Liquid products from oxidative thermal treatment of oil sludge with different oxygen concentrations of air


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Abstract Oxidative thermal treatment of oil sludge with different oxygen concentrations of air by using a dynamic thermogravimetric (TG) reaction system is investigated. The experimental conditions employed are: gas flow rate of 50 cm³/min (value at 298 K) for 300 mg dry waste, a constant heating rate of 5.2 K/min, the oxygen concentrations in air of 1.09, 8.62 and 20.95 vol. % O₂, and the temperature (T) range of 378~873 K. From the experimental results, the residual mass fractions (M) are about 78.95, 28.49, 8.77 and 4.13 wt. % at the oxidative T of 563, 713, 763 and 873 K for the case with 20.95 vol. % O₂, respectively. The values of M with 8.62 and 1.09 vol. % O₂ at T of 873 K are 4.87 and 9.44 wt. %, respectively. The distillation characteristics of the oil portion of liquid products (condensates of gas at 298 K) from the oxidative thermal treatment of oil sludge with 20.95 vol. % O₂ at T of 378~873 K is close to those of commercial gasoline. Nevertheless, the liquid product contains a large amount of water. The distillation characteristics of the oil portions of liquid products with 8.62 and 1.09 vol. % O₂ at T of 378~873 K are close to those of diesel and fuel oils, respectively. The oil quality with 8.62 vol. % O₂ is better than that with 1.09 vol. % O₂. However, the liquid product with 8.62 vol. % O₂ still contains a large amount of water; nonetheless, that with 1.09 vol. % O₂ is with negligible water. Compared with the oil product of nitrogen pyrolysis, the oil quality with 1.09 vol. % O₂ is better. Certainly, low oxygen conditions (i.e. 1.09 vol. % O₂) not only accelerate the thermal reaction of oil sludge, but also at the same time avoid or reduce the production of water. Further, from the analysis of benzene (B), ethylbenzene (E), toluene (T) and iso-xylene (X) concentrations of the oil portion of liquid products, the BETX concentrations of oil with 20.95 vol. % O₂ are higher than those with 8.62 and 1.09 vol. % O₂. The yields of liquid products with 20.95, 8.62 and 1.09 vol. % O₂ at T of 378~873 K are 31.96, 34.42 and 37.3 wt. %, respectively. From the experimental results, the improvement effects of oxygen on the qualities of the oil portion of liquid products are obvious. The above technique not only formats good quality gasoline and diesel oils but also reduces large amount of oil sludge. If the oil exists with water, it may be obtained by further separation or collected by fractional condensation.

Keywords Incineration; oil sludge; resources recovery; thermal oxidative decomposition

Introduction Owing to the advantages of resources and energy recovery, some thermal treatment techniques (such as pyrolysis, gasification and oxidative thermal decomposition) on solid wastes are increasingly emphasized. In the petroleum refineries, a lot of oil sludges accumulate from refining processes. The major sources of oil sludges include the oil storage tank sludge, the biological sludge, the dissolved air flotation (DAF) scum, the American Petroleum Institute (API) separator sludge and the chemical sludge. In Taiwan, most of oil sludges are from the oil storage tank sludge and the biological sludge of refinery wastewater treatment plant (1). The previous study (2) reported the proximate, elemental and heating value analyses of the target oil sludge with combustible of about 59 wt. %, carbon of about 84 wt. % (dry basis), and low heating value of wet basis of about 24,537 kJ/kg.

One of the current major methods to dispose of oil sludge is incineration. The incinerators used are aggregate types such as fluidized bed combustion, circulating fluidized bed
combustion (CFBC), kiln, rotary, rack, and step-type furnaces with combustion temperatures of 1,073–1,173 K (3–7). Sankaran et al. (7) investigated a fluidized – bed incineration of three different oil sludge wastes using a pilot plant facility. Under the 1,073 K of ignition burner, 1,273 K of after burner and 50 to 100% excess air, the trial runs conducted in the fluid bed incinerator system showed that more than 98% combustion efficiency and 99% incineration efficiencies were achieved for all three types of oil sludge wastes. Incineration has been deemed an effective method for destroying the majority of organic constituents to innocuous carbon dioxide and water. Besides, the incineration system can recover waste heat; however, the heat recovery efficiencies are not good enough. Other methods considered for the disposal of oil sludge are: (1) pyrolysis of oil sludge (8–9), (2) landfarming with microbial treatment to convert the hydrocarbons to combustible gases, (3) use in a delayed coker, (4) utilization for industrial bitumen, and (5) separation of water and sediment at elevated temperature by the use of diluents and emulsifiers with subsequent burning (6, 8–14). Landfill has pollution risks if stabilization of oil sludge is not complete. It may pollute groundwater and cause health problems (10). Landfarming and composting require a large surface area and usually take a long time to complete. They also cause air pollution problems (12, 14). The organic compounds of oil sludge include some aromatics and polyaromatic hydrocarbons (PAHs) that are carcinogenic, while some inorganic compounds may contain toxic heavy metals (13, 15). Three PAHs – phenanthrene (phA), fluoranthene (fluA), and pyrene (pyr) – were detected from a bench-scale study (13). The study indicated that with a small excess air of 20 vol. % and short nominal gas residence times (0.7–1.2 sec), the fluidized-bed incineration of an industrial waste at 773–1,073 K (500–800°C) emitted priority PAHs in the 2,506–5,930 µg/Nm³ range (13).

