Effects of External Heat Flux and Exhaust Flow Rate on CO and Soot Yields of Acrylic in a Cone Calorimeter

Sun-Yeo Mun, Jae-Ho Cho and Cheol-Hong Hwang *

Department of Fire and Disaster Prevention, Daejeon University, 62 Daehak-ro, Dong-Gu, Daejeon 34520, Korea; fayamun@gmail.com (S.-Y.M.); fayajaeho@gmail.com (J.-H.C.)
* Correspondence: chehwang@dju.ac.kr; Tel.: +82-42-280-2592

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Abstract: The effects of changes in irradiance level (external heat flux), exhaust flow rate, and hood height on CO and soot yield were examined using a cone calorimeter. Black acrylic, having similar constituents as polymethyl methacrylate, was used as a combustible, and external heat fluxes ranging from 15 to 65 kW/m² were considered. Both auto and spark ignitions were applied as ignition methods. The difference in auto and spark ignition methods had no effect on CO and soot yields, or on the mass loss rate (MLR), heat release rate (HRR), and effective heat of combustion (EHC), which are global parameters of fire. As the external heat flux increased, the mean MLR and HRR linearly increased while the EHC remained constant. When the external heat flux increased, the mean mass flow rates of CO and CO₂ had a directly proportional relationship with the mean MLR. Consequently, CO and CO₂ yields remained constant regardless of the external heat flux. In contrast, the mean mass flow rate and mean MLR of soot were linearly proportional as opposed to directly proportional, and the soot yield thus increased linearly with external heat flux. Variations in the exhaust flow rate and hood height, which can alter the velocity and temperature fields in post-flame and plume regions, had almost no impact on CO and soot yields, as well as on MLR and HRR. The results of this study are expected to provide improved insight into conventional approaches on the recognition of CO and soot yields as unique properties of each combustible.

Keywords: cone calorimeter; black acrylic; external heat flux; CO yield; soot yield; exhaust flow rate

1. Introduction

Reaction-to-fire (flammability), which indicates how combustibles respond to fire or heating, is often considered for quantitatively evaluating fire risks and hazards through various fire test standards, in addition to fire endurance (or resistance) [1]. In particular, cone calorimeters that are based on ISO 5660-1 [2] and ASTM E1354 [3] are commonly used for assessing the flame-retardant nature of solid combustibles in an open space, and for measuring combustion properties; further, they have been recognized as the most critical bench-scale apparatus in the fire safety field [4,5]. Specifically, simulated fire environments can be embodied by controlling the incident radiant heat flux on the surface of a solid combustible using a cone calorimeter. The ignition time, mass loss rate (MLR), heat release rate (HRR), effective heat of combustion (EHC), and combustion products, including toxic gases and smoke, can also be measured [6]. These data are used to evaluate the various fire risk factors such as the pyrolysis, flammability, and fire spread rate of solid combustibles. Clearly, caution is needed when directly associating the results of a bench-scale cone calorimeter experiment conducted using a specimen of limited size (10 mm square) with the complicated fire behaviors in full-scale models [1,7,8]. However, the experimental results of a cone calorimeter can be useful in understanding thermal and chemical characteristics per unit area of combustibles in the thermal environment of a controlled fire. Furthermore, information on various physical input parameters is provided to enable the numerical prediction of the risk of a full-scale fire. Numerous reports on
the cone calorimeter apparatus, test data, and engineering applications are systematically explained in Ref. [9].

The effective heat flux on the specimen surface of a cone calorimeter can be determined by the thermal balance of the irradiance (external heat flux), flame heat flux, and re-radiated heat flux. Among these heat fluxes, the external heat flux supplied by a cone heater is the most fundamental and important control variable in a cone calorimeter. In general, an external heat flux value below 20 kW/m$^2$ is applied to examine the ignition and flammability, and a range of 25–30 kW/m$^2$ may be applied for the fire spread. In addition, a higher external heat flux of 50 kW/m$^2$ is applied to discuss compartment fires after flashover, as well as to measure combustion properties. In practice, an external heat flux of 35 or 50 kW/m$^2$, which has a higher reproducibility of measurement results, has commonly been applied in previous studies [10,11]. Considering the degree to which the thermal conditions of combustible surfaces in compartment fires have a quantitatively very large scale or vary significantly over time, applications of an appropriate external heat flux should be examined, which accurately correspond to each of the fire growth stages of ignition (incipient)—growth—fully developed—decay or the considered fire scenario.

