



Research paper

Mechanical impregnation of Pd-Sn/alumina and Cu-Mn/graphite on charcoal to minimise carbon monoxide emissions

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HIGHLIGHTS

- Charcoal was modified to reduce carbon monoxide (CO) emissions.
- The residual CO was only 3.5% when charcoal was impregnated with 1% (w/w) Pd-Sn/alumina.
- The residual CO was only 16.7% when charcoal was impregnated with 5% (w/w) Cu-Mn/graphite.
- Catalyst loading and lower temperatures promoted CO oxidation.

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ABSTRACT

This study investigated how to minimize carbon monoxide (CO) emissions from charcoal by impregnating with Pd-Sn/alumina and Cu-Mn/graphite. Samples were heated isothermally with continuous monitoring of residual CO using electrochemical and infra-red sensors. With 0.2 wt% Pd-Sn/alumina, 26.9% and 44.4% were recorded as lowest and highest residual CO. On the other hand, when 2 wt% Cu-Mn/graphite was used, 15.6%, and 25.3% were observed as lowest and highest residual CO. The activity of the catalysts decreased with temperature and increased with catalyst loading. This method could be used on briquettes, wood boiler chips and other solid carbonaceous materials to minimise CO emissions.

1. Introduction

Charcoal from woody biomass is one of the high energy materials (calorific value ≈ 30 MJ/kg) used for cooking and heating. As it burns, charcoal releases several by-products that are dependent on its properties and the prevailing conditions. Complete combustion yields mainly carbon dioxide (CO₂) and moisture while incomplete combustion yields carbon monoxide (CO), carbon dioxide, particulate matter, volatile organic compounds, carbonyls among others [1]. Charcoal usage has led to a lot of unintentional CO poisoning resulting in the death of many people with countless near misses and chronic injuries [2–5]. On the other hand, CO poisoning from charcoal has been used as a method to commit suicide [6–9].

Efforts have been made through combustion equipment design to achieve near-complete combustion [10–14] for maximum CO oxidation. However, these systems have not been very successful, and they still expose charcoal users to high concentrations of CO. Other researchers have resorted to CO oxidation using metal/metal oxide catalysts or several combinations.

The unique adsorption properties and reactivity of CO on metal/oxide surfaces have enabled researchers to oxidize it to CO₂. The chemisorption behavior of CO on metals has been reported to vary considerably, with the heats of chemisorption increasing with the metal surface density for platinum, rhodium, and ruthenium. For palladium and iridium, a reverse order was observed; heats of chemisorption followed the trend – Pd \approx Ir > Pt > Rh > Ru \approx Ni > Co \gg Cu. There is a general decrease in heats of chemisorption on metal surfaces with CO and O₂ coverage. Oxygen is chemisorbed dissociatively on metal surfaces, with the heats of dissociative chemisorption decreasing in the order: W > Mo > Fe > Co > Ir \approx Ru > Rh \approx Ni > Cu > Pt > Pd > Ag > Au [15].

The presence of a supporting material has a crucial effect on the activity of metal/oxide catalysts. For example, CuO is unstable when not supported, and the oxidation state of copper usually varies depending on temperature and the CO:O₂ ratio. The three oxidation states (Cu²⁺, Cu⁺ and even Cu⁰) may coexist, during a reaction. Addition of a support like zirconia or alumina to CuO increases its activity by

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10–200-fold. Supported copper oxide catalysts are also more tolerant to potential poisons like SO_2 . The support enhances the co-existence of Cu^{2+} , Cu^+ , and Cu^0 species especially when appropriate pre-treatments are applied or by using the right set of supports. However, the catalyst is deactivated by moisture [15].

Manganese/oxides work best with other elements, like copper, cobalt, Nickel, and Lanthanum, forming manganites. This combination enhances Mn as a catalyst for oxidation of CO. It forms three principal oxides: MnO_2 , Mn_2O_3 or Mn_3O_4 . Mn_2O_3 is the most stable and very active. It has four polymorphs, denoted as alpha-, beta-, gamma-, and delta- MnO_2 . Alpha and delta- MnO_2 are the most active polymorphs for CO oxidation compared to gamma- and beta- MnO_2 . This is attributed to the strength of the Mn-O bond (alpha < delta < gamma < beta); with the strongest Mn-O bond responsible to less activity of the corresponding oxide [15].

