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How to Reduce Polycyclic Aromatic Hydrocarbons (PAHs) from Industrial Boilers under the Context of Thailand?

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Abstract: PAH emissions from several types of industrial boilers (i.e., two different size classes of boilers namely, a small-scale Light Fuel Oil boiler (LFO) and a medium scale Heavy Fuel Oil boiler (HFO)), fuel types (i.e., heavy oil, diesel, biodiesel, natural gas, biomass materials) and boiler's operating conditions (i.e., slumber mode and full frame mode) were investigated by literature review. The sum of 30 PAHs emitted from LFO and HFO was 17,060 and 9,906 ng mg^{-1}, respectively. Another report on PAH emissions from small wood boiler showed the values varied from 66-180 mg MJ fuel input^{-1} depending on the load of the boiler. Operating conditions of industrial boilers also play an important role in governing PAH emissions from the stacks. For instance, the PAH emissions from 50 kW Arimax 340 fixed retort system, biomass boiler were relatively low in "slumber condition" in comparison with those of "full frame mode" regardless of numerous types of biomass materials (i.e., larch, chestnut, oak and an unspecified mixture) used for the examination. Since, Thailand is currently facing both environmental and energy crisis, the use of shoot and leaf from sugarcane coupled with stem from cassava appear to be the most practical choice that can provide alternative biomass fuels with comparatively low PAH emissions.

Key words: PAHs, industrial boilers, biomass, Thailand, energy crisis

INTRODUCTION

In response to the Stockholm Convention, the ESEA (East and South East Asia) countries are committed to reduce/eliminate UP-POPs emission releases. The ESEA Forum, formally launched on October 5, 2007, is a programmatic regional initiative of UNIDO on the introduction of the Best Available Technique/Best Environmental Practice (BAT/BEP) measures on priority sectors defined by participating countries. The main objective of the Forum is to serve as a platform for information dissemination and exchange of experiences between countries in the region on different aspects of implementation of BAT/BEP and provide regular reporting on the impact of these in the industrial sectors cited in Annex C of the Convention (Stockholm Convention, 1997). Countries have been grouped based on their priority sectors of interest as mentioned in annex C of article 5 of Stockholm Convention (Stockholm Convention, 1997).

The regional project "Demonstration of BAT and BEP in the Fossil fuel-fired utilities and Industrial boilers in response to the Stockholm Convention on POPs", officially approved for full implementation by the Global Environmental Facility (GEF) in April 2010, is the first integral sectorial project of the ESEA BAT/BEP Forum. In accordance with the relevant resolutions of the third session of the Conference of the Parties (COP3) of the Stockholm Convention (SC), the overall objective of the regional project aims at reducing and where feasible, eliminating unintentionally produced POPs (UP-POPs) releases (in particular PCDDs- Polychlorinated-dibenzo-para-dioxins and PCDFs-Polychlorinated-dibenzofurans) by enhancing guidelines and guidance on BAT/BEP for fossil fuel-fired utilities and industrial boilers through addressing specific features of industry, common practices in the region and related socio-economic considerations. In addition, the project also targets the identification of possible options for the simultaneous reduction of PCDD/PCDFs and CO_2 from fossil fuel-fired utilities and industrial boilers in response to Stockholm Convention and Climate Change requirements. While, it focuses on the introduction of BAT/BEP measures, it also considers increasing energy efficiency, as required in Annex C Part V B (a) (iv) of the convention (Stockholm Convention, 1997). The evaluation of the mercury emissions by specific monitoring programs has been added afterwards according to the raising concerns on these pollutants. Under outcome 4.1 of the project, several activities related to capacity building in BAT and BEP built through training programs including regular curricula for graduates and government officials and through technical in-plant training for boiler operators of private and public sectors have been defined. Regional capacity building of human resources will be created through the development and implementation of training workshops for university students and boiler operators on environmentally-sound boiler technologies.

Apart from PCDD/PCDFs and CO_2 from fossil fuel-fired utilities and industrial boilers, PAHs are widely considered as carcinogenic substances by-product of imperfect combustions. As a consequence, it is also crucial to adopt BAT/BEP for reducing PAH emissions from fossil fuel-fired utilities and industrial boilers. Overall, the aims of this study are: (1) To review the effects of boiler types on PAH emissions, (2) To assess the influences of fuel types and combustion conditions on PAH releases from boilers, (3) To examine industrial boiler types, future and market trends in Thailand, (4) To evaluate the trends of energy consumptions and biomass used in industrial boilers in Thailand and (5) To recommend the best solution for reducing PAH emissions from industrial boilers under the context of Thailand.

EFFECTS OF BOILER TYPES ON PAH EMISSIONS

Various studies have investigated the impacts of boiler types on the degree of PAH emissions. For instance, vapor and particulate PAHs from two different size classes of boilers namely, the small scale (20-25 kW) and the medium scale (4-15 MW), were examined. As illustrated Table 1, the sum of 30 PAHs released from a small-scale Light Fuel Oil boiler (LFO) and a medium scale Heavy Fuel Oil boiler (HFO) was 17,060 and 9,906 ng mg^{-1}, respectively (Kaivosoja *et al*., 2013). Another study on small wood boiler for domestic heating revealed the levels of PAH emissions ranged from 66-180 mg MJ fuel $input^{-1}$ differing largely on the load of the stove that also affects their distribution in the different phases (Riva *et al*., 2011). As the load of the boiler enhances, the PAHs are largely detected in the particulate phase and increase also its average molecular weight. The combustion condition is another crucial parameter in governing PAH emissions, particularly from pulp and paper power boilers burning salt-laden wood waste (Leclerc *et al*., 2006). It appears that the incomplete combustion responsible for the formation of PAHs and PCDD/PCDF precursors from pulp and paper boilers. In addition, PCDD/PCDF and PAH emissions were observed to largely enhance with lower oxygen concentrations at the boiler exit.

