1Continuous hydrogen production from non-aqueous phase bio-oil via chemical 2looping redox cycles

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6ABSTRACT

7 Chemical looping of bio-oil is a promising route to convert this low-quality fuel to pure hydrogen
8with inherent gas separation and low energy penalty. In that the oil is liable to form coke during the
9heating process, the current chemical looping cycles usually suffer from low hydrogen purity and
10poor OC recyclability. In this paper, we proposed a strategy of adding steam in FR to suppress coke
11formation and enhance the hydrogen purity. To perform the chemical looping cycles, we first built a
12dual fluidized bed and attained the optimal operating conditions. The results showed the higher
13hydrogen purity, yield and good recyclability at 950 °C. Afterwards, we investigated effects of the
14steam to oil ratios on hydrogen purity, yield and the recyclability of oxygen carrier, and found
15adding steam in the fuel reactor was an efficiency way to enhance the hydrogen purity. The results
16suggested the hydrogen purity can reach 98%; nevertheless, it suppressed the hydrogen yield
17simultaneously. In terms of the redox performance of oxygen carrier, we also found the steam can
18weaken the reduction reactions, and therefore increased the particle recyclability. Our current study
19suggested the enhancement of the hydrogen purity was at the cost of the suppression in hydrogen
20yield, and we need to find a compromise between the hydrogen yield and the purity to pursue high
21system efficiency.

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241. **Introduction**

25 Biomass has stimulated increasing attention in recent decades due to its large source abundance,
26net zero carbon emission, and especially the ability to produce renewable oils to reduce the
27dependence on petroleum . One of the most promising approaches to attain this liquid fuel is the
28biomass flash pyrolysis with the aqueous phase oil hydrotreatment, that is advantageous in terms of
29the high yields of specific and well-defined oil as well as the avoidance of energy-intensive
30distillation process . Unfortunately, two tough challenges should be overcome prior to scale-up this
31technology for industrial use. On one hand, large amount of hydrogen is required in upgrading the
32aqueous phase oil in order to lower its oxygen content. On the other hand, the non-aqueous phase
33oil, a major by-product during the oil separation, is difficult to be utilized . Under this circumstance,
34the use of non-aqueous phase oil as a feedstock to produce hydrogen for the aqueous phase oil
35hydrotreatment seems to be an ideal way to breakthrough.

36 With respect to the hydrogen production technologies, steam reforming is well established and
37commercially dominated thanks to the high economic efficiency and good technical maturity . In
38this method, fuels are subject to a two stage process including steam reforming to produce syngas
39and a water-gas shift reaction to maximize the hydrogen yield. Consequently, a large amount of CO₂
40is mixed in the products and must be separated using processes such as Pressure Swing Adsorption
41(PSA) or Monoethanolamine (MEA) scrubbing; this results in intensive energy penalties and the
42loss of up to 30% of the produced hydrogen . In addition, since the increasing pressures on abating
43the greenhouse gas effects, generation of a pure and easily sequestered CO₂ waste stream is
44necessary to facilitate the subsequent CO₂ compression and storage.

45 Chemical looping is an emerging alternative approach to produce hydrogen with intrinsic CO₂

46sequestration . In this process, gaseous fuels derived from the oil pyrolysis reduce the oxygen
 47carrier (OC) material, giving rise to the oxygen-deficient OC and a gas mixture of CO₂ and H₂O.

48Oil pyrolysis:

49OC reduction (CO and H₂ as the representatives):

50 Then, steam was employed to regenerate the OC material with hydrogen production (R6 and R7):

51Steam oxidization:

53 Over the above cycles, pure and isolated H₂ and CO₂ can be attained after condensing the gas
 54streams, avoiding the complicated and expensive multistep separation processes. At present, the
 55feasibility of this technology has been demonstrated using a wide range of gaseous fuels , including
 56CO, syngas, CH₄ and carbonaceous fuels from coal/biomass gasification. The results showed good
 57operability and hydrogen purity over 95% when using this method to generate hydrogen. However,
 58the success in chemical looping of gaseous fuels cannot be directly extended to that of bio-oils; the
 59reason is that the lignin derivatives obtained from the biomass pyrolysis, tend to re-polymerize
 60during the heating process. This leads to the coke formation (pyrolytic lignin) and creates problems
 61that affects the reactor feed system and operation, accelerates OC deactivation, and more
 62importantly, pollutes the hydrogen stream . One example was the work carried out by Bleeker et al .
 63They used crude bio-oil as a feedstock to promote the chemical looping for hydrogen production.
 64The results confirmed the serious coking in the reduction period, which led to fast deactivation of

65OC and produced considerable amount of gas contaminants in SR (R8 and R9). To the best of our
66knowledge, no such reports concerning suppressing the coke formation in chemical looping of oil
67have been found to date.

