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Toxic emissions from smouldering combustion of wood and derived char with a case study of CO build-up in an ISO container

Abstract

Carbon monoxide (CO) from the use of biomass solid fuels has caused several fatalities in the United Kingdom. This study was undertaken to evaluate the amount of CO from five species of wood sawdust, and charcoal with a case study of CO in a confined ISO container. Laboratory experiments were conducted at temperatures between 350 and 600 °C under flowing air. Results showed a strong dependence of CO emissions on temperature and airflow. Sawdust emitted CO levels as high as 298 mg/g while charcoal released 495 mg/g as highest. The CO emissions recorded in the ISO container were above the recommended exposure limits due to poor ventilation.

Key words: Carbon monoxide, sawdust, charcoal, temperature, airflow, confined space

1 Introduction

Carbon monoxide (CO) produced by the combustion of carbonaceous solid fuels in air can accumulate in confined spaces and interfere with the human oxygen-carrying capacity of blood [1]. It is a potent yet odourless asphyxiant, with levels as low as 5000 ppm causing death in less than 30 min. In Denmark, between 2008 and 2012, there was approximately one accidental death per year from the burning of charcoal indoors [2]. In the UK, CO/gas safety records indicate that 3% of the 719 deaths due to unintentional CO poisoning between 1995 and 2016 were caused by barbeques [3]. In 2012, a young girl died in a tent in The New Forest [4], and Nicholas Holmes also died in a camper van in the same area and year [5]. Hannah Thomas Jones died in Shropshire in 2013 from the same causes [6]. There have been

several other reports of unintentional/suicide carbon monoxide poisoning in confined spaces from biomass usage [7] [8] [9] [10] [11] [12]. One of the authors of this article was the survivor of a similar accident, in which his partner died [13]. In this incident, the couple were convinced that the fire was out when they took the barbeque into their tent. This tragic accident was the event that prompted the studies described in this article.

Ideally, the combustion products of carbonaceous fuels would be entirely converted to CO₂, moisture and other harmless products at all temperatures because these are far less toxic than CO and the combustion reaction would be thermodynamically more efficient. The relative amounts of CO released by solid fuels during combustion can be influenced by the combustion temperature and by the amount of oxygen in the air. Solid fuels like sawdust and charcoal burn at their surfaces, where fuel-rich conditions predominate and the amount of air (oxygen) is likely to be insufficient for complete combustion [14]. The fuels generally reach temperatures of 700–800 °C during natural combustion. However, more literature and information is needed about the effects of mid-level temperatures (300–600 °C) on the emission of CO from burning sawdust and charcoal.

Compressed sawdust briquettes have found wide applications in domestic and industrial applications as alternatives/supplements to wood logs, charcoal and fossil fuels [15], [16]. Derived from wood waste materials, wood sawdust briquettes are easy to make with simple technologies and low production costs [17], [18]. Wood waste in UK constituted 1.645 million tonnes in 2018 while packaging materials (paper & cardboard) constituted 4.749 million tonnes. Wood constituted 1.31 million tonnes in 2016 (Department for Environmental Food & Rural Affairs – DEFR - Government Statistical services) [19]. An estimated 10 million tonnes of ‘post-farm gate’ food waste is thrown out across the UK every year, of which only 1.8 million tonnes was recycled as per 2016 [19]. Forestry waste and agricultural wastes [20] are also good raw materials for making compressed sawdust

logs/briquettes. Conversion of such carbonaceous materials to useful energy is a viable solution, to fill the energy gap left by the declining fossils as well as reducing the wastes sent to landfills and minimising deforestation.

The use of raw biomass materials for heating in fireplaces has been ongoing for many years since the invention of fire. The use of wood boilers since the 1970s and subsequent developments until today saw a remarkable stride in the utilisation of biomass materials in homes [21], [22]. However, the combustion of such carbonaceous materials emits several pollutants of which CO and CO₂ constitute over 80% of the total emissions [23].

Quantifying the emissions from raw biomass combustion is vital to assess the burden against which sustainable solutions can be sought to minimise the danger of human intoxication especially from CO. Much as acute exposure to CO emissions from raw carbonaceous waste has been reported [24], [25], there is continuous exposure to chronic levels of pollutants [26]. Several studies have analysed CO emissions from biomass materials: Bhattacharya *et al.* [27] compiled the data for emissions of CO from wood used in developing countries and the emission values were in the range 50 – 300 g/kg. However, some portable wood burning stoves [28] were reported to be efficient at minimising CO emissions to as low as 0.3 – 1.6 mg/g.

Much as wood and wood sawdust are used extensively, the derived product – charcoal, has found even more wide application due to high energy content, less smoke, easy of ignition and transport among other advantages. However, since the elemental carbon is more concentrated in charcoal than wood logs or wood sawdust, the amounts of CO emitted from incomplete combustion of charcoal are considerably higher. In one investigation of CO emissions from indoor barbecue charcoal, the authors tested temperatures in the range 450–550 °C with linear air flow rates of 10 and 20 L/s in a tube furnace [29]. In their study, temperature had no significant influence on CO emissions during the combustion of charcoal,

but the effect of air flow was not discussed. A comparison of emissions from flaming and smouldering biomass and other solid fuels revealed that smouldering fuel produces more CO than flaming fuel [30]. An analysis of the emissions from coal braziers revealed that high ventilation rates reduce the levels of CO and other emissions from burning coal [31].