The PAH emissions from 50 kW, Arimax 340 fixed retort system biomass boiler were further investigated under two main operating conditions; 'slumber' with no load on the boiler and low combustion temperatures, 'full flame', the normal operating mode of the boiler characterized by 100% load and high combustion temperatures (Bignal *et al*., 2008). Various types of biomass fuels were also examined (i.e., larch, chestnut, oak and an unspecified mixture). For the vapor phase, there is no significant difference on PAH distribution between slumber and full frame mode. However, there is a trend that HMW PAHs (particularly 6-ring congeners) in particulate phase were predominant in slumber mode irrespective of fuel types (Table 2).

Table 1: PAH content in PM_1 (ng mg^{-1}), sum of 30 PAHs PM_1 (ng mg^{-1}, mg MJ^{-1}) and sum of genotoxic PAHs PM_1 (ng mg^{-1}). The genotoxic PAHs (WHO/IPCS, 1998) are typed in bold. PAH results from pellet combustion are presented by Lamberg *et al*. (2011), Tapanainen *et al*. (2011) and Kaivosoja *et al*. (2013)

PAHs in PM_1 (ng mg^{-1})	Wood before ESP 1	Wood after ESP 1	LFO	HFO 1	Pellet
Naphthalene	<DL	<DL	4.8	<DL	0.2
Acenaphthylene	<DL	<DL	2.3	<DL	<DL
Acenaphthene<DL	<DL	<DL	4.1	<DL	<DL
Fluorene	<DL	<DL	31	<DL	<DL
Phenanthrene	0.8	2.1	335	80	0.6
Anthracene	<DL	<DL	19	2.8	<DL
1-Methyphenanthrene	<DL	<DL	206	13	0.1
Fluoranthene	20	172	4314	533	1.7
Pyrene	24	310	4685	53	2.1
Benzo (c) phenanthrene	0.8	100	839	400	0.1
Benao (a) anthracene	0.8	278	2060	773	0.1
Cyclopenta (c, d) pyrene	<DL	<DL	120	<DL	0.2
Triphenylene	0.2	36	354	242	0.1
Chrysene	0.8	222	2071	1778	0.1
5-Methylchrysene	<DL	<DL	<DL	1.5	<DL
Benzo (b) fluroanthene	<DL	25	486	2153	0.1
Benzo (k) fluroanthene	<DL	14	285	1637	<DL
Benzo (j) fluroanthene	<DL	19	342	1002	0.1
Benzo (e) pyrene	<DL	14	276	687	0.2
Benzo (a) pyrene	<DL	8.1	250	25	0.1
Perylene	<DL	<DL	28	14	<DL
Indeno (, 2, 3-cd) pyrene	<DL	<DL	68	250	<DL
Dibenzo (a, h) janthracene	<DL	<DL	6.6	66	<DL
Benzo (g, h, I) perylene	<DL	<DL	208	170	0.2
Anthanthrene	<DL	<DL	11	<DL	<DL
Dibenzo (a, l) pyrene	<DL	<DL	<DL	<DL	<DL
Dibenzo (a, e) pyrene	<DL	<DL	<DL	<DL	<DL
Coronene	<DL	<DL	53	26	<DL
Dibenzo (a, i) pyrene	<DL	<DL	<DL	<DL	<DL
Dibenzo (a, h) pyrene	<DL	<DL	<DL	<DL	<DL
Sum of 30 PAHs (ng mg^{-1})	47	1200	17,060	9906	6.0
Sum of genot. PAHs (ng mg^{-1})	23	887.64	11,978	9770	3.0
Sum of 30 PAHs (mg Mj^{-1})	0.013	0.0007	0.0015	0.20	0.0001
PAHs/PM_1 (%)	0.005	0.12	1.7	0.99	0.0006

<DL: Below detection limit

INFLUENCES OF FUEL TYPES AND COMBUSTION CONDITIONS ON PAH RELEASES FROM BOILERS

It is well known that the hydrocarbon fuel combustion particles are remarkably responsible for adverse health effects (Laden *et al*., 2000; Lanki *et al*., 2006; Penttinen *et al*., 2006). Several epidemiological and

Table 2: Mean percentage distribution (±standard deviation) of individula PAHs during full flame (F) and slumber (S) mode (Bignal *et al*., 2008)

	Gas phae		Particulate phase		Total	
Compound	F	S	F	S	F	S
Napthalene	55.6±24.9	48.5±25.5	27.4±45.4	0±0	54.0±24.3	47.2±25.2
Acenaphthylene	6.7±8.0	17.7±7.30	0±0	0±0	6.3±7.6	17.0±73
Acenaphthene	1.4±4.3	0.7±0.40	0±0	0±0	0.9±2.4	0.6±0.4
Fluorene	2.7±3.7	5.3±2.60	1.5±4.2	0.3±0.5	2.3±2.9	5.1±2.6
Phenanthrene	22.0±22.8	18.2±15.3	0.1±0.3	1.4±2.9	16.0±12.0	16.4±13.3
Anthracene	12±1.0	1.6±1.60	0.2±0.4	0.1±0.2	1.1±0.9	1.4±1.2
Fluranthene	6.2±6.3	4.4±6.60	5.8±9.0	2.3±1.6	6.0±6.2	3.7±4.3
Pyrene	3.4±2.7	3.2±5.20	10.1±20.5	2.8±2.1	3.4±2.7	2.6±3.4
Benz[α]anthracene	0.1±0.1	0.2±0.30	3.0±4.3	2.4±3.0	0.2±0.3	0.2±0.2
Chrysene	0.2±0.2	0.2±0.40	5.0±7.0	2.9±2.8	0.3±0.3	0.2±0.3
Benzo[b]fluoranthene	0.2±0.7	0.1±0.10	12.2±19.2	6.5±6.4	2.9±8.8	0.6±1.4
Benzo[k]fluoranthene	0.2±0.9	0.0±0.00	8.3±12.6	4.7±5.8	2.6±8.8	0.2±0.3
Benzo[α]pyrene	0.1±0.2	0.0±0.10	4.1±7.7	6.3±9.8	0.6±1.5	0.2±0.4
Indeno [1,2 ,3 -cd]pyrene	0.1±0.3	0.0±0.00	1.2±18.3	38.3±14.8	2.0±5.4	2.5±4.5
Dibenzo[α, h]anthracene	0.0±0.1	0.0±0.00	1.5±2.4	2.0±2.0	0.1±0.4	0.2±0.3
Benzo[g, h, i]perylene	0.0±0.2	0.0±0.00	8.7±13.1	30.0±12.0	1.3±3.7	1.9±3.5

