Fuel 102 (2012) 709–715

Contents lists available at SciVerse ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Experimental study of carbon monoxide for woods under spontaneous ignition condition

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HIGHLIGHTS

- ▶ We investigated CO release rate and CO yield of wood samples by spontaneous ignition.
- ▶ A model predicted CO yield of wood under heat flux and moisture content was developed.
- ▶ Woods' thickness show little effect to the peak CO release rate.
- ▶ Decrease of peak CO release rate is not obvious as heat flux is higher than 50 kW/m^2.
- ▶ Moisture reduces CO release rate and postpones time to peak CO release rate.

ARTICLE INFO

Article history:
Received 1 November 2011
Received in revised form 20 May 2012
Accepted 12 June 2012
Available online 23 June 2012

Keywords:
Autoignition
Wood
Carbon monoxide
Moisture content
Cone calorimeter

ABSTRACT

Toxic gases are significant in fire risk evaluation. Previous studies have focused on their characteristics by piloted ignition. Spontaneous ignition is a complex phenomenon that combustible materials are ignited by internal heating, without the spark plug. Comparing with piloted ignition, process of spontaneous ignition is much closer to the development of real fire. Therefore, carbon monoxide (CO) of six species of wood samples under external heat flux by spontaneous ignition in a cone calorimeter was investigated. Results showed that influence of thickness to peak CO release rate can be ignored, but time to peak is postponed with a higher thickness. Peak CO release rate decreases with a higher external heat flux, but the decrease is not obvious when heat flux increases from 50 to 75 kW/m^2. The flame also has influences to the CO release rate. A sharp decrease of CO release rate happens shortly after ignition and a second peak is near the end of the experiment. Moisture reduces CO release rate and postpones time to peak CO release rate. An empirical model of CO yield of wood samples under different external heat flux and moisture content by spontaneous ignition was developed. This empirical model can be used not only for fire risk evaluation, but also for modeling input and validation.

1. Introduction

Carbon monoxide (CO) in enclosure fires is the most important factor in fire deaths. Roughly two-thirds of all deaths resulting from enclosure can be attributed to the presence of CO, which is known to be the dominant toxicant in fire deaths [1]. Occupational Safety and Health Administration (OSHA) set exposure limits of CO at 35 ppm, and the exposure to higher concentrations can be detrimental to human in health and possibly result in death [2]. Carbon monoxide of woods is significant in fire risk evaluation, also very important in modeling input or validation [3–5].

Production of CO may be affected by several aspects. Babrauskas [6] noticed that for woods a substantial decrease in CO yield with increasing irradiance. Chung and Spearpoint [7] mentioned that CO yield depends on materials burning and ventilation conditions. Flame also has influences to the production of CO. Mulholland et al. [8] have found that CO yield has a peak shortly after ignition and a second peak near the end of the test. Grotkjar et al. [9] observed a dramatic increase of CO_2/CO ratio when a change from pyrolysis/smouldering to flaming ignition. Previous studies [10–13] also mentioned that moisture is found to have influence to CO yield. Moisture dependent CO yields are important in fire risk evaluation, however, very few studies have focused the effects of moisture for woods under external heat flux.

This paper investigated CO of six species of wood samples under different external heat flux and moisture content by spontaneous ignition in a cone calorimeter. The objectives of this study are:

- To predict CO yield of wood samples under different external heat flux and moisture content by spontaneous ignition.

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0016-2361/$ - see front matter © 2012 Published by Elsevier Ltd.
http://dx.doi.org/10.1016/j.fuel.2012.06.053

- To identify the influences of thickness, external heat flux, moisture to CO release rate and CO yield when woods are positioned under external heat flux by spontaneous ignition; and
- To provide input parameters or validation data for numerical modeling of wood samples under different external heat flux and moisture content by spontaneous ignition.

2. Methodology

2.1. Materials

Measured properties of wood samples are listed in Table 1. The sample sizes are 100 mm × 100 mm with different thicknesses, such as 10 mm, 20 mm, and 30 mm.

Samples were put under ambient environment for more than 24 h. Moisture contents of wood samples were then measured according to the ovendry method [14] by chamber furnace. In the furnace, temperature inside kept at a range of 102–105 °C to drive off the moisture. Periodical re-weighing were taken until no further weight loss was registered. Moisture content (wet basis) provided in Table 1 are the average of three different thicknesses. Dry wood in this table means no moisture exits inside wood samples, and wet wood represents wood samples with moisture content are about 0.11.

