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Catalytic reforming of tar during gasification. Part I. Steam reforming of biomass tar using ilmenite as a catalyst

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ABSTRACT

Ilmenite, a natural iron-containing mineral, has been investigated as an inexpensive catalyst for the steam reforming of volatiles (tar) from the pyrolysis of mallee woody biomass. The results indicate that ilmenite has good activity for the steam reforming of tar into gases due to its highly dispersed iron-containing species. The supply of external steam, in addition to the H_2O and CO_2 produced during the pyrolysis of biomass, plays an important role in minimising the formation of coke on the catalyst surface and thus the catalyst activity. The catalyst deactivation due to coke formation has more adverse effects on the reforming of larger aromatic ring system with steam than that of smaller ones. In addition, the supply of additional oxygen at low concentration changed the outcomes of tar reforming mainly because oxygen activated the smaller aromatic ring systems and polymerised them into larger aromatic ring systems in the gas phase.

1. Introduction

Biomass gasification is the core of many low-emission technologies to convert biomass into more valuable fuels or chemicals [1–5]. Tar reduction is one of the most important aspects of biomass gasification because tar can cause difficulties for the operation of downstream equipments and poison catalyst, incurring high cost of maintenance [3,4]. Physical methods of tar removal, such as liquid scrubbing, usually require the gasification product gas to be cooled down, leading to the loss of overall thermal efficiency, and create a waste liquid stream that must be further treated for disposal. Tar reforming, especially catalytic reforming, is a more attractive method to decrease the concentration of tar in the gasification product gas because tar can be destroyed through reforming reactions at high temperature inside the gasifier or immediately downstream the gasifier without creating a waste liquid stream.

Natural minerals, such as dolomite and olivine, are inexpensive and can be used to catalyse the reforming of tar. Although dolomite shows good catalytic activity for tar reforming, it is fragile resulting in the need of frequent catalyst replacement [6–12]. Olivine is another inexpensive catalyst for the reforming of tar [13–17] with high attrition resistibility. However, the catalyst needs to be pre-treated to obtain high activity for tar reforming and is easily deactivated [16] e.g. due to the loss of Fe dispersion. Despite intensive studies using natural minerals as catalysts, the reaction pathways for tar reforming, including the roles of support, remain poorly understood.

Biomass volatiles, including tar, are a mixture of many different compounds of widely different structures. The reforming of aromatic ring systems is a key consideration because they are particularly prone to form coke on the catalyst surface and are largely responsible for many problems associated with tar during the utilisation of the gasification product gas. Little is known about the relative difficulties in reforming the small and large aromatic ring systems in the complex volatiles, particularly when the catalyst is partially deactivated due to coke formation.

In this study, ilmenite, naturally occurring as a mineral and principally consisting of iron oxides and titanium dioxide with high attrition resistibility, is used as a catalyst for the steam reforming of biomass tar derived from the *in situ* pyrolysis of mallee wood. In addition to the quantification of tar yield, UV-fluorescence spectroscopy [18,19] is used to semi-quantify the extent of reforming of aromatic ring systems, including the differentiation of the relative reforming difficulties of smaller and larger aromatic ring systems in the tar. The functions of iron oxides and titanium dioxide in ilmenite and the possible reaction pathways on ilmenite will also be discussed.

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2. Experimental

2.1. Materials

Natural ilmenite (Tiwest Joint Venture, Western Australia, Table 1. 106–150 μm) and iron oxides (Sigma–Aldrich, Fe_2O_3, >99%, <50 nm, Fe_3O_4, >98%, <5 μm) were directly used as catalysts for the steam reforming of biomass tar.

Australian mallee biomass was chosen in this study. The mallee biomass, with a lot of special features, is grown in Western Australia to combat the dryland salinity problem and represents a substantial biomass resource for energy and chemicals [20–26]. A woody mallee biomass sample (90–180 μm) was used in this study and its whose proximate and ultimate analyses are given in Table 2. The biomass was pyrolysed to generate volatiles *in situ* for subsequent reforming. The wood was dried at 105 °C for overnight. Any residual moisture in the biomass or the moisture re-adsorbed into the biomass during handling/storage was taken into consideration in the calculation of the yields of tar and coke.

2.2. Steam reforming of biomass tar

A two-stage fluidised-bed/fixed-bed quartz reactor (Fig. 1) was used for the catalytic steam reforming of biomass volatiles (tar). The quartz reactor is 37 mm in diameter. Its top and bottom stages are 30 mm and 130 mm in length, respectively. The distance between the catalyst bed and the inlet of steam supply is about 30 mm.

The two-stage reactor was heated up in a furnace and the two stages were kept at the same temperature during a steam reforming experiment. Two thermocouples were inserted into the reactor, as is shown in Fig. 1 to measure the temperature of the top frit (top stage) and the temperature distribution in the bottom stage.