In studies that examined the effects of external heat flux on pyrolysis and the fire behaviors of solid combustibles, Chen et al. [12] verified that the transformed ignition time $(1/t_{ig})^{0.55}$ or $1/t_{ig}$ linearly increases, and this was considered to identify thermally thick or thermally thin materials with respect to the changes in external heat flux for commercial flame retardant materials within the range of 20–60 kW/m$^2$. Moreover, the peak and average MLR, as well as the HRR, all increased linearly with respect to the heat flux. On the contrary, the thermal thickness, which indicates the thermal penetration depth of the material at ignition, decreased with heat flux. Li et al. [13] confirmed that the MLR increases linearly with respect to the external heat flux for polymethyl methacrylate (PMMA) flames, and that the flame height is linearly dependent on the $2/3$ power of MLR. Scudamore et al. [14] verified that significant changes are observed in the ignition time, HRR, and smoke specific extinction with respect to the external heat flux (20–75 kW/m$^2$) for 25 plastic materials. The researchers also proposed that the examination of the heat flux levels for responding to a developing and a developed fire is important when considering the environment in which materials are applied. As shown in previous studies mentioned above, the importance of the effects of external heat flux are sufficiently known in a fire risk evaluation using a cone calorimeter in which the flammability, pyrolysis, HRR, and smoke production rate are taken into account. However, there is a lack of research on the effects of the external heat flux on the generation of carbon monoxide (CO) and soot, which are major hazards in a fire.

CO is a typical incomplete combustion product of hydrocarbon fuels, and the inhalation of CO is a major cause of death in fires. The generation of soot reduces visibility, which hinders the evacuation and fire extinguishing activities of firefighters, while the increased radiant heat owing to soot may increase the flame spread and burning rate [15,16]. Therefore, it is important to predict the amount of CO and soot generated from various combustibles in a fire environment when attempting to accurately evaluate the associated fire risks. The yield, which is defined as the ratio of the mass production rate of chemical species to the mass reduction rate of fuel, is often used to determine the amount of CO and soot generated in a fire, in addition to the generation factor and emission index, which have the same meaning [17,18]. The product emission yields for various combustibles obtained from a bench-scale cone calorimeter are directly used to evaluate the quantitative risks of hazardous materials, while providing useful information for extrapolating full-scale fire scenarios [1].

In general, the emission of CO in buoyant nonpremixed (diffusion) flames found in fires is generated from the imbalance of the production rate and oxidation rate. When the reaction pathway of hydrocarbon fuels is examined, CO is generated through the very complicated process of oxidation reactions, and then CO is converted to CO$_2$ mainly by reacting with OH. The reaction of CO+OH is relatively slower than other radical reactions,
and therefore, the CO that is not oxidized is eventually discharged [18]. Conceptually, the emission of CO may increase if there is an insufficient amount of additional air required for the generated CO to be oxidized or an insufficient residence time for the oxidation reaction to occur [19]. If this principle of CO generation is applied to an experimental environment of a cone calorimeter, where the air is sufficiently supplied to an open space, the mixing of CO and air may not have a significant impact on CO emission. In contrast, the changes in MLR and flame height according to the external heat flux [13] may influence the residence time in the region, satisfying the oxidation reaction conditions (temperature and oxygen concentration) of CO.

For soot, which has more complicated generation characteristics than CO, the flame temperature and residence time in the high-temperature region are known to be dominant parameters for controlling soot formation in a flame [20]. In fires involving hydrocarbon fuels, the flame temperature has a critical influence on soot formation starting from fuel pyrolysis, which corresponds to an endothermic reaction, to soot oxidation. When the flow rate of fuel changes, the changes in air entrainment and flame strain rate near the stoichiometric flame surface may cause the flame temperature to change, while the soot and flame temperature affect each other owing to radiation heat transfer. In addition, a sufficient residence time in the high-temperature region is required for complex chemical reactions included in the complicated soot generation path, including gas-phase precursor formation, soot nucleation, soot surface growth, particle coalescence, agglomeration, and soot oxidation [21,22]. The residence time can vary substantially depending on the flame height, which is affected by the fuel type and flow rate. Specifically, the residence time for soot formation in the buoyancy-controlled coflow flame is dependent on the flame height, which is proportional to $QS$, where $Q$ is the volumetric flow rate of the fuel gas mixture, and $S$ is the stoichiometric molar oxidizer-to-fuel ratio of the mixture [23,24]. MLR, which is the mass flow rate of a gaseous substance that has been pyrolyzed in a cone calorimeter, increases with the external heat flux, while the flame height is linearly dependent on the $2/3$ power of MLR [13]. The changes in MLR with respect to the external heat flux in a cone calorimeter may change the flame temperature owing to the changes in air entrainment, flame strain rate, and radiation. The residence time may also vary depending on the flame height [25–28]. Consequently, the amount of soot, as well as the soot properties, can vary significantly depending on the external heat flux. Furthermore, quantitative changes in the soot yield with respect to external heat flux need to be examined sufficiently, considering the nonlinear nature of complicated chemical kinetics and various factors that are related to soot formation.

