Pyrolytic product characteristics of biosludge from the wastewater treatment plant of a petrochemical industry

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ABSTRACT

Biosludge was produced from the wastewater treatment plant of a petrochemical industry. The element compositions of pyrolytic residues, CO, CO_2, NOx, SOx, total hydrocarbons and detailed volatile organic compounds of pyrolytic gas, and C, H, N, S content and compositions in biofuel were determined in this study. Generally, 75–80% water content in sludge cakes and about 65–70% weight of water vapor and volatile compounds were volatilized during the drying process. Propene, propane, 1-butene, n-butane, isobutene, toluene and benzene were the major volatile organic compounds (VOCs) of the pyrolytic gas, and the concentrations for most of the top 20 VOC species were greater than 5 ppm. C_5–C_9 compounds contributed 60% by weight of biofuel; 4-hydroxy-4-methyl-2-pentanone was the highest species, accounting for 28–53% of biofuel at various pyrolytic temperatures. Based on the dried residues, there was 8.5–13% weight in pyrolytic residues, 62–82% weight in liquid products (water and crude oil) and 5.8–30% weight in the gas phase after pyrolytic processing at 500–800 °C. Finally, 1.5–2.5 wt% liquid fuel was produced after the distillation process. The pyrolytic residues could be reused, the pyrolytic liquid product could be used as a fuel after distillation, and the pyrolytic gas could be recycled in the pyrolytic process to achieve non-toxic discharge and reduce the cost of sludge disposal.

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1. Introduction

Biological process is an important aspect of wastewater treatment, but sludge is an inevitable major byproduct, and its disposal can cause serious environmental problems. In addition, sludge treatment can account for a high portion of the capital and operating costs of a wastewater treatment facility [1]. Therefore, sludge disposal is an important part of wastewater treatment. Landfilling, incineration, or use in agriculture are the methods typically used to dispose of biosludge [2]. However, the disposal of sludge on reclaimed land is no longer a viable solution [3] because farmland sludge applications are limited by the uptake capacity of the soil in addition to potential pollution by heavy metals [4]. Incineration, however, can provide a large volume reduction and result in energy recovery [5], while the residue can be used for road surfacing, building materials and metal reclamation [6]. However, the pollution control of sludge incineration should be done with disposal in mind. Therefore, reuse of residues and products after the disposal of sludge should be carefully considered.

Recently, work done in Germany produced a "synthetic crude oil" from sewage sludge in an oxygen-free environment at 300–350 °C [7,8]. Thermal liquefaction of sewage sludge has also been developed by other researchers at higher temperatures (400–700 °C) [1,9].

Some workers used the sewage sludge mixed with other materials (e.g., coal and putrescible garbage, etc.) [10,11] or directly added the sludge to the cement kiln process [12,13] for disposal. Alternatively, researchers have focused on the pyrolysis of sewage sludge in an oxygen-free atmosphere, wherein the organic matter was transformed into liquid oil and gases containing hydrocarbons [1,14,15]. The residual solid, i.e., char, can be used as an adsorbent if it is pyrolyzed under controlled conditions or chemically treated [16]. The resultant adsorbents can be used in air and water pollution control and in odor removal from sewage treatment processes [17–19].

The reuse of digested sludge on farmland is limited by the uptake capacity of the soil and the high concentration of toxic organic constituents and heavy metals [4]. Additionally, in many countries, including Taiwan, landfill treatment is limited by land cost and land use. Incineration provides a large volume reduction and results in improved energy efficiency, although the scrubbing cost of the pyrolytic exhaust is high. The pyrolysis of sewage sludge in an oxygen-free atmosphere in fluidized beds has been proposed

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by Kaminsky [20], and other wastes, i.e., waste tire, have also been reused by the pyrolysis process [21].

Currently, the petroleum industry disposes of its sludge via landfilling and incineration. With incinerators such as fluidized bed furnaces or reactor-type furnaces, the combustion temperature can be up to 800–900 K. The residues include fly ash from incinerated municipal sewage sludge that must be landfilled. These methods are far from satisfactory under current recycling philosophies. In addition, the biomass contains a high proportion of hydrocarbon compounds that may be used as a secondary raw material. Although many studies have investigated reuse technologies for sludge, most have focused on the characteristics of pyrolytic residues, liquid products or pyrolytic gas. The effective reuse of sludge is based on consideration of detailed information about such factors as the operating parameters of the pyrolysis process and the compositions of the residues, liquid products, pyrolytic gas, etc.

