Pyrolysis of wood pellet in the presence of oxygen carriers in a fluidised bed coupled with a DBD reactor for tar quantification

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Abstract

The pyrolysis of wood in the presence of chemical looping agents including Fe₂O₃, mayenite-supported CuO and mayenite-supported Cu₂O was studied from 773 to 1173 K. A continuous tar quantification system, based on a DBD reactor downstream of the fluidised bed, was developed to allow quantification of the tar formed. An oxygen-containing plasma was used to convert volatiles and tars to measurable carbon-containing species, mainly CO, CH₄, and CO₂. It was found that pyrolysis of the wood in alumina sand produced CH₄, CO, CO₂, tar and char as the main products. Tar cracking was observed above 1073 K, and this mainly generated CH₄. Both Fe₂O₃ and mayenite-supported Cu-based oxides were effective for *in situ* combustion of the pyrolysis products, particularly tar, at temperatures exceeding 873 K. Mayenite-supported CuO showed the highest reactivity. The results showed the potential of using metal oxides for direct combustion of biomass, and particularly converting the tarry products during devolatilisation. The better activity of mayenite-supported CuO compared to Fe₂O₃ and Cu₂O in these experiments was mainly due to the ability of CuO to release gaseous oxygen at higher temperatures.

Keywords: biomass, chemical looping combustion, DBD reactor, online tar quantification, Fe₂O₃, mayenite-supported CuO.

1. Introduction

Chemical looping combustion (CLC) is a way of combusting a fuel using oxygen supplied from a solid metal oxide (commonly referred to as an oxygen carrier) and produces CO₂, undiluted by nitrogen. Oxygen carriers are typically transition metal oxides able to give up oxygen by reduction whilst oxidising a fuel (in a fuel reactor). The reduced oxides are regenerated by air (in an air reactor), which allows the oxygen carriers to be used in the next combustion cycle. The reactions are:

where Mtl represents some transition metal. The implication of CLC is that it avoids the mixing of CO₂ produced with a large proportion of N₂ (normally the fuel is combusted in air). This saves the energy that would have been required to separate the CO₂ and N₂ for carbon capture.

The CLC of fuels has been widely studied with both naturally occurring oxide minerals (such as ilmenite) and synthetic oxygen carriers, which usually consist of Fe, Ni, Mn, Cu, either used on their own or supported on inert materials such as Al₂O₃, ZrO₂, MgAl₂O₄ [1–8]. Among these materials, oxides of Mn and Cu have the ability to release gaseous oxygen at high temperatures, known as chemical looping oxygen uncoupling (CLOU). CLC was initially applied to gaseous fuels. According to reaction R-1, the oxygen carriers convert the gaseous fuel to CO₂ and H₂O. For a solid fuel, *e.g.* coal- or biomass-derived char, it is unlikely to occur through a direct solid-solid reaction. Thus, application of CLC to solid fuels either uses CLOU materials or converts the solid fuels into gaseous fuels by gasification (either *in-* or *ex-situ*). Liquid fuels such as tar have been studied only recently, normally based on model compounds due to the complexity of tar. Mendiara *et al.* [9] investigated the removal of toluene by selective reforming in a chemical looping system (in TGA and a lab-scale fixed bed reactor), using four oxygen carriers (NiO/MgAl₂O₄, NiO/NiAl₂O₄, Mn₃O₄/Mg-ZrO₂, and FeTiO₃). Their study compared the extent of carbon deposition of toluene on the four oxygen carriers and found that the addition of water reduced carbon deposition. Ryden *et al.* [10] investigated CLC of kerosene with Ni-, Mn-, Cu- and Fe-based oxygen carriers in continuous operation. They reported 95% - 99% conversion of carbon

in the fuel to CO₂. Biomass has been studied extensively in CLC systems [11–13]. Zeng *et al.* [13] proposed a chemical looping pyrolysis-gasification system for syngas production with a two-zone fuel reactor; in the first zone the biomass was pyrolysed and in the second zone steam was introduced to gasify the char and convert the pyrolysis products to give high H₂/CO ratio syngas. In a chemical looping system (or indeed any thermochemical conversion), the biomass fuel will first be heated and release volatile matter. This volatile matter represents a large proportion of the calorific value of the fuel, and if unconverted, the higher molecular mass species can condense as “tars” which can adversely affect down-stream equipment. The primary volatile components often undergo secondary reactions, either forming lighter species and being cracked to carbon, or forming larger species. The presence of solids in a reactor can have a profound effect on the fate of the volatiles and the formation of tars. Tars have often been a problem during gasification of biomass, and interaction with solids has been proposed as a way of converting these tars to lighter species, either in the primary gasification reactor, or by processing the gas downstream, *e.g.* the use of dolomite or catalytically active minerals such as olivine, nickel catalysts *etc.* [14]. In a chemical looping system, the volatiles are immediately exposed to solids which can react with them, potentially leading to a much more efficient combustion of the volatiles. Sarvaramini and Larachi [15] have studied CLC of biomass volatiles that came from torrefaction at ~ 300°C. They found up to 99% of the carbon released from birch wood torrefaction was converted to CO₂ by Fe₂O₃ in a fixed bed reactor at 600°C. However, the effectiveness of different solids for the conversion of the volatiles still requires further investigation, partly owing to the difficulties in measuring the volatiles or “tars” produced during experiments.

Measurement of tar content is challenging and usually done in a continuous system, from which the tars can be collected for a reasonable period, before being analysed off-line. This analysis can either be gravimetric [16] or based on other methods such as GC/MS to identify the complex mix of species [17]. This leads to a difference in the definition of tar, depending on how the tar is collected. Reported tar collection methods include the IEA tar measurement protocol (where six chemical solvents and water/ice bath are used for), the dust and tar measurement method (which aims to measure dust and tar from heavily polluted gases at the same time) *etc.* [17]. These methods require multiple stages,

involving the use of chemicals and heating/cooling treatment of the gas line, and usually need a considerable amount of time. Nunes *et al.* [18] adopted a simpler approach for tar collection in the investigation of tar formation and destruction in a fixed bed reactor from biomass fuels: a tar trap tube, which was immersed in liquid N₂, was attached to the main reactor for the condensation of tar from upstream. The tar trap was then washed offline with a mixture of methanol and chloroform for further analysis. In batch experiments, measurements of tar are difficult owing to the rapid release of volatiles and the difficulty of collecting sufficient amounts for analysis. Chern [19] attempted to solve this problem by using a multiport valve with loops to rapidly collect gas samples and store them for later GC analysis. This allowed speciation, but it was laborious.

In this study, the effectiveness of typical chemical looping agents: Fe₂O₃, CuO and Cu₂O (both CuO and Cu₂O were supported on mayenite), for the conversion of volatile matter is investigated. The effect of the oxygen carriers on the product distribution of a batch pyrolysis of biomass in a fluidised bed were studied and compared with that achieved in a nominally ‘inert’ bed of alumina sand. Both types of oxygen carriers have been investigated for chemical looping combustion. Copper oxide differs from the other two, in that it can release gas phase oxygen at chemical looping temperatures; this effect has been proposed as method of improving the conversion of gaseous and solid fuels (*i.e.* CLOU combustion [20]).

To enable online quantification of the unconverted volatile matter (referred to as “tar” here), an oxygen-containing dielectric barrier discharge (DBD) plasma reactor was used to convert the tar produced from the fluidised bed to lighter detectable species (mostly CO₂ and CO), enabling the quantification of the carbon in the tar. DBD plasma reactors have been widely studied for the abatement of volatile organic compounds (VOCs) [21–24]. The excited species in the plasma (here a plasma containing O₂ and O-containing excited species) can oxidise and crack hydrocarbons to detectable species. By comparing the amounts of detectable species when the gas has been treated with plasma with when it has not, an estimate of the carbon contained within the volatile species can be made. Owing to the placement of the trap at 0°C, this “tar” that consists of all the carbon-containing species would have condensed from the analysed gas. This differs from the IEA tar measurement protocol, but is similar to the method used

by Nunes *et al.* [18]. Of course, this relies on assumption that all of the higher molecular mass components are completely converted to detectable species, which has been evaluated by the overall carbon balance in the experiments.

