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Unlocking the potential flame-retardant mechanisms of extracellular polymeric substances recovered from municipal sludge

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ABSTRACT

Limited understanding of the thermal properties and flammability of extracellular polymeric substances (EPS) from municipal sludge has constrained their use in fire safety applications. This study investigates the thermal stability and flame retardancy of EPS derived from secondary sludge, waste sludge, and digested sludges. Comprehensive analyses of chemical composition, activation energy, char formation, and heat and gas release during pyrolysis and combustion reveal potential flame-retardant mechanisms. All EPS from different types of sludge can release both free-radical scavenging compounds and non-flammable gases during combustion to reduce fire propagation in the gas phase. In the condensed phase, EPS demonstrate their char-forming capability as a major flame-retardant mechanism to diminish heat release rate due to the presence of nitrogen, phosphorus, and sulfur elements. While nitrogen-based compounds in EPS contribute to flame-retardant mechanisms in both phases, phosphorus and sulfur mainly act in the condensed phase. Additionally, EPS from secondary sludge show the highest activation energy (372.3 kJ/mol) and ignite 24 s later than other EPS. Cone calorimeter tests confirm that EPS from secondary sludge have superior fire-resistant properties, with increased char contents (31.2 %) and enhanced thermal stability compared to other EPS. This study provides the first comprehensive assessment of EPS as eco-friendly flame retardants, advancing wastewater sludge valorisation and fire safety applications.

1. Introduction

Flame retardancy is vital for a wide range of products, including electronics and electrical devices, furnishings, building materials, and transportation systems [1]. According to the US Fire Administration, 1504,500 fire incidents were reported in 2022, resulting in significant loss of life and economic damage [2]. Many flame retardants have been developed to reduce the risk of ignition and inhibit the spread of fire. However, conventional flame retardants, such as halogenated flame retardants, have been restricted in European countries due to their adverse effects on human health and the environment [3]. Consequently, bio-based flame retardants have been explored as an alternative to conventional ones due to their nontoxic, eco-friendly, safe for human use, and low cost [4]. Recently, extracellular polymeric substances (EPS) have gained attention as a promising bio-based flame retardant since they are generated from renewable sources [5].

EPS, a mixture of polymers produced by microorganisms to form microbial aggregates in wastewater sludge, play a role in floc formation, settling and dewatering sludge in wastewater treatment plants (WWTPs) [6]. The chemically extracted EPS contains polysaccharide (PS), protein (PN), and humic-like substances (HS) [7]. The flame-retardant properties of EPS can possibly be attributed to the presence of charring agents (e.g., PS, HS), nitrogen compounds (e.g., PN), and phosphate groups in the polysugars [8]. Therefore, EPS are expected to be a novel nitrogen-phosphorus flame retardant [9]. However, there are no studies that fully report the flame-retardant mechanisms of EPS. Recent research about the flame-retardant properties of EPS on flax fabric [10] and polypropylene [11] demonstrated that EPS can create a char layer after burning to protect the material. In agreement, Li et al. [12] also found that EPS can reduce the heat release rate of linen fabric due to

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char formation. However, these works only focused on the char-forming capability of EPS and did not provide experimental data to elucidate the actual flame-retardant mechanisms.

The flame-retardant mechanisms of materials are directly associated with three stages of the combustion process, including the gas phase, condensation phase (char formation), and heat cycle [13]. Combustion initiates when sufficient thermal energy is supplied to reach the materials' ignition points. The rapid decomposition of materials releases volatile gases, which interact with oxygen to generate fire, smoke, and heat. In this case, the flame retardant with high thermal stability can shield and isolate the material from heat/energy sources, preventing the combustion process. The thermal stability of a flame retardant is represented by their activation energy (AE) value – a minimum energy requirement for decomposing. When the fire happens, the pyrolysis behaviour indicates how the polymer can inhibit and extinguish the fire by acting within the condensed and gas phases [14]. In the condensed phase, flame retardant forms a char layer to block heat transfer and prohibit the supply of external oxygen for the fire [14]. Meanwhile, the action of flame retardant in the gas phase relates to free radical scavenging to terminate the chain reaction of fire and diluting oxygen supplied by non-combustible gases (e.g. CO_2 and H_2O). Understanding the flame-retardant mechanisms is important to the development of effective flame retardants.

In general, EPS can be recovered from many types of sludges, such as aerobic granular sludge [15], aerobic activated sludge [16], and anaerobic digested sludge [17]. Although activated sludge from wastewater treatment plants is currently a major waste globally, with ten million tons of dry matter produced annually, recovery of EPS from this source is still less focused than aerobic granular sludge [16]. Therefore, the study of flame retardancy of EPS from activated sludge in this context not only contributes to the advancement of material science but also addresses the sludge management problem in activated sludge wastewater treatment plants [18]. In the activated sludge wastewater treatment plants, there are different sludge types that can be used as a source of EPS, including secondary sludge, waste sludge and digested sludge. The locations of these types of sludge are shown in Fig. 1. EPS are firstly synthesised by organic degradation of aerobic bacteria in the secondary sludge matrix. After this stage, the secondary sludge is mixed with the primary sludge, which mainly contains organic fibre, grease, and solid, to create a waste sludge. Therefore, EPS recovered from this waste sludge are expected to have more organic contents than EPS from secondary sludge. The waste sludge is finally fed to an anaerobic digestion tank to generate biogas, and the solid residues after this process, named digested sludge, can also be used to extract EPS. The content of EPS ranges 6 – 54 % of volatile solid content in secondary sludge and 10 – 30 % of volatile solid content in digested sludge [17]. According to Liu et al. [19], the changes in metabolic pathways and microbial consortium make a significant difference in the EPS structures and properties. For example, the EPS from secondary sludge have better gelling properties than EPS obtained from digested sludge [18]. However, during anaerobic digestion, the PN in EPS can be hydrolysed and decomposed, providing aromatic groups for promoting the formation of HS [7]. The HS content could be responsible for seed-coating applications of EPS [20]. However, regardless of the sources, the thermal-flammability properties and flame-retardant mechanism of EPS have not been reported yet, causing major challenges for the use of EPS in flame-retardant and other polymeric applications. Therefore, it is necessary to investigate the thermal and flammability properties of EPS from these types of sludges for practical purposes in sludge management and flame-retardant applications.

To the best of our knowledge, most studies on the EPS have focused on their application with limited investigation into their thermal and flammability properties. The current study explores the underlying pyrolysis mechanisms responsible for flame-retardant properties of EPS derived from municipal wastewater sludge. EPS was extracted using the base-acid method [16,21] from three types of sludges. The chemical and morphological properties of the recovered EPS were analysed to evaluate their differences. The pyrolysis behaviours, thermal stability, and flammability properties of EPS were also comprehensively investigated by determining activation energy, heat release, and characteristics of char and gases released during the pyrolysis. As a result, the proposed flame-retardant mechanisms of EPS were holistically evaluated. The findings highlight the potential of EPS derived from wastewater sludge as flame retardants, contributing to a more sustainable wastewater treatment process and fostering innovation in material development.

2. Materials and methods

2.1. Materials

The sludge used in this study has been collected from the Māngere wastewater treatment plant, operated by Watercare Service in Auckland, New Zealand. The plant is designed to treat 350,000 m^3 of wastewater per day. An overview of wastewater treatment process at the plant, along with specific locations for sludge sample location, is shown in Fig. 1. In this study, secondary, waste, and digested sludges were