In this work, we focused on the elemental composition of the pyrolytic residue of biosludge, which was taken from a petrochemical wastewater treatment plant and pyrolyzed in a nitrogen atmosphere. In addition, the pyrolytic residue, liquid product and pyrolytic gas compositions were determined in this study, providing detailed baseline information for the reuse of biosludge.

2. Experimental

2.1. Raw material

Biosludge samples were obtained from a petrochemical wastewater treatment plant in Kaohsiung, Taiwan, where the biosludge results from microorganism reproduction. A single 300-kg biosludge cake was sampled for all experiments to avoid the risk of obtaining different biosludge characteristics from samples taken at different times. Biosludge was stored at 4 °C until it was pyrolyzed. Two kilograms of the biosludge sample were dried in an oven at 105 °C for 24 h in each run. Raw biosludge cakes had a total solids content of 10.5 ± 0.8 wt% and a volatile solids concentration of 63.5 ± 5.3 wt%. The biosludge cakes were conditioned and dried at 105 °C. Carbon, oxygen, hydrogen, nitrogen and sulfur concentrations were 28.0%, 34.4%, 4.5%, 4.2%, and 1.8%, respectively.

2.2. Pyrolysis process

Pyrolysis was carried out in an isothermal reactor heated by a horizontal electric furnace. At the beginning of each run, 40 g of pretreated biosludge (irregular spherical shape with a diameter of 1.0–1.5 cm) was placed in the middle of a quartz tube (internal diameter 30 mm and length 70 cm). High purity (99.995%) nitrogen was used as the purging gas, which flowed through the sample bed at $2\,l\,min^{-1}$. The reactor was heated to the designated temperature at a rate of $15\,K\,min^{-1}$. For the pyrolytic study, the biosludge was dried at 100–105 °C to reduce the moisture content. In addition, the sludge could not be completely pyrolyzed at 300–400 °C, but some experimental data are included as a reference in this study (Tables 1, 2 and 5). Therefore, the biosludge pyrolysis experiments were mainly conducted at pyrolysis temperatures ranging from 500 to 800 °C. After pyrolysis, the reactor was cooled to room temperature before the pyrolysis residue was removed for quantification and characterization. The biosludge pyrolysis residue was weighed on an analytical balance (Mettler-Toledo, model AB204-S, Switzerland, weighing limit is less than 0.1 mg).

2.3. Chemical compositions of pyrolytic residues

To obtain a stabilized pyrolysis residue weight, 30 min was chosen as the optimal pyrolysis time in these experiments based on a previous study [22]. The nitrogen, carbon, hydrogen, and oxygen constituents were analyzed with an element analyzer (Heraeus CHN-O Rapid Element analyzer, USA). Sulfur and chloride concentrations were measured with a Tacussel Coloumax 78 (USA) element analyzer. Sulfanilic acid and 1-chloro-2,4-dinitrobenzene were used as standards.

Biosludge pyrolysis residue was digested with a mixture of $HNO_3:HClO_4:HF$ in a 3:5:2 proportion. The digested acid mixture was analyzed to determine the trace elements. A Perkin Elmer OPTIMA 3000 ICP-AES was used to determine the Al, Ca, Fe, K, Mg, Na, S, Co and Zn concentrations. Additionally, a SCIEX Elan Model 5000 ICP-MS manufactured by PerkinElmer was employed to determine the As, Ba, Cd, Cr, Cu, Mn, Ni, Pb, Sb, Se, Sr, Ag and V concentrations. Analysis was performed on five samples in duplicate for quality assurance and quality control.

2.4. Chemical composition of biofuels

Generally, fuel derived from biomass can be considered biofuel. But in this study, pyrolytic liquid and gas were the main biofuels obtained from biosludge.

The pyrolysis liquid was distilled to separate the oil from the liquid. The temperature program for distillation was as follows: heating to 120 °C ($20\,°C\,min^{-1}$) for 10 min to remove water and then heating to 250 °C ($10\,°C\,min^{-1}$) for 15 min to collect liquid oils. After that, the temperature was increased to 350 °C ($10\,°C\,min^{-1}$) for 10 min, which volatilized most of the liquid and left some char in the bottom of the distillate bottle. Over 80% of the liquid oil was collected at 200–250 °C. The composition of the pyrolysis oil was measured via gas chromatography with mass spectrometry.

