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Investigation of polycyclic aromatic hydrocarbons (PAHs) formed in three-phase products from the pyrolysis of various wastewater sewage sludge



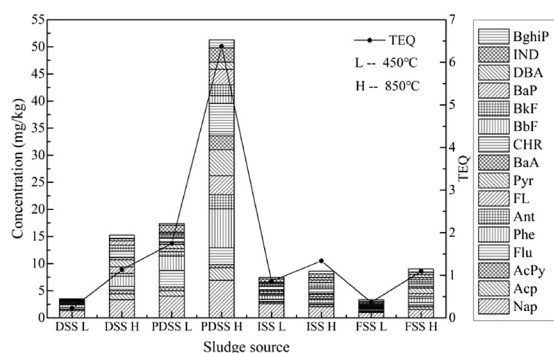
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GRAPHICAL ABSTRACT

PAHs content distribution and TEQ values in pyrolysis liquid products of sludge from different sources



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ABSTRACT

This study investigated the presence and concentration of 16 U.S. EPA priority controlled PAHs in gas, bio-oil and residues from the pyrolysis of different sewage sludges. We studied the temperature as a key influential factor for the formation of 16 targets PAHs and the effect of sludge source on the distribution of different molecules' PAHs were analyzed. Results showed that most of the 16 PAHs were formed during sludge pyrolysis and mainly ended up in bio-oil and gas. The distribution of PAHs in bio-oil was mostly dependent on pyrolysis temperature. With the increase of pyrolysis temperature from 450°C to 850°C, it has been observed an increase of PAHs concentration in the bio-oils as follows: 16 % (ISS), 1.3 % (food manufacture wastewater sludge, FSS), 194 % (printing and dyeing wastewater sludge, PDSS), 334 % (DSS). 2, 3 and 4-ring PAHs dominate, and their total mass proportion is over 70 %. In gas, the types and concentrations of PAHs were less than in bio-oil. PAHs yield in solid was very low, and a trace content of PAHs of 0.0161 mg kg⁻¹ was detected from the solid after the pyrolysis of DSS, while PAHs in solid for ISS and FSS are even non-existent and would cause fewer environmental problems.

1. Introduction

Disposal of dewatered sewage sludge as a by-product after

wastewater treatment plants is a significant environmental concern throughout the world. The quantity and types of contaminants contained in sludge pose a challenge for its effective disposal. To dispose of

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a large amount of produced sludge, its reuse technology in an environmentally friendly way has attracted much attention [Syed-Hassan et al., 2017; Folgueras et al., 2013; Zhou et al., 2014; Wang et al., 2016]. As a result of the significant calorific value (5000–6000 KJ/Kg) of dried sewage sludge in comparison with wood (15000–17000 KJ/Kg), the use of thermochemical conversion technologies provide an interesting disposal way to produce different chemicals using sewage sludges as starting materials. The physical and chemical properties of sewage sludge are influenced by the origin of wastewater and its treatment processes they result from. The chemical reagent and wastewater treatment processes used in different wastewater treatment plants also impact the chemical properties and components of the resulting sludge.

In China, except for domestic municipal wastewater, industrial wastewater treatment is being one production source of the massive amount of sewage sludge due to the rapid development of modernization and industrialization. The production of municipal sludge in cities and industrial sludge was 43.82 million tons and 40 million tons in 2018, respectively. The dispose of sludge in landfills has been completely banned in China and its stabilization, harmlessness and resource treatment and disposal are therefore being encouraged. Pyrolysis was reported as an economical and environmentally acceptable disposal way for the treatment of sewage sludge, which can reduce more than 50 % of sludge volume and stabilize the organic components [Chan and Wang, 2018]. An additional positive outcome is that such treatments can produce solid materials with adsorption property [Patryk et al., 2014], high heating value syngas and valuable chemicals from the obtained bio-oil [Magdalena and Patryk, 2016; Tsai et al., 2009a; Shen and Zhang, 2003].

The pyrolysis bio-oil typically consists of a complex chemical mixture of organic compounds, with the composition and yield changing with sludge source and used pyrolysis process conditions [Shen and Zhang, 2003; Tsai et al., 2009a, 2009b]. In the process of pyrolysis of sludge, some persistent organic pollutants were also formed, such as PAHs (polycyclic aromatic hydrocarbons). There are 16 kinds of PAHs that appeared on the US EPA (Environmental Protection Agency) priority controlled pollutants list. Their release is drawing great public attention due to their substantial toxicity and carcinogenic, teratogenic, and mutagenic characteristics. The thermal chemical process of fuel and biomass and is a public issue in China influence the extensive emission of PAHs. Investigations on the formation of PAHs during the thermal treatment of sewage sludge in the environment has extensively studied by some researchers [Chen et al., 2014; Deng et al., 2009; Waqas et al., 2014]. Researchers [Shen and Zhang, 2003; Tsai et al., 2009a, 2009b] studied the distributions of PAHs in pyrolysis liquid from different types of sewage sludge. It was noted that PAHs formation mostly depends on its thermal conditions. However, there is not much available information about the influence of sludge source on the generation of PAHs in the resulting pyrolysis products.

Sewage sludges from various industrial and municipal wastewater treatment were sampled to comprehensively study the generation mechanism of 16 PAHs in the pyrolysis process of different types of sludges. The sampled sludge was pyrolyzed to collect bio-oils, gas and solid residues. In this study, the 16 USEPA PAHs were quantified regarding their generation and distribution in the gas, bio-oil, and solid residues. The temperature as a key influential factor was determined, and indications of the different aromatic molecules PAHs produced were obtained. The yield of each phase and PAHs distribution influenced by temperatures were analyzed to help with understanding generation and their transport mechanism of PAHs. The obtained results could also be significant in achieving suitable methods of various sludges disposal environmentally friendly.

Table 1

The proximate analysis of different sewage sludge (dry base).

