed little activity for destructing NO\textsubscript{x} precursors even at high temperature, whereas the char-supported iron catalyst exhibited high activity for decomposing NO\textsubscript{x} precursors.

The activities of the char-supported iron catalyst for decomposing NO\textsubscript{x} precursors were impartial to both bark and leaf.

The hydrolysis of HCN and the decomposition of NH\textsubscript{3} are consecutive reactions for removing NO\textsubscript{x} precursors during the steam reforming process. Almost all of HCN was hydrolysed and converted into NH\textsubscript{3} during the steam reforming process. NH\textsubscript{3} could be decomposed into N\textsubscript{2} if the contact time was long enough.
6.4 References


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Chapter 7

Changes in char structure and specific reactivity of the spent char-supported iron catalyst after the steam reforming of biomass tar
7.1 Introduction

Catalytic reforming is frequently considered as an important part of the steam gasification of biomass in order to convert tar into syngas [1-3]. Large numbers of catalysts have been reported for decomposing tar. Natural minerals are inexpensive catalysts [4-10]. However, their activities for tar removal are comparatively low and some of them are extremely friable in the catalytic reactor. Ni-based catalysts have high activity [11-16], but they are expensive and can be easily deactivated or poisoned in the reforming process.

Previous investigations claimed that the chars and/or the char-supported catalysts with low cost have high activity for tar reforming (Chapter 4) [17, 18]. They can be simply burned/gasified to recover the energy without the need of regeneration after deactivation. It is also known that volatile-char interactions can cause the volatilisation of alkali and alkaline earth metallic (AAEM) species, which is likely to decrease the char reactivity [19, 20]. In addition, the interactions of volatiles and char would inevitably involve the deposition of volatile components to form soot on char surface [21]. Therefore, research on char conversion of fresh and spent catalysts in air was worth for the disposal of catalysts. The changes in char reactivity due to volatile-char interaction during reforming are an important consideration for the disposal of spent catalyst via gasification.

The reactivity of carbon in char is influenced by the char structure [22, 23], as well as the properties of catalytic species (e.g. concentration, physicochemical form and dispersion) such as alkali and alkaline earth metallic species (AAEM) in the carbon skeleton [19, 20]. X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy and Raman spectroscopy can be used to investigate the structural features of coal chars [24-26]. The XRD technique is suitable to characterize highly ordered crystalline carbon materials (e.g. graphite). The FT-IR spectroscopy has been employed to study the functional groups in carbon material. While Raman spectroscopy has been used for the characterisation of both crystalline and amorphous carbons [24-26], limited success has been achieved in characterising the coal char until recently when a novel Raman spectroscopic method was developed in our group to characterise the structure of the amorphous carbon in char [22, 27, 28].
In this Chapter, fresh and spent catalysts were investigated with FT-Raman spectroscopy and thermogravimetric analysis (TGA) in order to elucidate the changes in char properties and specific reactivity after the catalysts were used for the steam reforming of biomass tar.

7.2 Results and discussion

7.2.1 Structural features of fresh and spent char-supported iron catalysts

Figure 7-1 exhibits the total Raman peak area in the region 800-1800 cm\(^{-1}\) of chars after being used as catalysts in the steam reforming process. The Raman intensity is affected by the Raman scattering ability and light absorptivity of the char [27, 29]. Electron-rich structures such as O-containing functional groups that have high Raman scattering ability would enhance the observed Raman intensity. Oppositely, the condensation of aromatic ring systems that improve light absorptivity would result in low Raman intensity [27, 28]. Although iron would increase the O-containing functional groups during the initial stage of the steam gasification and the preparation of the catalyst [30], the data (Figure 7-1a) reveal that the O-containing functional groups in the char-supported iron catalyst failed to produce a resonant effect to enhance the Raman intensity. These were similar to the results of Na-form and Ca-form char as the O-containing functional groups, particularly carboxylates or adsorbed carbonate-like structures, in the partially gasified Na-form and Ca-form chars are not directly associated with their Raman-active carbon structures [22, 23]. Therefore, the H-form char catalyst showed higher total Raman peak area than the char-supported iron catalyst. The changes in char structure after the steam reforming process were tiny at different temperatures.

