Advances in biosolids pyrolysis: Roles of pre-treatments, catalysts, and co-feeding on products distribution and high-value chemical production

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ARTICLE INFO

ABSTRACT

Biosolids (stabilised sewage sludge) are solid residuals from the wastewater treatment process and are considered important bioresource. Therefore, the valorisation routes of biosolids, particularly those involving thermochemical treatment, demand further attention. Among these thermochemical conversion strategies, the pyrolysis technique converts biosolids into potentially valuable products (biochar, bio-oil, and pyrolysis gas). The traditional approach to biosolids pyrolysis involves the conversion of the numerous organic and inorganic constituents under the same conditions in a single reactor. This approach suffers from many technical and economical limitations around product selectivity, conversion kinetics, product yields, and product application potential. Prominent is the production of heavy metals (HMs) concentrated biochar and nitro-oxygenated and polyaromatic hydrocarbons contaminated bio-oil. The role of feedstock pre-treatments, catalysts and co-feeding in mitigating some of these challenges is getting immense research attention, for which a critical review is necessary. This work provides an overview of the development in biosolids pyrolysis, covering the various effects of pretreatment, catalysts, and co-processing in influencing the thermal degradation behaviour, pyrolysis kinetics, product distribution, and product properties. A comprehensive review of the recent literature shows that chemical pre-treatment of biosolids can concurrently achieve demineralisation, HMs removal and hydrolysis, which add further value to the overall pyrolysis upcycling of the treated biosolids. Various catalysts additives such as metal oxides, metal salts, and zeolites can facilitate a range of desired reactions and inhibit pollutants release during biosolids pyrolysis. Co-feeding with a range of feedstocks introduces numerous synergetic benefits on product yield and qualities during the conversion process. Furthermore, these feed or process modifications to biosolids pyrolysis influence the distribution of value-added chemical components (such as hydrocarbons, ammonia, phenols, and levoglucosan) in the bio-oil, which were critically reviewed. The integrated approach to biosolids pyrolysis through sole or joint pre-treatment, catalysis and co-feeding could bring about a new route in biosolids valorisation. Finally, the work concludes with key challenges and provides perspectives for future research.

1. Introduction

Biosolids, otherwise known as stabilised sewage sludge, are unavoidable by-product of municipal wastewater treatment plants (WWTPs). A typical biosolids composition (wt% dry basis) from urban WWTPs is around 5–10% moisture, 30–50% inorganic matter, 10–21% proteins, 2–17% lipids, and 15–30% carbohydrates [1]. The numerous biosolids' organic and inorganic constituents could be a precursor for energy, fuels, and bio-based materials production via various valorisation routes depicted in Fig. S1. Nevertheless, biosolids management poses a challenge to WWTPs operation, which has so far identified only a few viable solutions around volume reduction and stabilisation through composting and land application [2]. The global traditional biosolids management varies, with about 50% beneficiated to agricultural land,

20% landfilled, and the balance either stockpiled or incinerated [3,4]. However, several concerns related to air and soil pollution are restricting these options, worsened by the declining quality of biosolids due to the emergence of persistent organic, inorganic and microbial contaminants [5]. Common contaminants in biosolids include per-and poly--fluoroalkyl substances, surfactants, pharmaceuticals, pesticides, microplastics, heavy metals, bacterial biomass and pathogens [6–8]. For biosolids that cannot be used conventionally in agricultural soils due to high contaminants levels, thermal treatment for resource recovery can be the most favourable management pathway and should dominate other routes soon [9]. Dried biosolids are considered a bioenergy resource largely due to their considerable volatile content (30–88 wt%) and calorific value (11–26 MJ/kg) [10]. Of all the thermochemical treatment techniques (Fig. S1), pyrolysis is the most widely studied process for converting biosolids into biochar with bio-oil and py-gas as co-products while reducing the waste volume by 50–70%, destruct persistent organic contaminants and pathogens, and eliminate odour problems [11,12].

Research works that have investigated biosolids pyrolysis can be classified into five groups [13]: thermal degradation behaviour and kinetics of biosolids pyrolysis [14–18]; analytical pyrolysis of biosolids [2, 5,13,19–22]; biosolids pyrolysis mainly for biochar [5,23–25]; pyrolysis of biosolids for obtaining syn-gas [2,26–28], and biosolids pyrolysis mainly for liquid production [13,29–35]. Table S1 provides an overview of bench-scale biosolids pyrolysis studies. Earlier works on biosolids pyrolysis focus on the production of biochar (or upgraded to activated char), which has found a range of applications, including biofertiliser in agricultural soils [25,36–38], catalysis [5,28,39,40], adsorption [23,41, 42], contaminated land remediation [43,44], and energy generation [45,46]. However, during pyrolysis, the HMs in biosolids are largely retained in the biochar at higher concentrations. The elevated HMs load is of great concern for the direct land application of the biochar [2]. Studies involving agricultural trials of biosolids-derived biochar have suggested that the HMs are less bioavailable to plants compared to the biosolids feed, and biochar addition mitigates the leaching of HMs [24, 36,47]. Nevertheless, the long-term fate of these metals remains largely unclear, and unless this concern is alleviated through further development, land application of biosolids-biochar may be limited. Biosolids pyrolysis, mainly for liquid production, has been extensively investigated [2,13,19,30]. Biosolids-derived bio-oil has features typical of conventional bio-oil with relatively low oxygen and high water, nitrogen, and sulphur contents compromising important fuel properties and high risks of emission of potentially harmful gases if combusted [29,31, 48]. Upgrading through catalytic post-treatment and hydrocracking is laborious and expensive [1]. Biosolids bio-oil also contains considerable amounts of polycyclic aromatic hydrocarbons (PAHs), which could limit valuable applications [5,49,50]. Pyrolysis gas from biosolids consists mainly of H_2, CO, CO_2, CH_4 and light hydrocarbons such as C_2H_2, C_2H_4, C_2H_6, and C_3H_8 with an energy density of 5–20 MJ/m^3 depending on the pyrolysis temperature [2,51,52]. Alongside these gaseous components, several N, S and Cl-bearing gaseous pollutants such as HCN, NOx, H_2S, HCl, COS and CH_3SH are emitted. There is a need for extensive gas cleaning and emission capture system to improve the attractiveness of biosolids pyrolysis gas for energy recovery. Biosolids pyrolysis process is highly endothermic; however, the products' calorific value is higher than that of the feed. Therefore, it has been demonstrated that a biosolids pyrolysis plant can run in energy-neutral mode by keeping a product fraction (usually biochar) while sacrificing the other two product streams for pyrolysis energy generation [51–54]. Any excess energy can be used for drying the feed or directed for other use onsite. However, for biosolids pyrolysis to be attractive from a commercial point of view, all product streams should have a market value; thus, there is a need to identify advanced process development in a biorefinery context.

Research has focused on pre-treatment, catalysis and co-feeding to enhance value capturing from biosolids pyrolysis and its products.

Biosolids' unstructured and heterogeneous composition is crucial in determining their thermal decomposition to high-value products [18], [2]. Through pre-treatment techniques, biosolids composition can be tailored to meet specific pyrolysis products' properties and application requirements. Biosolids pre-treatment before pyrolysis have several benefits: remove minerals and ash-forming elements which have deleterious effects on product formations, hydrolyse the recalcitrant components for easy thermal devolatilisation, and reduce HMs contents in the char [55–58]. The use of catalysts in various forms for improving the pyrolytic conversion of biosolids has also been largely studied with several benefits, including pollutant degradation, tar cracking, lowering the activation energy, and increased process selectivity [14,28,40,55]. Finally, the co-pyrolysis of biosolids with a range of feedstocks is another useful intervention in HMs reduction in the char, high bio-oil yield, and improved product properties through beneficial synergistic effects [59–62].

So far, there are several reviews dedicated to the thermochemical (in general) and pyrolysis (in particular) conversion of biosolids to biochar, bio-oil and pyrolysis gas either as a sole or joint product of the process [2,13,24,63–68]. These reviews have examined the critical effects of biosolids physiochemical properties and pyrolysis process conditions on product distribution and compositions, biosolids' pyrolysis mechanisms and kinetics, and various product application routes. Hence, the current work does not seek to duplicate efforts in those areas. Also, most biosolids pre-treatment works were focused on enhancing the anaerobic digestibility and methane production from primary and waste-activated sludge [69–72]. The pre-treatment of digested biosolids, particularly for improving their downstream pyrolytic conversion, is a growing research area and requires an in-depth understanding of the state-of-the-art. Despite several research studies demonstrating the prospects of integrated pyrolysis with pre-treatment, catalysis, and co-feeding for improving biosolids conversion process, product quality and high-value chemical production, there are limited reviews in this domain [65,73]. Specifically, the effects of pre-treatment, catalysts and co-feeding on biosolids pyrolysis behaviour and kinetics as well as product distribution and attributes were not captured extensively in the previous reviews. Additionally, the influence of sole or combined pre-treatment, catalysis and co-feeding in the pyrolytic conversion of biosolids to high-value chemicals demands a critical review. In sum, no review paper has captured the three process improvements on biosolids upcycling via the pyrolysis route.

Therefore, this paper provides a comprehensive review of pre-treatment, catalysis, and co-pyrolysis as individual or combined process routes in advancing the pyrolytic conversion of biosolids. The review started with an in-depth discussion of the roles of inherent metals on biosolids pyrolysis, making a case for pre-treatment strategies. After that, the biosolids pre-treatment process was examined for multiple goals such as demineralisation, HMs removal, hydrolysis, and components recovery. Then the effects of pre-treatment, catalysts and co-feeding on biosolids' thermal degradation behaviour and kinetics, pyrolysis product distributions and product attributes were reviewed. Furthermore, pre-treatment, catalysts and co-feeding effects on biosolids pyrolysis to high-value chemical components such as hydrocarbons, ammonia, phenols, and levoglucosan were extensively explored. Finally, critical challenges and research gaps were identified, and perspectives on future research were provided.

2. Inherent metals in biosolids: effects on pyrolysis and mitigation approach

Depending on the source and stabilisation methods, biosolids may contain roughly equal weights of organic and inorganic matter [64,74]. Generally, organic matter, unlike inorganic matter, decomposes rapidly during pyrolysis and distributes into gas, liquid and solid phases. The major inorganic constituents in biosolids are macro components of Al, Ca, Fe, Mg, Na, K, P, and Si and traces of micro components of Zn, Cl, Cr,

Cu, Mn and Ti [75,76]. These elements can be free or as salts forming oxides, carbonates, sulphates and allied salts compounds with the organic matrix [77]. The concentration of typical inorganic constituents in biosolids and their derived biochar at different pyrolysis temperatures are summarised in Table 1. Generally, these inorganic minerals in the biosolids are retained in the char after pyrolysis but in a higher concentration following the substantial decrease of organic matters during pyrolysis (Table 1). During pyrolysis, the behaviours of these metals are deleterious to a larger extent; inorganic constituents can get trapped by new organic compounds formed during pyrolysis [78], and in other cases, some macro and micro elements get volatilised [79]. For instance, Zhang et al. [80] observed that Hg almost completely partitioned in the oil and gas product fractions during biosolids pyrolysis as low as 300 °C while Cd and As had less than 10% recovery in the biochar at 650 °C. Similarly, only about 90% of alkali metals (Na and K) were retained in biochar obtained from biosolids pyrolysis at 900 °C [81]. The released metals and bounded metals participate in volatiles-volatiles and volatiles-char interactions, significantly influencing product formation via the catalytic alteration of several thermolysis reactions [82]. Detailed insights into the transfer routes of inorganic matter during pyrolysis and associated roles in product formation are provided in Leijenhorst et al. [83]. The specific impact of inorganic elements and minerals during pyrolysis has been investigated in several studies, and their fate is largely influenced by pyrolysis conditions and metal species [82–85].

Inherent biosolids inorganics, particularly the ash-forming alkali and alkaline earth metals (AAEMs), play key roles in the pyrolysis process, impacting product yield and attributes. These native inorganic materials can modify the activity and selectivity of primary and secondary decomposition reactions during pyrolysis [86]. For instance, the AAEMs are known to catalyse the ring-opening of pyranose bonds and inhibit the cleavage of glycosidic bonds, facilitating the production of low-molecular-weight oxygenate compounds [87]. In addition, hydrocarbon yields were found to decrease monotonically with increasing AAEMs concentration in biomass [84]. AAEMs are also known to facilitate water formation during pyrolysis through fragmentation and dehydration reactions [88]. AAEMs can partition into bio-oil catalysing series of undesired recombination and repolymerisation reactions due to their high reactivity causing thermal instability and ageing. AAEMs and other metals promote char cracking, producing more gas at the expense of organic-rich oil production [55]. Unlike AAEMs, the effects of inherent HMs on the biosolids pyrolysis process and product characteristics remain inadequately explored [89,90]. Nevertheless, their

presence in the biochar and possible migration to the bio-oil and gas products are highly undesirable and could limit the useful valorisation of biosolids pyrolysis products if not removed.