Fuchs et al. [16] found that the rate of adsorption of CO was controlled by the oxidation of CO using palladium. The adsorption on the metal surface follows the Langmuir-Hinshelwood mechanism [17,18]. Bi et al. [19] found that the CO oxidation activity of Pd/NaZSM-5 decreased with the increase of calcination temperature and increased with the increase of Pd concentration. The decreased activity with calcination could be linked to the increase in crystallinity of the support and decrease in metal/support interaction [20].

Kondrat et al. [21] found that the ability to control phase formation (Cu-oxides and Mn-oxides) in Cu-Mn/support catalyst with heat treatment allows their catalytic potential for CO oxidation to be assessed. The presence of the CuMn_2O_4 phase within the catalyst mix is linked to high activity for CO oxidation. Retention of carbon dioxide as a by-product as well as contact with moisture poisons the catalyst, however, expelling the moisture at moderate temperatures restores the catalytic activity [22]. The activity of Cu-Mn generally decreases with temperature [23]. Highly homogeneous catalysts are found to be more active than less homogeneous ones for ambient temperature oxidation of CO [24].

All the studies mentioned above have done CO oxidation by passing the gas through/over a catalyst either in a fixed bed or a reactor of some sort. Up-to-date, there has not been any study focusing on ensuring the safety of charcoal by impregnating it with catalysts. This study differentiates itself by mechanically mixing the catalysts with charcoal to form a product with high homogeneity. Commercial Pd-Sn/alumina and Cu-Mn/graphite have been used in this study. Different concentrations of the catalysts were mixed with the charcoal mechanically, and the catalyst activity was tested by heating the product isothermally at different temperatures in the range 300–600 °C with residual CO measurement and recording. The catalyst activity was tested by monitoring the residual CO evolved as a function of temperature and catalyst concentration.

2. Methodology

2.1. Materials

Charcoal used in this study was produced using a controlled laboratory muffle furnace by pyrolysis of wood in a sealed retort heated for 4 h at 500 °C. This charcoal was ground by a laboratory vibratory pulverizer (Essa LM2 pulverizing mill) and sieved through a 210 μm mesh. Commercial catalysts, Pd-Sn/alumina and Cu-Mn/graphite purchased from Moleculite Products Limited were mechanically mixed together with the charcoal in different proportions (0.2w%, 1w%, 2w%, 5w% – catalyst) in a mortar and pestle to achieve a homogeneous product.

2.2. Material characterisation

The commercial catalysts Pd-Sn/alumina and Cu-Mn/graphite as well as the catalyst treated charcoal were characterised using thermogravimetric analysis (TGA), X-Ray Diffraction (XRD), and X-Ray Fluorescence (XRF). Thermogravimetric analysis was performed on a Mettler Toledo DSC/TGA3+ in an air environment at 50 ml/min, with a non-isothermal mode. Diffraction patterns were recorded with a Panalytical X'Pert diffractometer using Cu-K α radiation. The powdered catalyst was loaded on to low background scattering (off-cut silicon) XRD holders. A PIXcel strip detector was used to collect data as stepped scans across an angular range of 10–80 2 θ degrees. The quantities of elements present in the ash were analysed using the SEA6000VX bench-top X-ray fluorescence instrument manufactured by Seiko instruments (Nano technology Incorporated). The measurement conditions used were; a sample standard (RTC-CRM002-100G from LGC) and a Rhodium tube as the target. The analysis conditions were; measurement time (100 s), collimator/spot size (1.2 \times 1.2 mm), tube voltage (50 kV), tube current (314 μA – in Auto mode), no filter and He purging environment.

2.3. Testing catalyst activity

Approximately 200 mg of the catalyst impregnated charcoal was tested for residual CO evolution. Charcoal samples were weighed (on an HF-300G analytical balance with an accuracy of ± 0.002 g) into a quartz boat and loaded into a quartz tube (diameter = 35 mm, length = 550 mm) in a horizontal Carbolite tube furnace, which had been pre-heated to a set temperature with a regulated constant air flow. The experiments were conducted isothermally, and the temperature of the furnace was controlled using a Eurotherm CTFI-1200 controller. Samples were heated at 300, 320, 340, 360, 380, 400, 420, 440, 460, 480, 500, 520, 540, 560, 580, and 600 °C, (with a combined uncertainty