In order to gain a better understanding of their structural features, Raman spectra of different chars were curve fitted using 10 Gaussian bands (Table 2-8). The chars from the brown coal feature the presence of small and large aromatic ring systems, which are mainly represented by the D band (no less than 6 fused benzene rings) and the Gr, Vl and Vr bands (amorphous carbon structure), mainly due to aromatic ring
systems with 3-5 fused benzene rings together with some limited contribution by larger ring systems [27]. Therefore, the ratio between the intensity of D band and the total intensities of Gr, Vl and Vr bands reflects the ratio between the large aromatic ring systems and the small aromatic ring systems typically found in amorphous carbon [27, 28].

Figure 7-2 illustrates the band intensity ratio $I_D / I_{(Gr+Vl+Vr)}$ as a function of in-stream time at different temperatures. The ratios can provide detailed information about the structure of char during the steam reforming. The ratio, $I_D / I_{(Gr+Vl+Vr)}$, increased with elevating temperature and prolonging in-stream time. The parallel study found that the thermal effect at low temperature ($< 700 \, ^{\circ}C$) could not lead into significant ring condensation in char during steam gasification [31]. Also, as all catalysts underwent gasification at 800 °C during preparation steam or H radicals would be difficult to open/recombine the rings in the catalyst at temperatures lower than 800 °C. With increasing temperature and prolonging in-stream time, the gasification/consumption of small aromatic ring systems and O-containing functional groups would result in the relative decrease in $I_{(Gr+Vl+Vr)}$. Meanwhile, the recondensation/regeneration of aromatic ring systems would enlarge $I_D$. Therefore, both of them contributed to the increase in $I_D / I_{(Gr+Vl+Vr)}$ ratio.
Figure 7-1. Total Raman peak area (800-1800 cm\(^{-1}\)) of chars after being used as catalysts in the steam reforming of mallee wood tar. (a, different reforming temperatures, feeding 10 minutes; b, 800 and 850 °C, different reforming time)
Chapter 7 Changes in char structure and specific reactivity of the spent catalyst

Figure 7-2. The ratio of band peak areas $I_D/I_{(Gr+Vr+Vl)}$ of chars after being used as catalysts in the steam reforming of mallee wood tar. (a, different reforming temperatures, feeding 10 minutes; b, 800 and 850 °C, different reforming time)
7.2.2 Specific reactivity of fresh and spent char-supported iron catalysts

The specific reactivity of the spent catalysts after being used in steam reforming was determined using a TGA in air at 400 °C. Figures 7-3 and 7-4 depict the specific reactivity of chars as a function of char conversion. It was found that the reactivity of spent H-form char catalysts were similar to fresh one (Figure 7-3b), which indicated that the coke deposit and AAEM recondensation from bio-volatiles, if any, had little effects on the specific reactivity of the char. On the contrary, the specific reactivity of spent char-supported iron catalyst was higher than that of new char-supported iron catalyst for all reforming temperatures (Figure 7-3a).

Figure 7-3a shows that the type of the peak was similar and the specific reactivity of the char increased with elevating temperature (500-800 °C). From the above FT-Raman data (Figure 7-1), the Raman-active carbon structures of the char were similar from 500 °C to 800 °C, which resulted in the similar peak type of the specific reactivity. Besides the char structure, the activity of the iron-containing species played important roles in the combustion for the reactivity measurement at 400 °C. Iron oxide tended to be reduced to high activity metallic iron at high reforming temperature [32-34]. It is thus speculated that the catalytic activity of the iron-containing species in the char would increase after the steam reforming at high temperature, which would finally enhance the specific reactivity of the char-supported iron catalyst. Furthermore, the iron-containing species in the catalyst improved O-containing functional groups at the beginning of gasification in the catalyst [30]. These O-containing functional groups would be consumed quickly in subsequent combustion which would attribute into the increase in reactivity.

The peak of the specific reactivity of spent char-supported iron catalyst at 850 °C was shifted to higher char conversion level (Figure 7-3a). Previous researchers indicated that the gasification reactions would occur around the active sites of the catalyst [22, 23]. The char structure changed significantly at the reforming temperature of 850 °C. The large aromatic ring systems increased and the small aromatic ring systems decreased compared with new char-supported iron catalyst. Therefore, the iron-containing species locating in/associating with small molecules would have plenty chances to relocate during the steam reforming at 850 °C. Finally,
the relocated iron-containing species can act as a catalyst, resulting in the peak shift during combustion at 400 °C (Figure 7-3a).

