Determination of particle-bound polycyclic aromatic hydrocarbons emitted from co-pelletization combustion of lignite and rubber wood sawdust

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Abstract. Determination of particle-bound Polycyclic Aromatic Hydrocarbons (PAHs) emitted from co-pelletization combustion of lignite and rubber wood sawdust in a horizontal tube furnace is investigated using High Performance Liquid Chromatography with coupled Diode Array and Fluorescence Detection (HPLC-DAD/FLD). The particle-bound PAHs based on the mass concentration and the toxicity degree are discussed in the different size ranges of the particulate matters from 0.07-11 μm. In the present study, the particle-bound PAHs are likely abundant in the fine particles. More than 70% of toxicity degree of PAHs falls into $PM_{1.1}$ while more than 80% of mass concentration of PAHs falls into $PM_{2.5}$. The addition of lignite amount in the co-pelletization results in the increasing concentration of either 4-6 aromatic ring PAHs or high molecular weight PAHs. The high contribution of 4-6 aromatic ring PAHs or high molecular weight PAHs in the fine particles should be paid much more attention because of high probability of human carcinogenic. Furthermore, the rubber wood sawdust pellets emit high mass concentration of PAHs whereas the lignite pellets emit high toxicity degree of PAHs. By co-pelletized rubber wood sawdust with lignite (50% lignite pellets) has significant effect to reduce the toxicity degree of PAHs by 70%.

1. Introduction

Thailand is the largest global natural rubber production and exportation. Most of 700 cooperatives is located in the Southern Thailand. In order to dry the rubber sheets, the rubber woods are burnt to produce heat and smoke. The rubber woods are also burnt in order to generate the electricity like coal. The rubber wood burning was reported that it emitted very high particulate matters and Polycyclic Aromatic Hydrocarbons (PAHs) [1,2]. Unlike, lignite combustion generated high bottom ash and toxic heavy metals. However, the toxic elements in lignite may relate or increase the toxicity degree of PAHs. The emitted particles and the particle-bound PAHs can be the significant sources of the human health effects and the ambient air.

The PAHs concentration could be found in the raw materials and output residues. Verma et al [3] reported the PAHs in the coal power plant. The coal, raw material, existed 4,542 µg/kg of total PAHs, while the fly ash and bottom ash existed 32.4 and 10.1 µg/kg of total PAHs, respectively. Most of high molecular weight PAHs concentrated on the coal and the fly ash, whereas the low molecular weight PAHs on the bottom ash. The high molecular weight PAHs cause more human health impacts than the low molecular weight. Meanwhile, the rubber wood burning in the workplace was reported that it emitted 10 folds of particle-bound PAHs in comparison with the ambient air [2]. Most of particle-bound PAHs accumulated in the fine particles [1,2,4]. The high concentration of PAHs either in the workplace or ambient air should be concerned especially the workers' health. By blending lignite and rubber wood sawdust, the PAHs emission might be traded. Al-Naiema et al [5] reported that co-firing coal with oat hulls by 50% would lead to the reduction of particulate matters and PAHs by 90% and 40%, respectively but there was insignificantly effect of pollutants above on 3.8% wood chips blends. The particulate matters and PAHs will increase, decrease or remain stable depending on the properties/blending ratios of fuels and combustion conditions.

The PAHs formation has been studied on the various types of fuels, raw chunk blending, excess air, combustion temperature, moisture, and combustion system [1–6]. However, the study of particle-bound PAHs formation emitted for co-pelletization combustion is still remained in the initial information point and rarely identified the risk evaluation. The understanding of PAHs is important since they can accumulate in the particulate matters, which deposit surrounding the workplace or transport in a long distance in the ambient air. The PAHs impact seriously to the human health especially the carcinogenic and repository symptom depending on the size fraction of particles/particulate matters. The fine particles can penetrate deeply into the lung especially in the end of bronchus and alveolus areas rather than the coarse particles. The different size fraction of particles leads to the different health outcome. Therefore, the PAHs components related to the emitted particle size fraction are essentially determined.