Separation and Recovery Systems, Inc. (SRS) introduced a new generation of dryer technology, the MX-2500, for the treatment of refinery wastes and secondary materials including API sludges, DAF float, and slop oil emulsion solids (16). Ayen and Swanstrom (3) tested a low temperature thermal treatment process for petroleum refinery waste sludges coded as waste codes K048, K049, K050, K051 and K052 under the RCRA (Resources Conservation and Recovery Act). In the previous study, the one-, two- and three- reaction models were proposed to predict the pyrolysis experimental results (2). This is reasonable regarding the complex compositions of oil sludge. Extensive study has been reported (8) elsewhere on the analyses of major products obtained from the pyrolysis of oil sludge.

The investigation on the incineration of oil sludge has been carried out by using the fluidized-bed technique (7). The detailed kinetic equations deduced by the extension of Friedman method (17) of oxidative thermal decomposition of oil sludge were proposed by Shie et al. (18). Including the pyrolysis reactions, the overall oxidative thermal decomposition of oil sludge can be adequately described by a five – parallel – reaction model (18). The oil sludge is in both pyrolytic and oxidative thermal decomposition conditions. The effects of oxygen content and temperature on the gas emission and solid residue from the oxidative thermal decomposition of oil sludge were investigated by Shie et al. (19). Conesa et al. (20) proposed a kinetic model for the combustion of tyre wastes and indicated that the mass loss takes place in four steps. Their kinetic model involves three pyrolysis reactions and one oxidative reaction. This implies that oxygen takes part in the thermal degradation reaction mainly at the later reaction steps and higher reaction temperatures. The effects of oxygen content on the mass conversion at a constant heating rate are not obvious. However, the final residues of oxidative decomposition are lower than those of sole pyrolysis. In general, the solid waste incineration involves oxidizing the waste in excess air and at a high temperature. In the combustion systems of solid waste, an initial step of pyrolysis can occur producing organic volatiles and residues containing char and tar. In the next step, the residue of char or tar was then oxidatively reacted. The organic volatiles were also oxidatively...
decomposed in the postcombustion chamber. The oxidatively decomposed process is exothermic. The combustion heat released, in turn, can supply the heat needed for the endothermic pyrolysis reactions (20).

Wey et al. (21) performed oxidative pyrolysis of mixed solid waste by sand bed and free-board reaction in a fluidized bed under an oxygen-deficient atmosphere (air factor at 0.25–0.76) and lower temperature (813–903 K). The primary gas and residue tend to produce alkyl and alkene compounds rather than being oxidized to produce CO, CO₂ and H₂O because the oxygen is in short supply. Lee et al. (22) found that the effects of oxygen concentration (0–6.5 vol. %) on the yield and production rate of product gas are minor for the pyrolysis of waste tires. With increasing pyrolysis temperature, the gas yield and energy recovery increase, but the oil yield decreases, whereas the char yield remains constant (22).

The previous studies provided some useful results on thermal treatment of oil sludge but gave no data about the quality of the liquid products of the oxidative thermal treatment of oil sludge with different oxygen concentrations of air. Thus, the experiments are performed to establish the effects of operating conditions, especially the oxygen concentrations of air, on the quality of liquid products. The oxidative thermal decomposition is conducted by the use of a dynamic thermogravimetric (TG) reaction system at the temperature-programmed heating rate of 5.2 K/min in 1.09, 4.83, 8.62 and 20.95 vol. % O₂ atmosphere. The liquid products are collected and analyzed by the elemental analyzer, gas chromatography – thermal conductivity detector (GC-TCD), and gas chromatography – flame ionization detector (GC-FID).

**Experimental**

**Materials**

The oil sludge used in this study is sampled from the crude oil storage tank of a typical petroleum refinery plant located in northern Taiwan. The oil storage tank sludge accumulates at the bottom of the tank, where crude oil, product oil, vapor, slop, asphalt, etc. are stored, and is taken out during periodic tank cleaning and dumped separately from other sludges in ponds with or without covers (3). The oil sludge sample is dried in a recycle ventilation drier for 24 h at 378 K before use. Nitrogen gas, with 99.99% purity, and air gas, with 20.95% O₂, for the purge gas are purchased from Ching-Feng-Harng Co. Ltd. in Taipei, Taiwan.

**Apparatus and procedures**

*Thermogravimetry (TG).* The lab-scale apparatus and detailed description of experimental procedures for the oxidative thermal decomposition of oil sludge are the same as in the previous study (18, 23, 24). The heating rate employed for the analysis of oxidative thermal decomposition products is 5.2 K/min. The gas flow rate is 50 cm³/min (value at 298 K).

**Sampling.** The mass of oil sludge used for the experimental sampling of oxidative thermal decomposition products is 300 ± 0.5 mg. The products are divided into solid residues, liquid products (condensable liquid, 298 K) and noncondensable emission gases (298 K). The emission gases are passed through two condensing tubes immersed in a 298 K water bath, and the condensates are the liquid products. The program – raising temperature range for collecting products is 378–873 K. The connecting glass line between the furnace and condensing tube is wrapped with a thermal belt at 410 K.

**Analysis.** A Hewlett Packard (HP 5890) GC with an injector port and a FID is used for the quantitative analyses of liquid products. The chromatographic column is a Supelco fused silica capillary column (SPB-5, 30 m, 0.53 mm i. d., 1.5 µm film thickness). An integrator
from Hewlett Packard (HP 3395) is connected to the GC for graphing and integrating purposes. The operation conditions for simulation distillation of liquid products and commercial oils are set as follows: injector temperature 393 K, detector temperature 473 K, column temperature following the sampling injection is held at 313 K for 1 min, programmed to 573 K at 10 K/min, and finally stayed at 573 K for 50 min, nitrogen carrier gas flow rate 3.5 mL/min, nitrogen make-up gas 26 mL/min, and sample volume 0.1 µL.