2.2. Apparatus

Cone calorimeter as a frequent used equipment for piloted or spontaneous ignition experiments was used in this study [15]. Wood samples were put in horizontal orientation on specimen holder. External heat fluxes of 25, 50, and 75 kW/m^2 were chosen for this study, which means low, middle and high external heat flux. Fig. 1 shows a view of wood sample in cone calorimeter.

2.3. Procedure

Before experiments, gas analyzers and external heat flux were first calibrated accordingly. Wood samples were then secured on a specimen holder and placed under the heater horizontally. The edges and rear surface of the specimens were covered with aluminum foil for insulation. Change in weight was dynamically recorded using the built-in weighting device. A sample was considered ignited when visible flame was first observed. Spark plug was not used during the whole experiment.

2.4. Repeatability

Due to large number of experimental groups, it is impossible to repeat each experimental group. Several experimental groups have been repeated to identify the repeatability of experiments. Fig. 2 shows repeated experiments given by CO release rate. It is observed that the repeatability of experiments is good.

3. Results and discussion

3.1. CO release rate

Types and quantities of gas produced by a combustion process depend on a combination of factors including flammability of the fuels, the chemical composition, and the specific condition of fire scenario [16]. Carbon monoxide release rate of six species of wood samples were measured by gas analyzer in cone calorimeter.

Table 1
Measured properties of wood samples.

Species	Material	Grain orientation	Dry wood	Wet wood	
			Average density (kg/m^3)	Average density (kg/m^3)	Average moisture content
Softwood	Pine	Along	392.7	446.8	0.121
Hardwood	Beech	Along	566.6	632.4	0.104
	Cherry	Along	494.6	557.6	0.113
	Oak	Along	804.0	897.3	0.104
	Maple	Along	673.4	748.2	0.100
	Ash	Along	610.6	680.0	0.102

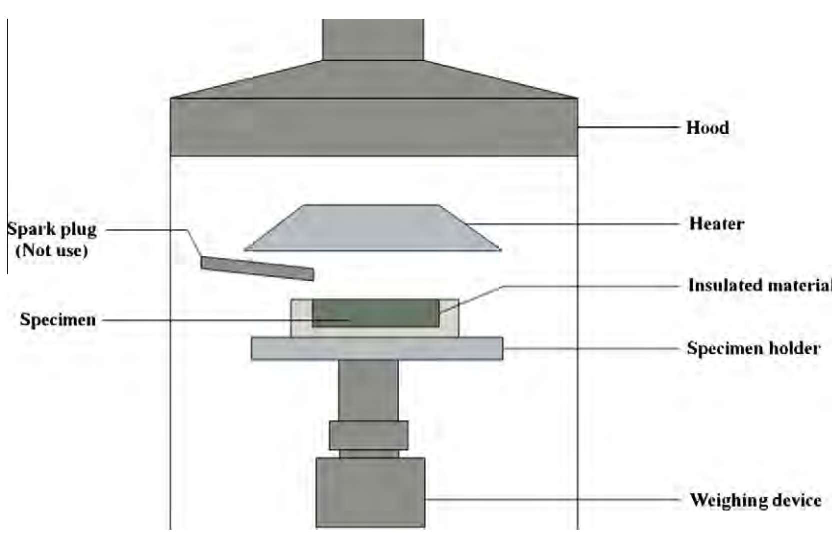

Fig. 1. A view of wood sample in cone calorimeter.