Following the active participation of the metals in the pyrolysis process, they primarily end up in the char residue due to their relatively thermal stability under pyrolysis conditions. As the AAEMs are undesirable in liquid and gaseous product phases, excessive amounts of inorganic species in the solid product can limit biochar properties and applications [91]. For instance, if the biochar is intended for use as activated char in adsorption/catalysis, the high levels of minerals can hinder the biochar porosity by restricting the penetration of activating agents into inner pores [92]. Native metals in biosolids were reported to interact with organic carbon stability during pyrolysis, thereby weakening the biochar carbon sequestration potential and inhibiting the conversion rates of organic matter [93]. Wang et al. [94] observed that the high minerals components in biosolids biochar altered the surface chemical functional groups considerably. The authors demonstrated that the abundance of oxygenated polar groups on the biochar was due to the ash-catalysed reactions of surface moieties during pyrolysis. The high ash contents in biosolids could retard stable polycyclic aromatic carbon formation that determines biochar stability [95]. Specifically, high levels of Si in biochar would reduce metal impregnation efficiency during a post-treatment modification [96]. Moreover, silica in the ash could promote metal sintering on melting at high calcination temperatures, reducing the degree of metal dispersion [97]. Lastly, the high levels of ash-forming minerals in biosolids would require higher pyrolysis temperature for its biochar pore structure to be fully developed compared to low-ash-containing biomass biochar [64].

On the other hand, inherent biosolids metals can facilitate the cracking of volatiles and char during pyrolysis to minimise tar formation and maximise syngas production. Metals (such as transition metals), either in the form of ions or in their zero-valent state, can be added to biosolids to introduce active sites in the resultant char for catalysis of several reactions, for example, methane decomposition [98], hydrogen production [97,99], and tar reforming [95]. The impregnation of metal salts on carbon materials may introduce functional sites to produce application-specific biochar [100]. Nevertheless, pre-treatment and post-treatment synthesis of biosolids or their derived char can interfere with the role of the inherent metals on physicochemical, thermochemical and structural morphology, which could be beneficial or otherwise in their application areas. Therefore the native mineral matters in biomass exhibit hybrid effects on the pyrolysis process and product attributes depending on the type of inorganic species and pyrolysis

Table 1
Typical inorganic constituents in biosolids and their derived biochar.

Components	Biosolids	Biochar production temperature (°C)			References
		350–500	550–650	700–900	
Proximate properties (wt% dry basis)					
VM[a]	28–74	10–37	6–21	5–16	[23,109–114]
Ash	24–69	41–81	44–84	62 – 95	[109,110,113,115–120]
Major Metals (mg/kg)					
K	26 – 7470	49–10300	2300–17800	2910 – 19663	[38,110,111,121–126]
Na	34–3490	51–5400	52–7400	1209–8110	[111,125–127]
Mg	750–22600	1200–41300	2240–49700	2300–37000	[111,118,128–130]
Ca	1500–54300	2000 – 77000	2300–77000	3400–110000	[110,111,129–131]
Fe	379–30000	508–40800	2550–41700	2800–43100	[110,111,123]
Al	1600–43200	1929–75700	4380–78400	5500–90700	[111,124,130,131]
Trace Metals (mg/kg)					
Cu	20–1000	38– 1900	90–2000	110–2200	[81,112,127,131,132]
Zn	4.4–2580	5.9–2822	172–3368	170 – 2300	[111,123,129,133]
Ni	12–112	17–147	28–160	32–195	[22,112,128,129,133–135]
Pb	0.2–3740	8–5120	27–5250	56–5200	[38,109,130,136]
Cd	0.4–169	0.5–235	1.5–2310	0.24–123	[22,109,110,120,129,130,137]
As	< 3–84	1–188	< 1 – 247	< 1–50	[22,109,112,127,132,137–140]
Co	2–20	4–1000	3–4000	–	[38,119,121,128,138]
Cr	1 – 449	3 – 586	3 – 690	25–630	[125,127,130,133,134,136]

[a] Volatile Matter

conditions [101,102].

Biosolids pre-treatment can mitigate the deleterious effects of the inherent metals during pyrolysis by either washing out the metals or passivating the activity of the metals [103]. The former occurs through the lixiviation of soluble cations in an ion-exchange reaction with a proton from acid (Fig. S2). The latter involves the infusion of chemical solvents into biosolids, which changes the feed's electronic structure by forming stable metal salts resistant to normal catalytic functions [104, 105]. The pyrolysis of minerals-deficient biosolids and pristine biosolids (with the full spectrum of inherent minerals) can help understand the influence of minerals on biosolids pyrolysis [56]. While this method provides insight into the overall role and impacts of internal biosolids minerals on pyrolysis performance, it lacks specificity on a particular metal as most pre-treatment techniques are not selective in removing certain metals at the cost of others. Also, the pre-treatment process, particularly at high severity conditions, can alter the treated biosolids' physicochemical and structural properties [106]. Thus, the pyrolysis behaviour of demineralised biosolids compared with raw biosolids may not reflect the exact impact of the metals due to significant variations in physiochemical attributes. A way to mitigate this potential challenge is to carefully select pre-treatment conditions that will remove most minerals and, at the same time, cause the least modifications to the structural and physicochemical properties of the treated biosolids. Robust analytical characterisation of the pre-treated biosolids to assess compositional stability is crucial [106].

The other approach to studying the pyrolytic role of biosolids minerals is to impregnate mineral-free biosolids (obtained through pretreatment steps) with various basic and acidic oxides or metal salts to attain biosolids enriched with specific components of interest [78,107, 108]. The pyrolysis of metal-infused biosolids and raw biosolids will help understand the effects of indigenous metals in biosolids pyrolysis. However, a critique of this approach is the non-competitive chemical structure of metal-impregnated biosolids with the naturally metal-enriched biosolids. Removing the native metals and minerals by pre-treatment modifies the biosolids matrix to some degree, and adding metals/minerals cannot produce the exact structure typical of raw biosolids containing that metal component [56]. Hence, the assumed role of added metals on biosolids' pyrolysis performance may not accurately represent the role of the native metal in biosolids. Nevertheless, this method provides specificity to the role of metals and minerals in biosolids pyrolysis as the feed is enriched with a specific metal component. Whichever approach is taken to elucidate the pyrolytic role of biosolids minerals, pre-treatment for demineralisation is fundamental.

3. Biosolids pre-treatment: techniques and objectives

Several pre-treatment techniques, such as chemical, physicochemical, biological, and thermochemical have been explored on lignocellulosic biomass integrated processing [141,142]. For biosolids, the range of pre-treatment techniques that have been used to achieve various goals is summarised in Table 2. Chemical solvents such as acids, alkalis, surfactants, and ionic liquids have advanced biosolids valorisation for resource recovery. For example, Abouelela et al. [143] demonstrated the use of acid-assisted protic ionic liquids for the fractionation and decontamination of industrial biosolids into lipids and

carbohydrate/protein-rich solids while simultaneously removing HMs. Other works have also reported the use of organic solvents and ionic liquids with various acid and alkali for the recovery of lipids and cellulose from primary biosolids for biodiesel and bioethanol production, respectively [144–147]. The low cost of acids and industrial maturity of acidpre-treatment processes [148] have favoured acid as the most extensive and popular pre-treatment agent used to achieve multiple objectives (Table 2). However, some concerns such as corrosiveness and generation of toxic waste streams are typical limitations. Biosolids components fractionation and hydrolysis (see Supplementary Information), demineralisation, and HMs removal can enhance the pyrolysis upcycling of treated biosolids to high-quality products. Acid pre-treatment of biosolids can concurrently achieve these objectives and is further examined in this section.

3.1. Demineralisation of biosolids using acids

The removal of water-insoluble metals requires acidic solutions for their leaching. Low pH values of acids are generally favourable for metal ions solubilisation. Since most metals and their ions are basic, they react with acid through ion-exchange mechanisms at electroneutral conditions [158]. Thus acids have a leading role in demineralisation [159]. Studies involving biosolids demineralisation using acids are summarised in Table 3. It can be observed that the demineralisation efficiency of biosolids using acid is generally between 20% and 50%, which is relatively lower compared to leaching efficiency from other biomass materials. For instance, Nan et al. [93] reported an 89%, 82%, 85%, and 52% deashing efficiency from barley grass, peanut hull, cow manure, and biosolids, respectively, under the same demineralisation conditions. The low demineralisation rate of biosolids indicated the presence of water and acid-insoluble inorganic sediments. Additionally, the metals can be bound to organic matter in biosolids, reducing the exchangeable fractions of the metals available for leaching [77]. Common minerals species found in biosolids and their ash are quartz (SiO_2), calcite ($CaCO_3$), calcium aluminosilicates ($CaAl_2Si_2O_8$.4 H_2O), aluminium phosphates ($Al_2(PO_4)(OH)_3$), ferric hydroxides ($FeOOH$), and calcium phosphate ($Ca_9(PO_4)_6PO_3OH$) [55,93,149]. Hence the major mineral-bearing elements in biosolids are P, Fe, Al, Ca, and Si. Silica is hardly removed during biosolids demineralisation with common acids, Ca extraction is limited in H_2SO_4 (the popular leaching solvent) due to the formation of poorly soluble $CaSO_4$ hydrates, and Fe extraction is generally enhanced at high leaching temperatures [56,160]. Therefore the low deashing efficiency of biosolids can be connected to high Si and Ca contents in biosolids [75]. Hakeem et al. [106] observed that higher acid concentration and low temperature gave the best deashing results for biosolids treated at 25–100 °C with 1–5% H_2SO_4. However, the demineralisation process was limited by Si and Ca removal, and only a modest 50% reduction in ash content was achieved. It is suggested that a two-stage demineralisation process using acid and alkali could increase the removal of mineral components further. The effectiveness of alkalis (typically KOH and NaOH) in removing silicates, aluminates and carbonates-based minerals, as well as sulphides in coal, have been reported [161–163]. Numerous studies demonstrated that acid washing is the most effective technique for diverse mineral removal in biosolids with varying levels of demineralisation efficiency [55,56,74,93].

Table 2
Biosolids pre-treatment techniques for various objectives.

Pre-treatment types	Acid	Alkali	Physico-chemical	Ionic liquids	Biological	Chelating agents	Hydrothermal
Pre-treatment objectives							
Components recovery[145,149–151]	✓	✓		✓	✓		
Components hydrolysis[144,145]	✓	✓		✓	✓		✓
Demineralisation/deashing[55,56]	✓	✓	✓			✓	
HMs removal[77,152–155],	✓			✓	✓	✓	✓
Anaerobic digestibility and dewaterability[69,70,156,157]	✓	✓	✓		✓		✓

Table 3

Demineralisation studies of biosolids using acids.

Feedstock	Pretreatment agents	Pretreatment conditions	Demineralisation efficiency* (%)	Remarks	Refs.
Digested sewage biosolids	1.0 M H_2SO_4	ambient temp, 12 hr	41.6	AAEMs were completely removed. Silica content increased by 30%.	[55]
Dewatered biosolids	5% HCl	ambient temp, 6 hr	21.6	AAEMs oxides were reduced by at least 50%. All minerals content reduced except for silica and TiO_2	[56]
Dried biosolids	2.0 M HCl	60 °C, 6 hr, 1:5 solid/liquid (g/ml)	–	Only Si was detected in the ash of the demineralised sample	[75]
Dried municipal biosolids	A mixture of 27% HCl and 9% HF	12 hr agitation then heating at 80 °C for 6 hr	19.0	Ca and Al are the dominant metals in the treated sample. Si and Fe removal rates exceeded 98% and 60%, respectively	[160]
Dried digested biosolids	1–5% H_2SO_4	25–100 °C, 2 hr, 1:10 solid/liquid (g/ml), 600 rpm	23–50	Ca removal was limited due to precipitation as $CaSO_4$ hydrates. Silica contents increased in all treated biosolids	[106]
Dried biosolids	0.5 M HCl and 0.5 M HF	Room temp; 1:30 solid/liquid (g/ml), 24 hr	51.5	The low ash removal rate indicated the presence of insoluble inorganic sediments	[93]
Digested and dried biosolids	3 M HCl	Room temp; 1:20 solid/liquid g/ml, 120 rpm, 48 hr	33.7	Biosolids used contained 49.2% volatile matter and 42.2% ash content	[74]

*estimated by taking the percentage difference of total minerals contents (wt%) in demineralised and raw biosolids or by the percentage difference in the ash contents before and after demineralisation

Corrosion of process reactors/vessels and the need for additional chemicals for neutralisation are also peculiar challenges with strong acid demineralisation [164]. As a result, dilute acids (<5%) demineralisation can be performed at moderate to higher temperatures, referred to as thermal acidolysis or thermo-chemical pre-treatment [165].

3.2. Acid pre-treatment of biosolids for HMs removal

Biosolids can be severely contaminated with toxic HMs in concentrations higher than the safe limit prescribed by many legislations [4, 65]. These metals are present in various forms and exhibit different behaviour regarding chemical interaction, mobility, bioavailability and potential toxicity [166]. While pyrolysis can degrade organic and microbial contaminants in biosolids, it typically increases the concentration of HMs in the derived biochar [24]. Hence pyrolysis cannot sufficiently deal with the problem of elevated metals contamination in biosolids unless coupled with either a pre- or post-treatment step. However, the pre-treatment of biosolids may be desired over the post-treatment of the derived biochar as the metal concentration are relatively lower in the biosolids than in the biochar [24]. Also, depending on the pyrolysis conditions, some low boiling point HMs (such as Hg, As, and Cd) volatilised and partitioned into bio-oil and gas fractions and may reduce their final remediation potential in the biochar [58,80]. Moreover, HMs are more readily leachable in biosolids than the resultant biochar due to increased metal stability and chemical transformation during pyrolysis [129]. Pyrolysis favoured the transformation of the mobile fraction of HMs to residual fraction at high temperature, immobilizing HMs in the char [58].