In the present study, the particle-bound PAHs emitted from co-pelletization combustion of lignite and rubber wood sawdust in a horizontal tube furnace are investigated using High Performance Liquid Chromatography with coupled Diode Array and Fluorescence Detection (HPLC-DAD/FLD). The particle-bound PAHs are determined in different size ranges of particulate matters from 0.07-11 µm. Moreover, their aromatic rings and toxicity degree are also discussed.

2. Materials and Methods

2.1. Materials
Lignite and rubber wood sawdust were adapted from Mae Moh, Lampang and Rattapoom, Songkhla, Thailand, respectively. Both materials were co-pelletized with 10% starch as binder by screw press. Further detail of raw materials and co-pelletization could be taken from a previous study [7].

2.2. Particle sampling from combustion experiment
The pellets were burnt in a horizontal tube furnace with an inserted quartz column (ID = 55 mm, OD = 60 mm, and L = 850 mm) and heating zone (OD = 60 mm and L = 650 mm) (figure 1). Eleven-selected pellets (3.5-4 L:D ratio) were inserted into the central heating zone of quartz column and burnt at room temperature to 700 ℃ with 5 ℃/min of heating rate and 20 min holding time. Dry clean air approximately 1.6 L/min was purged into the furnace to combust the pellets. In order to reduce the temperature and moisture content, the exhaust was diluted with a dilutor (OD = 35 mm and L = 800 mm) include a mixing tube (L = 70 mm) by the dry clean air. The particulate matters and the flue gas were respectively sampling using an Anderson cascade impactor with an initial filter stage (ANIF) model Dylec NA200 (Tokyo Dylec, Japan) and a gas analyzer model Testo 350XL (Testo, Germany).

The binder-less quartz filters Pallflex 2500QAT-UP (D = 80 mm, Pall Corporation, USA) were used in ANIF. The flow rate of ANIF was controlled at 28.3 L/min by a rotameter at the staked top of ANIF. The filters were treated for 72 h in room temperature and 50% of relative humidity.
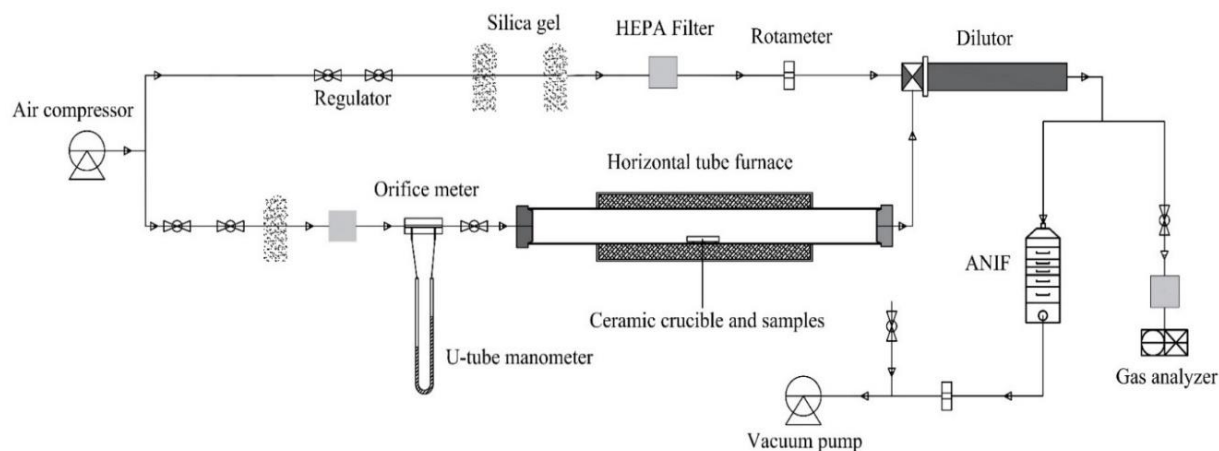
Figure 1. Schematic diagram of combustion system.