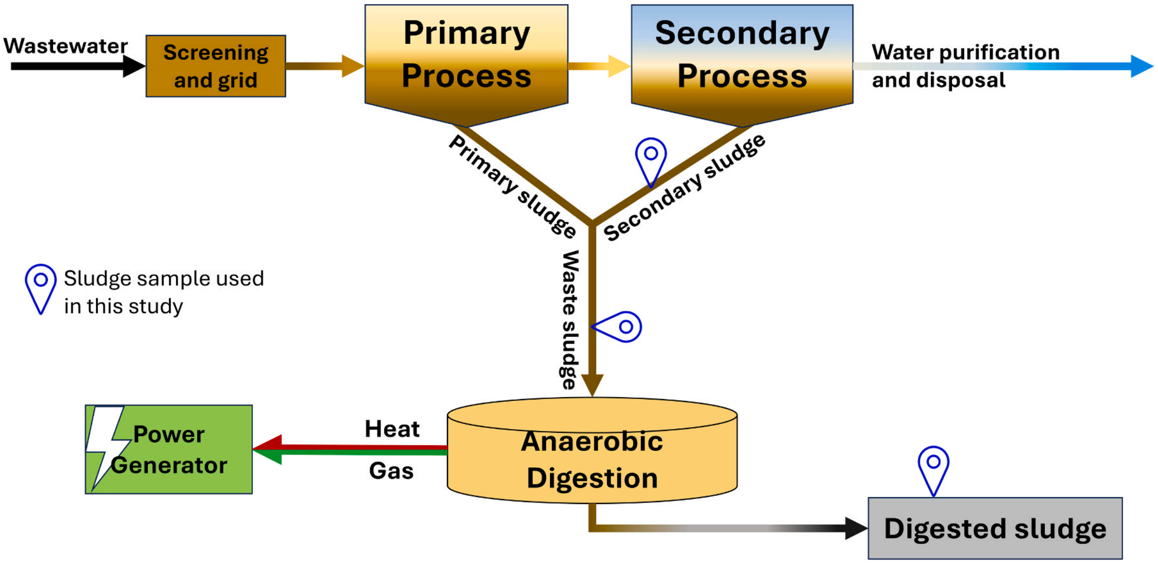


Fig. 1. Summarised wastewater treatment process and the sludge used in this study.

collected for recovery of EPS. The waste sludge is defined as a mixture of primary and secondary sludges.

Before extracting EPS from the three types of sludge samples, all sludge materials were autoclaved at 121 °C and 221 kPa for 30 min using the 385ELC-D equipment (Tuttnauer, Australia) and then stored at 5 °C for further study [22]. The purpose of this step is to stop the bioactivity of microorganisms in the sludge sample, which can change the sludge composition over time and pose potential risks for humans and the environment. The general properties of the sterilised sludge samples are shown in Table S1.

2.2. Recovery of EPS from different types of sludges

EPS from different sludge types were recovered following the base-acid method [16,21]. Briefly, 3.0 g of sludge (total solids) was mixed with 100 mL of distilled water before adding 1.0 g NaOH. The amount of total solids was calculated by the different masses of samples before and after drying at 105 °C for 24 h. The extraction process was conducted at 80 °C for 30 min with a stirring rate of 200 rpm. After extraction, the sludge residues were removed by centrifuging at 7000 rpm for 10 min to obtain supernatant. The supernatant samples were adjusted to pH 2.2 by HCl 1 M to precipitate EPS. The EPS were collected by centrifugation at 7000 rpm for 15 min and then rinsed with distilled water several times to remove salts. The samples were finally dried in a convection oven at 50 °C overnight. All the experiments were repeated at least three times with the same sludge. The EPS extracted from secondary sludge, waste sludge, and digested sludge were denoted as SSE, WSE, and DSE, respectively.

2.3. Physical, chemical and morphological characterisation

The total solids, volatile solids (VS), and ash contents of sludge and EPS were determined by the standard methods described in APHA [23]. The chemical functional groups of EPS were identified using a Nicolet iS50 ATR-FTIR Spectrometer (Thermo Fisher Scientific, USA) with a wavenumber from 4000 to 400 cm^{-1}. The aromatic groups of EPS were measured using a UV- 2700i (Shimadzu, Japan) from 800 nm to 200 nm. The morphology and elemental analysis of EPS were performed using a SEM-EDX (ZEISS GeminiSEM 460, Germany).

2.4. Thermal characterisation

2.4.1. Thermogravimetric analysis

The thermal degradation profiles of EPS from different types of sludge were identified by TGA equipment (Q5000, TA instruments, USA) with different heating rates (10, 20 and 30 °C/min). A sample with an initial weight of 10–15 mg was placed on the crucible and then heated to 850 °C under nitrogen atmosphere with a flow rate of 50 mL/min. The experiment was conducted with at least two replications.

2.4.2. Activation energy

Activation energy (AE) is an essential parameter in the thermal degradation kinetics of materials. The high activation energy indicates that the material has high thermal stability, which is promising for flame-retardant applications. In this study, AE was calculated using Flynn–Wall–Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS) methods, as expressed in Eqs. 1 and 2, respectively:

$$\text{FWO equation}: \ln\beta = c - 1.052\frac{E}{RT} \tag{1}$$

$$\text{KAS equation}: \ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{Eg(\alpha)}\right) - \frac{E}{RT} \tag{2}$$

where β is the heating rate (°C/min), *c* is a constant, E is activation energy (kJ/mol), R is the ideal gas constant (8.314 J/mol·K), and T is the absolute temperature (K). A is the pre-exponential factor (s^{-1}), and g(α) is a function of the conversion rate (α), calculated by Eq. 3:

$$\text{Conversion rate}: \alpha = \frac{W_o - W_i}{W_o - W_f} \tag{3}$$

where W_i, W_o, and W_f (mg) are the weights of the sample at i, initial, and final temperatures, respectively.

2.5. Cone calorimeter

The fire reaction properties of EPS were measured using a cone calorimeter (FTT, United Kingdom). A 12 g sample was pressed into a circular pellet with dimensions of 50 mm× 50 mm x 2 mm (diameter x diameter x thickness) and placed in an aluminium pan for measurement. The sample was mounted using a metal box with insulation cotton. The external heat flux was set at 35 kW/m^2 [24]. The test was conducted in triplicate, and the results are presented as mean values ± standard deviation.

2.6. Pyrolysis coupled with gas chromatography-mass spectrometry (Py-GCMS)

The gases released from EPS during pyrolysis under inert conditions were detected using a Py-GCMS. First, 2 mg of EPS was put in a stainless-steel sample cup before being subjected to pyrolyser. The pyrolyser (Multi-Shot Pyrolyser EGA/PY 3030D, Shimadzu, Japan) was heated from room temperature to 600 °C at a heating rate of 10 °C/min and held for 30 s. The final temperature was selected according to the TGA results. The volatiles released during the pyrolysis were subjected to GC (GCMS-QP2020 NX, Shimadzu, Japan) with an interface temperature of 300 °C, a slit ratio of 1:100, and pure helium as carrier gas at a flow rate of 1 mL/min. The GC system was equipped with an Ultra ALLOY-5 capillary column (30 m x 0.25 mm×0.25 μm). The GC oven was initially held at 40 °C for 2 min, then heated to 320 °C with a heating rate of 20 °C/min and finally held at 320 °C for 5 min before the program ended. The MS detector with an ion source of electrons scanned from 35 to 600 amu was used. The compounds were identified using the NIST mass spectra library.