For the analysis of H$_2$O and oxygen contents, a China Chromatography 8900 GC equipped with a TCD and a Supelco packing column (60/80 carbonxen-1000, 15 ft, 2.1 mm i. d.) is used. An integrator from Hewlett Packard (HP 3396) is connected to the GC. The operation conditions for analyzing H$_2$O content are set as follows: injector temperature 393 K, detector temperature 373 K, column temperature following the sampling injection held at 373 K for 20 min, helium carrier gas flow rate 35 mL/min for A and B columns, and sample volume 0.5 µL. The operation conditions for analyzing oxygen content are set as follows: injector temperature 393 K, detector temperature 373 K, column temperature following the sampling injection held at 353 K for 20 min, helium carrier gas flow rate 35 mL/min for A and B columns, and sample volume 500 µL.

The elemental analysis for the liquid products is made on a Perkin-Elmer, Norwalk, CT2400 elemental analyzer with 0.3 wt % accuracy, i.e. C, H and N analyzed with Heraeus CHN-O-RAPID, and S, Cl with Tacussel Coulomax 78 automatic coulometric titrator.

**Chemicals.** The principal liquid standards for establishing the calibration curve are the same as in the precious study (8). The liquid standards for the elemental analyzer are sulfonilic acid, 1-chloro-2, 4-dinitrobenzene, 3,5-dinitrobenzoic acid, acetanilide, benzoic acid and stearic acid.

Quantitative analysis of liquid products is based on the calculation using the linear calibration response equations of standards. The equation is generated for each of the liquid standards using a minimum of five different concentrations with three replicates at each concentration. All correlation coefficients ($r^2$) of linear calibration response curves are greater than 0.996.

**Results and discussion**

**Oxidative thermal decomposition of oil sludge**

The oil sludge used in this study is sampled from the crude oil storage tank of a typical petroleum refinery. The oxidative thermal decomposition reactions are significant in the range 415~931 K and the reaction scheme is complex (18). The temperature difference between final and initial reactions ($\Delta T = T_f - T_i$) increases as the heating rate increases at a fixed oxygen concentration ([O$_2$]). However, except for the case of 100% N$_2$, the value of $\Delta T$ decreases as the oxygen concentration increases at a fixed heating rate (18). Below 613 K, pyrolysis reactions are predominant. Including the pyrolysis reactions, the overall oxidative thermal decomposition of oil sludge can be adequately described by a five – parallel – reaction model. That oxidative thermal decomposition model can be used both in sole pyrolysis ([O$_2$] = 0) and oxidative thermal decomposition ([O$_2$] < 20.95 vol. %) of oil sludge (18). It seems that when oxygen-free pyrolysis occurs, the oil sludge degrades or devolatilizes to produce noncondensable gases, liquid oils and solid residues. If oxygen is present, the oil sludge proceeds not only with the pyrolysis to produce volatile, nonvolatile gases and solid residues but the oxidization with oxygen also produces lower molecular weight volatile hydrocarbons and combustion gases; meanwhile, the pyrolysis volatile gases react continuously with the oxygen to produce CO, CO$_2$, H$_2$O and others before emission.
Qualities of liquid products
The liquid products are mostly collected in the first condensing tube immersed in a 298 K water bath. Since water exists in the liquid products at the conditions of 20.95 and 8.62 vol. % O₂, the liquid products are divided into two levels (upper and lower) after steady state. The liquid products are collected and divided seven ways so as to investigate the effects of different oxygen concentrations of air on the quality of the liquid products. They are referred as TOL – air – U – 873 (A), TOL – air – L – 873 (B), TOL – air – mixed – 873 (C), TOL – air – mixed – 763 (D), TOL – air – mixed – 713 (E), TOL – 8.62% O₂ – mixed – 873 (F) and TOL – 1.92% O₂ – mixed – 873 (G). TOL – air – U – 873 (A) is the upper level liquid product at 378–873 K for 20.95 vol. % O₂, while TOL – air – L – 873 (B) is for the lower level liquid product at 378–873 K for 20.95 vol. % O₂. TOL – air – mixed – 873 (C) is the mixture of upper and lower level liquid products at 378 – 873 K for 20.95 vol. % O₂. In the mixed liquid, the upper and lower levels contain about 13.62 and 86.37 wt. %, respectively. TOL – air – mixed – 763 (D) is the mixed liquid product at 378–763 K for 20.95 vol. % O₂, while TOL – air – mixed – 713 (E) is the mixed liquid product at 378–713 K for 20.95 vol. % O₂. TOL – 8.62% O₂ – mixed – 873 (F) is the mixed liquid product at 378–873 K for 8.62 vol. % O₂, while TOL – 1.09% O₂ – mixed – 873 (G) is the mixed liquid product at 378–873 K for 1.09 vol. % O₂. The liquid products and some commercial oils are analyzed for the different boiling points (bps) by GC, according to the Standard Test Method for Boiling Range Distribution of Petroleum Fractions, proposed by the ASTM D-2887 method. Excluding water content, one notes that five portions of the organic components of liquid products are separated as listed in Table 1. The simulated distillation results are shown in Figure 1. The results including water content are listed in Table 2. Also, with the inclusion of water content, elemental analyses of oxidative decomposition liquid products, pyrolysis oil and some commercial oils are listed in Table 3.