Several pre-treatment methods have been investigated for removing HMs in biosolids. The washing of biosolids with solvents such as acids [167,168], ionic liquids [143,153], chelating agents [166,169], surfactants [170], and ferric salts [171–173] have been reported. Other methods include microbial leaching [155,174], electrodeposition [57], supercritical fluid extraction [175,176], hydrothermal [177,178], and ultrasonic technique [179,180]. Acidification with mineral and organic acids has short operation times and high removal efficiency of multiple metals compared to other methods [152]. Table 4 summarises studies using acids to remove common HMs in biosolids. When mixed with biosolids, the acid solubilises the HMs and leaches them into the solution through ion exchange of protons (H^+) from the acid with the metal ions, according to Eq. 1 [152]. Therefore, the rate of metal solubilisation is controlled by the pH (H^+ concentration) of the extracting solution besides operating variables such as contact time, solids loading, temperature, and agitation speeds [152]. However, the success of acid leaching for HMs removal depends on the chemical fractionation of the metals within the biosolids matrix [181]. Heavy metals in biosolids can be operationally defined in four different fractions i) exchangeable (ionised form), ii) reducible (bound with carbonates and Fe-Mn oxides), iii) oxidisable (bound with organic matter), and iv) residual (bound with silicates and recalcitrant organic matter [182]. Usually, the exchangeable (acid-soluble) fractions are easy to remove, followed by the reducible and oxidisable fractions, while the inert (residual) fraction is hardly removed through chemical leaching. Hence, both the pH and the oxidation-reduction potential of the extracting solvent jointly enhance HMs removal in biosolids [167]. The trivalent HM ions such as Fe and Cr are more difficult to remove than the divalent ions such as Cu, Zn, Ni and Cd due to the competitive uptake of H^+ by the more reactive HMs from the acid [183]. Gheju et al. [169] observed that HNO_3 and HCl could not extract Cr, while Cu, Cd and Pb had the least extraction affinity for all acids tested. Pb is known to have poor leachability with H_2SO_4 due to the formation of $PbSO_4$, which is sparingly soluble in water, and Cu is the most challenging HM to extract in biosolids using acids due to the high affinity of Cu with organic ligands [167]. A composite or sequential washing process combining two or more extraction reagents (acids, chelating agents, and oxidising agents) can achieve a higher removal rate of HMs from biosolids [184]. Lower pH (higher acid concentration), longer residence time, lower solid concentration, smaller particle size, and higher agitation speed support high extraction rates of HMs from biosolids at ambient temperature [77] (Table 4). However, higher temperature (preferably <100 °C) can shorten the extraction time due to improved mass transfer, low pulp density and higher diffusion rates of metal components [185]. Acidolysis and redoxolysis are the dominating mechanisms governing HMs dissolution from biosolids [173].

$$Biosolids \quad (M) + Acid \quad (H^+) \quad \rightarrow Biosolids + M^{z+} + Acid \quad (1)$$
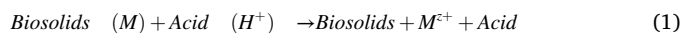
Optimum extraction pH with mineral acid is usually between 1.0 and 2.5 and 3.0–4.0 for organic acids, at which extraction of most metals can be around 50% [186]. However, the optimum conditions varied widely between metals due to differences in the initial concentration of the metals in the biosolids and their chemical form within the biosolids matrix [181]. Therefore, the extraction trend of most HMs in an acidic medium has not been largely consistent, even under similar leaching conditions (Table 4). Following the leaching of the HMs into the acidic solution (leachate), it is necessary to recover the HMs from the extracting solution to prevent adverse environmental impacts associated with the disposal of the metal-laden aqueous acidic stream. Hydrometallurgical processes may be the suitable way to utilise this secondary waste stream [187]; however, the concentration of the metals in the leachate needs to be attractive for recovery. Chemical precipitation, solvent extraction, adsorption, and selective ion exchange resin are the most common techniques for HMs recovery in aqueous solutions [154]. A comparison of the performance of each technique and their limitations

Table 4

Acid pre-treatment studies of biosolids for HMs removal.

Biosolids source	Acid type	Pre-treatment conditions	Metals Removal (%)						Refs.
			Cd	Cr	Cu	Ni	Pb	Zn	
Municipal digested biosolids	Citric	1:10 S/L, room temp., 200 rpm, 6 hr, pH 2	2.5	44.8	2.5	20	4.0	47.5	[169]
	Nitric	1:10 S/L, room temp., 200 rpm, 6 hr, pH 1	7.5	~0	1.5	19.5	4.9	28.5	
	Hydrochloric	1:10 S/L, room temp., 200 rpm, 6 hr, pH 1	9.0	~0	5.5	11.5	3.5	26.5	
	Oxalic	1:10 S/L, room temp., 200 rpm, 6 hr, pH 2	4.8	5.0	2.0	6.0	~0	7.5	
Municipal biosolids	Sulphuric	1:5 S/L, 10% v/v acid, 25 °C, 30 min		68	38	53	4	72	[195]
		1:5 S/L, 20% v/v acid, 25 °C, 30 min		82	58	55	5	68	
		1:5 S/L, 10% v/v acid, 80 °C, 30 min		64	54	62	8	70	
		1:5 S/L, 20% v/v acid, 80 °C, 30 min		99	86	74	11	72	
Metal plating biosolids	Sulphuric	2% w/v solids, 25 °C, 120 rpm, 48 hr, pH 2	58	11	69	69	55	72	[155]
Printed circuit board biosolids	Sulphuric	0.5% solids (w/v), 103 °C, 2 hr, 250 rpm, 0.05 M acid	~100	75	~100	85		84	[196]
		0.5% solids (w/v), 103 °C, 2 hr, 250 rpm, 0.5 M acid	~100	98	~100	99		100	
		4% solids (w/v), 103 °C, 2 hr, 250 rpm, 0.05 M acid	~100	~0	~70	78		65	
		4% solids (w/v), 103 °C, 2 hr, 250 rpm, 0.5 M acid	~100	90	~100	99		99	
Municipal biosolids	Sulphuric	1:3 S/L (g/ml), 1 N acid, room temp., 1 hr	57	29	20	72	37	78	[194]
	Nitric	1:3 S/L (g/ml), 1 N acid, room temp., 1 hr	52	27	24	75	100	74	
	Hydrochloric	1:3 S/L (g/ml), 1 N acid, room temp., 1 hr	60	28	56	77	100	86	
	Phosphoric	1:3 S/L (g/ml), 8.5% acid, room temp., 1 hr	72	35	6	80	65	77	
Industrial biosolids	Nitric (microwave-assisted)	1:6 S/L, 1 N acid, < 150 μm PS, 30 min, 1000 W			90	92		92	[77]
		1:20 S/L, 1 N acid, < 150 μm PS, 30 min, 1000 W			94	95		97	
	Sulphuric (microwave-assisted)	1:6 S/L, 1 N acid, < 150 μm PS, 30 min, 1000 W			92	95		81	
		1:20 S/L, 1 N acid, < 150 μm PS, 30 min, 1000 W			94	97		90	
Municipal and industrial biosolids	Citric (ultrasound-assisted)	1:10 S/L, 0.2 M acid, pH 2.7, 25 °C, 20 min		35.4	13.1	40.2		53.5	[197]
	Citric	1:10 S/L, 0.2 M acid, pH 2.7, 25 °C, 24 hr		34.8	12.7	40.0		52.5	
Digested biosolids (municipal)	Sulphuric	1:5 S/L (g/ml), 20% acid, room temp., 15 min		76	12	67	39	60	[198]
	Nitric	1:5 S/L (g/ml), 20% acid, room temp., 15 min		68	9	70	49	53	
	Hydrochloric	1:5 S/L (g/ml), 20% acid, room temp., 15 min		71	29	80	46	62	
	Phosphoric	1:5 S/L (g/ml), 20% acid, room temp., 15 min		53	10	53	42	47	
Metal plating biosolids	Sulphuric	1:5 S/L, 100 g/l acid, room temp, 700 rpm, 24 hrs		98.2	88.6	98.0	5.6	99.2	[199]
		1:5 S/L, 200 g/l acid, room temp, 700 rpm, 24 hr		99.2	77.6	95.4	4.9	89.8	
		1:20 S/L, 100 g/l acid, room temp, 700 rpm, 24 hr		98.8	84.1	99.2	2.5	96.3	
		1:20 S/L, 200 g/l acid room temp, 700 rpm, 24 hr		82.3	79.0	88.4	4.0	88.6	
Digested biosolids (municipal)	Sulphuric	0.5 g solid/200 ml liquid, pH 1.5, room temp		20.3	57.8	75.0	27.6	82.3	[200]
	Nitric	0.5 g solid/200 ml liquid, pH 1.5, room temp		18.9	65.5	73.6	45.1	72.1	
	Hydrochloric	0.5 g solid/200 ml liquid, pH 1.5, room temp		13.2	60.7	63.6	30.7	85.9	
Digested biosolids (municipal)	Sulphuric	1:10 S/L (g/ml), 3% acid, 25 °C, 600 rpm, 30 min	68.0		67.3	47.2		87.5	[106]
		1:10 S/L (g/ml), 3% acid, 63 °C, 600 rpm, 30 min	81.3		73.9	52.8		93.7	
		1:10 S/L (g/ml), 5% acid, 63 °C, 600 rpm, 30 min	78.9		95.5	60.8		86.0	

can be found in these reviews [188,189]. Chemical precipitation is the most widely studied and less laborious method [190]. Common precipitants, including alkalis such as CaO, NaOH, NaHCO₃, and sulphides such as NaS, H_2S, or FeS [152], can precipitate metals out of solution which can be recovered as mixed metal salts for smelter processing or as potential metal hydroxides salts for heterogenous catalysis reactions [191]. Adsorption using activated char, biochar, or other porous materials can uptake metal ions from the leachate stream [192,193]. Yoshizaki and Tomida [194] demonstrated the recovery of HMs and phosphoric acid from the leachate of municipal biosolids using cation-exchange resin. Three times recycling of the recovered phosphoric acid yielded a competitive removal efficiency of HMs. All HMs except As and Cr were almost entirely removed by the resin; over 70% of As and Cr was recovered.

4. Pyrolysis of pre-treated biosolids

4.1. Effects on biosolids thermal degradation behaviour

The derivative thermal degradation (DTG) profile of raw biosolids usually divides the overall degradation regimes into three: dehydration (100–220 °C), devolatilisation of organic matter (220–650 °C) and char cracking (>650 °C) [64,106,201]. Devolatilisation of organic matter results in massive weight loss attributed to the decomposition of carbohydrates, proteins and lipids. This stage is usually likened to the degradation of conventional lignocellulosic biomass components (hemicellulose, cellulose and lignin) – an analogy reached from the degradation temperature point of view and not from compositional resemblance [151,202]. Hemicellulose degrades in the temperature range of 150–315 °C, cellulose degradation occurs between 315 and 400 °C, whereas lignin decomposes at a higher and wider temperature

range of 250–700 °C [75]. The pre-treatment of biosolids using 2 M HCl and 60 °C to remove metals showed three clear and distinct degradation peaks with maxima temperature at 208, 247 and 421 °C, respectively, compared to 227, 323, and 440 °C for the raw biosolids (Fig. 1(A)) [75]. The DTG thermograph in Fig. 1(B) showed six clear peaks (I–VI) in the raw biosolids degradation profile. Peak I and peak II were attributed to the loss of moisture and light volatiles, respectively, while peaks III–V represent the major mass loss due to the decomposition of organic matter and peak VI was ascribed to the loss of inorganics, usually carbonates [106]. Pre-treatment temperatures influenced the thermal decomposition behaviour of the treated biosolids. For instance, the peaks (II and VI) associated with the decomposition of light volatiles and inorganics completely disappeared in all treated biosolids DTG. This observation suggested that acid treatment of biosolids, irrespective of severity conditions, caused a loss of light volatiles (leachable organics) and minerals.

The peaks associated with organics decomposition persisted in all treated samples but at different intensities. All DTG peaks of demineralised biosolids were shifted to lower temperatures compared with the raw biosolids (Fig. 1). This was in agreement with the study of Nan et al. [93], who observed a shift of the maximum peak degradation to a lower temperature (270 °C) during the thermal degradation of demineralised biosolids compared to 300 °C for the raw biosolids. Meanwhile, Tang et al. [56] observed a slight increase in the maximum peak degradation temperature of demineralised biosolids to 300 °C from 280 °C for raw biosolids. During demineralisation, biosolids' structure might change caused by metal removal, which could delay or hasten the degradation of organic macromolecules. Mineral removal can facilitate the thermal degradation of biosolids components, although this is usually common at the initial decomposition stage. Mineral removal is known to inhibit char cracking which generally occurs at the later stage of pyrolysis. Regarding degradation intensity, biosolids pre-treatment usually results in a higher weight loss rate. For instance, relative to the raw biosolids, a higher weight loss rate was observed for demineralised biosolids obtained at mild conditions of temperature and acid concentration (25–63 °C and 5% v/v (< 1 M) H_2SO_4) (Fig. 1(B)) [106], similar to the findings in Nan et al. [93] and Tang et al. [56]. In contrast, Shao et al. [75] observed a lower weight loss rate in the pyrolysis of demineralised biosolids obtained at 5 M HCl and 60 °C in Fig. 1(A). This suggests that biosolids demineralisation may lower the initial degradation temperature but may not increase the rate of such degradation (lesser amounts of organic matter are decomposed probably due to loss of volatiles during the pre-treatment steps), particularly when the pretreatment is

performed at high temperatures and/or acid concentration (see sample S4 in Fig. 1(B)). The variations in the thermal behaviour of demineralised biosolids can be attributed to differences in the levels of compositional alterations caused by the pre-treatment process and differences in demineralisation conditions [203]. The effect of acid pre-treatment on biosolids pyrolysis activation energy (Ea) is limited in the literature. Tang et al. [56] found that up to 330 °C, acid-washing increased the Ea by 8–40% and at higher temperatures up to 600 °C, the pyrolysis Ea was similar for both raw and treated biosolids. The decrease in Ea for the raw biosolids relative to the demineralised feed confirmed the catalytic effect induced by the inherent minerals.