68 In this paper, we focused on reducing the coke formation in chemical looping to enhance the
69hydrogen purity. For continuous hydrogen production, we built a dual fluidized bed to carry out the
70reduction and oxidization reactions, and obtained the optimal operation conditions in terms of
71higher hydrogen purity, yield as well as stable OC activity. Based on a fact that the oil
72decomposition can be promoted with the help of some oxidants, we introduced steam to FR to limit
73the coke formation currently. To evaluate the chemical looping in the presence of steam in FR, the
74effects of the steam to oil ratio in FR on hydrogen purity, yield and recyclability were also
75investigated.

762. Material and methods

772.1. Materials

78 Austrian MAC iron ore, an iron-based natural material, was used as OC in this work. The as
79received particles were firstly calcined at 1000 °C for 6 h in air atmosphere to attain adequate
80mechanical strength, and then crashed and sieved to the size range of 0.02-0.045 mm. The chemical
81analysis of the samples is listed in Table 1.

82 The crude bio-oil was produced by Shandong Tairan Co. Ltd in a 1000-ton pilot-scale cotton
83stalks pyrolysis unit. The in-situ separation of the oil was achieved by adding water into the oil
84condenser, aging for several days and drawing away the supernatant aqueous fraction. The
85deposited fuels were referred to as the non-aqueous phase oil to be used for producing hydrogen.
86The density of the oil is 1270 kg.m⁻³, and the ultimate analysis and water content of the oil are listed
87in Table 2.

882.2. *The experimental set-up*

89 A dual fluidized bed, consisting of a fuel reactor (FR), a steam reactor (SR), two cyclones and a
90 loop seal, was built to carry out the chemical looping reduction and oxidization reactions. The SR
91 had an inner diameter of 79 mm and a total height of 890 mm, in which hydrogen was produced and
92 OC was regenerated. Generally, FR was designed as a bubbling fluidized bed to increase the gas
93 residence time because of the inferior kinetics of OC reduction compared with the steam
94 oxidization. Nevertheless, a practical bubbling fluidized bed FR still suffered from low efficiency
95 because most of the gaseous fuels were centralized in bubbling phase and free to OC reduction
96 reactions during chemical looping. Moreover, we found the oil was decomposed violently in high
97 temperatures according to our tentative study on the bubbling fluidized bed FR; this led to the low
98 residence time of fuels and the instability of the operation. To address these problems, we designed
99 a stacked FR in our current study that consisted of a lower bed A (inner diameter 22 mm, total
100 height 1150 mm) and upper bed B (inner diameter 35 mm, total height 560 mm). The lower bed was
101 used to increase the gas-solid contact time and abate the influence of oil decomposition on the
102 system stability; the upper bed was operated in fast fluidization regime, providing the driving force
103 of the particle circulation. The reduced OC materials entrained in FR gas stream was captured by a
104 cyclone and regenerated in SR. Under the control of a loop seal, a desirable amount of particles
105 returned into FR, thus finishing a chemical looping redox cycle.

106 To reach the high temperatures required in the redox reactions, two reactors were placed in
107 electric ovens with a temperature controller monitoring and adjusting the bed temperatures. The
108 steam used in the experiments was provided by a vapor generator, and the inlet N₂ were introduced
109 for promoting the fluidization of the system. The loop-seal was aerated at two locations: the supply
110 chamber (which improves the fluidization of the downward particles and delivers them to the

111 recycle chamber) and the recycle chamber (which enables the particles crossing over the threshold
112 and entering into the SR). The schematic of the experimental set-up was shown in Fig. 1.