Effects of oxygen concentrations on liquid products. From Table 1 and Figure 1, under the conditions of 20.95 vol. % O₂ and 378–873 K, the oil portion of liquid A contains, by wt. %, about 0.19 light naphtha, 13.11 heavy naphtha, 65.7 light gas oil and 21.0 heavy gas oil, respectively. Thus, the oil portion of liquid A is close to the diesel oil but has much heavy gas oil. As for the oil portion of liquid B, it contains about 9.98 light naphtha, 65.52 heavy...
naphtha, 23.49 light gas oil and 1.01 heavy gas oil, respectively. The comparison of distillation results indicates that the oil portion of liquid B is close to the gasolines (such as 98, 95, 92 unleaded gasolines and gasolines). The oil portions of liquid C (mixture of A and B) contains about 8.65 light naphtha, 58.38 heavy naphtha, 29.24 light gas oil and 3.73 heavy gas oil, respectively. The quality of the oil portion of liquid C is between gasoline and diesel oil but closer to gasoline. Under the conditions of 8.62 vol. % O₂ and 378–873 K, the oil portion of liquid F contains about 0.16 light naphtha, 14.53 heavy naphtha, 80.94 light gas oil and 4.37 heavy gas oil, respectively. The oil portions of liquid F is close to the diesel oil. As for the case with 1.09 vol. % O₂ and 378–873 K, the oil portion of liquid G contains about 0.03 light naphtha, 9.63 heavy naphtha, 56.82 light gas oil, 33.52 heavy gas oil and 0.01 vacuum residue, respectively. The oil portion of liquid G is close to fuel oil. Comparison with the case of sole pyrolysis (8), the pyrolysis oil (TPL) contains 0.72 light naphtha, 12.28 heavy naphtha, 66.58 light gas oil, 10.85 heavy gas oil and 9.57 vacuum residue, respectively. With the increase of oxygen concentration, the qualities of the oil portions of liquid products improve. However, from Table 2, liquids A, B, C and F contain water of about 10.68, 83.92, 73.94 and 80.99 wt. %, respectively. The liquid G and TPL do not contain water. At high oxygen concentration conditions (such as 20.95 and 8.62% O₂), the liquid products contain a large amount of water, while, at quite low oxygen concentration (such as 1.09% O₂) or no oxygen (pyrolysis), there is no water produced. This is reasonable because oxygen may react with carbon and H of oil sludge to produce CO, CO₂ and H₂O, respectively. There seems to be a critical oxygen concentration point that leads to the production of CO, CO₂ and vapor H₂O. When the amount of vapor H₂O exceeds the saturation concentration, some water is then condensed. Comparison of the two liquid oils of 1.09 vol. % O₂ (liquid G) and sole pyrolysis (TPL) indicates that both do not contain water; however, the vacuum residue of liquid G is lower than that of TPL. Certainly, low oxygen conditions (i.e. 1.09 vol. % O₂) not only enhance the thermal reaction of oil sludge, but also at the same time avoid or reduce the production of water. It is unexpected that the amount of water produced by the case of 8.62% O₂ is greater than that of 20.95% O₂. This may be due to the experimental errors caused by some uncollected substances that are coated on the walls of the collection line. The improvement effects of using lean oxygen on the qualities of the oil portions of liquid products are obvious.

Effects of final temperatures on liquid products. In order to elucidate the temperature effects on the liquid products, one also analyzes the liquid products for the case with 20.95 vol. % O₂ at different temperatures (378–763 (liquid D) and 378–713 K (liquid E)). From Table 1 and Figure 1, the oil portion of liquid D contains about 9.67 light naphtha, 63.77 heavy naphtha, 24.58 light gas oil and 1.98 heavy gas oil, respectively. The oil portion of liquid D is close to gasolines (including 98, 95 and 92 unleaded gasolines and gasolines). The oil portion of liquid E contains about 14.18 light naphtha, 71.28 heavy naphtha, 13.75 light gas oil and 0.79 heavy gas oil, respectively. From this result, the quality of the oil portions of liquid E is better than those of commercial gasoline and liquid D. Comparison of liquids C (378–873 K), D, and E indicates that a decrease of final temperature increases the qualities of the oil portions of the liquid products. This may be because a higher final temperature devolatilizes and produces high molecular weight hydrocarbons (HCs).

Further, Table 2 illustrates that liquids C, D and E contain about 73.94, 80.96, and 81.42 wt. % water, respectively. As the final temperatures increase, the water content of liquid products decreases. This indicates that the reactions of oxygen with C to form CO and CO₂ are more favorable than that with H to form H₂O at higher temperatures. On the other hand, at lower temperatures, more lower molecular weight HCs, which react easier with oxygen to produce H₂O than high molecular weight HCs, might be formed.
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* a: TOL, TPL, GL, DL, FL, HL: total oxidative decomposition liquid product, total pyrolysis oil, gasoline, diesel oil, fuel oil and heavy oil; A: upper level TOL at 378–873 K with air.; B: lower level TOL at 378–873 K with air.; C: mixed TOL at 378–873 K with air.; D: mixed TOL at 378–763 K with air; E: mixed TOL at 378–713 K with air; F: mixed TOL at 378–873 K with 8.62% O2; G: mixed TOL at 378–873 K with 1.09% O2; b: unit: in wt. %. c: numbers in parentheses are standard deviations (σ_n–1). d: heating rate (HR) = 5.2 K/min. e: negligible.
Table 2 Distillation characteristics of oxidative thermal decomposition liquid products (including water) in this study, pyrolysis oil and some commercial oils a, b, c, d