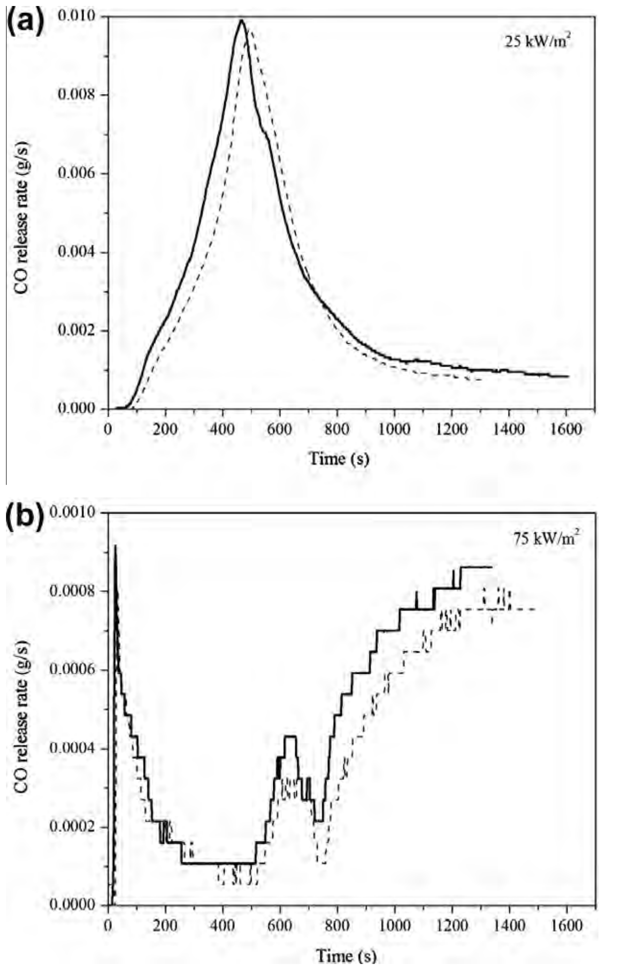

Fig. 2. Repeatability of experiments is good: (a) 10 mm thickness dry wood; and (b) 20 mm thickness wet wood.

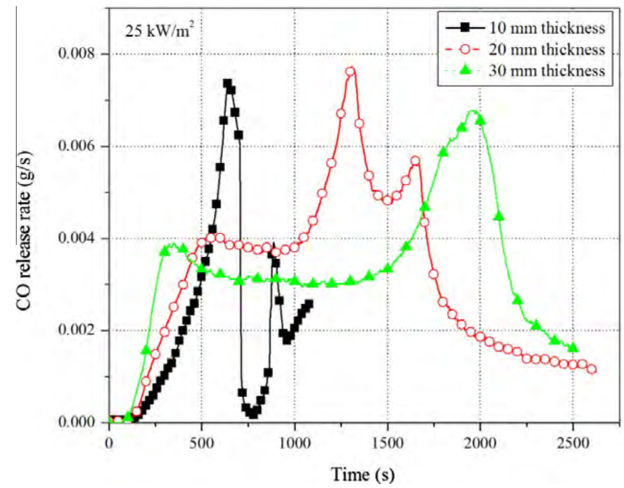

Fig. 3. CO release rate of beech dependent on thickness under 25 kW/m^2 external heat flux.

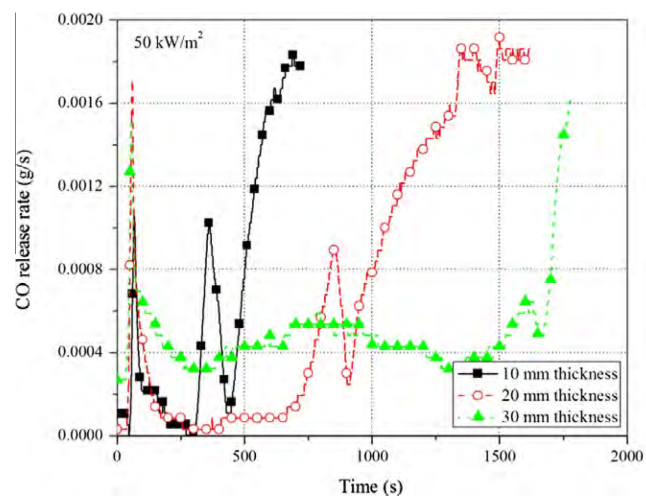

Fig. 4. CO release rate of beech dependent on thickness under 50 kW/m^2 external heat flux.

Fig. 3 shows CO release rate of beech dependent on thickness when they are put under 25 kW/m^2 external heat flux. It is observed that thickness has little effect to the peak CO release rate. However, time to peak is postponed with a higher thickness. This may be because the temperature of thin wood slabs increase faster than thick one when they are positioned under the same external heat flux. The main chemical components of wood include cellulose, hemicelluloses and lignin, which have specific temperature ranges of decomposition [17]. The temperature range of decomposition for cellulose is 240–350 °C, hemicelluloses is 200–260 °C, and lignin is 280–500 °C. Decomposition processes of cellulose, hemicelluloses and lignin then start earlier for a thinner wood sample. For wood samples under 25 kW/m^2 by spontaneous ignition, no visible flame was observed during whole experimental time.

