

1 (Revised MS to ES&T)

2 Reducing PAH Emissions from the Iron Ore Sintering
3 Process by Optimizing Its Operation Parameters

4 *Yu-Cheng Chen¹, Perng-Jy Tsai^{1,2*}, Jin-Luh Mou³*

5 ¹Department of Environmental and Occupational Health, Medical College, National Cheng Kung
6 University, 138, Sheng-Li Road, Tainan 70428, Taiwan

7 ²Sustainable Environment Research Center, National Cheng Kung University, 1 University Road,
8 Tainan 70101, Taiwan

9 ³Department of Occupational Safety and Health, Chung Hwa University of Medical Technology, 89,
10 Wenhwa 1st St., Rende Shiang, Tainan 71703, Taiwan

11

12 *Correspondence author: Perng-Jy Tsai, Department of Environmental and Occupational Health,
13 Medical College, National Cheng Kung University. 138, Sheng-Li Rd., Tainan 70428, Taiwan. Tel.:
14 +886-6-2353535 ext. 5806; Fax: +886-6-2752484; E-mail address: pjtsai@mail.ncku.edu.tw

15 **Running Title:** Determining optimal operation condition for reducing PAH emissions in the iron ore
16 sintering process by using Taguchi experimental design.

1 Abstract

2 This study was set out to reduce polycyclic aromatic hydrocarbon (PAH) emissions from the iron ore
3 sintering process by optimizing its operation parameters obtained from the Taguchi experimental design.
4 Four operating parameters, including the water content (Wc; range = 6.0–7.0 wt %), suction pressure
5 (Ps; range = 1000–1400 mmH₂O), bed height (Hb; range = 500–600 mm) and type of hearth layer (HL;
6 including sinter, hematite, and limonite) were selected and conducted on a pilot-scale sinter pot to
7 simulate various sintering operating conditions of a real-scale sinter plant. We found that the resultant
8 optimal combination (Wc = 6.5 wt%, Hb = 600 mm, Ps = 1400 mmH₂O, and HL = limonite) could
9 reduce the emission factor of total BaP equivalent concentration (EF_{BaPeq}) up to 57.6% in comparison
10 with the current operating condition of a real-scale sinter plant (Wc = 6.5 wt %, Hb = 550 mm, Ps =
11 1200 mmH₂O, and HL = sinter). Through the ANOVA analysis, we found that Ps and Hb were the top
12 two parameters affecting total EF_{BaPeq} (accounting respectively for 70.9% and 21.2% of the total
13 contribution of the four selected parameters). By examining both the sinter productivity and sinter
14 strength, the values obtained from the optimal combination were quite comparable to those of the
15 current operating condition. The above results further confirm the applicability of the obtained optimal
16 combination for the real-scale sinter plant.

17 Keywords: PAH emission, iron ore sintering, operation parameters, optimal combination, Taguchi
18 experimental design

19

1 **Introduction**

2 Polycyclic aromatic hydrocarbons (PAHs) and their derivatives could be formed during the
3 incomplete and/or inefficient combustion of fossil fuels. PAHs are semi-volatile compounds presenting
4 in the ambient air in not only the gas phase, but also the particulate phase through condensation or
5 adsorption of gas-phase PAHs on the surface of particles (1). PAHs are known to be harmful to human
6 health. Some PAHs, such as benzo[*a*]pyrene (BaP), and Cyclopenta[*c,d*]pyrene (CYC) and
7 dibenz[*a,h*]anthracene (DBA), have been classified into *Group 1* and *Group 2A*, respectively, by the
8 International Agency for Research on Cancer (IARC) (2). Many countries have also regulated the
9 ambient air quality standards or proposed the limit value for the BaP (3). PAHs found in the outside
10 ambient air can be generated both from the natural sources (such as forest fires and volcanic eruptions)
11 and the anthropogenic sources (such as industrial combustion, traffic emission, and waste incineration)
12 (4–6).

13 The iron and steelmaking is a highly energy-intensive process requiring burning of fossil fuels,
14 including coal and coke and is known as one of the significant PAH emission sources (7–9). As
15 reported by Ravindra et al., (3) and Bjørresth and Ramdahl (10) studies, PAHs emitted from iron and
16 steel industries have been recognized as the second major source in Europe, accounting for 12.0–20.2%
17 of yearly total PAH emissions. In an integrated iron and steel plant, the iron ore sintering process plays
18 an important role on PAH emissions due to its extremely large flue gas volume. Iron ore sintering is an
19 agglomeration process to convert iron ore fines (raw mixture) into lumpy agglomerates. In the
20 preliminary stage of sinter making process, water was sprayed onto the raw mixtures in the mixing
21 drum to increase the granular sizes for enhancing the permeability of the sinter bed. During sintering,
22 the raw mixtures were first ignited by gas-fueled (nature gas) burns situated at the beginning of the steel
23 belt conveyer. Then, the sinter bed was heated to temperature of ~1000 °C or above. Suction air passes
24 through the sinter layer by means of wind legs and a fan, which moves the melting/combustion zone to
25 the down layer to produce sintered products.

1 The sintering process has been developed for several decades in the iron and steel manufacturing
2 industry. Traditionally, air pollution control devices (APCDs) for the control of PAH emissions have
3 been widely used to reduce their environmental impacts. Nevertheless, most sinter plants have faced the
4 dilemma regarding how to continuously upgrade their APCDs in order to comply with stricter and
5 stricter emission standards adopted in their countries. In order to comply with future PAH emission
6 standard and decrease the cost resulting from upgrading the end-pipe PAH control devices, it is
7 important to develop an effective method for directly reducing PAH generations during the sintering
8 process. Therefore, to optimize operating conditions in order to reduce PAH formations via oxidation
9 reaction might provide a promising solution. In addition to the property of the sinter raw mixture, the
10 four operating parameters, including the water content (Wc), suction pressure (Ps), bed height (Hb) and
11 type of hearth layer (HL), are major factors affecting combustion conditions during the iron ore
12 sintering process (11-13). Among these four parameters, the content of Wc in the sinter bed might
13 affect the adsorption of PAHs on the surface of particles and the solubility of PAHs in water or might
14 affect the heating value of coke in combustion; the magnitude of Ps affects the air (or oxygen) supply
15 which might play an important role in the oxidation reaction related to PAH formations (14); Hb affects
16 the thickness and temperature profile of the combustion zone of the sinter bed and in consequence
17 affects the contents of unburned hydrocarbon compounds during the sintering process (15); and the type
18 of the HL might affect the catalytic oxidation reaction associated with PAH formations (13, 16). All
19 these operating parameters have been used to control the structure of the sinter bed to simulate various
20 operation conditions for the sintering process in many studies (11, 17-19). It is known that the cost
21 reduction and the sinter production are the major concerns of the real-scale sinter plant rather than
22 PAHs reduction. As a result the selected iron ores might come from numerous mine sources because of
23 cost and quality considerations and result in considerable variations in the contents of the sintering raw
24 mixture. Therefore, it would become impractical for changing the contents of the sintering raw mixture
25 in a real-scale sinter plant simply for reducing its PAH emissions. Therefore, to seek for an optimal

1 combination of Wc, Ps, Hb and HL for reducing PAH formations during the sintering process might
2 provide a promising solution.