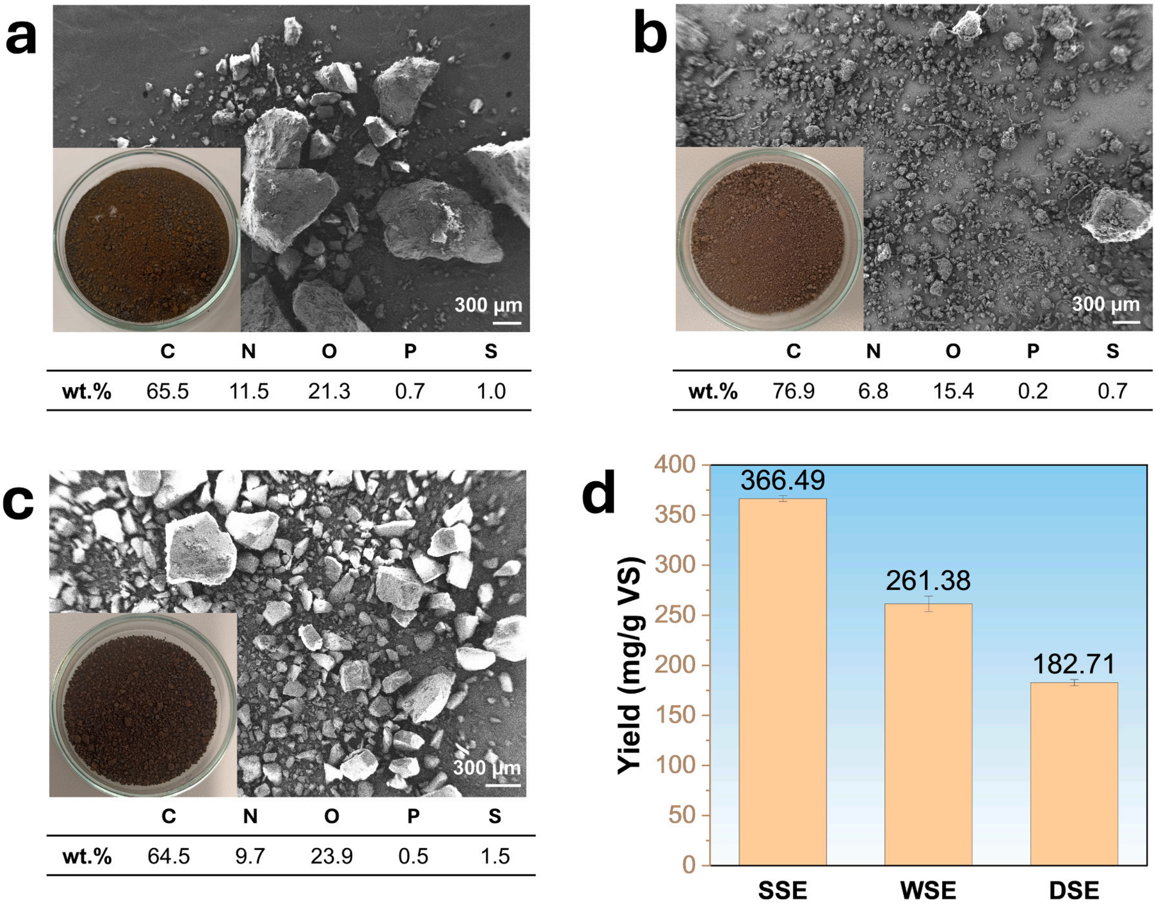
2.7. Condensed phase analysis

The char formation mechanisms of EPS were determined using a furnace (Nabertherm, Germany) and FTIR spectroscopy. In particular, the EPS were burned at different temperatures (20, 250, 350, 450, 600, and 900 °C) for 10 min. The temperature points were selected based on the DTG results (Section 3.2.1), representing the start and end of each thermal degradation zone. The char residues obtained were characterised by ATR-FTIR (Nicolet iS50 FTIR Spectrometer, Thermo Fisher Scientific, USA) with a wavenumber from 4000 to 400 cm^{-1}. Furthermore, the char obtained after burning in a cone calorimeter was analysed by SEM coupled with an EDX detector (ZEISS GeminiSEM 460, Germany) for detecting microstructure and elemental contents. The graphitic structures and the hybridisation states of carbon atoms within the residual char were also determined by Raman spectroscopy (Horiba Jobin-Yvon, France). The graphitisation degree of char, relating to the microcrystalline carbonaceous structure and pore diameter of the carbon layer, was calculated from the Raman spectrum. The results of EDX and Raman spectroscopy presented in this study were the mean values of at least three different points of samples.

3. Results and discussion

3.1. Chemical properties of EPS

The physical appearance and SEM images of EPS from different types of sludge are shown in Fig. 2. The SSE and DSE are dark brown powders, while WSE appears to be a light brown powder. The variations in the



(a)

	C	N	O	P	S
wt.%	65.5	11.5	21.3	0.7	1.0

(b)

	C	N	O	P	S
wt.%	76.9	6.8	15.4	0.2	0.7

(c)

	C	N	O	P	S
wt.%	64.5	9.7	23.9	0.5	1.5

Fig. 2. The physical appearance and SEM-EDX results of SSE (a), WSE (b), and DSE (c), and their extraction yield (d).

colour of EPS are attributed to the PN [25] and PS contents [26]. The extraction yields of the EPS are shown in Fig. 2d. The secondary sludge has the highest extraction yields, followed by waste sludge and digested sludge, due to the different EPS concentration in each sludge. During secondary treatment, microorganisms convert organic matter in wastewater into biomass, producing significant amounts of EPS in the sludge matrix. In contrast, anaerobic digestion transforms organic materials into biogas, which can reduce the EPS content [17]. Waste sludge, typically a mixture of primary and secondary sludge, has a lower EPS content because primary sludge contains no EPS. Consequently, secondary sludge provides a richer source of EPS compared to waste or digested sludge [17]. However, the combination of primary and secondary sludge also notably increases the organic content of WSE, as evidenced by the elevated carbon (C) content, reaching the maximum of 76.9 %. The reason is that the primary sludge mainly contains organic fibre, grease, and solid, thus improving the organic contents in EPS. In addition, nitrogen (N), phosphorus (P), and sulfur (S) are detected in all EPS. While the amount of P and S is relatively low across all samples, the N content is higher, reaching up to 11.5 % in SSE, followed by DSE and WSE. In the flame-retardant system, the presence of N-, P-, and S- containing compounds can enhance the flame-retardant efficiency of materials [27]. The C content also suggests the materials can create more char to protect the underlying layers during combustion.

3.2. *Thermal properties*

3.2.1. *Thermal decomposition profiles of EPS*

Thermal properties are essential for understanding the flammability characteristics of EPS [28]. The thermal decomposition of the materials in nitrogen is associated with the gasification and carbonisation processes, which are very important for flame retardants [28]. Fig. 3a-c illustrates the thermal decomposition behaviour of EPS from different types of sludge in a nitrogen atmosphere from 100 °C to 850 °C. The shapes of DTG and TGA curves remain unchanged at different heating rates, suggesting that the reaction mechanisms are not influenced by the changes in heating rate. However, the variation in the DTG curves of the EPS indicates the differences in their thermal properties. The TGA/DTG profiles of all EPS in different heating rates are shown in Table 1.

Generally, the thermal decomposition processes of all samples can be divided into three zones within a range of 140 °C to 600 °C. The Zone I (140 – 300 °C) can be associated with the degradation of lipid (LP) [29] and PN I [30]. Zone II, ranging from 300 °C to 400 °C, corresponds to the decomposition of PS and PN [31], with a mass loss of 22.4–43.6 %. It is noteworthy that there is a small shoulder in zone III, between 400 °C and 500 °C, which is only observed in cases of SSE and DSE. The third zone can be attributed to the decomposition of the PN and HS [32]. The residues from the TGA results can indicate char formation during the combustion, which is also an important factor in flame retardants. The char residues of EPS vary depending on the heating rates (β). At $\beta = 20$ and 30 °C/min, the char contents produced by SSE reach the highest values of 27.1 % and 29.6 %, respectively. However, at $\beta = 10$ °C/min, the char residues of SSE (25.2 %) are slightly lower than that of DSE (25.8 %). When the heating rates increase, the char content formed from SSE becomes higher than that of DSE and WSE. Therefore, it can be concluded that char generated from SSE is more stable than others under high energy supply conditions.

3.2.2. *Activation energy of EPS*

Activation energy (AE) is the minimum energy required to break down the structure of EPS. Fig. 3d and e demonstrate AE values of EPS

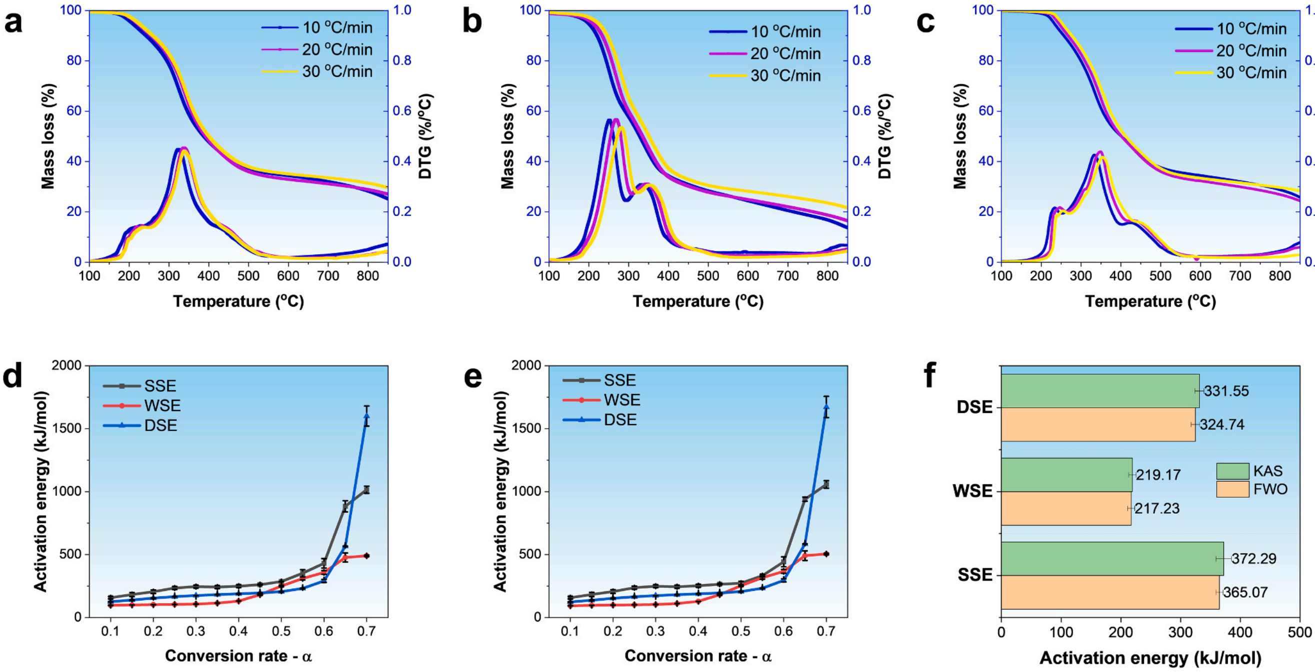


Fig. 3. TGA and DTG curves of EPS, including SSE (a), WSE (b), and DSE (c) in nitrogen; the activation energy curves with respect to conversion rates of EPS using FWO (d), and KAS (e); the overall activation energy values of EPS (f).