Fig. 4 shows CO release rate of beech dependent on thickness when they are put under 50 kW/m^2 external heat flux. Similarly, the thickness is observed to have little influence to the peak values, and time to peak get longer with a higher thickness. The range of ignition time for these wood samples is 39–46 s [18]. It is noticed from the figure that a sharp decrease of CO release rate happens shortly after ignition and a second peak is near the end of the experiment. Mulholland et al. [8] found the similar phenomenon during the experiments of woods. Grotkjar et al. [9] observed a dramatic increase of CO_2/CO ratio when a change from pyrolysis/smouldering to flaming ignition. This may due to the influences of flame. When flame is presented, oxidation reaction of CO may be accelerated, and more CO change into CO_2. The production of CO can be expressed by a two-steps reaction:

$$\begin{cases} \text{Step 1}: \ \text{Wood} + O_2 \rightarrow H_2O + CO + \text{others products} \\ \text{Step 2}: \ CO + 0.5O_2 \rightarrow CO_2 \end{cases} \quad (1)$$

According to this two-steps reaction, a dramatic decrease of CO may be because reaction rate of step 2 increases dramatically when flame is presented. Huggett [19] obtained heat release from a complete combustion involving conventional organic fuels is 13.1 kJ/g of oxygen consumed. After ignition, heat release increases dramatically, representing a higher oxygen consumption. Some part of oxygen may then be used in step 2, leading to a increase of CO_2 and decrease of CO.

Fig. 5 shows CO release rate of beech dependent on thickness under 75 kW/m^2 external heat flux. Peak CO release rate happens at the end of experiment. According to the situation of 25 and 50 kW/m^2, the release rate may increase if the experiments last a little longer. So it might be gained that the thickness still has little effect to the peak CO release rate. The range of ignition time for these wood samples is 13–20 s [18]. Similarly, it is observed that a sharp decrease of CO release rate happens shortly after ignition and a second peak is near the end of the experiment.

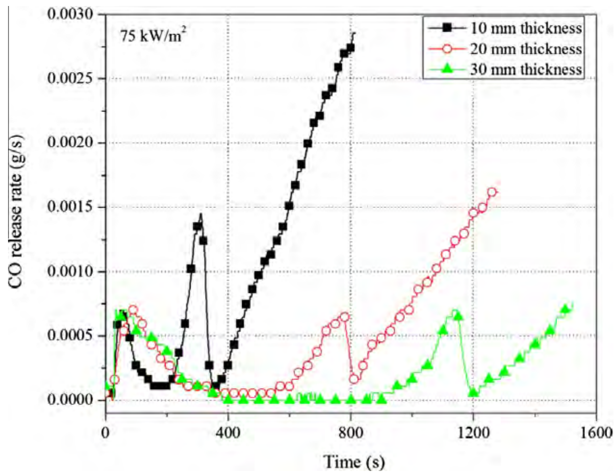

Fig. 5. CO release rate of beech dependent on thickness under 75 kW/m^2 external heat flux.

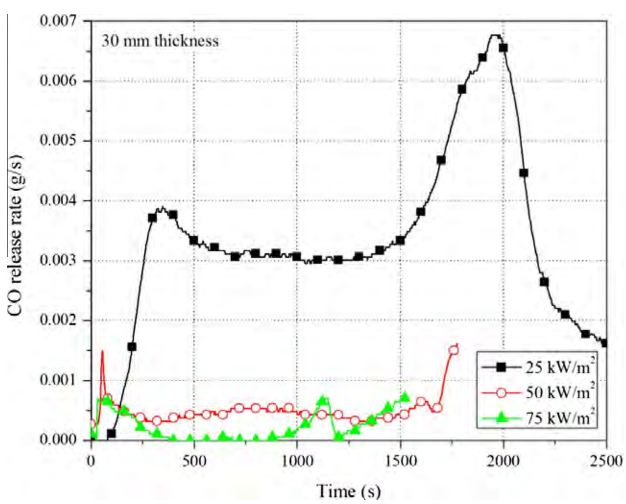

Fig. 6. CO release rate of beech dependent on external heat flux.

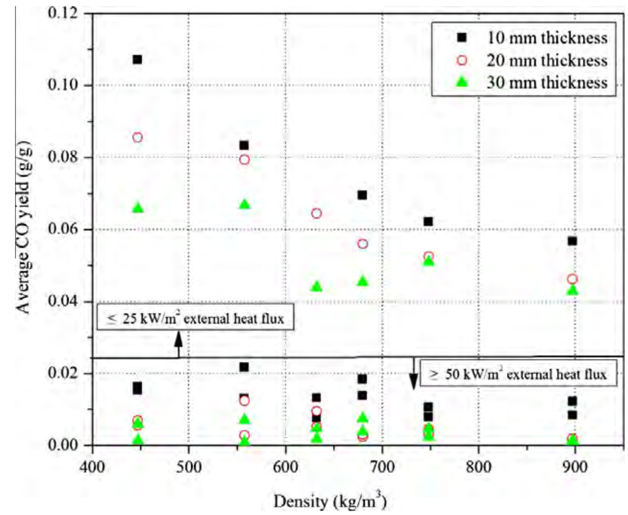

Fig. 7. Influence of density to average CO yield.