Several studies have been carried out to investigate CO emissions from charcoal under normal combustion conditions. Ojima [32] investigated the rate of CO generation from burning charcoal to determine the ventilation required in a room to maintain the CO levels below the Japanese national threshold. Evans and Emmons [33] produced an equation for burning charcoal which linked the CO/CO₂ ratio to temperature.

The desire to minimise heat loss in confined spaces has resulted in embracing double glazed window or door houses as a new fashion. This has its own drawbacks: combustion pollutants easily built-up leading to chronic and sometimes acute exposures. For the case of CO, since it is colourless and odourless, the victims are taken unaware with feeling of tiredness, headache, and similar conditions which are related to other ailments. It is natural that when a person gets such feelings, they resort to resting/sleeping. In such a CO environment, the consequences may be fatal or sustaining serious injuries.

Confined spaces usually have incomplete mixing of air [34], [35] and hence pollutants from combustion form different layers with concentrations increasing with height depending on ambient temperature and air buoyancy within the confined space. The longer a solid fuel is burnt in a confined space, the higher the likelihood that CO levels will go beyond the set threshold limit values [36]. Burning barbecue charcoal with ignition enhancers usually produces smoke during the first stages which many users avoid due to unpleasantness, but it usually clears away soon. However, the maximum concentrations of CO are produced during the smouldering phase when there is no smoke [37].

Different organisations have set maximum exposure limits for CO; the WHO [38,39] has established 100 mg/m³ (90 ppm) for 15 minutes, 60 mg/m³ (50 ppm) for 30 minutes, 30 mg/m³ (25 ppm) for 1 hour, 10 mg/m³ (10 ppm) for 8 hours. The Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for CO is 50 ppm parts of air (55 mg/m³) as an 8-hour time-weighted average (TWA) concentration. The National Institute for Occupational Safety and Health (NIOSH) has established a recommended exposure limit (REL) for CO of 35 ppm (40 mg/m³) as an 8-hour TWA and 200 ppm (229 mg/m³) as a ceiling. The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned CO a threshold limit value (TLV) of 25 ppm (29 mg/m³) as a TWA for a normal 8-hour workday and a 40-hour workweek [40],[41].

The main goal of most recent studies has been to facilitate the design of more efficient cooking stoves [42], [43], [44] and ventilation systems [32], the development of standards for stoves [43] and biomass space-heating equipment [45], the comparison of solid fuel emissions [46], the design and building of air samplers, and the development of low-emission combustion technologies. In this study we investigated the effect of temperature and air flow on CO emissions during the mid-temperature smouldering combustion of wood sawdust and wood charcoal in a tube furnace system under flowing air. We also give a detailed case study of CO accumulation in confined space. The aim was to determine in more detail the role of temperature and airflow during the combustion of solid fuels, with the emphasis on CO emissions, during the smouldering phase and the factors influencing CO build-up in confined spaces and the appropriate preventive measures.

2 Methodology

2.1 Sawdust

The samples were obtained from five different wood species: ash (*Fraxinus Excelsior*), beech (*Fagus Sylvatica*), elder (*Sambucus Nigra*), lilac (*Syringa Vulgaris*), and Hazel (*Corylus Avellana*). These were crushed using a laboratory vibratory pulveriser and sieved through a 210 μm mesh. The samples were dried in an oven at 110 °C overnight and kept in sealed containers for subsequent analysis. The proximate and ultimate analysis for these samples are shown in **Table 1**. The calorific values were determined using a method described elsewhere [47]. For determination of carbon monoxide (CO) emissions, triplicates of 200 mg samples were pyrolysed under air at temperatures between 300 – 450 °C using a method described in our previous work [48]. The duration of the experiments varied between 5 – 7 minutes. The experiments were terminated when the data logger registered zero concentration for CO meaning that the concentrations were below the detection limit of the sensor. The triplicates for each parameter were averaged to give a single data set.

2.2 Charcoal

The char samples were prepared in the laboratory in a furnace at 500 °C isothermal temperature for four hours. Upon cooling, the charcoal samples were ground to fine powder using an Essa LM2 pulverising mill and were sieved through a 210 μm mesh before drying in an oven at 105 °C and storing in a sealed container. The moisture content, volatile matter, fixed carbon and residual ash were determined as per the method described in our previous work [49].

For determination of carbon monoxide (CO) emissions, triplicates of 200 mg samples were heated under air at temperatures between 350 – 600 °C using a method previously described in our previous work [48].

Table 1: Ultimate, proximate analysis and heating values of the samples.

