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Effect of Excess Air Levels on PAHs Content in Smoke During Charcoal Combustion in Grilling Process

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Abstract: Charcoal grilling may lead to carcinogenic PAHs contamination of grilled food from incomplete combustion of charcoal. The objective of this study was to determine the effect of complete combustion of charcoal on PAHs content in smoke during the grilling process. Firstly, proximate and ultimate compositions of the charcoal were determined to identify the amount of air required for combustion according to stoichiometry. Different excess air levels consisting of stoichiometric air, 60, 100 and 150% excess air during combustion of charcoal on 16 PAHs released in smoke were studied. Moreover, CO and CO_2 concentrations were measured. The use of excess air decreased the emission factor of CO and increased the emission factor of CO_2. The 16 PAHs contents in smoke produced from charcoal combusted with stoichiometric air, 60, 100 and 150% excess air were 73.62, 51.78, 27.68 and 19.23 µg/kg dry charcoal, respectively. The use of excess air during charcoal combustion resulted in significantly lower PAHs contents in the smoke. Therefore, the use of excess air during charcoal grilling is one way to reduce the risk of PAHs contamination in grilled food.

Keywords: Charcoal; Complete combustion; Excess air; Grilling; PAHs.

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1. Introduction

Charcoal grilling is a cooking process that uses the moderate to high temperature from charcoal to create color and texture in foods, especially the unique smoky flavor which cannot find in the electric or gas grilling [1]. However, charcoal combustion during the grilling may generate and release the carcinogenic polycyclic aromatic hydrocarbons (PAHs*)* in the smoke that adhere to the surface of grilled foods [2] [3].

PAHs are the group of compounds that consist of at least two fused benzene rings. The United States Environment Protection Agency (US EPA) [4] has classified 16 of PAHs as priority pollutants. According to EU Regulation No. 201/8351 [5] for heat treated meat products (i.e. grilling and barbecuing) the maximum level of benzo[a]pyrene and the maximum level of sum of 4 PAHs consisting of benzo[a]pyrene, chrysene, benzo[a]anthracene and benzo[b]fluoranthene are 0.005 and 0.03 µg/g of wet weight, respectively.

Theoretically, PAHs may be formed during the incomplete combustion of fuel [6]. In case of biomass such as charcoal, many studies [2] [3] reported that volatile matter in charcoal was related with PAHs released in smoke during combustion. High volatile matter resulted in high PAHs content in smoke [3]. To reduce PAHs in smoke in order to decrease PAHs contamination in charcoal grilled food, many methods were proposed to decrease volatile matter in charcoal such as using high carbonization of 1,000 °C during charcoal production [3], pre-heating or burning charcoal to release volatile matter before using grilling [2]. However, these methods resulted in a decrease in yield or weight of charcoal before grilling, leading to an increase in charcoal cost. Other method to decrease PAHs in smoke during combustion was the addition of excess air to complete combustion of fuel [7, 8]. This led to the use of all charcoal including volatile matter for providing the energy by complete combustion. Gulyurtlu *et al.* (2003) [7] showed that the addition of 20 – 80% excess air to burn the coconut shell with particle size in range of 1-3.15 mm in fluidized bed resulted in a decrease in PAHs and CO emission which indicated the incomplete combustion. Moreover, an increase in air flow rate for combustion of coal with particle size of 4.75 mm in fixed bed led to reduce PAHs formation [8]. Although the addition of excess air has been successfully used to decrease PAHs emission due to complete combustion, there is only limited research in the lump charcoal combustion during the grilling process. As excess air required for complete combustion depends on the fuel characteristics, the lump charcoal for food grilling may require different excess air level compared to pulverized coal due to different surface area to volume ratio.

The objective of this work was to study the effect of the excess air levels on 16 PAHs content in charcoal smoke during charcoal combustion in grilling process. Firstly, the proximate and ultimate compositions of the commercial mangrove charcoal were determined to calculate the stoichiometric air required for complete combustion of charcoal. Different excess air levels consisting of stoichiometric air, 60, 100 and 150% excess air during combustion of charcoal with 5-7 cm diameter on 16 PAHs were studied. The PAHs released in smoke during charcoal combustion were collected and analyzed using Gas Chromatography-Mass Spectrometry (GC-MS). Moreover, CO and CO_2 emission during charcoal combustion were also measured to indicate the complete combustion.