Sewage sludge (SS)	W/%	A _d /%	V _d /%	FC _d /%	H _d /MJ. kg ⁻¹
DSS	2.02	40.07	53.69	4.22	13.5
PDSS	2.49	43.79	49.85	3.87	13.02
FSS	1.38	50.69	44.09	3.84	6.58
ISS	3.48	59.03	33.44	4.05	5.48

W – moisture content, V_{ad}-volatile matter content, A_{ad} - the amount of ash, M_{ad} - the moisture content, FC_{ad} -The fixed carbon content, H_d- heating value, d – dried basis weight.

2. Materials and methods

2.1. Material

Four kinds of sewage sludge were collected from different wastewater treatment plants of Zhejiang, China, including domestic wastewater sewage sludge (DSS) in Linan, Printing and Dyeing wastewater sewage sludge (PDSS) in Xiaoshan, industrial mix wastewater (ISS) in Hangzhou, and food manufacture wastewater sewage sludge (FSS) in Fuyang, respectively. The raw sewage sludge underwent mechanical dewatering, but no aerobic digestion before sampling. It was dried in a lab-scale air convection oven at 105°C to a constant weight. Table 1 showed Proximate and ultimate analysis of the used sludge on air dry basis, which were determined according to the National Testing Standard of Proximate Analysis of Coal (GB/T 212–2008) in China. The fixed carbon content was calculated based on mass balance. Standard for determination of carbon and hydrogen in coal (GB/T 476–2008), Standard for determination of nitrogen in fuel (GB/T 19227-2008) and Standard for determination of total sulfur in coal (GB/T 214–2007) were applied to determine the contents of C, H, N, and S in sludge. The content of oxygen was determined by difference. The net calorific value (Q) was determined based on GB/ T213-2008.

Here, Table 1 The proximate analysis of different sewage sludge (dry base)

2.2. Sampling of three-phase pyrolysis products

The sampled sewage sludge was pyrolyzed to collect three-phase products, bio-oil, gas and solid. Fig. 1 shows the experimental setup. The furnace and the collection procedure of resulted pyrolysis products were described in detail in an early study [Hu et al., 2019]. To assess the reproducibility of the installation and the experimental operation, a series of representative experiments of sludge pyrolysis were replicated, such as pyrolysis of various sludge at 850 °C and 450 °C. Base on the comparison of the yields, chemical compositions of pyrolysis products for the replicates, it was found that the errors between the obtained results of the replicate were below 10 %. Approximately 25 g of dried sludge was added into the furnace for each test. The pyrolysis experiments were done by heating the furnace to its final temperature with a 30 °C/min heating rate and 10 min of residence time at the final temperature. Two representative pyrolysis temperatures (low and high) were selected to compare the effect of temperature on PAHs formation in three-phase products, including 450 °C and 850 °C. The syngas outlet was passed through three consecutive condensers placed in ice-water baths. The nitrogen at a flow rate 1 L/min was kept to prevent the pyrolysis gas from accumulating in the furnace and avoid the impact of potential oxygen. The condensed oil was retrieved using dichloromethane and kept for further chemical analysis. The uncondensed syngas was passed through a XAD-2 resin column and a set of dichloromethane (DCM) scrubbing solutions in ice baths, which could absorb PAHs and other non-condensed compounds in the gas effluent, and was finally collected using sampling bags. After completed each pyrolysis experiment, the solid sample has been cooled down to room temperature in an inert atmosphere before the solid was collected.

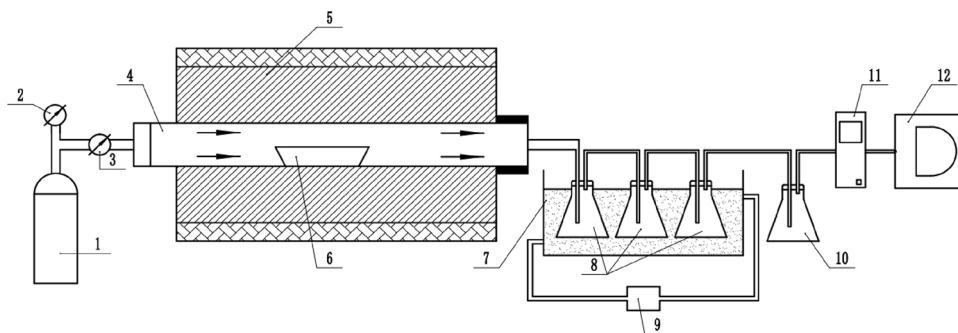


Fig. 1. Schematic diagram of sewage sludge pyrolysis equipment.

The yields of pyrolysis oil and solid were obtained by calculating the mass of recovered products over the mass of sludge feed. The yield of pyrolysis syngas was calculated by the mass difference over the mass of sludge feed. The residue, condensed oil, resin and DCM were respectively saved and were separately analyzed for PAHs in solid, liquid and gas phases.

Here, Fig. 1 Sewage sludge pyrolysis system to collect syngas, bio-oil and solid

2.3. PAHs analysis

US EPA method 8100 was selected as a reference to measure PAHs, with a slight change in the bio-oil and solid products pretreatment. The operation procedure of pretreating bio-oil and PAHs analysis were reported in the authors' previous work [Hu et al., 2013, 2019]. The duplicated experiments of the PAHs analysis were conducted for each sample to ensure the accuracy of the data. The 16 targets PAHs were determined using GC-MS CP3800-Saturn 2000. One microliter of the sample was injected into the capillary column with an auto-sampler. More detailed information regarding the quality control of PAHs analysis was reported in the authors' earlier publication [Hu et al., 2013]. In this study, the accuracy and repeatability for the pretreatment method of bio-oil and solid residue and GC-MS analysis methods were verified by running blank measurement and recovery measurements with edible oil and PAHs standards. The recovery efficiencies of the target PAHs were between 80 % and 99 %. The 16 target PAHs concentrations in the dried sewage sludge were analyzed and determined based on The National Measurement Standard of Determination of PAHs in Oil (SN/T 1877.3-2007; ISO 18,287:2006 (E)). The gas sample included XAD-2 resin and DCM. The XAD-2 resin was extracted using the obtained DCM. Then the resulting DCM was concentrated to 1 drop to transform the solvent to hexane. The sample continued to be concentrated and fixed to 100 mL using hexane. The 0.1 u L of the fixed sample was introduced to GC/MS analysis.