3 In this study the Taguchi experimental design was used to determine the optimal operating
4 combination for reducing PAH formations during the sintering process. In addition, two important
5 indexes (i.e. the sinter productivity and sinter strength) widely used for characterizing the quality of the
6 sintering products were also examined to further ensure the optimal combination obtained from the
7 Taguchi experimental design can be used in the real-scale sinter plant.

8 **Material and Methods**

9 **The Pilot Scale Sinter Pot and Its Operating Procedures.** A pilot scale sinter pot was used in this
10 study to simulate the real-scale sintering process (Fig. 1). It has been widely used in pilot tests for iron
11 ore and steel industries for improving their sinter production (12, 20) and the control of their emitted
12 air contaminants (such as PCDD/Fs) (21, 22), although the volume of this sinter pot (0.051 m³) is quite
13 small as in comparison with the real-scale sinter plant (400 m³). This sinter pot included a pot body
14 (inner diameter = 330 mm, height = 600 mm), an ignition hood, and a windbox connected to an exhaust
15 duct. Six kilogram of hearth layer (particle diameters = 10–15 mm, thickness = 40 mm) were placed
16 inside the sinter pot. The temperature profiles and related chemical reactions that presumably occurred
17 in the sinter pot during combustion were also illustrated in Fig. 1. Results associated with the zone
18 combustion process of the sinter pot have been described in details in the previous studies (21–22).
19 Outlet gas temperature was measured by three type-k thermocouples located in the windbox to monitor
20 sintering scenario during the combustion process. During sintering, the designated ignition temperature
21 in ignition hood was specified at 1150–1200 °C for 1.5 min and then held in another 1.5 min for
22 keeping heat. During this period (i.e., starting from the ignition to the removal of the ignition hood) the
23 suction pressure inside the sinter pot was controlled at 800 mmH₂O by using an electromagnetic valve.
24 After this, the suction pressure was raised to 1200 mmH₂O and then kept constant throughout the end of

1 the sintering process. The total sintering time was around 35 min depending on the experimental
2 conditions.

3 The sintering raw mixture used in this study was directly obtained from the real-scale sinter plant. Its
4 contents and the analyzed chemical compositions show in Table 1.

5 **The Taguchi Experimental Design.** The Taguchi experimental design is a powerful tool that
6 provides a simple, efficient and systematic approach to optimize operating conditions under designated
7 ranges of all selected parameters. The details of the Taguchi experimental design can be seen in the
8 Supporting Information (SI). The working steps for the Taguchi experimental design include: (1)
9 selection of operation parameters; (2) determination of the number of levels for each selected parameter;
10 (3) selection of the appropriate orthogonal array and arrangement of operation parameters to the
11 orthogonal array; (4) conducting experiments based on the arrangement of the orthogonal array; (5)
12 analysis of the experimental results using the S/N ratio and ANOVA analyses; (6) selection of the
13 optimal combination of levels for the selected operation parameter; and (7) verification of the above
14 optimal combination by conducting a confirmation experiment (23, 24).

15 **Selected Operation Parameters, Levels and Orthogonal Array.** Four operation parameters (and
16 their testing ranges), including water content (Wc; 6.0–7.0 wt %), suction pressure (Ps; 1000–1400 mm
17 H₂O), bed height (Hb; 500–600 mm), and types of hearth layer (HL; including sinter (containing 70%
18 Fe₂O₃ and 7% Fe₃O₄; Fe in total accounting for 58.1% of total weight), hematite (containing 88%
19 Fe₂O₃ and 7% FeO·OH; Fe in total accounting for 64.1% of total weight), and limonite (containing 40%
20 Fe₂O₃, 45% FeO·OH and 6% H₂O; Fe in total accounting for 63.3% of total weight)) were selected in
21 this study. The selected ranges of the above four parameters were determined based on the past
22 operation experience of the selected sinter plant and the published references (17, 25–26). A specific
23 combination of the four selected operation parameters (i.e., Wc = 6.5 wt %, Ps = 1200 mmH₂O, Hb =
24 550 mm, and type of HL = sinter) being currently used in the real-scale sinter plant was served as the
25 reference combination. SI Table S1 shows the selected three levels for each operation parameter based

1 on its designated range. SI Table S2 shows an $L9(3^4)$ orthogonal array (with four columns and nine
2 rows) used in this study according to the Taguchi experimental design (23). Since the experimental
3 design was orthogonal, it was possible to discriminate the effect of each individual parameter at each
4 designated level. As shown in SI Table S2, nine combinations of the four selected operation parameters
5 were chosen for conducting experiments. Subjected to the cost associated with samplings, sample
6 analyses and sinter pot operation, each experiment were repeated twice ($n = 2$) in this study.

7 **PAH sampling.** For each experiment, the flue gas samples were collected from the duct located at
8 the downstream of the windbox of the pilot sinter pot (see Fig 1) by using a PAHs Sampling System
9 (PSS; Li-The Co., Kaoushing, Taiwan) (27). Because the instability of the airstream occurred during the
10 first five minutes of the sintering process (i.e., the time needed for adjusting the suction pressure to
11 reach the designated level), the flue gas of the first five minute was not collected. As a result, the
12 sampling time for each flue gas sample was ~30 min. During sampling, the flue gas (including particle-
13 and gas-phase PAHs) was sampled iso-kinetically throughout each batch sintering. The details of the
14 PAH sampling method can be seen in the SI.

15 **PAH analysis.** For each collected sample, both its glass fiber filter and PUF/resin cartridge were
16 Soxhelt extracted in a mixed solvent (n-hexane and dichloromethane v:v = 1:1) for 24 hours. The
17 extract was concentrated by purging with ultra-pure nitrogen to 2 ml, cleaned-up and then re-
18 concentrated to exactly 1.0 ml. The contents of 22 PAH compounds were determined by using a gas
19 chromatograph with a mass selective detector (GC/MS) and a computer work station. Detailed
20 analytical methods and conditions were included in the SI or presented in our previous works (27–28).