The catalyst was pre-loaded into the top stage before the reactor was heated up. The bottom stage was a fluidised-bed reactor. Silica sand with a particle size range of 212–300 μm was used as the bed material. The wood particles were entrained in a feeder and fed into the fluidised-bed at 100 mg/min via an injection probe cooled with 1 L/min of cooling water. The feeding of biomass only commenced when the reactor had reached and stabilised at the target temperature. On entering the hot fluidised sand bed, the wood particles would be heated up rapidly, at a rate exceeding $>10^3–10^4$ K s^{-1}, to generate volatiles, which were then carried directly into the top stage for *in situ* reforming therein.

The steam was generated from the water fed directly into the reactor with an HPLC pump (Alltech 426). The steam entered the reactor at a location in between the two stages. Therefore, no external steam was supplied to the bottom stage and the woody biomass was pyrolysed in argon.

The flow rate of the argon gas (>99.999%) used to entrain and feed the woody particles into the reactor was fixed at 1 L/min. The flow rate of the fluidising gas (argon) was 0.72–1.50 L/min to ensure that the total gas flow rate passed through the reforming top stage in the reactor would result in unchanged residence time even when the reforming temperature was changed from 500 to 850 °C. The concentration of steam was always maintained at 15 vol% in the gas stream. In some experiments, oxygen (1000 ppm and 3000 ppm of the total gas flow rate) was supplied into the reactor to reform the volatiles (tar) with steam and O_2.

Table 1
Metal elemental analysis (wt% on dry basis) of ilmenite determined with ICP-AES following borate fusion and acid dissolution of the ashed samples.

	Fe	Ti	K	Mg	Na	Ca	Al	Si
Ilmenite	23	36	<0.01	0.2	<0.01	<0.01	0.5	<0.01

Table 2
Proximate and ultimate analyses of mallee biomass.

	Proximate analysis (wt%)			Ultimate analysis (wt%)					
	Ash[a]	Volatile matter[b]	Fixed carbon[b]	C[b]	H[b]	N[b]	S[b]	Cl[b]	O[b,c]
Mallee wood	0.9	81.6	18.4	48.2	6.1	0.15	0.01	0.04	45.5

[a] Dry basis.
[b] Dry and ash-free basis.
[c] By difference.

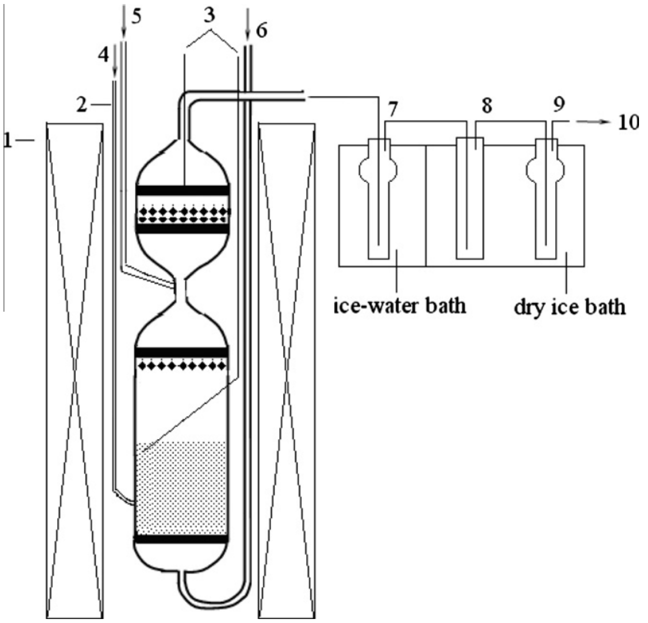

Fig. 1. A schematic diagram of the experimental set-up for the steam reforming of biomass volatiles (tar). 1, two-zone electrical furnace; 2, water-cooled probe; 3, thermocouples; 4, biomass particles and argon; 5, steam or H_2/and O_2; 6, argon; 7, 1st trap with a frit and 50 ml solvent; 8, 2nd trap with a thimble filter, wire mesh and 40 ml solvent; 9, 3rd trap with a frit and 30 ml solvent; 10, gas outlet (to vent).

Immediately after the feeding of biomass was completed, the reactor was quenched by being lifted out of the furnace. The fluidizing gas passed continuously through the reactor in order to prevent any oxidation during the quenching. The coke yields were measured by weighing the reactor before and after the experiment. Our blank experiments without feeding biomass confirmed the validity of this method. The estimated reproducibility of coke yield is about ±0.4 wt%.

