Comparison of polycyclic aromatic hydrocarbons emission from thermal treatment of petroleum sludge cake in the presence of different additives

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This study evaluates effectiveness of 4 additives [CaO, Ca(OH)2 + NaHCO3, H2O2, and FeSO4 + H2O2] in thermal degradation of hazardous polycyclic aromatic hydrocarbons (PAHs) in petroleum sludge cake. Residual concentrations of 16 priority PAHs were determined using GC-MS. Total PAH conc. was found as: gas, 3.11 × 10^-4 - 4.36 × 10^-4 ppmv; particulate, 7.92 × 10^-5 - 5.24 × 10^-4 mg/m^3; and residue, 1.37 × 10^-4 - 1.07 × 10^0 µg/g. Total toxicity equivalence of PAHs relative to that of benzo[a]pyrene (BaP) was found as: gas, 3.11 × 10^-7 - 4.41 × 10^-7; particulate, 3.87 × 10^-7 - 3.85 × 10^-5; and residue, 6.17 × 10^-7 - 9.65 × 10^-3. Ca(OH)2 + NaHCO3 was most suitable due to least emission of high molecular weight PAHs, lower equivalent carcinogenicity of products, and lower concentrations of PAHs in gas, particulate and residue.

Keywords: Additives, Petroleum sludge cake, Polycyclic aromatic hydrocarbons (PAHs), Thermal treatment

Introduction

Petroleum sludge (world production, 230,000 million tons per annum) contains1: hydrocarbons, 10-30; solids, 5-20; and water, 50-85%. A major cause of hazardous characteristics of sludge is the presence of polycyclic aromatic hydrocarbons (PAHs). United States Environment Protection Agency (USEPA) has identified 16 PAHs as priority compounds1,2 (Table 1). Toxicity equivalence factor (TEF) of PAHs reflects their relative carcinogenic potential as a quantitative cancer risk with reference to benzo[a]pyrene (BaP)3,4. Liu et al5 found lung cancer risk among foundry workers higher due to gaseous phase PAH exposure than particulate phase. Rojas et al6 calculated total toxicity equivalent concentration (TEC) from TEF to compare toxicity of particulate emission and found no significant difference in TEC from diesel and palm oil based biodiesel (B15). Biological treatment (bioremediation & phytoremediation) is not commonly used to degrade PAHs due to low yield, long treatment duration and process performance unpredictability1. Among chemical treatment (permanganate oxidation), Brown et al7 reported that BaP, Pyr (pyrene), Phe (phenanthrene), and Ant (anthracene) were reduced 54-72% in 30 min using 160 mM KMnO4, whereas Flu (fluorene) and Chr (chrysene) were reduced 8-13%. Ball-milling technique showed good degradation for low molecular weight (LMW, 2-3 rings) PAHs, but has no information on high molecular weight (HMW, ≥ 4 rings) PAHs degradation8. ElectroChemical GeoOxidation (ECGO) treatment for eliminating PAHs from solidified crude oil showed that priority PAHs were not detectable after 74-124 day test period9. Dadhkah & Akgerman10 employed sub-critical water and hydrogen peroxide (H2O2) to degrade PAHs in soil to undetectable level. Nam et al11 observed enhanced biodegradation of PAHs in former manufactured gas plant soils; combination of biodegradation with a modified Fenton reaction yielded 85% degradation of 4 and 5-ring PAHs. Kiln incineration12 (820-1600°C) completely degrades all priority PAHs. High operating temperature requires significant energy input that translates into high treatment cost; $475-1350 per cubic yard12 (or $328-843 per m^3)13. Chou et al14 conducted thermal treatment of synthetic PAH-
contaminated soil using a rotary kiln incinerator (700-900°C), and observed that soil washing was required to enhance PAH removal. CaO showed the best performance among calcium and magnesium based additives in PAH removal during fluidized-bed incineration of feedstock containing PVC. NaHCO₃ spray improved PAHs removal in incinerator flue gas.

This study compares effects of 4 additives in thermal degradation of PAHs in petroleum sludge cake (PSC) at 650°C using indirect heating. Priority PAHs in flue gas (gas and particulate phases) and residue (ash) after thermal treatment of PSC were quantified.

### Experimental Section

**Petroleum Sludge Cake (PSC)**

PSC samples were collected from sludge treatment plant of a local petroleum refinery in Malaysia. Samples were placed in dark glass bottles and stored at 4°C in a cold room. Prior to PAH extraction, PSC samples were placed in a dessicator cabinet and brought to room temperature (RT).

