

## LEAD IMMOBILIZATION AND PYROLYSIS OF LEAD-CONTAINING OIL SLUDGE

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### ABSTRACT

Recovery of organic composition is a sustainable way to deal with lead-containing refinery oil sludge; it is different from traditional methods of solidification, landfill, and incineration. The objective of this study is ( i ) to recover condensables and non-condensibles by low-temperature pyrolysis, and ( ii ) to immobilize lead compounds with inorganic sorbents of  $Al_2O_3$  or  $SiO_2$ . We expected to immobilize lead compounds to a TCLP level of less than 5.0 ml/l through the application of waste heat released from refinery flue gases, other than just to recover the organic composition in the refinery oil sludge. The results indicate that pyrolysis temperature is an essential factor that affects the extent of lead immobilization; a higher pyrolysis temperature reduces the TCLP value of lead species. The addition of inorganic sorbents also lowers lead TCLP value. The condensables can be further distilled into 50% gasoline, 35% diesel, and 15% heavy oils of higher boiling point.

### INTRODUCTION

Unlike fossil fuels, the output of solar, wind-mill, hydraulic, and geothermal energies are too minimal to be the main energy sources in Taiwan. Energy from nuclear fission is also limited due to the insufficiency of uranium mine; it is not well accepted by the civilians either. The supply of petroleum, like natural gas, can only last for ca. 50 years due to its limited resource in earth. The supply of coal may last longer, but only for ca. 200 years. It is critical to effectively utilize the fossil fuels that have been prevailing energy source thus far, before any alternative energy can be found. To transform low-rank fossil fuels and to effectively retrieve energy from spent plastics (1-4) are important research topics at present. It is also a waste of energy to landfill or incinerate the refinery oil sludge that has been produced in a substantial amount, other than the emission of air pollutants and the contamination of soil/underground water with organic and lead compounds. We pyrolyze the lead-containing refinery oil sludge to recover oil and to immobilize lead compounds. The experimental parameters include pyrolysis temperature, type of inorganic sorbents, the anal-

ysis and characterization of organic products, and the lead TCLP value after each pyrolysis run.

### EXPERIMENTAL

The pyrolysis reactor was made of Pyrex glass that was inserted into a 304 stainless steel furnace. The feeding port, carrier gas inlet, thermocouple port, and the organic vapor outlet was connected to the top end of the Pyrex reactor via a 4-way sand ground glass joint (3, 4). Pyrolysis heat was electrically supplied through a Ni/Cr wire. The organic vapor produced by pyrolysis was carried out from the Pyrex reactor by the carrier gas through the organic vapor outlet, which was connected to a condenser. The condensables were collected into a flask, which was located beneath the lower end of the condenser; while the non-condensables flew out of the top of the condenser (and) into a tube furnace to be combusted into  $H_2O$  and  $CO_2$ . The  $H_2O$  and  $CO_2$  were, respectively, adsorbed with anhydrous  $CaCl_2$  and  $NaOH$  pellets.  $SO_2$  and  $HCl$  in the flue gas were absorbed with 3%  $H_2O_2$  solution.

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### Chemicals and Instruments

1. Thermalgravimetry Analyzer (TGA): TG 1000, polymer laboratories (Epsom) Ltd., UK.
2. Fourier Transform Infrared Spectrometer (FTIR): BIO-RAD FTS-40, USA.
3. Flame Atomic Absorbency Spectrometer (FAAs): HITACHI Z-6100, Japan.
4. Nuclear Magnetic Resonance Spectrometer (NMR): Varian UNITY-300, USA.
5. Tube furnace: Yang-Cheng Co., Taiwan.
6. TCLP device: Associated Design, USA.
7. PbNO<sub>3</sub>: Riedel-de Hean, R. G. grade, Germany.
8. HNO<sub>3</sub>: Merck, 70% R. G. grade, Germany.
9. H<sub>2</sub>O<sub>2</sub>: Riedel-de Hean, 30% R. G. grade, Germany.
10. HF: Riedel-de Hean, 40% R. G. grade, Germany.
11. Kaolin: AKIMA 35, Associated Kaolin Industries, Malaysia.
12. Al<sub>2</sub>O<sub>3</sub>: A-21, Sumitomo Chemical Co., Ltd., Japan.
13. SiO<sub>2</sub>: Riedel-de Hean, R. G. grade, Germany.