2.3. Analysis of particle-bound polycyclic aromatic hydrocarbons
The particulate matters on each stages of ANIF were extracted by ultrasonic extraction technique in order to analyze the PAHs. The extraction was operated with dichloromethane in the cooled ultrasonic cleaner twice for 20 min (99 Hz and <10 ℃). The dimethyl sulfoxide (DMSO) was added into the extraction after filtering with the filler papers and 0.45-µm PTFE syringes. After that, the solution was evaporated by a rotary evaporator model Rotavapor-R (Büchi, Switzerland) with cooling system to remove dichloromethane. After evaporating, acetonitrile was added and homogeneously mixed. The PAHs solution was finally filtrated with the 0.45-µm PTFE syringes and stored in the refrigerator at 4±2 ℃ for the next PAHs analysis.

Table 1. Aromatic rings and toxic equivalence factors of sixteen priority PAHs listed by US EPA.

PAHs	Abbr.	Aromatic rings	TEF
Naphthalene	NAP	2	0.001
Acenaphthylene	ACY	3	0.001
Fluorene	FLU	3	0.001
Acenaphthene	ACE	3	0.001
Phenanthrene	PHE	3	0.001
Anthracene	ANT	3	0.01
Fluoranthene	FLA	4	0.001
Pyrene	PYR	4	0.001
Benzo(a)anthracene	**BaA**	**4**	**0.1**
Chrysene	**CHY**	**4**	**0.001**
Benzo(b)fluoranthene	**BbF**	**5**	**0.1**
Benzo(k)fluoranthene	**BkF**	**5**	**0.01**
Benzo(a)pyrene	**BaP**	**5**	**1**
Dibenz(a,h)anthracene	**DahA**	**5**	**1**
Benzo(g,h,i)perylene	BghiP	6	0.01
Indeno(1,2,3-cd)pyrene	**IcdP**	**6**	**0.1**

Bold words: Probably human carcinogenic PAHs listed by US EPA [8–10]

PAHs are hydrocarbon compounds with two or more aromatic rings released from the combustion of fuels, or found in the emission and fuels. The sixteen particle-bound PAHs as shown in table 1 were analyzed by High Performance Liquid Chromatography with coupled Diode Array and Fluorescence

Detection (HPLC-DAD/FLD) model Hewlett Packard series 1100 (Hewlett Packard, USA) and Inersil ODS-P C-18 reversed-phase column connected with 5-μm Inersil guard (5-μm particle size, 4.6-mm diameter, 250-mm length). The combination of DAD and FLD detection was the powerful technique when NAP, ACE, FLU, and ACY provided the weak signals on the FLD detection, especially ACY. The portion of extracted PAHs was automatically injected into the column approximately 20 μL while the mixture mobile phases of acetonitrile and ultra-pure water were operated with the gradient condition mode of acetonitrile at flow rate 0.5 mL/min (table 2). Timing of PAHs detection was set following the optimum excitation and emission wavelengths of detectors (table 3)**.** In addition, the PAHs peaks were calibrated with the standard PAHs ($R^2 = 0.99$). The blank filters were prepared for the PAHs analysis. The corrected PAHs were applied by subtracting the blank PAHs. The PAHs recovery was 72-138% depending on individual PAHs.

Table 2. Gradient condition of PAHs analysis.

Time (min)	Acetonitrile (%)	Ultra-pure water (%)	Flow rate (mL/min)
0	70	30	
10	70	30	
25	90	10	
27	99	1	
30	100	0	0.5
75	100	0	
76	70	30	
80	70	30	

Table 3. Optimum wavelength of sixteen PAHs with diode array and florescence detection.

Time (min)	Fluorescence		Diode Array	PAHs
	λ Excitation (nm)	λ Emission (nm)	λ Wavelength (nm)	
0	280	340		NAP, ACE, FLU, ACY (except ACY not detected in florescence)
23	250	400		PHE
29	286	433		ANT, FLA
31	331	392	254	PYR
34	264	407		BaA, CHR, BbF, BkF BaP, DahA, BghiP
65	294	482		IcdP
72	280	340		-
80	280	340		-