Nevertheless, the activity of the iron-containing species is not only affected by the char structure of the catalysts but also by the properties of the iron-containing species. It was observed clearly in Figure 7-4 that the specific reactivity of the char-supported iron catalyst in air at 400 °C decreased with prolonging in-stream time. The changes of char structure and the properties of the iron-containing species in the catalyst would contribute to the trend. Firstly, the char would become much more ordered with increasing in-stream time as the H radical was able to penetrate deep into the char to initiate/enhance the ring condensation reactions [22, 23]. The ring condensation reaction would result in the loss of O-containing functional groups and the relocation of the iron-containing species onto large aromatic ring systems, which would finally cause the shift/elimination of the specific reactivity peak. Secondly, the particle size of the iron-containing species enlarged and the dispersion of the iron-containing species decreased with increasing in-stream time due to the consumption of the carbon support and the agglomeration of the iron-containing species, which would reduce its activity for its combustion in air at 400 °C.
Figure 7-3. Specific reactivity of char after being used as catalysts in the steam reforming of mallee wood tar at different temperatures (a), char-supported iron catalyst; (b), H-form char catalyst. (1, new catalyst; 2, after being used at 500 °C; 3, after being used at 600 °C; 4, after being used at 700 °C; 5, after being used at 800 °C; 6, after being used at 850 °C)
Figure 7-4. Specific reactivity of char after being used as catalysts in the steam reforming of mallee wood tar for different feeding time. (a, 800 °C; b, 850 °C)
7.3 Conclusions

The total Raman peak area of the H-form char catalyst was higher than that of the char-supported iron catalyst. It changed slightly after the steam reforming process at different temperatures. The total Raman peak area of the spent catalysts decreased with prolonging in-stream time. The ratio of $I_D/I_{(G_r+V_l+V_r)}$ rose when temperature reached 800 °C or when the in-stream time was extended.

The specific reactivity of the spent H-form char catalyst was similar to the new catalyst. However, the specific reactivity of the char-supported iron catalyst changed significantly after the steam reforming at different temperatures because of the changes in the properties of the char and the iron-containing species in the catalyst.
7.4 References


Chapter 7 Changes in char structure and specific reactivity of the spent catalyst


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Chapter 7 Changes in char structure and specific reactivity of the spent catalyst


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Chapter 8

Conclusions and recommendations
8.1 Introduction

The purpose of the study is to investigate iron-based catalysts with low cost and high activity for the steam reforming of biomass volatiles. In the study, natural ilmenite ore (Western Australia), novel char-supported catalysts were used for the reforming of biomass tar with steam. The performances of these catalysts were evaluated under a wide range of experimental conditions. The characterizations of new and spent catalysts were analyzed and discussed. The main conclusions from the present study are listed below.

8.2 Conclusions

8.2.1 Catalytic steam reforming of tar on ilmenite ore during biomass gasification

- Ilmenite had activity for reforming tar with steam. TiO$_2$ in ilmenite could mainly act as a support to inhibit sintering and agglomeration, whereas the highly dispersed iron-containing species contributed to its high and consistent activity.

- While the external steam exhibited little effect on the thermal cracking and reforming of tar in the gas phase under the current experimental conditions of short residence time, it affected the steam reforming of tar on ilmenite significantly. Tar was mainly converted into coke on the catalyst at low temperature, whereas it was primarily reformed into gas on ilmenite at high temperature in the presence of the external steam.

- Low concentration oxygen significantly changed the compositions of volatiles in the gas phase by activating and converting the small aromatic ring systems into new large aromatic ring systems. Finally, it changed the apparent performance of ilmenite for reforming tar with steam.
8.2.2 Importance of support in iron-based catalysts during the steam reforming of biomass tar

- The H-form char catalyst can only show some activity for tar reforming until the operating temperature reached 800 °C, whereas the char-supported iron/nickel catalysts exhibited much higher activity for the steam reforming of tar than the H-form char catalyst.
- Compared with the char-supported nickel catalyst, the inexpensive char-supported iron catalyst may have significant economical advantages in industrial applications since it had similar activity to the former at high temperature.
- The surface and structural proprieties of support played important roles for the activities of the catalysts and the reaction pathways on the catalysts. Ilmenite and the char-supported iron catalyst contained similar active phases but presented different activities.
- Kinetic parameters indicated that the reaction pathways of the steam reforming of tar on the char-supported catalysts were similar but they were different from the reactions on ilmenite.
- Char would not only carry out the functions (like TiO\(_2\) in ilmenite) to disperse the active phases in the catalyst but also interact with them to improve the catalyst activity for the steam reforming of tar.