A gas chromatography (GC) apparatus coupled with a mass spectrometry (MS) apparatus (GC–MS, model QP-2010; Shimadzu, Japan) was used to analyze the composition of biofuels. The temperature program using the DB-5 column (0.25 mm × 30 m, 0.25 μm film thickness, Agilent J&W) was as follows: 60 °C for 10 min, then raised from to 325 °C at a rate of 5 °C per min; injector and detector temperatures 250 °C; carrier gas nitrogen ($2\,ml\,min^{-1}$); detector dual FID; split ratio 1:30; and injection of 0.5 μl. GC peaks were identified by comparing the MS fragmentation pattern and relative retention time with those of the reference compounds available. The relative proportions of the biofuel constituents were expressed as percentages obtained by FID peak-area normalization.

2.5. Pyrolytic gas analysis

2.5.1. Chemical compositions of pyrolytic gas

Pyrolytic gases including CO, CO_2, SO_2 and NOx of sludge pyrolysis was measured by an infrared gas analyzer (ZSV, Fuji Electric System Co. Ltd., Japan). In addition, total hydrocarbons were analyzed by a heated hydrocarbon analyzer (Model 300-HFID, California Analytical Instruments, USA).

2.5.2. VOC in pyrolytic gas analysis

Volatile organic compound (VOC) samples were collected in glass bottles, and three to five duplicate runs were carried out to obtain representative samples. Pyrolytic gases were sampled from the exhaust pipeline and analyzed by the US EPA Method 18 integrated bag method [23]. Five consecutive samples were collected at each pipe at $0.5\,l\,min^{-1}$ (Gilian Personal Air Sampler) to yield average concentrations during the pyrolysis process.

VOC species were pre-concentrated in a purge-and-trap system (Entech 7100 instrument) and subsequently analyzed in a GC/MS (HP-6890 Gas Chromatograph and HP 5973N Mass Spectrometer). The GC was equipped with a fused silica capillary column (non-polar RTx-1, 105 m × 0.25 mm ID × 1.0 μm film thickness). Calibration standards were prepared by diluting a certified stan-

Table 1
Major element content (%) of pyrolytic residues ($n = 5$[a]).

Temperature (°C)	Residue elements content (%)			
	C	H	N	S
105	28 ± 3.5	4.5 ± 0.1	4.2 ± 0.3	1.8 ± 0.3
400	25 ± 2.5	2.4 ± 0.7	4.0 ± 0.7	2.5 ± 0.4
500	22 ± 0.4	1.1 ± 0.3	2.9 ± 0.4	3.0 ± 0.5
600	21 ± 1.0	1.0 ± 0.3	2.3 ± 0.4	3.2 ± 0.4
700	17 ± 0.5	1.0 ± 0.2	1.9 ± 0.2	3.4 ± 0.4
800	15 ± 2.9	0.8 ± 0.3	1.7 ± 0.2	3.6 ± 0.7

[a] n is sample number.

dard gas (56 Enviro-Mat Ozone Precursor, Matheson, USA) with ultra high purity nitrogen (99.995%) in dilution bottles. VOC analysis included the analysis of halogenated VOCs and the standard gases prepared by Matheson Gas Products, Georgia, USA.

The performance of the GC/MS was evaluated with perfluorotributylamine for quality control. The relative standard deviation for all VOCs was <15%, the accuracy ranged from $92 \pm 5\%$ (propane) to $103 \pm 9\%$ (p-ethyltoluene), and the method detection limit varied from 0.01 (n-decane) to 0.12 (n-butane) ppb.

3. Results and discussion

3.1. Raw material and pyrolytic residues

3.1.1. Major element composition

The oven-dried biosludge and the pyrolytic residues were analyzed for carbon, hydrogen, nitrogen, sulfur, and chlorine content using an elemental analyzer. Table 1 shows the results of element contents in the pyrolytic residue: carbon from 15% to 28%, hydrogen from 0.8% to 4.5%, nitrogen from 1.7% to 4.2%, and sulfur from 1.8% to 3.6%, respectively. Chlorine was not detected (<0.01%) in any residue or biosludge. Based on another study [10], oxygen content was high (32–38%) in biosludge. Therefore, the other elemental fraction could be the oxygen. The percentage of each element in the pyrolysis residue, except for sulfur, was less than that of the oven-dried biosludge. When pyrolytic temperatures increased, the elemental content (C, H, and N) decreased in the residues. The results also revealed that the amount of carbon, nitrogen, and hydrogen from the residues decreased when the pyrolysis temperature was

raised from 400 to 800 °C, suggesting that the carbon, nitrogen, and hydrogen were desorbed, but the sulfur was not. The residue sulfur content increased as the pyrolysis temperature increased throughout the experimental temperature range. This may be attributed to the fact that the sulfur forms stable high-boiling-point compounds (high bond energy of sulfur compound) with other pyrolysis products; therefore, the sulfur compound could be volatilized at a higher temperature [24,25].