4.2. Effects on products distribution and attributes

Numerous research efforts on biosolids pre-treatment focused on producing activated char via chemical activation pre or post-pyrolysis (Table S2). Also, substantial works on biosolids pre-treatment were coupled to an analytical pyrolysis set-up to understand thermal degradation behaviour and kinetics (as discussed in Section 4.1). There are limited research investigations on biosolids pre-treatment integrated to applied pyrolysis for all product analyses, particularly bio-oil compositions and properties [55,204]. Pre-treatment can have different effects on biosolids pyrolysis products' yield and quality due to possible changes in physicochemical properties such as the decrease in ash contents (and increase in the volatile matter) and modification of surface morphology and functional groups [106]. The excessive dissolution of total solids, including volatile matter, during pre-treatment is undesirable if the treated biosolids are to be converted via pyrolysis to valuable products. Hence, the pre-treatment must be performed under mild conditions to have minimal impact on the organic matter available for the downstream pyrolysis process. Also, since the raw biosolids and treated biosolids are usually different in terms of ash (or volatile matter) contents, the product yields after pyrolysis are assessed on an ash-free or volatile matter basis. For instance, concerning the loss of total solids (TS), the pre-treatment of biosolids with HCl and acetic acid caused about 8–26 wt% reduction in TS, and it was 16 wt% for NaOH treatment [204]. H_2SO_4 treatment caused about 25–45% loss in TS in another work [106]. The volatile matter (VM) of acid-treated biosolids was largely similar to the raw biosolids [204], whereas a 3 wt% decrease in VM was reported by Wei et al. [160], and ~10 wt% increase in VM was reported by Hakeem et al. [106]. Acid pre-treatment of biosolids can be more of demineralisation rather than hydrolysis process if performed under mild conditions to limit the loss of organic matter. However, alkalis have high
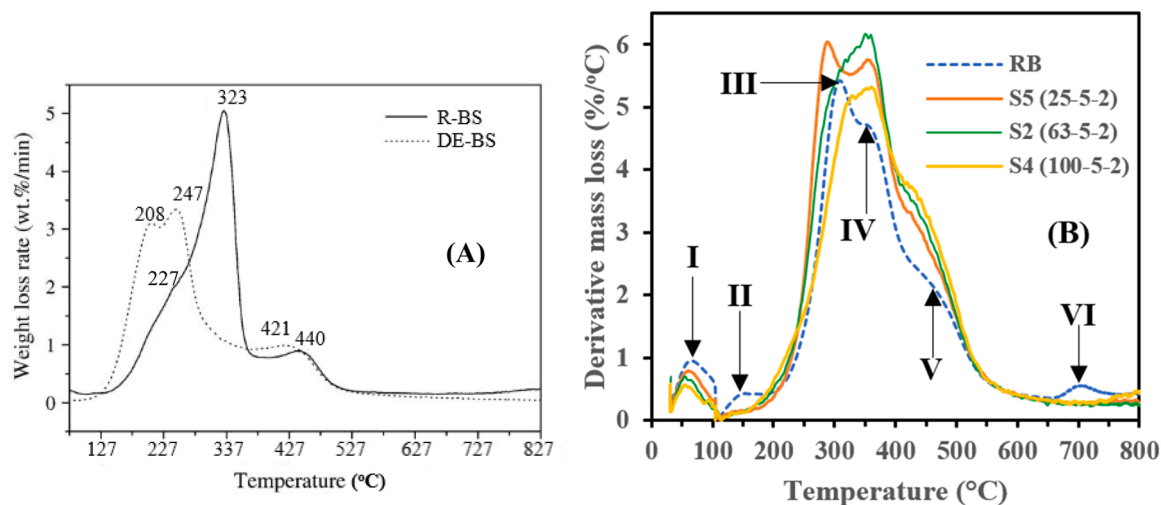

Fig. 1. Effects of pre-treatment on thermal degradation of biosolids (A) raw biosolids (R-BS) vs demineralised biosolids (DE-BS) at 2 M HCl and 60 °C for 6 hr [75] (B) raw biosolids (RB) vs demineralised biosolids (S5, S2, and S4) at different H_2SO_4 pre-treatment conditions (temperature–acid concentration–time); e.g., S5 (25−5−2) refers to demineralised biosolids obtained at 25 °C with 5% v/v H_2SO_4 for 2 hr [106].

organic matter hydrolysis ability leading to substantial loss of VM, suggesting that using alkali for biosolids pre-treatment can reduce the organic matter conversion to oil during pyrolysis [204].

Pyrolysis temperature and feedstocks' volatile matter are the key factors affecting oil yields during pyrolysis. Bio-oil yields (on a dry ash-free basis) from acid and alkali-treated biosolids ranged from 47 to 50 wt% and were 3–6 wt% higher than the untreated biosolids (44 wt %) [204]. Pyrolysis of demineralised biosolids usually gave lower bio-char yields due to the prior removal of ash forming elements, which enhances the devolatilisation of organics to generate lower solid residues. For instance, the biochar yield from demineralised biosolids was 43 wt% (with an ash content of 54.4 wt%) compared to a yield of 48 wt % (with an ash content of 70.5 wt%) from raw biosolids [93]. Similarly, in another work [106], the biochar yield from raw biosolids (having an ash content of 30 wt%) was 51 wt%, while the biochar yield from treated biosolids (having an ash content of 17 wt%) was 36 wt%. The higher the demineralisation efficiency of biosolids, the lower the biochar yield; generally, the higher the ash content of biomass, the higher the char yield at a given pyrolysis temperature [205]. However, when the biochar yield is expressed on a dry ash-free basis, it is typical for the biochar yield from demineralised biosolids to be higher relative to the raw biosolids biochar yield [93]. This is because pre-treatment facilitated the removal of labile carbon in biosolids, thereby increasing the amount of fixed carbon reaching the biochar. Biosolids pre-treatment can increase the carbon sequestration potential of the resulting biochar as well as the calorific value. Higher carbon (3.5–30.1%) retention in biochar was obtained from demineralised biosolids compared to the raw biosolids [93,106]. Pre-treatment caused a reduction of oxygen-containing functional groups such as C=O, O=C–O, and C–O, and promoted C–C/C=C bonds, producing biochar with a higher degree of aromatisation [93]. However, no significant influence of pre-treatment was reported on the evolution of small molecules (such as CO_2, CH_4, $C_2H_4O_2$, C_3H_6O, $C_3H_6O_2$, and C_4H_4O) during the pyrolysis of demineralised and raw biosolids [93]. Lastly, biosolids pre-treatment produce biochar of overall lower HMs contents, higher fixed carbon, and lower ash contents compared to raw biosolids biochar. The retention and migration characteristics of the HMs during pyrolysis were impacted by pre-treatment [106].

5. Catalytic pyrolysis of biosolids

Catalytic pyrolysis of biosolids is a well-explored research area with the aim of increasing conversion and selectivity and lowering energy consumption. Commonly used catalysts include metal salts, metal (alkaline earth and transition metals) oxides, and zeolites [75,206,207]. Based on the nature of the contact between catalysts and feed materials, catalysts that are effective for this application can be classified into two groups: the primary catalysts and the secondary catalysts [208]. Primary catalysts are considered to have direct contact with biosolids through normal dry mixing or wet impregnation. The in-situ catalysis (using primary catalysts by dry mixing) is the most common approach to biosolids catalytic pyrolysis, where the catalysts materials are used as additives or as bed materials [5,14]. Secondary catalysts are not mixed with the biosolids feed but are used in a secondary process downstream of the main pyrolysis process. This set-up is commonly called ex-situ catalysis, usually for tar cracking, gas cleaning and bio-oil upgrading [209].

5.1. Effects on biosolids degradation behaviour and pyrolysis kinetics

Shao et al. [75] investigated the role of metal oxides (Al_2O_3, Fe_2O_3, TiO_2, ZnO and CaO) addition on the pyrolysis of HCl-demineralised biosolids up to 1100 K. The pyrolysis of demineralised biosolids blended with Fe_2O_3 and ZnO slowed down the decomposition of organic matters to generate more chars. In contrast, the addition of Al_2O_3, CaO and TiO_2 enhanced the degradation of organic components to produce

less solid residues. Al_2O_3 and TiO_2 increased the overall kinetics of pyrolysis while CaO, Fe_2O_3 and ZnO retarded pyrolysis kinetics in terms of conversion rates. However, all the metal oxides added were found to accelerate the initial degradation rate of biosolids samples, occurring at 429–435 K as opposed to 448 K for the raw biosolids [75]. Mineral removal from biosolids samples prior to pyrolysis changed the physicochemical structure, further modified by the presence of CaO, TiO_2, and ZnO. Overall, the catalytic effects of the metal oxides on the pyrolysis of demineralized biosolids samples varied significantly across the decomposition stages of biosolids' organic components. Blending lime with biosolids was reported to improve the thermal stability of the biosolids [210]. Devolatilisation rate increased from 0.20 %/°C to 0.50 %/°C for limed-added biosolids. However, the maximum degradation temperature shifted from 280 °C for raw biosolids to 450 °C for lime-blended biosolids. The loading of lime had a critical influence on the pyrolysis conversion of the biosolids matrix in terms of degradation rate, kinetics, and heat flow [210]. For example, the heat requirement per gram of weight loss during the pyrolysis of lime-blended biosolids at 340–550 °C slightly increased at a proportional rate of $Ca(OH)_2$ added. On the contrary, at higher temperatures (550–700 °C), adding lime up to 85 mass% lowered the pyrolysis heat requirement by 17–73% [210].

In another study, Tang et al. [76] observed that the pyrolysis profile of biosolids and the rate of weight loss was proportional to the amounts of MgO added (Fig. 2(B)), similarly to the observations with CaO addition (Fig. S3). CaO and MgO-blended biosolids produced more char residues than raw biosolids, indicating that mineral addition retarded biosolids decomposition to a certain extent. Minerals also lowered the degradation rate, and the degree of reduction increased with the increase in the amount of minerals added. At a temperature above 580 °C, biosolids pyrolysis was impeded to some extent by the presence of MgO, whereas the presence of CaO facilitated the decomposition of the organic constituents. Meanwhile, in another work, adding Fe_2O_3, Al_2O_3 and SiO_2 to biosolids did not significantly change its thermal decomposition behaviour [99]. Patel et al. [14] observed that the thermal decomposition of biosolids in the presence of different additives increased the maximum weight loss rate with degradation behaviour shown in Fig. 2(A). Mineral addition facilitated the devolatilisation of biosolids components which was contrary to the observations of Tang et al. [76] (Fig. 2(B)). However, the addition of minerals did not appreciably decrease the pyrolysis Ea in both studies. Also, a similar mean Ea (21.8–28.8 kJ/mol) were observed during the pyrolysis of biosolids with various minerals [75]. Drastic reduction (up to 95%) in Ea was only observed for degradation regimes above 500 °C, where char cracking might be initiated. On the contrary, pyrolysis Ea was found to reduce for MgO/CaO blended biosolids between 170 and 430 °C, while the Ea increased at higher temperatures up to 600 °C and decreased afterwards at 750 °C [76]. Adding Fe_2O_3 or red mud lowers the mean Ea of biosolids pyrolysis by 13.9 and 20.1 kJ/mol, respectively, whereas SiO_2 and Al_2O_3 did not change the pyrolysis Ea (189–191 kJ/mol) [99]. The dependency of pyrolysis Ea on biosolids fractional conversion in the presence of SiO_2 was unchanged compared to the raw biosolids indicating that SiO_2 was inert throughout the pyrolysis process. The use of primary catalysts in biosolids pyrolysis was beneficial in lowering the pyrolysis Ea only at higher fractional conversion ≥ 70% [99]. However, the change in pyrolysis Ea is a function of pyrolysis temperature, minerals type and blending ratio, and kinetic model used. Generally, minerals addition to pyrolysis is favourable at the char cracking stage for lowering Ea but can increase the initial energy requirement at the devolatilisation stage [14,75,78,206].