2.3. Sampling and analysis of tar

Tar was captured with three tar traps connected in series all filled with a mixture of HPLC-grade chloroform and methanol (80:20, vol). The volumes of solvents used in these three traps were approximately 50, 40 and 30 mL, respectively. The solvents in the traps were used to enhance heat transfer and, more importantly, dissolve the tar immediately to avoid the blockage of the thimble and/or the frit in the traps. The first trap with a frit was placed in an ice-water cold bath (0 °C) to condense the steam in the gas. The condensation of steam in this trap avoided the blockage of the next trap that had a thimble surrounded by wire mesh and was immersed in a dry ice bath (−78 °C) to capture the tar. The thimble and wire mesh were used to enhance the absorption 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 in the solution) 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 little (<10% of the intensity for the second trap) small aromatic rings (i.e. colourless tar). Hence, the solution in the third trap was used to wash other traps and the outlet of the reactor after the experiment to minimise the use of solvents. The recovered tar solutions from all three traps were mixed well and weighed accurately before it was stored in a freezer for further analysis.

The tar yield was determined by quantifying the tar concentration in the solution. A certain amount of tar solution (about 1–2 mL, accurately weighed) was put onto an aluminium tray and dried at 35 °C for 4 h to evaporate all solvents and water, beyond which little further weight loss took place. Thus, 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 h. The residues in the solvents themselves were determined by blank experiments and considered in the calculation of the tar concentration. The estimated reproducibility of tar yield determination is about ±0.3 wt%.

A Perkin–Elmer LS50B luminescence spectrometer with a 1 cm light path length was used to record the UV-fluorescence spectra of the tar [19]. The tar solution obtained from an experiment was diluted with methanol (Uvasol for spectroscopy; purity (GC): ⩾99.9%) to 2 ppm and 4 ppm (wt). The synchronous spectra were recorded with a constant energy difference of $-2800\ \mathrm{cm}^{-1}$ together with slit widths of 2.5 nm and a scan speed of $200\ \mathrm{nm} \cdot \mathrm{min}^{-1}$. Each spectrum shown here represents the average of four scans. At the same concentration, the fluorescence intensity was multiplied by the tar yield to display the fluorescence intensity on the basis of 'per gram of biomass (db)' [27,28].

2.4. Characterizations of the catalysts

X-ray diffraction (XRD) patterns of the fresh and spent ilmenite catalysts were scanned by using a D8 ADVANCE diffractometer with Cu Kα radiation and lynxeye detector (40 mA and 40 kV) at a scan rate of $2^\circ\ \mathrm{min}^{-1}$ and a step size of 0.02°.

3. Results and discussion

3.1. Effects of temperature on tar reforming

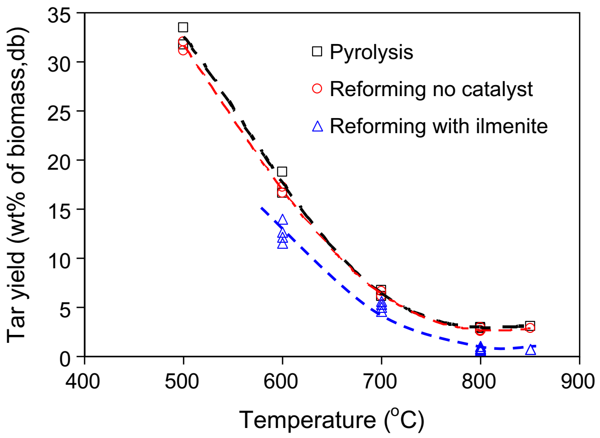

Fig. 2. The tar yields of mallee wood after reforming without/with ilmenite (10 g) at different temperatures. (The total gas flow rates of argon were 2.50 L/min at 500 °C, 2.21 L/min at 600 °C, 1.98 L/min at 700 °C, 1.80 L/min at 800 °C and 1.72 L/min at 850 °C, respectively. The concentration of steam was always maintained at 15 vol% in the gas stream.)

Fig. 2 shows the tar yields of mallee wood after reforming without/with ilmenite at different temperatures. It was found that, regardless of the use of ilmenite catalyst, the tar yield decreased with increasing temperature due to enhanced thermal cracking and possible homogeneous reforming (see below). The tar yields after pyrolysis were similar to those after reforming without a catalyst at a given temperature, indicating that the external steam has little effects on the further thermal cracking/reforming of tar in the gas phase, which is in broad agreement with literatures [29]. It is believed that the large amounts of steam and carbon dioxide produced from the pyrolysis of biomass in the bottom stage would have already reformed some reactive compounds/structures of volatiles (e.g. aliphatics and O-containing groups) in the gas phase even in the absence of the steam externally supplied. In other words, the pyrolysis in the bottom stage and subsequent reactions in the freeboard and in the top stage were actually a self-reforming process: tar was reformed by H_2O, CO_2 etc. all as a part of the volatiles. What was left would have more stable structure and lower reactivity. Therefore, the enhancement of volatile/tar reforming by the externally added steam was very limited especially at low temperature. Therefore, the tar yields after pyrolysis were similar to those after the steam reforming without catalyst.

