

Effect of excess air on polycyclic aromatic hydrocarbons removal from petroleum sludge using thermal treatment with additives

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Petroleum sludge contains polycyclic aromatic hydrocarbons (PAH) which are hazardous compounds due to their toxic and carcinogenic-mutagenic characteristics. The United States Environmental Protection Agency has identified 16 of these compounds as priority pollutants. This study evaluates the effectiveness of excess air addition in thermal removal of priority PAH from petroleum sludge treated in a rotary-drum electric heater at 650°C with Ca(OH)₂ (1 mole) + NaHCO₃ (1 mole) (1:1) additives. The concentrations of PAH in flue gas and residue phases were determined using Gas Chromatography-Mass Spectrometry (GC-MS). The samples were extracted with acetonitrile by ultra-sonication prior to GC-MS analysis. The concentrations of 2-3 ring PAH, 4-6 ring PAH, suspect carcinogenic PAH, ΣPAH and ΣTEF were also determined. Excess air addition was found to be instrumental in PAH removal.

Keywords: Thermal treatment, Excess air, Additives, Polycyclic aromatic hydrocarbons (PAH), Petroleum sludge cake.

Introduction

Petroleum sludge is a major waste produced from the petroleum refining industry. Oil production and petroleum refining processes generate considerable amount of petroleum sludge worldwide as wastes; an estimated 230,000 million tonnes each year. Typically, the sludge contains 10-30% total petroleum hydrocarbons (TPH), 5-20% solids and 50-85% water. The polycyclic aromatic hydrocarbons (PAH) content of the sludge is about 550 mg/kg TPH¹. The sludge is a major hazardous petroleum waste due to the presence of harmful organic compounds such as PAH which have toxic and carcinogenic-mutagenic characteristics^{2,3}. Out of the known more than 10,000 PAHs, with about 200 tested as possible carcinogens, the United States Environmental Protection Agency (USEPA) has identified 16 as priority compounds⁴. The 16 priority PAH are: Naphthalene (Nap; 2-rings, C₁₀H₈), Acenaphthylene (Acy; 3-rings, C₁₀H₈), Acenaphthene (Ace; 3-rings, C₁₀H₁₀), Fluorene (Flu; 3-rings, C₁₃H₁₀), Phenanthrene (Phe; 3-rings, C₁₃H₁₀),

Anthracene (Ant; 3-rings, C₁₃H₁₀), Fluoroanthene (Fla; 4-rings, C₁₆H₁₀), Pyrene (Pyr; 4-rings, C₁₆H₁₀), Benzo[a]Anthracene (BaA; 4-rings, C₁₈H₁₂), Chrysene (Chr; 4-rings, C₁₈H₁₂), Benzo[b]Fluoranthene (BbF; 5-rings, C₂₀H₁₂), Benzo[k]Fluoranthene (BkF; 5-rings, C₂₀H₁₂), Benzo[a]Pyrene (BaP; 5-rings, C₂₀H₁₂), Indeno[1,2,3-cd]Pyrene (Ind; 6-rings, C₂₂H₁₂), Dibenzo[a,h]Anthracene (DbA; 6-rings, C₂₂H₁₄), and Benzo[g,h,i]Perylene (BPer; 6-rings, C₂₂H₁₂). Toxicity equivalence factor (TEF) of the priority PAH reflects their relative carcinogenic potential as a quantitative cancer risk estimate with reference to the specific compound benzo[a]pyrene or BaP^{2,3}. TEF of the priority PAH are: Nap 0.001, Acy 0.001, Ace 0.001, Flu 0.001, Phe 0.001, Ant 0.01, Fla 0.001, Pyr 0.001, BaA 0.1, Chr 0.01, BbF 0.1, BkF 0.1, BaP 1.0, Ind 0.1, DbA 5.0, and BPer 0.01. Thermal treatment, especially kiln incineration (typical temperature of 820 to 1600°C), can completely degrade all priority PAH. The high energy requirement and operational cost, however, are of concern. Some studies on thermal removal of PAH conducted by employing additives such as lime, sodium, metal and metal oxides with or without excess air supply are summarised in Table 1⁵⁻¹¹. Recently, Pakpahan *et al*¹²