toxicological findings have also revealed that aerosols, from hydrocarbon fuel combustion, may cause adverse effects (Jalava *et al*., 2006; Happo *et al*., 2008). Among other air pollutants occurred during the incomplete fossil fuel combustions, PAHs are one of the major carcinogenic and mutagenic substances released from industrial boilers. Although, the emissions of PAHs largely depend on the combustion conditions, operating conditions and types of fuel burned, numerous researches have evaluated the influences of fuel types on the level of PAH emissions. For instance, Naph, Ace and Fluo were three dominated low molecular weight PAH species in Down Fired Combustor (DFC) of the Research Boiler's (RB) baghouse using Middle Kittanning[1] and upper freeport seam coals[2] as fossil fuels with the emission factors varied from 80-320 μg kg^{-1} as illustrated in Fig. 1-2 (Pisupati *et al*., 2000). A similar study was conducted by analyzing PAHs emitted from 25 industrial boilers using 21 Heavy Oil (HO), two diesel, a co-combustion of Heavy Oil and Natural Gas (HO+NG) and a co-combustion of Coke Oven Gas and Blast Furnace Gas (COG+BFG) boilers (Li *et al*., 1999). Total PAH concentration (i.e., the sum of 21 individual PAHs) in the flue gas emitted from 25 boiler stacks varied from 29.0-4,250 μg m^{-3} with the average of 488 μg m^{-3}. It is interesting to note that the percentage contributions of 2, 3 and 4 ring PAHs were 54.7, 9.47 and 15.3%, respectively (Table 3). Naph was the main PAH congener detected at the stack flue gas. The Emission Factors (EFs) of total-PAHs were 13,300, 2920, 2880 and 208 μg kg fuel^{-1} for the heavy oil, diesel, HO+NG and COG+BFG fueled-boiler, respectively (Table 4). In addition, another study underlined the relatively low emission contents of Pyr and B[α]P from industrial boilers using biodiesel in comparison with those emitted from heating oil (Macor and Pavanello, 2009). The effects of temperature and residence time on PAH formation were also investigated by measuring PAH contents in both particulate and gaseous phases. Analytical results revealed that no significant differences were found in the emissions of particulate PAHs with respect to the fuel type while PAH concentrations in the vapor-phase samples increased as a function of temperature (Pisupati *et al*., 2000). By using a receptor model called Positive Matrix Factorization (PMF), the main emission sources of PAHs in the region of Dalian, China collected in winter were coal-fired boiler (72%) followed by traffic average (20%) and gasoline engine (8%) (Wang *et al*., 2009).

Despite of its renewable and worldwide available fuel used for residential heating in small-scale firings during winter, the wood combustion is widely considered as a major source of carcinogenic PAHs during winter period. It was discovered that emissions of PAHs were comparatively lower in pellet oven and log wood boiler under complete combustion compared to incomplete combustion and emissions were higher in pellet oven than log wood boiler. Based on the field measurements during cold period in 2009, an approximately 44% of the particulate PAHs were detected having carcinogenic potential in Dettenhausen and Bechtoldsweiler, Germany (Bari *et al*., 2011). As a consequence, these facts

[1]Kittanning coal refers to coal seams in the Kittanning cyclothem of the Pennsylvanian Epoch. The Lower Kittanning is coal No. 5, while the Middle Kittanning is coal No. 6

[2]The upper freeport coal seam (Pennsylvanian, Allegheny group) of West Virginia, Pennsylvania and Maryland is largely mined-out with many closed, above-drainage mines that are discharging acid mine water (2006 Philadelphia Annual Meeting (22-25 October 2006))