**Thermal Treatment**

Thermal treatment of PSC (500 g) using reactor system (Fig. 1) was conducted in a rotary drum electric
heater at 650°C (< incineration temp.) with 30% excess air supply using 4 additives [CaO (1 mole) (Add 1); Ca(OH)₂ (1 mole) + NaHCO₃ (1 mole) (Add 2); H₂O₂ (5% vol, 1 l) (Add 3); and FeSO₄ (1 mole) + H₂O₂ (5% vol, 1 l) (Add 4)]. Concentrations of 16 priority PAHs in flue gas [gas absorbed on Amberlite XAD-4 adsorbent and particulate (total suspended particulate) on quartz filter] and residue were determined using Gas Chromatography-Mass Spectrometry (GC-MS). Samples were extracted by ultra-sonication using acetonitrile prior to GC-MS analysis. Rotary drum heater is an assembly of two concentric cylinders (effective length, 0.6 m; outer cylinder, 0.3 m I.D.; and inner cylinder, 0.2 m O.D.) with heating chamber being the space between them. Outer cylinder rotated at 20 rpm. Heating was provided by a 9 kW ceramic electric heater capable of raising the chamber’s temperature to > 700°C. Other components included an air blower (capacity, 190 l/min), a stack with a sampling train and a control panel. All experiments were carried out in triplicate.

Sampling Procedure and Sample Extraction

Flue gas (gas and particulate phases) collection setup followed emission sampling train of USEPA MM5 Method¹⁸. Flue gas trapping line consisted of a quartz filter (1.0 µm, 42 mm diam, Whatman) to collect particulate, and 2.5 g of Amberlite XAD-4 adsorbent (20 - 60 mesh, Sigma Aldrich) to capture remaining PAHs in gas phase. Sampling duration was 40 min for each batch. Residue was collected manually through collecting door of rotary-drum electric heater. PAHs were extracted from PSC residue, particulate collected on quartz filter, and Amberlite XAD-4 adsorbent using ultra-sonication. Sonication, modified by SW-846 Method 3550B, can be employed with a relatively small amount of solvent, short time intervals and good recovery (75-101%; 58-120%) of analyte.

Standard Solution for Calibration

Seventeen standard solutions (conc.: 0.001, 0.002, 0.004, 0.008, 0.01, 0.02, 0.04, 0.08, 0.1, 0.2, 0.4, 0.8, 1.0, 2.0, 4.0, 6.0, and 9.0 ppm) were prepared from stock solution of PAHs mixture standard (Restek Corp). Each standard was dissolved in acetonitrile and spiked with 200 µl of 5.0 ppm PAHs internal standards [D₁₀-acenaphtene, D₁₀-phenanthrene, and D₁₂-perylene (Supelco)] in a 2 ml brown vial prior to GC-MS analysis. Plot of peak area ratios against concentrations of standard solution showed coefficient of determination (R²) to be over 0.900.

GC-MS Analysis

Quantitative analysis of individual PAHs in samples was carried out by comparing with the corrected peak areas of PAHs in standard mixture with internal standard²⁰,²¹. This study used 6890N GC, 5973N MS with 7683 auto-injector (Agilent Technologies) and SIM Mode to determine PAH concentrations (Fig. 2) based on USEPA Method 8270D. GC-MS was equipped with an Agilent J & W capillary column (30 m long, 0.25 mm
Diam, 0.25 µm film thickness) with: carrier gas helium (He) flow, 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°C/min to final temperature 270°C.

Analytical Method Validation

Recovery efficiency of 16 priority PAHs in a quartz filter (1.0 µm, 42 mm diam, Whatman, n = 3); and Standard Reference Material (SRM) Urban Dust 1496b NIST (n = 6) was determined to validate accuracy of ultra-sonication extraction method using acetonitrile as solvent\textsuperscript{20,22}. Samples of SRM (60 mg) were weighed using a 4-decimal digit analytical balance. Each sample was dissolved in 25 ml of polar solvent acetonitrile (Merck, HPLC Grade). Solutions were then extracted at 37 Hz with 100% sonicator power (Elma, Transsonic Digitalis) at a controlled temperature of 10°C for 30 min. After filtration with a 45 µm nylon syringe (Sartorius), extract was concentrated using a vacuum rotary evaporator (Buchi Rotavapor R-215) at 57 mbar and 30°C to get a concentrate (1.0 ml), which was redissolved in 25 ml acetonitrile and re-concentrated until 500 µl and topped up with acetonitrile to 1.0 ml. Finally, aliquot was spiked with 200 µl of 5.0 ppm internal standards D\textsubscript{10}\textsuperscript{10}-acenaphthene, D\textsubscript{10}\textsuperscript{10}-phenanthrene, and D\textsubscript{15}\textsuperscript{12}-perylenne (Supelco) prior to analysis using GC-MS. Samples of quartz filter were also extracted following SRM procedure.