113 2.3. Test procedure

114 Prior to the experiments, the total bed inventory of 6 kg was loaded in SR, while purging N₂ to
115 drive the solid circulations until the pressure drop of FR and SR kept largely unchanged. The steam
116 was introduced from the bottom of the SR with a constant flow rate of 13.33 sccm (water), and the
117 flow rates of inlet N₂ was controlled at 20000 sccm, 5000 sccm, 3333.33 sccm respectively to
118 accommodate the FR, SR and loop seal fluidization. The bed temperatures were set at 850 °C for SR
119 and 850 °C-1000 °C for FR. When all the operation parameters stabilized, oil was introduced into
120 the FR lower bed continuously at a constant flow rate of 2.39 sccm. At the same time, a small
121 fraction of the exhaust gas was extracted to a cooler and a silica gel desiccator, and then collected in
122 gas bags for analysis. An Emerson multi-component gas analyzer was used to measure the
123 concentration of CO₂, CH₄, CO and H₂ with a detection range of CO₂ (0~100%, 0.01% uncertain),
124 CH₄ (0-10%, 0.01% uncertain), CO (0-100%, 0.01% uncertain), O₂ (0-25%, 0.01% uncertain), and
125 H₂ (0-50%, 0.1% uncertain).

126 2.4. Data evaluation

127 To facilitate the comparison of gas concentration of each component, the gas concentration (f_i),
128 N₂ free basis, can be obtained by:

$$f_i = x_i / (x_{CO} + x_{CO_2} + x_{CH_4} + x_{H_2}) \quad (10)$$

129 Gas production of specie i ($\dot{n}_i$) can be calculated based on a N₂ mass balance method:

$$\dot{n}_i = \int_{t_1}^{t_2} \dot{n}_{out} x_i dt \quad (11)$$

130 With

$$\dot{n}_{\text{out}} = \dot{n}_{\text{N}_2,\text{in}} / x_{\text{N}_2,\text{out}} = \dot{n}_{\text{N}_2,\text{in}} / (1 - x_{\text{CO}} - x_{\text{CO}_2} - x_{\text{CH}_4} - x_{\text{H}_2}) \quad (12)$$

where x_i was the concentration of specie i measured by the gas analyzer, $\dot{n}_{\text{in}}$ and $\dot{n}_{\text{out}}$ were the total inlet and outlet volumetric gas flow rate; respectively.

Carbon conversion of the oil (X_C) was defined as the accumulated amount of carbon in the outlet gas streams divided by the total amount of carbon in the bio-oil heavy fraction and can be calculated by:

$$X_C = \int 12\dot{n}_{\text{out,FR}} (x_{\text{CO}_2,\text{FR}} + x_{\text{CO,FR}} + x_{\text{CH}_4,\text{FR}}) / 0.0224 dt / \int \rho_{\text{oil}} n_{\text{oil}} f_c dt \quad (13)$$

Where n_{oil} was the oil feeding rate, ρ_{oil} was the oil density and f_c was the carbon content of the oil which was shown in Table 2.

Hydrogen yield was defined as the hydrogen production in SR per unit volume of oil, which can be calculated by:

$$\gamma_{\text{SR}} = \dot{n}_{\text{outSR,H}_2} / n_{\text{oil}} \quad (14)$$

To evaluate the effects of adding steam in FR on the overall chemical looping, the gross yield of H_2 in both FR and SR was also compared in terms of different steam to oil ratios, and it can be calculated by:

$$\gamma = (\dot{n}_{\text{outSR,H}_2} + \dot{n}_{\text{outFR,H}_2}) / n_{\text{oil}} \quad (15)$$

3. Results

3.1. Test profile

According to the work by Bleeker et al, oil was rapidly decomposed into gaseous products when feeding into FR at temperatures higher than 800 °C, that implied the oil pyrolysis was not the rate-limiting step and the resultant gas products would determine the subsequent chemical looping reactions. Therefore, in this section, the oil pyrolysis in a sand bed was performed first.