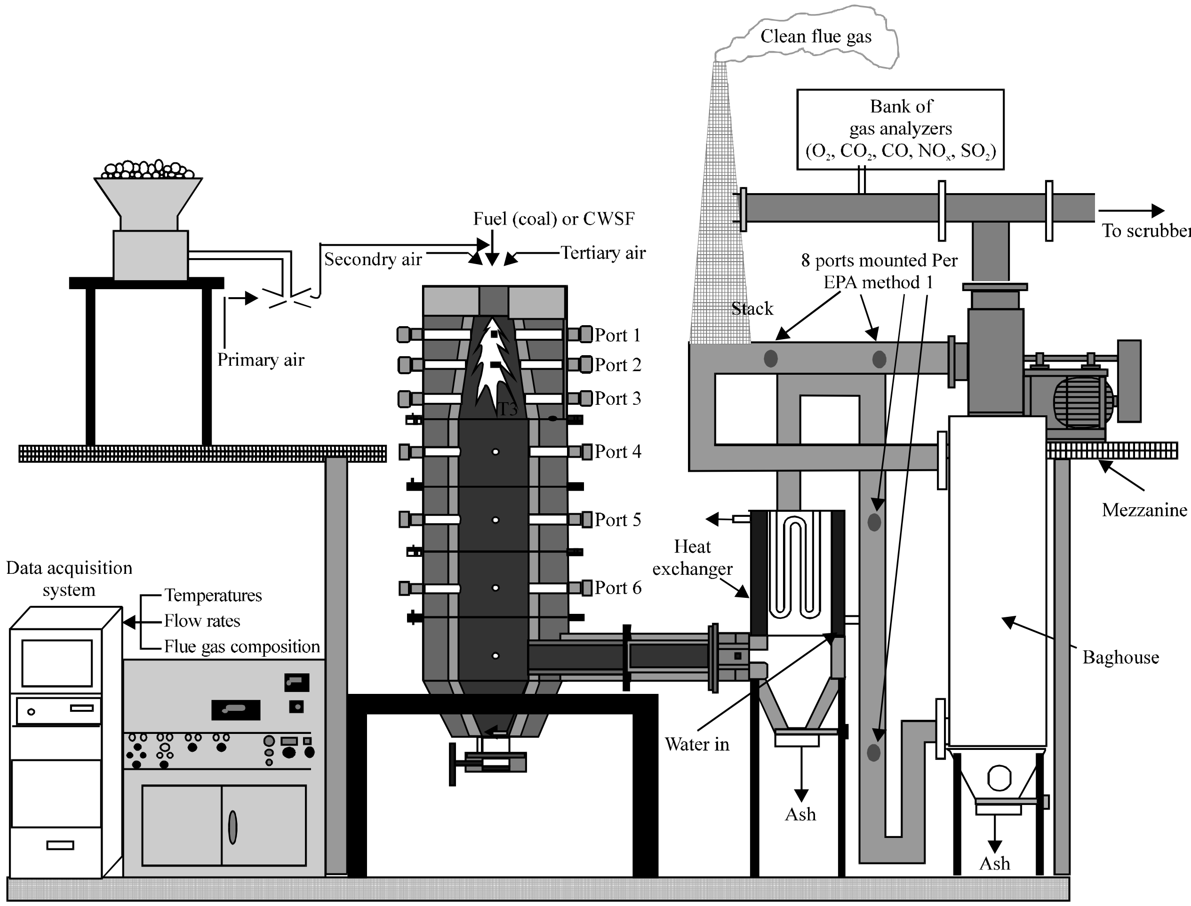

Fig. 1: Schematic diagram of the DFC (Pisupati *et al*., 2000)

Table 3: Fraction of PAH-homologue mass (F%) counted for the total-PAH mass (Li *et al*., 1999)

	PAH (%)					
Stack No.	2-ring	3-ring	4-ring	5-ring	6-ring	7-ring
H-1	26.2	45.6	23.1	4.25	0.40	0.02
H-2	72.8	21.6	4.25	1.60	0.01	ND
H-3	79.1	6.57	12.8	1.64	0.13	0.003
H-4	63.0	7.19	20.6	8.9	0.31	0.12
H-5	52.2	3.42	41.8	2.33	0.11	0.09
H-6	93.3	4.01	0.39	0.97	0.78	0.51
H-7	38.5	8.77	9.13	35.1	8.33	0.12
H-8	18.2	20.8	19.4	19.1	20.3	2.40
H-9	22.6	5.99	29.1	30.6	10.8	0.90
H-10	42.4	11.5	14.6	24.0	7.29	0.20
H-11	44.6	7.65	15.5	22.6	9.32	0.29
H-12	93.3	2.50	1.54	1.52	1.06	0.05
H-13	40.7	8.28	11.7	19.8	18.7	0.77
H-14	59.6	5.60	12.3	13.1	9.04	0.20
H-15	44.7	9.92	12.0	15.9	17.1	0.11
H-16	74.7	3.89	2.39	13.2	5.82	0.07
H-17	95.9	0.64	0.41	1.89	1.18	ND
H-18	96.3	0.81	0.82	1.16	0.71	0.15
H-19	34.6	6.16	4.95	25.3	25.9	3.09
H-20	36.8	6.20	3.28	29.6	23.0	1.16
H-21	47.0	2.32	1.09	19.7	29.6	0.02
D-1	35.3	6.82	53.4	4.11	0.19	0.09
D-2	72.7	13.7	1.49	8.13	1.01	3.02
HG-1	64.3	24.8	7.89	2.80	ND	0.18
CB-1	17.9	1.90	7.84	1.79	0.01	ND
Mean	54.7	9.47	15.3	12.4	7.66	0.54