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Table 1—Effect of temperature and additives on PAH removal

Process	Results	References
Incineration of waste oil sludge with additive: PE plastic, excess air: 22-86% at $T \leq 850^\circ\text{C}$	~93% ($1,250 \text{ ng/m}^3$) of the 16 priority PAH emitted in gas phase.	Li <i>et al</i> ⁵
Coal atmospheric fluidized bed combustion with additive: limestone, excess O_2 : 20% at $T = 900^\circ\text{C}$	Lowest emission of total PAH.	Mastral <i>et al</i> ⁶
Coal-fired fluidized bed combustion with excess O_2 : 2.5-7%	Emission of LMW PAH (2-3 rings) increased when excess O_2 was increased, while HMW PAH (4-6 rings) decreased.	Liu <i>et al</i> ⁷
Coal fluidized bed combustion with additive: limestone, excess O_2 : 10% at $T = 850^\circ\text{C}$	Most of PAH were emitted in ash rather than in gas phase.	Mastral <i>et al</i> ⁸
Incineration of benzene with additive: NaOH, $\text{Ca}(\text{NO}_3)_2$ at $T = 740^\circ\text{C}$	Less emission of the 16 priority PAH in ash phase by added $\text{Ca}(\text{NO}_3)_2$. Need air/ O_2 supply for optimisation.	Cheng <i>et al</i> ⁹
PAHs formation mechanism in pyrolysis of cellulose with excess O_2 : 5-10% at $T = 300\text{-}650^\circ\text{C}$	Addition of O_2 to the carrier gas (He) significantly reduced the overall yield of PAH.	McGrath <i>et al</i> ¹⁰
Bituminous coal combustion with additives Cu and CuO at $T = 600\text{-}1200^\circ\text{C}$	Cu and CuO promote PAH formation during coal combustion.	Yan <i>et al</i> ¹¹

showed that thermal degradation of PAH in petroleum sludge at 650°C with additives $\text{Ca}(\text{OH})_2 + \text{NaHCO}_3$ (1:1) yielded lowest emission of PAH in gas, particulate and residue (ash) phases compared to the additives CaO , H_2O_2 and $\text{H}_2\text{O}_2 + \text{FeSO}_4$.

The main objective of this study is to investigate the effect of excess air on thermal degradation of PAH using $\text{Ca}(\text{OH})_2 + \text{NaHCO}_3$ as additives. The 16 priority PAH remaining in the flue gas (gas and particulate phases) and ash (residue phase) after thermal treatment of petroleum sludge were quantified.

Materials and Methods

Petroleum Sludge Cake

Petroleum sludge cake samples were collected from the sludge treatment plant of a local petroleum refinery in Malaysia. The samples were placed in dark glass bottles and stored at 4°C in a cold room. Prior to extraction, the samples were placed in a desiccator cabinet and brought to room temperature.

Thermal Treatment and Sampling

Thermal treatment of petroleum sludge cake was conducted in a rotary-drum electric heating chamber^{12,13} at a temperature of 650°C , using additives $\text{Ca}(\text{OH})_2$ (1 mole) + NaHCO_3 (1 mole) (1:1). The treatment was conducted with (30%) and without excess air addition. The heater consisted of two concentric cylinders: the I.D. of the outer cylinder was 0.3 m, the O.D. of the inner cylinder was 0.2 m, and the effective length of the cylinders was 0.6 m. Sludge cake samples for thermal treatment were mixed with the additives and placed in the space between the cylinders. The outer cylinder rotated at 20 rpm during operation. Heating was provided using

a 9 kW ceramic electric heater housed in the inner cylinder. The heater assembly also included an air blower, stack with a sampling train and a control panel. The sampling procedure followed the emission sampling train of USEPA modified method 5 (MM5 Method)¹⁴. The flue gas sampling probe contained 5 g Amberlite XAD-4 adsorbent (20-60 mesh, Sigma Aldrich) and housed a Whatman 1.0 μm , 42 mm diameter quartz filter to capture PAHs in the gas phase and to collect particulates respectively. The sampling duration was 40 minutes for each batch of sludge sample subjected to thermal treatment. Residue was collected manually through the collection door at the bottom of the rotary-drum electric heater.