As listed in Table 3, we can find that the higher temperature suppressed the formation of CH_4 and

150CO₂ but favored the H₂ production; particularly, CO was independent on the operating temperature.
 151The competition relationship of CH₄ and H₂ can be easily attributed to the endothermic methane
 152crack reaction ($\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$). Based on a fact that OC possessed higher reactivity with CO and H₂
 153than that with CH₄, the higher operating temperature resulting in more CO and H₂ would be better
 154for the subsequent reduction process. However, the carbon conversion was unsatisfactory no matter
 155which temperature was tested. The results listed in in the last column in table 3 suggested the
 156maximum value of only 70% at 950 °C. Compared with the results using crude oil, this confirm the
 157non-aqueous bio-oil was more liable to form the solid carbon.

158 Fig.2 shows the gas concentrations, N₂ free basis, as a function of reaction time at 950 °C.

159Clearly, the profile could be easily divided into three stages of region I for time t=0 min to t=70 min,
 160region II for t= 70 min to t= 130 min, and region III for t= 130 min to t=200 min. Initially, the
 161starting material was in the form of hematite; by virtue of the preferred thermodynamics in hematite
 162reduction, almost all the reducing gas (CO, H₂, CH₄) was absorbed and the outlet stream contained
 163high purity of CO₂. Therefore, this reduction period was suitable for producing or sequestering
 164CO₂. With respect to SR, there was no hydrogen produced in this stage, evidencing the magnetite
 165reduction had not occurred. In contrast, some carbonaceous gases were observed and CO₂ was
 166produced in high concentration. The gas composition can be due to the gas leakage from FR to SR
 167and the subsequent water-gas shift reaction in SR. When the reduction reaction progressed to 70
 168min (region II), CO, H₂ broke through and CO₂ dropped dramatically, the point at which it can be
 169deduced that the starting material of Fe₂O₃ exhausted and the reduction to FeO or Fe occurred. The

intensified reduction in this stage endowed the OC with the ability to crack water and produce hydrogen. As a result, we observed a surge in hydrogen concentration in SR (Fig. 2b). Based on the evolutions of FR gas compositions in region II, it should be noted that the CO_2/CO ratio tended to be stabilized. This implied the compromise between oxygen releasing and accepting rates of OC. After 130 min (region III), the two rates became comparable and OC composition kept largely unchanged. At this moment, the dual bed system stabilized and hydrogen with a purity of 84% was attained.

3.2. *Effects of the operation temperature on redox performances*

The effects of the operating temperature on the redox performance are shown in Fig. 3. As can be seen, the results identified 950 °C was an optimal operating temperature in terms of the higher CO_2 and H_2 concentrations. This can be ascribed to more CO and H_2 produced at higher temperatures and the endothermic characteristics of these reduction reactions. However, we observed a slight decrease in CO_2 and H_2 concentrations when further evaluating the temperature to 1000 °C; this was possibly due to the lower carbon conversion at this temperature (Table 3). The hydrogen yield at 1000 °C was proved higher than that at 950 °C (Fig. 4), and the increase in hydrogen yield maybe original from the reduction of OC by oil coke. To confirm this hypothesis, the carbon conversion of oil under the OC bed was calculated. As shown in Fig. 4, we can find that the presence of OC can promote the oil pyrolysis significantly when comparing with the results under the sand bed. More importantly, this promotion was greater at 1000 °C than that at 950 °C.

To evaluate the recyclability of OC material, the 600 min long-term experiments were performed as well. As a whole, the hydrogen purity and yield decayed continuously with the cyclic time

191increased (Fig. 5, 6). It was, not surprisingly, a result of the OC deactivation, *i.e.* the nanoparticle
192growth that can proceed through transport of molecular or monoatomic species between individual
193particles (Ostwald ripening) or through coalescence and migration of particles (sintering) . This
194deactivation generally led to the shrinkage in material surface area (Table 4), and therefore
195increased the diffusion energy barrier (OC has a very limited path length in ion diffusion) .
196Comparing with the hydrogen yield in different reduction temperatures, we have found higher
197temperature could give rise to higher yield (Fig. 4). Unfortunately, the increase in temperature
198accelerated the OC deactivation (Fig. 5, 6), and negatively affected the hydrogen production.
199Therefore, the hydrogen yield at 1000 °C was lower than that at 950 °C after 600 min long-term
200tests.