Table 1

TGA data of EPS from different types of sludges at various heating rates.

Samples	β (°C/min)	Zone I		Zone II		Zone III		Residues at 850 °C (%)
		T_{max1} (°C)	DTG (%/°C)	T_{max2} (°C)	DTG (%/°C)	T_{max3} (°C)	DTG (%/°C)	
SSE	10	229.78	0.15	323.29	0.45	428.08	0.14	25.19
	20	231.77	0.15	337.22	0.45	442.47	0.14	27.07
	30	236.80	0.14	338.95	0.44	453.11	0.12	29.62
WSE	10	251.65	0.57	334.62	0.31	-	-	13.70
	20	268.64	0.57	344.94	0.31	-	-	16.46
	30	281.72	0.53	352.32	0.31	-	-	21.65
DSE	10	234.12	0.22	333.25	0.43	423.31	0.16	25.78
	20	246.61	0.22	348.77	0.44	430.12	0.17	26.44
	30	254.28	0.20	354.21	0.42	450.60	0.16	28.40

β: heating rate, Tmax i: the peak temperature at zone i, DTG: the corresponding DTG values at Tmax temperature.

from different sludges at various conversion rates, which are calculated from the fitting curves of the FWO and KAS equations (Figure S1). Notably, by α = 0.50, the trends of the AE plots against α values are consistent and gradually increase, regardless of different types of sludges, implying the similarities in thermal behaviour in this range. The corresponding temperatures of α = 0.50 are around 300 °C for WSE, 350 °C for SSE, and DSE, aligning with the decomposition of the LP, PN I and PS. After this point, the AE values of EPS from different types of sludges exhibit significant differences. In α = 0.50 – 0.75, the AE values of DSE significantly increase from 205.9 to 1600.9 kJ/mol. At α = 0.75, the AE value of DSE is extremely higher than that of other EPS, indicating high thermal stability of char formed. The temperature in this stage of 0.50 – 0.75 corresponds to the decomposition of PN and HS. Therefore, it suggests that PN and HS can enhance the AE value of EPS. Similarly, Li et al. [32] also have reported that the AE values of HS at α = 0.5 – 0.75 can reach 433.10 – 550.96 kJ/mol for FWO method. Although the AE values of SSE do not significantly increase in α = 0.50 – 0.75, the overall AE value of SSE is highest compared to other EPS, with values of 372.3 kJ/mol for KAS and 365.1 kJ/mol for FWO due to the higher AE values of SSE at α = 0.10 – 0.65. This means SSE require more energy to be decomposed at temperatures below 400 °C; otherwise, DSE can form a stable char at higher temperatures (400 – 600 °C). Interestingly, the overall AE values of all types of EPS in this study are higher than that of some bio-flame retardants, such as industrial lignin (104 – 168 kJ/mol) [33] and phytic acid (39.7 – 55.1 kJ/mol) [34].

3.3. Fire reaction properties

The forced combustion behaviour of EPS was detected using cone calorimeter, and fire reaction properties are shown in Fig. 4 and Table 2. The average time to ignition (TTI) of WSE is 16 s, while SSE and DSE ignite later than WSE. The results are aligned with AE values of EPS, where SSE have the highest AE values at a low-temperature range (< 400 °C). Moreover, the higher N and P contents in SSE compared to other samples also play an important role in delaying ignition [35].

As shown in Fig. 4, the HRR and THR of WSE are significantly greater than those from SSE and DSE, indicating that WSE are more flammable than others. After ignition, WSE burns intensely, reaching a sharp peak HRR (PHRR) of 818.2 kW/m^2 in 50 s. On the other hand, the PHRR values of SSE and DSE are 419.6 kW/m^2 and 431.0 kW/m^2, respectively. Furthermore, they take 75 s (SSE) and 68 s (DSE) to reach their PHRR. Additionally, the THR values for SSE and DSE are lower than those for WSE. Both time to PHRR (t-PHRR) and TTI are key factors in evaluating the possibility of rescue and escape from the fire [36]. Alongi et al.[37]

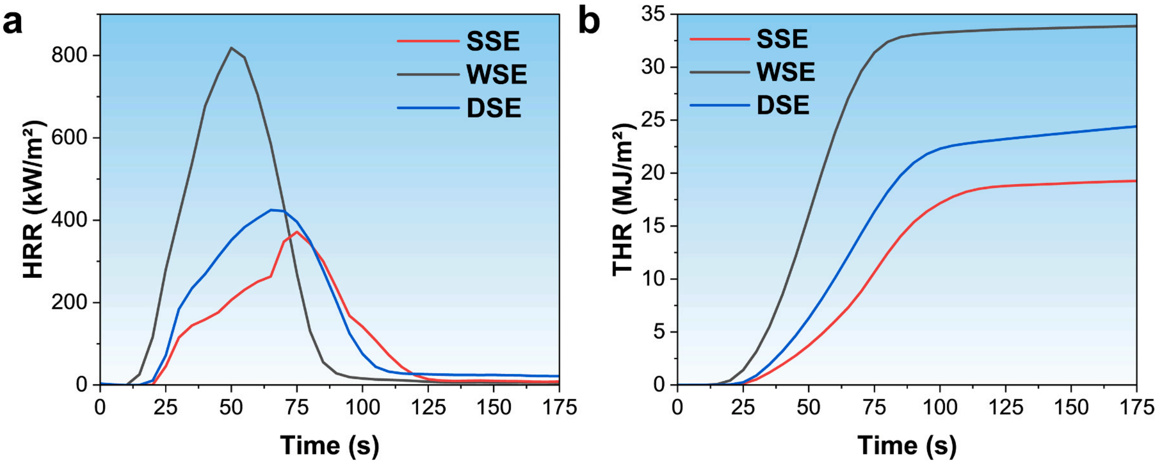


Fig. 4. Heat release rate - HRR (a) and total heat release - THR (b) of EPS from different sludge sources using a cone calorimeter.

Table 2
Cone calorimetry data of EPS from different types of sludge.

Flammability characteristics	TTI (s)	PHRR (kW/m^2)	t-PHRR	THR (MJ/m^2)	TSR (m^2/m^2)	TSP (m^2)	Av-COY (kg/kg)	Av-CO_2Y (kg/kg)	Char residues (%)
SSE	24.33 ± 2.89	419.59 ± 35.09	75 ± 0.00	18.71 ± 3.49	366.83 ± 19.87	2.88 ± 0.23	0.03 ± 0.01	1.25 ± 0.03	31.17 ± 1.25
WSE	16.33 ± 3.06	818.17 ± 29.27	50 ± 0.00	33.29 ± 0.34	409.17 ± 12.16	3.21 ± 0.17	0.02 ± 0.00	1.49 ± 0.36	23.83 ± 1.83
DSE	22.33 ± 3.06	430.98 ± 27.40	68 ± 2.89	23.06 ± 0.13	476.26 ± 16.82	3.66 ± 0.13	0.03 ± 0.00	1.34 ± 0.03	28.33 ± 1.67

TTI: time to ignition, PHRR: peak heat release rate, t-PHRR: time to reach peak heat release rate, THR: total heat release rate, TSR: total smoke production rate, TSP: total smoke production, av-COY: average CO yielded, av-CO_2Y: average CO_2 yielded.

reported that the TTI of pure DNA and casein are 1 and 2 s under heat flux of 35 kW/m^2, while DNA only takes 8 s to reach PHRR. Both DNA and casein have been known as effective flame retardants. Therefore, the higher TTI and t-PHRR of SSE and DSE, compared to casein and DNA under the same heat flux, suggest that the material can prolong the ignition and provide escape time. In addition, SSE and DSE exhibit higher char residues than casein, indicating that EPS can protect the incorporated polymer by forming a char layer. The trend of char residues observed in the cone calorimeter testing is consistent with that obtained from TGA, further confirming these findings.