Sample name	Ultimate analysis (wt%)				Proximate analysis (wt%)				HHV ^e (MJ/kg)	Source
	N	C	H	O*	M ^a	VM ^b	FC ^c	RA ^d		
Lilac wood	0.30	49.19	6.63	43.87	5.8	73.2	19.5	1.5	19.15	This study
Ash wood	0.35	49.12	6.64	43.89	5.3	71.0	20.6	3.1	19.12	This study
Ash tree	<0.1	48.9	5.9	44.9	7.6	86.8	12.3	0.9	17.23	[50]
Hazel wood	0.51	48.41	6.60	44.48	4.9	75.7	18.2	1.2	18.75	This study
Elder wood	0.27	48.88	6.49	44.36	6.3	71.7	19.3	2.5	18.86	This study
Beech wood	0.35	49.07	6.67	43.92	5.8	75.8	17.7	0.8	19.12	This study
Lilac char	0.62	83.44	2.74	13.21	3.5	11.7	80.9	4.0	32.18	This study
Ash char	0.49	80.67	2.80	16.04	4.1	13.8	78.2	3.9	30.87	This study
Hazel char	1.08	83.11	2.81	13.00	3.8	12.0	80.5	3.7	32.13	This study
Hazel nut shell	-	75.00	5.50	40.60	-	20.6	77.1	2.3	-	[51]
Elder char	0.49	83.79	2.93	12.79	3.9	11.5	80.6	4.1	32.52	This study
Beech char	0.74	80.58	2.74	15.95	5.2	14.5	75.9	4.3	30.79	This study
Beech wood char	0.30	89.00	1.70	9.00	-	-	-	-	-	[52]
Beech char	-	80.00	2.00	18.00	-	-	-	-	-	[53]
Coal char	1.16	82.74	3.56	12.54	2.0	11.3	80.1	6.5	32.68	This study
Bituminous coal	1.60	81.30	5.30	10.80	14.6	35.2	46.2	4.0	-	[54]
Commercial char	0.25	84.02	2.15	13.58	4.3	9.5	60.4	25.9	31.86	This study
Bagasse char	0.47	79.40	3.60	16.60	-	27.0	64.0	10.5	-	[55]

*Determined by difference, ^aMoisture content, ^bVolatile matter, ^cFixed carbon, ^dResidual ash, ^eHigher heating value

2.3 CO emission computation

The overall amounts of the CO were determined by first calculating the area under the concentration-time curve using Eq 1, and then presenting the data in ppm.s,

$$A_T = \sum_{t_0}^{t_f} t_n C_n \quad (1)$$

where A_T , t_0 , t_f , t_n and C_n are the total area under the CO curves, initial time, final time, n^{th} time, and concentration at the n^{th} time, respectively. The total area was then used to calculate the total moles of CO evolved using Eq 2, which involves the air flow rate and molar volume over the time of the experiment.

$$X_i = \frac{A_T Q}{60 V_{\text{rtp}} 10^6} \quad (2)$$

where X_i , Q and V_{rtp} are the moles of CO, air flow rate, and molar volume at room temperature and pressure, respectively. The CO emissions (mg/g) were calculated by determining the mass of CO (Moles x relative molecular mass x 1000) and dividing it by the dry basis mass (in grams) of the original sample.

2.4 A case study of CO in the ISO container

The experiments were carried out in a 33m³ ISO container with a double door (dimensions = L x H = 2.34m x 2.28m) and no windows. However, the container was not air tight even in the fully closed position. One kilogram (1kg) of barbecue charcoal in a paper bag was loaded on to a barbecue pan that was fixed on a 25kg type load cell which had been calibrated prior to the experiments. Three K type thermocouples were inserted into the charcoal before it was ignited. The thermocouples and load cell were connected to a Squirrel data logger that recorded the temperature and mass loss of the charcoal during the experiments. Two fans (10cm diameter) were fixed one on each side of the BBQ pan blowing air at a velocity of 3.5m/s towards the charcoal to allow quick distribution of combustion gases in the ISO container.

The CO emissions were recorded by auto-logging PHD6 instruments fitted with CO electrochemical sensors. The CO recording instruments were placed inside the container at 30cm above the floor and near the door at 150cm above the floor. These PHD6 instruments also recorded room temperature. For safety of the research team, another set of CO sensor was placed outside the container fitted with a suction pump to draw effluent gases from near the BBQ inside the container. This was connected to the data logger that was checked routinely to monitor the concentrations of CO. Once the CO concentrations went below 10ppm, the experiment was terminated. Four domestic CO alarms (Kidde type, model 10LLDCO) were installed near the ceiling of the container. These were used to record the time when the alarm went off from the start of each experiment as they responded to time-weighted-average exposures and the maximum concentrations recorded during each run. Each set of experiments was repeated three times.

A portable weather station was installed just outside the container for monitoring wind speed, humidity, temperature, and dew point. The wind speeds were in the range 3.53 to 6.5

(m/s), the outside temperatures were in the range 17.3 to 19.6 (°C), pressure of approximately 1020.7 mbar, and the dew point was in the range 12.2 to 15.2 (°C). The mass of charcoal used per experiment was in the range 900 – 930 g. Each experiment lasted about 2 hours.