2013.3. *Enhancement on hydrogen purity*

202 According to the above experiments, we can concluded that 950 °C was an optimal operating
203temperature in terms of the higher H₂ concentration and yield as well as good recyclability.
204However, we have confirmed that the hydrogen purity in this selected temperature remained not
205desirable, *i.e.* hydrogen purity reached only 84% in 950 °C that cannot satisfy the practical use, such
206as hydrogen-powered fuel cells, directly as fuels or hydrodeoxygenation of aqueous phase bio-oil
207proposed in the current work. Therefore, some approaches to enhance the hydrogen purity are
208required.

209 In this section, three strategies to improve the current processes were proposed. One is to conduct
210the oil pyrolysis in a separated reactor and utilize the resultant gaseous fuels to react with OC, thus
211the solid carbon is isolated with no chance to participate in the subsequent redox reactions. Another
212method is to absorb the gas impurities using processes such as Pressure Swing Adsorption (PSA) or
213Monoethanolamine (MEA) scrubbing as was employed in the methane steam reforming .

Obviously, these two solutions will inevitably result in intensive energy penalties, extra capital costs as well as the increase in technical complexity. Since the gas contaminations in hydrogen stream were produced by the steam gasification of oil coke in SR, the hydrogen purity will be inherently enhanced if we can minimize the coke formation during oil pyrolysis period. Thermodynamically, the oil decomposition can be promoted with the help of some oxidants. For instance, when water was introduced into FR, the coke would be burnt to carbonaceous gases; the gas impurities produced by the steam gasification of coke could be released in FR directly. As a result, the coke to be transported into SR can be inherently separated and the hydrogen could be in-situ purified. To confirm this hypothesis, the steam was introduced during the reduction period at 950 °C, and the role of steam in redox performance was evaluated.

Fig. 7 shows the effects of steam to oil ratio on the hydrogen concentration and yield. As can be seen, the hydrogen purity was improved as the steam to oil ratio increased, *e.g.* the hydrogen purity reached over 98% at steam to oil ratio of 2.5. This can be expected as the solid carbon had been burnt in FR. Nevertheless, the steam gasification of solid carbon, which was considered as a major source of the gas pollutants, contributed the hydrogen yield as well (R8 and R9); that implied part of hydrogen was eliminated along with the gasification of solid carbon in FR. As illustrate in Fig.7, the steam added in FR played a negative effect on hydrogen yield. At steam to oil ratio of 2.5, we can attain high hydrogen purity of over 98%, whereas the hydrogen yield was only 480 ml.ml⁻¹ oil. On the contrary, if the hydrogen yield required to be maximized, the system can provide only 83.7% hydrogen purity. To sum up, hydrogen purity and hydrogen production were in a competing relationship, and the enhancement of the hydrogen purity was at the cost of the suppression in hydrogen yield.

Under this circumstance, we need to find a compromise between the hydrogen yield and the

237purity to pursue high system efficiency. For the currently proposed aqueous phase
238hydrodeoxygenation, the hydrogen purity over 95% is required; the current result suggests the
239steam to oil ratio of 1.5 is preferred, under which we can attain a hydrogen purity of 96% and a
240relatively higher yield of 635 ml.ml⁻¹ oil. With respect to the gross yield of H₂ in both FR and SR, a
241slight decrease can be observed (Table 5); this is possibly due to the weakened water-gas shift
242reaction in FR. Compared with the case without steam in FR, the coke was reformed in SR. With
243the help of the intensified oxidization atmosphere, the water gas shift reaction can occur
244successfully and drag the reaction to produce more hydrogen. However, when water was added,
245most of the coke was reformed in FR where the reduction atmosphere was dominated, thus the
246reforming of CO was suppressed thermodynamically.

247 The long-term test was also carried out to evaluate the cyclic performance under different steam
248to oil ratios. The results, not surprisingly showed the hydrogen yield and purity was declined with
249the cycling time elapsed (Fig. 8). More importantly in this test, we found the deterioration of cyclic
250performance was much slower in terms of higher steam to oil ratios, *e.g.* the hydrogen purity, when
251steam to oil ratio was 2.5, decreased by 2% after 600 min long-term experiments that was in
252contrast to 4% if no steam was added; this result indicated adding steam in FR was also a promising
253approach to mitigate the OC deactivation. The reasons can be ascribed to the reduction level of OC;
254according to Bauer–Glaessner diagram , more steam in OC reduction can efficiently suppress the
255formation of metallic iron, which was reported as a major cause to particle sintering. For the oil
256hydrodeoxygenation, we need to ensure the hydrogen purity over 95%, but the purity decrease to
25794.8% after 600 min running. Our current experiments suggested that we could adjust the steam to
258oil ratio during the chemical looping operation to meet the desirable hydrogen purity.