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<td>1.64</td>
<td>2.25</td>
<td>1.84</td>
<td>2.63</td>
<td>0.03</td>
<td>0.03</td>
<td>0.72</td>
<td>8.49</td>
</tr>
<tr>
<td>343–366 K</td>
<td>0.04</td>
<td>0.13</td>
<td>0.18</td>
<td>0.09</td>
<td>0.43</td>
<td>0.01</td>
<td>0.01</td>
<td>0.48</td>
<td>2.67</td>
</tr>
<tr>
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<td>10.54</td>
<td>15.21</td>
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<td>9.63</td>
<td>12.28</td>
<td>64.37</td>
<td>70.95</td>
</tr>
<tr>
<td>366–477 K</td>
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<td>0.48</td>
<td>0.73</td>
<td>0.21</td>
<td>0.25</td>
<td>0.28</td>
<td>0.04</td>
<td>7.96</td>
<td>2.21</td>
</tr>
<tr>
<td>light gas oil</td>
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<td>3.78</td>
<td>7.62</td>
<td>4.68</td>
<td>2.55</td>
<td>15.39</td>
<td>56.82</td>
<td>66.58</td>
<td>26.59</td>
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<td>477–616 K</td>
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<td>0.59</td>
<td>0.86</td>
<td>0.2</td>
<td>0.77</td>
<td>0.25</td>
<td>3.15</td>
<td>9.6</td>
<td>3.4</td>
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<td>0.83</td>
<td>33.52</td>
<td>10.85</td>
<td>0.54</td>
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<tr>
<td>616–811 K</td>
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<td>0.04</td>
<td>0.19</td>
<td>0.04</td>
<td>0.15</td>
<td>0.04</td>
<td>3.09</td>
<td>5.79</td>
<td>0.51</td>
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<td>vacuum residue</td>
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<td>~0</td>
<td>~0</td>
<td>~0</td>
<td>~0</td>
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<td>~0</td>
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<td>water</td>
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<td>73.94</td>
<td>80.96</td>
<td>81.42</td>
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<td>0.02</td>
<td>4.74</td>
<td>0.08</td>
<td>(&lt;0.001)</td>
<td>ND</td>
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a, b, c, d, e: same as in Table 1. f: ND: nondetectable concentration
Elemental analyses of liquid products. From Table 3, due to the large amounts of water content in the liquid products, carbon contents in the oxidative thermal decomposition liquid products are quite low and between 11.73–19.6 wt. % (not including the case of 1.09 vol. % O₂). The carbon content of liquid G is 77.7 wt. %, and is close to 95 unleaded gasoline. Comparison of liquid G, TPL (8), DL, and 95 unleaded GL indicates that the mole ratios (H/C) of liquid G, TPL, DL and 95 unleaded GL are 1.92, 1.57, 1.83 and 1.65, respectively. All of them belong to the aromatics organic compounds (with H/C of 1.0–2.0). It is noted that the sulfur content in the liquid B (containing water) is about 0.26 wt. %, while that in the oil portion of liquid B is about 0.04 wt. %. Therefore, the oil portion of liquid B is a lower sulfur gasoline. The sulfur content in commercial gasoline is close to 0.1 wt. % (21).

Benzene (B), toluene (T), ethylbenzene (E) and iso-xylene (X) in liquid products. The amounts of benzene (B), toluene (T), ethylbenzene (E) and iso-xylene (X) in the oils affect the qualities of oils. Without including the water contents, Table 4 lists the BETX concentrations in the oil portions of oxidative thermal decomposition liquid products, the sole pyrolysis oil and some commercial oils. Those including the water contents are listed in Table 5. From Table 4, the total BETX concentrations of the oil portions of oxidative thermal decomposition liquid products are between 0.4887–8.6302 wt. %. The highest total concentration of BETX in the oil portions is liquid D (20.95 vol. % O₂, 378–763 K) and the lowest is liquid F (8.62% vol. O₂ mixed- unleaded). With the inclusion of water content, the total BETX concentrations of liquid products are between 0.0929–1.8969 wt. %. The highest one is liquid C (20.95 vol. % O₂, 378–873 K) and the lowest is again liquid F. From the results, with the water contents, the total BETX concentrations increase with the final temperature. The BETX concentrations of oil portions with 20.95 vol. % O₂ are generally higher than those with 8.62 and 1.09 vol. % O₂. As compared to the sole pyrolysis oil, the total BETX concentrations of all oxidative thermal decomposition liquid products and their oil portions are higher than that of pyrolysis oil (0.0261 wt. %). According to Table 4 or 5, the total BETX concentrations of commercial gasolines (98, 95 and 92 unleaded GLs, and gasoline) and diesel oil are between 16.51–24.4351 and 0.472 wt. %, respectively. From the B, E, T and X concentrations, 98 unleaded gasoline is close to 95 unleaded gasoline, while 92 unleaded gasoline is close to gasoline. The total concentrations of BETX of four commercial gasolines are higher than those of oxidative thermal decomposition liquid

Table 3  Elemental analyses of oxidative thermal decomposition liquid products (including water) in this study, pyrolysis oil and some commercial oils a, b, c, d

<table>
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<th>TOL-air-</th>
<th>TOL-air-</th>
<th>TOL-air-</th>
<th>TOL-air-</th>
<th>TOL-air-</th>
<th>95</th>
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<tr>
<td></td>
<td>8.62 %</td>
<td>1.09 %</td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>U-873</td>
<td>A</td>
<td>B</td>
<td>C</td>
<td>D</td>
<td>E</td>
<td>GL</td>
</tr>
<tr>
<td>TOL-air-</td>
<td>8.62 %</td>
<td>1.09 %</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>L-873</td>
<td>(A)</td>
<td>(B)</td>
<td>(C)</td>
<td>(D)</td>
<td>(E)</td>
<td>(F)</td>
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<tr>
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<td></td>
<td></td>
<td></td>
<td>(G)</td>
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<tr>
<td>C</td>
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<td>1.73</td>
<td>16.21</td>
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<td>9.25</td>
<td>9.43</td>
<td>9.32</td>
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<td>0.053</td>
<td>0.063</td>
<td>0.13</td>
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<tr>
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<td>NA</td>
<td>NA</td>
<td>NA</td>
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</tr>
<tr>
<td>Cl</td>
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<td>0.07</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
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<td>1.35</td>
<td>1.45</td>
<td>1.24</td>
<td>1.74</td>
<td>6.27</td>
</tr>
</tbody>
</table>

a, c, d: same as in Table 1. b: units: in wt. % for C, H, N, S, Cl; in wt./wt. for C/H ratio. e: NA: not analyzed. f: numbers in brackets are relative errors ((|X₁ – X₂|/0.5 (X₁ + X₂)) ×100%)

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products. The total BETX concentration of the oil portion of liquid F (0.4888 wt. %) is very close to commercial diesel oil (0.472 wt. %). It is especially noted that the total BETX concentration of liquid G (1.09 vol. % O₂, 378–873 K) is higher than that of diesel oil, while the simulated distillation result of liquid G is close to fuel oil.