5.2. Effects on product distributions

The distribution of biosolids pyrolysis products can vary in the presence of catalysts materials. Table 5 summarises catalytic pyrolysis studies using different catalysts materials and their effects on product yields. Irrespective of the catalyst materials, pyrolysis conditions such as
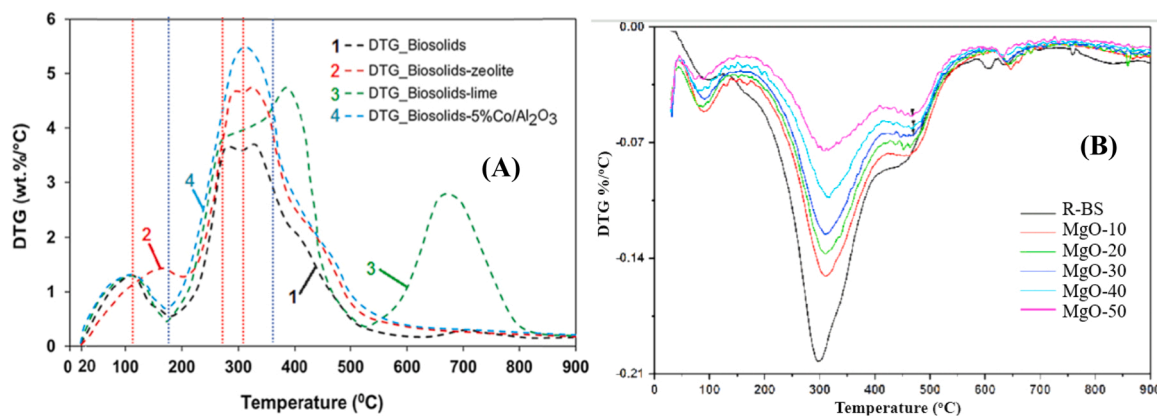
Fig. 2. Influence of minerals addition on the thermal decomposition behaviour of biosolids (A) biosolids with various additives [14] (B) MgO addition to biosolids - Raw biosolids (RS) and MgO-blended biosolids at 10–50% mass ratios [76].

temperature and pyrolysis types (conventional vs microwave) had a remarkable impact on product yields. For instance, at the same temperature and similar feed composition, microwave pyrolysis generally produce lower gas and higher oil yields compared to conventional heating [211]. This is due to the lower residence time of vapours and less interaction of volatiles and char in microwave systems. From Table 5, acidic (e.g., metal salts and zeolites) and basic (e.g., metal oxides/hydroxides) catalysts are the two common types of materials used in the catalytic pyrolysis process. Generally, acidic catalysts such as HZSM-5 increase biochar yield and reduce tar formation (decrease bio-oil yield), while the basic catalysts decrease biochar yield relative to the product yields from uncatalysed pyrolysis [208]. Acid-based catalysts are known for their excellent tar reforming ability due to the availability of protons for hydrocracking reactions, whereas basic catalysts have superior char cracking ability [212]. The acidity of catalysts, particularly Brønsted acidity, is critical for cracking oxygenates in the pyrolysis vapours. Empirically, the cracking activity of solid acid catalysts such as ZSM-5, zinc oxide, silica-alumina and Al-MCM-41 can be correlated to their acidity [213]. Also, the nature of catalysts mixing with the biosolids can influence the product yields differently. For example, the wet-impregnation of CaO with biosolids increased biochar yield [214], contrary to other studies that reported that CaO addition generally decreases biochar yield [5,215]. This is because the wet-infusion method can passivate the char cracking ability of the added metal components through the formation of thermally stable salts resistant to normal catalytic functions [104]. Lastly, carbon-based catalysts in the form of biochar or activated char were not observed to influence biochar yield but rather promote gas production through secondary cracking of higher molecular weight volatiles at high temperatures. The mechanism of biochar/activated char catalysis can be attributed to combination of surface areas, microporosity, metals, and surface functional groups [40,216]. In conclusion, it can be observed that the effects of catalysts on the product distribution and selectivity is dependent on catalysts type, catalyst loading, pyrolysis set-up (conventional vs microwave, slow vs fast, and reactor configurations), biosolids compositions (volatiles and ash) and reaction mechanisms of each catalyst material.

5.3. Effects on gaseous pollutants emission

Mineral addition to biosolids can facilitate desulphrisation and denitrogenation reactions and mitigate the release of gaseous pollutants during pyrolysis. For instance, $Ca(OH)_2$ addition promoted the transformation of S and N components in biosolids resulting in a lesser content of pollutants (H_2S, pyrrole-N, NOx) [210]. $Ca(OH)_2$ addition produced biosolids-char with lower aromaticity and hydrophilicity, in which the dominant speciation of C, N, and S was C–H group,

pyridine-N, and sulphonic- and sulphide-S, respectively. The pyrolysis of biosolids mixed with different mass ratios (10–50 wt%) of calcined CaO and MgO gave higher absorbance of pyrolytic volatiles with a stronger enhancement from CaO [76]. MgO suppressed the release of pollutants (H_2S, HCN, NH_3) and nitro-aromatics compounds, while the addition of CaO fostered the release of NH_3 and HCN. However, both minerals effectively lower the release of S-containing pollutants (COS, SO_2, CH_3SH) and inhibit the transformation of N to NO_2. Sun et al. [222] suggested that alkaline earth oxides (MgO/CaO) can be an effective catalyst in pollutants degradation as well as good sulphur fixation agents. The performance of three catalysts materials (CaO, biosolids ash and Al_2O_3) was assessed for the degradation of S-, N-, and Cl-bearing gaseous pollutants during biosolids pyrolysis [222]. Biosolids-derived ash and CaO remarkably reduce H_2S emission at lower temperatures; however, the strength of biosolids ash was weak at higher temperatures. CaO, Al_2O_3 and biosolids ash were limited in suppressing NH_3 release, and only CaO considerably lowered the evolution of HCl due to the formation of $CaCl_2$ and hydration of calcium oxide consistent with the work of Park et al. [223]. The cracking of pyrolysis volatiles in the presence of CaO and La_2O_3 in a fixed bed set-up at 450 °C lowered the chlorine content in the biosolids bio-oil drastically [223]. Chlorine concentration was reduced from 498 ppm in the raw bio-oil to 73 ppm by CaO and 78 ppm by La_2O_3 attributed to the formation of metal chlorides (CaClOH and LaOCl) by chlorination and hydration of the metal oxides catalysts. CaO was found to have a stronger sulphur fixation effect for both H_2S and COS. Han et al. [224] reported that CaO fostered the release of oxygen and nitrogen substituted heavy PAHs in biosolids at 450 °C while it decreased light substituted PAHs. $Ca(OH)_2$ hindered the transformation of nitrile-N in char to HCN, enriching the char with N [225]. Although high nitrogen content in char is potentially attractive as a fertilizer; however, the plant-available N in most biochar is unclear at present [226].

5.4. Effects on products composition and properties

Furthermore, the catalytic pyrolysis of biosolids can impact the distribution of components in the bio-oil as well as the properties. Patel et al. [14] observed that the catalytic pyrolysis of biosolids in the presence of lime, 5% CO/Al_2O_3 and zeolite considerably impact the evolution of non-condensable gases, hydrocarbons, carboxylic acids and oxygenates. All additives increase gaseous volatiles (CO_2, CO and CH_4), whereas only 5% CO/Al_2O_3 and lime considerably increased hydrocarbon and carboxylic acid formation. Lin et al. [220] studied the pyrolysis of biosolids impregnated with KOH, H_2SO_4, $ZnCl_2$, $FeSO_4$, and H_3BO_3. All the five additives reduced bio-oil yield, and except for $ZnCl_2$, all other materials greatly improved bio-oil quality with respect to HHV, density, viscosity and carbon content. Alkali addition promoted

Table 5

Pyrolysis of biosolids with various catalysts materials: influence on product distribution.

Catalysts	Process conditions	Products yields (wt% dry basis)[a]			Observations	Ref.
		Bio-oil	Biochar	Gas		
Metal oxides						
CaO	Bed material, Slow pyrolysis, bubbling fluidisation, 20 g BS, 500 °C, 1 hr r.t., 1:1 BS to cat.	27.6 (24.2)	31.1 (44.7)	41.4 (31.2)	CaO influence on product distribution was prominent at higher temperatures. CaO addition decreases char yield and enhances secondary char and tar cracking to gas. Lime cracked the oxygenate compounds (C-O) in oil to form $CaCO_3$. Biochar surface areas declined in the presence of lime	[5]
	700 °C	28.8 (36.8)	26.8 (38.0)	44.5 (25.2)		
	900 °C	25.4 (28.0)	21.8 (31.3)	52.9 (40.8)		
TiO_2	Dry mixing, TG-study, 10 mg feed, 827 °C, 10 °C/min 1:10 cat to BS	–	38.2 (42)	–	The effects of the additives on biosolids organic devolatilisation can be ranked as Fe_2O_3 <ZnO<No-catalyst<Al_2O_3 <CaO<TiO_2. Solid residue formation was increased by Fe_2O_3 and ZnO but decreased by others	[75]
ZnO		–	42.4 (42)	–		
Al_2O_3		–	41.2 (42)	–		
CaO		–	38.8 (42)	–		
Fe_2O_3		–	42.7 (42)	–		
CaO	Wet mixing with BS, fixed bed, 600 °C, 0.2 g/min feed rate, 10 min reaction time	30(46)	60(49)	10(5)	CaO destructs S-containing compounds in bio-oil from 4.6% to 1.5%. CaO promoted H_2 and CO generation through the ring-opening reactions of aromatic hydrocarbons	[214]
Fe_2O_3	Dry mixing, Fixed bed, 30 g BS, 500 °C, 30 °C/min, 30 min r.t., 1 wt% cat.	34.5 (32.5)	55.5 (58.8)	10(8.7)	Fe_2O_3 shows no significant effect on bio-oil compositions. The catalyst improved the devolatilisation of biosolid's organics to more oil and less char but did not enhance tar cracking. The bio-oil HHV was improved slightly, and the gas calorific value was not improved.	[217]
	3 wt% cat.	37.5 (32.5)	51.0 (58.8)	11.5 (8.7)		
	10 wt% cat.	39.1 (32.5)	48.7 (58.8)	12.2 (8.7)		
Al_2O_3	Dry mixing, Microwave pyrolysis, 30 g BS, 550 °C, 1:10 cat to BS	19.4 (17.5)	–	–	LHV and chemical energy of the bio-oil increased by 11% and 19%, respectively. Al_2O_3 promoted direct devolatilisation of biosolids organics to hydrocarbons	[218]
Fe_2O_3		22.6 (17.5)	–	–	LHV and chemical energy of the oil increase by 17% and 56%, respectively. Fe_2O_3 had inhibitory effects on oxygenate formation, which improved the heating value of the oil	
Composite alumina	Dry mixing, Fixed bed, 35 g BS, 500 °C, 50 min, 1:1 BS to cat	45.2 (47.3)	34.0 (35.1)	20.8 (17.6)	The ratio of the organic phase to the liquid product was higher. The catalyst promoted the reforming of the liquid product.	[219]
Al_2O_3	Dry mixing, Fixed bed fast pyrolysis, 10 g feed containing 10 wt% cat, 800 °C, 30 min r.t.	27 (36.5)	57.0 (47)	16.0 (16.5)	At the same temperature, only Fe_2O_3 and red mud could produce more gas. H_2 yield increased by 111% and 56% with the addition of Fe_2O_3 and Al_2O_3, respectively. All additives could not lower the PAHs content in the oil	[99]
SiO_2		25 (36.5)	58.5 (47)	16.5 (16.5)		
Fe_2O_3		21 (36.5)	56.0 (47)	23.0 (16.5)		
Red Mud		23.5 (36.5)	56.5 (47)	20 (16.5)		
CaO	Dry mixing, Microwave pyrolysis, 30 g BS, 10 wt% cat, 700 °C	13.6 (21.6)	55.0 (68.0)	31.4 (10.4)	Both catalysts aided the devolatilisation of BS organic matter. CaO was a better tar cracking catalysts to favour gas production than Fe_2O_3. CaO enhanced aromatic hydrocarbon formation while Fe_3O_2 inhibited phenol formation	[215]
Fe_2O_3		22.6 (21.6)	60.0 (68.0)	17.4 (10.4)		
Metal salts and hydroxides						
$FeSO_4$	Wet impregnation, Microwave pyrolysis, 400 °C, 3.5 kg feed containing ~67 g catalyst/kg feed	27.6 (29.2)	–	–	All additives reduce bio-oil yield but influence the bio-oil compositions and properties differently. For instance, all catalysts except for $ZnCl_2$ increased the oil's calorific value. All additives reduced the bio-oil density similarly, but $FeSO_4$ gave the lowest reduction in the oil's viscosity	[220]
$ZnCl_2$		23.7 (29.2)	–	–		
KOH		24.1 (29.2)	–	–		
Acid and Zeolites						
HZSM-5	Microwave fast pyrolysis, 550 °C, 15 g BS, 1:1 BS to cat.	16.5 (23.5)	54 (44.5)	30(32)	HZSM-5 addition did not improve bio-oil yield; rather, it increased char yield. Substantial increase in aromatic hydrocarbon	[221]
H_2SO_4	Wet impregnation, Microwave pyrolysis, 3.5 kg feed containing 68 g catalyst/kg feed, 400 °C	19.3 (29.2)	–	–	Sulphuric acid reduced bio-oil yield more than boric acid due to the enhanced reduction of water, metals and polar groups in BS by strong acid treatment. This decreased the microwave heating rate remarkably. Both acids slightly increased the oil carbon and nitrogen content	[220]
H_3BO_3		25.7 (29.2)	–	–		
Biochar-based catalysts						
Biosolids derived biochar	Slow pyrolysis, bubbling fluidisation 700 °C, 35 °C/min, 1 hr r.t., 1:1 BS to cat ratio	48.8 (36.8)	36.8 (38.0)	14.4 (25.2)	Biochar assisted the devolatilisation of biosolids organics leading to high bio-oil yield	[5]
Biosolids derived activated char		16.9 (36.8)	40.1 (38.0)	43.0 (25.2)	The high surface area of activated char increased aromatic yield by 63% and lower formation of nitrogenated by 39%, and polyaromatics by 73%	[5]
Biosolids derived biochar	Fixed bed reactor, 700 °C, 15 °C/min, 30 min r.t., 1:1 BS to cat ratio	21.5 (36.5)	43.5 (44.5)	34.5 (19.0)	The ratio of feed to catalyst has a negligible influence on biochar yield but considerably influences oil and gas yields. A higher catalyst amount increases gas yield and decreases oil yield. Bio-oil HHV decreased considerably from 8.1 MJ/kg to 1.6 MJ/kg due to the high water contents of the bio-oil. Gas HHV increased by over 100%.	[28]
	2:1 BS to cat ratio	26.5 (36.5)	42.5 (44.5)	29.7 (19.0)		

Table 5 (*continued*)

Catalysts	Process conditions	Products yields (wt% dry basis)[a]			Observations	Ref.
		Bio-oil	Biochar	Gas		
					Energy recovery was shifted from bio-oil to gas using biochar-based catalysts.	