3.4. Gas release analysis

The flame-retardant mechanisms in the gas phase are governed by two processes. The first process involves decomposing the material into volatile compounds under anaerobic conditions, such as light hydrocarbons, bio-syngas, and bio-oil. The second process involves the oxidation of these volatile compounds into non-combustible gases, such as carbon monoxide (CO) and carbon dioxide (CO_2). The volatile compounds released from EPS pyrolysis at 600 °C have been analysed using Py-GCMS. The total ion chromatogram of the volatile products is shown in Fig. 5, and the corresponding products are listed in Table S2.

Under anaerobic conditions, EPS are decomposed via carbonylation and carboxylation reactions, releasing CO_2 and other volatile compounds. CO_2 has been known as a non-combustible gas, which can dilute the oxygen concentration supplied for combustion. The volatile products detected by Py-GCMS mainly include esters, carboxylic acids, aldehydes, nitriles, and several other hydrocarbons, as shown in Table S2. Surprisingly, lipid-derived compounds, such as fatty acids and steroids, account for a significant portion of the gases released in WSE. These compounds are predominantly flammable and easily cracked, releasing hydrocarbons, leading to the increased HRR and THR of WSE. Many nitrogen-containing compounds formed due to the decomposition of PN are also detected in the gas phase. These compounds belong to groups of alkoxyamines and polyimide-derived compounds. The formation of these N-compounds can help quench free radicals, contributing to reducing the fire spread [28]. In addition, some compounds that could be from the decomposition of PS and HS, like furan derivatives and phenolics, are also reported to interact with •OH, •H, and •O free radicals to reduce fire propagation. Therefore, the lower HRR and THR of SSE and DSE than those of WSE can be attributed to the better distribution of these compounds. The findings indicate that EPS can have scavenging free radical effects on the gas phase, which helps reduce fire propagation. Furthermore, no P- and S-containing compounds have been detected in the gas phase, implying that the effects of these compounds in the gas phase are insignificant.

The second process is related to the oxidation reaction of combustible gaseous products (e.g. hydrocarbon, ketones, etc.) to release smoke, CO, and CO_2 in the gas phase. In a real fire, the harm caused by toxic gases and smoke released during combustion is even more severe than heat release. Therefore, reducing smoke production during combustion is of paramount importance. Table 2 shows that the total smoke production (TSP) of SSE is the lowest at 2.9 m^2. Surprisingly, the TSP of DSE (3.7 m^2) is higher than that of WSE (3.2 m^2), which implies that DSE have less fire safety than WSE. At the same time, SSE produces less CO and CO_2 yields than others, which is beneficial for fire safety.

3.5. Char analysis

3.5.1. Functional groups of char

The char formation of EPS is an important characteristic for determining the potential of the material as a flame retardant. In this study, the char created after the simulated combustion process at different temperatures is assessed via FT-IR, as illustrated in Fig. 6. In ambient temperature, all EPS have the same functional groups constituted by hydroxyl group (-OH) and aminoacidic group (-NH) at 3400 cm^{-1}, C-H

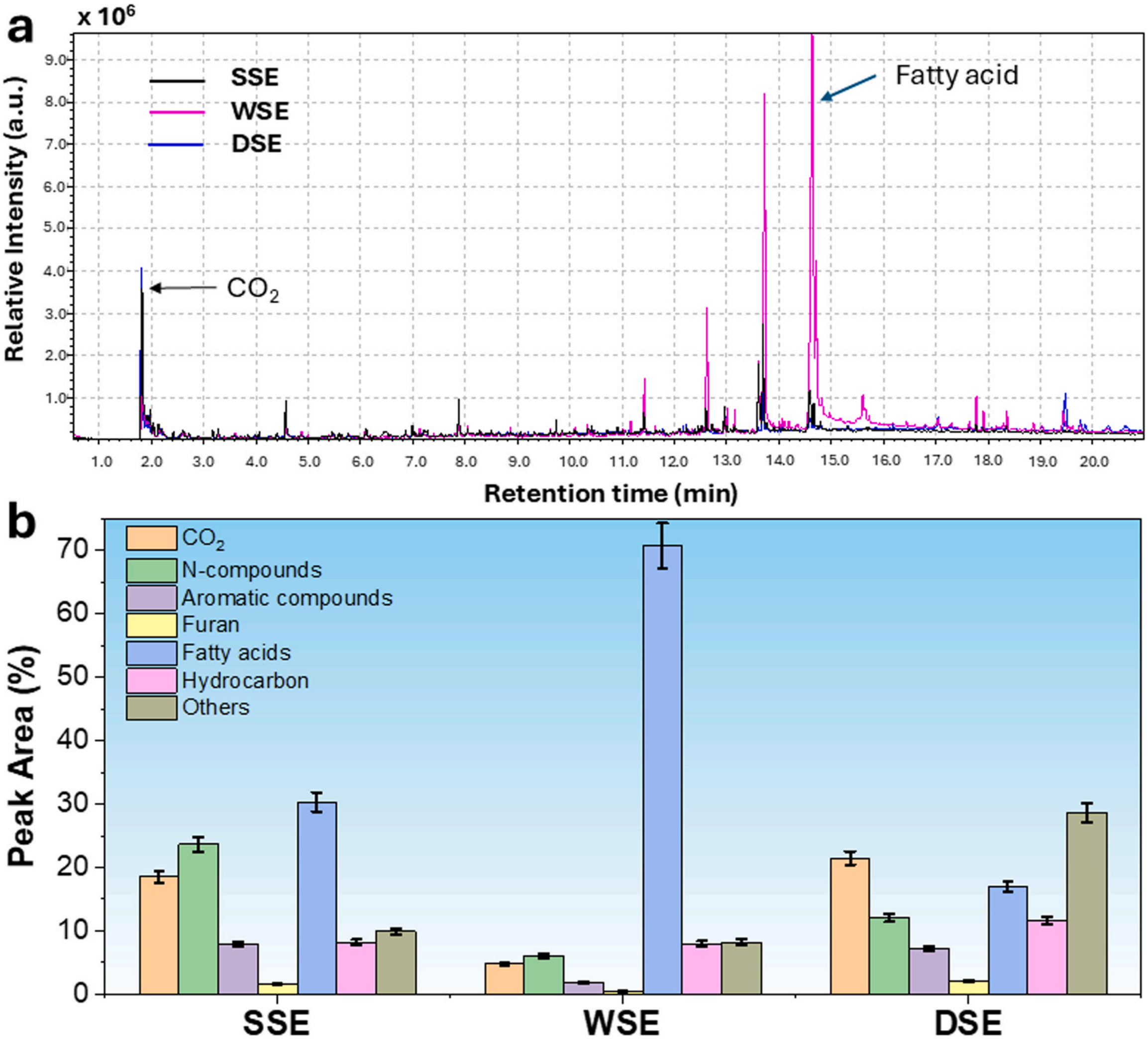


Fig. 5. Pyrograms (a) and product distribution (b) obtained from Py-GCMS of EPS.

stretching groups of PS, PN, and lipids (LP) at 2850 cm^{-1} and 2920 cm^{-1}[38]. The PN structure can be characterised by amide I band at 1620 – 1720 cm^{-1} (C-O and C-N stretching), amide II bands at 1510 – 1530 cm^{-1} (C-H and N-H stretching), and amide III at 1210 cm^{-1} (C-N stretching) [39]. The peak at 1027 cm^{-1} corresponds to the C-H plane bending group of PS [40].