3 Results and discussion

3.1 Wood sawdust

3.1.1 Effect of temperature

The experiments were conducted for the temperature range 300-450 °C for two main reasons: (i) below 300 °C, the emissions of CO were too low to be detected; (ii) above 450 °C, the combustion process transformed from smouldering to flaming. Hence, any experiment in which no gaseous concentrations were detected within the first 5 minutes was terminated and disregarded. Likewise, for any experiment where the combustion system transformed from smouldering to flaming was also terminated and disregarded.

The tendency of combustion to transform from smouldering to flaming could be related to the concentration of volatiles within the sawdust samples. However, some studies suggest that some mineral elements, especially potassium, enhance the temperature of samples leading to enhanced combustibility [56].

The concentration of CO (mg/g) at each temperature can be seen in **Table 2**. The essential gases produced during smouldering are CO and CO₂ accounting for over 80% [57] of the total gaseous emissions. Except for beech and ash (*Fraxinus*) (at 300 °C only), all samples registered CO values in the range $150 \leq \text{CO} \leq 250$ mg/g for all temperatures. These results are consistent with the 50 – 300 mg/g detected by Burnet *et al.* [58] from wood fire stoves but higher than the 0.3 – 1.6 mg/g detected by Cheng-Wei [28] emitted by portable household warming devices. The influence of temperature on emissions of CO from this study cannot be generalised. Beech and hazel samples showed a general increase; lilac CO

emissions remained almost constant, Ash (*Fraxinus*) CO emissions increased at 300 – 350 °C followed by a decrease to 450 °C. Elder showed a general decrease in CO emissions with temperature attributed to enhanced combustion efficiency [59]. Xiao *et al.* [60] determined the emissions of CO from a moving grate boiler to be in the range 49-56 mg/g. The amounts of CO emissions recorded in our study are high, and without sufficient ventilation, these values could lead to acute exposure symptoms in a healthy individual especially in a confined space.

3.1.2 Effect of airflow

There was a general decrease in CO emissions with airflow **Table 2**. This could be due to the increased turbulence created by the supply of increased air, which resulted in better combustion of volatile matter [61], [62]. This may also be due to the complete combustion of smaller particles and unburned carbon [59]. None the less the obtained values exceed the WHO limits. Casey et al. [63] determined the CO time-weighted averages in several homes in Navajo of Japan and found the values (>40 ppm per eight hour weighted average) to exceed the recommended levels.

Table 2: Effect of temperature and airflow on emissions of CO $\pm$ STD (mg/g) from wood sawdust samples. The values were computed with one standard deviation.

Sample	Temperature (°C)				Airflow (L/min)			
	300	350	400	450	0.72	1.24	1.71	2.2
Lilac wood	122.7 $\pm$ 3.4	124.0 $\pm$ 7.8	117.5 $\pm$ 6.6	128.3 $\pm$ 5.6	129.5 $\pm$ 12.8	125.6 $\pm$ 4.5	123.4 $\pm$ 8.5	114.1 $\pm$ 4.0
Elder wood	172.3 $\pm$ 3.9	167.2 $\pm$ 6.8	162.4 $\pm$ 4.5	161.8 $\pm$ 14.1	165.6 $\pm$ 8.2	176.6 $\pm$ 7.8	167.2 $\pm$ 5.9	159.1 $\pm$ 7.8
Hazel wood	-	185.01 $\pm$ 3.8	245.5 $\pm$ 8.1	258.0 $\pm$ 8.6	233.7 $\pm$ 5.7	230.6 $\pm$ 4.5	242.6 $\pm$ 8.9	211.1 $\pm$ 6.9
Ash wood	136.6 $\pm$ 8.8	204.5 $\pm$ 8.4	189.7 $\pm$ 10.9	169.8 $\pm$ 10.5	201.2 $\pm$ 13.9	182.1 $\pm$ 7.9	155.6 $\pm$ 4.2	170.0 $\pm$ 10.7
Beech wood	98.9 $\pm$ 8.1	170.2 $\pm$ 6.8	173.6 $\pm$ 9.0	166.0 $\pm$ 5.9	179.3 $\pm$ 6.2	153.6 $\pm$ 4.0	131.7 $\pm$ 7.9	159.0 $\pm$ 6.1

3.1.3 CO evolution profile from wood sawdust

Average data values were produced for each triplicate analysis. All CO evolution pattern followed a comparable trend similar to that reported elsewhere [23] and reached the

minimum values at periods between 300 – 500 seconds for all samples. For this reason, lilac (*Syringa vulgaris*) was chosen to represent all the other sawdust samples **Figure 1** for the evolution profiles. The key observations were: (i) The time required to attain the maximum CO concentration and the total time of the experiment decreased with increase in temperature across all airflows. This was attributed to the quick degradation of the cellulose, hemicellulose and lignin components with increase in temperature. (ii) There was a general increase in the maximum concentration of CO with an increase in temperature across all airflows. This was related to the early-peak-phenomena in which the concentration of products is directly proportional to temperature (iii) For a particular temperature, the maximum CO concentrations decreased with an increase in airflow. This was attributed to CO oxidation by oxygen in the air.