PAH Analytical Procedure

Sonication extraction (SW-846 Method 3550B) with acetonitrile solvent was conducted to extract PAH from the Amberlite XAD-4 adsorbent, particulate collected on quartz filter, and residue^{15,16}. For calibration, stock solution of a PAH mixture standard (Restek Corp) was used to prepare standard solutions of 17 concentrations from 0.001ppm to 9.0 ppm. PAH in the samples were determined using a 6890N GC, 5973N MS with 7683 auto-injector (Agilent Technologies). SIM Mode was used to determine the PAH concentrations based on USEPA Method 8270D. The GC-MS was equipped with an Agilent J & W capillary column of 30 m length, 0.25 mm diameter, and 0.25 μm film thickness. The operating conditions were: carrier gas Helium (He) flow rate 1.0 mL/min, injection volume 10 μL , splitless injection at 275°C , detector at 280°C , and initial oven temperature 70°C held for 2 min, then increased at $8^\circ\text{C}/\text{min}$ to final temperature 270°C .

PAH Analytical Validation

Prior to quantification of PAH in the samples, the analytical procedure was validated based on recovery of the 16 priority PAH in three samples of particulates collected on quartz filter (Whatman 1.0 μm , 42 mm diameter) and in six samples of the Standard Reference Material (SRM) Urban Dust 1496b NIST. 60 mg samples of SRM were weighed and dissolved in 25 mL of the polar solvent acetonitrile (Merck, HPLC Grade). The solutions were extracted at 37 Hertz (Hz) with 100% sonicator power (Elma, Transsonic Digitals) at a controlled temperature of 10°C for 30 minutes followed by filtration with a 45 μm nylon syringe (Sartorius). The extract was concentrated using a vacuum rotary evaporator (Buchi Rotavapor R-215) at 57 mbar pressure and 30°C temperature until around 1.0 mL. The concentrate was then re-dissolved in 25 mL acetonitrile and re-concentrated until around 500 μL and topped up with acetonitrile to 1.0 mL. Finally, the aliquot was spiked with 200 μL of 5.0 ppm internal standards D₁₀-acenaphthene, D₁₀-phenanthrene, and D₁₂-perylene (Supelco) prior to analysis using GC-MS. The same procedure was followed for extraction of quartz filter samples.

Results and Discussion

Quality Control of PAH Analytical Procedure

Table 2 shows the detection limit (DL) and percentage recovery of the PAH varied from 0.03 to

Table 2—Analytical Detection Limit (DL) and recovery efficiency of the 16 priority PAH

PAH	DL (ng/m ³)	% Recovery (n=3)	SRM Certified Value (n=6) ($\mu\text{g/kg}$)	Validation Method Measured Value ($\mu\text{g/kg}$)
Nap	0.04	106 $\pm$ 5	-	-
Acy	0.03	103 $\pm$ 1	-	-
Ace	0.26	106 $\pm$ 6	-	-
Flu	0.03	103 $\pm$ 8	-	-
Phe	0.05	101 $\pm$ 7	4.14 $\pm$ 0.37	2.73 $\pm$ 0.38
Ant	0.22	95 $\pm$ 16	0.43 $\pm$ 0.08	0.50 $\pm$ 0.03
Fla	0.08	101 $\pm$ 12	6.45 $\pm$ 0.18	5.20 $\pm$ 0.79
Pyr	0.08	99 $\pm$ 11	5.29 $\pm$ 0.25	4.37 $\pm$ 0.70
BaA	0.08	80 $\pm$ 12	2.21 $\pm$ 0.07	2.12 $\pm$ 0.14
Chr	0.09	91 $\pm$ 12	3.05 $\pm$ 0.06	3.11 $\pm$ 0.32
BbF	0.42	99 $\pm$ 8	6.45 $\pm$ 0.64	7.10 $\pm$ 1.01
BkF	0.35	80 $\pm$ 14	1.91 $\pm$ 0.03	1.69 $\pm$ 0.11
BaP	0.15	85 $\pm$ 8	2.51 $\pm$ 0.09	2.01 $\pm$ 0.22
Ind	0.45	95 $\pm$ 16	3.18 $\pm$ 0.72	2.45 $\pm$ 0.05
DbA	0.72	95 $\pm$ 14	0.29 $\pm$ 0.02	0.31 $\pm$ 0.01
BPer	0.66	90 $\pm$ 13	4.01 $\pm$ 0.91	2.47 $\pm$ 0.08