3. Results and discussions

In this study, results regarding concentration distribution and mass proportion of PAHs generated during the pyrolysis were expressed as mg PAH of 1 kg target sample and % of the total target PAHs, respectively. The data regarding the 16 PAHs are displayed and classified by the number of the benzene ring and their distribution profiles.

The high-ring PAHs means more than five rings PAHs, including benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), indeno(1,2,3-cd)pyrene (InD), dibenzo(a,h)anthracene (DBB), benzo(g,hi)perylene (BghiP). The middle-ring PAHs means four rings PAHs, including fluoranthene (FL), pyrene (Pyr), benzo(a)anthracene (BaA), chrysene (CHR). The low-ring PAHs means two and three rings PAHs, including naphthalene (Nap), acenaphthylene (Acpy), acenaphthene (Acp), fluorene (Flu), phenanthrene (Phe), and anthracene (Ant) [Hu et al., 2014]. The toxic Equivalent Quantity (TEQ)

values were calculated using the toxic equivalent factor (TEF) concept. This has been done to characterize the carcinogenic properties of PAH more precisely, to evaluate the influence of sludge sources on the harmful health effect of the resulted pyrolysis products, and to characterize the real toxicity. The toxic equivalent factor (TEF) was employed by comparing every compound with the BaP owning the highest value of TEF [Nisbet and Lagoy, 1992].

3.1. PAHs concentrations in sewage sludges

Some researchers reported that sewage sludge contains organic pollutants such as PAHs [Khadhar et al., 2010; Dai et al., 2007]. The distributions of 16 PAHs in sewage sludge from different sources were analyzed, including their contents, types, and TEQ-value, as shown in Fig.2. The concentration of 16 PAHs in different sludges was varied as their source. The total content of 16 PAHs in DSS was the highest, followed by ISS, PDSS and FSS, which were 1.61 mg/kg, 1.57 mg/kg, 1.14 mg/kg and 0.59 mg/kg, respectively. Bghip, FL, Pyr, BbF and DBA occupy the highest contents among the detected PAHs in DSS. For PDSS, the contents of NaP, Phe, CHR and BkF are higher than other PAHs. The mass proportion of PAHs with different rings is also varied as their source. 4-ring PAHs have the highest mass proportion, ranging from 27.93 % (ISS) to 34.15 % (PDSS). 6-ring PAHs in PDSS and FSS have the lowest mass proportion, which is 10.4 % and 9.4 %. 3-ring PAHs in DSS and ISS have the lowest mass proportion, which is 8.3 % and 11.3 %, respectively. It was reported that the PAHs in the raw sewage sludge was about 0.251 mg/kg, a rather low value for sewage sludge since it varied from 0.096 to 7.718 mg/kg for nine samples from Tunisia [Khadhar et al., 2010]. As a result of the complex source of the four kinds of sewage sludge, the effect of the origin of sewage sludge on their PAHs concentrations will not be further discussed in this study. It needs relevant information to explore the source of PAHs, such as treatment methods of wastewater, the chemical composition of wastewater, which will be investigated in future research work. But the effect of original PAHs in sewage sludge on the generation of PAHs in pyrolysis products was discussed in this study.

The TEQ-value of PAHs in four sludges was 0.03547 (FSS) < 0.11 (PDSS) < 0.17 (DSS) < 0.18 (ISS), which was basically consistent with the variation trend of total PAHs contents in different sludge. The TEQ value of PAHs in ISS is slightly higher than that in DSS, which is contrary to the concentration distribution trend of the PAHs. This may be because the toxicity equivalent factor (TEF) of BaP in ISS is 0.064, which is higher than that of DSS (0.052).

Here, Fig. 2 The contents of PAHs in four kinds of sewage sludges and their TEQ values

3.2. Product yields

Fig. 3 (a) and (b) show the yields of gas, bio-oil and solid residues generated from the pyrolysis of DSS, PDSS, FSS and ISS at the low temperature (450 °C) and the high temperature (850 °C), respectively.

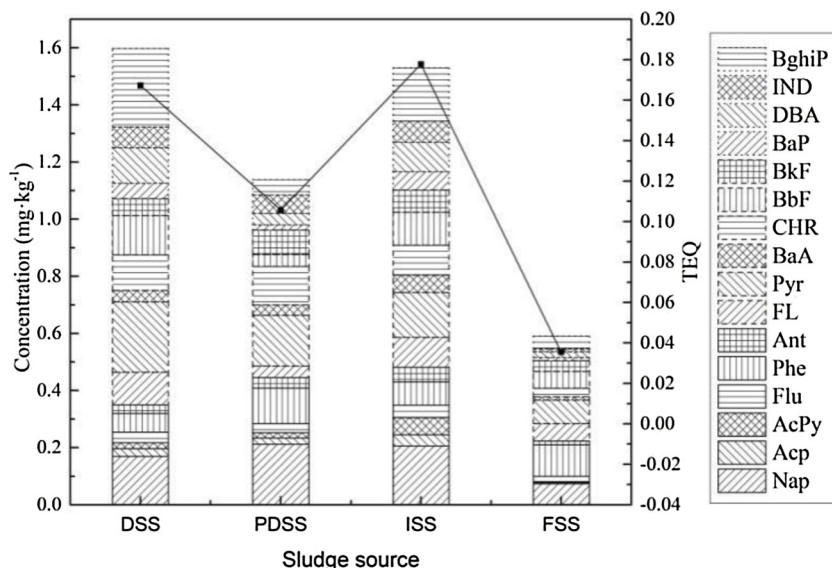


Fig. 2. The contents of PAHs in four kinds of sewage sludges and their TEQ values.