Based on the principle of CO and soot generation, the changes in external heat flux in a cone calorimeter can be predicted to lead to changes in the MLR, flame height, flame temperature, and residence time, with a high possibility of ultimately inducing changes in CO and soot yields. However, the effects of the external heat flux are not sufficiently considered when measuring CO and soot yields in a cone calorimeter, where the measurement values at a specific external heat flux arbitrarily selected by researchers are recognized as unique combustion properties of each combustible [29]. In particular, the constant value of a specific fuel is applied for CO and soot yields, which are required as crucial input parameters in a fire risk analysis based on fire simulations [30]. As a result, a risk analysis based on fire simulations may produce quantitative errors that cannot be neglected.

In studies conducted on the effects of the external heat flux on CO and soot yields in a cone calorimeter, Paul [6] reported that the CO yield increases linearly, while no significant changes in CO$_2$ yield are observed as the external heat flux is increased (within the range of 25–75 kW/m$^2$) for PMMA. On the other hand, Luche et al. [31] reported that the CO yield decreases slightly, while the CO$_2$ yield increases slightly with the external heat flux (within the range of 15–60 kW/m$^2$). When the measurement results were inspected in detail, however, the CO yield was 0.008 g/g when the external heat flux was 20 kW/m$^2$ or below, and the CO yield was constant at 0.006 g/g when the external heat flux was within the range of 25–60 kW/m$^2$. Despite the identical test methods and conditions such
as the application of the cone calorimeter, PMMA, and spark ignition based on ISO 5660-1, the variation trends of the CO yield with respect to the changes in external heat flux differed; unfortunately, the soot yield was not measured in these studies. In a study that examined both CO and soot yields, Abu-Bakar et al. [32] reported that CO and soot yields both increase linearly with the external heat flux (within the range of 25–75 kW/m²). There are fundamental limitations with respect to gaining a concrete understanding of CO and soot formation based on CO and soot yield measurements using a cone calorimeter. Nonetheless, previous studies [6,31,32] simply reported the measurement results, thus failing to fully understand the effects of the external heat flux on the CO and soot yields. The differences in the quantitative values of CO and soot yields measured in a cone calorimeter may be attributable to the differences in the detailed dimensions of the apparatus, proficiency of the researchers, and measurement uncertainties. Moreover, considering that pseudo-steady-state burning is generally not present in solid combustibles, a significant difference may result from the selection of measurement starting and end points in order to obtain the average data [6]. As the measurement results of previous studies are not consistent, valid trends of CO and soot yields due to the changes in external heat flux must be examined again carefully.

Accordingly, this study experimentally analyzed the combustion properties according to the irradiance level (external heat flux) using a cone calorimeter. Black acrylic having similar constituents as PMMA was used as a combustible, and external heat fluxes that range from 15 to 65 kW/m² were considered. Auto-ignition and spark ignition were all applied as ignition methods. The ignition time, MLR, HRR, EHC, CO, CO₂, and soot yields were measured. In particular, it highlighted the need to re-examine the trend of changes in CO and soot yields when there are changes in the external heat flux as a primary parameter. In addition to the external heat flux, the effects of the changes in the exhaust flow rate and hood height, which can influence air entrainment, flame height, and thermal quenching, on the CO and soot yields were also examined. The results of this study are expected to provide improved insight into conventional approaches on the recognition of CO and soot yields as unique properties of each combustible, which are crucial for evacuation and personal safety.

2. Experimental Method and Conditions
2.1. Material
CO and soot yields are known to quantitatively vary significantly depending on the type of combustible [29]. Black PPMA is most widely used as a reference material when evaluating the relevance of the cone calorimeter apparatus setup and when directly comparing the measurements of other researchers [31,33–37]. PMMA, which is a well-known noncharring polymer, generates a combustible gas when melted by heat, and has a similar fire phenomenon as oil fires. Unlike charring polymers (ABS, PVC, PC, etc.), which exhibit complicated pyrolysis and heat transfer phenomena owing to the formation of a char layer, PMMA does not have residuals after combustion, and entails a relatively simpler pyrolysis process. To minimize the difference in measurements due to differences in detailed components of PMMA in an experiment conducted using a cone calorimeter, it is recommended to use standard PMMA in which the ignition time, HRR, and EHC are satisfied within an appropriate range [38]. This study used a polymer that is produced using a cell casting method, that has similar components as standard PMMA, and that is generally easily sourced. The material was named black acrylic as a matter of convenience because the certificate of test of PMMA was not provided by the manufacturer.