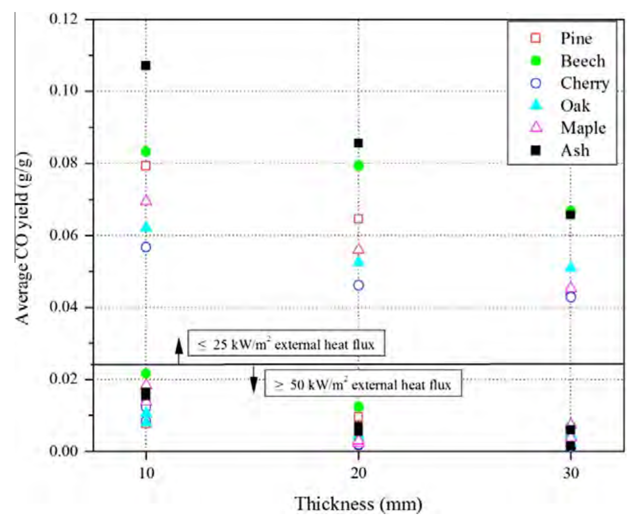

Fig. 8. Influence of thickness to average CO yield.

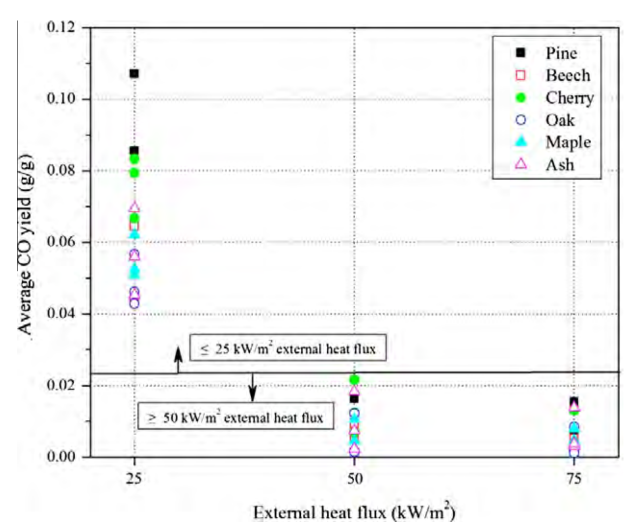

Fig. 9. Influence of external heat flux to average CO yield.

Fig. 6 shows CO release rate of beech dependent on external heat flux. It is observed that external heat flux has obvious effect to the CO release rate. Peak CO release rate gets much higher with a lower external heat flux. Peak CO release rate decreases when external heat flux increases from 50 to 75 kW/m^2, but the decrease is not obvious.

3.2. CO yield

Previous studies [20] showed that it is not possible to predict, from an additivity law, pyrolysis gas yields of any biomass from its composition in cellulose, hemicelluloses and lignin. Therefore, correlation between CO yield and other factors, such as density, thickness, external heat flux, will be analyzed.

Fig. 7 shows influence of density to the average CO yield (Y_{CO}). It is observed that average CO yield decreases exponentially with density. It might be gained that the Y_{CO} correlates linearly with ρ^{-c}.

Fig. 8 shows the influence of thickness (L) to average CO yield. Similarly, average CO yield has a decreasing trend when thickness is getting higher. It may be gained that the average CO yield has a linear correlation with L^{-d}.

Fig. 9 shows the influence of external heat flux to average CO yield. When heat flux is 50 or 75 kW/m^2, average CO yield is less than 0.025 g/g. Average CO yield is greater than 0.04 g/g when heat

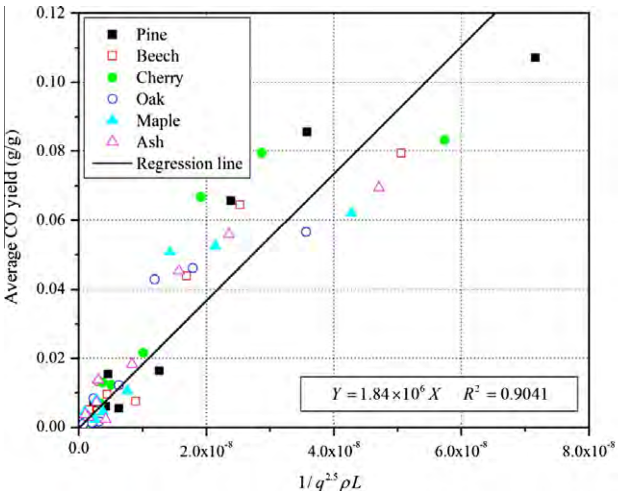

Fig. 10. Correlation between average CO yield and other properties.

flux is 25 kW/m^2. Also these data may present that the average CO yield correlates linearly with $\dot{q}''^{-b}$.