The tar yields dropped significantly when ilmenite was employed in the top stage of the reactor to act as a catalyst for tar reforming. Tar molecules may be activated in two ways. Firstly, the tar molecules may be activated in the gas phase. This is because the volatiles produced from the pyrolysis of biomass contained abundant radicals that would react with tar molecules to form activated tar fragments, e.g. by H- and CH_3-abstraction in the gas phase. The activated tar fragments may be adsorbed on the catalyst for further reforming reactions. Secondly, the tar molecules may be activated directly through chemisorption on the catalyst surface. These activated tar fragments would be reformed into gas by two pathways on the catalyst surface: direction steam reforming into gas and/or coke formation followed by the subsequent gasification of the coke. At low temperature, the high coke yields indicated that the coke formation was more significant than the gas formation through steam reforming on ilmenite (Fig. 3). This is mainly because of the low reactivity of steam at low temperature and therefore the activated tar fragments would combine together easily on the surface of the catalyst to form coke, which was hard to gasify at

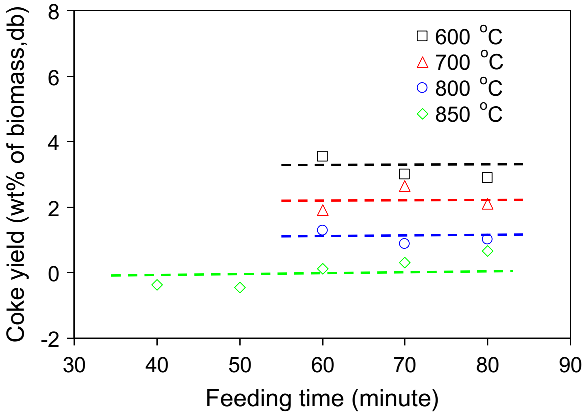

Fig. 3. The coke yields of mallee wood after reforming with ilmenite (10 g) at different temperatures. (The total gas flow rates of argon were 2.21 L/min at 600 °C, 1.98 L/min at 700 °C, 1.80 L/min at 800 °C and 1.72 L/min at 850 °C, respectively. The concentration of steam was always maintained at 15 vol% in the gas stream.)

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 gas-phase cracking, the reactivity of steam enhanced, the activity of ilmenite improved; all combine to enhance the gas formation through direct catalytic reforming. Furthermore, the coke gasification rate would also increase with increasing temperature to result in the rapid gasification of coke even if the coke was formed.

Aromatic ring systems (a term [18,19] commonly used to represent the key aromatic ring moieties without referring to the substitutions) in the tar that would cause deposits easily in downstream equipments are the major concern of gas quality. The tar yields cannot always reflect the changes in aromatic ring systems because aromatic ring systems are only a part of tar that has other structures such as aliphatic and O-containing functional groups. Therefore, UV-fluorescence spectroscopy was used to characterize aromatic ring systems in the tar. In order to minimise 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 were about half of those of 4 ppm, illustrating that 4 ppm was low enough to minimise the self-absorption effects.

Fig. 4 displays the constant energy synchronous spectra of mallee wood tar solutions after the steam reforming with/without ilmenite (10 g) at different temperatures. In broad agreement with the corresponding tar yields in Fig. 2, 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 only 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.

The data in Fig. 4 clearly indicate that ilmenite had good 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 ilmenite 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 (Fig. 3). 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.

3.2. The roles of external steam in the competition between reforming and coke formation on catalyst surface

While the above 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 reactions 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 steam injection methods (continuous and pulsed injections)