2. Experimental

2.1. Experimental setup

The experimental setup consisted of a fluidised bed reactor, a DBD plasma reactor and a chilled trap before a train of gas analysers, as shown in Fig. 1. The fluidised bed reactor was a quartz tube (i.d. 29 mm, o.d. 32 mm), with a porous distributor positioned 110 mm above the gas inlet at the bottom. The sampled gas from the fluidised bed mixed with a stream of air prior to passing through the DBD reactor. All flows were metered and controlled *via* variable area flow meters equipped with valves. The DBD reactor and the sampling line connecting it to the fluidised bed were externally heated (refer to 2.4.1 for operating temperatures) by heating tapes (Omega, STH051). The stream leaving the DBD reactor was passed through a trap immersed in ice water and consisting of a tube packed with CaCl_2 and ceramic beads, and plugged with glass wool at each end to remove tar, water and carbon fines, before the gases were analysed by Fourier transform infrared spectroscopy (FTIR) (ThermoFisher Scientific, NICOLET iS10) and a paramagnetic oxygen analyser (ABB, EL3020) positioned after the FTIR. The configuration of the DBD reactor is shown in Fig. 2. It consisted of two metal electrodes, with the high voltage electrode being a stainless-steel rod (diameter of 25.0 mm, length of 80 mm) and the ground electrode being a stainless-steel tube (i.d. 36.0 mm). A quartz tube (i.d. 26.0 mm, o.d. 30.0 mm) covering the high voltage electrode was used as the dielectric barrier, leaving a gap (3.0 mm) between the outer surface of the quartz tube and the inner surface of the ground electrode for the plasma discharge and to allow the sampled gas to flow through. The DBD reactor was sealed by two Teflon end-caps, which also provided electrical insulation and support for the electrodes. Alternating voltage ranging from 13.2 to 15.2 kV (peak to peak) at a frequency of ~ 22 kHz was supplied to generate plasma *via* a plasma generator (PVM500-2500, Information Unlimited).

Figure 1 Process flow diagram of the experimental set-up.

Figure 2 Configuration of the downstream plasma reactor.

2.2. Materials

2.2.1. Wood pellets

The received wood pellets were crushed to 4.0 - 4.2 mm. They were air dried at ambient environment for 24 hours prior to being fed into the fluidised bed. The results of elemental analysis and proximate analysis of the wood sample are shown in Tables 1 and 2.

Table 1 Elemental analysis (air dried).

Element	Mass %
Carbon	46.33
Hydrogen	6.12
Nitrogen	0.00
Oxygen (balanced)	47.55

Table 2 Proximate analysis (air dried).

Composition	Mass %
Moisture	8.53
Volatile matter	75.21
Fixed carbon	15.83
Ash	0.42

2.2.2. Materials used as the fluidised bed

Here, the fluidised bed consisted of particles (sieve size of 355 - 425 μm) of alumina sand, Fe_2O_3 , mayenite-supported CuO or Cu_2O . The alumina sand was sieved, and washed in de-ionised (DI) water, followed by drying at 393 K for 24 hours prior to use. The bulk density of alumina sand was 2200 kg/m^3 . The voidage of the alumina sand, 0.44, was measured by filling a packed bed of alumina sand of water just to the surface and recording the volume of water added, giving a particle density of 3930 kg/m^3 . Fe_2O_3 was prepared from iron oxide powers (Fisher Scientific; mean diameter of 10 μm with purity > 95 wt%). Iron oxide powder was granulated using DI water, with a mass ratio of iron oxide powder to DI water of 10:1. The mixing was carried out in a commercial mixer. The resulting granules were sieved to 355 to 600 μm , followed by the calcination of the agglomerated particles at 1273 K for 6 hours in air. The Fe_2O_3 particles were then crushed and sieved to 355 - 425 μm , giving a bulk density of 1760 kg/m^3 . The estimated particle density of Fe_2O_3 , assuming the particles formed a close-packed bed with a voidage of ~ 0.40 [25,26] was 2930 kg/m^3 . The preparation of mayenite-supported CuO followed the method described in Ref. [27]. The support, mayenite, helped to increase the mechanical strength and prevent deactivation of CuO in a fluidising environment and at high temperatures. The

particles had a composition of 60 wt% CuO, 23 wt% Al₂O₃ and 17 wt% CaO. Similarly, based on a voidage of ~0.40 of mayenite-supported CuO, and a measured bulk density of 1200 kg/m³, an estimated particle density of 2000 kg/m³ was obtained for mayenite-supported CuO.

Mayenite-supported Cu₂O was prepared from the mayenite-supported CuO by fluidising in a bed of N₂ at 1173 K until no oxygen was detected. When fluidised in N₂, CuO decomposed to Cu₂O; further decomposition to Cu was avoided either by its own equilibrium with the trace amount of O₂ with the ambient and/or the slow reaction kinetics. To ensure consistency, a single batch of mayenite-supported Cu₂O was prepared and divided equally between experiments.

2.2.3 Characterisation of the oxygen carriers

X-ray diffraction (XRD) analysis of the oxygen carriers were performed using an Empyrean PANalytical diffractometer (Cu K_α radiation with a voltage of 40 kV and current of 40 mA) with a scan range from 5° to 80° in 2θ and step size of 0.0167°. The diffractograms obtained were compared with references from Inorganic Crystal Structure Database (ICSD) for phase identification.

2.3. Plasma SED measurement

Specific energy density (SED) was used to characterise the density of plasma energy within the downstream plasma reactor and is given by

$$SED = \frac{P}{Q},$$

where P is the power input (W), Q is the gas flow rate (L/s) (all the flow rates here are expressed at 293 K and 1 atm) passed through the reactor. The power input is related to the frequency f of the AC supply by:

$$P = E \times f.$$

The energy input per cycle E is [28],

$$E = \int_0^t V(t) I(t) dt = \int_0^t V(t) dq,$$

where $V(t)$ is the voltage, $I(t)$ is the current and q is the charge. Thus, the power can be determined from the V - q Lissajous diagram. The voltage was measured using a high voltage probe (TESTEC, 1000:1, 30 kV, 50 MHz) with the sensing head connected to the high voltage electrode. The charge was obtained from the voltage (Tektronix probe, P6015A, 1:1) across a 1 μ F capacitor, connected in series between the reactor ground electrode and earth. Both the voltage and charge signals were collected simultaneously using an oscilloscope (Tektronix, TDS 3012) in X-Y mode. A typical V - q Lissajous curve is presented in Fig. S1 (refer to Supplementary materials S1).

2.4. Operating conditions and tar measurement

2.4.1 Operating conditions

The fluidised bed was loaded with ~ 20 ml of bed material (*i.e.* alumina sand, Fe_2O_3 , mayenite-supported CuO, or mayenite-supported Cu_2O), and fluidised by pure N_2 with a flow rate of ~ 3 L/min. The temperature of the bed was varied from 773 to 1173 K, giving the ratio of superficial velocity to minimum fluidising velocity U/U_{mf} of: 1.7 to 3.4 in alumina sand; 3.0 to 5.8 in mayenite-supported CuO; 3.0 to 6.0 in mayenite-supported Cu_2O ; 2.0 to 4.0 in Fe_2O_3 . The value of U_{mf} was calculated using the correlation of Wen and Yu [29]. The air stream entering the sampling line was set to ~ 0.45 L/min, and the total flow rate of the sampling line was set to 0.90 L/min. The temperature of the sampling line was kept at 573 K and the plasma reactor at 523 K. After each experiment, the fluidising gas was switched from N_2 to air to burn off any char remaining in the fluidised bed; and the amount of CO and CO_2 from the burn-off was measured to determine the yield of char. For every experiment, 0.0538 ± 0.0002 g of wood was fed. Sufficient bed material was provided in each batch experiment for full conversion of the carbon content in wood to CO_2 , assuming Fe_2O_3 was reduced to Fe_3O_4 , CuO to Cu_2O , and Cu_2O to Cu. The duration of the experiment was set to be equal to the pyrolysis time for the fuel, assuming that this can be determined by noting when CH_4 was no longer detected. Each experiment was repeated three times.