We also observed the appearance of a secondary peak towards completion of the emission profiles especially at low airflow rates and low temperatures. The second peak was attributed to CO emissions from devolatilised char which is rich in carbon.

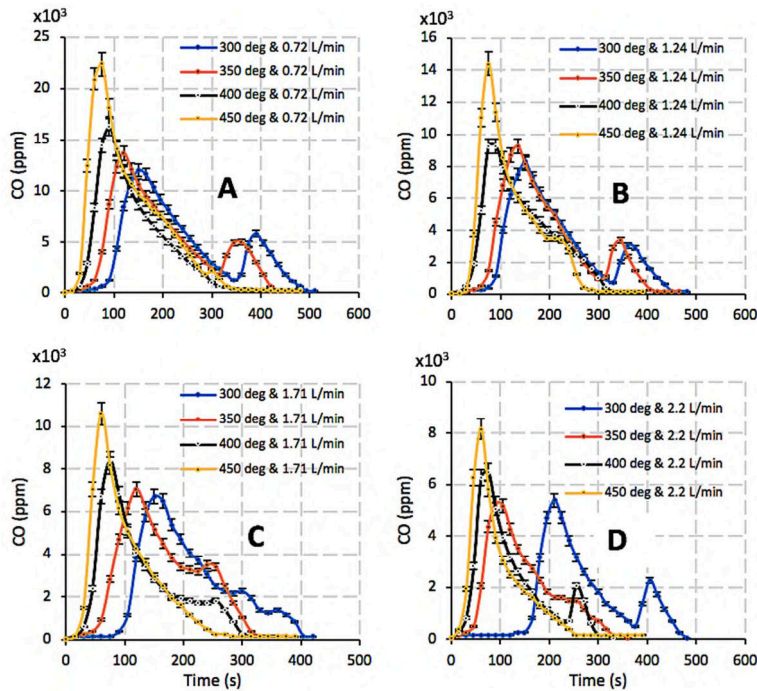


Figure 1: CO emission profile for lilac (*Syringa vulgaris*) representing the profiles for all sawdust samples in this study. A – at 0.72 L/min; B – at 1.24 L/min; C – at 1.71 L/min and D – at 2.2 L/min airflow rates.

3.2 Charcoal

The proximate and ultimate analysis values of charcoal shown in **Table 1**, are consistent with other studies [64], [65]. The low volatile matter content of commercial charcoal could be attributed to the temperature at which it was manufactured; high temperatures remove most of the volatiles [29].

3.2.1 Effect of temperature and air flow

There was a general decrease in CO emissions with temperature across all airflows **Table 3**. The CO evolution profile followed a general pattern shown in **Figure 2** for all charcoal samples. The initial CO evolution is a typical zero order followed by a first order decay until most of the carbon is consumed. Apart from beech charcoal, the rest of the charcoal samples showed a general decrease in CO emissions with airflow **Table 4**.

Table 3: Effect of temperature on emissions of CO $\pm$ STD (mg/g) from charcoal samples. The values were computed with one standard deviation.

Sample	Temperature ($^{\circ}$ C)					
	350	400	450	500	550	600
Commercial charcoal	98.1 $\pm$ 9.6	198.0 $\pm$ 9.9	258.2 $\pm$ 10.2	265.3 $\pm$ 11.8	245.9 $\pm$ 15.2	236.6 $\pm$ 15.6
Lilac charcoal	303.9 $\pm$ 10.2	287.5 $\pm$ 3.2	275.4 $\pm$ 7.0	257.5 $\pm$ 13.9	251.3 $\pm$ 10.3	296.47 $\pm$ 5.5
Ash charcoal	299.0 $\pm$ 12.8	286.6 $\pm$ 13.6	300.6 $\pm$ 17.7	291.3 $\pm$ 11.7	273.0 $\pm$ 16.0	272.2 $\pm$ 10.2
Elder charcoal	301.9 $\pm$ 14.5	331.8 $\pm$ 7.0	324.4 $\pm$ 14.7	305.4 $\pm$ 19.9	272.2 $\pm$ 10.5	275.7 $\pm$ 13.2
Hazel charcoal	347.9 $\pm$ 11.5	397.6 $\pm$ 12.6	465.5 $\pm$ 11.8	495.0 $\pm$ 10.5	403.6 $\pm$ 9.8	363.7 $\pm$ 12.1
Beech charcoal	300.6 $\pm$ 12.1	328.6 $\pm$ 15.4	334.1 $\pm$ 15.6	327.9 $\pm$ 17.0	308.5 $\pm$ 17.9	276.0 $\pm$ 10.7

The time-dependant decay of CO emissions is probably related to the turnover of surface complexes, their attachment (weak or strong) and subsequent loss. At any point on the decay curve, the rate of release (calculated from ppm data and flow rates as moles/s) can be related to the remaining mass of charcoal, and “rate constants” calculated.