3.1.2. Trace element composition

Trace element compositions in the pyrolysis residues of biosludge are summarized in Table 2. Ca, Al, Fe, Mg and Zn content were high in the dried raw material and pyrolytic residues. The results obtained for Zn, Ni, and Cr content were in the same range for both this study and the study of Dai et al. [26], but Cu, Pb and Cd were low and As was high in our study. Some elemental concentrations were toxic, i.e., Cd was 0.2–0.8 µg g⁻¹, Se was 0.8–9.6 µg g⁻¹, Cr was 24–68 µg g⁻¹, Pb was 4.4–17 µg g⁻¹, As was 41–135 µg g⁻¹, and Cu was 49–73 µg g⁻¹. The As and Cr content were in the range of that reported by Rauckyte et al. [27], but Cd and Pb were lower than in their study. Mn, Ni, S, V, and Sr could be concentrated after high-temperature pyrolysis. In contrast to other elements in pyrolytic residues, Cd concentration decreased because it was volatile at temperatures higher than 600 °C [28]. In addition, Zn, Pb and Se could be volatilized at high temperature. Based on other studies, the pyrolytic residue could be used as brick for construction material [29,30], as an adsorbent for pollution control [16,31], and as a bio-fertilizer for soil improvement [32,33].

3.2. Liquid product

3.2.1. Yield of pyrolytic products

Generally, the water content of sludge cakes obtained from the wastewater treatment plant of the petrochemical industry was 75–80%. Fig. 1 shows the biosludge reuse process and the mass fraction of the solid, liquid and gas phases. In the first step, the sludge cake was dried at 105 °C in an oven. At this step, about 65–70% weight of water vapor and volatile compounds was volatilized. The drying sludge residues were put into an electric furnace with influent nitrogen gas for pyrolysis at 500–800 °C. Results indicated that pyrolytic residues accounted for 8.5–13% of the weight, liquid prod-
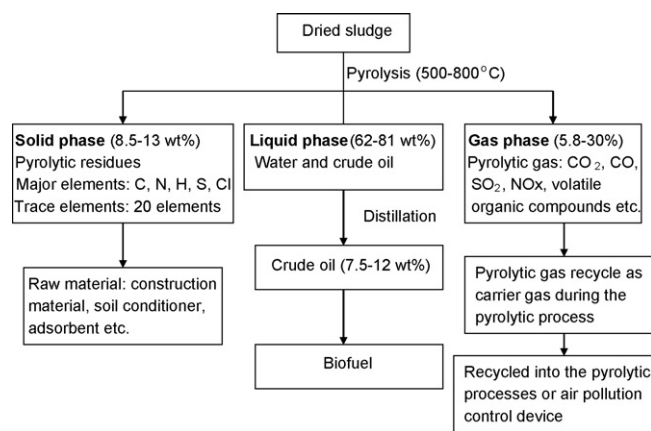
Table 2
Trace element content (mg-element/g-residue) of pyrolytic residues ($n = 5$[a]).