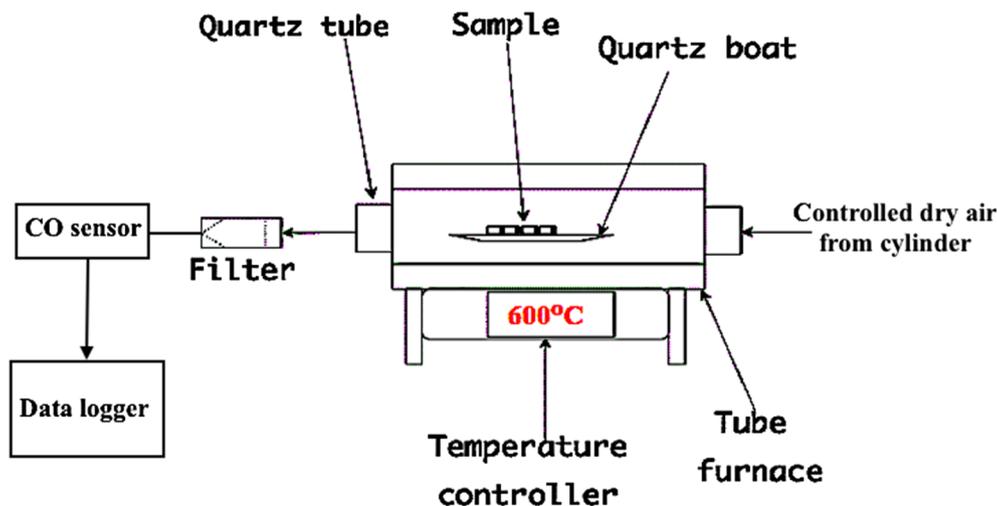


Fig. 1. Schematic of the experimental setup for CO quantification.

of $\pm 5^\circ\text{C}$) and at an air flow rate of 2 ± 0.1 (L/min) (all values are \pm combined uncertainty). Air flow was controlled by a calibrated ($R^2 = 0.99$) Platon rotameter flow meter. The CO was channelled through a $0.8\text{-}\mu\text{m}$ cellulose membrane filter, to remove any smoke particles, to a CO sensor which gave an output to a Squirrel 1200 data logger and recorded voltages at a rate of four data points per minute Fig. 1. The logger display was regularly inspected during the heating period until the reading had fallen to zero CO (indicating emissions were below the detection limit for the sensor). The sensor was calibrated by injecting measured volumes of pure CO from a gas-tight syringe into several Tedlar bags which had been filled with air from a cylinder at a known flow rate for a known length of time. Calibration graphs were constructed to cover the range of concentrations that the sensors could measure. The calibration graph ($R^2 = 0.99$) was used to calculate the concentrations of CO. All CO measurement experiments were performed in triplicate.

2.4. Percentage residual CO

The residual amount of carbon monoxide were computed from Eq. (1);

$$CO_{rT}(\%) = 100 - \left(\frac{CO_0 - CO_c}{CO_0} \right) * 100 \quad (1)$$

where CO_{rT} , CO_0 , and CO_c are the residual CO at any temperature T, carbon monoxide from untreated charcoal and carbon monoxide from catalyst treated charcoal.

3. Results and discussion

This study reports charcoal made safer from CO released by impregnating it with Cu-Mn and Pd-Sn based catalysts. The decomposition profiles of catalysts under air have been reported using thermogravimetric analysis. Phase composition of the as-received, and heat-treated catalysts were analysed using XRD. The composition of the resulting ash after combustion was analysed with XRF. The residual CO recorded as mole CO per mole carbon burnt are presented for untreated charcoal and catalyst-treated-charcoal as a function of temperature.

3.1. Thermogravimetric analysis of catalysts

Fig. 2 shows the TG and DTG thermographs for the Cu-Mn/graphite and Pd-Sn/Alumina catalysts obtained in air (50 ml/min) environment at $10^\circ\text{C}/\text{min}$ heating rate. The first peak on the Pd-Sn/alumina profile at 114°C corresponds to the loss of physically bound moisture; the second