2.4.2 Tar/volatile quantification

A method to allow the online quantification of the total amount of carbon in the tar was developed; whilst the composition of the tar can be of interest, it is beyond the scope of the current study. In the current study, to measure the carbon in the tar produced at one experimental condition, two identical experiments were required, one with plasma and the other without. To have identical experimental conditions, the wood mass, flow rate, N₂ to air ratio of the two experiments need to be strictly controlled. The difference in the signals from FTIR between experiments, one with the plasma on and the other off was, analysed (*i.e.* two separate experiments were carried out with other conditions being the same). In the first experiment without the plasma, the sampled gas passes through the sample line and heavy molecular mass species are condensed in the tar trap. In the second, identical experiment, the gases pass through the active plasma reactor, and are converted and oxidized (*via* the added air) to smaller and detectable carbon-containing species.

Tar is a complex mixture of condensable hydrocarbons; here, for simplicity, tar was defined as any carbon-containing gaseous species, except CO, CO₂ and CH₄, that was unable to pass through the tar trap un-converted. This definition means that other light hydrocarbons, not condensed at 0°C are also included in the “tar” measurement. If quantified by the FTIR, it would be possible to correct for these lighter carbon-containing species, since they are detectable. However, in the experiments performed here, as shown in Fig. 5 for example, the gas after the tar trap (even with no plasma active) contained only trace amounts of other carbon-containing species, predominantly traces of acetic acid. In these experiments, it would appear that, other than CH₄, CO, and CO₂, most of the remaining carbon in the volatile matter was contained within species which condensed at 0°C, *i.e.* tarry species.

Assuming that tar can be converted to CO, CH₄ and CO₂ completely, the amount of carbon in the tar entering the sampling system is given by:

$$m_{C,tar} = \sum_{i=CO,CO_2 \text{ or } CH_4} m_i^{on} - \sum_{i=CO,CO_2 \text{ or } CH_4} m_i^{off},$$

where m_i^{on} and m_i^{off} are the masses of carbon in the carbon-containing species i (CO, CO₂ or CH₄) that entered the sampling system for the separate experiments with the plasma on and off, respectively.

Here, m_i^{on} and m_i^{off} were determined by taking the integral of the rate of species i that entered the sampling system and detected by FTIR, $R_i(t)$, over pyrolysis time from t_0 to t_a :

$$m_i = \int_{t_0}^{t_a} R_i(t) dt.$$

The above equation gives the mass of carbon entering the sampling system over the duration of an experiment. To obtain the total amount of carbon in each species, for instance in tar, the ratio of the total gas flow rate in the fluidised bed, F_{FB} , to the flow rate into to the sampling line F_{sampling} was used:

$$M_{C,\text{tar}} = m_{C,\text{tar}} \times \frac{F_{FB}}{F_{\text{sampling}}},$$

where $M_{C,\text{tar}}$ is the total amount carbon in the tar produced in the fluidised bed.

Following each experiment, the residual amount of carbon remaining in the bed was measured by burning off using air. The carbon balance was calculated by:

$$m \% = \frac{(\sum_i m_i^{\text{off}} + m_{C,\text{burn-off}} + m_{C,\text{tar}}) \times \frac{F_{FB}}{F_{\text{sampling}}}}{M_{C,\text{total}}} \times 100 \%,$$

$$M_{C,\text{total}} = M_{\text{wood,total}} \times x_C,$$

where $M_{\text{wood,total}}$ is the total mass of wood fed into the fluidised bed, and x_C is the weight fraction of elemental carbon in the wood. $M_{C,\text{total}}$ is the total carbon content in the wood fed. $m_{C,\text{burn-off}}$ is the amount of carbon in the char determined by burn-off in air, after pyrolysis time t_a :

$$m_{C,\text{burn-off}} = \int_{t_a}^{t_b} R_{\text{CO,burn-off}} + R_{\text{CO}_2,\text{burn-off}} dt,$$

where $R_{\text{CO,burn-off}}$ and $R_{\text{CO}_2,\text{burn-off}}$ are the rates of production of CO and CO₂ (expressed as equivalent mass of carbon and corrected for dilution in the sampling system) during burn-off from t_a to t_b .

The yield of gaseous species i , Y_i is then,

$$Y_i = \frac{m_{(i,\text{off})} \times \frac{F_{FB}}{F_{\text{sampling}}}}{M_{C,\text{total}}}.$$

The yield of tar Y_{tar} is

$$Y_{\text{tar}} = \frac{M_{\text{C,tar}}}{M_{\text{C,total}}},$$

and the yield of char Y_{char} is

$$Y_{\text{char}} = \frac{m_{(\text{C,burn-off})} \times \frac{F_{\text{FB}}}{F_{\text{sampling}}}}{M_{\text{C,total}}}.$$

Additionally, the change in composition of the gases can affect the total flow rate through the sampling line. In particular, the generated tar (without plasma) appeared to block the sampling line, leading to an increased pressure drop and causing a change in the total flow rate through the line. To resolve the issue for the purpose of tar measurement, a correction for the change in flow rate was applied. See S2 in Supplementary materials for the correction of the flow rate.

3. Results

3.1 Characterisation of the oxygen carriers

XRD analysis of fresh Fe_2O_3 , mayenite-supported CuO and Cu_2O particles were carried out, as shown in Fig. 3. The diffractogram of Fe_2O_3 sample showed a predominant Fe_2O_3 phase with some unidentified impurities. In mayenite-supported CuO, the dominant phases are $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (mayenite) and CuO. The diffractogram of mayenite-supported Cu_2O particles shows that CuO had mostly been reduced to Cu_2O (the main peaks of the CuO phase at 35.59° and 38.78° are barely visible) whilst the mayenite phase remained unchanged.

Figure 3 XRD diffractograms of fresh (a) Fe_2O_3 , (b) mayenite-supported CuO and (c) mayenite-supported Cu_2O , where the collection codes of the references used from ICSD are 15840 for Fe_2O_3 , and 241243 for $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$, 69758 for CuO , and 172174 for Cu_2O .

3.2 Tar measurements

3.2.1 Identification of product species

Figure 4 shows the IR spectra of the gases leaving the DBD reactor in the absence of additional oxygen (denoted by “pure” N₂) and when air is mixed in to the gases prior to the DBD reactor (giving ~ 8.3 vol% oxygen). N₂ was used to fluidise a bed of alumina sand in each case. When wood was fed into the fluidised bed, the gas contained species produced from wood pyrolysis. The significant peaks at around 630 - 710 cm⁻¹, 2280 - 2380 cm⁻¹, and 3580 - 3770 cm⁻¹ are typical peaks of CO₂. The main product measured when the plasma was running in N₂ was CO₂. The CO₂ peaks in N₂ might have come from contamination in the system, or have been an artefact of the background subtraction. The FTIR is very sensitive to CO₂, so the small peak corresponds to a negligible amount of CO₂. When the mixture of N₂ and air (*i.e.* no pyrolysis products) passed through the plasma reactor, the products leaving the plasma reactor were N₂O, NO₂, NO, and CO₂; no clear CO peak was detected. However, the sensitivity of the FTIR to CO is much lower than CO₂, so detecting any conversion of trace quantities of the CO₂ to CO in the plasma would have been difficult. In Fig. 4, only the main peaks of N₂O and NO are marked, because the secondary peaks overlapped those for CO, CH₄ and CO₂. Ozone is often formed in plasma reactor in the presence of air [30], but was not observed here. It might be that any ozone produced quickly decomposed in the heated environment and reacted with N₂ to form more stable species NO, N₂O and NO₂. This is in agreement with the findings of Huu *et al.* [24]. They studied methane removal using a plasma-catalytic hybrid reactor, and showed that increasing the temperature of a plasma reactor significantly decreased the ozone concentration in the product stream, *e.g.* with a clear ozone signal at 303 K but no signal at 573 K.