Product yields showed an evident difference resulted from the various sludge source and the operating pyrolysis temperature. Among them, the solid has the highest yield, ranging from 52.6 % for DSS to 75.7 % for ISS, followed by the bio-oil yields, ranging from 19.9 % (ISS) to 43 % (DSS). The gas-phase product yields are the lowest, especially for DSS, only 4.25 %. At high-temperature pyrolysis, the yields of solid and liquid products after the pyrolysis of four sludges were still very high. However, it is also noted that an increased temperature resulted in the reduction of the solid product yields for the four sludges, which are decreased to 62.3 % (FSS), 49.2 % (PDSS), 68.0 % (ISS) and 49.1 % (DSS). The highest yield of bio-oil is 43 % from DSS, and the lowest is 20 % for ISS. The bio-oil yields of PDSS and FSS are similar, which are 30 % and 27 %. The variation on the yields could be mainly due to the sludge source and their ash contents. ISS is generated after various industrial wastewater treatment and contained a relatively lower content of volatile matter, while DSS mainly comes from domestic sewage, which contains abundant organic matter.

Here, Fig.3 the yields of the pyrolysis products from the four kinds sewage sludge

3.3. PAHs in bio-oil

Temperature is the most investigated parameters in PAHs formation

[Dai et al., 2014a; Qin et al., 2017]. It can be noted that 16 kinds of PAHs were all detected out in the obtained bio-oil, but their fraction distribution was quite different, as shown in Fig.4. Among the four kinds of bio-oils, 2, 3 and 4-ring PAHs dominate, and their total fraction proportion is over 70 %. NaP has the highest mass proportion, ranging from 22.9 % for PDSS to 37.0 % for DSS, followed by Phe (14.3 %) and Flu (1 7.5 %, Phe (9.1 %) and BghiP (8.9 %). The proportions of 5-ring and 6-ring PAHs produced from FSS were much higher than that in other sludges, which are 20 % and 13 %, respectively. Because of the difference in chemical characteristics of PAHs with different ring numbers, the formation rules of different rings PAHs in the thermochemical conversion process are also discussed in the literature [Zhang et al., 2016; Muhammad et al., 2014].

When the pyrolysis temperature rises from 450°C to 850°C, the mass proportion of 16 PAHs has changed significantly. For instance, NaP in bio-oil from DSS decreased at most by weight of 42 %. Other 2, 3 -ring PAHs also slightly decreased, while 4 ring PAHs and the high-molecules` PAHs in bio-oil of DSS and PDSS increased. For ISS, the mass proportion of high-molecules` PAHs in bio-oil increases. Also, it can be seen that higher temperatures at pyrolysis can promote the generation of middle and high molecules` PAHs in bio-oils. It has been elucidated in the literature that a high-temperature environment promotes the formation of PAHs with more than 4 rings [Dai et al., 2014a, 2014b;

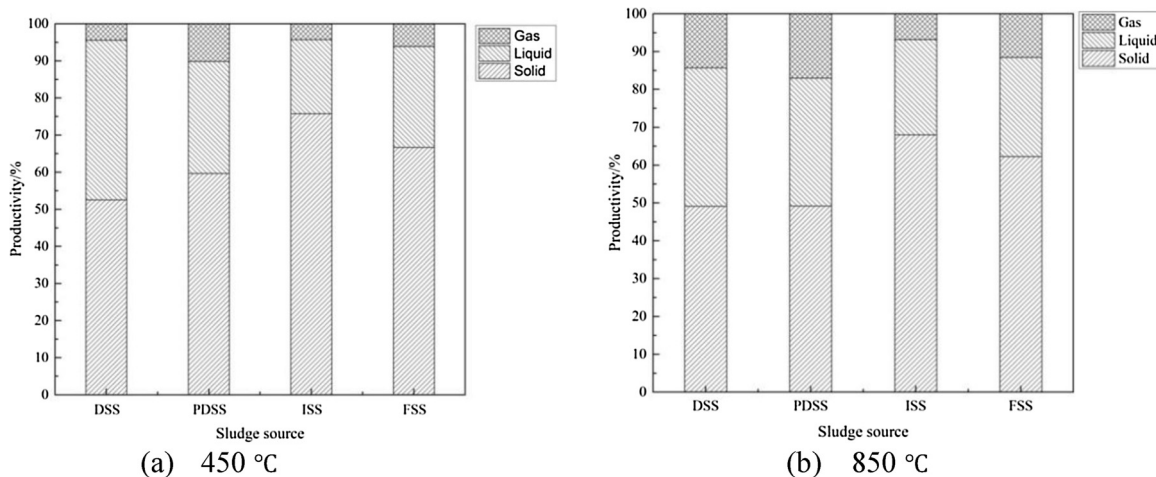


Fig. 3. the yields of the pyrolysis products from the four sewage sludge.

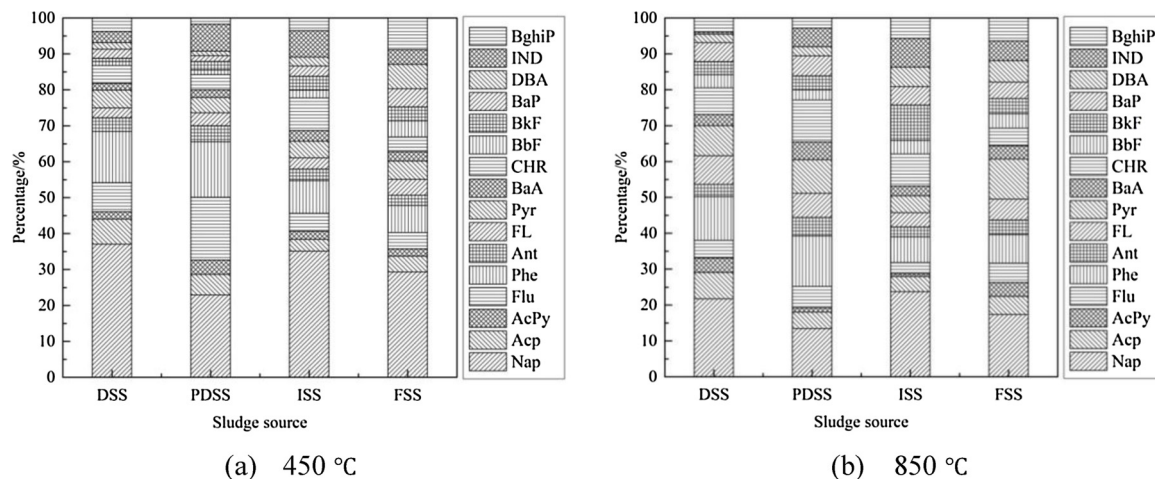


Fig. 4. The mass proportions of 16 PAHs in bio-oil from the pyrolysis four kinds of sewage sludge.