2.2. Experimental Conditions
To examine the effects of changes in the external heat flux, exhaust flow rate, and hood height on CO and soot yields for black acrylic, an open-cone calorimeter illustrated in Figure 1 was produced based on ISO 5660-1 [2]. This apparatus was designed to be utilized as a controlled atmosphere cone calorimeter (CACC) [39] to examine the variation in the
ignition characteristics of solid combustibles with the oxygen concentration. Specifically, an open-cone calorimeter can be embodied by opening the front and rear back sides. Compared to the original open-cone calorimeter, by performing numerical simulations [40,41] and experiments comparing results with previous studies, it has been adequately proven that a limited open area due to external housing has no effect on measurement data (ignition time, HRR, yield, etc.). The HRR was measured based on the oxygen consumption technique [42,43], and was calibrated up to 8 kW using propane fuel. The MLR of black acrylic was measured using a load cell. To minimize the measurement errors of a load cell due to radiant heat, the apparatus was designed so that coolant is supplied outside the box in which the load cell is installed.

![Schematic of a cone calorimeter and photograph of test section.](image)

The external heat flux, which is the primary parameter of this study, was varied within a wide range of 15–65 kW/m². The calibration of the external heat flux was performed by a Schmidt Boelter gauge at the specimen location. The surface area of the specimen was 100 mm × 100 mm, and the actual surface area receiving radiant heat from the specimen holder was 0.0088 m² (94 mm × 94 mm). The maximum value of HRR, the penetration time of heat in the depth direction, and the CO yield can be markedly affected by the thickness of the specimen [44]. Thus, the specimen thickness was fixed at 10 mm in this study. The distance between the specimen surface and the bottom of the cone heater was fixed at 0.025 m. The cross-sectional mean velocity inside a duct was measured using a blade-shaped pitot tube (Debimo 125, KIMO) and a differential pressure transmitter (MS-311-LCD, Dwyer). To ensure that the volume flow rate of the exhaust hood was consistently supplied, the hood was operated for 10 min before the experiment, and then a gas analyzer was calibrated. The experiment was repeated at least three times for each specimen to obtain the mean and standard deviation of the measurement data.

To ignite solid combustibles in a cone calorimeter, the spark ignition and auto-ignition methods can be applied. The pilot ignition process is controlled by pyrolysis, while the auto ignition process is known to be dependent on the gas-phase reaction, as well as the pyrolysis [36]. Therefore, to examine the effects of an ignition process on burning characteristics, including the CO and soot yields according to an ignition method, both the spark ignition and auto ignition methods were considered in this study.

Figure 2 shows the images of the cone heater and the schematics of two exhaust hood heights (h) considered in this study. The exhaust flow rate and hood height (vertical height from the specimen surface to the bottom of the hood) based on ISO 5660-1 are 24 L/s and 0.25 m, respectively. As mentioned in the introduction, the changes in MLR with respect to the external heat flux induce changes in the flame height, thus significantly affecting CO
and soot yields accordingly. As an additional parameter that may affect the flame height, the changes in the exhaust flow rate may change the entrainment of the surrounding air, which can also significantly affect the flame height due to flame stretch. Therefore, under the condition where external heat flux is fixed at 50 kW/m², five different conditions of exhaust flow rate within the range between 24 and 86 L/s were applied. A flame generated in a cone calorimeter undergoes periodic fluctuation owing to buoyancy; the maximum height of the instantaneous flame can be positioned inside the hood. An exhaust hood height of 0.55 m was also considered in addition to 0.25 m in order to examine the effects of direct impingements when a flame or high-temperature plume crashes on the surface of the upper part of the hood having low temperature and high thermal conductivity. As the hood height increases, overflow of exhaust gas occurs in a low exhaust flow rate; thus, only the results of the 72 L/s condition were compared.

![Figure 2. Photographs of a cone heater and the schematics of exhaust hood heights considered.](image)

2.3. Calculation of CO and Soot Yields

As shown in Figure 1, the CO yield was calculated using the cross-sectional mean temperature ($T_d$), flow rate ($V_d$), volume fraction of CO ($X_{CO}$) measured within the exhaust duct, and MLR measured with a load cell. The CO yield ($y_{co}$) is expressed as the ratio of the time-averaged mass flow rate ($\bar{m}_{co}$) of CO to MLR ($\bar{m}_f$), as shown in Equation (1).

$$y_{co} = \frac{\bar{m}_{co}}{\bar{m}_f}$$  (1)

As mentioned in the introduction, selecting start and end points in the time averaging process of the measurement data can have a significant effect on quantitative changes in physical quantities. In particular, in studies involving cone calorimeters, various criteria have been applied to define $\bar{m}_f$ during the entire burning time [16,38,45]. In this study, $\bar{m}_f$ was calculated as the mass variation ($m_{t0} - m_{t10}$) of the section corresponding to between 10% ($t_{10}$) and 90% ($t_{90}$) of the entire mass loss using Equation (2); $\bar{m}_{co}$ was calculated using Equation (3) [38].