2. Experimental

Commercial mangrove charcoal was purchased from Khao Yeesarn (Samutsongkram, Thailand). Mangrove charcoal samples with diameter in the range of 5–7 cm were cut to obtain 4 cm length. Sorbent tubes were purchased from Supelco (ORBO 1500 PUF/XAD-2/PUF, Bellefonte, USA). Diethyl ether, hexane and dichloromethane were purchased from RCI Labscan (Bangkok, Thailand). Sodium sulfate anhydrous was purchased from Carlo Erba (Renningen, Germany). Sixteen PAHs mixed standards solution in cyclohexane concentration 10 ng/μL was purchased from Sigma-Aldrich (Darmstadt, Germany).

2.1 Determination of charcoal compositions

Proximate and ultimate analysis were carried to measure composition of mangrove charcoal. For proximate analysis, charcoal compositions in terms of moisture content, volatile matter, ash and fixed-carbon were determined according to ASTM D1762 [9]. For ultimate analysis, charcoal compositions in terms of elemental carbon, hydrogen and nitrogen were measured according to ASTM D3178 [10] and elemental sulfur was measured according to ASTM D4239 [11]. The ultimate analysis was used to estimate the amount of the stoichiometric air required for the complete combustion.

2.2 Determination of effect of excess air levels on PAHs in smoke during charcoal combustion

In charcoal grilling, the smoke generated from incomplete combustion of the charcoal is the one of the factors affecting PAHs contamination in grilled food. Therefore, to decrease the PAHs in smoke during charcoal grilling, the effect of the complete combustion by varying the excess air levels including stoichiometric air, 60, 100 and 150% excess air on 16 PAHs in smoke was determined. Furthermore, CO and CO_2 concentration formed during charcoal combustion were also measured to indicate complete combustion reactions.

The stoichiometric air and different excess air levels required for charcoal combustion were calculated through the chemical combustion equations of the carbon, hydrogen and sulfur components in charcoal obtained from the ultimate analysis. However, ash was neglected in the combustion analysis as the incombustible substances [12]. In addition, the combustion equation of fuel-bound nitrogen was negligible [13]. The different air levels were varied by changing the air velocity. Therefore, the air velocity for stoichiometric air and 60, 100 and 150% excess air was 0.25, 0.5, 1 and 1.5 m/s, respectively.

The experiments were carried out as shown in Figure 1. Charcoal was combusted in the chamber. The emission gas including CO and CO_2 were measured by flue gas analyzer (AVL SESAM i60 FT SII, AVL, Germany). The PAHs in smoke were collected using sorbent tube connected with the air pump (AP-40, Resun, Shenzhen, China) to pump smoke at 2 L/min of flow rate.

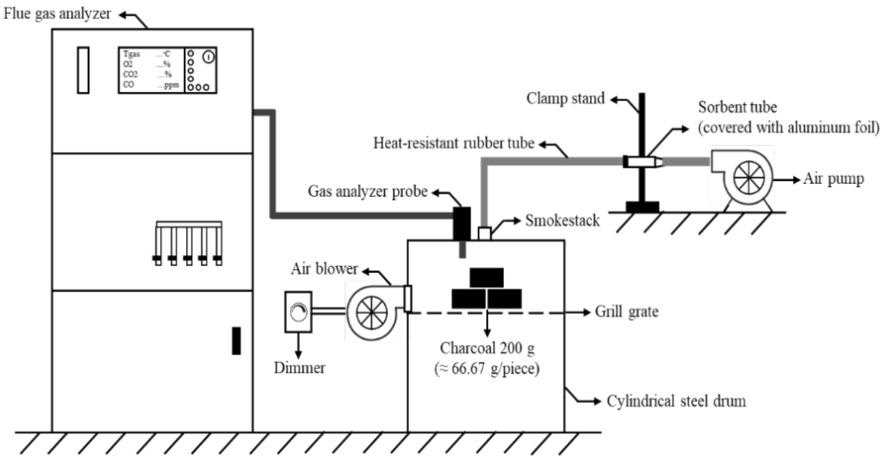

Figure 1. Schematic diagram of charcoal combustion and smoke collection system

In each experiment, 200 g of charcoals were ignited by LPG for 5 min before placing on the grill grate in combustion chamber. The air blower (Toto, Electric Air Pump, China) connected with a dimmer (RK-2000, Reckon, Bangkok, Thailand) to adjust air velocity was used to supply air during charcoal combustion. The ambient air entering in the combustion chamber was measured using an anemometer (435, Testo, Lenzkirch, Germany). The air temperature and relative humidity were 30-32 °C and 60-65%, respectively. Charcoals were burnt with horizontal air flow. Each experiment was performed in triplicate.