21 **Evaluation of Sinter Productivity and Sinter Strength.** The sinter productivity, expressed in tons
22 per square meter of grate area of sintering machine per day, was calculated from the sintering time, the
23 cross-sectional area of the pot grate, and the weight of sinter product recovered from the test (by
24 removing the loss of the weight of hearth layer). The sinter strength was measured by using a modified
25 ISO 3271 test method (29).

1 **Data Analysis.** In this study, the total PAH concentration was defined as the sum of the
2 concentrations of the selected 22 PAH compounds. In addition, PAH contents were further divided into
3 three categories (LMW-, MMW- and HMW-PAHs) according to their molecular weights (see in SI
4 Table S3).

5 Because BaP has been known to be the most carcinogenic PAH compound, the carcinogenic
6 potency of each collected sample was also determined in terms of its BaP equivalent concentration
7 (BaP_{eq}). To calculate the BaP_{eq} for each individual PAH species, it requires the use of its toxic
8 equivalent factor (TEF) for the given species relative to BaP carcinogenic potency. Each selected TEF
9 corresponding it's PAH compound has been reported by our previous works (27, 30). The carcinogenic
10 potency of the total BaP_{eq} was estimated as the sum of individual BaP_{eq} of the 22 PAH compounds. In
11 the present study, considering the variations in flow rate, sintering time, and charging weight of
12 feedstock among different experimental combinations, the emission factor of total BaP_{eq} ($EF_{BaP_{eq}}$;
13 $\mu\text{g}/\text{kg}$ -feedstock) was calculated to compare for reducing the environmental impact purpose. [The details](#)
14 [associated with the calculation of \$EF_{BaP_{eq}}\$ can be seen in the SI.](#)

15 The S/N ratio based on the concept of the-lower-the-better was used to characterize $EF_{BaP_{eq}}$. The
16 details of the calculated equations including the S/N ratio and its predicted value for the optimal
17 combination can be seen in the SI. In addition, the analysis of variance (ANOVA) was used to
18 investigate the effect of each individual parameter on $EF_{BaP_{eq}}$.

19 **Results and Discussion**

20 **Concentrations and Characteristics of PAHs Emitted from the Sintering Process.** The SI Figure
21 S1 shows the fractions of 22 PAHs (mean and range) obtained from each of the nine selected
22 experimental combinations as using Test A-sintering raw mixture. The most abundant PAHs presented
23 in sequence were NaP, AcPy, Flu, PA and Acp. Table 2 further classifies the above concentrations into
24 LMW-, MMW-, and HMW-PAHs, gas- and particle-phase PAHs, total PAH, and total BaP_{eq}

1 concentrations. The mean total PAH and BaP_{eq} concentrations were 504 $\mu\text{g}/\text{Nm}^3$ (range = 355–673
2 $\mu\text{g}/\text{Nm}^3$) and 5.35 $\mu\text{g}/\text{Nm}^3$ (range = 2.80–7.41 $\mu\text{g}/\text{Nm}^3$), respectively. The total PAHs was mostly
3 contributed by gas-phase PAHs (mean = 479 $\mu\text{g}/\text{Nm}^3$) accounting for 95.1% (range = 93.2–97.7%)
4 emissions of total PAHs. The LMW-PAHs was the most dominant PAH homologue (mean = 473
5 $\mu\text{g}/\text{Nm}^3$) accounting for 93.8% (range = 90.9–94.6%) emissions of total PAHs. Because of the high
6 volatility of LMW-PAHs, the above results further confirm that most PAHs were in the form of the gas
7 phase. In contrast, the MMW- and HMW-PAHs, although were know with higher carcinogenic
8 potencies, were the least and second least dominant homologues (mean = 10.3 and 20.8 $\mu\text{g}/\text{Nm}^3$,
9 respectively) accounting respectively for 2.04% and 4.13% (range = 1.53–2.85% and 3.12–6.52%,
10 respectively) emissions of total PAHs. Table 2 also shows the emission factor of total BaP_{eq} (total
11 EF_{BaPeq}) for each combination. We found that the mean total EF_{BaPeq} for the nine selected experimental
12 combinations was 23.4 $\mu\text{g}/\text{kg}$ -feedstock (range = 10.9–34.2 $\mu\text{g}/\text{kg}$ -feedstock). Due to the intrinsic
13 differences in flow rate, sintering time and charging weight of the nine selected experimental
14 combinations, it should be noted that the trend in magnitude of total EF_{BaPeq} was somewhat different
15 from that of total BaP_{eq} concentrations. The above result clearly indicates the importance of using total
16 EF_{BaPeq} to determine the optimal combination for reducing PAH emissions from the sintering process.

17 **Comparison of PAH Characteristics and Concentrations between This Sinter Pot and Sinter**
18 **Plants.** Table 3 shows PAH characteristics (including profile, homologue distributions, particle- (sinter
19 pot = 4.3%; sinter plant = 6.7%) and gas-phase (sinter pot = 95.7%; sinter plant = 86%) distribution)
20 and concentrations (including mean total concentration (sinter pot = 504 $\mu\text{g}/\text{Nm}^3$; sinter plant = 778
21 $\mu\text{g}/\text{Nm}^3$) and EF_{PAHs} (sinter pot = 2364 $\mu\text{g}/\text{kg}$ -feedstock; sinter plant = 3160 $\mu\text{g}/\text{kg}$ -feedstock)) obtained
22 from the present study and real-scale sinter plants (7, 31). We found above both results were
23 comparable indicating our results could be representative of iron metallurgy.

24 **S/N Ratios and ANOVA Analysis.** In this study, the total EF_{BaPeq} obtained from the nine selected
25 experimental combinations were used to calculate S/N ratio. The S/N ratios of the four selected

1 parameters in three designated levels according to the orthogonal array of the experimental arrangement
2 were presented in SI Table S4. We found that the resultant S/N ratios fell to the range from -20.5 to -
3 29.7 dB. SI Table S5 shows mean S/N ratios of the four selected parameters in each of their three
4 designated levels. For each selected parameter, the difference between maximum S/N ratio and its
5 corresponding minimum S/N ratio (i.e., max-min) represents the effect of the given parameter on
6 determining total EF_{BaPeq} . Based on this, we found that the effects in sequence for the four selected
7 parameters on total EF_{BaPeq} were: Ps (5.29 dB), Hb (3.07 dB), HL (1.14 dB) and Wc (0.81 dB). Figure 2
8 shows the trend of the resultant S/N ratios for each selected parameters at the three designated levels
9 affecting total EF_{BaPeq} . Both Ps and HL shared the same trend in their resultant S/N ratios (i.e., first
10 decreased then increased). The above trend was different from that of Wc (i.e., first increased then
11 decreased) and Hb. The combination of Wc (= 6.5 wt %), Ps (= 1400 mmH₂O), Hb (= 600 mm), and
12 HL (= limonite) were found with the highest S/N ratio for each of the four selected parameters, and
13 hence was considered as the optimal operation condition for reducing PAH emissions.