With wood fed into the fluidised bed, the pyrolysis products entered the sampling system. A comparison between the spectra with wood fed into fluidised bed with the plasma on (SED of 1027 J/L) and off, is presented in Fig. 5. With the plasma running, the products after the plasma reactor were mainly N₂O, NO₂, NO, CO₂, CH₄ and CO. The main gaseous products from wood pyrolysis without downstream plasma, and having passed through the cold trap, were CO, CO₂, and CH₄. Some other absorption peaks at ~ 950, 1700, and 3050 cm⁻¹ were also observed in Fig. 5, which can be attributed to the peaks of

acetic acid. There was no significant acetic acid signal after the plasma treatment, suggesting that plasma converted the acetic acid to other species, most likely to CO or/and CO₂. The plasma reactor also seems to have converted some of the CH₄, because of the lower intensity of the CH₄ signals observed when the sampled stream was subjected to plasma discharge. It should also be remembered that any heavier hydrocarbons that passed through the sampling system unconverted, would have been removed before the FTIR by the cold trap.

Figure 4 FTIR spectra of species in different gaseous environment in the presence of plasma discharge with fluidised bed loaded with alumina sand and fluidised in N₂.

Figure 5 FTIR spectra of gaseous products with/without plasma running with wood fed into the fluidised bed (in N₂) of alumina sand at 873 K.

3.2.2 Effect of plasma power and carbon balance

- **Effect of plasma power**

The effect of the supplied power on the destruction of the carbon-containing compounds inside the plasma reactor was also investigated. This was carried out with a bed of mayenite-supported CuO fluidised by pure N₂ at 873 K. The reason for testing the system in the bed of mayenite-supported CuO was that it is more reactive than Fe₂O₃ for combustion and thus expected to generate the lowest amount of tar, and hence would require the most sensitive measurements. Figure 6 gives mole fraction of primary carbon-containing species leaving the plasma reactor after a batch of wood had been added to the fluidised bed, as a function of increasing plasma input power (from 0 to 17.1 W, corresponding to SED values from 0 to 1027 J/L). The time taken for complete pyrolysis in each experiment was reproducible (~30 s), as shown in Fig. 6. It can be seen that as the SED was increased, the mole fraction of CO increased accordingly, while CO₂ was not affected significantly. The apparent rate of production of CH₄ decreased with the increase in the plasma power. This suggests that when the tar was transported into the hot plasma reactor, most of the tar was converted into CO and some of the CH₄ produced from pyrolysis was burned. The observations here were similar to those of Huu *et al.* [24] and Baylet *et al.* [31]. They both investigated CH₄ conversion using DBD. Under operating conditions similar to the current study (>200°C, and a gas mixture of N₂/O₂/CO₂ in the plasma reactor, and similar DBD geometry), they found CH₄ in plasma was converted primarily into CO, with a small proportion converting to CO₂.

Figure 6 Mole fraction of carbon-containing gaseous species detected (with dilution by air) at 873 K in a fluidised bed of mayenite-supported CuO of for different SED values of the plasma reactor, (a) CO, (b) CO₂, (c) CH₄.

Figure 7 Overall mole fraction profiles of carbon-containing gaseous species ($\text{CO} + \text{CO}_2 + \text{CH}_4$) detected (with dilution by air) at 873 K in a fluidised bed of mayenite-supported CuO, under different SED values of the plasma reactor.

Figure 7 shows the overall mole fraction of all carbon-containing species detected by FTIR. The measurement system has ~ 18 seconds response time (time taken for the FTIR signal change from 5% to 95 % of full response to a step change). Any difference between the curves would suggest a difference in the amount of carbon in tar being burned in the plasma. The difference between the curves with no plasma and plasma with a SED of 1027 J/L, gives the rate of conversion of the carbon in tar to detectable carbon-containing species, and hence the tar content of the gas entering the sample line. This difference in the total mole fraction of carbon in $\text{CH}_4 + \text{CO} + \text{CO}_2$ is shown in Figure 8 for wood pyrolysing at 873 K in mayenite-supported CuO. Figure 8 would allow the rate of tar production to be measured as a function of time; however, in this case (with an experiment lasting only ~ 30 s, and a mixing time of 18 s), the result is strongly influenced by mixing in the sample line and would require deconvolution. Future studies looking at rates of pyrolysis would require further optimisation of the time response (which here is dominated by the FTIR) of the sample system. Here, however, total quantities, the main interest, are unaffected by the sampling system response time.

Figure 8 Additional total molar fraction of carbon in detectable species (CO, CH₄ and CO₂) upon activation of plasma. The sample was pyrolysed in a bed of mayenite-supported CuO. at 873 K.

- **Carbon balance**

No visible deposits of tar or carbon fines were observed in the trapping tube. As shown in Table 3, good carbon balances (0.89 – 0.94) were obtained when plasma was present. The overall carbon balance increased a little with an increase in plasma SED from 400 to 1027 J/L, but not by a significant amount. Increasing the power seems only to result in more significant conversion of CH₄ to CO. Most of the produced tar in the fluidised bed had been combusted (or converted to methane) in the presence of plasma at low power, thus further increase in power did not result in an increase in the overall rate of conversion to (CH₄+CO+CO₂).

Table 3 Total carbon balance as CO, CO₂ and CH₄ under different plasma SED (base on pure carbon as the tar compound), with the fluidised bed in mayenite-supported CuO and at 873 K.

SED (J/L)	Total carbon balance (air-dried)
0 (no plasma)	0.73±0.02
400	0.89±0.02
685	0.90±0.03
776	0.92±0.02
900	0.93±0.02
1027	0.94±0.02

Though relatively high carbon balances were observed in Table 3, they were not as high as close to unity, and the operating temperature of the fluidised bed might have an effect on this. The investigations of the effects of temperature and bed materials in the following sections were all carried out with plasma SED of 1027 J/L. Table 4 summarized the results of carbon balance under each experimental condition, with change in the fluidising bed material and operating temperature. It was found that an increase in the temperature of the fluidised bed led to an improved carbon balance. The improved carbon balance with increased temperature suggests that either i) tar produced at higher temperatures was easier to convert in the plasma reactor, or ii) the hotter fluidised bed results in higher temperatures in the stream of gas and volatile matter entering the sampling line, and thus less likely to condense. The possibility of i) seems less likely to dominate here. Tars can be broadly classified into primary, secondary and tertiary tars, depending on their formation conditions [32]. The secondary and tertiary tar come from the primary tar, and the primary tar products are destroyed before tertiary tar appeared. Primary tar products usually appear in the temperature range between 500 to 800°C, and tertiary tar starts to be generated from at 750°C and above [33]. Tertiary tar products are believed the most stable and difficult to crack catalytically [34]. Therefore, it is reasonable to predict that tars produced from higher temperatures in the fluidised bed should be harder to convert in the plasma reactor, unless there is some different activation route of plasma cracking.

Overall, the fact that the carbon balance is close to unity indicates that the majority of the carbon in the tars was fully converted to detectable species in the oxygen containing plasma.

Table 4 Total carbon balance with the fluidised bed loaded with different bed materials and at temperatures from 773 to 1173 K (based on pure carbon as the tar compound).