Element	105 °C	500 °C	600 °C	700 °C	800 °C
Al	4.72 ± 0.40	6.42 ± 0.62	9.50 ± 1.06	7.44 ± 1.99	8.46 ± 1.19
Ba	0.058 ± 0.001	0.083 ± 0.015	0.289 ± 0.285	0.091 ± 0.002	0.114 ± 0.005
Ca	65 ± 1.5	72 ± 2.8	113 ± 35	98 ± 18	94 ± 11
Cr	0.049 ± 0.002	0.048 ± 0.005	0.061 ± 0.001	0.068 ± 0.006	0.024 ± 0.004
Cu	0.049 ± 0.002	0.060 ± 0.001	0.073 ± 0.006	0.064 ± 0.002	0.073 ± 0.001
Fe	2.44 ± 0.200	2.86 ± 0.54	3.90 ± 0.52	3.33 ± 0.45	3.17 ± 0.36
K	0.177 ± 0.014	0.244 ± 0.031	0.322 ± 0.030	0.293 ± 0.010	0.358 ± 0.032
Mg	3.24 ± 0.25	4.767 ± 0.273	5.47 ± 0.45	5.82 ± 0.47	5.22 ± 0.11
Mn	0.082 ± 0.004	0.109 ± 0.003	0.134 ± 0.001	0.135 ± 0.006	0.185 ± 0.007
Na	0.382 ± 0.004	0.725 ± 0.021	0.953 ± 0.046	0.852 ± 0.061	1.34 ± 0.06
Ni	0.049 ± 0.001	0.071 ± 0.005	0.089 ± 0.005	0.085 ± 0.007	0.115 ± 0.002
Zn	1.94 ± 0.11	2.82 ± 0.18	3.55 ± 0.14	2.92 ± 0.11	0.973 ± 0.025
S	0.493 ± 0.013	0.785 ± 0.014	0.988 ± 0.017	0.967 ± 0.007	1.14 ± 0.04
Sr	0.519 ± 0.042	0.819 ± 0.097	1.01 ± 0.06	0.965 ± 0.000	1.16 ± 0.08
As	0.075 ± 0.014	0.041 ± 0.009	0.046 ± 0.005	0.083 ± 0.022	0.135 ± 0.002
Cd	0.0008 ± 0.0002	0.0006 ± 0.0001	0.0007 ± 0.0001	0.0004 ± 0.0001	0.0002 ± 0.0002
Pb	0.013 ± 0.003	0.0090 ± 0.0011	0.0140 ± 0.0025	0.0169 ± 0.002	0.0044 ± 0.0004
V	0.0014 ± 0.0002	0.0019 ± 0.0001	0.0021 ± 0.0003	0.0031 ± 0.0002	0.0036 ± 0.0002
Co	0.004 ± 0.002	0.0027 ± 0.0003	0.0022 ± 0.0004	0.0025 ± 0.0007	0.0010 ± 0.0007
Se	0.015 ± 0.002	0.0010 ± 0.0001	0.0054 ± 0.0069	0.0096 ± 0.0058	0.0008 ± 0.0004
Sb	0.015 ± 0.0005	0.0020 ± 0.0002	0.0057 ± 0.0066	0.0080 ± 0.0027	0.0015 ± 0.0001
Ag	0.0005 ± 0.0001	0.0005 ± 0.0001	0.0010 ± 0.0001	0.0005 ± 0.0001	0.0010 ± 0.0001

[a] n is sample number.

Fig. 1. Pyrolytic concept and mass fraction of biosludge reuse.

ucts (water and crude oil) for 62–81%, and the gas phase for 5.8–30%. Furthermore, the liquid product was distilled to product oil. There was 1.5–2.5 wt% of oil based on the original sludge cake. Domínguez et al. [34] investigated pyrolysis of sludge by an electric furnace; in their results, char was 10%, water was 59%, oil was 0.9% and gas was 30%. The product yields were similar to those obtained in this study, and the oil product was a little higher. The main components of biofuel were C (68–73%), H (10–11%), N (5.4–6%), and S (0.3–0.4%) with the pyrolytic temperature at 500–800 °C (shown as Table 3). In addition, the chlorine content was less than 0.01%. The carbon content increased slightly with an increase in pyrolytic temperature.

Hydrogen, nitrogen and sulfur contents did not vary significantly in the biofuel at different pyrolytic temperatures. The heat values of liquid products are 8600–10100 kcal kg^{-1}, similar to the values obtained with H_2O (10–20%) and diesel emulsion liquid [35,36].

3.2.2. Biofuel compositions (carbon number and composition fraction)

The pyrolysis liquid consisted of aqueous (containing primarily water and water-soluble organics including alcohols, ethers, aldehydes, carboxylic acid, etc.) and oil fractions. Pyrolytic oils are complex mixtures of organic compounds with a wide variety of chemical groups. Generally, pyrolysis of sludge yielded liquid products that contained significant amounts of oxygenated compounds and unacceptable amounts of nitrogen and possibly sulfur [37]. The standards of chemical compositions of biofuel are difficult to obtain; therefore, the chemical content of the biofuel could not be quantified in this study. Therefore, mass spectrometry was applied to identify the potential chemical species and measure their fraction by the peak area of the spectrum. Similar semi-quantifiable methods were applied in other work [34,37,38].