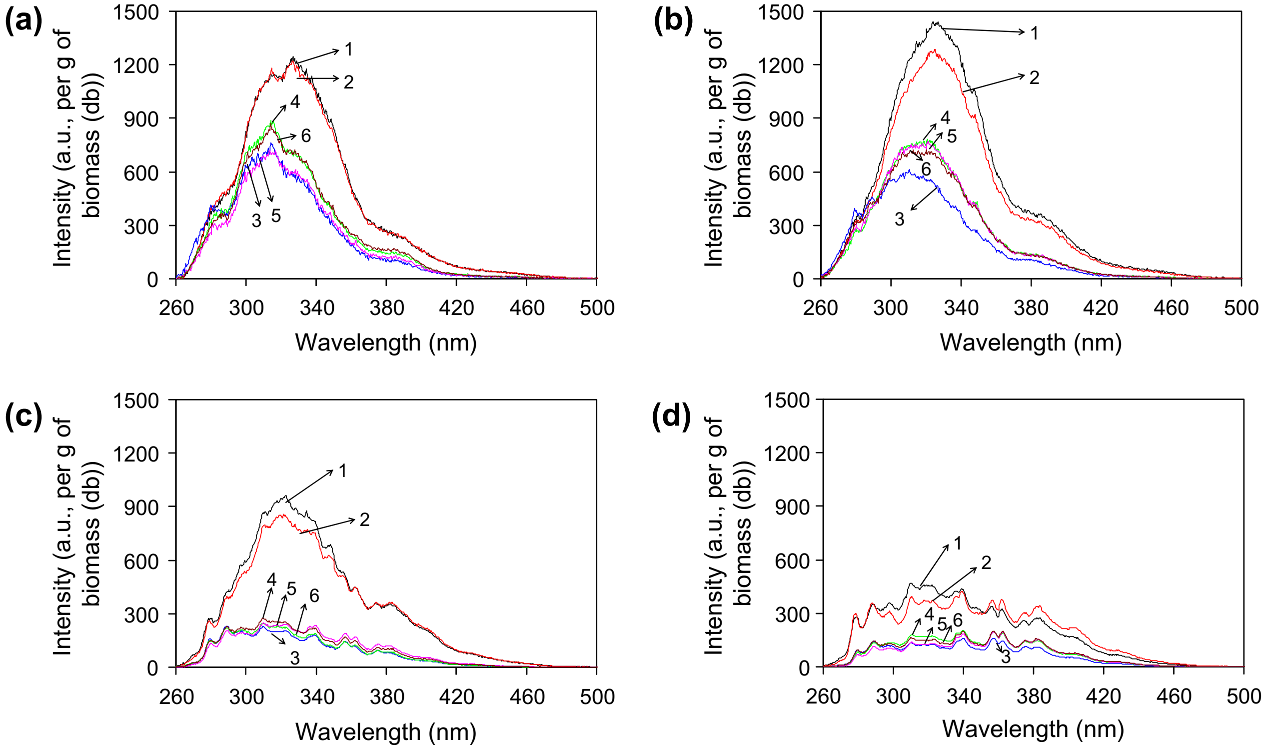

Fig. 4. Constant energy (−2800 cm^{-1}) synchronous spectra of mallee wood tar solutions (4 ppm) produced using 10 g ilmenite as catalysts at different temperatures and feeding times. (a) 600 °C; (b) 700 °C; (c) 800 °C; (d) 850 °C (1, pyrolysis; 2, reforming without catalyst; 3, ilmenite 50 min; 4, ilmenite 60 min; 5, ilmenite 70 min; 6, ilmenite 80 min).

were used to investigate the reaction pathways and the effects of the external steam during the catalytic reforming of biomass tar on ilmenite catalyst in the absence and presence of the external steam. When pulsed steam injection was used, the length of time to supply steam and not to supply steam in the same experiment was the same; this time length was either 20 s, 40 s or 60 s.

It was observed that the tar yield after the steam reforming with the continuous steam injection was lower than those after the steam reforming with the pulsed steam injection (Table 3). As was stated above, tar could be reformed by two pathways on the surface of the catalyst, direct steam reforming into gas or/and coke formation and subsequent gasification. In the presence of the sufficient (external) steam, the activated tar fragments would be continuously 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 sufficient (external) steam. In the absence of sufficient steam, the coke structure would further condense to become less reactive. With the accumulation and further condensation of coke on the catalyst, the activity for tar reforming decreased, resulting in high tar yields from the reforming with the pulsed steam injection.

As is shown in Fig. 5, the activity of ilmenite for reforming the aromatic ring systems decreased when the external steam was injected discontinuously (in pulses) into the reactor. Additionally, the activity of ilmenite dropped with extending the time during which no steam was supplied. The results in Fig. 5 further show that the requirements to reform the small and large aromatic ring systems are different. Compared with the reforming of the small aromatic ring systems, the reforming of the large ones 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. In fact, the reforming of large aromatic ring systems would likely require many adjacent 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 sufficient (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 contiguous active sites on the surface of the catalyst. Hence, the catalyst would lose the activity for reforming large aromatic rings. In contrast, the reforming of the small aromatic ring systems would still have chance to be reformed on the catalyst because they need fewer vacant sites to be adjacent to each other. With prolonged time in the absence of sufficient/external steam, the accumulated coke would continuously cover active sites on the surface of the catalyst, causing the loss of its activity for the steam reforming of all aromatic ring systems.