### Pyrolysis Procedure

After the assembly of Pyrex reactor, 304 s.s. furnace, Ni/Cr heating wire, the collection set-up for pyrolysis-produced organic vapor, tube furnace, and the adsorption/absorption tubes after the tube furnace, the entire assembly was purged with N<sub>2</sub>. The electric heating system was kept on during the purging process. The lead-containing refinery oil sludge was fed into the Pyrex reactor as soon as a stable pre-set pyrolysis temperature was reached. After the pyrolysis, the residue inside the reactor is collected and subsequently extracted according to the TCLP method. The Pb concentration in the TCLP extract was then determined with an FAAs. The refinery oil sludge and the pyrolyzed samples are also subjected to the analyses of TGA, elemental composition (C, H, S, Cl, N, O), and total Pb content with microwave-assisted digestion/FAAs. The condensables collected were subjected to simulated distillation, and then were analyzed with FTIR and NMR. The non-condensables were burnt into H<sub>2</sub>O, CO<sub>2</sub>, SO<sub>2</sub>, and HCl. H<sub>2</sub>O and CO<sub>2</sub> are, respectively, adsorbed with anhydrous CaCl<sub>2</sub> and NaOH pellets. SO<sub>2</sub> and HCl are absorbed with a 3% H<sub>2</sub>O<sub>2</sub> solution. The refinery oil sludges pyrolyzed in this study were artificially doped with 10000 and 40000 ppm Pb (in form of Pb(NO<sub>3</sub>)<sub>2</sub>).

Table 1. Heating content of residue of pyrolyzed refinery oil sludge

Pyrolysis temperature (°C)	Heating content of residue (Kcal/Kg)
200	3044.5
300	1430.9
400	608.6

Table 2. Product partition of pyrolyzed refinery oil sludge (%)

Pyrolysis temperature (°C)	Product		
	Solid residue	Condensables	Non-condensables
200	56.3	36.3	7.4
300	49.7	42.4	7.9
400	46.3	45.0	8.7

### RESULTS AND DISCUSSION

The three main constituents in the refinery oil sludge are determined to be 33% ash, 43% water and some organic content that vaporizes at 105°C (for 3-5 days), and 24% organic content that remained liquid or solid at 105°C (for 3-5 days). The weight contents of S and Cl in the refinery oil sludge were determined to be 876 and 842 ppm, respectively. Due to its high viscosity, the refinery oil sludge was difficult to mix thoroughly. Table 1 shows the heating values of the residues that remained in the reactor after the pyrolysis. The heating values are 608.6 ~ 3044.5 Kcal/Kg depending on the pyrolysis temperature. Basically, the residues were all dry.

The heating value of the residue from the 200°C-pyrolysis run was the highest one among all residues due to its lowest pyrolysis temperature; while the 400°C-pyrolysis run gave the residue of the lowest heating value of 608.6 Kcal/Kg.

Table 2 demonstrates the weight distribution of solid residue, condensables, and non-condensables after the pyrolysis of the refinery oil sludge. The residue percentage decreases from 56.3% for the 200°C run to 46.3% for the 400°C run; while the weight percentage of both the condensables and non-condensables increases as the pyrolysis temperature is raised from 200°C to 400°C.