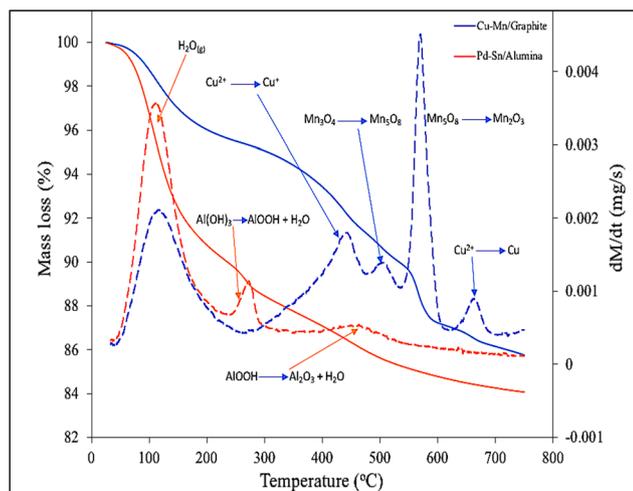


Fig. 2. TG and DTG for the Cu-Mn/graphite and Pd-Sn/alumina catalysts obtained in air (50 ml/min) environment at $10^\circ\text{C}/\text{min}$ heating rate.

peak at 272°C corresponds to the loss of chemically bound moisture from $\text{Al}(\text{OH})_3$ to form AlOOH . The third peak at 467°C corresponds to the final loss of chemically bound moisture from AlOOH to form Al_2O_3 . For the Cu-Mn/graphite TG and DTG profile, the first peak at 114°C corresponds to the loss of physically bound moisture. The second peak at 450°C corresponds to the conversion of Cu^{2+} to Cu^+ . The third peak at 500°C corresponds to the conversion of $\text{Mn}^{2.7+}$ to $\text{Mn}^{3.2+}$. The fourth peak at 550°C corresponds to the conversion of $\text{Mn}^{3.2+}$ to Mn^{3+} and the peak at 660°C could be attributed to the formation of copper metal from its ions. All these phase transformations are supported by X-Ray diffraction analysis performed on the catalysts at as-received samples and after heat treatment at 600°C discussed in the next section.

3.2. X-ray diffraction

Fig. 3(1) and (2) show the diffractograms of Cu-Mn/graphite and Pd-Sn/alumina. The phases MnO_2 (PDF - 30-820), CuMn_2O_4 (PDF -74-2422) and Graphite (PDF - 23-64) were identified in the as-received Cu-Mn/graphite catalyst. After heat treatment at 600°C for 3 h, $\text{Cu}_{1.5}\text{Mn}_{1.5}\text{O}_4$ (PDF - 35-1030), Mn_5O_8 (PDF - 20-718), Mn_2O_3 (PDF - 2-898) and graphite (PDF - 23-64) were identified. The presence of Mn_5O_8 , Mn_2O_3 in the heat treated catalyst is consistent with the observations of Augustin et al. [25] who monitored phase transformations of manganese oxides by in-situ calcination of Mn(II) glycolate. In their study, Mn_3O_4 at 18.0° was formed at about 185°C after the Mn(II) glycolate peaks had disappeared. The decreasing intensity of Mn_3O_4

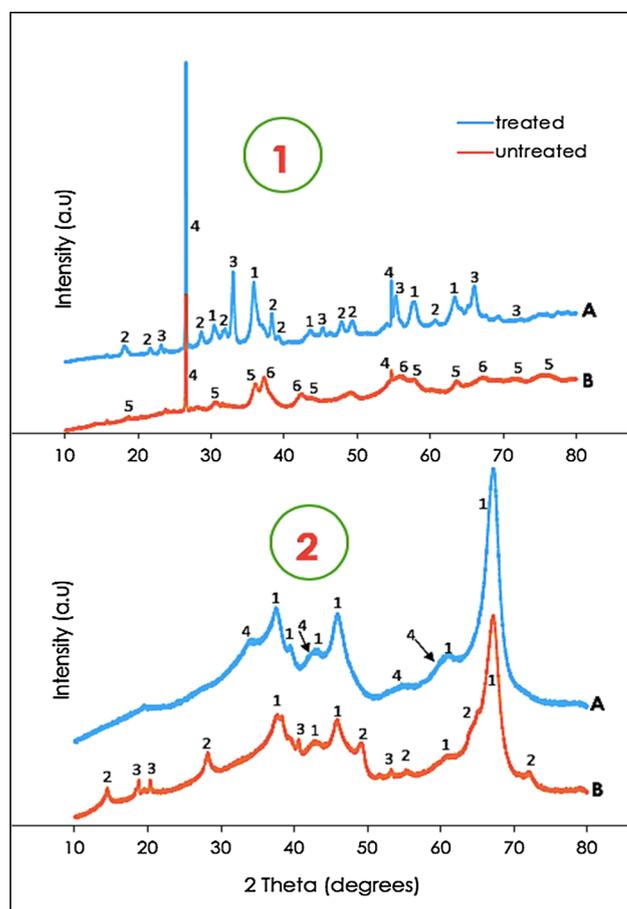
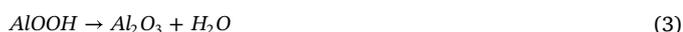