$$\bar{m}_f = \frac{(m_{t0} - m_{t10})}{(t_{90} - t_{10})}$$  (2)

$$\bar{m}_{co} = \frac{\int_{t_{10}}^{t_{90}} Y_{co}(t) \bar{m}_e(t) dt}{(t_{90} - t_{10})}$$  (3)

where $Y_{co}$ is the mass fraction of CO, which was converted using the equation $Y_{CO} = X_{CO} MW_{CO} / MW_{air}$. $\bar{m}_e$ indicates the mass flow rate within the exhaust duct, which was calculated using the equation $\bar{m}_e = \rho_e A_D V_D$. Moreover, $MW$, $A_D$, and $V_D$ indicate the
molecular weight, area of the exhaust duct, and average velocity within the exhaust duct, respectively. The density inside the exhaust duct ($\rho_e$) is calculated as the mean temperature measured at three different locations in the radial direction. For most fire calculations, the average molecular weight of exhaust gases is similar to that of air, and it was assumed that the value is primarily determined by temperature \[29\]. Specifically, $\rho (\text{kg/m}^3)$ is calculated based on $352.8/T(K)$.

Regarding the calculation of the soot yield ($y_{\text{soot}}$), the light extinction coefficient has the relationship of optical path distance ($L$) and permeation rate based on Bouguer’s law, as shown in Equation (4) \[46\].

$$k(t) = -\ln(I(t)/I_0)/L$$  

(4)

Here, $I_0$ and $I$ represent the voltage of a photo transistor before and after ignition, respectively. The mass concentration of the smoke ($m_{\text{soot}}$) can be calculated using Equation (5), $k_m$ is the mass specific extinction coefficient, which is dependent on the fuel in which hydrocarbon fuels have a coefficient of 8.4, while wood materials have a coefficient of 7.6 \[29\]. Then, the mass flow rate of the smoke ($\dot{m}_{\text{soot}}$) is expressed as the product of the volume flow rate ($V_e$) within the exhaust duct, as shown in Equation (6). Finally, $y_{\text{soot}}$ was calculated using Equation (7).

$$m_{\text{soot}}(t) = k(t)/k_m$$  

(5)

$$\dot{m}_{\text{soot}}(t) = m_{\text{soot}}(t)V_e(t)$$  

(6)

$$y_{\text{soot}} = \bar{m}_{\text{soot}}/\bar{m}_f = \left[ \int_{t_{10}}^{t_{90}} m_{\text{soot}}(t)dt / (t_{90} - t_{10}) \right] / \bar{m}_f$$  

(7)

3. Results and Discussion

3.1. Burning Characteristics of Black Acrylic According to External Heat Flux

To evaluate the relevance of experimental methods and the setup of a cone calorimeter, Figure 3 illustrates the ignition time according to the external heat flux under auto and spark ignition conditions. Quantitative errors that may be generated owing to the specimen components were verified by comparing standard PMMA and black acrylic applied in this study. In addition, the ignition time of PMMA was compared with the findings of previous studies \[33,37\]. Figure 3a shows the experimental results obtained where the auto-ignition method was applied; all conditions below 40 kW/m$^2$ were excluded where ignition did not occur during an exposure time of external heat flux for 30 min or longer \[2\]. The ignition time gradually decreased with the external heat flux, and there was almost no quantitative difference between black acrylic and standard PMMA. Moreover, the relative error between the measurements in this study and the previous study \[37\] is very similar, about 3.5%.

Figure 3b shows the results obtained within an external heat flux range of 15–65 kW/m$^2$ under the spark ignition condition. The results of this are quantitatively very similar to those of a previous study conducted under identical experimental conditions. The standard deviation (vertical error bar) from repeated experiments was largest under the condition of 15 kW/m$^2$, while the reproducibility of measurements was fairly high under the condition of 30 kW/m$^2$ or greater. The relative error between the measurements with the previous study \[33\] is very similar, about 9.5% at 15 kW/m$^2$ and about 4.8% above 30 kW/m$^2$. Thus, the reliability of the experimental methods and cone calorimeter apparatus applied in this study is guaranteed, while the results of black acrylic are quantitatively very similar to the results of standard PMMA, as shown in Figure 3.
Figure 3. Ignition times as a function of external heat flux for the auto and spark ignitions.

