Supplementary Information

Figure S.1. Equilibrium diagram for the reaction of Fe$_2$O$_3$ with CO produced using factsage (a thermodynamic modelling software) that calculates equilibrium constants based on a minimisation of Gibbs free energy approach.

Figure S.2. Equilibrium diagram for the reaction of Fe$_2$O$_3$ with CO in the presence of Al$_2$O$_3$. The data was calculated using Factsage (a thermodynamic modelling software) that calculates equilibrium constants based on a minimisation of Gibbs free energy approach.
S.1 Char yield determination method description

Char yields were determined by comparing the carbon content of the gas produced as the char bed was combusted in 10 mol.% O\(_2\), 90 mol.% N\(_2\) after the biomass pyrolysis phase with the carbon content of the char retrieved after an experiment without the burn-off step (determined via elemental CHN analysis) (eq. 1-2).

\[
C_{\text{char,g}} = Q_{\text{out,293K}} \cdot A_r C \left( \frac{x_{\text{CO}_2}}{M_r \text{CO}_2} + \frac{x_{\text{CO}}}{M_r \text{CO}} + \frac{x_{\text{CH}_4}}{M_r \text{CH}_4} \right) \quad \text{(Eq 1)}
\]

\[
 W_{\text{char}} = C_{\text{char,g}} \cdot \left( A_r C \cdot x_{C,\text{char}} \right) \quad \text{(Eq 2)}
\]

\(C_{\text{cha,g}}\) is the carbon content of the char (in wt.%) as determined from the concentrations of CO\(_2\), CO and CH\(_4\) measured at the outlet of the reactor; \(Q_{\text{out,293K}}\) is the total flow rate at the outlet of the reactor at 293 K and 1 bar\(_a\) (temperature and pressure of the gas analysers); \(A_r C\) is the atomic mass of carbon; \(x_i\) is the mole fraction of gaseous species \(i\) in the gas stream exiting the reactor; \(M_r i\) is the relative molecular mass of gaseous species \(i\); \(W_{\text{cha}}\) the total calculated weight of char (including ash); \(x_{C,\text{char}}\) is the mole fraction of C in the char where \(A_r C \cdot x_{C,\text{cha}}\) is the mass fraction of C in the char as determined from elemental CHNS analysis of the char (Perkin Elmer 2400).

S.2 Size exclusion chromatography (SEC) method description

The SEC setup consisted of a Mixed D column (300mm long, 7.5mm ID) with a polydivinylbenzene packing (5 \(\mu\)m particle size, Polymer Laboratories UK). SEC analysis of the tars was via a tried and tested method that has been used at Imperial College for many years [1-5]. Tar samples were dissolved in n-methyl-2-pyrrolidone (NMP) which acted as the mobile phase. The column was operated at 353 K (80 °C) and an NMP flow rate of 0.5 ml min\(^{-1}\). Elution from the column was monitored with a Kauner diode array smartline 2600 detector. The detector measures UV absorbance at 300 nm of the separated sample as it elutes from the column. Data was recorded and area normalised, to enable comparison of tar samples generated under different conditions.
Figure S.3. SEC analyses of the tars recovered from the fast pyrolysis of 0.10 g of beech wood in the two-stage reactor loaded with (a) the 100Fe OC material and (b) 60Fe40Al OC material in both their oxidised and reduced forms under an atmosphere of 15 mol.% CO$_2$, balance N$_2$. 
Figure S.4. Light microscope images of (a-b) the coked 100Fe(S) OC particles and (c-d) coked 60Fe40Al OC particles retrieved after exposure to the biomass pyrolysis products under conditions of (a,c) 15%CO$_2$ PreRed and (b,d) 15%CO$_2$ PostRed. The strand of wire featured in each of the figures was 200 µm in diameter and was included for scale.

References