Bed material	Bed temperature (K)	Carbon balance
N ₂ fluidised bed with alumina sand	773	0.86±0.02
	873	0.85±0.04
	973	0.96±0.02

	1073	1.02±0.05
	1173	1.04±0.03
N ₂ fluidised bed with Fe ₂ O ₃	773	0.85±0.03
	873	0.88±0.03
	973	0.98±0.02
	1073	0.94±0.03
	1173	1.00 ± 0.03
N ₂ fluidised bed with Mayenite-supported CuO	773	0.91 ± 0.03
	873	0.94±0.02
	973	0.96±0.02
	1073	0.98 ± 0.03
	1173	0.97±0.03
N ₂ fluidised bed with Mayenite-supported Cu ₂ O	773	0.92±0.03
	873	0.96±0.03
	973	0.98±0.03
	1073	1.00±0.02
	1173	0.99±0.03

3.3 Pyrolysis of wood in alumina sand

Figure 9 gives the yield of each carbon-containing species including CO, CO₂, CH₄, tar and char from wood pyrolysis in alumina sand. The error bars show the range of results for three repetitions. Alumina sand is considered inert, thus chemical interaction with the wood particle is expected to be minimal. According to Fig. 9, an increase in temperature promoted the production of gases. The yield of CH₄ increased from less than 0.1 % to 1.9 % on a weight basis from 773 to 1073 K, with a maximum value of 2.5 % at 973 K. Then, a sharp increase in CH₄ yield from 1073 to 1173 K was observed; meanwhile, there was a decrease in the yield of tar (in contrast to the gradual increase of tar yield from 773 to 1073 K). This suggests that the CH₄ could have come from the cracking of tar when the bed temperature is above 1073 K. Below 1073 K, the tar could have been mainly primary tar, which is consistent with the results by Evans and Milne (1997) [33]. When the temperature increased to 1173 K, there could have

been a conversion of primary tar to secondary or tertiary tar, resulting the generation of CH_4 . The yield of char was determined from the CO and CO_2 produced during the burn-off period after pyrolysis. The char content gradually decreased from $\sim 29\%$ to $\sim 17\%$ due to more significant decomposition as the temperature increased from 773 to 1173 K.

Figure 9 Yield (mass of carbon / mass of carbon in the fuel) of different carbon-containing product species in a bed of alumina sand from 773 to 1173 K.

3.4 Pyrolysis of wood with Fe_2O_3

Figure 10 gives the yield of each product in a fluidised bed of Fe_2O_3 . According to Fig. 10, at 773 K, tars were the most significant product, $\sim 34\%$ (of carbon). As the temperature increased, the amounts of CO_2 significantly increased and became dominant at high temperatures. Comparing the results with those in the bed of alumina sand (Fig. 9), the yield of CO was similar in the two different bed materials from 773 to 973 K; beyond 973 K, the amount of CO produced in the Fe_2O_3 bed fell, probably because the Fe_2O_3 started to convert CO from 973 K. The yield of tar was also found to be lower in Fe_2O_3 from 873 to 1173 K, whilst the yield of CO_2 was much higher, indicating combustion of pyrolysed tar by Fe_2O_3 to mostly CO_2 , when the temperature exceeded 873 K. From 773 to 1073 K, the yield of CH_4 in Fe_2O_3 was higher than that in alumina sand; at 1173 K, the value was lower. It seems that CH_4 is also a

product from the reaction between tar and Fe_2O_3 at low temperatures. When the temperature increased to 1173 K, Fe_2O_3 became reactive for the conversion of CH_4 . Conversion of CH_4 by Fe_2O_3 -based materials usually occurs at temperatures above 1123 K, depending on the composition, preparation method and particle size of the material [35,36]. The char yields in the beds of alumina sand and Fe_2O_3 were similar, indicating no direct solid-solid reaction between char and Fe_2O_3 .

Figure 10 Yield (mass of carbon / mass of carbon in the fuel) of different carbon-containing species in a bed of Fe_2O_3 from 773 to 1173 K.

3.5 Pyrolysis of wood with mayenite-supported CuO and Cu_2O

Figure 11 shows the yield of each product in a fluidised bed of CuO supported on mayenite. Comparing Figs. 11 and 9, mayenite-supported CuO was effective in combusting pyrolysis products *in situ*. The products of pyrolysis were converted mainly to CO_2 , especially at 1173 K, where CO_2 constituted of ~ 87 % of the products. Comparing the results with the pyrolysis in Fe_2O_3 , mayenite-supported CuO exhibited higher reactivity for the conversion of pyrolysis products to CO_2 . Similar to Fe_2O_3 and alumina sand, there was no significant solid-solid reaction between mayenite-supported CuO and char from 773 to 1073 K. When the temperature reached 1173 K, mayenite-supported CuO consumed most

of the char generated. This high reactivity of mayenite-supported CuO at 1173 K could have come from the change in the form of oxygen supply. CuO tends to release significant amount of gaseous oxygen [37] and form Cu₂O: $\text{CuO} = \text{Cu}_2\text{O} + \text{O}_2$. At low temperatures, this effect can be ignored. At 1173 K, due to the presence of gaseous oxygen, there seem to have been both gas-gas reaction between gaseous pyrolysis products and released oxygen, and solid-gas reaction between char and the released oxygen. The effect of released oxygen from CuO at higher temperatures was further confirmed by comparing the results from a bed of Cu₂O (which does not release oxygen).

Figure 11 Yield (mass of carbon / mass of carbon in the fuel) of different carbon-containing products species in a bed of mayenite-supported CuO from 773 to 1173 K.

Figure 12 shows the pyrolysis of wood chips in a bed of mayenite-supported Cu₂O. For each temperature, with and without plasma, experiments were carried out consecutively, with no regeneration between the two (to prevent re-oxidation to the CuO). The amount of oxygen available in the Cu₂O was always in excess of that needed for complete combustion (*i.e.* ~ 0.88 g of Cu₂O was needed for every 0.0538 g wood) for two experiments. To remove any systematic effect of the order in which the experiments were performed, experiments were repeated with the order of the two reversed; this showed the results were not influenced by the conversion of the oxygen carrier. After two

experiments at each temperature, the bed was burned off in air to quantify the amount of char. The amount of char at each temperature was then obtained by taking half of carbon content in CO and CO₂ generated during burn-off.

Figure 12 Yield (mass of carbon / mass of carbon in the fuel) of different carbon-containing products species in a bed of mayenite-supported Cu₂O from 773 to 1173 K.

4 Discussion

4.1 Approach to tar quantification

The use of an oxygen containing DBD plasma to convert volatile (*i.e.* tarry) species was shown to give good results in the experiments outline here. The key uncertainty was whether the plasma was able to convert all the species entering the sampling line into species detectable by the gas analyser. The good carbon balances obtained here, showed that for these experiments, all the carbon could be accounted for correctly, indicating complete or near complete conversion of the tars. Ideally, the downstream analysis of the gases could use relatively cheap infra-red analysers, rather than the more costly FTIR used here. Here, the carbon in the tar was defined to be any material that condensed in the trap at 0°C that was not carbon in CH₄, CO₂ or CO. Any lighter species entering the plasma reactor that did not condense would have produce erroneous values. In this particular case, using an FTIR confirmed that only trace amounts of such species were produced, and not in sufficient quantity to substantially alter the carbon balance. As noted, in the introduction, the definition of “tar” is somewhat arbitrary and must

either be related to a standard or it is effectively defined by how it is collected. The choice of the 0°C is in line with other works [38,39], which also used trapping system in ice bath for tar collection from upstream. The trapping system used here could be modified to change the tars collected, if required. However, here the main interest was in being able to account for the fate of the carbon released by the volatile matter.