There are no significant changes in the chemical structures of EPS at temperatures up to 250 °C, indicating that the EPS structure remains stable below this temperature threshold. At 350 °C, further degradation occurs, as evidenced by the disappearance of peaks at 3500 cm^{-1}, 2900 cm^{-1} and 1500 cm^{-1}, which correspond to OH groups, C-H stretching, and C═C stretching, respectively. Until 450 °C, the functional groups of these EPS are dominant by C-H stretching (2900 cm^{-1}), C═C stretching (1650 cm^{-1}), and C═O stretching (1725 cm^{-1}), indicating the strong carbonisation reaction during this stage. By increasing the temperature, all EPS-based materials show a broad peak at 1022 cm^{-1}, corresponding to C-O-C and P-O-C bonding [41]. The formation of P species demonstrates the high thermal stability of char residues. While the degradation of EPS is mostly completed at 600 °C, the peaks at 1022 cm^{-1} and 900 cm^{-1} (P-O-P groups) still remain until 900 °C. It is likely that inorganic materials, such as hydroxyapatite, are present in the char, contributing to the formation of thermally stable char [12]. Kim et al.[10] have also detected the presence of hydroxyapatite in the char residues of EPS from granular sludge.

3.5.2. *Char structures*

To elucidate the potential flame-retardant function of EPS in the condensed phase, the visualisation and micrographs of char residues from different EPS are analysed by SEM, as illustrated in Fig. 7. All samples exhibit a “blowing effect” due to the release of N_2, NH_3, and CO_2 gases during decomposition. The “blowing effect” suggests that the materials can retain the combustible gases interacting with oxygen and reduce the heat provided for decomposition [42]. However, this effect and the heat generated during combustion impose stress on the char layer. Thus, to be an effective barrier in the condensed phase of flame retardant, the char layer should have compactness, structural integrity and thermal stability. The char layer of WSE is densely dotted with holes and cracks (Fig. 7f). While the char layer from DSE can keep its continuous surface, though it shows signs of shrinkage during combustion. The microstructure of the DSE char layer also shows high porosity but less than that of WSE. In contrast, SSE forms an expanded, smooth-surfaced char layer with a compact structure and only a few holes. Therefore, SSE char layer tends to be more thermally stable than others. The charring behaviours of different EPS are summarised in Fig. 7k, illustrating the interaction of heat, gas and condensed phases.

During combustion, WSE form a char layer with a high porous structure, which allow for exposing flammable gases from decomposition and increasing heat transfer from fire to raw materials. Although DSE char layer also contains several holes, it demonstrates a greater tolerance to the pressure exerted by heat and released gases. As a result,

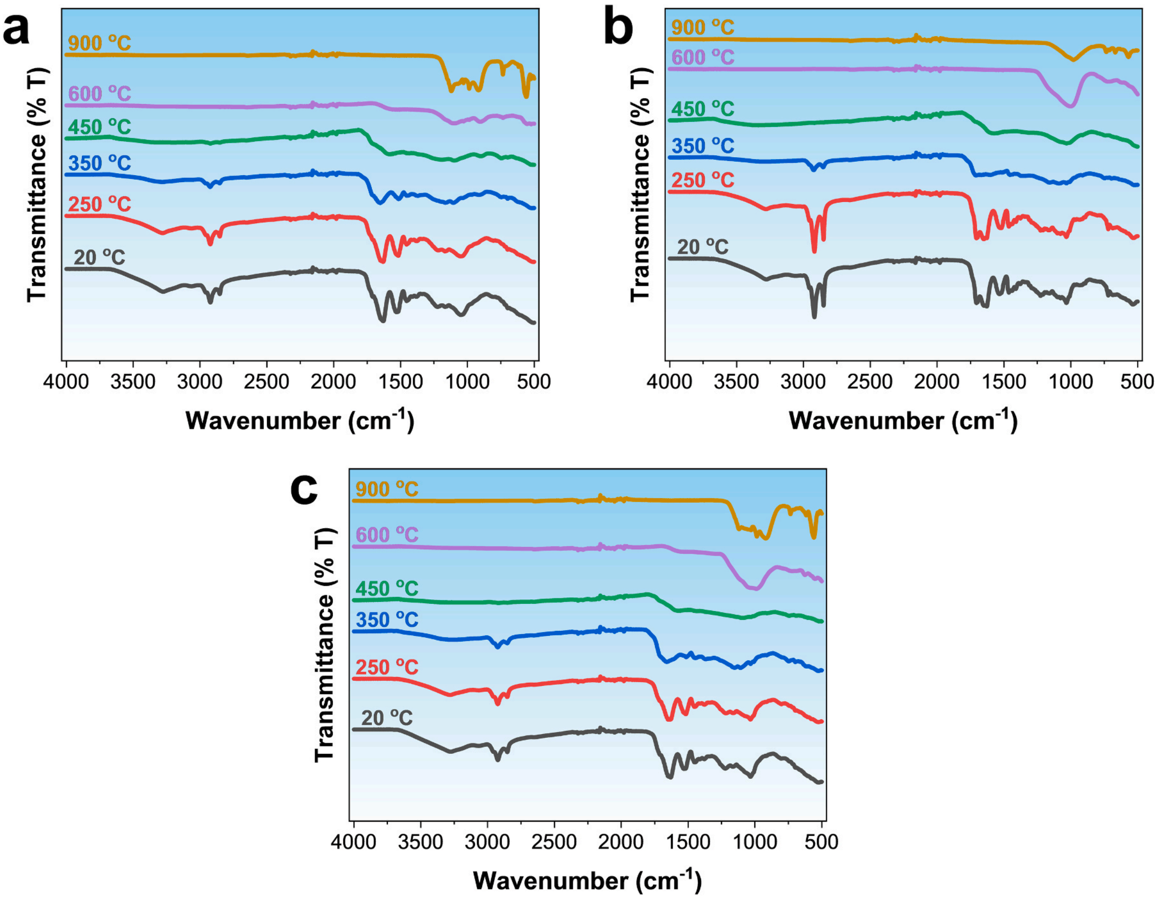


Fig. 6. FT-IR spectra of char residues from SSE (a), WSE (b), and DSE (c) at different temperatures.

DSE have lower PHRR, THR and higher char residue than those of WSE. Among EPS, the char layer formed by SSE is an outstanding barrier for preventing the propagation of flammable gases, insulating against heat transfer, and slowing down decomposition. The advantageous properties of char residues of SSE can be explained by their elemental contents and graphitisation degree, as shown in Fig. 8.

As illustrated in Fig. 8, the SSE char layer possesses the highest C and N contents of 69.2 % and 9.0 %, respectively, and the lowest O content of 17.6 %. In addition, the presence of N, P, and S elements in the char layer can suggest strong thermal stability. According to Sun et al. [43], the P and N elements can catalyse carbonisation and reinforce the char layer against heat and flame. Moreover, the presence of the P element is consistent with the FT-IR results where the P elements can persist at 900 °C. Although the P content in the char layer of WSE (5.1 %) is higher than SSE (3.9 %), the WSE char layer is still cracked due to lower carbon content than that of SSE. This instability may stem from the higher O/C ratio (0.71) in WSE char, which contrasts sharply with its N/C ratio (0.04) and P/C ratio (0.09). These disparate ratios reflect an inconsistent distribution of C-N and C-P bonds in the WSE char layer, resulting in a less stable structure. On the other hand, the O/C, N/C, and P/N ratios of the SSE char layer are relatively balanced, contributing to a more even and stable structure. For DSE, the thermal stability of the char layer can be attributed to the highest P and S contents of 6.23 % and 0.47 %, respectively, compared to those from other EPS. While the O/C ratio (0.67) of the DSE char layer is still higher than N/C (0.07), and P/C (0.12) ratios, this structure maintains a continuous surface despite the highest gas released. According to Qi et al. [42], the S element has synergistic effects with P, promoting its flame-retardant properties in the condensed phase. These findings align with the graphitisation degree of the char layer determined using Raman spectroscopy. In general, the Raman spectrum of each sample has two peaks, defined as D and G bands. The D band at 1360 cm^{-1} is related to the disordered carbon structure, while the G band at 1580 cm^{-1} is associated with the C-C vibration. The graphitisation degree of char is characterised by the intensity ratio of D bands and G bands (I_D/I_G). The smaller I_D/I_G ratio indicates the higher microcrystalline carbonaceous structure and smaller pore diameter of the char layer, which means better protective efficiency. As shown in Fig. 7, the I_D/I_G ratio of EPS char layer follows the sequence of DSE (1.48) < SSE (1.49) < WSE (1.82). The results provide evidence that char layers of SSE and DSE are denser and stronger than that of WSE. The reason can be due to the higher N, P, and S elemental contents of SSE and DSE than those of WSE.