[a] values in parenthesis are the respective product yield from the non-catalytic biosolids pyrolysis process

hydrocarbon production while acid treatment favoured the formation of heterocyclics, ketones, alcohols and nitriles. $ZnCl_2$ was a better catalyst than $FeSO_4$ in terms of higher selectivity to a few components. Meanwhile, in another study, adding Fe_2O_3, SiO_2, Al_2O_3 and red mud did not influence the biosolids pyrolysis product distributions [99]. However, Fe_2O_3 and Al_2O_3 increased H_2 yield by 50.7–268.5% and 10.3–56.0%, respectively, at 700–900 °C [99]. Morni et al. [227] studied the effects of two metal oxides catalysts (NiO and MoO_3) and ZSM-5 catalysts on the composition of bio-oil obtained from biosolids pyrolysis. Both metal oxides catalysts substantially promoted the formation of phenols, ketones and furans. Ketonisation and aldol condensation reactions are facilitated over metal oxides catalysts, promoting C-C coupling reactions via dehydration by oxygen removal [228]. ZSM-5 catalysts reduced acids and alcohol formation by 96% and 67%, respectively and remarkably increased aromatic hydrocarbon by over 300% [227].

Yu et al. [229] observed that Ni-based catalysts (NiO and Ni_2O_3) had higher activities towards converting biosolids to more bio-oil and gas with stronger enhancement from Ni_2O_3. CaO favoured the production of H_2-rich syngas, whereas Ni-based catalysts generated CO-rich syngas due to the promotion of CO_2 and steam reforming reactions by Ni. The addition of $CaCO_3$ rather than CaO decreased H_2 yield, evident by the stimulation of reverse-water gas shift and dry reforming of methane reactions by $CaCO_3$. Kim and Parker [204] observed that alumina-free zeolite catalysis of biosolids did not influence bio-oil yields; rather, it resulted in lower char yields and higher gas yields. The addition of zeolite was useful for generating pyrolysis gases by facilitating the conversion of volatile solids to gases and char cracking to gases. Ren et al. [230] reported that adding $Ca(OH)_2$ to biosolids increased carbon retention, surface area, alkalinity, and chemical oxidation stability of the biochar, enhancing its potential for carbon sequestration when used as a soil amendment. Agrafioti et al. [23] observed that the impregnation of biosolids with K_2CO_3 and H_3PO_4 enhanced the leachability of specific HMs from their biochar, whereas HMs were highly immobilised in non-impregnated biosolids biochar.

5.5. Secondary catalysts

Few studies have investigated the ex-situ catalytic pyrolysis of biosolids. Azuara et al. [1] and Wang et al. [226] performed ex-situ catalytic pyrolysis of biosolids by passing pyrolysis vapours over HZSM-5 catalyst bed. The bio-oil contains light hydrocarbon components due to enhanced cracking of the pyrolytic tar, and further reaction increased the yields of CO and CO_2. However, this observation was highly influenced by pyrolysis temperature and catalysis temperature, facilitating decarbonylation and decarboxylation reactions. Xie et al. [221] found that microwave-assisted ex-situ catalytic pyrolysis of biosolids using HZSM-5 was optimal at 550 C, marked by higher hydrocarbons and the lowest proportions of oxygen- and nitrogen-containing compounds in the bio-oil. In these studies, the effects of catalysts are largely inconsequential on the product yields, particularly the biochar. Nutrients and HMs are highly retained in the biochar due to little interaction of the char with the catalyst material during pyrolysis. Hence, catalyst deactivation (pore blocking) by the char inorganics might be mitigated or even eliminated in *ex-situ* catalytic pyrolysis processes than in-situ catalytic setup. Also, it could be easier to control the catalytic reaction when pyrolysis and catalysis stages are not lumped together as in the in-situ approach and allow for easy recovery of the catalyst materials.

However, catalyst poisoning by tar and the need for two-process stages are typical challenges in ex-situ catalysis.

6. Biosolids co-pyrolysis

Biosolids share many similarities with most biomass materials in physiochemical attributes, enhancing its co-processing with a wide range of feedstocks [2]. Co-pyrolysis of biosolids can improve the conversion efficiency and assist in elevating some compositional and application deficiencies in biosolids-derived products, such as lowering HMs content in biochar, destruction of nitrogenated and PAHs compounds in bio-oil, and enhancing biochar surface morphology [9]. Due to biosolids' high ash content and low calorific value, co-processing with lignocellulosic biomass may positively affect product yields and quality. The potential advantage of mixing biosolids with lignocellulosic biomass is the low ash, HMs, nitrogen and sulphur contents which can lower pollutants release and retention during biosolids pyrolysis. Polymer wastes such as polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), nylons, and tires have a very high H/C ratio given that they are the product of petroleum and natural gas. Plastics have high combustible contents, no ash and negligible oxygen (nitrogen and sulphur) contents which are important parameters for improving liquid product yield and quality during pyrolysis [231]. Notably, PVC has considerable chlorine contents (~57 wt%); therefore, co-processing biosolids with PVC can increase the risks of Cl-contamination and associated emissions [232]. Although there are no reported works on the co-pyrolysis of biosolids with PVC, other works have demonstrated that the co-processing of PVC with biomass and coal inhibited dehydrochlorination reaction from the synergistic interactions of ash materials on Cl fixation [233]. Nonetheless, plastic wastes are considered good feedstock for pyrolysis and can be a good co-reactant in enhancing the pyrolytic conversion of biosolids to light liquid fuels. Non-plant biomass such as animal manure, poultry litter, food waste, algae, paunch waste, and other readily biodegradable materials are generally classified as organic wastes. Given the high inherent moisture and nutrient (N, S and P) contents of these feedstocks, their co-treatment with biosolids can benefit from the catalytic ability of biosolids ash in desulphurisation and denitrogenation reactions during pyrolysis [182, 234,235].

6.1. Effects on the thermal degradation behaviour

The feedstock type and the mixing ratio with biosolids can significantly impact the thermal degradation behaviour of biosolids. When biosolids were mixed with various plastics materials, LDPE-blended biosolids had the maximum weight loss rate (11–19 %/min) and lowest residual mass (26–30%), while polyester-blended biosolids had the lowest weight loss rate (3 %/min) and highest residual mass (40%) [236]. Biosolids were observed to largely control all mixed feeds' degradation kinetics at low plastic mixing ratios and beyond 500 °C as all the plastic materials decompose almost completely at 500 °C [236]. However, where the plastic to biosolids ratio is extreme ($\geq$4), the particular plastic decomposition behaviour governs the degradation kinetics. On the contrary, Lin et al. [237] observed that the change and trend of the DTG profiles of bagasse-blended biosolids were largely similar to the degradation profile of 100% bagasse even at equal blending ratio. Similarly, the decomposition behaviour of biosolids was

completely different in the presence of pinewood sawdust and digested manure at the same mixing conditions [62,238]. Variation in biochemical compositions and physicochemical properties will drive the pyrolysis behaviour of biosolids mixed with other feed materials. However, it is common for the thermal degradation profile of the mixed feed to be in between the individual feed's degradation profile, suggesting that both materials influenced the degradation behaviour (Fig. 3 (A)). The synergy of such interactions during the thermal degradation usually arises from the shift (change) of initial and final devolatilisation temperatures, peak degradation temperatures, and the intensity of the maximum weight loss rate relative to the observation in 100% biosolids pyrolysis [237] (Fig. 3(B)). For instance, Dong et al. [239] found that mixing biosolids (BS) with rice straw (RS) at various ratios shortened the pyrolysis temperature range from 157 °C to 614 °C for 100% BS to 186–491 °C for mixed feeds compared to 219–431 °C for 100% RS. The addition of RS increased the initial (from 157 °C to 186 °C) but decreased the final (from 614 °C to 491 °C) devolatilisation temperatures, similar to the findings of Shuang-quan et al. [240]. On the contrary, Lin et al. [237] reported that the addition of bagasse to biosolids decreased both initial and final devolatilisation temperatures. The initial pyrolysis temperatures for the mixed feeds were 177–186 °C compared to 197 °C for 100% BS, and the final temperature was 559–564 °C compared to 965 °C for 100% BS. However, the study observed that the maximum weight loss rate was nearly doubled even at the lowest biomass blend ratio. Meanwhile, another work found that the conversion rates and degradation temperatures of biosolids mixed with pinewood sawdust remained relatively unaltered compared to the behaviour in individual parent materials [241].

The synergistic interactions during the co-pyrolysis of biosolids with biomass are largely inconclusive. Alvarez et al. [62] observed that the synergy in the thermal degradation behaviour of biosolids mixed with pinewood occurred only for the lipids degradation stage and the lipid degradation peak in 100% biosolids shifted from 200 °C to 150 °C for the blended feed. No interactions were found for carbohydrates and protein degradations at higher temperatures ≥ 300 °C. Zhu et al. [241] and Zaker et al. [242] concluded that there were no obvious mutual interactions between biosolids and co-feeds components during co-pyrolysis as the calculated and experimental degradation profiles completely overlap over a wide temperature range. In contrast, Shuang-quan et al. [240] derived that the co-pyrolysis of biosolids and rice straw had obvious chemical interactions, which is not just a simple summation of behaviour from individual feedstocks. The commonly used approach to elucidate the synergistic effects during co-pyrolysis (Eq. 2) is a simplified assumption that the pyrolytic characteristics of the co-components follow the behaviours of the parent materials in an additive manner. However, during pyrolysis, the interaction is much more complex, and changes in the thermal degradation behaviour of components are dynamic and occur rapidly, which cannot be thoroughly observed in thermal analysis instruments such as the TGA. The synergy is highly dependent on the relative pyrolysis rates, the particle-volatiles, particle-particle, and volatiles-volatiles contact, and the matching of the release of individual fuel radical intermediates [241].

$$DTG_{blend} = DTG_{F1}.X_{F1} + DTG_{F2}.X_{F2} \qquad (2)$$

Where X_{F1} and X_{F2} are the mass fraction of feedstock 1 and feedstock 2 in the mixed feed, respectively; and DTG_{blend}, DTG_{F1}, and DTG_{F2} represent the mass loss of the blends, feedstock 1 and feedstock 2, respectively, at the same process conditions.

6.2. Effects on pyrolysis kinetics

The effects of co-feeding on biosolids pyrolysis activation energy (Ea) have not been consistent. The blending of LDPE with biosolids (1:1 blend) showed a positive synergistic effect on the co-pyrolysis Ea (37.3 kJ/mol), which was lower than the average of individual feedstock pyrolysis (30.0 kJ/mol for 100% biosolids and 187.4 kJ/mol for 100% LDPE) [242]. When rice straw (RS) was added to biosolids (1:1), the mean Ea for the co-pyrolysis was reduced from 460.5 kJ/mol (100% biosolids) to 275.9 kJ/mol [239]. In another study, the addition of RS to biosolids (1:1) increased the co-pyrolysis Ea from 20 kJ/mol in 100% biosolids to 49 kJ/mol in the blended feeds [240]. The addition of sawdust at ≥ 50% blend with biosolids did not change the mean co-pyrolysis Ea (151–155 kJ/mol); however, at a lower sawdust proportion (25%), the Ea was increased to 175 kJ/mol [241]. The observation was indifferent when another kinetic model was used. The co-pyrolysis of rice husk and biosolids had Ea of 45–65 kJ/mol, similar to the pyrolysis of pure biosolids (52–68 kJ/mol) in the devolatilisation region [243]. It appears that the overall mean Ea might not be suitable to elucidate the effects of co-processing on the degradation kinetics due to the convolution of mutual synergistic interactions of the feedstocks in the entire pyrolysis process. Depending on the co-feedstock and the co-pyrolysis temperature, the main synergy on pyrolysis kinetic is usually observed at the organic devolatilisation stage (200–600 °C, α = 0.1–0.6) and tar/ash cracking stage (>600 °C, α > 0.6). Moreover, pyrolysis Ea is a function of the thermal degradation rate (β) and the instantaneous fractional conversion (α) of the feedstock [15]. It is necessary to study the effects of co-feeding on the pyrolysis Ea at different values of α at a constant value of β. Based on this approach,
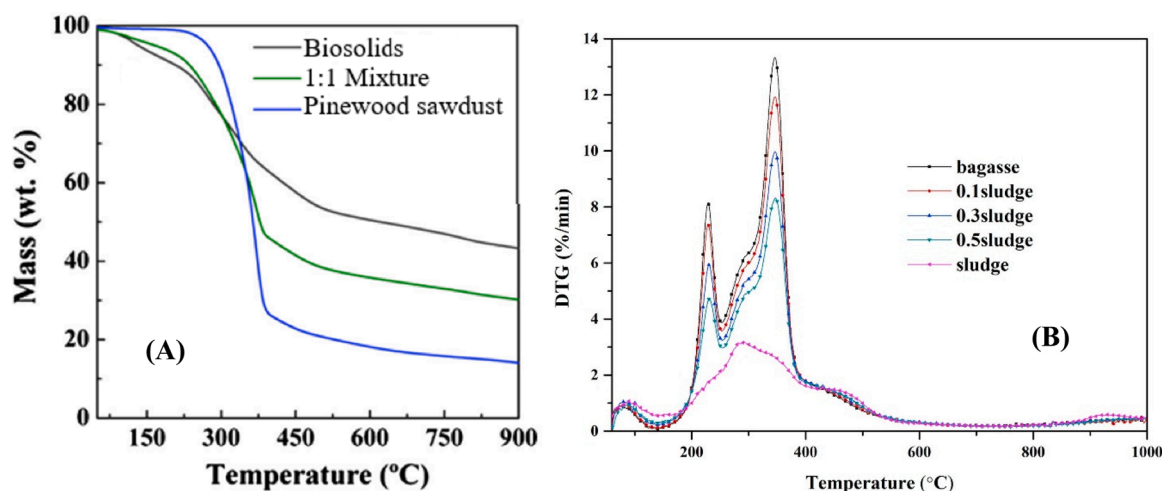

Fig. 3. Thermal degradation profile of biosolids blended with biomass (A) biosolids mixed with equal mass of pinewood sawdust [62]; (B) biosolids (sludge) mixed with bagasse at various mass fractions (0.1–0.5) [237].