Based on the results from Figs. 7 to 9, the average CO yield may can be expressed as:

$$Y_{CO} = a\frac{1}{\dot{q}''^{b}\rho^{c}L^{d}} \quad (2)$$

where Y_{CO} is the average yield of CO, g/g; and a is the coefficient.

Taking the logarithm of both sides, it is gained that:

$$\log Y_{CO} = \log a - b\cdot\log\dot{q}'' - c\cdot\log\rho - d\cdot\log L \quad (3)$$

It is obtained that a, b, c, and d are 1.84×10^{6}, 2.5, 1, and 1, respectively, by using linear regression method. A correlation between average yield of CO and $1/\dot{q}''^{2.5}\rho L$ is shown in Fig. 10.

The correlation between average CO yield and heat flux, density, and thickness can be given as:

$$Y_{CO,wet} = 1.84\times10^{6}\frac{1}{\dot{q}''^{2.5}\rho L} \quad (4)$$

where $Y_{CO,wet}$ is the average CO yield of wet wood samples (about 0.11 moisture content), g/g.

From this equation, it is known that the external heat flux has a great influence to the average CO yield, which can be proved by Fig. 9. It is also noticed that the average CO yield of wood sample is inversely proportional to density and thickness.

4. Influences of moisture

4.1. CO release rate

Fig. 11 shows CO release rate of wet and dry oak under external heat flux. It is noticed that moisture has influences to the CO release rate. A higher CO release rate is observed with dry wood. Peak CO release rate of dry wood happens earlier than those of wet wood. It is observed that moisture postpones the time to peak CO release rate, and reduces CO release rate as well.

Under external heat flux, moisture inside woods start to evaporate when temperature is higher than 100 °C. For wood samples with a higher moisture content, energy used for water evaporation increases. Temperature inside then rises slower as less energy can be used for heating up. As production of CO depends on temperature, lower temperature mean less production of CO. Kaewluan and Pipatmanomai [12] obtained a similar result that average bed temperature of woodchip was reduced from about 760 °C by about 60 °C when moisture content increases from 9.5% to 25.5%. Houck and Tiegs [21] also mentioned that high moisture reduces combustion temperature and hence combustion is more incomplete.