14 In this study, the ANOVA analysis was used to prioritize effects of the four selected parameters on
15 determining total EF_{BaPeq} . The result shows that Ps ($p < 0.01$) and Hb ($p = 0.021$) were the significant
16 parameters accounting for 70.9% and 21.2%, respectively, of the total contribution of the four selected
17 parameters (SI Table S6). The above result was consistent with that found in previous studies (14, 15,
18 19, 32). Thomas et al., (14) and Ledesma et al. (32) have indicated that PAH compounds decreased at
19 high oxygen concentrations (i.e. high air supply passing through combustion zone during sintering
20 process), in accordance with their destruction by oxidation. The high Hb was close to ignition hood that
21 might result in a wider melting/combustion zone in the sinter bed, leading to more complete coke
22 combustion and less PAH formations during the sintering process (15, 19). For the result of Wc,
23 although the effect was not significance ($p = 0.665$), it should be noted that the optimal Wc found at the
24 middle level (i.e., 6.5 wt %) might be worth further discussion. Kasai et al. (33) and Haga et al. (34)
25 have indicated that the increase of Wc in sinter raw mixtures could increase the permeability of
26 sintering bed and combustion efficiency (due to the abundant coke breezes and limestone fines coating

1 on the surface of particles), and hence results in reducing PAH formations during sintering processes.
2 On the other hand, Gulyurtlu et al. (35) have indicated that the high level of water content could result
3 in local quenching of the combustion reactions, which in turn could lead to PAH formations. Based on
4 these, it is not so surprising to see that the lowest total $EF_{BaP_{eq}}$ was found at the middle level (i.e., 6.5 wt
5 %) rather than at 6.0 wt % or 7.0 wt %. For the type of HL, we found that the use of limonite could
6 slightly decrease total $EF_{BaP_{eq}}$ in comparison with the use of sinter as the HL of the sinter pot, although
7 the above effect was not significance ($p = 0.467$). Cieplik et al. (13) have indicated that limonite could
8 exhibit higher potent catalytic activity of oxidation than that of hematite. However, Guélou et al. have
9 reported that Fe content might play an important role in catalytic oxidation of carbon monoxide, and the
10 higher Fe content might result in the less PAH formations (36). The above inference is consistent with
11 what we have found in the three selected types of HL in their Fe contents (i.e., hematite (64.1%) \cong
12 limonite (63.3%) > sinter (58.1%)). Nevertheless, the insignificant effect associated with the types of
13 HL used in this study might mainly because the depth of the HL was too thin to have sufficient reaction
14 time for the formation of PAHs during sintering process. In addition, it should be noted that other
15 physical parameters of HL, such as the particle size and porosity, could also be important factors
16 affecting PAH formations. Therefore, the net effect of HL on PAH formations warrants the needs for
17 further research in the future.

18 **Comparison PAH emissions between the Reference and the Optimal Operation Combination.**

19 Table 4 shows the total $EF_{BaP_{eq}}$ and the S/N ratio obtained from the reference combination (i.e, Wc =
20 6.5 wt %, Ps = 1200 mmH₂O, Hb = 550 mm, and HL = sinter) and the resultant optimal combination
21 (i.e., Wc = 6.50 w%, Ps = 1400 mmH₂O, Hb = 600 mm, and HL = limonite). The total $EF_{BaP_{eq}}$ and its
22 corresponding S/N ratio for the reference combination were found as 28.6 μ g/kg-feedstock and -29.1
23 dB, respectively. For the predicted optimal combination, its total $EF_{BaP_{eq}}$ and S/N ratio (predicted based
24 on the SI eq 4) were found as 10.9 μ g/kg-feedstock and -20.5 dB, respectively. The difference in the
25 above two S/N ratios (= 8.6 dB) indicating that the use of the optimal combination would result in a

1 decrease in total $EF_{BaP_{eq}}$ up to 61.9% in comparison with the reference combination. For confirmation
2 purpose, experiments ($n = 2$) were conducted as using Test B-sintering raw mixture based on the
3 specification of the reference combination and the resultant optimal combination. The resultant mean
4 total $EF_{BaP_{eq}}$ obtained from the reference combination and the confirmation combination were found as
5 60.3 and 25.6 $\mu g/kg$ -feedstock, respectively (Table 4). The decrease $EF_{BaP_{eq}}$ from the reference
6 combination to the optimal combination (confirmation experiments) was up to 57.6% (range =
7 54.3–60.8%). The above similar decreases in total $EF_{BaP_{eq}}$ further confirm the applicability of the
8 obtained optimal combination for reducing PAH formations during the sintering process.

9 Figure 3 shows PAH concentrations (including 2- to 7-ringed PAHs, and LMW- MMW- and HMW-
10 PAHs in the particle- and gas-phase, respectively) obtained from the sinter pot operated under the
11 reference combination and the optimal combination for the confirmation purpose. While operated under
12 the optimal combination, gas-phase MMW- and HMW-PAH concentrations decreased significantly (=
13 72.9% and 67.4%, respectively) in comparison with that of the reference combination. In contrast, gas-
14 phase LMW-PAHs increased up to 31.2%. The above results might be because MMW- and HMW-
15 PAHs were much easier to be cleaved into LMW-PAHs under the optimal combination than that of the
16 reference combination. For particle-phase PAHs, all selected PAH homologues (particularly for HMW-
17 PAHs) decreased consistently from the optimal to the reference combination. The above results indicate
18 that the use of the optimal combination could significantly reduce high molecular weight PAH
19 formations. Considering the formation mechanisms HMW-PAHs were similar to those of PCDFs
20 during the sintering process (37), our results might provide another solution to suppress PCDD/F
21 formations in the future.

22 **Sinter Productivity and Sinter Strength of the Reference and Optimal Operation Combination.**

23 Although the resultant optimal combination was able to reduce PAH emissions, it is important to
24 examine its impact on the sinter productivity and sinter strength for practical reason. In this study, we
25 found that the sinter productivity and sinter strength for the reference combination were 38.9 $t/m^2/day$

1 and 71.1%, respectively. The above values were quite comparable to those found for the optimal
2 combination (=39.5 t/m²/day and 70.2%, respectively). Therefore, it is concluded that the use of the
3 optimal combination determined by the Taguchi experimental design for the sintering process could
4 effectively reduce PAH emissions without interfering with the quantity of its sinter products.