ND: Not detectable

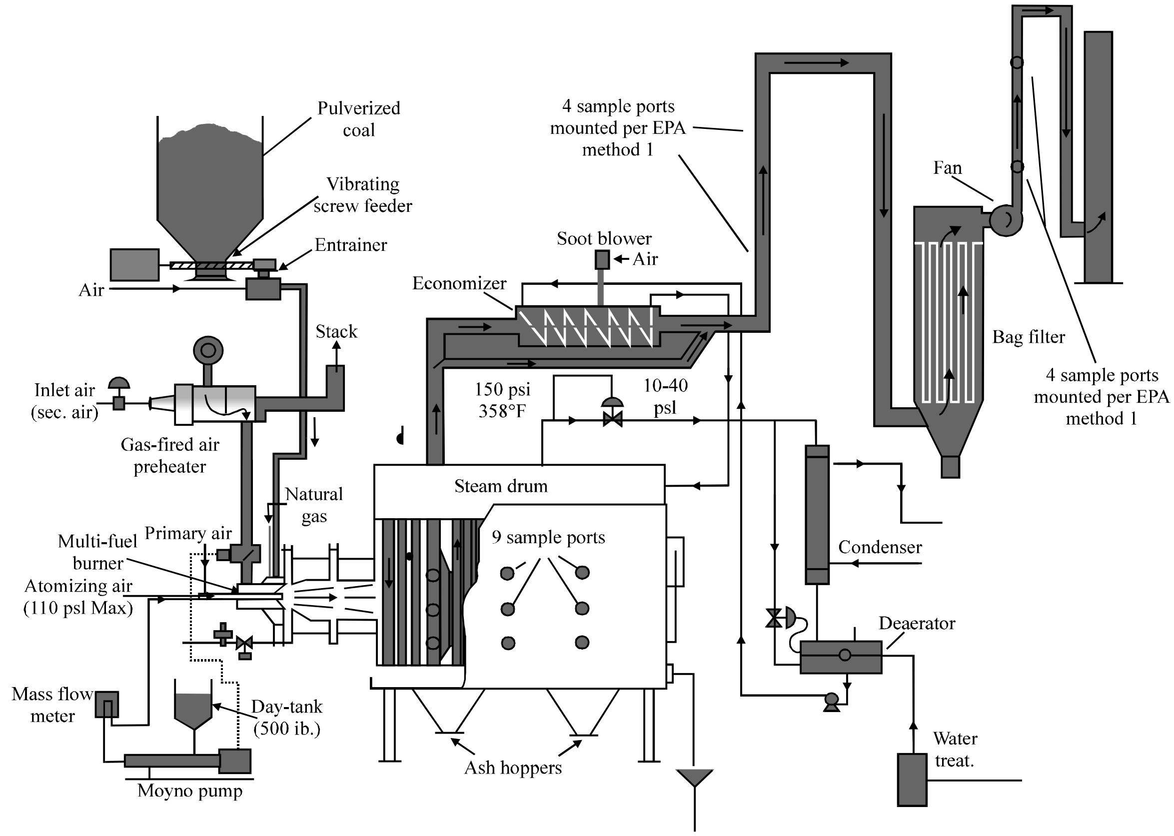

Fig. 2: Schematic diagram of the RB (Pisupati *et al*., 2000)

Table 4: Mean emission factor of PAHs for the various fueled-boilers presented by the unit of μg PAH kg^{-1} fuel consumed (Li *et al*., 1999)

	Fueled-boiler			
PAHs	Heavy oil	Diesel	HO+NG	COG+BFG
Nap	10900	1263	1835	37.3
AcPy	68.8	21.4	10.1	0.05
Acp	68.9	47.3	22.9	0.10
Flu	340	68.3	72.5	1.55
PA	322	78.8	615	0.23
Ant	109	30.8	9.68	2.10
FL	381	1115	128	158
Pyr	357	108	86.8	4.68
CYC	30.8	4.25	7.00	0.33
BaA	33.1	8.10	3.55	ND
CHR	29.2	5.23	11.8	0.05
BbF	65.5	19.0	2.58	0.15
BkF	37.1	48.3	5.20	0.60
BeP	62.8	21.1	5.33	0.48
BaP	112	26.0	16.7	1.53
PER	38.2	10.2	8.93	0.10
IND	297	2.98	0.05	0.25
DBA	388	11.1	0.80	0.53
BbC	45.1	1.50	32.3	ND
BghiP	130	7.53	ND	ND
COR	24.7	20.3	5.13	ND
Total-PAHs	13300	2918	28	208

ND: Non-detectable

accentuate a crucial alarm of controlling PAH emissions from wood-fired winter heating in residential areas and propose adopting BAT such as controlled pellet stoves and boilers and wood chip firings.

Another study had investigated the speciation and concentration of PAHs on Lime Spray Dryer[3] (LSD) ash samples collected from the baghouse of a spreader stoker boiler (Sun *et al*., 2006). It was found that PAH contents in LSD ash were relatively low in comparison with those of other matrices such as soil and sediment (Ghosh *et al*., 2001; MDEP, 2002). For instance, the PAH contents in terrestrial soil samples varied from 0.5-4 mg kg^{-1} as informed by Massachusetts Department of Environmental Protection, which is 2-3 orders of degree higher than that in collected LSD ash (MDEP, 2002). Although, this study highlights the relatively low PAH contents in LSD ash in comparison with those of terrestrial soils, the authors raise concerns over a bioavailability study requests to be performed to verify that use or disposal of LSD ash is non-threatening (Sun *et al*., 2006).

[3]Lime Spray Dryer (LSD) ash is a residual material generated from processes used to remove sulfur dioxide from flue gas following coal combustion. In the LSD process, a fine spray of slaked lime ($Ca(OH)_2$) is injected into the scrubber and reacts with sulfur oxides resulting in the formation of dry calcium sulfate or calcium sulfite (Kadambi *et al*., 1998). The mixture of dry calcium sulfite/sulfate, along with fly ash, is collected as ''LSD ash'' by an electrostatic precipitator or a baghouse

INDUSTRIAL BOILER TYPES, FUTURE AND MARKET TRENDS IN THAILAND

Thai industry, in the early days, began with cottage industry or small-scale business by which family members used free time after crop harvesting to produce garments, woodcrafts and potteries for extra income. It was maintained in such manner until the industrial revolution brought modern manufacturing technology to the Kingdom. The first steam turbine power plant was established in early 1900s as fundamental infrastructure for national economic and social development and then wide variety of industries began as well as the use of industrial boilers. First generation of power boilers and heating boilers was mainly imported from Europe or United States. Despite the quality was guaranteed by international standards such as American Society of Mechanical Engineers (ASME) or British Standards (BS), there was no government agency, which particularly regulates the industrial affairs until the Ministry of Industry was founded in 1942 and Thai Industrial Standards Institute (TISI) in 1969. Thai industrial development is summarized in Fig. 3.