3. Results and Discussion

The sixteen PAHs such as NAP, ACE, FLU, ACY, PHE, ANT, FLA, PYR, BaA, CHR, BbF, BkF, BaP, DahA, BghiP, and IcdP are examined in the different size ranges of particulate matters from 0.07-11 μm. As seen in figure 2, the pellet combustion emits the low molecular weight PAHs (< 228 g/mol) higher than the high molecular weight PAHs (> 228 g/mol). The 0%, 50% and 100% lignite pellet combustion emits 97%, 91%, and 75% of low molecular weight PAHs, whereas 3%, 9%, and 25% of high molecular weight PAHs, respectively. In addition, the mass fraction of PAHs is mostly dominated by 25-67% of NAP and 23-29% of ACY. It is interested that the more $PM_{2.1}$ increases, the greater high molecular weight PAHs increases. The consequences of high molecular weight PAHs accommodated in the fine particles are the diffusivity of molecular weights, the vapor pressures of PAHs, the absorption between particle surface areas and organic matters, and transformation of gas phase to particle phase [11,12].

The PAHs can accompany either in the gas phase or particulate phase due to its vapor pressure (function of temperature) and its molecular weight. In general, the low molecular weight PAHs are anticipated in gas phase, whereas the high molecular weight in particulate phase with which the size distribution of particles are associated [11]. Most of PAHs is found in the fine particulate matters or in the gas phase anticipated with the small particles [1,2,13]. Moreover, more than 85% of total PAHs is accumulated on the particulate matters according to the literatures [11,14].

Figure 2. Composition profile of PAHs in different size ranges of particulate matters emitted from (a) 0% lignite pellet, (b) 50% lignite pellet, and 100% lignite pellet combustion.

In general, the non-carcinogenic and carcinogenic PAHs have been recognized to 2-3 aromatic rings and 4-6 aromatic rings of PAHs, respectively. As seen in figure 3, the 0% and 50% lignite pellet combustion are mostly abundant the 2-3 aromatic ring PAHs while the 100% lignite pellet combustion are mostly abundant the 3-4 aromatic ring PAHs. The 5-6 aromatic ring PAHs also increase when the lignite mount increase in the co-pelletiztion. The 4-6 aromatic ring PAHs contributed in the order of 0% (1181 ng/g fuel) > 50% (3349 ng/g fuel) > 100% (8200 ng/g fuel) lignite pellets combustion. The increment of mass concentration of 4-6 aromatic PAHs will more cause human carcinogenic, mutagen, and repository symptom. Meanwhile, Shen [11] reported that there was no significant effect of mass concentration of PAHs between the raw chunk fuel and densified fuel combustion; however, the densified fuel combustion significantly leads to the reduction of particulate matters and also the other pollutants. Hence, the toxicity degree of PAHs emitted from the co-pelletization combustion will be taken into accounts.
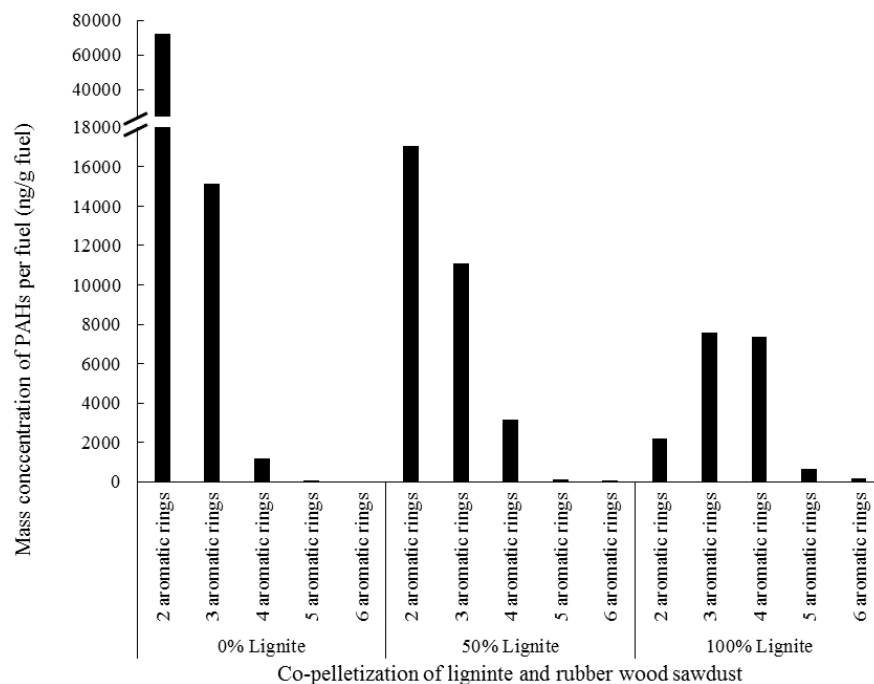
Figure 3. Total mass concentration of different aromatic ring PAHs emitted
from co-pelletization combustion of lignite and rubber wood sawdust.