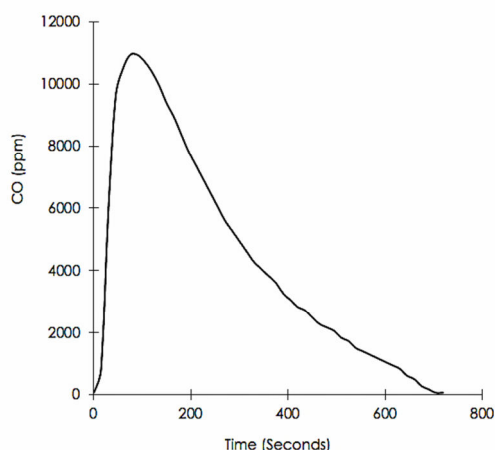


Figure 2: Typical profile for the release of CO from charcoal.

Table 4: Effect of airflow on emissions of CO $\pm$ STD (mg/g) from charcoal samples. The values were computed with one standard deviation.

Sample	Airflow (L/min)			
	0.72	1.24	1.71	2.2
Commercial charcoal	257.8 $\pm$ 16.1	210.9 $\pm$ 12.9	186.6 $\pm$ 12.7	212.7 $\pm$ 17.4
Lilac charcoal	265.4 $\pm$ 13.4	292.6 $\pm$ 17.7	282.7 $\pm$ 12.9	273.9 $\pm$ 13.3
Ash charcoal	264.0 $\pm$ 16.1	306.7 $\pm$ 10.2	291.2 $\pm$ 14.1	286.6 $\pm$ 14.3
Elder charcoal	318.8 $\pm$ 17.3	297.7 $\pm$ 12.7	286.7 $\pm$ 18.2	304.3 $\pm$ 13.6
Hazel charcoal	426.8 $\pm$ 10.2	421.6 $\pm$ 14.5	408.7 $\pm$ 14.6	391.6 $\pm$ 18.2
Beech charcoal	299.2 $\pm$ 16.7	303.2 $\pm$ 14.5	315.0 $\pm$ 11.9	333.0 $\pm$ 18.6

Although we did not measure the mass of charcoal continuously during the heating process, the number of moles remaining at any point can be estimated from the moles of CO and CO₂ released. The rate of CO production was linearly dependent on the amount of carbon remaining for most part of each experiment, **Figure 3**.

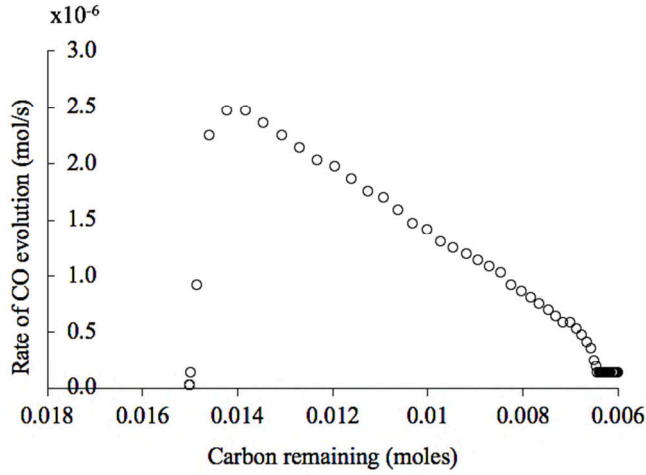


Figure 3: The rate of evolution of CO from char at 450°C and 1.71 L/min air flow.

Rate constants (k_s in units of 1/s) can be derived if the linear data for CO in **Figure 3** are used in Eq. 3 which shows a simple pseudo first-order reaction assuming $[O_2]$ is constant and the surface area of carbon decreases uniformly with mass. These data are shown in **Table 5**.

$$\frac{d[CO]}{dt} = k_s \cdot [Carbon] \quad (3)$$

Table 5: Values of k_s (1/s) for different temperatures and air flow rates
Temp (°C) (Air flow $\pm$ 0.01) (L/min)

	0.72	1.24	1.7	2.2
400	5.3×10^{-4}	3.9×10^{-4}	-	2.2×10^{-4}
450	5.3×10^{-4}	3.4×10^{-4}	2.7×10^{-4}	2.2×10^{-4}
500	4.5×10^{-4}	3.4×10^{-4}	2.7×10^{-4}	2.4×10^{-4}
550	7.7×10^{-4}	4.5×10^{-4}	2.8×10^{-4}	2.5×10^{-4}
600	8.8×10^{-4}	6.8×10^{-4}	3.6×10^{-4}	2.3×10^{-4}

We again observe an airflow effect, with low flows increasing the rate constant for CO evolution, and a temperature effect that is only manifested at the lower air flows.