2594. Discussion

2604.1. *Chemical looping for gas conditioning*

261 For a typical chemical looping cycle, 1 mol H₂ can be obtained no matter the input feedstock is 1
262mol CO, or 1 mol H₂ according to the overall oxygen mass balance (Fig. 9), so the net benefits are
263turning 1 mol CO to 1 mol H₂. Based on this hypothesis, one could note that chemical looping can
264be employed as an efficient way for gas conditioning. According to our current results, we attained
265nearly 2:1 H₂/CO syngas in total gas products (Fig. 3, FR and SR gas products) that is suitable for
266methanol synthesis. In a similar way, higher H₂/CO ratio can also be achieved through the
267adjustment on the solid flux and phase composition of OC, *e.g.* we can regulate the H₂/CO ratio to
2683:1 by chemical looping for synthetic natural gas production. Compared with the competing method
269(water-gas shift reaction), this approach possesses the accurate definition on the H₂/CO ratios
270without an extra gas conditioning unit. We anticipate this strategy can expand the applications of the
271chemical looping to produce more clean chemicals with CO₂ capture.

2724.2. *An novel fluidized bed for chemical looping hydrogen production with CO₂ capture*

273 As shown in Fig. 2, we can observe the large amount of H₂ and CO was free to react with OC
274particles, implying extensive energy penalty and great environmental concerns. In addition, the FR
275gas stream generally needs to have high CO₂ concentration for facilitating the subsequent capture
276and storage of the greenhouse gases. To meet these energy and environmental challenges, we
277proposed a novel fluidized bed in this section, and the corresponding chemical looping occurred in
278each reactor is also discussed.

279 In the chemical looping of iron oxides, the reduction of oxygen carrier would experience three
280different stages, ranging from Fe₂O₃ capable of absorbing CO and H₂ in a very low concentration, to
281Fe₃O₄ or FeO with significant thermodynamic limit when reduced by CO and H₂. The reduction of
282Fe₃O₄ or FeO was also considered as a major cause of the lost in CO and H₂. In this case, we

283proposed a stacked FR consisting of a lower bed A and upper bed B, as shown in Fig. 10. By
284regulating the fuel to OC ratio, the reduction of Fe_2O_3 and Fe_3O_4 can be separately performed. In
285bed A, there only involves the reduction of Fe_3O_4 instead of the reactions of Fe_2O_3 and Fe_3O_4
286occurred simultaneously. The unreacted CO and H_2 in this case are then introduced to an upper bed
287B where reduction of Fe_2O_3 was carried out. By virtue of the preferred thermodynamics, the
288remaining CO and H_2 can be completely absorbed by Fe_2O_3 with pure CO_2 emitted. In addition, the
289particle attrition associated with the high solid flux can be reduced since solid stream transported
290from FR to SR will no longer contain Fe_2O_3 in this unit. The proposed reactor rearranges the
291chemical looping in the reactors and the co-production of H_2 and CO_2 was expected to be achieved.

2925. Conclusion

293 In this work, hydrogen was successfully produced from non-aqueous bio-oil in a dual fluidized
294bed using the chemical looping redox cycle of Australian MAC iron ore. Considering higher
295hydrogen purity and yield, we confirmed 950 °C was the optimal operating temperature. However,
296the hydrogen purity remained not desirable due to the low carbon conversion of the oil. To address
297this problem, we proposed a method of adding steam in FR to eliminate the solid carbon, and
298investigated the effects of the steam to oil ratio on the redox performance. The results showed that
299adding steam in FR was an efficiency way to enhance the hydrogen purity. Nevertheless, it
300suppressed the hydrogen yield simultaneously. In addition, we found adding steam in FR can affect
301the reduction level of OC, and therefore mitigate the OC deactivation. As for the aqueous phase oil
302hydrodeoxygenation process, our current study indicated the steam to oil ratio of 1.5 was preferred,
303under which we can attain a hydrogen purity of 96% and a relatively higher yield of 635 ml.ml⁻¹ oil.