The mass concentration and toxicity degree of PAHs per fuel burning in the different size ranges of particulate matters emitted from 0%, 50% and 100% lignite pellet combustion are shown in figure 4. The particle-bound PAHs would consider to be abundant in $PM_{2.5}$ more than 80%, which presents a good agreement with the literatures [11,15]. The distribution of PAHs of 0% lignite pellet combustion contributes very high amount in each sizes as compared to the 50% and 100% lignite pellet combustion. The most abundant mass concentration of PAHs is in the particle sizes of 1.1-2.1 μm of 0% lignite pellet combustion, whereas in the finer particle sizes of 0.43-0.64 μm of 50% and 100% lignite pellet combustion (figure 4.a). On the other hand, the mass concentration of PAHs cannot judge its toxicity degree, so the toxicity degree of PAHs is calculated in BaP-TEQ basis (Benzo(a)Pyrene Toxic Equivalence Quotient) as following:

$$PAH_{total} = \sum (PAH_i \times TEF_i)$$

(1)

where PAH_{total} is the total PAHs (BaP-TEQ), PAH_i is the congener i of PAHs, and TEF_i is the toxic equivalence factor of PAHs congener i.

In contract to the mass concentration of PAHs, the toxicity degree of PAHs is massively abundant in 0.43-0.64 μm of 100% lignite pellet combustion (137.36 BaP-TEQ ng/g fuel) following 50% lignite pellet combustion (53.94 BaP-TEQ ng/g fuel). The 0% lignite pellet combustion is abundant in the particle sizes of 1.1-2.1 μm with less toxicity degree of PAHs (25.27 BaP-TEQ ng/g fuel) (figure 4.b). Furthermore, the total toxicity of PAHs of the 100% lignite pellet combustion is 3.7 folds of the 0% lignite pellet combustion while the total toxicity of PAHs of the 50% lignite pellet combustion is 1.3 and 0.35 folds of the 0% and 100% lignite pellet combustion, respectively. When the high molecular weight PAHs considered 4-6 aromatic ring of PAHs tend to emit in the fine particles, they will influent on the ambient air and human health. The fine particle-bound PAHs can undergo in the long distance with the atmospheric movement in contrast to the large particle-bound PAHs that tend to deposit in a short time around the combustion workplace. Therefore, the particle-bound PAHs should get much more attention on the fine particles.
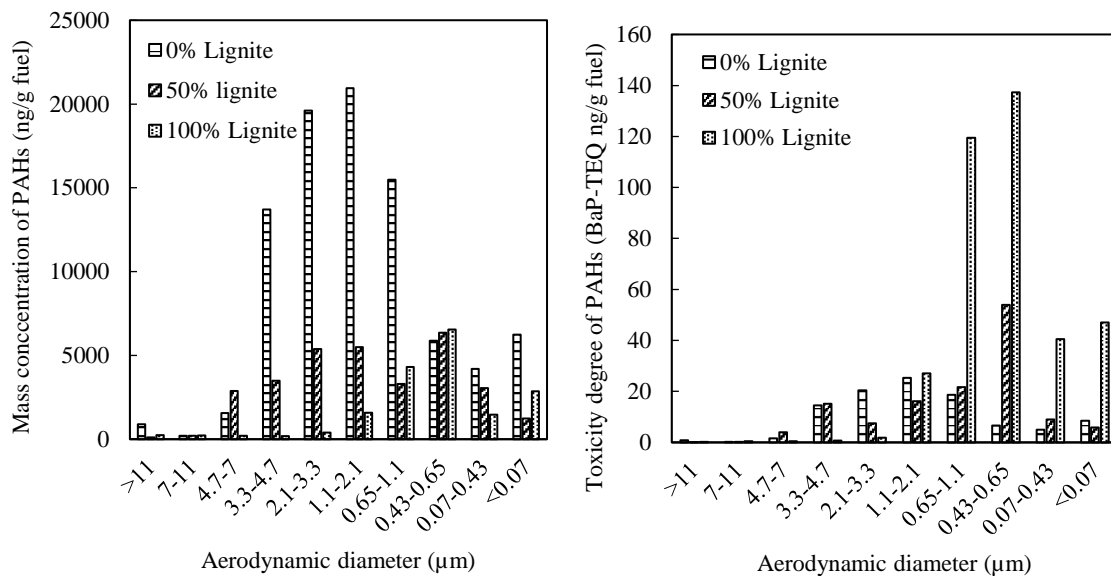
Figure 4. Concentration of PAHs emitted from co-pelletization combustion of lignite and rubber wood sawdust in different size ranges of particulate matters: (a) mass concentration of PAHs and (b) toxicity degree of PAHs.
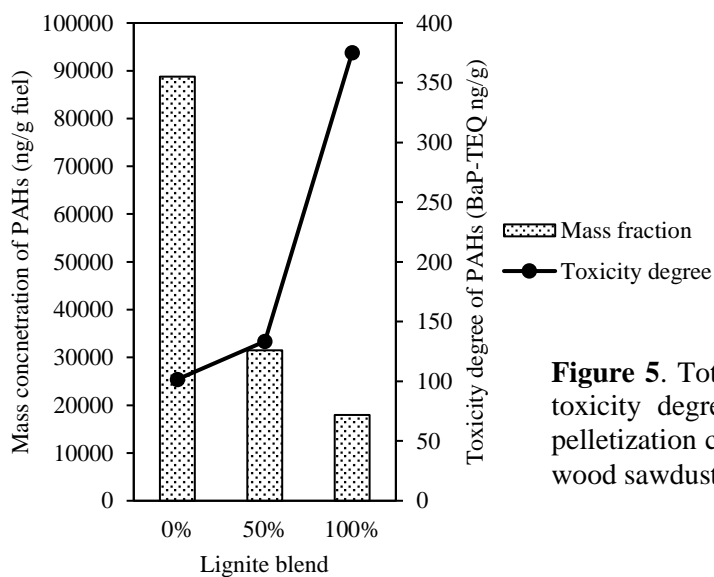