The detailed compounds of biofuel are shown in Table 4, which was created using the percentage of area of the chromatographic peaks. Results indicated that 4-hydroxy-4-methyl-2-pentanone (C_6) (28–53%), pentadecane (C_{15}) (1.2–9.5%), nonadecanenitrile (C_{19}) (1.1–6.5%), 3-methylindole (C_9) (1–4.2%), 4-hydroxypentan-2-one (C_5) (1.4–3.5%), heptadecane (C_{17}) (1.2–5.8%), cetyl alcohol (C_{16}) (1.6–2.6%), nitrobenzyl alcohol ($p+m$) (C_7) (1.5–3.0%) and nonadecane (C_{19}) (1.2–1.6%) were the major components found using GC/MS identification. Based on the carbon number fraction of bio-

Table 3
Major element compositions (%) of liquid product.

Pyrolytic temperature (°C)	Elements (%)				Heating value (kcal kg^{-1})
	C	H	N	S	
500	68 ± 3.8	11 ± 1.7	6.0 ± 0.4	0.35 ± 0.05	8585 ± 650
600	71 ± 7.5	9.8 ± 2.5	5.8 ± 0.5	0.42 ± 0.10	9560 ± 780
700	72 ± 4.3	9.7 ± 1.2	5.7 ± 0.7	0.34 ± 0.06	10130 ± 1020
800	73 ± 5.6	11 ± 0.8	5.4 ± 0.6	0.28 ± 0.05	9970 ± 560

Cl content was less than 0.01%.

Table 4
Typical compounds (%) detected in oil derived by the biosludge pyrolysis.

500 °C		600 °C		700 °C		800 °C	
Compounds	Area	Compounds	Area	Compounds	Area	Compounds	Area
4-Hydroxy-4-methyl-2-pentanone	48	4-Hydroxy-4-methyl-2-pentanone	36	4-Hydroxy-4-methyl-2-pentanone	53	4-Hydroxy-4-methyl-2-pentanone	28
Nonadecanenitrile	6.5	Pentadecane	9.5	Heptadecane	5.8	Indole	7.8
p-Cresol	4.0	Indole	4.8	4-Hydroxypentan-2-one	3.5	Tempidon	5.5
3-Methylindole	4.0	3-Methylindole	2.6	Octadecanonitrile	3.2	3-Methylindole	4.2
Indole	3.3	2-Hexyl-1-decanol	2.6	Cetyl alcohol	2.5	p-Cresol	3.3
4-Hydroxypentan-2-one	3.0	p-Cresol	1.8	Nitrobenzyl alcohol (p+m)	2.3	Nitrobenzyl alcohol (p+m)	3.0
2-Hexyl-1-decanol	2.7	Cetyl alcohol	1.6	Nonadecanenitrile	2.3	Phenol(JAN)	3.0
Cetyl alcohol	2.6	Nonadecane	1.6	Hexadecan-3-ol	1.7	1-Tridecene	2.2
Nitrobenzyl alcohol (p+m)	2.0	Nitrobenzyl alcohol (p+m)	1.5	Nonadecane	1.6	Tridecan	2.0
Tetracosane	1.8	Heptadecane	1.5	3-Aminocarbazole	1.3	Heptadecane	2.0
1-Octadecene	1.3	4-Hydroxypentan-2-one	1.4	Hexadecanamide	1.2	Cetyl alcohol	2.0
Heneicosane	1.3	n-Hexadecane	1.3	Heneicosane	1.2	4-Ethylphenol	1.8
Pentadecane	1.2	1-Heptadecene	1.3	3-Methylindole	1	4-Hydroxypentan-2-one	1.8
Heptadecane	1.2	Phenol	1.2			1-Tetradecene	1.8
Nonadecane	1.2	N-Hexadec-1-ene	1.1			n-Tetradecane	1.8
		Nonadecanentrile	1.1			N-Hexadec-1-ene	1.7
		Eicosane	1			3-Hexen-2-one	1.3
		Heneicosane	0.8			Nonadecane	1.2
		Tetracosane	0.8			Orthocresol	1.2
		1-Octadecene	0.6			Tropilidine	1.2
						Tetracosane	0.9
Amounted	84.1	Amounted	74.1	Amounted	80.6	Amounted	77.7

Table 5
Concentration of pyrolytic gas at the sludge pyrolysis.