Fig. 3. (1) – XRD profile of Cu-Mn/graphite catalyst: B – before heat treatment and A – after heat treatment at 600°C for 3 h. The numbers 1, 2, 3, 4, 5, and 6 represent the phases: $\text{Cu}_{1.5}\text{Mn}_{1.5}\text{O}_4$, Mn_5O_8 , Mn_2O_3 , C (graphite), CuMn_2O_4 , and MnO_2 respectively. (2) – XRD profile of Pd-Sn/alumina: A – before heat treatment and B – after heat treatment at 600°C for 3 h. The numbers 1, 2, 3, and 4 represent the phases: Al_2O_3 , $\text{AlO}(\text{OH})$, $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ and PdO respectively.

peaks was accompanied by an increase in the intensity of the Mn_5O_8 at about 350 °C. At 550 °C, the peaks assigned to Mn_5O_8 disappeared after the appearance of the more stable α - Mn_2O_3 reflection at 23.2°. Basahel et al. [23] also confirmed the presence of $Cu_{1.5}Mn_{1.5}O_4/CuO$ after calcination of Cu-Mn catalyst at 550 °C.

For Pd-Sn/Alumina catalyst, the phases $AlO(OH)$ (PDF- 83-2384), $Al_2O_3 \cdot 3H_2O$ (PDF- 1-287) and Al_2O_3 (PDF - 4-880) were identified in the as-received catalyst. After heat treatment at 600 °C for 3 h, Al_2O_3 (PDF - 4-880) and PdO (PDF - 882434) were identified. Alumina (Al_2O_3) is mainly manufactured from its hydroxide. If the mother material remains in the final product, it undergoes dehydration forming more crystalline phases with calcination until the most stable phase is formed. Eqs. (2) and (3), show the dehydration reactions of aluminium hydroxide forming alumina.



The masking of the Pd-Sn peaks in the background of the XRD profile before heat treatment could be attributed to their low concentrations in the catalyst mixture relative to the Alumina support. However, after heat treatment at 600 °C, the aluminium hydroxide peaks disappeared, hence, palladium oxide phase could be noticed. This observation is consistent with that of Bi et al. [19].

3.3. X-ray fluorescence

The concentrations of trace elements in the residual ash were SiO (43.8 wt%), CaO (29.8 wt%), P_2O_5 (13.8 wt%), K_2O (10.6 wt%), FeO (0.9 wt%), MgO (1.2 wt%), and Al_2O_3 (0.7 wt%). The concentrations of trace elements in charcoal could affect the activity of the catalysts arising from trace metal-catalyst reactions/poisoning. Morris et al. [26] showed that palladium catalysts activity could be slowed by sulphur and phosphorus. Secondly, build-up of product gases from combustion also deactivates the palladium catalysts. Palladium catalysts could be regenerated with organic polar solvents. Sulphur also poisons copper catalysts during methanol synthesis which involves reaction of CO with hydrogen [26]. However, the impact of these trace elements on catalyst activity was not investigated in this study.

3.4. The activity of Cu-Mn/graphite and Pd-Sn/alumina catalysts for CO oxidation

Catalysts act by adsorption/chemisorption of species onto their surfaces where reactions later take place. Carbon monoxide is adsorbed onto the Pd (1 1 1) at the binding sites (Atop, Bridge, FCC, and Hcp). Chen et al. [27] observed that lower saturation coverage of CO and lower CO binding energies contributes to the outstanding activity on Pd surfaces. Hsu et al. [28] found that the Mn dopant facilitates oxygen vacancy formation, while the Mn adatoms may restrain oxygen vacancy formation. The physisorbed CO, and chemisorbed CO species were also observed on the Mn catalyst. Janki et al. [29] found that oxygen atoms on Pd surface increase the binding energy due to lateral repulsion between oxygen atoms and Pd surface. Oxygen interaction with Pd brings about a strong electrostatic repulsion between adsorbates which is responsible for the adsorption energy to decrease with increasing coverage. There is a general decrease in heats of chemisorption on transition metal surfaces with CO and O_2 coverage and could be linked to the metallic radius of the metals [15].