**Solid residues or ash from oxidative thermal decomposition of oil sludge**

*Residual masses of oxidative thermal decomposition of oil sludge.* Under constant heating rate (5.2 K/min), the elemental components of solid residues at different oxidative thermal decomposition temperatures (T) and oxygen concentrations (O₂) can indicate the reaction extents. From the experimental results, the residual mass fractions (M) are about 78.95, 28.49, 8.77 and 4.13 wt. % at T of 563, 713, 763 and 873 K for 20.95 vol. % O₂, respectively (19). The values of M for 8.62, 4.83 and 1.09 vol. % O₂ at T of 873 K are 4.87, 7.94 and 9.44 wt. %, respectively (19). In the sole pyrolysis, the M is 13.1 wt. % at T of 873 K (8). It indicates that the extent of oxidative thermal decomposition increases with the oxygen concentration. The oxidative thermal decomposition of oil sludge helps the volume reduction of oil sludge dramatically. A higher oxygen concentration would enhance the oxidative thermal decomposition reactions and reduce the residual mass.

**Metal analyses of residual masses.** In the process of oxidative thermal decomposition, some volatile trace metal species may be released with the gaseous products and partially condensed in the liquid oil. The presence of metal species may then affect the quality of liquid oil. Also, the concentrations of metal elements in the solid residues and TCLP (toxicity characteristics leaching procedure) leachates in turn decide the disposal methods. The results of the metal element analysis of the solid residues of oxidative thermal decomposition are summarized in Table 6. Note especially the dramatic reduction for Hg metal element, which, at 873 K, is reduced by 94.95 wt. %, based on the mass of dry oil sludge. The other metal elements do not have significant reductions. The significant reduction of Hg (94.95 wt. %) during the thermal process is reasonable due to its low evaporating point (with boiling point (bp) of 629.6 K). Comparison with sole pyrolysis (8) indicates that the Hg in the pyrolysis residual masses also reduces dramatically (about 99 wt. % reduction). However, the metal elements of Pb and Ba reduce about 80 wt. % in sole pyrolysis (8), but they do not reduce in the oxidative thermal decomposition case. This may be because Pb and Ba were converted to the high melting point compounds of PbO (with melting point (mp) of 1161 K) and BaO (with mp of 2196 K) in oxidative reactions. The concentration of total metal element (Cₘₑ) of initial dry basis oil sludge is 15,728 mg/kg (ppmw). As the temperature increases, the values (column c) of Cₘₑ of solid residues (at different temperatures) also increase. The value of Cₘₑ of solid residues at 873 K is 455,850 mg/kg and 28.98 times to that of initial dry basis oil sludge and that is far higher than that in the sole pyrolysis case (5.28 times). This is because the residual mass fraction (4.13 wt. %) of the oxidative thermal decomposition of oil sludge at 20.95 vol. % O₂ is lower than that (13.1 wt. %) of pyrolysis.

**Mass balance of liquid products, solid residues and emission gases**

Under the oxidative thermal decomposition temperatures of 378–873 K, the variations of input and output masses with temperature for the oxidative thermal decomposition of dry oil sludge are listed in Table 7. The yields of liquid products relative to the initial dry oil sludge, in wt. %, with 20.95, 8.62 and 1.09 vol. % O₂ at T of 378–873 K are 31.96, 34.42 and 37.3 wt. %, respectively. Nevertheless, the oil portions of liquid products relative to the initial dry oil sludge, in wt. %, with 20.95, 8.62, 1.09 vol. % O₂ and sole pyrolysis (8) at T of 378–873 K are 8.33, 6.54, 37.3 and 69.63 wt. %, respectively. The residual mass fractions
### Table 4 BTEX concentrations in oil portions (organic components excluding water) of oxidative thermal decomposition liquid products in this study, pyrolysis oil and some commercial oils

| TOL-air | TOL-air | TOL-air | TOL-air | TOL-air | TOL-air | TOL-air | TOL-air | TOL-air | TOL-air | TOL-air | TOL-air | TOL-air | TOL-air |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
|         | U-873   | L-873   | mixed-763 | mixed-713 | mixed-873 | mixed-763 | mixed-713 | mixed-873 | mixed-763 | mixed-713 | mixed-873 | mixed-763 | mixed-713 | mixed-873 |
| (A)     | (B)     | (C)     | (D)     | (E)     | (F)     | (G)     | (H)     | (I)     | (J)     | (K)     | (L)     | (M)     | (N)     | (O)     |
| Benzene (mg/kg) | 752.45 (264.76) | 67863.86 | 58716.5 | 50277.83 (3054.74) | 27973.04 (2669.89) | 215.23 (35.33) | 20.55 | 19477.11 | 20539.5 | 80695.64 | 87934.59 | 348.64 |
| Toluene (mg/kg) | 3271.57 (497.41) | 10242.45 (2100.86) | 9291.99 | 23576.38 (1882.25) | 2174.42 (317.87) | 1113.13 (109.95) | 7.57 | 68623.31 | 70556.06 | 56262.62 | 64980.5 | 1740.11 |
| Ethylbenzene (mg/kg) | 3467.6 (241.46) | 2611.07 (471.62) | 2727.47 | 1958.42 (46.18) | 2997.26 (101.96) | 1254.66 (514.8) | 123.78 | 26681.42 | 28518.36 | 66046.73 | 56523.15 | 801.70 |
| Iso-xylene (mg/kg) | 673.99 (28.21) | 2270.74 (488.48) | 2053.04 | 10489.72 (425.74) | 2421.49 (19.49) | 9572.9 (828.98) | 418.69 | 50318.16 | 48812.97 | 32586.1 | 34913.2 | 1829.1 |
| Totalb wt. % | 0.7266 | 8.2988 | 7.2789 | 8.6302 | 3.2737 | 0.4888 | 1.0941 | 0.0261 | 16.51 | 16.8427 | 24.3591 | 0.472 |