Scanning electron microscopy, **Figure 4**, revealed that the wood char retains much of the micrometre-sized porous structure of the wood from which it was derived. Wood charcoal probably burns in much the same way on all surfaces similar to propellant grains [66] extruded with voids down their length so that as the external surface shrinks during burning,

simultaneously the internal surface grows to maintain the overall surface area thus conferring a near constant burn rate. Hence, the assumption that surface area depends on the mass of charcoal could be true.

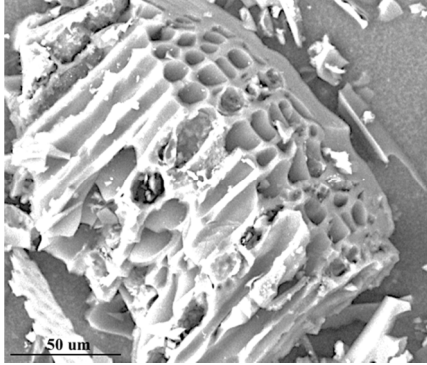


Figure 4: Scanning electron microscopy image for wood charcoal

3.2.2 ΔG as a predictor of reaction feasibility

Several reactions may take place during char combustion leading to production of CO, including the following:



We predict that reactions 4 become less favourable as the temperature increases, whereas 5 become more favourable because the former involve a decrease in gas-phase species and the latter an increase. Reaction 6 does not occur at temperatures below 973 K [67].

There are many other factors to consider. The product ratios (CO/CO₂) may reflect the different active sites present on each char surface associated with cationic trace metal impurities that act as catalysts [68]. Although our experiments involved isothermal combustion, the actual char temperatures could have been higher because metal impurities can enhance the burning temperature of char [69]. There is evidence for CO conversion to CO₂ at the char surface by the catalytic action of the char mineral matter [70]. It is also

possible that the decrease in CO amounts with temperature are due to secondary processes taking place in the charcoal pores, promoting the conversion of CO to CO₂.

Our results highlight the dangerous assumption that charcoal fires do not produce CO merely because they are not glowing red hot. Radiant heat should be an indicator of continuing combustion. Initial results with this charcoal sample suggest that there are steps that could be taken to encourage secondary conversion of CO to CO₂ in these systems and that this may be as simple as selecting the most suitable wood for charcoal preparation.

3.3 Case study of CO in the ISO container

3.3.1 CO at different positions in the container

The results clearly show that the CO values recorded at 150 cm above floor (near the door) were higher than those recorded at 30 cm above floor (extreme end inside the container), **Figure 5**. This could be explained by the movement of heavy, moist and fresh air from the outside displacing dry, warm and polluted air from charcoal combustion to the upper parts of the container [71]. Secondly, the buoyant air movement and the temperature difference within the ISO container was a major factor contributing for movement of CO to the upper parts of the ISO container [72]. This emphasises two very important considerations during cooking/heating: to keep the door and windows open to allow entry of fresh air [73] and to move at the lower side as possible (in a crawling position) as we exit any confined space on fire. As expected, the amounts of emissions relative to the door position were in the order; fully closed > half open > fully open. Even in the fully closed-door position, fresh air could enter since the door was not air tight [74].

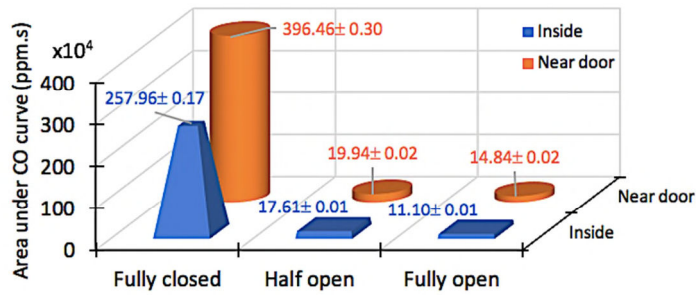


Figure 5: Area under the CO curves for the different door positions during the ISO container experiments. The value for the fully-closed-near-door has been reduced x10 to fit well on the plot.

There was a steady decline in charcoal temperature recorded during the fully closed-door session reaching its lowest value (159°C) at the end of the experiment compared to the fully open and half open-door positions which had the lowest charcoal temperature as 442 and 500 °C respectively. This could be attributed to low air flow within the container during the fully closed-door position, hence, residual ash built-up on charcoal surfaces and could not be easily removed due to low airflow rates. This also explains the high amounts of CO recorded during this experiment due to low purging compared to the fully open and the half open door positions. Additionally, due to constant blowing of air, the temperature during the fully open and half open experiments was maintained above 440°C [75] throughout the experiment compared to the fully closed-door position where the charcoal temperature declined continuously to as low as 159°C.

The fully open-door experiment took about 110 minutes, the half open experiment took about 120 minutes while the fully closed-door experiment took the longest time of close to 140 minutes. This could be due the oxidation of charcoal by incoming air: the higher the airflow, the faster the oxidation [76].