3.6. *Proposed flame-retardant mechanisms of EPS*

The proposed flame-retardant mechanisms of EPS are shown in Fig. 9. Based on our findings, EPS exhibits flame-retardant mechanisms not only in condensed but also in gas phases.

In ambient conditions, EPS can act as an energy barrier to delay ignition due to the high AE. For example, SSE, with an AE of 372.29 kJ/mol, prolong the TTI to 24 s compared to 16 s for WSE, which have a lower AE of 219.17 kJ/mol. According to Zhu et al. [44], a higher AE corresponds to a greater energy barrier for thermal decomposition, which can slow down the pyrolysis reaction. Liang et al. [45] also compared the flame-retardant performance of two different lignin-epoxy flame-retardant composites. They found that the alkaline lignin-epoxy composites with lower activation energy showed higher THR and pHRR values than lignin@ammonium polyphosphate-epoxy composites. When a fire breaks out, PS, PN I, and LP are decomposed at low temperatures, releasing volatile compounds that cause combustion. However, the phenolics and N-compounds in the gas phase can interact with free radicals to diminish fire propagation [28]. Afterwards,

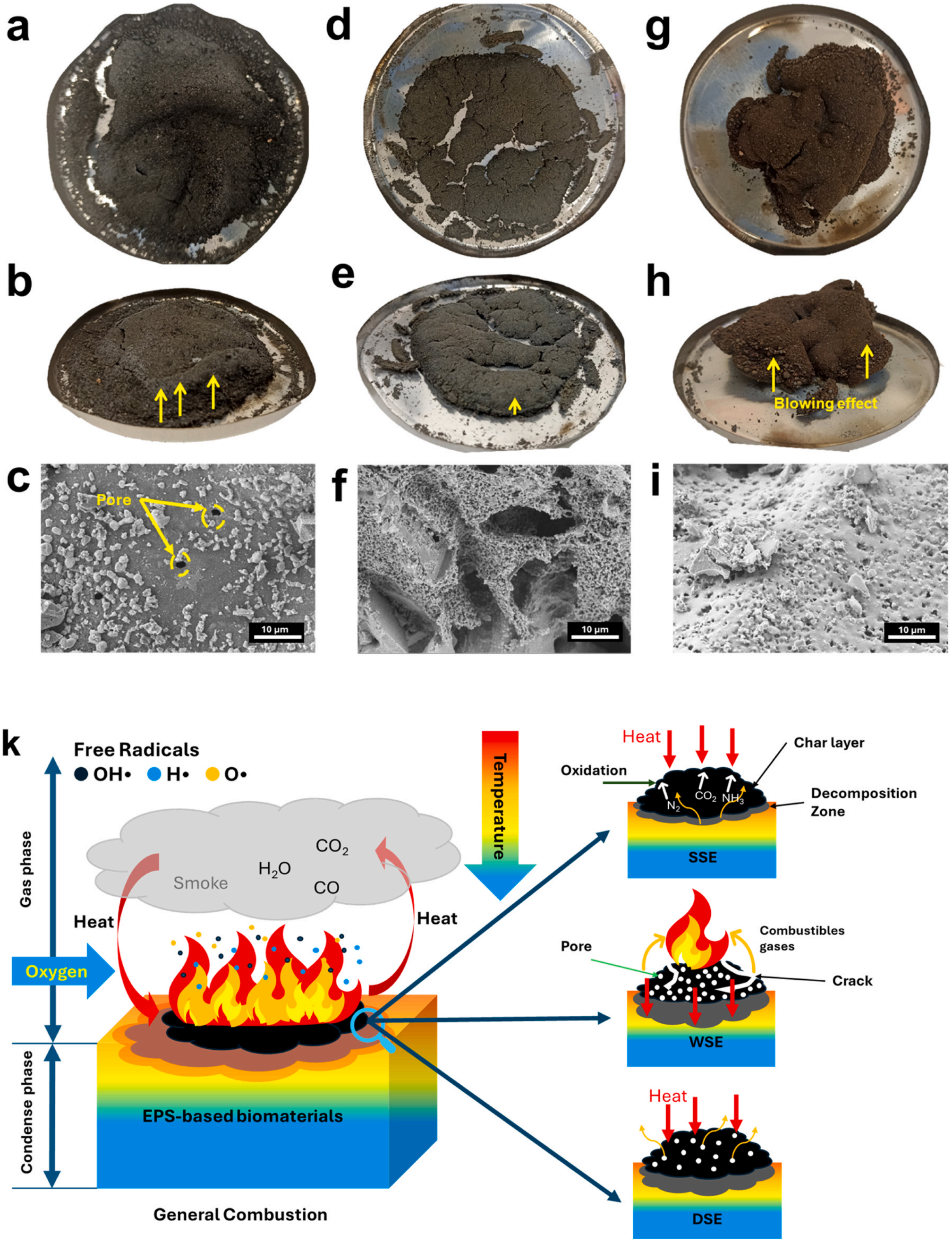


Fig. 7. Digital photos and SEM images of the char residues after burning in a cone calorimeter from SSE (a-c), WSE (d-f), and DSE (g-i) and the charring behaviours of different EPS (k).

these volatiles are oxidised to emit non-flammable gas to dilute the oxygen supplied to the fire. Furthermore, EPS form effective char to reduce the flammability of materials in the condensed phase. Based on the results above, it has been identified that HS and PN II contribute to char formation within the temperature range of 350 – 600 °C primarily due to their aromatic components. The EPS initiate to form char at 250 °C and continue to develop an effective char layer because of the release of P, N, and S elements. The char layer between EPS and a heat source can act as a physical barrier that prevents heat and mass transfer between gas and condensed phases, resulting in slower combustion. Therefore, the structured char layer of SSE and DSE is a reason for their lower THR and HRR compared to those of WSE. Leong et al. [46] claimed that N content has a significant positive correlation with the flame-retardant properties of recombinant proteins in *Escherichia coli.* This can suggest the main role of PN in the flame-retardant properties of EPS.

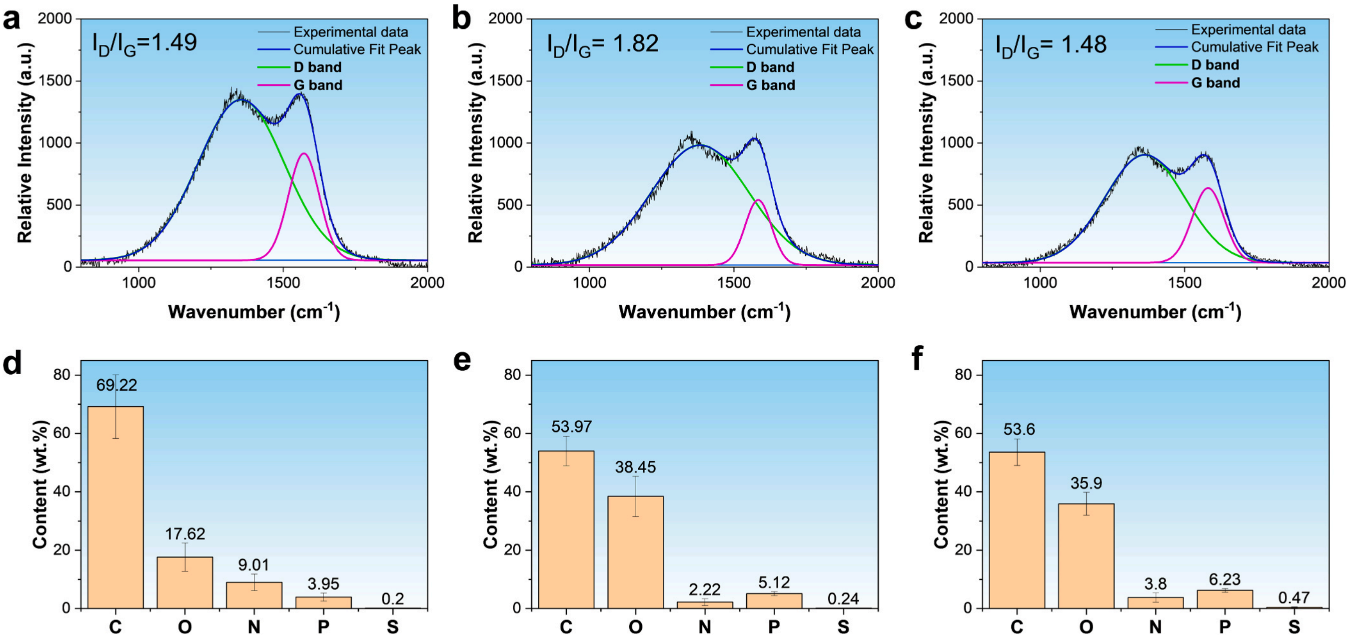


Fig. 8. Elemental contents and Raman spectra of the char residue after burning in a cone calorimeter from SSE (a and d), WSE (b and e), and DSE (c and f).