5 **Acknowledgements**

6 We thank the China Steel Corporation (CSC) in Taiwan for funding this research project. We also
7 thank the staffs at CSC for providing testing materials and facilities.

8 **Supporting Information Available**

9 Information about the details of Taguchi experimental design, sampling and analytical methods,
10 conditions, data analysis, six additional tables and one figure. This material is available free of charge
11 via the Internet at <http://pubs.acs.org>.

1 Literature Cited

- 2 (1). Coutant, R. W.; Brown, L.; Chuang, J. C.; Riggin, R. M.; Lewis, R. G. Phase distribution and
3 artifact formation in ambient air sampling for polynuclear aromatic hydrocarbons. *Atmos.*
4 *Environ.t* **1988**, *22*, 403–409.
- 5 (2). International Agency for Research on Cancer (IARC), Vol. 92 (in preparation), Polycyclic
6 Aromatic Hydrocarbons: Summary of Data Reported and Evaluation **2007**.
7 <http://monographs.iarc.fr/ENG/Meetings/92-pahs.pdf>.
- 8 (3). Ravindra, K.; Sokhi, R.; Grieken, R. V. Atmospheric polycyclic aromatic hydrocarbons: Source
9 attribution, emission factors and regulation. *Atmos. Environ.* **2008**, *42*, 2895–2921.
- 10 (4). Marr, L. C.; Kirchstetter, T. W.; Harley, R. A.; Miguel, A. H.; Hering, S. V.; Hammond, S. K.
11 Characterization of Polycyclic Aromatic Hydrocarbons in Motor Vehicle Fuels and Exhaust
12 Emissions. *Environ. Sci. Technol.* **1999**, *33*, 3091–3099.
- 13 (5). Omar, N. Y. M. J., Abas, M. R. B., Ketuly, K. A., Tahir, N. M. Concentrations of PAHs in
14 atmospheric particles (PM-10) and roadside soil particles collected in Kuala Lumpur, Malaysia.
15 *Atmos. Environ.* **2002**, *36*, 247–254.
- 16 (6). Dyke, P. H.; Foan, C.; Fiedler, H. PCB and PAH releases from power stations and waste
17 incineration processes in the UK. *Chemosphere* **2003**, *50*, 469–480.
- 18 (7). Yang, H. H.; Lai, S. O.; Hsieh, L. T.; Hsueh, H. J.; Chi, T. W. Profiles of PAH emission from
19 steel and iron industries. *Chemosphere* **2002**, *48*, 1061–1074.
- 20 (8). Almaula, S. Polycyclic Aromatic Hydrocarbons from Steelmaking. *Environ. Forensics* **2005**, *6*,
21 143–150.

- 1 (9). Tsai, J. H.; Lin, K. H.; Chen, C. Y.; Ding, J. Y.; Choa, C. G.; Chiang, H. L. Chemical
2 constituents in particulate emissions from an integrated iron and steel facility. *J. Hazard. Mater.*
3 **2007**, *147*, 111–119.
- 4 (10).Bjorseth A.; Ramdahl T. *Handbook of Polycyclic Aromatic Hydrocarbons*; Marcel Dekker:
5 New York, 1985.
- 6 (11).Maeda, T.; Fukumoto, C.; Matsumura, T.; Nishioka, K.; Shimizu, M. Effect of adding moisture
7 and wettability on granulation of iron ore. *ISIJ Int.* **2005**, *45*, 477–484.
- 8 (12).Kamijo, C.; Matsumura, M.; Kawaguchi, T. Sintering behavior of raw material bed placing large
9 particles. *ISIJ Int.* **2005**, *45*, 544–550.
- 10 (13).Cieplik, M. K.; Carbonell, J. P.; Munoz, C.; Baker, S.; Kruger, S.; Liljelind, P.; Marklund, S.;
11 Louw, R. On Dioxin Formation in Iron Ore Sintering. *Environ. Sci. Technol.* **2003**, *37*, 3323–
12 3331.
- 13 (14).Thomas S.; Wornat M. J. The effects of oxygen on the yields of polycyclic aromatic
14 hydrocarbons formed during the pyrolysis and fuel-rich oxidation of catechol. *Fuel* **2008**, *87*,
15 768–781.
- 16 (15).Mitterlehner, J.; Loeffler, G.; Winter, F.; Hofbauer, H.; Schmid, H.; Zwittag, E.; Buergler, T. H.;
17 Pammer, O.; Stiasny, H. Modeling and simulation of heat front propagation in the iron ore
18 sintering process. *ISIJ Int.* **2004**, *44*, 11–20.
- 19 (16).Imai, T.; Matsui, T.; Fujii, Y.; Nakai, T.; Tanaka, S. Oxidation catalyst of iron oxide suppressing
20 dioxin formation in polyethylene combustion. *J. Mater. Cycles. Waste. Manag.* **2001**, *3*, 103–
21 109.
- 22 (17).Nath, N. K.; Mitra, K. Optimisation of suction pressure for iron ore sintering by genetic
23 algorithm. *Ironmak. Steelmak.* **2004**, *31*, 199–206.

- 1 (18).Kawaguchi, T.; Kamijo, C.; Matsumura, M. The sintering behavior of raw material bed placing
2 large particles. *Tetsu to Hagane* **2006**, *92*, 779–787.
- 3 (19).Yang, W.; Choi, S.; Choi, E. S.; Ri, D. W.; Kim, S. Combustion characteristics in an iron ore
4 sintering bed–evaluation of fuel substitution. *Combust. Flame* **2006**, *145*, 447–463.
- 5 (20).Higuchi, K.; Kawaguchi, T.; Kobayashi, M.; Hosotani, Y.; Nakamura, K.; Iwamoto, K.;
6 Fujimoto, M. Improvement of Productivity by Stand-support Sintering in Commercial Sintering
7 Machines, *ISIJ Int.* **2000**, *40*, 1188–1194.
- 8 (21).Kasai, E.; Harjanto, S.; Terui, T.; Nakamura, T.; Waseda, Y. Thermal remediation of PCDD/Fs
9 contaminated soil by zone combustion process, *Chemosphere* **2000**, *41*, 857–864.
- 10 (22).Harjanto, S.; Kasai, E.; Terui, T.; Nakamura, T. Formation and transport of PCDD/Fs in the
11 packed bed of soil containing organic chloride during a thermal remediation process,
12 *Chemosphere* **2002**, *49*, 217–224.
- 13 (23).Taguchi, G. *Introduction to quality engineering: designing quality into products and processes*;
14 Asian Productivity Organization: Tokyo, Japan, 1987.
- 15 (24).Yang, W. H.; Tarng, Y. S. Design optimization of cutting parameters for turning operations
16 based on the Taguchi method. *J. Mater. Process. Tech.* **1998**, *84*, 122–129.
- 17 (25).Yang, W.; Ryu, C.; Choi, S.; Choi, E.; Lee, D.; Huh, W. Modeling of combustion and heat
18 transfer in an iron ore sintering bed with considerations of multiple solid phases. *ISIJ Int.* **2004**,
19 *44*, 492–499.
- 20 (26).Oyama, N.; Sato, H.; Takeda, K.; Ariyama, T.; Masumoto, S.; Jinno, T.; Fujii, N. Development
21 of coating granulation process at commercial sintering plant for improving productivity and
22 reducibility. *ISIJ Int.* **2005**, *45*, 817–826.