Continuous industrial growth has yielded large number of industrial establishments. Government agencies (STB[4]) and certified institutions [5]still have insufficient capacity to provide training on boiler operation to both existing and new industrial operators. Most of existing certified institutions are clustered in Bangkok, which is convenient only for factories within central region. More certified institutions in other regions of the country will increase accessibility to boiler operation training, especially small- scale factory which is very cost-sensitive. During the past few years, there is a trend of operational safety and health in industrial boiler to have more stringent regulations and increasing awareness of operational safety and health at workplace significantly reduce the risk of serious accident.

For boiler's operating and maintenance approach, it tends to shift from "passive approach" (shutdown, breakdown or emergency) to "proactive approach" (preventive and corrective maintenance) as well as increasing awareness of environmental health impact from industrial boiler, especially adverse health effect of dioxin and furans. Market trend of industrial boiler reveals that local boiler supplier tends to move towards energy-efficient and environmentally-sound technology. The increasing oil and gas price drives higher demand of alternative energies, notably biogas or biomass. As Thailand is agro-industrial-based country, the availability of biomass can be good support to the use of biomass boiler. Biomass utilization through direct combustion or thermochemical conversion shows great potential for low-emission heat and power generation.

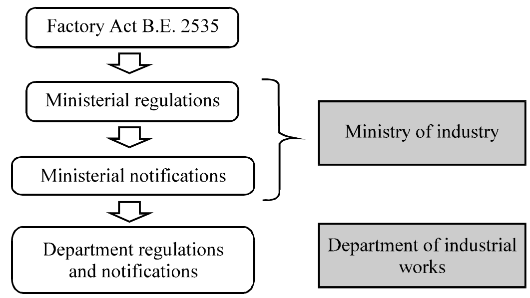

Fig. 3: Legal structure of industrial boiler use and safety in Thailand (Pokasoowan and Pongpiachan, 2013)

TRENDS OF ENERGY CONSUMPTIONS AND BIOMASS USED IN INDUSTRIAL BOILERS IN THAILAND

According to the survey conducted by Department of Alternative Energy Development and Efficiency, an industry, transportation and a household were three major sectors representing for 36.7, 35.8 and 15.1% of total energy consumptions, respectively. It is also interesting to note that a commercial sector and an agricultural sector contribute only 7.2 and 5.2%, correspondingly. There is a general trend that a transportation sector, factories, electric power plants and households rely on non-renewable energy such as natural gas, oil and coal. Beyond petroleum in 2010, predicted that the proved reserves energy since 2009, the use of energy is more or less the same and the production of the energy remains more or less constant are asfollows; oil can be used for 42 years, natural gas for 60 years and coal for 122 years. Alternatively, renewable energy is presently of interest as fuel and its use can meet 13.5% of the global energy demand (Varun *et al*., 2009).

[4]The Safety Technology Bureau (STB) is corresponding authority that factory must notify when serious accident occurs. When accident is reported, the bureau deploys an investigation team to observe and extract information from the accident scene, analyze for the cause of accident and finally summarize the case. There were 43 records of steam boiler explosion countrywide during 1978- 2007. However, the records shown in this report only present type of boiler, age of boiler, whether boiler design and fabrication conforms to the national standard, and whether the factory regularly perform boiler inspection

[5]Faculty of Industrial Technology, Petchaburi Rajabhat University, Industrial Technology Development Institute (ITDK), King Mongkut's University of Technology North Bangkok, Technology Promotion Association (Thailand-Japan), The Federation of Thai Industry, The Engineering Institute of Thailand, Safety and Environmental of work Development Association (SEDA)

Table 5: No. of boilers using biomass in Thailand (Sttayawuthiphong, 201 3)

Biomass type	No. of boilers	Total boilers capacity (ton h^{-1})
Bagasse	174	15,878.0
Wood (Chip, dust, etc.)	1,589	10,416.8
Rice husk	618	3,355.0
Oil palm (Palm fronds, empty fruit bunches, palm kernel shells, residue)	215	3,080.3
Wood + oil palm shell	23	682.1
Wood + bagasse	8	472.0
Corn peel	32	102.3
Coconut shell	16	65.1
Wood + rice husk	1	50.0
Wood + cirb cobs	5	38.3
Corn cobs	8	37.1
Coffee grounds	1	13.2
Wood + coconut shell	2	6.1
Sybean meal	2	5.6
Cotton shell	1	2.4
Banana peel	1	1.0
Total	2,696	34,205.3

Included boilers using biomass with fossil fuel such as wood, fuel oil

Table 6: Quantitative potential of biomass fuels in Thailand from EforE (Sattayawuthiphong, 2013)

		Energy potential	
Plants	Residue	TJ	ktoe
Rice	Husk	519.47	12.40
	Rice straw	57,210.10	1,366.18
Sugarcane	Bagasse	-	-
	Shoot and leaf	93,211.27	2,255.89
Cassava	Stem	93,873.63	2,241.70
	Starch from root	19,508.39	465.86
Corn	Cob	5,568.39	132.98
	Stem	17,701.08	422.70
Palm oil	Fiber	-	-
	Empty fruit bunch	5,625.65	134.34
	Shell	-	-
	Fond	-	-
Parawood	Sawdust	-	-
	Wood chip	6,701.77	160.25