2.2.1 Determination of gas emission during charcoal combustion

To indicate the complete combustion during charcoal combustion with different air levels, CO and CO_2 concentrations were measured and were presented as the emission factor which is the mass of the emission gas per mass of the fuel (g/kg of fuel). The emission factor of CO and CO_2 gas was calculated as following equation [14]:

$$EF_i = \frac{m_i}{m_{bw}} = \frac{10^{-3} V_a}{m_{fd}} \frac{W}{22.4} \frac{273.15}{T} \int_{t_0}^{t_f} {}_iC_i dt \tag{1}$$

where EF_i is the emission factor of gas i, m_{fd} is the mass of charcoal consumed during each test (kg), t_0 is the starting time of each test (s), t_f is the finishing time of each test (s), V_a is the gas volume flow rate (m^3/s), T is the temperature of entering air (K), W_i is the molecular weight of gas i (g/mol) and C_i is the sampling concentration of gas i (ppm).

2.2.2 Determination of PAHs during charcoal combustion

To determine the effect of the different excess air levels on PAHs, smoke during charcoal combustion was collected in sorbent tube as described above. Then, PAHs were extracted and 16 PAHs were analyzed using GC-MS.

PAHs were extracted from PUF and XAD-2 resin in sorbent tube using Soxhlet extraction according USEPA Method TO-13A [4]. Prior to extraction, the surrogate standard (50 µg/mL of pyrene-d_{10}) was spiked with 20 µL to each sample. The PUF and XAD-2 resin were put in each extraction thimble and placed in the Soxhlet apparatus. The 10% diethyl ether in hexane (350 mL) and dichloromethane (350 mL) was respectively added to the PUF and the XAD-2 resin and refluxed for 18 h in the dark at least 3 cycles/h. Next, the solvent was filtered through sodium sulfate anhydrous (10 g). Then, solvent was evaporated using a rotary evaporator (R215, Buchi, Flawil, Switzerland) until its volume was below 1 mL and then dissolved in 1 mL of hexane. Finally, the extraction was filtered through 0.2 µm membrane filter and transferred to a Teflon®-sealed screw-cap amber vial and flushed with N_2.

The 16 PAHs were analyzed by GC-MS with a 7890A GC system (Agilent Technologies, Canada) and a 5974C inert XL MS (Agilent Technologies, USA) with an auto-sampler. A DB-5MS column (30 m length x 0.25 mm i.d. with 0.25 µm of film thickness, Agilent Technologies, USA) was used. The oven temperature was programmed from 55 °C for 1 min to 100 °C at 2 °C/min, then to 320 °C at 5 °C /min and maintained at 320 °C for 3 min. Helium was used as the carrier gas. The detector temperature was 280 °C (Lynam 2008). Electron ionization was 70 eV. The mass in range of 45-450 m/z was detected using elected ion monitoring (SIM) mode. The standard calibration curves of 16 PAHs in range of 0-1,250 ppb were prepared with D8-napthalene (50 ppb) as the internal standard. The linear regression of each PAH was plotted. The correlation coefficients (r^2) was in range of 0.987-0.996 for 16 PAHs.

2.3 Statistical analysis

Statistical analysis was performed using Minitab 16. Analysis of variance (ANOVA) was performed followed by Tukey's test ($p < 0.05$). Each sample was analyzed in 2 replicates**. S**tandard deviation was calculated and the data was expressed in mean ± SD.

3. Results and discussion

3.1 Commercial charcoal compositions

Proximate and ultimate analysis of commercial mangrove charcoal are presented in Table 1. For proximate analysis, compositions in terms of moisture content, volatile matter, ash and fixed carbon of charcoal were 3.35, 46.98, 1.84 and 47.83%, respectively. The proximate composition of charcoal depended on many factors such as carbonization temperature of charcoal production [3] and properties of wood resources [15]. As commercial mangrove charcoal was traditionally produced in brick kiln at 500 °C of carbonization, resulting in a high volatile matter. For the ultimate analysis, the compositions by mass per 100 g charcoal were C = 73.27, H = 4.07, O =

17.15, N = 0.22 and S = 0.10, respectively. This ultimate analysis was used to estimate the amount of the stoichiometric air required for the complete combustion.