Wang et al. [244] reported 131 kJ/mol as Ea for biosolids pyrolysis at 50% fractional conversion, at the same value of α for 1:1 biosolids to rice husk mixed feed, the co-pyrolysis Ea was reduced to 119 kJ/mol. At a higher value of α (80%), the Ea for 100% biosolids pyrolysis was 292 kJ/mol, and it was reduced to 143 kJ/mol. Similarly, in the work of Bi et al. [245], the co-pyrolysis of peanut shells and biosolids gave a similar mean Ea in the first stage (α = 0.1–0.5) which was 132 kJ/mol for 100% biosolids, 134 kJ/mol for 1:1 mixed feed and 139 kJ/mol for 100% peanut shells. However, in the second stage (α = 0.5–0.9), there was a clear synergistic effects on the co-pyrolysis Ea which was 172 kJ/mol compared to 208 kJ/mol and 177 kJ/mol for pure biosolids and peanut shells respectively. There was a remarkable variation in the

Table 6
Summary of biosolids co-pyrolysis and effects on products distribution.

Co-feedstocks	Mixing ratios (mass %)	Pyrolysis Process Conditions	Experimental Products Yield (wt %)[a]			Calculated Products Yield (wt%)[b]			Synergistic effects[c]	Refs.
			Bio-oil	Biochar	Gas	Bio-oil (BO)	Biochar (BC)	Gas (GS)		
Wheat straw (WS)	20WS	Fast pyrolysis, 2 g feed, 900 °C, 500 ml/min N₂	74(72)	23(13)	3(15)	72.4	12.4	15.2	+BO,+BC,−GS	[246]
	40WS		78(72)	17(13)	5(15)	72.8	11.8	15.4	+BO,+BC,−GS	
	60WS		80(72)	12(13)	6(15)	73.2	11.2	15.6	+BO,+BC,−GS	
	80WS		82(72)	12(13)	6(15)	73.6	10.6	15.8	+BO,+BC,−GS	
Pinewood sawdust (PS)	50PS	Fast pyrolysis, 1 g/min, 500 °C, vapour r. t < 1 s, char r.t. 2 min	55(49)	33(46)	12(5)	62	31.5	6.3	−BO,+BC,+GS	[62]
Rice straw (RS)	30RS	Fixed bed, 600 °C, 30 min, 200 ml/min N₂	–	53(62)	–	–	53.9	–	−BC	[239]
	50RS		–	47(62)	–	–	48.2	–	−BC	
	70RS		–	40(62)	–	–	42.5	–	−BC	
Rice Husk (RH)	10RH	TG-study, 10 mg, 20 °C/min, 800 °C, 100 ml/min N₂	–	59(62)	–	–	58.7	–	+BC	[244]
	30RH		–	53(62)	–	–	52.2	–	+BC	
	50RH		–	47(62)	–	–	45.6	–	+BC	
	70RH		–	40(62)	–	–	39.1	–	+BC	
	90RH		–	34(62)	–	–	32.5	–	+BC	
Waste tires (WT)	33.3WT	Fixed bed slow pyrolysis, 50 kg, 550 °C, 2 hr	17(16)	66(67.5)	17 (16.5)	26.5	58.2	15.3	−BO, +BC,+GS	[248]
	50WT		20(16)	59(67.5)	21 (16.5)	31.8	53.5	14.8	−BO, +BC,+GS	
	66.7WT		30(16)	58(67.5)	13 (16.5)	37	48.8	14.2	−BO, +BC, −GS	
Low density polyethylene (LDPE)	25LDPE	TG-study, 5 mg, 1000 °C, 30 °C/min, 100 ml/min Argon flow	–	25.3 (39.7)	–	–	29.8	–	−BC	[242]
	50LDPE		–	19.7 (39.7)	–	–	19.9	–	≈BC	
	75LDPE		–	7.7 (39.7)	–	–	9.9	–	−BC	
Bagasse (BG)	90BG	TG-study, 5 mg, 700 °C, 10 °C/min, 5 ml/s N₂ flow	–	30(61)	–	–	29.2	–	+BC	[249]
	70BG		–	38(61)	–	–	36.2	–	+BC	
	50BG		–	46(61)	–	–	43.3	–	+BC	
Wheat straw (WS)	20WS	Fixed bed, 1 g, 20 °C/min, 600 °C, 10 min	48.8 (41.7)	32.6 (44.7)	19 (13.6)	45.4	38.9	15.8	+BO, −BC,+GS	[247]
	40WS		54 (41.7)	22(44.7)	24 (13.6)	49.0	33.0	18.0	+BO, −BC,+GS	
	60WS		64 (41.7)	10.5 (44.7)	25.5 (13.6)	52.7	27.2	20.1	+BO, −BC,+GS	
	80WS		66.2 (41.7)	7.3 (44.7)	26.5 (13.6)	56.3	21.3	22.32	+BO, −BC,+GS	
Digested manure (DM)	50DM	Stirred batch reactor, 300 g, 525 °C, 8 °C/min, 30 min	42(42)	48(51)	8(5)	38.5	49.5	8.5	+BO, −BC, ≈GS	[238]
Peanut shells (PS)	30PS	TG-study, 5 mg, 800 °C, 5 °C/min, 50 ml/min	–	51.2 (56.5)	–	–	50.3	–	+BC	[245]
	50PS		–	48.5 (56.5)	–	–	46.2	–	+BC	
	70PS		–	45.6 (56.5)	–	–	42.1	–	+BC	
Rice husk (RH)	50RH	Fixed bed, fast pyrolysis, 4 g, 450 °C, feed r. t 1–2 s	30(20)	58(76)	13(5)	31.5	58.5	9	−BO, ≈BC, +GS	[250]
Sawdust (SD)	50 SD		35(20)	55(76)	10(5)	39	51.5	10	−BO, +BC, ≈GS	
Alum sludge (AS)	50AS	Fluidised bed reactor operated at minimum fluidisation velocity, 500 °C, 1 hr	25 (35.5)	52(49.5)	23 (14.5)	28.8	56.8	14.8	−BO, −BC, + GS	[81]
	75AS		25.5 (35.5)	57(49.5)	17 (14.5)	25.4	60.4	14.9	≈BO, −BC, +GS	
	50AS	700 °C, 1 hr	29(39)	49(42)	23 (18.5)	33	49.7	17.5	−BO, −BC, +GS	[81]
	75AS		28(39)	53(42)	18 (18.5)	30	53.6	17.0	−BO, −BC, +GS	

[a] values in parenthesis are the respective product yield from the 100% biosolids pyrolysis;
[b] Calculated product yield from the co-pyrolysis process at the given conditions of temperature and mixing ratio calculated by $Y_{calc} = Y_{BS}X_{f,BS} + Y_{co-feed}(1 - X_{f,BS})$ where $X_{f,BS}$ is the mass fraction of biosolids in the mixed feed.
[c] Synergistic effect is interpreted as: (+) is positive synergy (when experimental yield > calculated yield), (−) is negative synergy (when experimental yield < calculated yield), and (≈) is no synergy (when experimental yield ≈ theoretical yield).

pyrolysis Ea of biosolids, biosolids equally mixed with LDPE as a function of conversion degrees. For example, at 10% conversion, the Ea for 100% biosolids was 146 kJ/mol, it was 77 kJ/mol for mixed feed and 324 kJ/mol for 100% LDPE. At the extreme 90% conversion, the pyrolysis Ea was 62 kJ/mol, 343 kJ/mol and 355 kJ/mol for biosolids, mixed feed, and LDPE respectively. The large scatter in reported values and trends of co-pyrolysis Ea can be attributed partly to variations in co-feedstocks properties and pyrolysis conditions and largely to differences in kinetic models and associated assumptions.

6.3. Effects on products distribution

The yield and attribute of the products from the co-pyrolysis process is a function of the interaction between the feedstock constituents, which can either be positive or negative synergistic effects. Positive synergy will occur when the interactions among co-feedstocks generate a higher total value than the sum of values accrued from individual feedstocks [192]. The synergy in product yield during co-pyrolysis can be determined using a similar equation to Eq. (2), where the theoretical yield is calculated as the sum of the individual product yield multiplied by the mass fraction of the corresponding feed in the mixture. Table 6 summarises the effects of co-feeding on biosolids pyrolysis product distribution, including synergistic interactions on the product yield. There is a considerable scatter on the influence of the co-feed materials on product yields largely due to variations in process conditions, including blending ratio and pyrolysis temperature. Generally, biomass addition to biosolids increases bio-oil and decreases char yields due to the beneficial influence of higher volatile matter and low ash content from biomass (Table 6). On the contrary, char and gas yields increased while oil yield decreased when alum sludge having lower volatile matter and higher ash content than biosolids, was used as co-pyrolysis feedstock [81]. However, there is usually a critical mixing ratio and pyrolysis temperature beyond which the co-feedstock synergy may not yield the desired interactions [246]. For instance, the synergistic effects of alum sludge addition to biosolids on product yields were profound at lower pyrolysis temperature (500 °C) and a 1:1 mixing ratio. At the extreme pyrolysis temperature of 900 °C and 3:1 (alum sludge to biosolids) mixing ratio, the effect of alum sludge was not obvious on the product yield [81]. This is because organic devolatilisation and tar/char cracking reaction phases where the catalytic ability of alum sludge is desired occur below 900 °C, and the amount of the co-feed (alum sludge) was excess for that required to crack volatiles. In another work [247], the feed mixing ratio strongly affects the gas compositions and the degree of the synergetic effect. The strongest synergetic effect on product yields occurred at 60 wt% wheat straw and 40 wt% biosolids, and the calculated product yields significantly deviated from the experimental yields (Table 6). At this mixing ratio, bio-oil yield increased by 53%, char yield decreased by 77%, and gas yield increased by 88%; when the mixing ratio was reversed between the two feedstocks; bio-oil yield increased by 30%, char yield decreased by 51%, and gas yield increased by 76% relative to 100% biosolids pyrolysis products. The synergy in char yield during the co-pyrolysis of biosolids with virgin LDPE at 25, 50 and 75 wt% LDPE feed proportion was only observed at temperatures ≤ 500 °C, no synergistic effects can be studied beyond 500 °C as LDPE completely decomposed at 500 °C with a char residue yield of ~0% [242]. However, at 1000 °C, the calculated char yield was higher than the experimental char yield at all mixing ratios, indicating that the presence of LDPE accelerated the decomposition process of biosolids resulting in the lower formation of char residues.

6.4. Effects on bio-oil compositions and properties

Aside from the influence on product yields, co-pyrolysis can impact the product attributes, such as bio-oil physicochemical properties and chemical compositions, HMs contents and stability in the biochar and surface morphology of the biochar, amongst others. Alvarez et al. [62]

found that a 1:1 blend of biosolids and pinewood sawdust produced a single stable phase bio-oil (instead of the usual two or three phases in biosolids bio-oil) composed mainly of 32 wt% water, 9 wt% nitrogenated compounds, and 49 wt% oxygenates with ketones and phenols being the dominant components. Different behaviour was observed in components speciation in the co-pyrolysis bio-oil relative to the 100% biosolids-derived bio-oil: carboxylic acids reduced by 17%; furans reduced by 70%; phenols increased by 13%; anhydrosugars increased by 98%, and hydrocarbons increased by over 100%. The significant variation in components distribution in the co-pyrolysis bio-oil suggests that the reaction pathway of the co-pyrolysis process changes owing to the interactions between biosolids and biomass components which may require further mechanistic studies to elucidate the extent of this change. Co-pyrolysis of biosolids and bagasse affects components distribution in the bio-oil. Increasing biosolids content in the feed decreased acetic acid, furfural and low-molecular-weight compounds (number of carbon atom ≤C7) while the contents of higher molecular weight compounds (>C7) increased. Minerals in the biosolids ash catalysed the ring-opening of furfural products and facilitated the combination of low-molecular weights oxygenates and carboxylic acids to >C7 compounds in the bio-oil [237]. The co-pyrolysis of biosolids and LDPE decreased char yield and increased liquid yield with increasing LDPE loading owing to an increase in hydrogen donation from LDPE to biosolids [242]. In another study, the slow co-pyrolysis of waste tires and wastewater biosolids (from olive mill) enhances bio-oil properties (partial deoxygenation, higher calorific value, and lower viscosity) but produced a negative synergy in the yield of bio-oil compared to that of biochar [248]. Nevertheless, the co-pyrolytic bio-oil properties were still inferior to commercial diesel. The authors further demonstrated that the slow co-pyrolysis of biosolids with waste tires was a better, simple and cheap bio-oil upgrading method than HZSM-5 catalytic hydrodeoxygenation of the 100% biosolids-derived bio-oil with respect to the oil physicochemical and chemical compositions. Ruiz-Gómez et al. [238] observed no synergy in product yields (except for organic-phase liquid) and calorific value from the co-pyrolysis of manure and biosolids. Some interactions were reported in the chemical composition of the liquid product phases – the proportion of fatty acids decreased, and aliphatic nitriles increased in the organic phase of the co-pyrolysed bio-oil compared to the predicted averages. The co-pyrolysis of biosolids with alum sludge influenced the bio-oil chemical composition considerably. At a pyrolysis temperature of 500 °C, aromatics compounds increased from 23% in 100% biosolids bio-oil to 48% in 1:1 mixed feed bio-oil; aliphatic compounds decreased from 22% to 9%, nitrogenated compounds decreased from 29% to 22% while polyaromatic compounds were ~0% in the co-pyrolysis oil [81]. The catalytic effects of alum sludge was obvious in cracking higher molecular weight compounds and improve aromatisation reactions. The enhanced tar cracking reactions facilitated by alum sludge increased the concentration of CO and H_2 in the co-pyrolysis gas relative to the 100% biosolids pyrolysis gas.