- 1 (27).Chen, Y. C.; Lee, W. J.; Uang, S. N.; Lee, S. H.; Tsai, P. J. Characteristics of polycyclic
2 aromatic hydrocarbon (PAH) emissions from a UH-1H helicopter engine and its impact on the
3 ambient environment. *Atmos. Environ.* **2006**, *40*, 7589–7597.
- 4 (28).Tsai, P. J.; Shih, T.S.; Chen, S. L.; Lee, W. J.; Lai, G. H.; Liou, S. H. Assessing the contents of
5 polycyclic aromatic hydrocarbons in the tollbooths of a highway toll station via direct and
6 indirect approaches. *Environ. Sci. Technol.* **2002**, *36*, 4748–5473.
- 7 (29).Iron ores – Determination of tumble strength, 3rd ed.; International Organization for
8 Standardization (ISO) 3271: Geneva, 1995.
- 9 (30).Tsai, P. J.; Shih, T. S.; Chen, S. L.; Lee, W. J.; Lai, G. H.; Liou, S. H. Assessing and Predicting
10 the Exposures of Polycyclic Aromatic Hydrocarbons (PAHs) and Their Carcinogenic Potencies
11 from Vehicle Engine Exhausts to Highway Toll Station Workers. *Atmos. Environ.* **2004**, *38*,
12 333–343.
- 13 (31).Ooi, T. C.; Aries, E.; Ewan, B. C. R.; Thompson, D.; Anderson, D. R.; Fisher, R.; Fray, T.;
14 Tognarelli, D. The study of sunflower seed husks as a fuel in the iron ore sintering process.
15 *Miner. Eng.* **2008**, *21*, 167-177.
- 16 (32).Ledesma, E. B.; Kalish, M. A.; Nelson, P. F.; Wornat, M. J.; Mackie, J. C. Formation and fate of
17 PAH during the pyrolysis and fuel-rich combustion of coal primary tar. *Fuel* **2001**, *35*, 1801–
18 1814.
- 19 (33).Kasai, E.; Rankin, W. J.; Gannon, J. F. The effect of raw mixture properties on bed permeability
20 during sintering. *ISIJ Int.* **1989**, *29*, 33–42.
- 21 (34).Haga, T.; Ohshio, A.; Nakamura, K.; Kozono, T. Control technique of the melting reaction in
22 sintering process by the fine part selective granulation of clayish iron ores. *Tetsu to Hagane*
23 **1997**, *83*, 103–108.

1 (35).Gulyurtlu, I.; Karunaratne, D. G. G. P.; Cabrita, I. The study of the effect of operating parameters
2 on the PAH formation during the combustion of coconut shell in a fluidised bed. *Fuel* **2003**, *82*,
3 215–223.

4 (36).Guélou, E.; Barrault, J.; Fournier, J.; Tatibouët, J. M. Active iron species in the catalytic wet
5 peroxide oxidation of phenol over pillared clays containing iron. *Appl. Catal. B-Environ.* **2003**,
6 *44*, 1–8.

7 (37).Iino, F.; Imagawa, T.; Takeuchi, M.; Sadakata, M. De novo synthesis mechanism of
8 polychlorinated dibenzofurans from polycyclic aromatic hydrocarbons and the characteristic
9 isomers of polychlorinated naphthalenes. *Environ. Sci. Technol.* **1999**, *33*, 1038–1043.

10 **Brief:** Using the Taguchi experimental design to identify the optimal operating condition provides
11 useful approaches for reducing PAH formations during the iron ore sintering process.

12 **Captions**

13 **Figures**

14 **FIGURE 1.** The schematic of the pilot scale sinter pot and the illustration of its zone combustion
15 process

16 **FIGURE 2.** Mean S/N ratios of the four selected operation parameters at the three designated levels

17 **FIGURE 3.** PAH concentrations (including 2- to 7-ringed PAHs, and LMW- MMW- and HMW-PAHs
18 in the particle- and gas-phase, respectively) obtained from the sinter pot operated under the reference
19 combination and the optimal combination for confirmation purpose

20 **Tables**

21 **TABLE 1.** The contents of sintering raw mixture and its chemical compositions in Test A and Test B

1 TABLE 2. The mean (range) of LMW-, MMW-, and HMW-PAHs, gas- and particle-phase PAHs, total
2 PAH, and total BaP_{eq} emission concentrations ($\mu\text{g}/\text{Nm}^3$) in the flue gas of the nine designed
3 experimental combinations and their corresponding emission factors of total BaP_{eq} (EF_{BaP_{eq}}; $\mu\text{g}/\text{kg}$ -
4 feedstock)

5 TABLE 3. The comparison of PAH profiles, homologues, gas- and particle-phase distributions (range),
6 mean (range) total concentration and EF_{PAHs} obtained from the present study with those data collected
7 from real-scale sinter plants.

8 TABLE 4. The emitted total EF_{BaP_{eq}} ($\mu\text{g}/\text{kg}$ -feedstock) and its corresponding S/N ratio (dB) obtained
9 from the reference operation combination and optimal operation combination (including both predicted
10 and that obtained from the confirmation experiments)