### Table 5 BTEX concentrations in oxidative thermal decomposition liquid products (including water) in this study, pyrolysis oil and some commercial oils

| TOL-air | TOL-air | TOL-air | TOL-air | TOL-air | TOL-air | TOL-air | TOL-air | TOL-air | TOL-air | TOL-air | TOL-air | TOL-air | TOL-air |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
|         | U-873   | L-873   | mixed-763 | mixed-713 | mixed-873 | mixed-763 | mixed-713 | mixed-873 | mixed-763 | mixed-713 | mixed-873 | mixed-763 | mixed-713 | mixed-873 |
| (A)     | (B)     | (C)     | (D)     | (E)     | (F)     | (G)     | (H)     | (I)     | (J)     | (K)     | (L)     | (M)     | (N)     | (O)     |
| Benzene (mg/kg) | 672.09 (236.48) | 10912.51 (404.18) | 15301.52 (575.15) | 9572.9 (581.62) | 5197.39 (496.07) | 40.99 | 154.72 | 20.55 | 19477.11 | 20539.5 | 80695.64 | 87934.59 | 348.64 |
| Toluene (mg/kg) | 2922.17 (444.29) | 1646.99 (337.82) | 2421.49 (490.51) | 4488.94 (274.8) | 968.17 | 413.36 | 1113.13 | 7.57 | 68623.31 | 70556.06 | 56262.62 | 64980.5 | 1740.11 |
| Ethylbenzene (mg/kg) | 3097.26 (215.67) | 419.86 (7.85) | 710.78 (114.72) | 372.88 (18.94) | 556.89 | 282.32 | 1254.66 | 123.78 | 26681.42 | 28518.36 | 66046.73 | 56523.15 | 801.70 |
| Iso-xylene (mg/kg) | 602.01 (25.2) | 365.13 (78.55) | 535.02 (110.95) | 1997.24 (135.81) | 196.15 | 192.61 | 8418.4 | 108.6 | 50318.16 | 48812.97 | 32586.1 | 34913.2 | 1829.1 |
| Totalb wt. % | 0.7294 | 1.3344 | 1.8969 | 1.6432 | 0.6919 | 0.0929 | 1.0941 | 0.0261 | 16.51 | 16.8427 | 24.3591 | 0.472 |
for 20.95, 8.62, 4.83 and 1.09 vol. % O₂ at T of 873 K are 4.13, 4.87, 7.94 and 9.44 wt. %, respectively (19). As for the gases, the total masses of CO and CO₂ produced decrease as the oxygen concentration decreases. The overall yields of the thermal treatment of oil sludge ((liquids + ash + gases excluding N₂ and O₂)/(oil sludge + O₂ consumed)), in wt. %, with 20.95, 8.62 vol. % O₂ and sole pyrolysis (8) at T of 378~873 K are 92.67, 85.36 and 86.9 wt. %, respectively. However, the recoveries of thermal treatment system ((liquids + ash + gases excluding N₂ + output O₂)/(oil sludge + input O₂)), in wt. %, with 20.95, 8.62 vol. % O₂ and sole pyrolysis (8) at T of 378~873 K are 98.64, 94.24 and 86.9 wt. %, respectively. The unbalanced deficiency of recovery may include 1) uncollected substances coating the walls of the collection line, 2) unidentified gaseous substances and 3) experimental errors.

Table 6 Analyses of metal elements in oil sludge and solid residues at different oxidative thermal decomposition temperatures of airf,g

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<th>713 K</th>
<th>763 K</th>
<th>873 K</th>
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<tbody>
<tr>
<td></td>
<td>a [Wet]</td>
<td>b Dry</td>
<td>c ppmw</td>
<td>d ppmw</td>
<td>e ppmw</td>
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<td>(810.07)</td>
<td>(1,027.6)</td>
<td>(953.39)</td>
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<td>(6.14)</td>
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<td>(3.17)</td>
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<td>14.1</td>
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<td>886</td>
<td>0.96</td>
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<td>11.28</td>
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<td>1.56</td>
<td>1.23</td>
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<td>(0)</td>
<td>(0.03)</td>
<td>(0.01)</td>
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<tr>
<td>Cd</td>
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<td>0.27</td>
<td>0.21</td>
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<td>(0.02)</td>
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<tr>
<td>Se</td>
<td>958</td>
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<td>(0.002)</td>
<td>(5.87)</td>
<td>(3.95)</td>
<td>(23.7)</td>
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<tr>
<td>Total</td>
<td>9,275</td>
<td>15,728</td>
<td>20,464.6</td>
<td>16,158.6</td>
<td>56,811.6</td>
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</table>

a: wet basis (reference 2). b: dry basis. c: based on mass of solid residues at different temperatures. d: based on mass of initial dry oil sludge. e: ppmw: ppm in wt. / wt., mg / kg. f: numbers in parentheses are standard deviations (sₓ−1). g: heating rate (HR) = 5.2 K/min