Another significant issue with the method for measuring tar used here is that it is time-consuming (*i.e.* requiring two experiments) and does not give an instantaneous online measurement. Other ways of carrying out the tar measurement were also attempted. Firstly, an idea of using two sampling lines was tested. The sampling line from the fluidised bed to the point where the air was introduced was unchanged. After the air mixing, the stream was divided into two, with 50% of the flow going to a “blank” reactor with the same dimensions as the plasma reactor prior to an analyser, the other going to the plasma reactor prior to FTIR. The difference between the signals from the two analysers indicates the amount of tar entering each sampling line. This method simplified the experimental procedure, as only one experiment was needed to measure the tar yield. However, it was found difficult to control the flow conditions in the two sampling lines to be perfectly identical. Any variation between the two flow rates led to significant differences in the results. Additionally, the error caused by the difference in calibration, and residence time of the two analysers (in addition to the FTIR, and an infrared photometer Uras26 ABB analyser was also used) could not be neglected. Practically, better engineering of the two sampling lines, more stringent control of the flow rates, and using identical analysers would largely increase the feasibility of the application of this method. Secondly, the plasma was pulsed on and off during one experiment. In a continuous pyrolysis process, where the tar fraction does not change with time, it is possible to apply this approach. However, the idea was found to be unsuitable for the experiments here because the response time of the plasma reactor (*i.e.* on/off) must be quick enough than the pyrolysis time. Here, the plasma system took ~ 5 seconds to fully activate or deactivate, which is not sufficiently short compared to ~ 30 seconds pyrolysis time here. Thus, although the method used here to quantify the tar worked well, more work is needed if this method is to be adapted for general use.

4.2 Reactivity of pyrolysis products with oxygen carriers

The order of reactivity of pyrolysis products (CO, CH₄, tar) with active bed materials can be determined by comparing Figs. 9, 10, and 11. According to Figs. 9 and 10, at the lowest temperature (773 K), the presence of Fe₂O₃ caused a slight decrease in CO and tar yields; the yield of CH₄ increased a little due to the decomposition of tar. Thus, CO and tar are more reactive towards the oxygen carriers than CH₄. This is consistent with the reported findings that the oxidation of CH₄ by oxygen carriers (*e.g.* Fe₂O₃) is usually more difficult than that of other carbon-containing species such as CO [40]. Comparing the product distribution at 773 K in alumina sand and mayenite-supported CuO, there was a clear increase in CO₂, and decrease in CO while no clear drop in tar yield in the bed of mayenite-supported CuO. In this case, CO was considered to react more readily with the active bed materials. Thus, the order of the reactivity of gaseous product species is likely to be CO > tar > CH₄.

Fe₂O₃, mayenite-supported CuO and mayenite-supported Cu₂O all helped tar abatement inside the fluidised bed within the short residence time (~ 1 second), as shown in Fig.13. The increase in temperature clearly improved the conversion of tar in the bed materials. Mayenite-supported CuO was especially effective for combustion at high temperatures (*e.g.* 1073 and 1173 K), exhibiting its potential as an oxidant for the direct combustion of biomass in a fluidised bed system.

Figure 13 Tar conversions in different fluidised bed conditions.

Mayenite has previously been shown to be an ideal support for CuO in chemical looping system if the CLOU effect is to be preserved [27]. Other support materials such as Al₂O₃ form mixed oxides with the copper oxide which can lead to agglomeration of the particles and reduce the partial pressure of oxygen [41]. At 1073 K, the oxygen mole fraction at atmospheric pressure produced by CuO should be about 0.0016; at 1173 K, it reached 0.018 (calculated from MTDATA [42]). Thus, at 1173 K, there could have been both gas-gas reaction between gaseous pyrolysis products and released oxygen, and solid-gas reaction between char and the oxygen.

Comparing the mole fractions of CO, tar and CH₄ in Figs. 11 and 12, reactivity of Cu₂O and CuO for the conversion tar was similar from 773 to 973 K. More CH₄ was detected in Cu₂O, indicating that CuO is more reactive than Cu₂O towards CH₄. When the temperature reached 1073 K, the yield of tar in CuO dropped whilst it remained high in Cu₂O. At 1173 K, the difference was more significant in that both tar and char still contributed a large portion to the total yield in a bed of Cu₂O, but not in CuO. The clear difference observed at 1073 and 1173 K suggests that gaseous oxygen from CuO is the primary cause for the reduction of in the amounts of char and tar at 1173 K.

5. Conclusions

- (1) A plasma system for the on-line continuous quantification of tar was designed and placed in the downstream of a fluidised bed. The plasma system was found to be effective for tar conversion. The method for tar quantitation worked well, giving good carbon balances. Improvements to the response time of the gas analysers, and better control of the flow rates would allow more rapid measurements of the rates of tar production.
- (2) Pyrolysis of wood with alumina sand in the fluidised bed was studied. It was shown that higher temperature promoted the production of gaseous products. Tar was found as the primary product from pyrolysis from 773 to 1173 K. When the bed temperature increased to above 1073 K, the tar formed cracked to CH₄.

(3) Fe_2O_3 , mayenite-supported Cu_2O , and mayenite-supported CuO were found effective for *in situ* conversion of tar in the fluidised bed. The tar was mostly combusted to CO_2 . Mayenite-supported CuO was found to be the most reactive with the pyrolysis products, and was particularly effective for converting tar and char at 1173 K due to its ability to uncouple oxygen. The results demonstrated the promising feasibility of CLC or CLOU of biomass, without any active fluidising gas.

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Supplementary materials

S1 V - q Lissajous curve

Figure S1 A typical V - q Lissajous curve from a typical experiment, with frequency of 22 kHz, and voltage 14.4 kV for the DBD reactor. The fluidised bed was operated at 873 K, with mayenite-supported CuO as the bed. The sampled gas from the fluidised bed was diluted by air before entering the DBD reactor. The energy input was obtained by taking the area enclosed by the curve.

S2 Correction of the flow

Without plasma

The change in composition of the gases can affect the total flow rate through the sampling line. In particular, the generated tar (without plasma running) appeared to block the sampling line. To resolve this issue for the purpose of tar quantification, a correction for the change in flow rate was applied. The air flow F_{air} introduced to mix with product flow from the fluidised bed was assumed to be constant at 0.45 L/min, and when there was no plasma (*i.e.* oxygen was not consumed) the oxygen in the air flow was used as a tracer species. The total flow rate in the sampling line during the experiment F_{total} could therefore be expressed as:

$$F_{\text{total}} = \frac{F_{\text{air}} \times 0.21}{x_{\text{O}_2}}.$$

Here, x_{O_2} is the mole fraction of oxygen detected by the ABB analyser, with 0.21 being oxygen mole fraction in undiluted air.

Ideally, if it is assumed that no change in sample gas flow occurs, the “ideal” mole fractions of product species detected by the analyser would be:

$$x_{i,\text{ideal}} = \frac{F_{\text{FB,initial}} \times y_i}{F_{\text{FB,initial}} + F_{\text{air}}} \quad \text{Eq.S1}$$

$$x_i = \frac{F_{\text{FB}} \times y_i}{F_{\text{FB}} + F_{\text{air}}} \quad \text{Eq.S2}$$

In Eq.S1, $x_{i,\text{ideal}}$ is the “ideal” mole fraction of the product species i detected by the analyser, assuming negligible change in the total flow rate. $F_{\text{FB,initial}}$ is initial flow rate of the gas stream that enters to the sampling line and y_i is the mole fraction of species i in the gas flow from the fluidised bed. For the non-ideal case (when flow rate changes), the flow rate of the gas from the fluidised bed, F_{FB} , will be lower than $F_{\text{FB,initial}}$, which leads to lower measured mole fractions of the product species i , x_i . By combining Eqs.S1 and S2 to eliminate y_i , and rearranging:

$$x_{i,\text{corrected}} = \frac{x_i \times F_{\text{total}} \times F_{\text{FB,initial}}}{F_{\text{total,initial}} \times F_{\text{FB}}},$$

where

$$F_{\text{total}} = F_{\text{FB}} + F_{\text{air}}.$$

Corrected, “ideal” mole fractions of the products species were used for the calculation of yields.