Fig. 4 shows the residual amounts of CO recorded for catalyst treated charcoal. The residual CO from catalyst-treated charcoal were recorded at temperatures 300–600 °C and 2 L/min dry compressed air flow were. The CO amounts followed a non-linear trend with temperature. Morris et al. [26] showed that Pd and Cu based catalysts are denatured at high temperatures through a sintering process. They proposed that use of reaction temperatures lower than 1/3 to 1/2 of the melting point of the metal catalysts would minimise catalyst sintering.

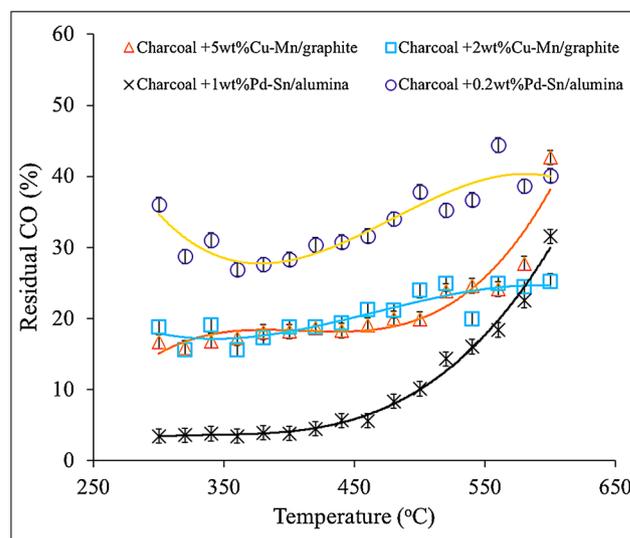


Fig. 4. Residual CO recorded for catalyst treated charcoal.

These observations are consistent with those of Ivanov et al. [30] and others [19,23].

On impregnation of the charcoal with 5w% Cu-Mn/graphite catalyst, the residual amounts of CO measured were 16.7% and 42.7% as lowest and highest. With 2w% Cu-Mn/graphite catalyst, the residual amounts of CO were 15.6% and 25.3% as lowest and highest. Increasing the amount of catalyst impregnated onto the charcoal increases the active sites for adsorption of CO and O_2 for better CO oxidation [15]. On the other hand, mixing of the charcoal with Pd-Sn/alumina released less CO than the Cu-Mn/graphite treated charcoal. With the 1w% Pd-Sn/alumina catalyst, only 3.5% and 31.6% were recorded as the lowest and highest residual CO amounts. When the concentrations were reduced to 0.2w%, the residual CO amounts recorded were 26.9% and 44.4% as the lowest and highest respectively. These data together with CO levels from charcoal without catalyst are provided in [supplementary data](#). The enhanced activity with catalyst loading is consistent with observations of Bi et al. [19].

4. Conclusions

In this study, charcoal was for the first time mechanically impregnated with catalysts to minimize carbon monoxide released during combustion. Two commercial catalysts were used: Pd-Sn/alumina and Cu-Mn/graphite. With 1 wt% of Pd-Sn/alumina impregnated on charcoal, 3.5% was observed as lowest residual CO. When the concentrations were reduced to 0.2 wt% Pd-Sn/alumina, 26.9% was recorded as lowest residual CO. On the other hand, when 5 wt% of Cu-Mn/graphite was impregnated, 16.7% was achieved as lowest residual CO. With 2 wt % Cu-Mn/graphite, 15.6% was achieved as lowest residual CO. Pd-Sn/alumina was a better catalyst for CO oxidation in this study. In all cases of catalyst testing, the activity decreased with temperature and increased with catalyst loading. The decreased activity of catalysts was due to formation of less active phases. It could also be due to trace elements in the ash formed as charcoal burnt. However, the effect of trace elements was not investigated in this study. This study could be scaled-up for commercial production of catalyst treated charcoal that is safer for domestic and industrial applications. The method could also be used for production of catalyst treated sawdust briquettes, wood boiler chips and other solid materials to minimise the amounts of CO released from combustion reactions.

Declarations of interest

None.

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Competing interests

The authors declare no competing interests.

Data availability statement

All the data associated with this work is available in this manuscript.

Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cplett.2018.11.041>.

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