Even when charcoal looks to be out of fire, it is not recommended to take it to any confined space. The best practice would be to empty the charcoal remaining into a waste/hot charcoal safety bin before storage of the BBQ grill. In the 33 m³ ISO container experiment

described above, CO values as high as 70ppm were recorded from only 270g of (charcoal+ residual ash) which had remained after the 1kg charcoal sample was burnt from the outside – this was done to simulate what some CO poisoning victims do after a BBQ meal. This implies that, any confined space smaller than the ISO container used in this study could have registered very high CO concentrations [77].

The domestic alarms also provided very important information. In the fully open position, the alarms went off at 22 to 25 minutes within the experiment. Once checked at the end of the experiments, they recorded maximum CO concentrations as 125 to 130ppm. In the half open door position, the alarms went off at 15 to 20 minutes within the experiment and they recorded 820 to 900ppm as maximum CO concentrations. In the fully closed-door position, the alarms went off at 2 to 6 minutes and they recorded 999ppm as maximum CO concentrations during those experiments. With the charcoal burnt from the outside and then taken inside the ISO container, the CO alarms went off after 40 minutes. According to the manufacturers of Kidde alarms [78], the alarm response times and CO concentration are shown in **Table 6**.

Table 6: CO concentrations and Kidde alarm response times

Carbon Monoxide Level	Alarm Response Time
40 ppm	10 hours
50 ppm	8 hours
70 ppm	1 to 4 hours
150 ppm	10 to 50 minutes
400 ppm	4 to 15 minutes

The experimental alarm response values (CO concentration and time) agree with the guide from the manufacturers of Kidde alarms. In the fully open-door position, the alarm response time was within the 15-minute allowable limits but outside the 1-hour limits of UK/EU/WHO [39] guideline. In the half open and fully closed-door positions, the recorded values all exceed the UK/EU/WHO guideline values for 15 minutes (100mg/m³ or 87.3ppm) and 1-hour (35mg/m³ or 30.6ppm) indoor exposures.

3.3.2 Experimental CO levels in relation to recommended exposure limits

In the fully closed-door position, the overall time-weighted-average (TWA) CO concentration for the entire experiment (2 hours and 20 minutes) at 150cm was 497ppm. This level is said to cause mild headache, fatigue, nausea and dizziness [38,79]. However, the one-hour time weighted average CO value was 751ppm. This value is close to 800ppm established by OSHA that causes serious headache and may trigger other symptoms that are life threatening. In the sitting position (at 30 cm), the one-hour time weighted average was 481ppm. These CO levels would cause mild headache, fatigue, nausea and dizziness (OSHA, WHO) [38].

In the half open door position, the overall time-weighted-average (TWA) CO concentration for the entire experiment (2 hours) at 150cm was 28ppm. According to WHO and OSHA, this level would not cause any immediate symptoms. However, the one hour TWA was 47ppm which is lower than the dangerous levels set by UK-EU-WHO-OSHA) [38] for 60 minutes CO exposures. In the sitting position height, (at 30 cm), the 2hour TWA was 25ppm. However, the one hour TWA was 37ppm which is higher than the 25ppm level set by UK-EU-WHO-OSHA) [38] for 60 minutes CO exposures.

In the fully open-door position, the overall time-weighted-average (TWA) CO concentration for the entire experiment (110 minutes) at 150cm was 22ppm-TWA. According to WHO and OSHA, this level would not cause any immediate symptoms. However, the one hour TWA was 30 ppm which is lower than the dangerous levels set by UK-EU-WHO-OSHA) [38], [80] for 60 minutes CO exposures (set in 2011, and 2005). In the sitting position (at 30 cm), the overall TWA CO concentration was 17ppm for the entire experiment (1 hour 50 minutes). However, the one hour TWA was 22 ppm which is lower than the levels set by UK-EU-WHO-OSHA) [38] for 60 minutes CO exposure. This CO level is also lower

than the levels set by UK-EU-WHO-OSHA for the 60 minutes (set in 2015) CO exposures in the standing position. However, low levels of CO exposure have been linked neurodevelopment disorders [81].

However, all the recorded CO values in this case study are higher than 20 ppm – long term exposure (8 hours) and the 100 ppm – short term exposure (15 minutes) set by the UK Health and Safety Executive 2018 [82].

Conclusions

In this study, the emissions of CO from wood sawdust and charcoal from the same wood species were evaluated. Sawdust emitted less CO than charcoal. Secondary, a case study of CO accumulation in a confined space was simulated using an ISO container. CO emission from wood sawdust were in the range 98.8 mg/g as lowest to 258.0 mg/g as highest across all temperatures and airflows. On the other hand, the CO emission from charcoal were in the range 98.1 mg/g as lowest to 495 mg/g as highest across all temperatures and 186.6 mg/g as lowest to 426.8 mg/g as highest across all airflows. There was a general decrease in CO emissions across all temperatures and airflows for both sawdust and charcoal except wood sawdust for which the CO emissions from each sample was affected differently by temperature. The amounts of CO emissions recorded in the ISO container increased with decrease in airflow within the container. Higher amounts of CO were recorded at the upper parts of the container compared to the lower parts. The ISO container case study elaborates the build-up of CO in enclosed environments and the importance of aeration.

Declaration of interest: None

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