for 20.95, 8.62, 4.83 and 1.09 vol. % O₂ at T of 873 K are 4.13, 4.87, 7.94 and 9.44 wt. %, respectively (19). As for the gases, the total masses of CO and CO₂ produced decrease as the oxygen concentration decreases. The overall yields of the thermal treatment of oil sludge ((liquids + ash + gases excluding N₂ and O₂)/(oil sludge + O₂ consumed)), in wt. %, with 20.95, 8.62 vol. % O₂ and sole pyrolysis (8) at T of 378~873 K are 92.67, 85.36 and 86.9 wt. %, respectively. However, the recoveries of thermal treatment system ((liquids + ash + gases excluding N₂ + output O₂)/(oil sludge + input O₂)), in wt. %, with 20.95, 8.62 vol. % O₂ and sole pyrolysis (8) at T of 378~873 K are 98.64, 94.24 and 86.9 wt. %, respectively. The unbalanced deficiency of recovery may include 1) uncollected substances coating the walls of the collection line, 2) unidentified gaseous substances and 3) experimental errors.
Conclusions

The effects of oxygen concentration and temperature on the liquid products from the oxidative thermal treatment of oil sludge are examined by a TGA reaction system at different oxygen concentrations with the heating rate of 5.2 K/min over the temperature range of 378~873 K. The higher oxygen concentration enhances the oxidative thermal decomposition reactions and reduces the residual mass. Also, the oxidative thermal treatment process is exothermic and can produce the heat for use in the endothermic pyrolysis reactions. This thus decreases the consumption of energy. The oil sludge can be effectively treated by the oxidative thermal treatment method. Certainly, low oxygen conditions (i.e. 1.09 vol. % O₂) not only enhance the thermal reaction of oil sludge, but also at the same time avoid or reduce the production of water. The above technique not only formats good quality oils but also reduces the amount of oil sludge. If the oil exists with water, it may be obtained by further separation or collected by the fractional condensation. This study greatly assists the proper design and operation of the oxidative thermal treatment of oil sludge.

Table 7 Mass balance of oxidative thermal decomposition in this study and pyrolysis of oil sludge a, b, c

<table>
<thead>
<tr>
<th></th>
<th>Air (20.95 % O₂)</th>
<th>8.62 % O₂</th>
<th>4.83 % O₂</th>
<th>1.09 % O₂</th>
<th>0 % O₂ (pyrolysis)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Input</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Oil Sludge</strong></td>
<td>300 (100)</td>
<td>300 (100)</td>
<td>300 (100)</td>
<td>300 (100)</td>
<td>300 (100)</td>
</tr>
<tr>
<td>O₂ in air</td>
<td>1315.54</td>
<td>462.84</td>
<td>303.3</td>
<td>68.44</td>
<td>ND</td>
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<tr>
<td>N₂ in air</td>
<td>4343.4</td>
<td>5020.89</td>
<td>5229.12</td>
<td>5434.62</td>
<td>5494.51</td>
</tr>
<tr>
<td><strong>Output</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Liquids</strong></td>
<td>95.88 (31.96)</td>
<td>103.26 (34.42)</td>
<td>NA</td>
<td>111.9 (37.3)</td>
<td>208.89 (69.63)</td>
</tr>
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<td>Oil</td>
<td>24.99 (8.33)</td>
<td>19.63 (6.54)</td>
<td>NA</td>
<td>111.9 (37.3)</td>
<td>208.89 (69.63)</td>
</tr>
<tr>
<td>Water</td>
<td>70.89 (23.63)</td>
<td>83.63 (27.88)</td>
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<td>ND</td>
<td>ND</td>
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<tr>
<td>Ash or residue</td>
<td>12.39 (4.13)</td>
<td>14.61 (4.87)</td>
<td>23.82 (7.94)</td>
<td>28.32 (9.44)</td>
<td>41.1 (13.7)</td>
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<td>Gases</td>
<td>481.92 (160.64)</td>
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<td>NA</td>
<td>10.71 (3.57)</td>
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<td>19.92 (6.64)</td>
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<td>NA</td>
<td>2.73 (0.91)</td>
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<td>NA</td>
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<tr>
<td>H₂O</td>
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<td>6.96 (2.32)</td>
<td>NA</td>
<td>NA</td>
<td>1.89 (0.63)</td>
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<tr>
<td>CO</td>
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<td>148.44 (49.48)</td>
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<td>0.66 (0.22)</td>
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<td>CO₂</td>
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<td>O₂ consumed</td>
<td>312.17</td>
<td>148.73</td>
<td>NA</td>
<td>NA</td>
<td>0</td>
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<tr>
<td>Overall yield</td>
<td>92.67</td>
<td>85.36</td>
<td>–</td>
<td>–</td>
<td>86.9</td>
</tr>
<tr>
<td>Recovery</td>
<td>98.64</td>
<td>94.24</td>
<td>–</td>
<td>–</td>
<td>86.9</td>
</tr>
</tbody>
</table>

a: collection range = 378–873 K, inlet gas flow rate = 50 mL/min and heating rate (HR) = 5.2 K/min. b: unit : in mg. c: numbers in parentheses are relative weight percent to initial dry oil sludge (300 mg). d: ND: non-detectable concentration. e: NA: not analyzed. f: overall yield of thermal treatment of oil sludge (wt. %) = (liquids + ash + gases excluding N₂ and O₂)/(oil sludge + O₂ consumed). g: recovery of thermal treatment system (wt. %) = (liquids + ash + gases excluding N₂ + output O₂)/(oil sludge + input O₂).
Acknowledgement
We express our sincere thanks to the National Science Council of Taiwan for financial support, under contract number NSC88-2211-E-002-021.

References
1. AAECC (Asian American Environmental Control Corporation) (1987). Refinery Solid Wastes Treatment and Management, Report, Submitted to Chinese Petroleum Corp. (Taiwan) by AAECC.