3.3. Effects of additional oxygen on tar reforming

Oxygen or air is usually used in industrial biomass gasifiers. Therefore, it is necessary to understand the effects of molecular oxygen on the performance of ilmenite. Table 4 lists tar and coke yields of mallee wood after reforming with ilmenite and low concentration O_2. It was found that the tar yields were similar and in the range of experimental error.

Table 3
Tar and coke yields of mallee wood after the steam reforming with ilmenite (5 g) using different steam injection methods at 850 °C.

	Tar yield (wt%, db)	Coke yield (wt%, db)
Continuous	0.7	0.6
Pulsing 20 s	1.5	3.0
Pulsing 40 s	1.7	3.5
Pulsing 60 s	1.9	3.9

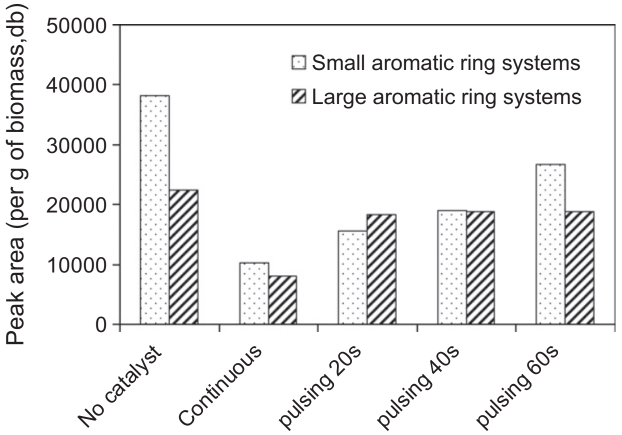

Fig. 5. Peak area of constant energy ($-2800\ \mathrm{cm}^{-1}$) synchronous spectra of mallee wood tar solution (4 ppm) after the steam reforming with ilmenite (5 g) using different steam injection methods at 850 °C (small aromatic ring systems, wavelength < 360 nm; large aromatic ring systems, wavelength > 360 nm).

Table 4
Tar and coke yields of mallee wood after the steam reforming with ilmenite (10 g) and additional O_2 at 800 °C and 850 °C.

	Tar yield (wt%, db)		Coke yield (wt%, db)	
	800 °C	850 °C	800 °C	850 °C
No O_2	0.9	0.8	1.0	0.5
1000 ppm O_2	0.7	0.5	1.8	1.5
3000 ppm O_2	0.7	0.4	0.7	1.0

As are shown in Figs. 6a and 6b, the tar produced with additional O_2 tended to have 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 a catalyst. There could be three potential effects by supplying external oxygen [30]. Firstly, it could enhance polycyclic aromatic hydrocarbons (PAH) production due to the increases in the radical concentration. Secondly, oxygen could change the formation pathway of PAH, causing selective production. Thirdly, it could decrease PAH yields due to deep/complete oxidation. The outcomes of the competition among these conflicting effects of additional oxygen vary according to the concentration of oxygen [30]. In our experiments, the concentration of oxygen was low and insufficient for combustion. As is suggested in the literature [31,32], low concentration oxygen would enhance aryl radicals by H- and/or CH_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 being further reformed in the gas phase. The net result is the formation of the large aromatic ring systems (as the products) at the expenses of small ones (reactants) in the tar. Our results in Fig. 6 suggest that the additional oxygen at low concentration appeared to have activated the smaller aromatic ring systems and polymerised them into new larger aromatic ring systems in the gas phase. The increase of the large aromatic ring systems would enhance the formation of coke on the catalyst surface.

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 (Fig. 6). According to the above discussion, the low concentration oxygen would be consumed to change the relative proportions of