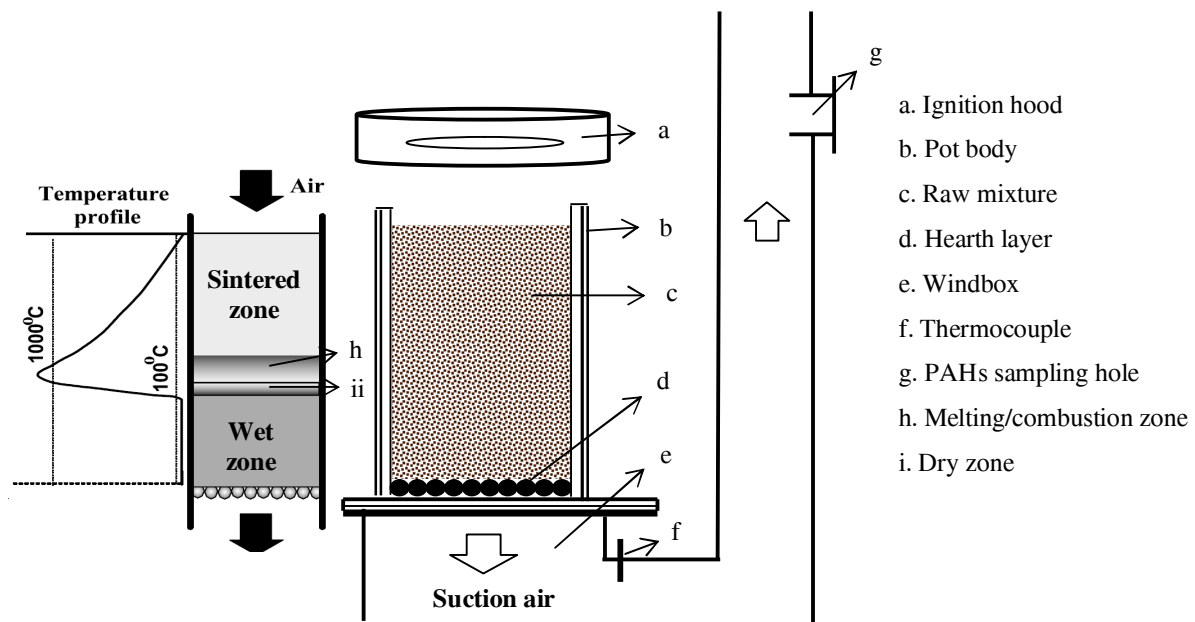


FIGURE. 1 The schematic of the pilot scale sinter pot and the illustration of its zone combustion process

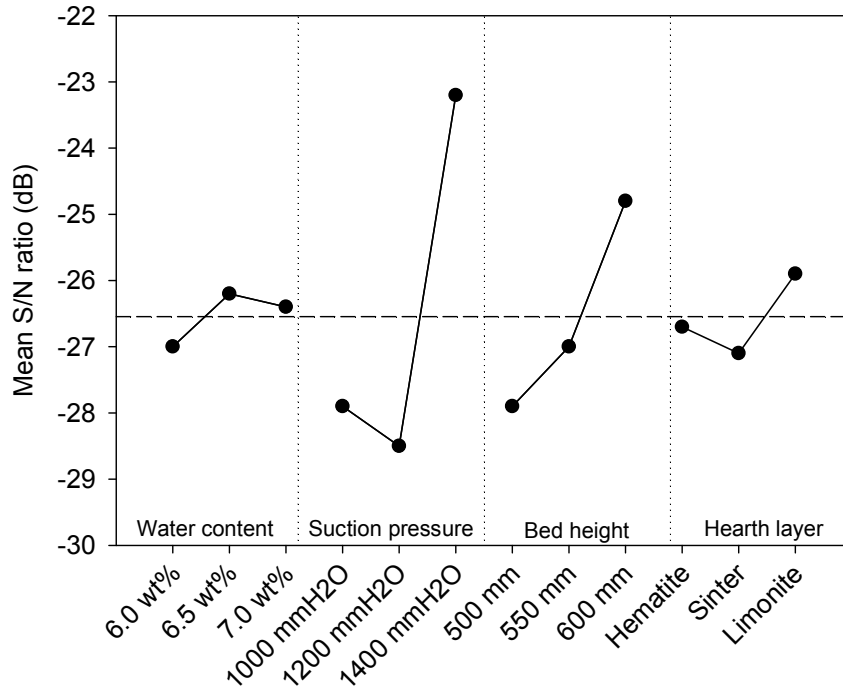
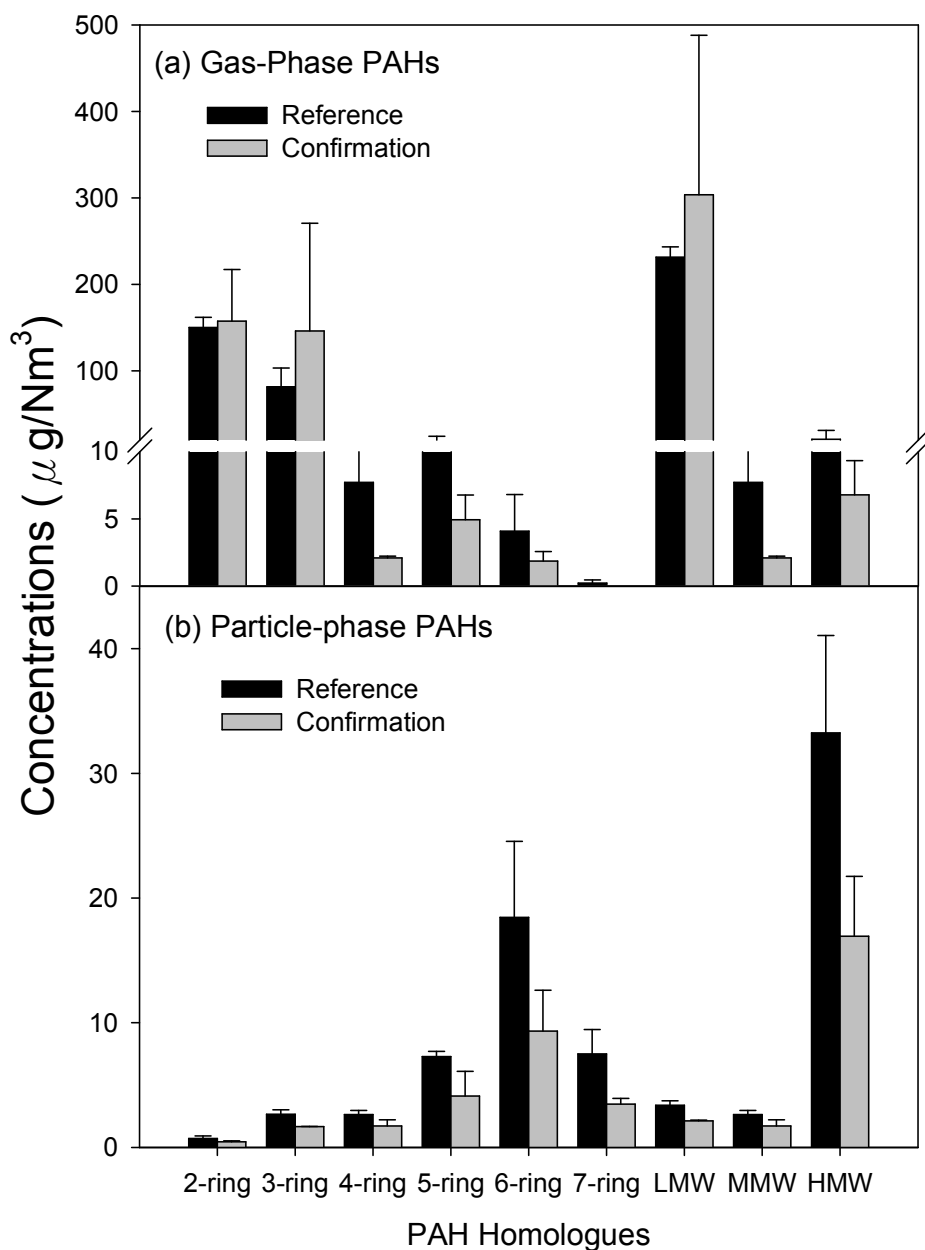