Figure S2 Mole fractions of CO₂ before and after correction of the flow, with operating conditions of a Fe₂O₃ bed at 873 K in the fluidised bed without plasma discharge in the DBD reactor. The measured mole fraction of O₂ is also shown. Note that the wood was fed into the fluidised bed at $t = 30$ s.

Figure S2 shows the results in a Fe₂O₃ bed at 873 K, without plasma running. The oxygen, which was expected to be inert, increased slightly when the wood was fed into the bed. The corrected CO₂ curve based on the measured oxygen curve is largely similar to that before correction, suggesting that the change in the flow did not have a significant effect on the concentration of CO₂ measured. A similar observation was made when using other gases and at different temperatures.

With plasma

In the case when there was plasma, oxygen from the air stream can no longer be used as the trace species, as it was consumed to burn the tar and possibly convert CO to CO₂. In order to correct for changes in the dilution, the oxygen concentration before the plasma reactor was required. It was assumed that the drop in the measured oxygen level was all used to burn the tar and possibly convert CO to CO₂. Assuming that the tar was oxygen-free, then the difference in total O₂ content in the CO and CO₂ between the experiments with and without plasma all comes from the oxygen being consumed. Oxygen was also being consumed to produce water during tar combustion, and this amount depends on the chemical formula of the tar:

The amount of oxygen consumed for converting the carbon in tar to CO and CO₂, $F_{O_2,C}$, is,

$$F_{O_2,C} = \left(\frac{1}{2}F_{CO,on} + F_{CO_2,on}\right) - \left(\frac{1}{2}F_{CO,off} + F_{CO_2,off}\right).$$

Here, $F_{O_2,C}$ is the molar flow rate of oxygen consumed for burning the carbon content of tar, $F_{CO,on}$ and $F_{CO_2,on}$ are respectively the mole flow rate of CO and CO₂ with plasma running, and subscript ‘off’ indicates the condition without plasma. Taking into account the stoichiometry of the tar, $F_{O_2,tar}$, the mole flow rate of oxygen consumed for burning the tar is,

$$F_{O_2,tar} = F_{O_2,C} * \left(1 + \frac{\frac{1}{4}y}{x}\right).$$

The flow of oxygen through the sampling line, in the absence of combustion, *i.e.* the flow entering the plasma reactor, is then

$$F_{O_2} = F_{O_2,tar} + F_{O_2,measured}.$$

Figure S3 shows the comparison of before and after correction to the flowrates of the mole fractions obtained from a bed of Fe₂O₃ at 873 K. In Figure S3 (a), the measured oxygen level significantly fell when the wood was dropped into the fluidised bed. All the three tar compounds could restore the oxygen

profile at the inlet of the plasma reactor, to close to the initial value, among which the correction based on pure carbon appeared to be the best. However, a tar compound should contain some hydrogen. The fact that pure carbon could restore the oxygen profile best is a combined effect of: 1) the tar itself might be mainly aromatics, which has very high C to H ratio; 2) the tar might contain some oxygen, which would lead to an over-estimation of the oxygen consumed for burning the carbon content in the tar; 3) incomplete combustion in the plasma reactor; 4) fluctuation in the background flow.

Figure S3 (b) gives the corrected CO_2 mole fraction based on an oxygen level restored using pure carbon tar compound. There is tiny difference between the corrected and the measured values, suggesting that with plasma running there is no need to correct for changes in dilution in the sampling line; qualitatively, little change in flow was observed when the plasma was active.

(a)

(b)

Figure S3 Mole fraction profiles at 873K in a Fe_2O_3 bed with plasma discharge a) measured oxygen mole fraction and calculated mole fraction at the inlet to the plasma reactor, based on different tar compound b) comparison of the CO_2 before and after correction of the flow. Note that the plasma was turned on at $t = 10$ s, and wood was fed into the fluidised bed at $t = 20$ s.

Reference

- [1] J. Adanez, A. Abad, F. Garcia-Labiano, P. Gayan, L.F. de Diego, Progress in Chemical-Looping Combustion and Reforming technologies, Prog. Energy Combust. Sci. 38 (2012) 215–282. doi:10.1016/j.pecs.2011.09.001.
- [2] L.-S. Fan, F. Li, Chemical Looping Technology and Its Fossil Energy Conversion Applications, Ind. Eng. Chem. Res. 49 (2010) 10200–10211. doi:10.1021/ie1005542.
- [3] T.A. Brown, F. Scala, S.A. Scott, J.S. Dennis, P. Salatino, The attrition behaviour of oxygen-carriers under inert and reacting conditions, Chem. Eng. Sci. 71 (2012) 449–467. doi:10.1016/J.CES.2011.11.008.
- [4] C. Dueso, M. Ortiz, A. Abad, F. García-Labiano, L.F. de Diego, P. Gayán, J. Adánez, Reduction and oxidation kinetics of nickel-based oxygen-carriers for chemical-looping combustion and

- chemical-looping reforming, *Chem. Eng. J.* 188 (2012) 142–154. doi:10.1016/J.CEJ.2012.01.124.
- [5] X. Zhao, H. Zhou, V.S. Sikarwar, M. Zhao, A.-H.A. Park, P.S. Fennell, L. Shen, L.-S. Fan, Biomass-based chemical looping technologies: the good, the bad and the future, *Energy Environ. Sci.* 10 (2017) 1885–1910. doi:10.1039/C6EE03718F.
- [6] P. Cho, T. Mattisson, A. Lyngfelt, Comparison of iron-, nickel-, copper- and manganese-based oxygen carriers for chemical-looping combustion, *Fuel*. 83 (2004) 1215–1225. doi:10.1016/j.fuel.2003.11.013.
- [7] H. Ge, L. Shen, H. Gu, S. Jiang, Effect of co-precipitation and impregnation on K-decorated Fe₂O₃/Al₂O₃ oxygen carrier in Chemical Looping Combustion of bituminous coal, *Chem. Eng. J.* 262 (2015) 1065–1076. doi:10.1016/j.cej.2014.10.021.
- [8] T.A. Brown, J.S. Dennis, S.A. Scott, J.F. Davidson, A.N. Hayhurst, Gasification and Chemical-Looping Combustion of a Lignite Char in a Fluidized Bed of Iron Oxide, *Energy & Fuels*. 24 (2010) 3034–3048. doi:10.1021/ef100068m.
- [9] T. Mendiara, J.M. Johansen, R. Utrilla, P. Geraldo, A.D. Jensen, P. Glarborg, Evaluation of different oxygen carriers for biomass tar reforming (I): Carbon deposition in experiments with toluene, *Fuel*. 90 (2011) 1049–1060. doi:10.1016/j.fuel.2010.11.028.
- [10] M. Rydén, P. Moldenhauer, T. Mattisson, A. Lyngfelt, M. Younes, T. Niass, B. Fadhel, J.-P. Ballaguet, Chemical-Looping Combustion with Liquid Fuels, *Energy Procedia*. 37 (2013) 654–661. doi:10.1016/j.egypro.2013.05.153.
- [11] T. Mendiara, a. Abad, L.F. de Diego, F. García-Labiano, P. Gayán, J. Adánez, Biomass combustion in a CLC system using an iron ore as an oxygen carrier, *Int. J. Greenh. Gas Control*. 19 (2013) 322–330. doi:10.1016/j.ijggc.2013.09.012.
- [12] H. Gu, L. Shen, J. Xiao, S. Zhang, T. Song, Chemical looping combustion of biomass/coal with natural iron ore as oxygen carrier in a continuous reactor, *Energy and Fuels*. 25 (2011) 446–455.

doi:10.1021/ef101318b.