0.72 ng/m³ and 80 to 106 % respectively. Thirteen PAH yielded greater than 90% recovery. Recovery of low molecular weight (LMW) i.e. 2-3 ring PAH was in the range of 95 to 106%. This was greater than the recovery for the high molecular weight (HMW) i.e. $\geq$ 4 rings PAH for which the recovery was 80 to 101%. A comparison of the measured concentrations of the 12 PAH and their actual concentrations in the SRM Urban Dust 1496b NIST was satisfactory; four PAH had percentage error less than 10%, six had error of 10 to 20%, and the last two PAH had more than 20% error.

Effect of Excess Air on Thermal Treatment of Petroleum Sludge Cake

Excess air is an influencing factor in thermal treatment processes. Table 3 and Figure 1 show concentrations of the 16 priority PAH (according to groups) emitted in gas, particulate, and residue phases after thermal treatment of the petroleum sludge cake. The total concentration of all 16 priority PAH (Σ PAH) in gas phase was 251 mg/m³ without excess air during treatment and it reduced to about 60% (150 mg/m³) when 30% excess air was supplied. A similar observation was made for the particulate phase wherein Σ PAH concentration was 2.44 mg/m³ and 1.63 mg/m³ without and with excess air, respectively. In the residue phase, Σ PAH for treatment with excess air was only about 5% (1,170 $\mu\text{g/g}$) of the concentration (22,190 $\mu\text{g/g}$) when no excess air was supplied. Compared to the initial Σ PAH concentration of raw sludge PAH (1.10×10^5 $\mu\text{g/g}$), 30% excess air supply was able to remove 99% of Σ PAH in residue phase, whereas with no excess air the degradation was 80%. Σ TEF values in gas, particulate and residue, with excess air, were 58, 33 and 16% of the corresponding values obtained with no excess air. With reference to the residue, over 99.7% Σ TEF degradation was obtained based on 824 $\mu\text{g/g}$ Σ TEF concentration in raw sludge. Carcinogenic PAH concentration followed a similar trend and yielded over 93.6% reduction when excess air was supplied. LMW (2-3 rings) PAH were in abundance (1.05×10^5 $\mu\text{g/g}$) compared to HMW (4-6 rings) PAH (4.77×10^3 $\mu\text{g/g}$) in the raw sludge. Thermal treatment of the sludge cake with excess air reduced LMW and HMW PAH by 99.2 and 93% respectively. Thus, excess air supply was beneficial to thermal degradation of PAH. The total concentration of PAH emissions after thermal treatment of petroleum sludge cake was nominal (Table 3). Thermal treatment

Table 3—Emission of priority PAH after thermal treatment of petroleum sludge cake

PAH compounds (groups)	Raw Sludge ($\mu\text{g/g}$)	Concentration of priority PAH					
		No excess air; Additive: $\text{Ca}(\text{OH})_2$ (1 mole) + NaHCO_3 (1 mole) (1:1); $T = 650^\circ\text{C}$			30% an excess air; Additive: $\text{Ca}(\text{OH})_2$ (1 mole) + NaHCO_3 (1 mole) (1:1); $T = 650^\circ\text{C}$		
		Gas (mg/m^3)	Particulate (mg/m^3)	Residue ($\mu\text{g/g}$)	Gas (mg/m^3)	Particulate (mg/m^3)	Residue ($\mu\text{g/g}$)
2-3 rings	1.05×10^5	251	2.43	19500	150	1.43	838
4-6 rings	4.77×10^3	0.417	0.326	2690	0.376	0.308	336
Carci. *	3.25×10^3	0.376	0.282	2360	0.348	0.119	207
ΣPAH	1.10×10^5	251	2.44	22190	150	1.63	1170
ΣTEF	8.24×10^2	0.627	0.027	12.3	0.366	0.009	1.98

*Carcinogenic PAH are BaA, Chr, BbF, BkF, BaP, Ind and DbA^{2,3,16}.