Table 3 represents the Pb TCLP value of the solid residue after the pyrolysis of the raw refinery oil sludge at various temperatures. Without pyrolysis, the Pb TCLP value of the raw refinery oil sludge is the highest (3.9 mg Pb/l). After the low-temperature pyrolysis (300°C and 400°C), it decreases to a non-detectable level ( $\leq 0.6$  mg Pb/l). The Pb TCLP value tends to decrease with the increase of the pyrolysis temperature. To simulate a high-Pb-content oil sludge (i.e., denoted as

Table 3. Pb TCLP values of pyrolysis residues at various temperatures of the raw refinery oil sludge

Sample	Pb TCLP value(mg/l)
Raw refinery oil sludge	3.9
200°C-pyrolysis residue	2.1
300°C-pyrolysis residue	≤0.6
400°C-pyrolysis residue	≤0.6

Table 4. Pb TCLP value of pyrolysis residue formed at 200°C with the addition of various sorbents

Sorbent addition	Pb TCLP value(mg/l)
no addition	260
Kaolin	110
Al <sub>2</sub> O <sub>3</sub>	140
SiO <sub>2</sub>	60

HPBS), we artificially spiked 10000 mg Pb (in the form of lead nitrate) into the raw refinery oil sludge. The effect of sorbent added to the HPBS on the Pb TCLP value was studied by pyrolyzing it at 200°C, and then (determine) the Pb TCLP value in the residue was determined. Table 4 shows that without sorbent addition, the Pb TCLP value is 260 mg/l; while it decreases to 110 mg/l with kaolin addition, to 140 mg/l with Al<sub>2</sub>O<sub>3</sub> addition, and to 60 mg/l with SiO<sub>2</sub> addition. This indicates that sorbent addition can effectively reduce Pb leaching; Pb is more immobilized.

The collected condensables contained both water and oils; some of them even became miscible for unknown reasons. They were subjected to a centrifuging process to separate each component. The percentages of water and oil in the condensables are listed on Table 5; H<sub>2</sub>O accounts for ca. three-fourths (in weight) of the condensables. The oil composition separated from the H<sub>2</sub>O portion was further analyzed with TGA, SMD, FTIR and NMR to understand its characteristics better. Figure 1 shows the TGA curves for the residues left after the pyrolysis of the oil sludge at various temperatures. The residue produced at higher pyrolysis temperature loses lesser weight due to its less organic content to start with the TGA test. The result of the SMD of the condensables is summarized on Table 6. There is not much difference in the SMD results between the 200°C and 300°C runs. The percentage of oil products with a boiling point less than 200°C is about 54% for the 200°C and 300°C runs. For the 400°C run, the corresponding percentage is less than

Table 5. The weight percentage of oil and water in the condensable product at various temperatures.

Pyrolysis temperature (°C)	Oil (%)	Water (%)
200	23.17	76.83
300	26.32	73.68
400	21.90	78.10

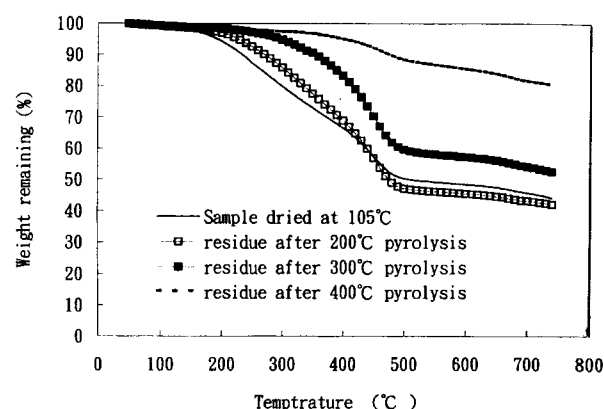


Fig. 1. TGA curves of the results obtained from experiments on residues produced at various pyrolysis temperatures.