Table 1. Proximate and ultimate analysis of the commercial mangrove charcoal

Charcoal compositions	Content
Proximate analysis (%wet basis)	
Moisture	3.30 ± 0.54
Volatile matter	43.51 ± 2.92
Ash	1.91 ± 0.43
Fixed Carbon	51.23 ± 3.04
Ultimate analysis (%weight)	
Carbon	73.27 ± 1.51
Hydrogen	4.07 ± 0.16
Oxygen	17.09 ± 1.40
Nitrogen	0.22 ± 0.06
Sulfur	0.10 ± 0.02

3. 2 Effect of excess air levels on emission gas and PAHs content during charcoal combustion in grilling process

In charcoal grilling, the smoke generated by incomplete combustion of the charcoal is the one of factors affecting PAHs contamination in grilled food [6]. To decrease PAHs in smoke from incomplete combustion of charcoal during grilling, the effect of the excess air levels consisting of stoichiometric air, 60, 100 and 150% excess air was studied. During charcoal combustion, emission gas consisting of CO and CO_2 were determined to indicate complete combustion. In addition, 16 PAHs in smoke were measured.

3.2.1 Effect of excess air levels on emission gas during charcoal combustion

To indicate whether the complete combustion occur during charcoal combustion with different excess air levels, emission gas consisting of CO and CO_2 in smoke was measured. The results showed that when the excess air level increased, the CO emission decreased, but the CO_2 emission increased. This indicated a decrease in an incomplete combustion with excess air level. However, at 150% excess air, CO still occurred, indicating the incomplete combustion. This might be due to the large size of lump charcoal. As charcoal in this study had a low surface area to volume ratio, resulting in the lower reaction between O_2 and fuel. Therefore, the addition of excess air 150% was insufficient for complete combustion of lump charcoal.

In addition, Table 2 shows the concentration of CO and CO_2 from charcoal combustion was calculated as the emission factor. The emission factor of CO decreased from 415 to 91 g/kg for stoichiometric air and 150% excess air, respectively. The emission factor of CO_2 increased from 1,539 to 2,428 g/kg for stoichiometric air and 150% excess air, respectively. This results were comparable with Bhattacharya *et al*. (2002) [16] who reported that emission factor of CO and CO_2 of mangrove charcoal (2 –5 cm) combustion in cook stove was in the range of 35 – 198 and 2,155 – 2,567 g/kg, respectively. These different values might be explained by that the emissions factor is dependent on combustion conditions such as fuel size and ash content [17] [18].

Table 2. Emission factor of CO and CO_2 gas from charcoal combustion at different air levels

Excess air level	Emission factor (g/kg dry charcoal)	
	CO	CO_2
Stoichiometric air	415.10±36.9^{a}	1,539.42+212.7^{b}
60% excess air	216.38+44.6^{b}	2.181.34+^{b}
100% excess air	174.64±37.7^{b}	2,504.51±113.4^{a}
150% excess air	91.81+8.9^{b}	2,428.04±292.7^{a}

* Different letters in the same column indicate significant differences ($p < 0.05$)

3.2.2 Effect of Excess Air Levels on PAHs Content during Charcoal Combustion

To determine the effect of excess air levels on PAHs content during charcoal grilling, the 16 PAHs in smoke from charcoal combustion with different excess air levels was measured. Table 3 shows the 16 PAHs content during charcoal combustion with stoichiometric air, 60, 100 and 150% excess air. The 16 PAHs were released about 73.62, 51.78, 27.68and 19.23 μg/kg dry charcoal for stoichiometric air, 60, 100 and 150%, excess air, respectively.

These results indicated that an increase in excess air for charcoal combustion decreased the 16 PAHs content released in smoke. This may be because at high excess air more oxygen could contact to the charcoal surface, resulting in high complete combustion reaction. This result was in an agreement with other studies [7] [19] which reported that the addition of the air into the combustion process led to significant decrease of the PAHs in smoke during pulverized coal combustion.