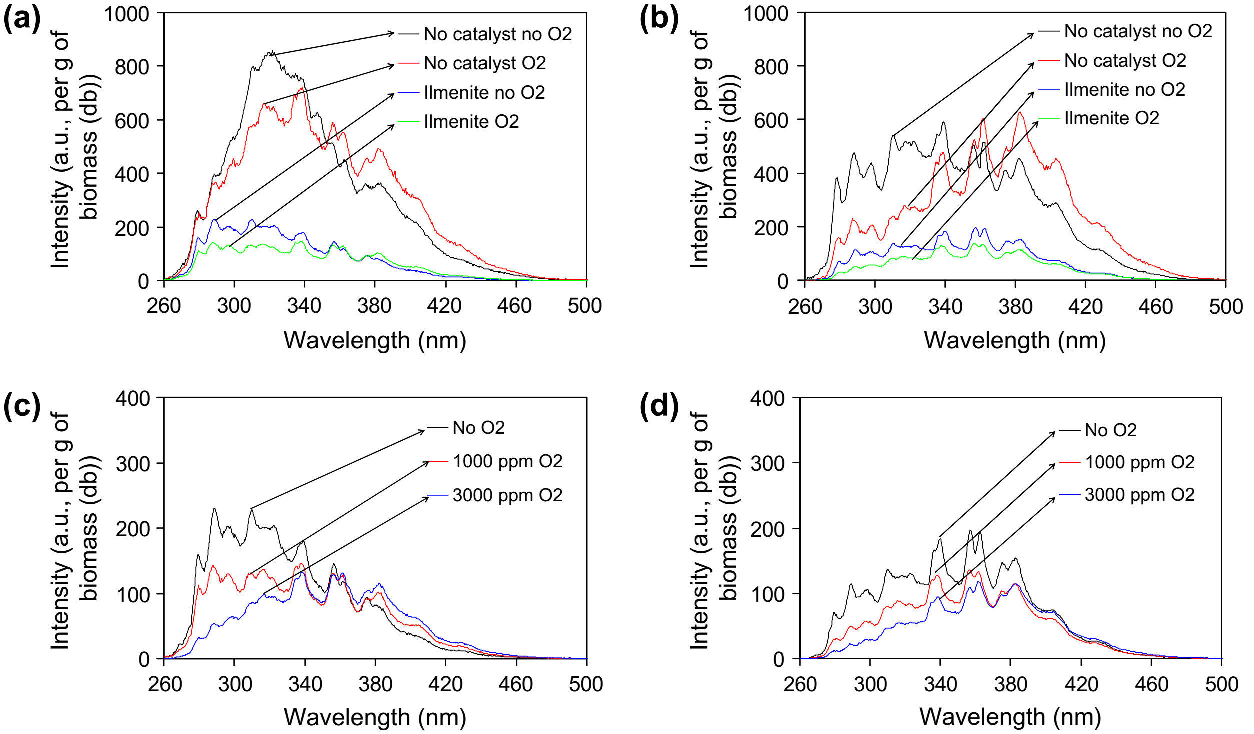

Fig. 6. Constant energy synchronous spectra of mallee wood tar solution (4 ppm) after the steam reforming with/without ilmenite (10 g) and additional O_2 at 800 °C and 850 °C. (a) 800 °C, 1000 ppm O_2, with/without ilmenite; (b) 850 °C, 1000 ppm O_2, with/without ilmenite; (c) 800 °C, ilmenite, different concentration O_2; (d) 850 °C, ilmenite, different concentration O_2.

smaller and larger aromatic ring systems in the gas phase even before they came into contact with the catalyst.

3.4. Iron-containing species acting as an active phase

Fig. 7 illustrates the XRD patterns of the ilmenite catalysts before and after experiments. In the raw ilmenite (Fig. 7a), only TiO_2 and Fe_2O_3 peaks were observed. In contrast, the spent ilmenite showed strong TiO_2 peaks, $TiFeO_3$ peaks as well as weak metallic iron peaks. These results demonstrated that Fe_2O_3 and/or other amorphous iron-containing species would be crystallised 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 the spent ilmenite, implying that the reduction of iron oxides occurred during the stream reforming. The crystal sizes of TiO_2 and $FeTiO_3$ in the spent ilmenite were calculated using the Scherrer equation (Table 5). Their crystal sizes did not appear to change significantly with increasing temperature because TiO_2 in ilmenite would primarily act as a support for the catalyst to 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.

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 Fig. 8, Fe_2O_3 exhibited higher activity for reforming the aromatic ring systems than Fe_3O_4. It is speculated that Fe_2O_3 may be reduced more easily than Fe_3O_4 by the partially reformed volatiles and the syngas product to form reduced iron species.

Further experiments were carried out to compare the catalytic activity of untreated and pre-reduced ilmenite. In these experiments, hydrogen (>99.999%) controlled by a mass flow controller (0.3 L/min) was used to reduce ilmenite *in situ* at 600 °C for 1 h before the steam reforming process. The data in Fig. 8 shows that the activity of pre-reduced ilmenite for breaking down the aromatic ring systems was slightly higher than that of ilmenite. These data reveal that the reduced forms of the iron-containing species would have higher activity for reforming tar than iron oxides. This observation is in broad agreement with the previous studies claiming that olivine with more surface iron and greater reducibility