Table 6. The results of the simulation distillation\* of condensables produced at various pyrolysis temperatures(°C)

Cumulative weight percentage (%)	Distillation temperature (°C)		
	200°C run	300°C run	400°C run
BP** 2%	-	-	126
4%	126	126	129
10%	135	135	138
20%	147	147	158
30%	164	164	182
40%	179	179	205
44%	183	183	217
46%	187	187	222
50%	192	192	233
54%	199	199	247
56%	203	203	253
60%	213	212	267
70%	237	236	309
80%	279	275	354
90%	351	338	417
92%	369	354	435
94%	392	375	457
96%	420	407	486
98%	469	472	527
FBP*** 99.5%	578	578	584

\* : By ASTM D 2887 Extended. \*\* : starting boiling point. \*\*\* : final boiling point.

40%. It should be noted that this portion of oil products could be further refined to produce gasoline to be the main product. Table 6 also shows that the percentage of oil products with a boiling point between 200 and 340°C that can be utilized as diesel, is ca. 36~40% for all three pyrolysis runs at 200, 300 and 400°C. The last portion of the oil products in Table 6 is the one with a boiling point greater than 340°C, which can be used as heavy oil; these range between 10 and 20%. The FTIR spectra of all pyrolysis residues show that the main functional groups detected are C=C and O-H; they are irrelative to the pyrolysis temperature. Similar results were also obtained for the

FTIR spectra of the condensables, except that there were strong H<sub>2</sub>O signal detected.

Typical NMR spectrum of the condensables is shown in Fig. 2. It shows that the octane number (RON) of the condensables is quite independent of the pyrolysis temperature; however, the content of aromatic hydrocarbon in the condensables decreases with the increase of the pyrolysis temperature as shown on Table 7. The non-condensables were combusted in a tube furnace to determine their contents of C, H, S, and Cl. The weight percentages of them was all quite low; the total percentage was between 7.4 and 8.7%.