Figures 4 and 5 illustrate the changes in MLR and HRR of black acrylic with respect to time under various external heat fluxes. Time from ignition may be generally used as the title of the x-axis. However, to examine the ignition phenomena in detail according to an ignition method, the time in the x-axis was proposed as the time at which the external heat flux is exposed to the specimen. The results illustrated in Figure 4 show that the MLR was higher after ignition as the external heat flux was higher, regardless of the ignition method, while the time to reach the maximum MLR was reduced. The difference in MLR in terms of the ignition method was clearly shown under the condition of an external heat flux of 40 kW/m², which is relatively low. In other words, the MLR value between 50 and 140 s was approximately 0.05 g/s when auto-ignition was applied, where MLR increased sharply after 25 s, which corresponds to the ignition time when spark ignition was applied. Specifically, under the auto-ignition condition, even if pyrolysis by external heat flux proceeds and combustible gas reaches the lower flammability limit, ignition would not occur if insufficient thermal energy is provided to initiate the gas-phase reaction. This moment is marked as the “only pyrolysis period” in Figure 4a. In contrast, forced ignition occurs when the lower flammability limit is reached through pyrolysis under the spark ignition condition [36]. Under the condition of a relatively lower external heat flux, excluding the delay in ignition time due to the inactivation of the gas-phase reaction that can occur in the initial phase of pyrolysis, the changes in HRR with respect to time showed very similar behaviors when compared to MLR, as illustrated in Figure 5.
To examine the global burning behaviors of acrylic with respect to the external heat flux, Figure 6a,b show integral values over time, as well as maximum and mean values that are related to MLR and HRR. TML and THR in the figure represent the total mass loss (kg) due to pyrolysis and total heat release (kJ) due to the gas-phase reaction, respectively. TML and THR showed constant values regardless of the external heat flux because the same specimen was applied. The maximum and mean values of MLR and HRR tended to linearly increase with the external heat flux, which was also observed in previous studies [12,13]. Furthermore, it was clearly shown that auto and spark ignitions, which showed different ignition phenomena under relatively low heat flux conditions, had no significant impact on global burning behaviors.

Figure 7 shows the effective heat of combustion values (EHC, kJ/kg) with respect to the external heat flux, indicating the thermal energy that can be emitted per unit mass of fuel in an actual fire environment in which incomplete combustion is taken into consideration. In this study, the EHC was calculated as the ratio of the mean HRR to the mean MLR (HRRmean/MLRmean). The average EHC in the figure was 25.575 kJ/kg, having a 3.7% relative error with respect to the average value for all external heat fluxes and ignition methods considered in this study. The measured EHC of the black acrylic is quantitatively similar to the EHCs (24–25 MJ/kg) of black PMMA measured within a wide range of external heat fluxes in previous studies [31,32,35,36]. Accordingly, the EHC measured in a cone calorimeter was almost not affected by the external heat flux and ignition method, while maintaining a constant value. From the perspective of global burning characteristics, a constant EHC value indicates that the combustion efficiency is similar with respect to the external heat flux [47]. However, CO and soot, which are incomplete combustion products,
have very small volume fractions compared to complete combustion products. Therefore, CO and soot yields according to external heat flux need to be further examined.

Figure 7. Effective heat of combustion as a function of external heat flux for the auto and spark ignitions.

3.2. Effect of External Heat Flux on CO and Soot Yields

Before examining the changes in CO and soot yields according to external heat flux, the mean mass flow rates of CO and soot according to the mean MLR, which were applied to calculate the yield, are illustrated in Figure 8. CO$_2$, which is a common complete combustion product, is also presented. The horizontal and vertical error bars in the figure indicate the standard deviation obtained during the process of calculating the average of the tests repeated at least three times. The mean mass flow rates of CO, CO$_2$, and soot measured in the exhaust duct clearly increased linearly with respect to the mean MLR. Quantitatively, the linear regression line in the figure shows that coefficients of determination ($R^2$) were all above 0.96. That is, the amount of CO, CO$_2$, and soot generated all had a linear relationship with respect to the mean MLR. More specifically, the mean mass flow rates of CO and CO$_2$ were directly proportional to the mean MLR, considering that the y-intercept of the linear regression lines shown in Figure 8a,b is near 0. In contrast, the y-intercept of the linear regression line in Figure 8c is a negative value that cannot be neglected, which implies that the mean mass flow rate of soot simply had a linearly proportional relationship with the mean MLR instead of a directly proportional relationship. As presented in Figure 6a, the mean MLR increased linearly with respect to the external heat flux, while the yields of combustion products are expressed as the ratio of $x$-axis values to $y$-axis values shown in Figure 8. Therefore, the yields of CO and CO$_2$ can have a constant value when the external heat flux increases, whereas the soot yield can be expected to vary. In addition, differences in ignition methods such as auto and spark ignitions had almost no influence on the mass flow rates of CO, CO$_2$, and soot.
Figure 8. Mean mass flow rates of CO, CO$_2$, and soot as a function of mean mass loss rate.