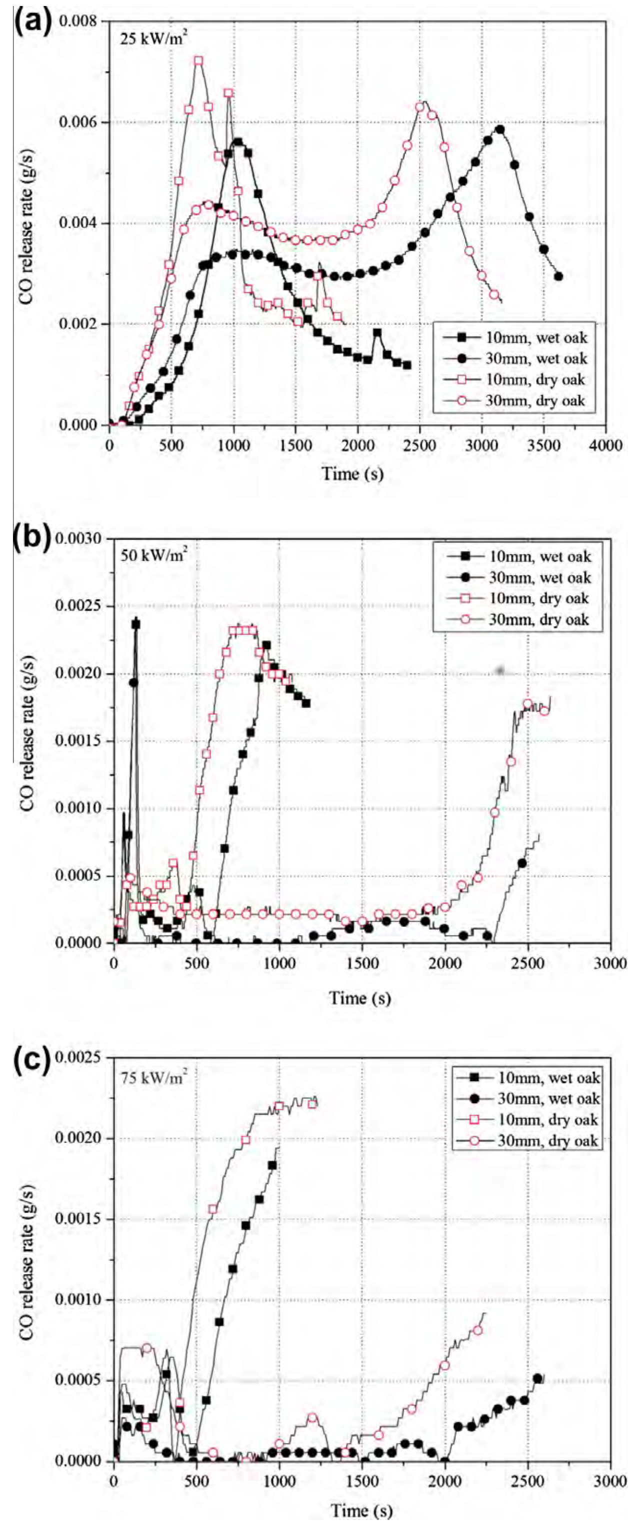

Fig. 11. CO release rate of wet and dry oak under external heat flux (a) 25 kW/m^2; (b) 50 kW/m^2; and (c) 75 kW/m^2.

As mentioned above, chemical components such as cellulose, hemicelluloses and lignin, decompose in specific temperature ranges, so these decomposition reactions are postponed under high moisture content, resulting in a delay of peak CO release rate.

4.2. CO yield

Fig. 12 shows a comparison of average CO yield between wet wood and dry wood. Average CO yield increases with a lower moisture content. However, the effect of moisture to the CO yield cannot be identified accurately by this figure as they have different densities.

For wet woods, average CO yield correlates linearly with $1/\dot{q}''^{2.5}\rho L$. For dry woods, average CO yield may also obey the same rule. Fig. 13 shows a correlation between average CO yield of dry wood and $1/\dot{q}''^{2.5}\rho L$. It is noticed that these two correlate well, which can be expressed by:

$$Y_{CO,dry} = 2.6 \times 10^6 \frac{1}{\dot{q}''^{2.5}\rho L} \quad (5)$$

where $Y_{CO,dry}$ is the average CO yield of dry woods (no moisture inside), g/g.

From Eqs. (4) and (5), it is noticed that average CO yield for both of wet woods and dry woods correlate linearly with $1/\dot{q}''^{2.5}\rho L$. From the coefficients of these two equations, it is known that average CO yield decreases with a higher moisture content. The effect of moisture to CO yield may can be represented by the coefficients. Kaewluan and Pipatmanomai [12] investigated the effect of moisture by

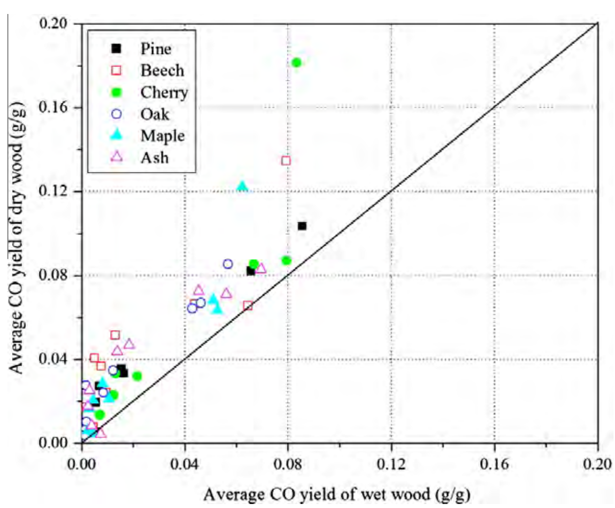

Fig. 12. A comparison of average CO yield between wet wood and dry wood.