FIGURE 2 Mean S/N ratios of the four selected operation parameters at the three designated levels



1

FIGURE 3 PAH concentrations (including 2- to 7-ringed PAHs, and LMW- MMW- and HMW-PAHs in the particle- and gas-phase, respectively) obtained from the sinter pot operated under the reference combination and the optimal combination for confirmation purpose

Table 1. The contents (wt %) of sintering raw mixture and its chemical composition (wt %)in Test A and Test B

Raw mixture	iron ore	coke breeze	anthracite	serpentine	marble	slurry	return fine ^a	Mini-pellet
Test A	52.8	3.99	1.84	0.421	1.98	0.562	31.5	1.50
Test B	61.1	1.88	1.92	0.647	2.94	0.888	30.4	0.241
Chemical composition	CaO	MgO	Al ₂ O ₃	SiO ₂	FeO	Total-Fe		
Test A	9.38	1.44	1.66	4.79	8.51	57.5		
Test B	9.31	1.16	1.80	2.80	6.72	58.2		

^a including return fine obtained from sinter plant and blast furnace; Test A: prediction experiments; Test B: confirmation experiments

Table 2. The mean (range) of LMW-, MMW-, and HMW-PAHs, gas- and particle-phase PAHs, total PAH, and total BaP_{eq} emission concentrations ($\mu\text{g}/\text{Nm}^3$) in the flue gas of the nine designed experimental combinations and their corresponding emission factors of total BaP_{eq} (EF_{BaPeq} ; $\mu\text{g}/\text{kg}$ -feedstock)

emission concentration	experimental combination									mean
	1	2	3	4	5	6	7	8	9	
LMW-PAHs	372 (349–395)	595 (485–704)	356 (285–427)	497 (458–536)	379 (332–425)	334 (324–344)	536 (519–552)	554 (528–579)	632 (627–636)	473 (334–632)
MMW-PAHs	10.7 (8.89–12.5)	9.79 (8.20–11.4)	9.52 (3.72–15.3)	8.12 (7.08–9.17)	7.69 (4.74–10.6)	5.70 (4.87–6.54)	12.4 (3.13–21.8)	9.94 (3.95–15.9)	19.2 (16.1–22.2)	10.3 (5.70–19.2)
HMW-PAHs	26.7 (23.9–29.5)	24.3 (22.3–26.2)	13.0 (11.9–14.1)	25.7 (15.7–35.8)	15.8 (15.1–16.5)	14.7 (11.1–18.3)	22.1 (16.6–27.6)	24.0 (9.65–38.3)	21.0 (18.6–23.3)	20.8 (13.0–26.7)
gas-phase PAHs	386 (366–406)	599 (491–707)	370 (289–451)	504 (461–548)	379 (331–428)	335 (317–354)	532 (518–546)	552 (526–580)	655 (643–666)	479 (335–655)
particle-phase PAHs	23.4 (22.0–24.5)	29.7 (24.5–34.8)	8.67 (3.54–13.8)	26.4 (11.0–41.7)	22.7 (16.8–28.6)	19.5 (18.2–20.9)	38.5 (21.1–56.0)	34.7 (13.0–56.5)	17.8 (16.9–18.7)	24.6 (8.67–38.5)
total PAHs	409 (391–428)	629 (516–742)	379 (303–454)	530 (503–559)	402 (359–445)	355 (347–362)	571 (539–602)	587 (582–593)	673 (662–682)	504 (355–673)
total BaP _{eq}	6.77 (6.03–7.51)	5.82 (4.59–7.05)	2.80 (2.47–3.22)	7.41 (4.06–10.8)	4.75 (4.34–5.15)	3.71 (3.20–4.23)	5.86 (5.06–6.66)	6.15 (2.46–9.83)	4.92 (4.08–5.76)	5.35 (2.80–7.41)
total EF _{BaPeq}	28.6 (27.2–30.0)	29.8 (19.9–39.7)	10.9 (8.60–13.1)	34.2 (18.9–49.5)	22.9 (19.7–26.0)	16.3 (15.4–17.2)	22.1 (19.6–24.5)	27.6 (13.6–41.6)	18.0 (14.7–21.4)	23.4 (10.9–34.2)

Table 3. The comparison of PAH profiles, homologues, gas- and particle-phase distributions² (range), mean (range) total concentration and EF_{PAHs} obtained from the present study with those data collected from real-scale sinter plants.

PAH emission results	Sinter plants (7, 31)	This study
the most abundant compounds	NaP, Ant, AcPy, FL, Flu; ¹ NaP, PA, Flu, Fl, Pyr	NaP, AcPy, PA, Flu, FL
homologue in order	2-ring > 3-ring > 4-ring > 5-ring > 6-ring > 7-ring	2-ring > 3-ring > 4-ring > 5-ring > 6-ring > 7-ring
gas- and particle-phase PAHs distribution (%)	Gas = 86 (78–96) Particle = 6.7 (1.3–12.1)	Gas = 95.7 (93.5–98.4) Particle = 4.3 (1.63–6.45)
avg. total PAHs ($\mu\text{g}/\text{Nm}^3$)	778 (555–1001); ¹ 277	504 (355–673)
avg. total EF_{PAHs} (EF_{PAHs} ; $\mu\text{g}/\text{kg}$ -feedstock)	3160 (2499–4245)	2364 (1036–3616)

¹ ref. (31)

1

2

3

Table 4. The emitted total $EF_{BaP_{eq}}$ (μ g/kg-feedstock) and its corresponding S/N ratio (dB) obtained from the reference operation combination and optimal operation combination (including both predicted and that obtained from the confirmation experiments).

testing results		reference operation combination	optimal operation combination	
			prediction	confirmation
Test A	total $EF_{BaP_{eq}}$	28.6	10.9	-
	S/N ratio	-29.1	-20.5	-
Test B	total $EF_{BaP_{eq}}$	60.3	-	25.6