Sanchez et al., 2009; Hu et al., 2014].

Here, Fig. 4 The mass proportions of 16 PAHs in bio-oil from the pyrolysis four kinds of sewage sludge.

The concentration distribution and TEQ-value of 16 PAHs in bio-oils were shown in Fig.5. Likewise, the average is based on two samples for each type. The experimental errors of the concentrations of 16 PAHs in the duplicated tests are less than 10 %. The total content of 16 PAHs in bio-oil produced by PDSS at 850°C was highest, which was 51.25 mg kg⁻¹. This would be explained that PDSS from the treatment of dyeing wastewater with the addition of chemical conditioning agents, such as slaked lime. The slacked lime could be an additive to promote more PAHs at 850°C.

With the increase of pyrolysis temperature from 450°C to 850°C, the increased rates of PAHs concentration in the four kinds of bio-oil were as follows: ISS (16 %) < FDD (1.3 %) < PDSS (194 %) < DSS (334 %). It can be seen that the pyrolyzed DSS gave rise to the highest increase of PAHs production, which may be related to the highest content of volatile matter in DSS.

Here, Fig. 5 PAHs content distribution and TEQ values in pyrolysis liquid products of sludge from different sources

When PAHs are classified by benzene ring number (Fig.6), the change is evident in this study: the 2-ring and 3-ring PAHs are dominant in all the bio-oils from the pyrolysis of four sludges. Especially for PDSS, the concentration of 2 and 3-ring PAHs is as high as 22.73 mg kg⁻¹,

which accounts for more than 70 % of the whole PAHs detected. According to the profile presented in Fig.6 (a) and (b), it can thus be deduced that PAHs with more rings are easily decomposed at a higher temperature.

Here, Fig. 6 The content distribution of high, medium and low ring PAHs in bio-oil

3.4. PAHs in gas phase product

Fig. 7 (a) and (b) show the mass proportions of 16 PAHs in gaseous products from the pyrolysis of four sludges. Variation of PAHs in the syngas along with the temperature and sources of sludge were similar to the bio-oil. However, the composition of PAHs in gas was somewhere different from that of bio-oil. Composition analysis of gas showed that only naphthalene (NaP), acenaphthene (AcP), fluorene (Flu), phenanthrene (Phe) and some 3-ring PAHs were detected in the resulted gas after the pyrolysis of ISS and FSS. And a trace amount of Flt was detected in the gas, which its mass ratio is 17.3 % (ISS) and 2.4 % (PDSS) at 450°C, 12.5 % (DSS) and 5.3 % (PDSS) at 850 °C, respectively. Six kinds of PAHs were detected in the gas from the pyrolysis of PDSS, as shown in Fig.7. Also, it was observed that the types of PAHs detected in gas obtained from the various pyrolyzed sewage sludge showed significant similarities, but different mass proportions. This may be due to its physical-chemical properties of solution equilibrium gas and liquid

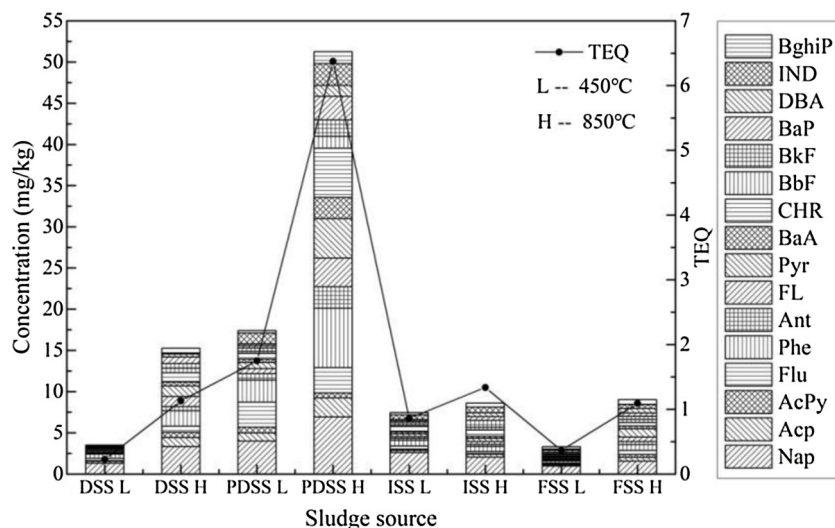


Fig. 5. PAHs content distribution and TEQ values in pyrolysis liquid products of sludge from different sources.

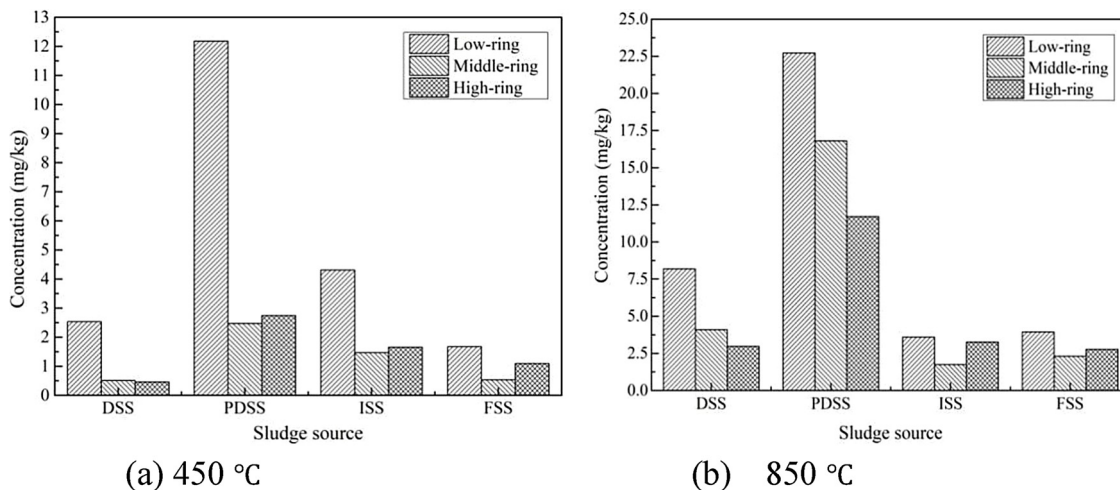


Fig. 6. The content distribution of high, medium and low ring PAHs in bio-oil.

phases.