Figure 5. Total mass concentration and total toxicity degree of PAHs emitted from co-pelletization combustion of lignite and rubber wood sawdust.

As shown in figure 5, the mass concentration of PAHs are presented in the order of 0% > 50% > 100% lignite pellet combustion in contracted to the toxicity degree of PAHs. However the total mass concentration of PAHs from the 0% lignite pellet combustion emits higher value than the 100% lignite pellet combustion, the toxicity degree of PAHs from the 100% lignite combustion is more effect to the human health. It is widely documented that the high moisture content, high volatile matter, and unstable medium combustion condition would happen the incomplete combustion and produce more particulate matters and even the mass concentration of PAHs while the toxicity degree of PAHs causes from the complex structures of co-pellets especially the complex aromatic structures of lignite and the mineral association of lignite [6,11,13]. It is worth noting that the lignite combustion alone should be much more concerned. By pelletized rubber wood sawdust with lignite (50% lignite pellets), the toxicity degree of PAHs can be reduced by 70% of total toxicity degree of PAHs.

4. Conclusion

By sampling the particulate matters associated with PAHs in the horizontal tube furnace and further analysing with HPLC-DAD/FLD, the characteristics of particle-bound PAHs emitted from co-pelletization combustion of lignite and rubber wood sawdust are obtained that: (1) the PAHs components are abundant by 25-67% of NAP and 23-29% of ACY; (2) the mass concentration of particle-bound PAHs decrease in addition of lignite, whereas 4-6 aromatic PAHs increase and even the toxicity degree of PAHs; and (3) by co-pelletized rubber wood sawdust with lignite (50% lignite pellets), the toxicity degree of PAHs can be reduced by 70% of total toxicity degree of PAHs, and the large contribution of PAHs appears in the fine particle size of 0.43-0.65 μm while the PAHs are massively abundant approximately 70% in $PM_{1.1}$.

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