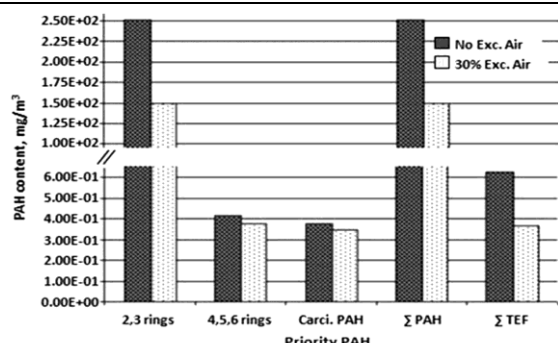
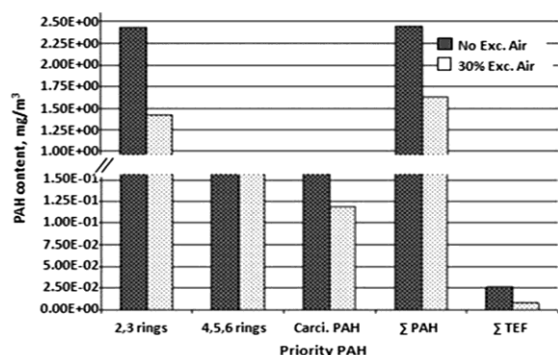
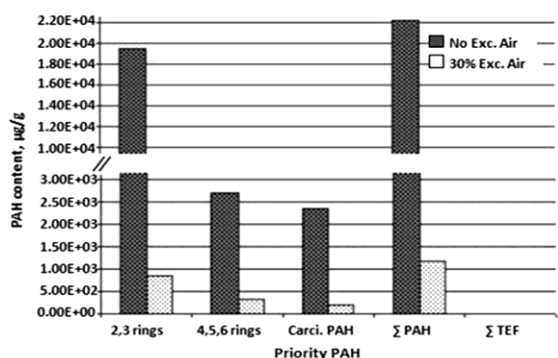
(a) PAH in gas phase (mg/m^3)(b) PAH in particulate phase (mg/m^3)(c) PAH in residue phase ($\mu\text{g/g}$)

Fig. 1—Typical emission of PAHs in gas, particulate and residue phases of petroleum sludge cake after thermal treatment at 650°C with (30%) and without excess air

without excess air supply was suspected to provide inadequate interaction between oxygen and radicals, and resulted in higher PAH emissions. Li *et al*¹⁷ conducted a study of plastic waste incineration with excess air supply and reported lowest PAH emission at 80% excess air and comparable amounts at 20 and 60% excess air. Wei and Wu¹⁸ as well as Mastral *et al*⁶ suggested more than 20% excess air is preferable to decrease PAH emission. Liu *et al*⁷ supplied excess air in the range of 15 to 45% for PAH emission reduction from coal combustion and the lowest emission resulted at 30 to 35% excess air supply. In the present study as well, 30% excess air was found to be effective. Besides degradation of PAH, excess air has benefits such as reduction of SO_2 and CO emissions¹⁹.

Conclusions

This study has profiled PAH emission in gas, particulate and residue phases from thermal treatment of petroleum sludge cake at 650°C using additives $\text{Ca}(\text{OH})_2$ (1 mole) + NaHCO_3 (1 mole) (1:1). A comparison was made between the treatment cases with 30% excess air supply and with no excess air. 30% excess air was found to be beneficial for thermal treatment of the sludge as it resulted in lower emission of ΣPAH , carcinogenic PAH, and ΣTEF . Up to 98.9%, 93.6%, and 99.8% removal of ΣPAH , carcinogenic PAH, and ΣTEF respectively was obtained with reference to their concentrations in the sludge.

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