Temperature (°C)	THC (ppm)	CO_2 (%)	CO (ppm)	SO_2 (ppm)	NOx (ppm)
105	16.8 ± 4.0	<0.002	78 ± 2.5	<0.001	0.46 ± 0.10
300	954 ± 345	0.32 ± 0.20	246 ± 52	0.092 ± 0.052	28 ± 13
500	3523 ± 1075	0.80 ± 0.35	1180 ± 468	1.31 ± 0.54	23 ± 6.8
600	8880 ± 5600	1.3 ± 0.5	3999 ± 1618	13 ± 7.3	32 ± 7.7
700	11821 ± 7700	1.7 ± 1.0	7379 ± 2872	13 ± 5.3	35 ± 5.7
800	11237 ± 2592	1.56 ± 0.25	4576 ± 1012	11 ± 2.7	25 ± 2.3

fuel, C_5–C_9 accounted for about 60%. In addition, the variation of the composition fraction of liquid biofuel at different pyrolytic temperatures may be caused by the cracking and reformulation of organic molecules at high temperature. But this study did not generate enough data to prove these phenomena. Some studies have provided a few concepts to explain the reaction of sludge pyrolysis, but they do not explain the temperature effect on pyrolytic products [10,34]. Further study is necessary to explain why chemical reformulation and cracking during the pyrolytic process cause the chemical composition variation in the pyrolytic liquid product.

According to Table 4, aliphatics (n-alkanes, alkenes and branched hydrocarbons), oxygenated compounds (oxygenated aromatics compounds, ketones, alcohols, etc.), and nitrogenated compounds were the main components in liquid biofuel. Although low aromatic and polar content is desired in fuels, they are very important as raw materials in industry, and the proteins and lipids in sludge are responsible for the polar and aromatic content in pyrolysis fuel. Ideally, the components in oil should be straight chain hydrocarbons, as these have a high heating value and lower viscosity. In this study, the biofuel contains a high portion of aliphatics, which is similar to the composition of fuel oil.

3.3. Pyrolytic gas compositions

3.3.1. Major gas constituents

The sludge was pyrolyzed at temperatures from 500 to 800 °C; then the liquid product was collected and the pyrolytic gas was measured. Table 5 shows the major gas composition during pyrolysis. Results indicate that the concentrations of major gas pollutants were low during the drying process at 100 °C. This data could be

regarded as reference information during the pretreatment process of drying. While the pyrolytic temperature was held at 500 °C, the concentration of pyrolytic gas was increased to reach a high of about 700 °C. Total hydrocarbon concentration was 1.2%, CO concentration was 0.7%, SO_2 was 13 ppm, NOx concentration was 35 ppm and CO_2 was 1.7% at 700 °C. Based on the gas concentration data, the pyrolytic gas could be recycled during the pyrolysis processes to reduce pyrolytic gas emission, and the pyrolytic gas could be concentrated as a fuel that could be used to reduce the cost of sludge reuse. The method could be useful for pyrolytic gas treatment and has been successfully used in a coal-fire power plant [39].

3.3.2. Volatile organic compounds

Generally, the pyrolytic gas was rich in hydrocarbon, so it could be combustible. Toxic components are another concern during the reuse of biosludge. The VOC compositions of pyrolytic gas are shown in Table 6. In this study, five samples were taken in each run based on the pyrolytic time and three to five runs were carried out for each pyrolytic temperature. Therefore, the data in Table 6 were the average concentration and standard deviation of 15–25 VOC samples. The high variation could be caused by the sampling times.

In addition, propene, propane, 1-butene, n-butane, isobutene, toluene and benzene were the major VOCs of the pyrolytic gas at 500–800 °C. The average concentration of propene was 148–392 ppm, propane was 116–152 ppm, 1-butene was 73–136 ppm, toluene was 63–94 ppm and benzene was 7.5–32 ppm at 500–800 °C. Most of the VOCs were greater than 5 ppm for the top 20 species. In addition, the aromatic compounds including styrene, isopropylbenzene, n-propbenzene, m-, p- and o-ethyltoluene, 1,3,5-

Table 6
Top 20 volatile organic compound concentrations (ppm) in the pyrolytic gas during biosludge pyrolysis.