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398**Table captions**

399**Table 1.** Chemical composition of the Australian MAC iron ore.

400**Table 2.** Ultimate analysis and water content of non-aqueous phase bio-oil /wt% (wet).

401**Table 3.** Gas compositions from the oil pyrolysis at different reaction temperatures.

402**Table 4.** BET analysis of the fresh OC and OC after cycles at different temperatures.

403**Table 5.** The hydrogen yield in FR and SR at different steam to oil ratios.

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421 **Figure captions**

422 **Fig. 1.** The schemetic of the experimental set-up.

423 **Fig. 2.** Gas concentrations, N₂ free basis, as a function of reaction time at 950 °C. (a) FR; (b) SR.

424 **Fig. 3.** The effects of the reduction temperature on the redox performance. (a) FR; (b) SR.

425 **Fig. 4.** Carbon conversion and hydrogen yield as a function of reaction temperatures.

426 **Fig. 5.** Hydrogen yield at different reduction temperatures as a function of reaction time.

427 **Fig. 6.** Hydrogen concentration, N₂ free basis, at different reduction temperatures as a function of
428 reaction time.

429 **Fig. 7.** Hydrogen concentration, N₂ free basis, and hydrogen yield as a function of steam to oil ratio.

430 **Fig. 8.** Cyclic performance as a function of steam to oil ratio (ζ).

431 **Fig. 9.** The principle of chemical looping for gas conditioning.

432 **Fig. 10.** The schematic of the proposed triple fluidized bed reactors. (A) FR lower bed; (B) FR
433 upper bed; (C) SR; (D) AR.

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The schemetic of the experimental set-up.

Fig. 2.
Gas concentrations, N₂ free basis, as a function of reaction time at 950 °C. (a) FR; (b) SR.

Fig. 3.
The effects of the reduction temperature on the redox performance. (a) FR; (b) SR.

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Cyclic performance as a function of steam to oil ratio (ζ).

Fig. 9.
The principle of chemical looping for gas conditioning.

Fig. 10.

The schematic of the proposed triple fluidized bed reactors. (A) FR lower bed; (B) FR upper bed; (C) SR; (D) AR.

Table 1.
Chemical composition of the Australian MAC iron ore /wt%.

	Fe ₂ O ₃	TiO ₂	SiO ₂	Al ₂ O ₃	CaO	Na ₂ O	MnO	Cr ₂ O ₃	K ₂ O
Sample	93.96	0.00	3.96	2.08	0.00	0.00	0.00	0.00	0.00

Table 2.

Ultimate analysis and water content of non-aqueous phase bio-oil /wt% (wet).

sample	C	H	O ^a	N	H ₂ O
bio-oil heavy fraction	57.18	6.75	35.65	0.42	18.54

^a by difference.

Table 3.

Gas compositions from the oil pyrolysis at different reaction temperatures.

Temperature (°C)	CO ₂ (%)	CO (%)	H ₂ (%)	CH ₄ (%)	Carbon conversion (%)
850	11.50	38.95	30.35	19.20	47.0657
900	8.61	39.66	33.83	17.91	55.6813
950	8.94	39.77	36.29	14.99	70.3746
1000	3.96	39.52	43.37	13.15	56.5320

Table 4.

BET analysis of the fresh OC and OC after cycles at different temperatures.

	fresh	850 °C	900 °C	950 °C	1000 °C
BET surface area (m ² /g)	1.7092	1.0231	0.8695	0.7954	0.6781

Table 5.

The hydrogen yield in FR and SR at different steam to oil ratios.

Steam to oil ratio	SR (ml.ml ⁻¹ oil)	FR (ml.ml ⁻¹ oil)	Total (ml.ml ⁻¹ oil)
0	863.6	47.6	911.2
0.5	787.4	103.8	891.2
1.0	685.8	197.7	883.5
1.5	635	243.4	878.4
2.0	533.4	341.4	874.8
2.5	482.6	390.8	873.4