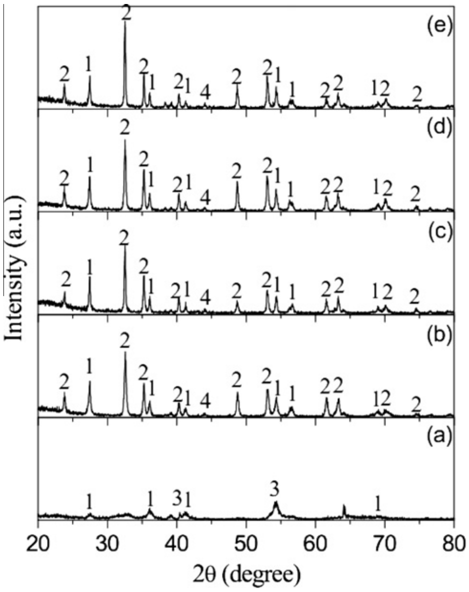

Fig. 7. XRD spectra of new and spent ilmenite after the catalytic steam reforming of mallee wood tar. (a) Raw ilmenite; (b) 600 °C, 80 min; (c) 700 °C, 80 min; (d) 800 °C, 80 min; (e) 850 °C, 80 min. Peaks labelled “1”, TiO_2; peaks labelled “2”, $FeTiO_3$; peaks labelled “3”, Fe_2O_3; peaks labelled “4”, Fe.

Table 5
Crystal sizes (calculated using the Scherrer equation) in the spent ilmenite after the steam reforming of mallee wood tar.

	$FeTiO_3$ (nm)	TiO_2 (nm)
600 °C, used for 80 min	42.3	42.3
700 °C, used for 80 min	42.2	44.9
800 °C, used for 80 min	44.3	43.3
850 °C, used for 80 min	42.2	43.4

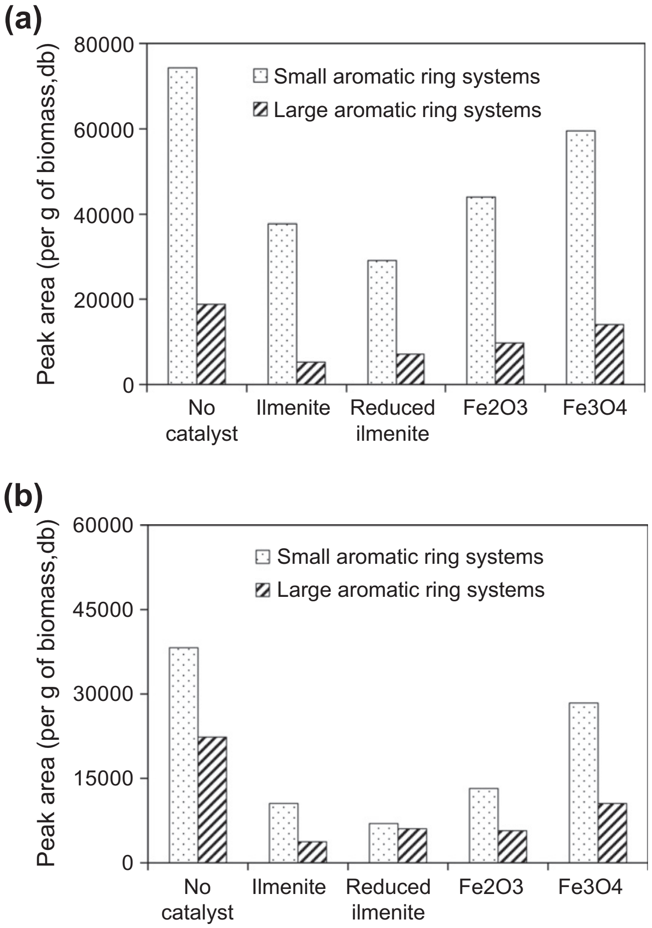

Fig. 8. Peak area of constant energy ($-2800\ cm^{-1}$) synchronous spectra of mallee wood tar solution (4 ppm) after the steam reforming with iron-containing catalysts. (a), 700 °C; (b), 850 °C. Small aromatic ring systems, wavelength < 360 nm; large aromatic ring systems, wavelength > 360 nm.

would have higher activity [17]. It is believed that the partially reformed volatiles and the syngas product would transform Fe^{3+} in the raw ilmenite into reduced forms, $TiFeO_3$ (Fe^{2+}) and/or metallic iron (Fe^0) during the initial steam reforming process.

4. Conclusions

Ilmenite, a natural iron-containing mineral in Western Australia, exhibited good activity for reforming tar from mallee biomass. The highly dispersed iron-containing species in ilmenite contributed to its high and consistent activity. While the externally supplied steam had little effect on the further thermal cracking and reforming of tar in the gas phase, it played an important role in the steam reforming of tar on the ilmenite catalyst. Tar was mainly converted into coke on the catalyst at low temperature, whereas it was primarily reformed catalytically into gas at high temperature in the presence of sufficient steam. Small and large aromatic ring systems in biomass volatiles behaved differently during reforming, possibly due to their different requirements for adjacent vacant sites on the catalyst surface. Low concentration oxygen significantly altered the relative proportion of smaller and larger aromatic ring systems during reforming.

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