| Compounds	500	600	700	800
Propene	148 ± 109	154 ± 119	281 ± 177	392 ± 274
Propane	152 ± 117	125 ± 91	136 ± 76	116 ± 77
Isobutane	35 ± 16	28 ± 6.8	32 ± 8.8	18 ± 6.8
1-Butene	73 ± 55	80 ± 57	116 ± 66	136 ± 97
n-Butane	39 ± 30	33 ± 23	32 ± 16	26 ± 19
trans-2-Butene	15 ± 11	17 ± 13	20 ± 11	21 ± 15
cis-2-Butene	9.7 ± 7.2	12 ± 8.4	14 ± 7.8	16 ± 11
Isopentane	8.9 ± 7.3	9.8 ± 5.2	8.2 ± 4.4	7.2 ± 4.2
1-Pentene	7.3 ± 7.2	9.8 ± 8.4	14 ± 10	17 ± 16
n-Pentane	12 ± 10	8.5 ± 6.5	7.7 ± 3.9	6.3 ± 4.3
Isoprene	11 ± 10	8.5 ± 6.9	7.6 ± 4.1	6.3 ± 4.5
cis-2-Pentene	5.9 ± 6.5	5.1 ± 1.9	2.4 ± 0.75	2.9 ± 1.9
1-Hexene	8.3 ± 7.3	9.6 ± 8.3	21 ± 14	23 ± 23
n-Hexane	10 ± 7.8	7.7 ± 4.6	4.4 ± 2.7	5.6 ± 2.4
Benzene	31 ± 9.4	7.5 ± 5.0	16 ± 9.8	32 ± 23
n-Heptane	6.6 ± 6.2	4.7 ± 3.4	15 ± 9.3	11 ± 12
Toluene	94 ± 47	63 ± 33	85 ± 46	90 ± 59
Ethylbenzene	8.5 ± 3.4	8.1 ± 2.8	5.6 ± 2.9	8.8 ± 5.7
m,p-Xylene	5.3 ± 0.84	5.9 ± 0.67	2.7 ± 0.89	5.7 ± 1.6
n-Undecane	7.5 ± 4.4	16 ± 0.50	7.0 ± 0.73	11 ± 1.2
Sum of top 20 species	687	613	863	953
Sum of 52 species	762	765	882	1061
Percent of top 20 species (%)	90	80	94	90
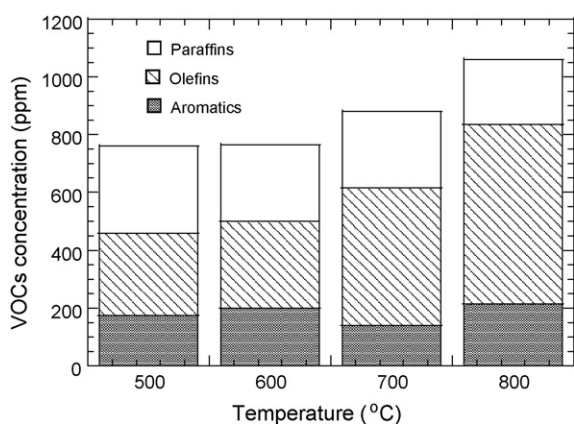
Fig. 2. VOC group concentration of pyrolytic gas during the sludge pyrolysis.

, 1,2,4- and 1,2,3-trimethylbenzene, and *m*- and *p*-diethylbenzene were higher than 2 ppm. These 20 species contributed 80–94% of the concentration fraction of 52 VOCs. The concentration of these VOCs was between 762 and 1061 ppm in the temperature range from 500 to 800 °C. However, the content of some of the toxic species (e.g., benzene, toluene, ethylbenzene and xylene) was high; therefore, the pyrolytic gas should be well disposed before emission. Based on the pyrolytic gas compositions, which were similar to the study by Karayildirim et al. [37], the content of combustible gas in pyrolysis gas is high.

Fig. 2 shows the VOC group profile for biosludge pyrolytic gas at 500–800 °C. Results indicated that olefins were 37–58%, paraffins were 21–40%, and aromatics were 16–26%. The olefin compounds were the major VOCs in pyrolytic gas of sludge, which may be attributed to the raw material of the petrochemical industry and the characteristics of biosludge (cells of microorganisms).

4. Conclusions

Biosludge can be reused to produce biofuels, combustible gas, and char residues after pyrolysis. The results of this study indicated that the Ca, Al, Fe, Mg and Zn contents were high in the dried raw material and pyrolytic residues. Some toxic element contents in residues were in the acceptable range for reuse. Liquid biofuel contained 68–73% C, 10–11% H, 5.4–6% N, and 0.3–0.4% S at the various pyrolysis temperatures. High polar and oxygenated compounds were measured in liquid biofuel, and their heat values were 9000–10,000 kcal kg^{-1}. In addition, propene, propane, toluene, benzene, and 1-butene were the major VOCs, and olefins were the main fraction of the pyrolytic gas. Benzene, toluene, ethylbenzene and xylene concentration were high in pyrolytic gas; therefore, the safe disposal of pyrolytic gas is necessary. The pyrolytic gas was rich in hydrocarbon; it could be recycled as a carrier gas during the pyrolysis process to reduce the exhaust volume. Based on the treatment procedures of biosludge, the sludge could be reused and safely disposed to reduce the environmental impact.

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