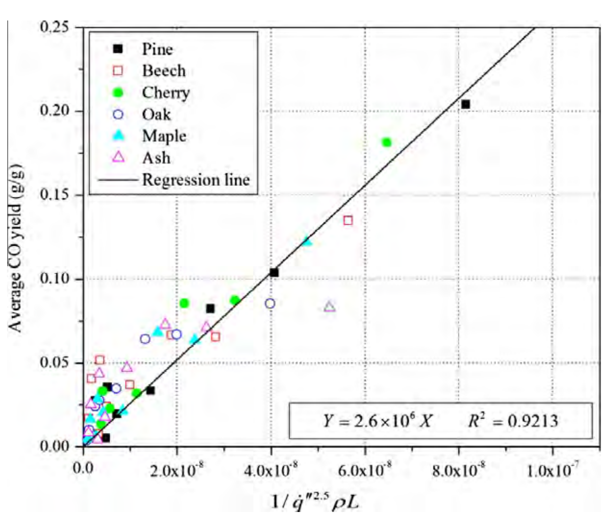

Fig. 13. Correlation between average CO yield and other factors.

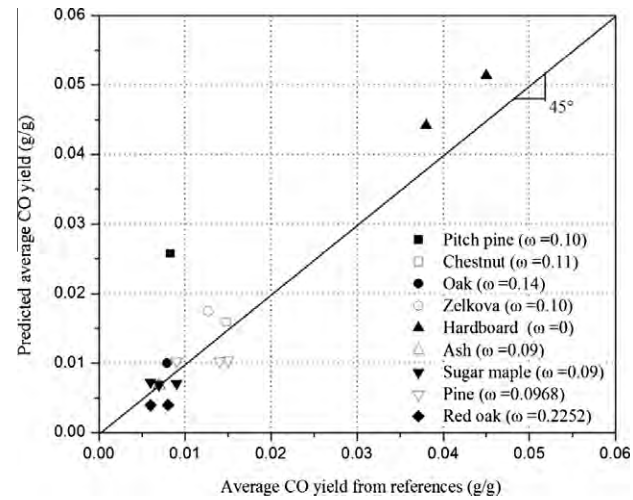

Fig. 14. Comparison between predicted CO yield and reference data.

varying the moisture content in woodchip at 0.095, 0.181 and 0.255. It was gained that minimal gas yield happens when moisture content is 0.181. Houck and Tiegs [21] showed that the lowest gas emissions occurs with wood moisture in the 0.13–0.20 range (wet basis). This means that gas yield does not always decrease when moisture content goes up. Maybe there exists a turning point. As mentioned above, it is known that gas yield keeps decrease under a range of moisture content from 0 to 0.13.

Due to a lack of references on the effect of moisture to the average CO yield, it is assumed that CO yield correlates linearly with moisture content when moisture contents are less than 0.13. Combining Eqs. (4) and (5), average CO yield of woods can be expressed by:

$$Y_{CO} = (2.6 - 6.9\omega) \times 10^6 \frac{1}{\dot{q}''^{2.5}\rho L} \quad (10 \leqslant L \leqslant 30) \quad (6)$$

where ω is the moisture content, 0–0.13; and ρ is the original density of dry woods or wet woods, kg/m^3.

Fig. 14 shows a comparison between predicted CO yield and reference data. For reference data [7,22–23], the range of moisture content for these wood samples is 0–0.2252. It is noticed that the predictions obey well with reference data.

5. Conclusion

This paper investigated carbon monoxide (CO) on the six species of wood samples under external heat flux by spontaneous ignition in a cone calorimeter. The following conclusions can be addressed:

(1) For CO release rate, thickness has little effect to peak values, but the time to peak is postponed with a higher thickness. Peak CO release rate decreases with a higher external heat flux, but decrease is not obvious when external heat flux increases from 50 to 75 kW/m^2.
(2) The flame also has influence to the CO release rate. A sharp decrease of CO release rate happens shortly after ignition and a second peak is near the end of the experiment. This may be because the flame accelerate the oxidation reaction of CO, leading to a decrease of CO and increase of CO_2.
(3) Time to peak CO release rate is postponed under the effect of moisture. And CO release rate decreases with a higher moisture content. This is because energy used for water evaporation increases with a higher moisture content. Temperature

then rises slower as less energy can be used for heating up. Chemical components such as cellulose, hemicelluloses and lignin, decompose in specific temperature ranges, so these decomposition reactions are postponed under high moisture content, resulting in a delay of peak CO release rate.

(4) Average CO yield is inversely proportional to external heat flux, thickness, and density. Average CO yield of wood samples under different external heat flux and moisture contents can be gained by:

$$Y_{CO} = (2.6 - 6.9\omega) \times 10^6 \frac{1}{\dot{q}''^{2.5} \rho L} \quad (10 \leqslant L \leqslant 30)$$

The empirical model and data in this study not only can be used to predict average CO yield of wood samples under different external heat flux and moisture content by spontaneous ignition, but also could be used for modeling input or validation of numerical models.

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