In Thailand, Department of Industrial Works (DIW), Ministry of Industry takes care of boiler using in the factories and Ministry of Labor Force takes care of boilers using in both industrial sector and general enterprise such as hospital and hotel, etc. However, database of boilers in Thailand is available only in DIW. Data of boilers using biomass from DIW, in August, 2012, are shown in Table 5. Industrial boilers used wood chips were predominant (i.e., 1,589 boilers) followed by rice husk (i.e., 618 boilers) and bagasse (i.e., 174 boilers). Apart from wood chips and rice husk, there is more space for other biomass materials such as residue from sugarcane, cassava, corn, palm oil and para wood. The quantitative evaluation of biomass fuels including rice, sugarcane, cassava, corn, palm oil and para wood were illustrated in Table 6. This information use data from "Guidelines on Biomass Fuel Management for Use as Alternative Energy at the Macro Level" which is the assessment of biomass potential in 2007. The analysis of potential biomass fuels remaining in Thailand found that correspond to potential, biomass fuels remaining in the same direction. Shoot and leaf from sugarcane as well as stem from cassava display the highest energy potential with the values of 93,211 and 93,874 TJ, respectively. It is also interesting to note that shoot and leaf of sugarcane has relatively low RH (9.20%), indicating the promising properties as biomass fuel with low PAH emissions. On the contrary, saw dust, chips and roots from para wood tend to produce higher PAH emissions because of its relatively high RH (55 %) coupled with its low heating value (6.57 MJ kg^{-1}) (Table 7).

RECOMMENDATIONS FOR REDUCING PAH EMISSIONS FROM INDUSTRIAL BOILERS UNDER THE CONTEXT OF THAILAND

Thai industry in the early days began with cottage industry or small-scale business by which family members used free time after crop harvesting to produce garments, woodcrafts and potteries for extra income. It was maintained in such manner until the industrial revolution brought modern manufacturing technology to the Kingdom. The first steam turbine power plant was established in early 1900s as fundamental infrastructure for national economic and social development and then wide variety of industries began as well as the use of industrial boilers. First generation of power boilers and heating boilers was mainly imported from Europe or United States. Despite, the quality was guaranteed by international standards such as American Society of Mechanical Engineers (ASME) or British Standards (BS), there was no government agency which particularly regulates the industrial affairs until the Ministry of Industry was founded in 1942 and Thai Industrial Standards Institute (TISI) in 1969.

Rapid economic growth and industrialization in Thailand raise concerns over the emissions of PAHs from industrial sectors, particularly incomplete combustions of fuels used in boilers. Several recommendations and suggestions for reducing PAH emissions from fossil fuel-fired utilities and industrial boilers can be described as follows:

- Based on small wood boiler for domestic heating, the PAH emissions are positively correlated with the loading of fuel. Therefore, the optimization of fuel load is essential crucial for PAHs reductions. The boiler operator should also optimize the oxygen level at the boiler exit since PCDD/PCDF and PAH emissions were observed to largely enhance with lower oxygen concentrations

Table 7: Quantitative potential of biomass of Thailand in 2007 (Sattayawuthiphong, 2013)

			Ratio of biomass		Quantity of	Heating		Factor of	Quantity of	Energy potential	
Plants	Production per year (M t)	Biomass	By product	(t rai^{-1})	biomass (M t)	value (MJ kg^{-1})	RH (%)	unuse residue	unuse biomass (M t)	TJ	ktoe
Rice	32.099	Husk	0.21		6.74	13.52	12.00	0.0057	0.038	519.47	12.40
		Straw	0.49		15.73	12.33	10.00	0.295	4.640	57,210.10	1,366.18
Sugarcane	64.4	Bagasse	0.58		37.35	7.37	50.73	0.00	-	-	-
		Shoot and leaf	0.17		10.95	15.47	9.20	0.55	6.021	93,211.27	2,225.89
Cassava	26.92	Stem	0.09		2.42	5.59	59.40	0.407	6.021	93,873.63	2,241.70
		Root	0.20		5.38	5.49	59.40	0.66	3.553	16,508.39	465.86
Corn	3.6	Cob	0.24		0.86	9.62	40.00	0.67	0.579	5,568.39	132.98
		Stem	0.82		2.95	9.83	42.00	0.61	1.801	17,701.08	422.70
Palm oil	6.39	Fiber	0.19		1.21	11.40	38.50	0.00	-	-	-
		Shell	0.04		0.26	16.90	12.00	0.00	-	-	-
		Empty fruit bunch	0.32		2.04	7.24	58.60	0.38	0.777	5,625.65	134.34
Parawood	207,607 (rai)	Sawdust		3	0.62	6.57	55.00	0.00	-	-	-
		Chip		12	2.49	6.57	55.00	0.41	1.021	6,701.77	160.25
		Root		5	1.04	6.57	55.00	0.95	0.986	6,478.90	154.72

- Since, there is a trend that HMW PAHs (i.e., high carcinogenic PAHs) in aerosols were predominant in "slumber mode" regardless of biomass material types, the boiler operator should set the combustion condition as "full frame mode" in order to decrease the level of 6-ring aromatic PAH congeners
- Heavy oil tends to produce relatively high EFs of total-PAHs in comparison with those of diesel, HO+NG and COG+BFG fueled-boiler. For those industrial boilers used biodiesel as fuels appears to produce less emissions of Pyr and B[a]P and thus the Ministry of Industry as well as Pollution Control Department, Ministry of Natural Resources and Environment should promote biodiesel as an environmentally friendly fuel compatible for boilers used in green industry concept
- During the past few years, the increasing oil and gas price forces higher need of substitute fuel, remarkably biomass or agricultural waste materials. Since Thailand is agro-industrial-based country, the availability of biomass can be good support to the use of biomass boiler. In this study, we found that shoot and leaf from sugarcane coupled with stem from cassava are promising biomass fuel due to its comparatively low RH with high energy potential. In other words, these agricultural waste materials can provide relatively high energy values with low PAH emissions and thus can be considered as one of most suitable green fuels under the context of Thailand

REFERENCES

Bari, M.A., G. Baumbach, J. Brodbeck, M. Struschka, B. Kuch, W. Dreher and G. Scheffknecht, 2011. Characterisation of particulates and carcinogenic polycyclic aromatic hydrocarbons in wintertime wood-fired heating in residential areas. Atmos. Environ., 45: 7627-7634.