- [13] J. Zeng, R. Xiao, H. Zhang, Y. Wang, D. Zeng, Z. Ma, Chemical looping pyrolysis-gasification of biomass for high H₂/CO syngas production, *Fuel Process. Technol.* 168 (2017) 116–122. doi:10.1016/j.fuproc.2017.08.036.
- [14] Y. Shen, K. Yoshikawa, Recent progresses in catalytic tar elimination during biomass gasification or pyrolysis—A review, *Renew. Sustain. Energy Rev.* 21 (2013) 371–392. doi:10.1016/J.RSER.2012.12.062.
- [15] A. Sarvaramini, F. Larachi, Integrated biomass torrefaction – Chemical looping combustion as a method to recover torrefaction volatiles energy, *Fuel.* 116 (2014) 158–167. doi:10.1016/J.FUEL.2013.07.119.
- [16] M. Xu, R.C. Brown, G. Norton, J. Smeenk, Comparison of a solvent-free tar quantification method to the International Energy Agency’s tar measurement protocol, *Energy and Fuels.* 19 (2005) 2509–2513. doi:10.1021/ef0501703.
- [17] T.A. Milne, R.J. Evans, N. Abatzoglou, Biomass Gasifier “Tars”: Their Nature, Formation, and Conversion, 1998. doi:10.2172/3726.
- [18] S.M. Nunes, N. Paterson, A.A. Herod, D.R. Dugwell, R. Kandiyoti, Tar formation and destruction in a fixed bed reactor simulating downdraft gasification: Optimization of conditions, *Energy and Fuels.* 22 (2008) 1955–1964. doi:10.1021/ef700662g.
- [19] J.-S. Chern, The pyrolysis and devolatilisation of coal in a fluidised bed, University of Cambridge, 1997.
- [20] T. Mattisson, A. Lyngfelt, H. Leion, Chemical-looping with oxygen uncoupling for combustion of solid fuels, *Int. J. Greenh. Gas Control.* 3 (2009) 11–19. doi:10.1016/j.ijggc.2008.06.002.
- [21] Y. Huang, S. Dai, F. Feng, X. Zhang, Z. Liu, K. Yan, A comparison study of toluene removal by two-stage DBD-catalyst systems loading with MnO_x, CeMnO_x, and CoMnO_x, *Environ. Sci. Pollut. Res.* 22 (2015) 19240–19250. doi:10.1007/s11356-015-5121-3.

- [22] J. Karuppiah, E.L. Reddy, P.M.K. Reddy, B. Ramaraju, R. Karvembu, C. Subrahmanyam, Abatement of mixture of volatile organic compounds (VOCs) in a catalytic non-thermal plasma reactor., *J. Hazard. Mater.* 237–238 (2012) 283–9. doi:10.1016/j.jhazmat.2012.08.040.
- [23] S. Sultana, A. Vandenbroucke, C. Leys, N. De Geyter, R. Morent, Abatement of VOCs with Alternate Adsorption and Plasma-Assisted Regeneration: A Review, *Catalysts*. 5 (2015) 718–746. doi:10.3390/catal5020718.
- [24] T. Pham Huu, S. Gil, P. Da Costa, A. Giroir-Fendler, A. Khacef, Plasma-catalytic hybrid reactor: Application to methane removal, *Catal. Today*. 257 (2015) 86–92. doi:10.1016/j.cattod.2015.03.001.
- [25] D.P. Haughey, G.S.G. Beveridge, Structural properties of packed beds — A review, *Can. J. Chem. Eng.* 47 (1969) 130–140. doi:10.1002/cjce.5450470206.
- [26] S.C. Reyes, E. Iglesia, Monte carlo simulations of structural properties of packed beds, *Chem. Eng. Sci.* 46 (1991) 1089–1099. doi:10.1016/0009-2509(91)85102-4.
- [27] W. Hu, F. Donat, S.A. Scott, J.S. Dennis, Kinetics of oxygen uncoupling of a copper based oxygen carrier, *Appl. Energy*. 161 (2016) 92–100. doi:10.1016/j.apenergy.2015.10.006.
- [28] K.H. Becker, U. Kogelschatz, K.H. Schoenbach, R.J. Barker, Non-equilibrium air plasmas at atmospheric pressure, 2005. doi:10.1016/0006-291X(79)91191-4.
- [29] C.Y. Wen, Y.H. Yu, A generalized method for predicting the minimum fluidization velocity, *AIChE J.* 12 (1966) 610–612. doi:10.1002/aic.690120343.
- [30] O. Karatum, M.A. Deshusses, A comparative study of dilute VOCs treatment in a non-thermal plasma reactor, *Chem. Eng. J.* 294 (2016) 308–315. doi:10.1016/j.cej.2016.03.002.
- [31] A. Baylet, P. Marécot, D. Duprez, X. Jeandel, K. Lombaert, J.M. Tatibouët, Synergetic effect of plasma/catalysis hybrid system for CH₄ removal, *Appl. Catal. B Environ.* 113 (2012) 31–36. doi:10.1016/j.apcatb.2011.10.026.

- [32] Prabier Basu, Biomass Gasification, Pyrolysis and Torrefaction: Practical Design and Theory, Academic Press, 2013.
- [33] R.J. Evans, T.A. Milne, Chemistry of Tar Formation and Maturation in the Thermochemical Conversion of Biomass, in: Dev. Thermochem. Biomass Convers., Springer Netherlands, Dordrecht, 1997: pp. 803–816. doi:10.1007/978-94-009-1559-6_64.
- [34] R. Luque, J.G. Speight, Gasification for Synthetic Fuel Production, 2015. doi:10.1016/B978-0-85709-802-3.00001-1.
- [35] S. Bhavsar, B. Tackett, G. Vesper, Evaluation of iron- and manganese-based mono- and mixed-metallic oxygen carriers for chemical looping combustion, Fuel. 136 (2014) 268–279. doi:10.1016/j.fuel.2014.07.068.
- [36] S.K. Haider, G. Azimi, L. Duan, E.J. Anthony, K. Patchigolla, J.E. Oakey, H. Leion, T. Mattisson, A. Lyngfelt, Enhancing properties of iron and manganese ores as oxygen carriers for chemical looping processes by dry impregnation, Appl. Energy. 163 (2016) 41–50. doi:10.1016/j.apenergy.2015.10.142.
- [37] F. Donat, W. Hu, S.A. Scott, J.S. Dennis, Characteristics of Copper-based Oxygen Carriers Supported on Calcium Aluminates for Chemical-Looping Combustion with Oxygen Uncoupling (CLOU), Ind. Eng. Chem. Res. 54 (2015) 6713–23. doi:10.1021/acs.iecr.5b01172.
- [38] D.K. Shen, S. Gu, The mechanism for thermal decomposition of cellulose and its main products, Bioresour. Technol. 100 (2009) 6496–6504. doi:10.1016/J.BIORTECH.2009.06.095.
- [39] S. Nakamura, U. Siriwat, K. Yoshikawa, S. Kitano, Development of Tar Removal Technologies for Biomass Gasification using the By-products, Energy Procedia. 75 (2015) 208–213. doi:10.1016/J.EGYPRO.2015.07.305.
- [40] S. Kwon, M. Fan, T.D. Wheelock, Catalytic Oxidation of CO and CH₄ as Well as Mixture of CO and CH₄ with Nano and Micro Fe₂ O₃, Environ. Eng. Sci. 24 (2007) 1065–1071. doi:10.1089/ees.2006.0227.

- [41] S. Chuang, J. Dennis, A. Hayhurst, S. Scott, Development and performance of Cu-based oxygen carriers for chemical-looping combustion, *Combust. Flame.* 154 (2008) 109–121. doi:10.1016/j.combustflame.2007.10.005.
- [42] R.H. Davies, A.T. Dinsdale, J.A. Gisby, J.A.J. Robinson, S.M. Martin, MTDATA-thermodynamic and phase equilibrium software from the national physical laboratory, *Calphad.* 26 (2002) 229–71. doi:10.1016/S0364-5916(02)00036-6.