Here, Fig. 7 the mass proportions of PAHs in gas

The PAHs' yields in gas are much lower than that of bio-oil, whether the pyrolysis conditions of high or low temperatures. The total concentration of PAHs in the gas from the pyrolysis of PDSS is much higher than that of other source sludge, which is 23.1 mg/Kg at 850°C and 9.9 mg/Kg at 450°C. It was observed that the total concentration of PAHs in the collected gas samples at 850°C is consistently higher than at 450°C. It was explained that the lower temperature caused the gas was more easily condensed. The gas yield was decreased as a result of the fewer PAHs to be blown out, so the increasing trend of PAHs production along with temperature was not as evident as in the liquid fraction. The increase of PAHs content in gas from 450°C to 850°C also could be due to the more prominent evaporation of PAHs from bio-oil. The increased temperature makes PAHs more difficult to condense in liquid products. The content of PAHs in the gas from the pyrolysis of ISS was the lowest (450°C, 1.64 mg kg⁻¹; 850 °C, 4.16 mg kg⁻¹). It was further indicated that the source of sludge had a very significant effect on the production of PAHs during thermal treatment. Since low-molecules' PAHs and a small number of middle-molecules' PAHs dominate in the gas and no high-molecules' PAHs with substantial toxicity, the TEQ values are relatively lower than that of bio-oil.

Here, Fig. 8 PAHs contents and TEQ values in gas

As a result from the low melting point and boiling point of 16 kinds of PAHs, PAHs in the gas phase from sludge pyrolysis products can be condensed entirely into liquid if sufficiently cooled. From the

analysis of data, it can be seen that the concentration of low molecules' PAHs in gas is similar to that in bio-oil. From Fig. 9 (a,b), it can be seen that low molecules' PAHs are dominant in gaseous products, followed by a small number of middle molecules' PAHs, and zero high-molecules' PAHs are detected. PDSS contributed the highest production of low-molecules' PAHs of 9.5 mg/Kg at 450°C and 22.5 mg/Kg at 850°C. With the pyrolysis temperature rising from 450 °C to 850 °C, the concentration of low molecules' PAHs in gas from the pyrolysis of the four sludges showed an obvious upward trend, which increased by 3.2 times, 1.3 times, 1.8 times and 2.7 times, respectively. Compared with low molecules' PAHs, the concentration of middle molecules' PAHs changed more smoothly. This is due to the pyrolysis of macromolecule organic matter in sludge to form small molecule organic matter, and the formation of a large number of PAHs with the middle molecules also partially occurs pyrolysis reaction.

Here, Fig. 9 The concentration distribution of different ring PAHs in gas

3.5. The distribution of PAHs in solid products

In this work, it was found that the content of PAHs in solid products from different sludge pyrolysis was very low and almost non-existent. At 750 °C, the concentration of PAHs in the solid residue from the pyrolysis of DSS peaked at 0.0161 mg kg⁻¹. At 450 °C and 850 °C, a trace content of PAHs of 0.005 mg kg⁻¹ was detected in the resulted residues. The contents of PAHs in solid from ISS, PDSS, FDD pyrolysis

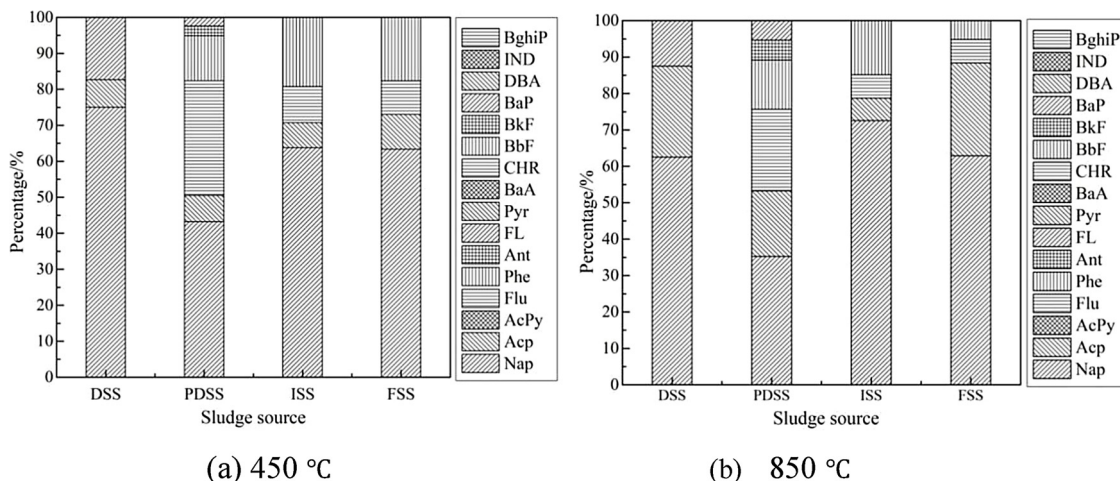


Fig. 7. the mass proportions of PAHs in gas.

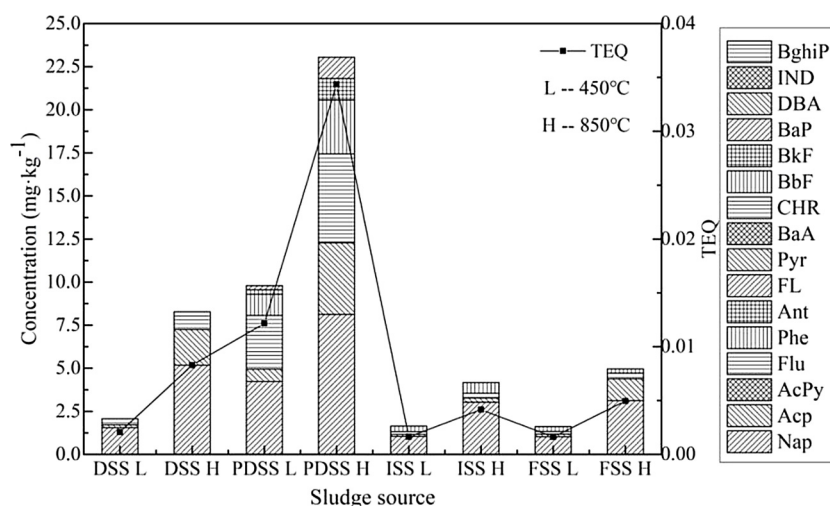


Fig. 8. PAHs contents and TEQ values in gas.