Bignal, K.L., S. Langridge and J.L. Zhou, 2008. Release of polycyclic aromatic hydrocarbons, carbon monoxide and particulate matter from biomass combustion in a wood-fired boiler under varying boiler conditions. Atmos. Environ., 42: 8863-8871.

Ghosh, U., J.W. Talley and R.G. Luthy, 2001. Particle-scale investigation of PAH desorption kinetics and thermodynamics from sediment. Environ. Sci. Technol., 35: 3468-3475.

Happo, M.S., M.R. Hirvonen, A.I. Halinen, P.I. Jalava and A.S. Pennanen *et al*., 2008. Chemical compositions responsible for inflammation and tissue damage in the mouse lung by coarse and fine particulate samples from contrasting air pollution in Europe. Inhalation Toxicol., 20: 1215-1231.

Jalava, P.I., R.O. Salonen, A.I. Halinen, P. Penttinen and A.S. Pennanen *et al*., 2006. *In vitro* inflammatory and cytotoxic effects of size-segregated particulate samples collected during long-range transport of wildfire smoke to Helsinki. Toxicol. Applied Pharmacol., 215: 341-353.

Kadambi, J.R., R.J. Adler, M.E. Prudich, L.S. Fan, K. Raghunathan, S.J. Khang and T.C. Keener, 1998. Flue Gas Desulfurization for Acid Rain Control. In: Dry Scrubbing Technologies for Flue Gas Desulfurization, Toole-O?Neil, B. (Ed.). Kluwer Academic Publishers, Boston/Dordrecht/ London, pp: 1-80.

Kaivosoja, T., P.I. Jalava, H. Lamberg, A. Viren and M. Tapanainen *et al*., 2013. Comparison of emissions and toxicological properties of fine particles from wood and oil boilers in small (20-25 kW) and medium (5-10 MW) scale. Atmos. Environ., 77: 193-201.

Laden, F., L.M. Neas, D.W. Dockery and J. Schwartz, 2000. Association of fine particulate matter from different sources with daily mortality in six U.S. cities. Environ. Health Perspect., 108: 941-947.

Lamberg, H., K. Nuutinen, J. Tissari, J. Ruusunen and P. Yli-Pirila *et al*., 2011. Physicochemical characterization of fine particles from small-scale wood combustion. Atmos. Environ., 45: 7635-7643.

Lanki, T., J. Pekkanen, P. Aalto, R. Elosua and N. Berglind *et al*., 2006. Associations of traffic related air pollutants with hospitalisation for first acute myocardial infarction: The HEAPSS study. Occup. Environ. Med., 63: 844-851.

Leclerc, D., W.L. Duo and M. Vessey, 2006. Effects of combustion and operating conditions on PCDD/PCDF emissions from power boilers burning salt-laden wood waste. Chemosphere, 63: 676-689.

Li, C.T., H.H. Mi, W.J. Lee, W.C. You and Y.F. Wang, 1999. PAH emission from the industrial boilers. J. Hazardous Mater., 69: 1-11.

MDEP, 2002. Technical update: Background levels of polycyclic aromatic hydrocarbons and metals in soil. Massachusetts Department of Environmental Protection (MDEP), Massachusetts, USA., pp: 1-5.

Macor, A. and P. Pavanello, 2009. Performance and emissions of biodiesel in a boiler for residential heating. Energy, 34: 2025-2032.

Penttinen, P., M. Vallius, P. Tiittanen, J. Ruuskanen and J. Pekkanen, 2006. Source-specific fine particles in urban air and respiratory function among adult asthmatics. Inhalation Toxicol., 18: 191-198.

Pisupati, S.V., R.S. Wasco and A.W. Scaroni, 2000. An investigation on polycyclic aromatic hydrocarbon emissions from pulverized coal combustion systems. J. Hazardous Mater., 74: 91-107.

Pokasoowan, C. and S. Pongpiachan, 2013. Occupational accidents in industrial boiler use in Thailand. A Survey Report, United Nations Industrial Development Organization.

Riva, G., E.F. Pedretti, G. Toscano, D. Duca and A. Pizzi, 2011. Determination of polycyclic aromatic hydrocarbons in domestic pellet stove emissions. Biomass Bioenergy, 35: 4261-4267.

Sattayawuthiphong, B., 2013. Biomass in Thailand. A Survey Report, United Nations Industrial Development Organization.

Stockholm Convention, 1997. Annex C, unintentional production. Stockholm Convention on Persistent Organic Pollutants, pp: 27-30. http://www.pops.int/documents/convtext/convtext_en.pdf.

Sun, P., L.K. Weavers, P. Taerakul and H.W. Walker, 2006. Characterization of Polycyclic Aromatic Hydrocarbons (PAHs) on Lime Spray Dryer (LSD) ash using different extraction methods. Chemosphere, 62: 265-274.

Tapanainen, M., P.I. Jalava, J. Maki-Paakkanen, P. Hakulinen and M.S. Happo *et al*., 2011. *In vitro* immunotoxic and genotoxic activities of particles emitted from two different small-scale wood combustion appliances. Atmos. Environ., 45: 7546-7554.

Varun, R. Prakash and I.K. Bhat, 2009. Energy, economics and environmental impacts of renewable energy systems. Renewable Sustainable Energy Rev., 13: 2716-2721.

WHO/IPCS, 1998. Selected non-heterocyclic polycyclic aromatic hydrocarbons. Environmental Health Criteria 202. International Programme on Chemical Safety, World Health Organization, Geneva.

Wang, D., F. Tian, M. Yang, C. Liu and Y.F. Li, 2009. Application of positive matrix factorization to identify potential sources of PAHs in soil of Dalian, China. Environ. Pollut., 157: 1559-1564.