8.2.3 Effects of feedstock on the performance of ilmenite ore during the steaming reforming of biomass tar

- Compared with wood, bark produced more solid products, whereas leaf generated more liquid products during pyrolysis. The properties of biomass changed the chemical composition of its volatiles and the influences became insignificant with increasing temperature.
- Tar including aromatic ring systems derived from wood, bark and leaf can be reformed effectively by ilmenite. However, prolonging feeding time
decreased the activity of ilmenite for reforming tar from bark and leaf.

Burning the accumulated coke, a more important factor than sintering, was an effective method for the reactivation of the spent ilmenite.

8.2.4 Decomposition of NO\textsubscript{x} precursors on the char-supported iron catalyst during the steam reforming of biomass tar

- NO\textsubscript{x} precursors were destructed effectively on the char-supported iron catalyst during the steam reforming process. The iron-containing species in the catalyst played an important role in the decomposition of NO\textsubscript{x} precursors.
- Effects of feedstock on the performance of the catalyst in terms of NO\textsubscript{x} precursors destruction were low.
- The hydrolysis of HCN and the decomposition of NH\textsubscript{3} are consecutive reactions during the steam reforming process. Almost all of HCN was converted into NH\textsubscript{3} during the steam reforming process. NH\textsubscript{3} could be decomposed into N\textsubscript{2} when the contact time was long enough.

8.2.5 Changes in char structure and specific reactivity of the spent char-supported iron catalyst after the steam reforming of biomass tar

- The total Raman peak area of the H-form char catalyst was higher than that of the char-supported iron catalyst. It changed slightly after the steam reforming process at different temperatures. The total Raman peak area of the spent catalysts decreased with prolonging in-stream time. The ratio of $I_D/I_{(G_r+V_l+V_r)}$ rose when temperature reached 800 °C or when the in-stream time was extended.
- The specific reactivity of the spent H-form char catalyst was similar to the new catalyst. However, the specific reactivity of the char-supported iron catalyst changed significantly after the steam reforming at different
temperatures because of the changes in the properties of the char and the iron-containing species in the catalyst.

8.3 Recommendations

1. It was seen in this study that ilmenite and the char-supported iron catalyst had high activity for reforming tar with steam. It is recommended that future studies investigate the composition of gas products under different operational conditions so as to control the quality of syngas and further elucidate the mechanisms of the reforming of light hydrocarbons.

2. The study proved that the support played an important role on the performance of the catalysts. Coke on the catalyst is one of the major problems of the catalyst deactivation. Therefore, the further investigations of coke properties, the mechanism of coke formation and the further kinetic study on the specific reactivity of the catalyst are recommended. In addition, the contributions of three main components of biomass (i.e. cellulose, hemicellulose and lignin) on the formation of coke and/or aromatic ring systems in volatiles are important to further understand the reaction mechanism and control the operating conditions.

3. Ilmenite has obvious catalytic activity but the activity appears low because of the support properties and iron dispersion as shown in Chapters 3 and 4. The potential ways to improve its activity are important to further study to meet the practical need, such as calcination (surface iron-containing species), reduction (reduced iron-containing species) or prohibition of coke formation. In addition, other characterizations, such as SEM, TEM, N\textsubscript{2} and CO\textsubscript{2} adsorption, could be used to further investigation of the catalysts.

4. It was observed from this study that low concentration oxygen could activate small aromatic ring systems and form large aromatic ring systems in volatiles before the catalytic steam reforming. Besides oxygen, CO\textsubscript{2} would be another major component of the gas phase in an industrial gasifier and its effect on the performance of the catalyst would be an important consideration in future reactor design.
5. The transportation and storage of biomass will not only consume large amounts of energy and operating cost but also cause pollutions. By converting biomass into bio-oil at the harvesting site, the handling, distribution, and storage problems of biomass can be resolved. Hence, the catalytic steam reforming of bio-oil is worthy to be investigated in future.