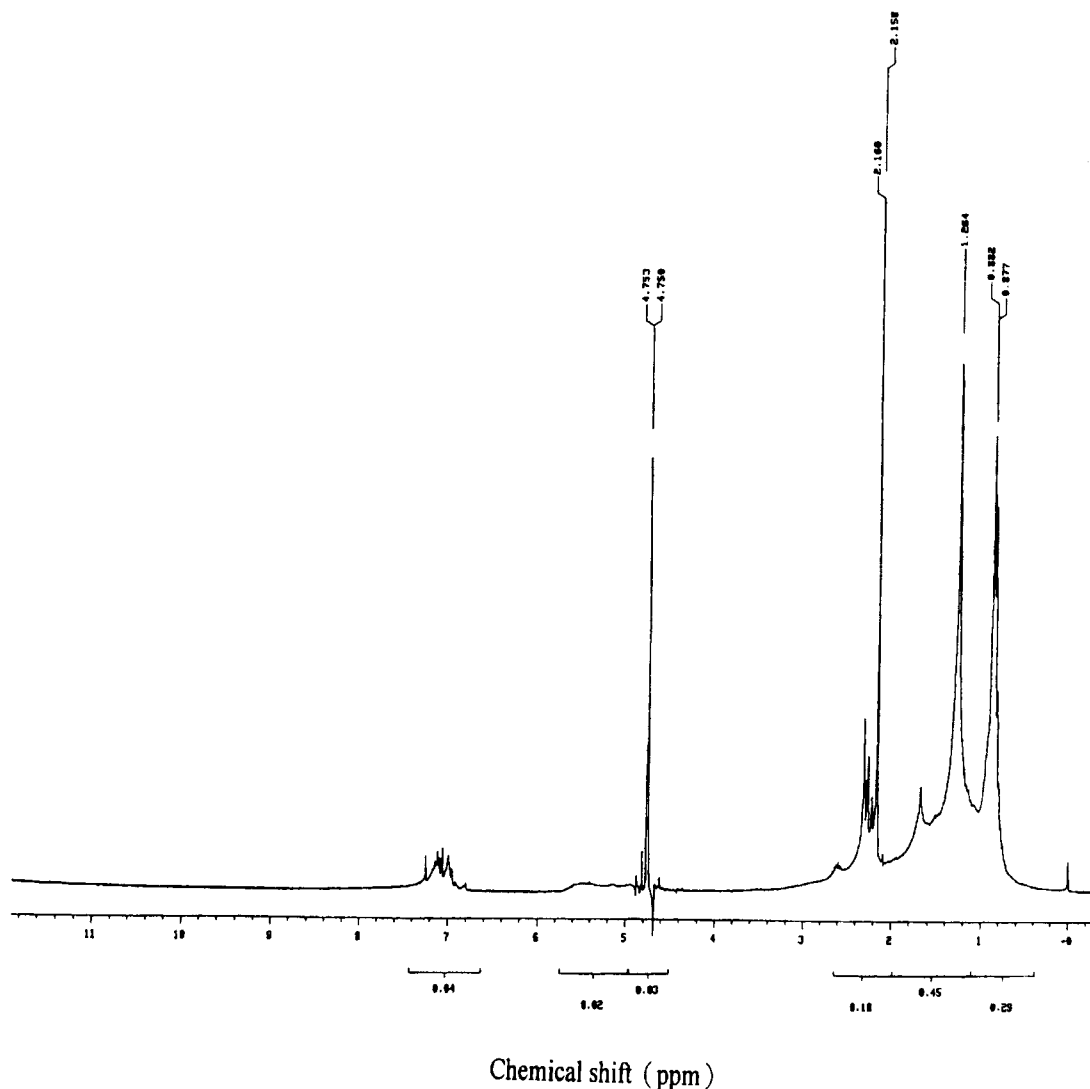


Fig. 2. The NMR spectrum of condensable oil product generated from 200°C pyrolysis of the refinery oil sludge.

Table 7. The NMR results of the condensables produced at various temperatures

Pyrolysis temperature(°C)	H <sub>aromatics</sub> (%)	H <sub>aliphatics</sub> (%)	RON value
200	13.89	86.11	70.26
300	7.08	92.92	70.26
400	6.21	93.79	70.18

## CONCLUSION

The great complexity and high viscosity of the real-world sludge samples result in a difficult mixing of the samples; this will possibly cause a poor datum repetition. It has been suggested that, unlike using the artificial samples, to apply this technique to real-world sludge samples, caution should be taken. The characteristics, except those revealed from the results from SMD, of the condensables obtained from pyrolysis at various temperatures (200-400°C) are not obviously different from each other. However, as pyrolysis temperature increases, the condensable percentage increases with a concomitant decrease in heating content of the pyrolysis residue. Although the pyrolysis at a higher temperature demands more energy input, the lead is better immobilized; therefore, in this aspect, lead should be regarded as a non-hazardous waste. This would reduce the cost to dispose of pyrolysis residues.

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## 含鉛廢油泥之裂解與鉛安定化

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**關鍵詞：** 煉油廠廢油泥、裂解、可凝結液態產物、鉛安定化、模擬蒸餾

### 摘 要

煉油廠所產生之含鉛廢油泥廢棄物之處理方式，除了固化、掩埋、焚化外，另一個較合乎永續理念為回收油品再利用。本研究目的有二：一為低溫裂解，回收液相可凝物（condensibles）及氣相之不凝物（non-condensibles）；二則藉由低溫及無機氧化物質，如  $\text{Al}_2\text{O}_3$ 、 $\text{SiO}_2$  成分安定化鉛。期望能利用煉油廠排放的低溫廢熱來處理廢油泥，安定化鉛，使鉛的毒性特性溶出濃度可達到法規規定的  $5.0 \text{ mg/l}$  以下，而趨向無害化；同時亦可回收廢油泥中之有機物質，充分達到資源化的目的。研究結果發現，溫度為影響鉛安定化之主因，較高溫度之裂解，其鉛溶出率較低；且添加不同吸附劑亦會影響鉛的溶出率。有機液相產物約有 50% 可提煉為汽油類，35% 可提煉柴油類，15% 為較高沸點之燃料油品質。