Figure 9 illustrates the changes in CO, CO$_2$, and soot yields with respect to the external heat flux. As shown in Figure 8, the mean mass flow rates of CO and CO$_2$ were directly proportional to the mean MLR, while MLR was known to increase linearly as the external heat flux increased. Accordingly, CO and CO$_2$ yields were 0.0070 and 2.3202 g/s, respectively, regardless of the external heat flux or ignition method, as shown in Figure 9a. For reference, the CO and CO$_2$ yields measured in this study were quantitatively very similar to the results of a previous study [31]. Constant CO and CO$_2$ yields with respect to the external heat flux imply that the ratio of CO/CO$_2$ was also constant. The ratio of CO/CO$_2$ is used for predicting CO generation in the hazard assessment of some room fire models in which the value is known to have a relatively consistent value in the given fuel and fire environments [48]. The ratio of CO/CO$_2$ was constant because the same ventilation conditions (a cone calorimeter in an open space) of fire as black acrylic were applied. As mentioned in the introduction, an increase in the external heat flux can induce changes in the flame height and residence time through an increase in MLR. However, the changes in these factors related to CO generation did not significantly impact CO emission in a cone calorimeter where the air is sufficiently provided, which is a meaningful implication. As illustrated in Figure 9b, the soot yield increased linearly with respect to the external heat flux, unlike the CO yield. This result was deduced because the mean mass flow rate and mean MLR of soot shown in Figure 9b were not in a directly proportional relationship. Considering previous studies on soot formation, an increase in the residence time due to flame height, which increases linearly at the 2/3 power of MLR, has contributed most significantly to the increase in the soot yield. It is clear that the flame temperature due to changes in air entrainment, flame strain rate, and radiation caused by changes in the external heat flux must have also affected the changes in soot yields in a complex manner. As the flame temperature, which has the greatest impact on soot formation, and residence time in the high-temperature region were not measured in this study, there were limitations with respect to the concrete interpretation of the changes in soot yield according to the external heat flux. However, the results shown in Figure 9b still provide important information in that caution is required in conventional approaches [29,30] where the soot yield measured at a specific external heat flux is applied as a unique combustion property of combustibles.
CO and soot yields owing to the following factors: air entrainment in post-flame and specifically, changes in the exhaust flow rate and hood height have the potential to affect plume regions, mixing rate of combustible gas and air, flame stretching by the suction flow of the hood, and direct quenching phenomena when a flame or high-temperature plume crashes on the surface of the upper part of the hood. The exhaust flow rate proposed in ISO 5660-1 is 24 L/s, while the hood height that corresponds to the vertical distance from the specimen surface to the bottom of the hood is 0.25 m. Considering that the exhaust flow rate is based on volume rather than on mass, however, it is difficult to maintain a constant volume flow rate inside the exhaust duct, where there is a significant temperature change in exhaust gas. That is, the exhaust flow rate and hood height can vary significantly in the experiment process and setup of a cone calorimeter according to the individual researchers. Therefore, examining the effects of changes in the exhaust flow rate and hood height on CO and soot yields will provide an opportunity to inspect quantitative errors on the dependence of reference values proposed in ISO 5660-1 can also be assessed.

In addition to the external heat flux, which was examined as a factor affecting CO and soot yields in a cone calorimeter, the exhaust flow rate and hood height can also be considered as factors that influence the formation and emission of CO and soot. More specifically, changes in the exhaust flow rate and hood height have the potential to affect CO and soot yields owing to the following factors: air entrainment in post-flame and plume regions, mixing rate of combustible gas and air, flame stretching by the suction flow of the hood, and direct quenching phenomena when a flame or high-temperature plume crashes on the surface of the upper part of the hood. The exhaust flow rate proposed in ISO 5660-1 is 24 L/s, while the hood height that corresponds to the vertical distance from the specimen surface to the bottom of the hood is 0.25 m. Considering that the exhaust flow rate is based on volume rather than on mass, however, it is difficult to maintain a constant volume flow rate inside the exhaust duct, where there is a significant temperature change in exhaust gas. That is, the exhaust flow rate and hood height can vary significantly in the experiment process and setup of a cone calorimeter according to the individual researchers. Therefore, examining the effects of changes in the exhaust flow rate and hood height on CO and soot yields will provide an opportunity to inspect quantitative errors on the dependence of reference values proposed in ISO 5660-1 can also be assessed.