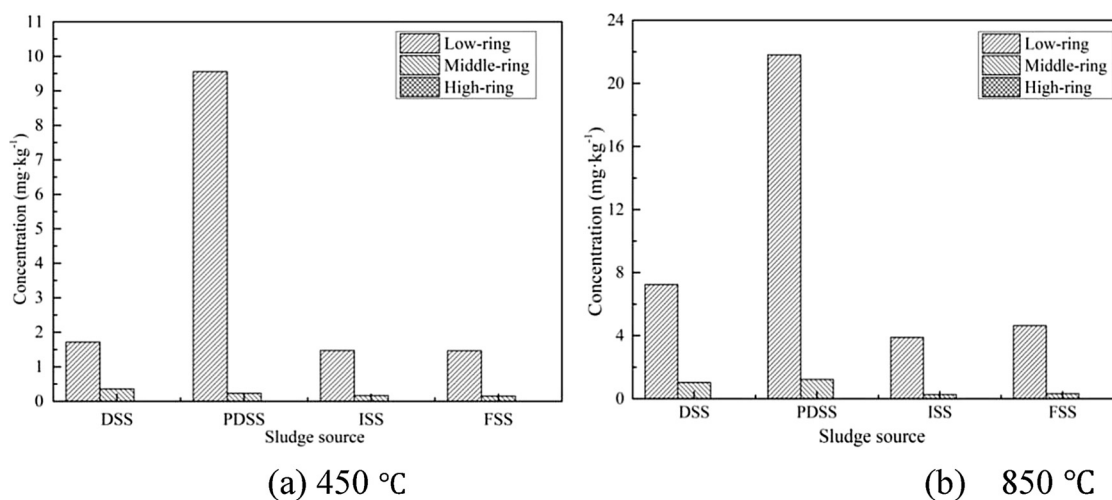


Fig. 9. The concentration distribution of different ring PAHs in gas.

were detected to be lower than that of the DSS. In some previous literature, it was reported that solid residues contained very low contents of PAHs [Xu et al., 2013]. Based on the Chinese legislation limit value (3 mg/kg) for agriculture use (GB 18918-2002), BaP was not existed in solid and far below the limit value, which is no longer an environmental problem for the solid proposal.

4. Conclusions

The formation of the 16 PAHs in three-phase products from the pyrolysis of different wastewater sewage sludge was characterized. The temperature as a key influential factor was investigated and the effect of sludge source on the formation of the different molecule's PAHs produced was characterized. The results indicate that most of 16 US EPA PAHs were generated during sludge pyrolysis and mainly ended up into the resulting pyrolysis bio-oil and gas.

Among all considered sludges, DSS contained the highest concentration of PAHs (1.61 mg/Kg), which is dominated by the middle-molecule PAHs. DSS also produced the highest yield of bio-oil (43 %), while ISS yielded the lowest (20 %). Gas yield from the pyrolysis of all sludges is the lowest than that of bio-oil and solid residues. In bio-oil, PAHs distribution was mostly dependent on pyrolysis temperature. I.e. higher temperature promotes more PAHs formation into bio-oils. With the increase of pyrolysis temperature from 450°C to 850°C, the increased rates of PAHs concentration in four kinds of bio-oils were as

follows: ISS (16 %), FDD (1.3 %), PDSS (194 %), DSS (334 %). 2, 3 and 4-ring PAHs dominate, and their total mass proportion is over 70 %. In gas, the types and concentrations of PAHs were less than that of bio-oil. Only naphthalene (NaP), acenaphthene (AcP), fluorene (Flu), phenanthrene (Phe) and some 3-ring PAHs were detected in gas obtained after the pyrolysis of ISS and FDD. Since low- molecule PAHs and a small amount of middle- molecules PAHs dominate in the gas and no high-ring PAHs with strong toxicity, the TEQ values are relatively lower than that of bio-oil. PAHs yield in solid was very low, and a trace content of PAHs of 0.0161 mg kg⁻¹ was detected from the solid after the pyrolysis of DSS, while PAHs in solid for ISS and FSS are even non-existent.

Author contribution section

YanJun Hu was the project leader, finished the design of the experiment, data analysis, conclusion, and paper writing.

YuanYuan Xia was in charge of the sampling of three-phase pyrolysis products, part of PAH analysis and other experiments, and paper writing.

Francesco Di Maio was in charge of data analysis and language improvement.

Fan Yu did the measurement of PAH using GC-MS and data analysis.