Results and Discussion

Quality Control of PAHs Analysis

Analytical validation method measured recovery efficiency of 16 priority PAHs in quartz filter and SRM Urban Dust 1496b NIST. Detection limit (DL) of GC-MS for each PAH was calculated as three times the standard deviation of blank concentration\textsuperscript{22}; values were 0.03 to 0.72 ng/m\textsuperscript{3} (Table 2). Recovery of 16 PAHs was 80-106% (13 PAHs with recovery > 90%). Recovery of 2-3 rings PAHs was 95-106%, while recovery for the remaining ≥ 4 rings PAHs was 80-101%. Comparison of measured concentrations of 12 PAHs and their actual concentrations in SRM showed error as: 4 PAHs, < 10%; 6 PAHs, 10-20%; and 2 PAHs, > 20%.

Evaluation of Additives for PAH Degradation

Distribution of 16 priority PAHs in gas, particulate and residue is shown (Fig. 3). Concentrations of 16 priority PAHs after thermal treatment of the sludge (Table 3) were multiplied by their respective TEF values (Table 1) to convert them into BaP equivalents [toxicity equivalent concentration (TEC)]. Summation of these values [ΣTEC (Table 3)] for each treatment was then compared to evaluate effectiveness of each treatment strategy. You\textsuperscript{21}, in a study on PAH emission from incineration of a mixture of municipal solid waste and coal with CaO as desulfurizer, reported ΣTEC in gas (0.0729032 mg/Nm\textsuperscript{3}) and residue (0.0002185 µg/g) phases; values are 5 and 1 orders of magnitude higher than the corresponding values.
obtained with CaO in this study. Incineration of waste oily sludge and polyethylene plastic resulted in ΣPAH emission in gas (0.606 mg/m$^3$), particulate (0.0418 mg/m$^3$), and residue (0.0418 mg/m$^3$).

Fig. 3—PAHs emission after thermal treatment of petroleum sludge cake using four additives at 650°C in a) gas phase (ppmv), b) particulate phase (mg/m$^3$), and c) residue phase (µg/g).

Table 3—Priority PAHs in gas, particulate and residue from thermal treatment of petroleum sludge cake using four additives at 650°C.

<table>
<thead>
<tr>
<th>PAH Compounds</th>
<th>Mean Concentration of PAHs</th>
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<tbody>
<tr>
<td></td>
<td>Add.: CaO</td>
</tr>
<tr>
<td></td>
<td>Gas (ppmv)</td>
</tr>
<tr>
<td>2-3 rings</td>
<td>4.17×10$^4$</td>
</tr>
<tr>
<td>4-6 rings</td>
<td>6.53×10$^7$</td>
</tr>
<tr>
<td>Carcinogenic*</td>
<td>2.01×10$^7$</td>
</tr>
<tr>
<td>ΣPAHs</td>
<td>4.18×10$^4$</td>
</tr>
<tr>
<td>ΣTEC</td>
<td>4.41×10$^7$</td>
</tr>
</tbody>
</table>

*Carcinogenic PAHs are BaA, Ch, Be, BbF, BkF, BaP, Ind and DbA$^{1,9}$

$^{5}$- and 6-ring PAHs were not detectable.
and residue (3.03 µg/g). Compared to the corresponding concentrations obtained in this study with additive Ca(OH)$_2$ + NaHCO$_3$, these values are 3, 2 and 2 orders of magnitude higher. PAH emission trend obtained in this study is similar to reported low (low molecular weight PAH dominant and 5 & 6 ring PAHs non-detectable in thermal treatment of PAH-contaminated soil at 700°C).

Thus, Add, Ca(OH)$_2$ + NaHCO$_3$ was found to be the most suitable option among additives employed because: i) it resulted in the lowest ΣPAH and ΣTEC in gas, particulate and residue (only Add$_3$ had lower concentrations in residue); ii) there were no suspect carcinogenic PAHs emitted in gas and residue phases; iii) carcinogenic PAHs emitted in particulate phase was the least among additives tested; iv) it yielded the lowest and least amount of 4-6 rings PAHs, which generally have higher carcinogenicity than 2-3 rings PAHs; v) it was the only additive, with no emission of 5 and 6 ring PAHs; vi) low levels (< 1.26 × 10$^{-3}$ mg/m$^3$) of some 4 ring PAHs were detected only in particulate phase; vii) low levels (< 3.00 × 10$^{-4}$ ppmv) of 2 and 3 ring PAHs were mainly in the gas and particulate phases; and viii) only Nap (1.33 × 10$^{-2}$ µg/g) was detected in residue phase.

Conclusions

PAH emissions from thermal treatment of PSC at 650°C using indirect heating and 4 additives were profiled in gas, particulate and residue phases. Lime based additives were found superior to other additives in PAH degradation. Overall, Ca(OH)$_2$ + NaHCO$_3$ was considered the most suitable due to least emission of HMW PAHs, absence of 5 and 6 ring PAHs, lower equivalent carcinogenicity of products and lower concentrations of PAHs in the gas, particulate and residue phases. Thus the use of Ca(OH)$_2$ + NaHCO$_3$ can be further explored for optimization of thermal treatment of PSC.

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