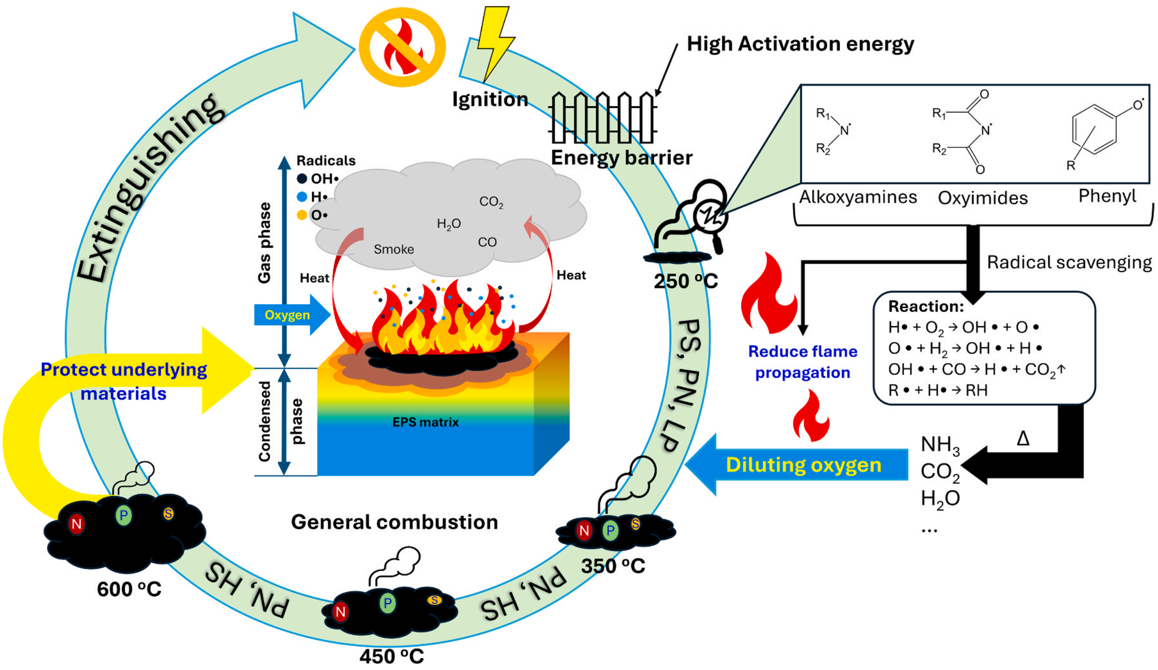


Fig. 9. Proposed flame-retardant mechanisms of EPS.

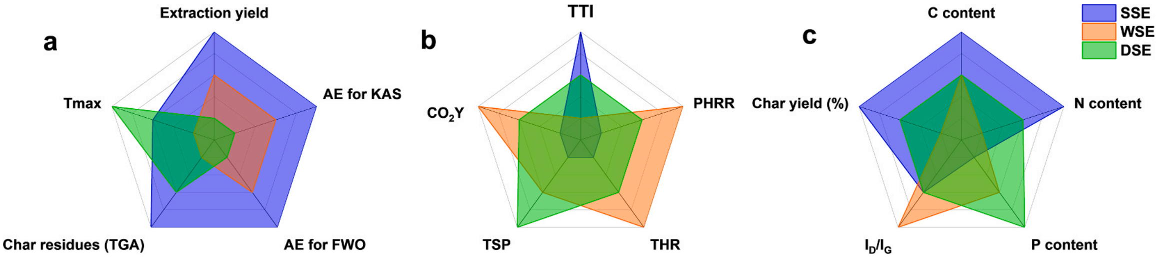


Fig. 10. Comparison properties of EPS from different types of sludges, including chemical-thermal properties (a), flammability (b), and char properties (c) for flame retardant applications.

3.7. Comparison of EPS for flame-retardant applications and future perspectives

Based on the results from the current research, the properties of EPS for flame-retardant applications are compared, as illustrated in Fig. 10.

While WSE are almost flammable, the SSE have the highest extraction yields, thermal stability, char-forming capabilities, and fewer toxicity gases, implying that SSE can be an effective flame retardant. Moreover, recovery of SSE could potentially have cost benefits for wastewater treatment plants, where the sludge residue, after extraction, can continuously take part in the anaerobic digestion process for methane and biogas production [47]. The fire performance and safety profile of DSE require improvement before it can be considered for application in flame-retardant materials, as its combustion is associated with the release of substantial amounts of toxic gases. A study on using DSE as a flame retardant could contribute to increasing the value chain of biosolids since they are currently used in low-economic applications, such as fertiliser and compost. Moreover, due to the high activation of SSE and DSE compared to some bio-flame retardants, such as lignin and phytic acid, these EPS have potential for use in flame-retardant packaging, where thermal properties are among the most important characteristics [22].

In this study, we found that nitrogen-based compounds in EPS conduct an important role for flame-retardant mechanisms in the gas and condensed phases, while phosphorus- and sulfur-based components exhibit flame-retardant effects predominantly in the condensed phase. Normally, nitrogen-containing compounds in EPS can mainly be found in protein and humic-like substances [48]. Furthermore, the phosphorus-based compounds can be associated with lipopolysaccharides [49] and phospholipids. These findings suggest that by controlling these component contents, we can improve the fire performance of EPS (as discussed in Section 3.5.2). In fact, controlling EPS composition can be done using different extraction methods. Liu et al. [50] have reported several methods to extract EPS with high polysaccharide content (21–78 %) but remaining other components (0.6 – 22 %). Similarly, our recent study [22] has found that the alkaline heating method can enhance the protein and humic-like substances content in EPS composition. Meanwhile, the physical process (e.g., sonication and centrifugation) can extract more polysaccharides.

Since EPS recovered from wastewater sludge is a novel and complex material, its application as a flame retardant is still in its infancy. According to Liu et al. [51], the flame retardant can play as an additive, a coating agent in the polymer matrix or join in polymerisation with other polymers. Therefore, the flame-retardant performance of EPS on polymer, fibre, or other combustible materials should be evaluated. Furthermore, the emission profile and potential toxicological effects of EPS as a flame retardant on human health and the environment are also an important research direction to fully evaluate the environmental sustainability of EPS-based flame retardants.

4. Conclusions

This study comprehensively analysed the flame-retardant mechanisms of municipal activated sludge EPS, revealing their potential as eco-friendly flame retardants. The flame retardancy of EPS from different types of sludges was assessed through chemical, thermal, and flammability properties. EPS has both gas-phase and condensed-phase flame retardant mechanisms. Gas-phase reactions involve the release of non-combustible gases that dilute oxygen and quench free radicals, while condensed-phase mechanisms are driven by the carbonisation facilitated by nitrogen, phosphorus, and sulfur groups in the EPS. The secondary sludge EPS demonstrated superior performance, with higher activation energy at a lower temperature (< 400 °C), delaying ignition by up to 24 s and exhibiting enhanced char formation and thermal stability. Secondary sludge EPS, with a high C, N, and P content, showed the lowest heat release rates. Unlike conventional flame retardants, the effectiveness of EPS arises from the interaction of their components, like proteins, polysaccharides, humics and lipids, warranting future research into their synergetic roles. This work demonstrates the feasibility of repurposing wastewater sludge-derived biopolymers as flame-retardants, contributing to circular economy practices and sustainable waste management.

CRediT authorship contribution statement

Krishnan Jayaraman: Writing – review & editing, Supervision, Methodology, Investigation, Conceptualization. **Nam Kyeun Kim:** Writing – review & editing, Supervision, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization. **Mark C.M. van Loosdrecht:** Writing – review & editing, Methodology, Investigation. **Yuemei Lin:** Writing – review & editing, Supervision, Methodology, Investigation, Conceptualization. **Wei-Qin Zhuang:** Writing – review & editing, Methodology, Investigation. **Tan Minh Le:** Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Conceptualization.

Declaration of Competing Interest

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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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2025.117907.

Data Availability

Data will be made available on request.

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