Figures 10 and 11 show MLR and HRR when the exhaust flow rate and hood height (h) change according to auto and spark ignitions under the fixed external heat flux condition of 50 kW/m². The exhaust flow rate was varied up to 86 L/s, including the reference condition of 24 L/s. Hood heights of 0.25 and 0.55 m were considered; however, for 0.55 m, the exhaust flow rate of 72 L/s at which overflow of exhaust gas does not occur was examined limitedly. As shown in Figure 10a, changes in exhaust flow rate under the conditions of h = 0.25 m and auto-ignition did not affect MLR significantly. The mean HRR of the section between 100 and 400 s was around 5.3 kW under all flow rate conditions that were quantitatively considered. The mean HRR was still around 5.1 kW when the hood height was increased to 0.55 m, thus proving that the effects of changes in hood height on MLR was negligible. The same trend was also observed under the spark ignition shown in Figure 10b. The results of HRR shown in Figure 11a,b indicate that HRR did not vary substantially according to the exhaust flow rate and hood height, thus resembling the results of MLR.
Figures 10 and 11 show MLR and HRR when the exhaust flow rate and hood height were changed. The results of soot yield, the value remained constant at 0.0184 g/g regardless of changes in the exhaust flow rate and hood height. Similar to the results of CO and CO\textsubscript{2} yields being constant with respect to the exhaust flow rate and hood height, the mean HRR was still around 5.1 kW when the hood height was increased to 0.55 m, thus proving that the effects of changes in hood height on global characteristics such as MLR and HRR, while the reference values proposed in ISO 5660-1 were deemed to be sufficiently representative.

Figure 10. Time histories of mass loss rate with the changes in exhaust flow rate and hood height (h) for auto and spark ignitions.

Figure 11. Time histories of heat release rate with the changes in exhaust flow rate and hood height (h) for auto and spark ignitions.

Figure 12 illustrates CO, CO\textsubscript{2}, and soot yields according to the exhaust flow rate for the two hood heights that were considered. As shown in Figure 12a, CO and CO\textsubscript{2} yields were constant at 0.0070 and 2.2030 g/g, respectively, regardless of the exhaust flow rate and hood height. Similar to the results of CO and CO\textsubscript{2} yields being constant with respect to the external heat flux in Figure 9a, the changes in the exhaust flow rate and hood height did not influence the CO and CO\textsubscript{2} yields. In Figure 12b, which shows the results of soot yield, the value remained constant at 0.0184 g/g regardless of changes in the exhaust flow rate and hood height, which is similar to the results of the CO yield. The hypothesis that changes in the exhaust flow rate and hood height will cause velocity and temperature fields in post-flame and plume regions to change as well, thus affecting CO and soot yields, was not supported. Although it was not presented in this study, the vertical (axial) velocity was measured on the specimen and at the cone heater outlet and bottom part of the exhaust hood. Nonetheless, it can be deduced that complicated fire phenomena due to changes in the exhaust flow rate and hood height had almost no effect on the changes in MLR and HRR or the CO and soot yields. Based on the findings above, variations in exhaust flow rate and hood height, which can be caused during the setup and experimental process by individual researchers, had a minimal impact on CO and soot yields, as well as on global characteristics such as MLR and HRR, while the reference values proposed in ISO 5660-1 were deemed to be sufficiently representative.
Figure 12. Variations in CO, CO$_2$, and soot yields with changes in exhaust flow rate and hood height (h).

4. Conclusions

This study experimentally analyzed combustion properties according to irradiance level (external heat flux) using a cone calorimeter. Black acrylic having similar constituents as PMMA was used as a combustible, and external heat fluxes within the range of 15–65 kW/m$^2$ were considered. Auto and spark ignitions were all applied as ignition methods. The ignition time, MLR, HRR, EHC, CO, CO$_2$, and soot yields were measured. In particular, the need to re-examine the trend of changes in CO and soot yields was highlighted when there were fluctuations in the external heat flux as the primary parameter. In addition to the external heat flux, the effects of changes in the exhaust flow rate and hood height on CO and soot yields were also examined. The major findings of this study are as follows.

Auto and spark ignitions that can be applied to a cone calorimeter exhibited diverse ignition phenomena depending on the occurrence of gas-phase reactions in the initial stage of pyrolysis under a relatively low external heat flux condition. However, the difference in the ignition method did not affect global parameters such as the MLR, HRR, and EHC, as well as CO and soot yields.

As the external heat flux increased, the mean MLR and HRR linearly increased, while the EHC remained constant. When the external heat flux increased, the mean mass flow rates of CO and CO$_2$ had a directly proportional relationship with the mean MLR. Consequently, CO and CO$_2$ yields remained constant regardless of the external heat flux. In contrast, the mean mass flow rate and mean MLR of soot were linearly proportional instead of directly proportional, and the soot yield thus increased linearly with the external heat flux.

The changes in the exhaust flow rate and hood height that can alter the velocity and temperature fields in post-flame and plume regions had almost no impact on the changes in CO and soot yields, as well as MLR and HRR. Accordingly, it can be deduced that there was no dependency of an individual researcher, who would be available during the experimental process or setup of exhaust flow rate and hood height, and the reference values proposed in ISO 5660-1 were sufficiently representative. The results of this study are expected to provide improved insight into conventional approaches on recognizing CO and soot yields as unique properties of each combustible, which are crucial for evacuation and personal safety.

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