However, in this study the 16 PAHs were still released in smoke during charcoal combustion with 150% excess air. This can be associated with incomplete combustion of charcoal as described in previous section that CO emission occurred during charcoal combustion at 150% excess air. This may be because lump charcoal with 5 cm diameter and 4-6 cm long was used in this study, resulting in the incomplete combustion due to low surface area to volume ratio of fuel [17].

Table 3. Concentrations of 16 PAHs in smoke from charcoal combustion with different excess air levels

PAHs	PAHs concentration (μg/kg dry charcoal)			
	Stoichiometric air	60% excess air	100% excess air	150% excess air
Naphthalene	57.99±30.89	45.52±3.90	22.22±1.96	15.38±3.11
Acenaphthylene	0.86±0.00	0.60±0.53	0.46±0.21	0.40±0.06
Acenaphthene	N.D.	0.06±0.53	0.19±0.24	N.D.
Fluorene	1.41±1.99	1.26±1.79	0.80±0.51	0.69±0.60
Phenanthene	8.45±3.66	2.59±3.58	1.69±0.96	1.19±0.75
Anthracene	1.52±0.20	0.57±0.81	0.34±0.21	0.40±0.17
Pyrene	1.09±0.65	0.83±1.18	1.67±1.13	0.82±0.29
Fluoranthene	1.01±0.04	0.32±0.45	0.25±0.18	0.21±0.09
Benzo[a]anthracene*	0.20±0.12	0.03±0.04	0.02±0.03	0.02±0.03
Chrysene*	0.11±0.16	N.D.	N.D.	N.D.
Benzo[b]fluoranthene*	0.26±0.04	N.D.	0.04±0.07	N.D.
Benzo[k]fluoranthene	0.14±0.20	N.D.	N.D.	0.04±0.07
Benzo[a]pyrene*	N.D.	N.D.	N.D.	N.D.
Indeno[1,2,3-c,d]pyrene	N.D.	N.D.	N.D.	N.D.
Dibenzo[a,h]anthracene	0.29±0.41	N.D.	N.D.	N.D.
Benzo[g,h,i]perylene	0.29±0.41	N.D.	N.D.	0.08±0.13
16 PAHs	73.62	51.78	27.68	19.23
*4 PAHs	0.57	0.03	0.06	0.02

Note: N.D. Mean not detected.

In addition, considering 4 PAHs and benzo[a]pyrene content according to regulation for grilled food, 4 PAHs decreased from 0.57 to 0.02-0.06 μg/kg dry charcoal for stoichiometric air and 60-150% excess air, respectively. No benzo[a]pyrene was observed in smoke for all charcoal combustion conditions in this study. Therefore, this study suggested that the addition of excess air for charcoal combustion during grilling led to a low risk of PAHs contamination for grilled food. However, as incomplete combustion still occurred as CO produced in charcoal smoke at 150% excess air. Therefore, the addition of more than 150% excess air for lump charcoal combustion during grilling process should be considered. However, many studied have reported that PAHs can be formed in too much excess air during combustion [7]. Moreover, the PAHs deposited onto grilled food should be studied to compare PAHs content in grilled foods with the EU regulation.

4. Conclusion

To reduce carcinogenic PAHs contamination on charcoal grilled food, the effect of the excess air levels to decrease the incomplete combustion of lump mangrove charcoal on PAHs in smoke was studied. The results showed that an increase in excess air level from stoichiometric air, to 150% excess air decreased CO emission and increased CO_2 emission. However, at 150% excess air CO emission was found during charcoal combustion with 150% excess air, indicating an incomplete combustion of charcoal. This may be due to low surface area to volume ratio of charcoal for oxygen in air to react during combustion. For 16 PAHs generated in charcoal smoke during the combustion, the different excess air levels significantly affected 16 PAHs content in smoke. For 4 PAHs according to EU regulation for grilled food, 4 PAHs decreased from 0.57 to 0.02-0.06 μg/kg dry charcoal for stoichiometric air and 60-150% excess air, respectively. In addition, no benzo[a]pyrene was observed in smoke for all charcoal combustion conditions in this study. Therefore, this study suggested that the use of excess air for charcoal combustion during grilling is one way to reduce the risk of PAHs contamination in grilled food. However, the addition of more than 150% excess air for lump charcoal combustion during grilling process should be considered as the incomplete combustion still occurred at 150% excess air. Moreover, the PAHs deposited onto grilled food should be taken into account in further study to compare PAHs content with the EU regulation.

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