Wenjing Yu was in charge of part of PAH analysis and PAH measurement using GC-MS.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- Chan, W.P., Wang, J.Y., 2018. Characterization of sludge for pyrolysis conversion process based on biomass composition analysis and simulation of pyrolytic properties. *Waste Manag.* 72, 274–286 DOI: 10.1016/j.wasman.2017.11.026.
- Chen, W.S., Han, J., Linbo Qin, L.B., Furuuchi, B., Mitsuhiro, H., 2014. The emission characteristics of PAHs during coal and sewage sludge Co- combustion in a drop tube furnace. *Aerosol Air Qual. Res.* 14, 1160–1167.
- Dai, J., Xu, M., Chen, J., Yang, X., Ke, Z., 2007. PAH and heavy metals in the sewage sludge from six wastewater treatment plants in Beijing, China. *Chemosphere* 66 (2), 353–361.
- Dai, Q.J., Jiang, X.G., Jiang, Y.F., Jin, Y.Q., Wang, F., Chi, Y., Yan, J.H., Xu, A.H., 2014a. Temperature influence and distribution in three phases of PAHs in wet sewage sludge pyrolysis using conventional and microwave heating. *Energy Fuels* 28, 3317–3325.
- Dai, Q.J., Jiang, X.G., Jiang, Y.F., Jin, Y.Q., Wang, F., Chi, Y., Yan, J.H., 2014b. Formation of PAHs during the pyrolysis of dry sewage sludge. *Fuel* 130, 92–99.
- Deng, W.Y., Yan, J.H., Li, X.D., 2009. Emission characteristics of dioxins, furans and polycyclic aromatic hydrocarbons during fluidized-bed combustion of sewage sludge. *J. Environ. Sci. China (China)* 21, 1747–1752.
- Folgueras, M.B., Alonso, M., Diaz, R.M., 2013. Influence of sewage sludge treatment on pyrolysis and combustion of dry sludge. *Energy* 55, 426–435.
- Hu, Y., Li, G., Yan, M., Ping, C., Ren, J., 2014. Investigation into the distribution of polycyclic aromatic hydrocarbons (PAHs) in wastewater sewage sludge and its resulting pyrolysis bio-oils. *Sci. Total Environ.* 473, 459–464.
- Hu, Y.J., Guan, Z.C., Zheng, X.Y., 2013. Analysis on polycyclic aromatic hydrocarbons (PAHs) in pyrolysis oil produced from municipal wastewater sewage sludge. *Chem. Eng. J.* 33, 67–72.
- Hu, Y.J., Yu, W.J., Wibowo, H., Xia, Y.Y., Lu, Y.J., Yan, M., 2019. Effect of catalysts on the distribution of polycyclic-aromatic hydrocarbon (PAHs) in bio-oils from the pyrolysis of dewatered sewage sludge at high and low temperatures. *Sci. Total Environ.* 667, 263–270.
- Khadhar, S., Higashi, T., Hamdi, H., Matsuyama, S., Charef, A., 2010. Distribution of 16 EPA priority polycyclic aromatic hydrocarbons (PAHs) in sludges collected from nine Tunisian wastewater treatment plants. *J. Hazard. Mater.* 183 (1), 98–102 2010-01-01.
- Magdalena, S., Patryk, O., 2016. Addition of biochar to sewage sludge decreases freely dissolved PAHs content and toxicity of sewage sludge-amended soil. *Environme. Polluti.* 218, 242–251.
- Muhammad, W., Sardar, K., Huang, Q., Brian, J., Reid, Cai C., 2014. The effects of sewage sludge and sewage sludge biochar on PAHs and potentially toxic element bioaccumulation in *Cucumis sativa* L. *Chemosphe.* 105, 53–61.
- Nisbet, I.C., LaGoy, P.K., 1992. Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs). *Regul. Toxicol. Pharmacol.* 16 (3), 290–300.
- Patryk, O., Anna, Z., Gerard, C., 2014. Stabilization of sewage sludge by different biochars towards reducing freely dissolved polycyclic aromatic hydrocarbons (PAHs) content. *Bioresour. Technol.* 152, 139–145.
- Qin, L.B., Han, J., Chen, W.S., Wang, G.G., Luo, G.Q., Yao, H., 2017. Simultaneous removal of SO₂ and PAHs by adding calcium-based additives during sewage sludge incineration in a fluidized bed incinerator. *J Mater Cycle Waste Manag.* 19, 1061–1068.
- Sanchez, M.E., Menendez, J.A., Dominguez, A., Pis, J.J., Martinez, O., Calvo, L.F., Bernad, P.L., 2009. Effect of pyrolysis temperature on the composition of the oils obtained from sewage sludge. *La Rev. Des Sci. Gest. Dir. Gest.* 33, 933–940.
- Shen, L., Zhang, D.K., 2003. An experimental study of oil recovery from sewage sludge by low-temperature pyrolysis in a fluidized-bed. *Fuel* 82, 1465–1472.
- Syed-Hassan, S.S.A., Wang, Y., Hu, S., Song, S., Sheng, S., Xiang, J., 2017. Thermochemical processing of sewage sludge to energy and fuel: fundamentals, challenges and considerations. *Renewable Sustainable Energy Rev.* 80, 888–913.
- Tsai, W.T., Lee, M.K., Chang, J.H., Su, T.Y., Chang, Y.M., 2009a. Characterization of bio-oil from induction-heating pyrolysis of food-processing sewage sludges using chromatographic analysis. *Bioresour. Technol.* 100, 2650–2654.
- Tsai, W.T., Mi, H.H., Chang, J.H., Chang, Y.M., 2009b. Levels of polycyclic aromatic hydrocarbons in the bio-oils from induction-heating pyrolysis of food-processing sewage sludges. *J. Anal. Appl. Pyrolysis* 86, 364–368.
- Wang, X.D., Li, C.X., Zhang, B., Lin, J.J., Chi, Q.Q., Wang, Y., 2016. Migration and risk assessment of heavy metals in sewage sludge during hydrothermal treatment combined with pyrolysis. *Bioresour. Technol.* 221, 560–567.
- Waqas, Muhammad, Khan, Sardar, Qing, Huang, Reid, Brian J., Chao, Cai, 2014. The effects of sewage sludge and sewage sludge biochar on PAHs and potentially toxic element bioaccumulation in *Cucumis sativa* L. *Chemosphere* 105, 53–61.
- Xu, Z.R., Chen, F.L., Xu, M.Z., Gong, M., 2013. Risk assessment of PAHs in solid residues from supercritical water gasification of sewage sludge. *Advanced Materials Research Vols.* 726-731, 2778–2781.
- Zhang, H., Xu, L., Zhang, Y.F., Jiang, M.C., 2016. The transformation of PAHs in the sewage sludge incineration treatment. *Front. Environ. Sci. Eng. China* 10 (2), 336–340.
- Zhou, H.B., Ma, C., Gao, D., Chen, T.B., Zheng, G.D., Chen, J., Pan, T.H., 2014. Application of a recyclable plastic bulking agent for sewage sludge composting. *Bioresour. Technol.* 152, 329–336.