6.5. Effects on biochar properties

Co-pyrolysis of biosolids and cotton stalks at 650 °C produced biochar with higher aromaticity (H/C ratio) and a more developed porous structure at the expense of biochar yield, cation exchange capacity and electrical conductivity [251]. The total contents of HMs in the co-feed biochar decreased with increasing biomass ratio. However, the metals retention factor in the biochar increase with increasing cotton stalk ratio, implying that the biosolids is the controlling feed for HMs retention in the biochar even at the extreme ratio of 10% biosolids to 90% cotton stalk [251]. In another study, a 50% co-feeding of biosolids with either sawdust or rice straw had little to no influence on the biochar aromaticity but decreased the BET surface area and pore volume by 7–45% and 10–55%, respectively, relative to 100% biosolids-derived biochar [252]. Alvarez et al. [62] reported about 28% reduction in the

specific surface area of biochar obtained from 1:1 mixture of pinewood sawdust and biosolids. Similarly, Rathnayake et al. [81] observed a significant reduction in biochar specific surface area when alum sludge was co-pyrolysed with biosolids at 500–900 °C. The BET surface area decreased from 29 m^2/g to 89 m^2/g in the 100% biosolids biochar to 17–41 m^2/g in the co-pyrolysis biochar. Increasing the ratio of alum sludge in the mixed feed further reduced the biochar surface area to 14–24 m^2/g. On the contrary, the addition of rice straw (30–70 wt%) to biosolids increased the derived char specific surface area considerably from 16 m^2/g in 100% biosolids biochar to 28–65 m^2/g in the co-pyrolysis biochar [239]. Also, the addition of wheat straw (20–80 wt %) to biosolids produced biochar with a specific surface area of 75–267 of m^2/g, which were significantly higher than that of 100% biosolids biochar (28 m^2/g) [246]. The biochar obtained from the co-pyrolysis of biosolids with rice husk (20–40 wt%) had a higher specific surface area (26–68 m^2/g) compared to ~20 m^2/g for the 100% biosolids biochar [244]. It can be concluded that the co-pyrolysis of biosolids with relatively low-ash containing feedstocks like agricultural residue and woody biomass will improve the derived char surface area. Pyrolysis process conditions such as temperature and heating rate also significantly influence the formation of micropore structure and specific surface areas [253].

The total HMs contents in the co-pyrolysis biochar can be significantly reduced by adding low HMs-containing biomass such as sawdust, rice straw or alum sludge in the mixed feed [81,252]. For instance, the Cu concentration in 100% biosolids biochar was reduced by 57% in the biochar produced from 1:1 (alum sludge to biosolids) mixed feed and by 80% in a 3:1 (alum sludge to biosolids) mixed feed [81]. The mobility and leaching toxicity of the HMs in the co-pyrolysis biochar could not be alleviated by biomass addition in the study of Huang et al. [252]. This observation contradicts the findings of many other works [59,60,81, 254]. The expected reduction in both the HMs contents and leachability in co-pyrolysis biochar is through dilution effects and the development of new functional groups on biochar surfaces which enhances the immobilisation of HMs due to the formation of stable organo-metallic complexes [255]. Wang et al. [60] co-blend biosolids with four plastics materials (PP, PE, PS and PVC) and found that all HMs contents except for Cd were reduced with different plastic addition. Relative to raw biosolids biochar, PE, PP and PS addition promoted the transformation of HMs speciation from readily leachable fractions to more stable fractions and enhanced HMs immobilisation in the co-feed biochar. PVC addition only facilitated the immobilisation of Cr and As in the biochar and exhibited clear activation effects on other HMs.

Wang et al. [182] observed that the co-pyrolysis of biosolids with kitchen waste and spent tea bags decreased biochar yield and HMs contents but increased carbon sequestration and aromaticity. The addition of hazelnut shells to biosolids in a co-pyrolysis process increased the microcosmic surface of the biochar, generated microporous structure, and transformed HMs from mobile fractions to stable fractions with increasing pyrolysis temperature [254]. Zhang et al. [256] reported that at the same temperature and mixing ratio, the co-pyrolysis of biosolids with bamboo sawdust was better for improving biochar aromaticity, while co-pyrolysis of biosolids with rice husk was better for HMs immobilisation in the biochar. Both of these beneficial outcomes occurred at an optimum co-pyrolysis temperature of 700 °C. Co-pyrolysis has a positive effect in decreasing the HMs concentration in the biochar, whereas pyrolysis temperature influence significantly the stability and potential toxicity of the metals in the char. The addition of co-feed biomass causes dilution effects on HMs concentration, and temperature affects the migration of the HMs into bio-oil and gas products during the pyrolysis process [109]. Mixing walnut shell with biosolids was beneficial in producing biochar with a well-developed porous structure [61]. At a mixing ratio of 3:1 (biosolids/walnut shell), the derived biochar showed optimum adsorption capacity for NH$_4^+$-N from water over a short pH range (7−9). However, the 100% biosolids biochar was more effective for PO$_4^{3-}$-P adsorption in water over

a wide pH range (4−12). The abundance of surface functional groups and metal oxides in biosolids biochar rather than surface areas controlled the adsorption of PO$_4^{3-}$-P because the adsorption rate was lower in all co-pyrolysis biochar, reaching zero in 100% walnut shell-derived biochar despite having the highest surface area and pore volume.

7. Biosolids pyrolysis for high-value chemical production

7.1. Biosolids bio-oil and utilisation potential

Under appropriate conditions, up to 70 wt% liquid products can be obtained from biosolids pyrolysis [257]. The liquid product separates into at least two layers having an aqueous phase and organic phase, usually in the ratio of 65:35 (v%), respectively [2], depending on the partial distribution of the oil components, feed and process conditions, and liquid recovery methods [258]. Induced phase separation is sometimes carried out using solvent, gravity, and centrifugation to enhance bio-oil physicochemical properties and its utilisation potential [29]. The difference in the numerous components' polarities and densities aids the phase separation in biosolids pyrolysis liquid. Each of the phases has distinct physicochemical properties. The pH of the whole liquid is slightly on the basic side (7.9–10.1) attributed to the high nitrogen content [1], density @ 20 °C in the range of 940–1250 kg/m^3, viscosity @ 20 °C is about 17 cSt and HHV of aqueous fraction < 20 MJ/kg, organic-rich fraction is 30–45 MJ/kg and whole liquid is 20–30 MJ/kg [29,257]. The organic phase has properties typical of bio-oil and can be refined similarly to traditional bio-oils [31].

The aqueous phase contains mostly polar compounds, including ammonia, acetonitrile, carboxylic acids, methanol, traces of monomeric and oligomeric sugars, and other hydrolysable organic compounds [29, 48,259]. The organic phase usually consists of aliphatic and aromatic hydrocarbons, phenols, carboxylic acids, fatty esters, and nitrogen-heterocyclic compounds [11,31,257]. Like other bio-oils, biosolids-derived oil also have high quantity of water and free oxygen content. High water content lowers the heating value significantly and limits its suitability as fuel, while high oxygen contents make fuel upgrading challenging [260]. The high oxygen content in bio-oil fractions could be a potential source of bio-based oxygenates chemicals due to the enhanced reactivity of the oil during further processing. However, the low molecular weight oxygenated compounds undergo several reactions such as repolymerisation, condensation, etherification, and esterification even at room temperature, causing thermal instability and ageing of the bio-oil [261].

Although no commercially viable uses of biosolids-based bio-oil have been found, energy recovery through combustion is the common application route [262]. The emerging biosolids pyrolysis technique is to capture the energy of bio-oil and non-condensable gases for autothermal pyrolysis process in an integrated combustion-pyrolysis set-up [54]. Fonts et al. [29] suggested that biosolids bio-oil can be employed as fuels in a lime kiln without further treatment. Utilising the liquid product from biosolids pyrolysis for energy production, either in the raw or refined forms, is promising. The perceived ability of bio-oil as a green fuel to replace petro-based liquid fuels in internal combustion engines sustains the research on maximising liquid products during the pyrolysis of biomass resources [263–266]. Some studies explored biosolids' bio-oil aqueous fraction as a substrate for fermentation [267–270], and it supports reasonably the growth of microorganisms up to a certain degree of tolerance. However, some toxic organic components in the liquid inhibit enzyme activities and reduce the process viability eventually. Similarly, the aqueous fraction of biosolids-derived bio-oil was used as a co-digestate for the anaerobic digestion of biomass [32,271].

7.2. The potential of biosolids bio-oil for value-added chemical production

Limited works are dedicated to the influence of biosolids feed and

pyrolysis process modifications on value-added chemical components in the biosolids-derived bio-oil [65,272]. Pyrolysis liquids derived from lignocellulosic biomass have potential as sources of valuable chemical production [273]. Attempts to utilise the range of compounds in the lignocellulosic biomass-derived bio-oil to produce platform chemicals are abundant in the literature [273–278]. Depending on the process conditions and feed compositions, a spectrum of valuable chemical components, including furfural, levoglucosenone, succinic acid, and phenols, can be produced (Fig. S4). However, given the distinct difference in the biochemical and physicochemical properties of lignocellulosic biomass and biosolids (Table S3), the chemical components (especially the sugar-derived) present in biomass-based bio-oil may not be found in biosolids bio-oil. The building blocks of plant-based biomass are hemicellulose, cellulose and lignin, whereas biosolids are made up of complex polysaccharides (from extracellular polymeric substances), proteins, lipids and inorganic materials. Therefore, biosolids pyrolysis to high-value chemicals will require tailoring the feed biochemical makeup and the process conditions to the targeted chemical components in the bio-oil. Table 7 summarises biosolids building block(s) from which potential platform chemicals can be derived. The range of platform chemicals in the biosolids-derived bio-oil can include nitriles, aliphatic hydrocarbons, phenols, ammonia, fatty acids, and esters. Table 8 shows the major chemical components and their concentrations in water-free biosolids bio-oil obtained at 500 °C. Water in bio-oil comes from the initial moisture content in the biosolids and through dehydration reactions catalysed by AAEMs and fragmentation of high molecular weight oxygenated compounds [88]. Aside from water, the bio-oil has several components (usually in dilute concentrations), making it a highly heterogeneous mixture (Table 8). The separation and recovery of the chemical components in the bio-oil is laborious, involving a series of multistep processes such as phase fractionation, solvent extraction, absorption, and distillation, amongst others [279]. Fonts et al. [272] assessed the production of value-added chemicals from biosolids-derived liquids by separating the bio-oil into heptane-soluble, DCM-soluble and HCl-soluble fractions. Aliphatic hydrocarbons, aliphatic nitriles and steroids are partitioned in the heptane-soluble fraction, while phenols and fatty acids separate in the DCM fraction and carboxylic acids and amides distribute in the acid-soluble fraction. The most attractive chemical components in the biosolids bio-oil cracked by γ-Al₂O₃ based on maximum possible production volume and price (kg/t biosolids) were ammonia, α-olefins, n-paraffins, aromatic hydrocarbons, nitriles, phenols, fatty acids, short carboxylic acids and indole [272].

7.3. Effects of pre-treatment, catalysts and co-feeding on the production and distribution of major high-value chemicals

Pre-treatment, catalysis, and co-feeding of biosolids can influence the distribution of bio-oil chemical components, as shown in Fig. 4. It can be seen that each additive feed, chemical and catalyst material

Table 7
Biosolids building blocks and derivable chemical components in the pyrolysis liquid [67,272].

Building block	Decomposition temperature (°C)	Decomposition components
Proteins	209–700	Phenols, heterocyclic non-aromatic amides, N-heterocyclic aromatic compounds, linear or branched short amides, pentose and cytosine-containing compounds
Lipids	200–635	Fatty acids, paraffins, olefins
Carbohydrates	164–497	Short chain carboxylic acids, ketones, hydrocarbons
Protein+lipids	200–600	Fatty nitriles
Protein+carbohydrates	164–700	Short aliphatic amides and nitriles

Table 8
Major components in bio-oil from pyrolysis of biosolids at 500 °C.

Components	Relative Contents (area%)[a]					
	[5]	[88][b]	[280]	[281]	[28]	[282][c]
Alcohols	5.82	2.08	–	4.65	2.97	2.2
Aldehydes		0.19	–	1.74	0.08	–
Aliphatic hydrocarbons	29.62	0.23	5.86	21.93	–	63.7
Amides	8.00	3.24	9.93	1.20	–	23.1
Amines	2.59	1.09	–	–	–	–
Aromatic hydrocarbons	22.55	0.33	9.21	2.46	1.81	27.9
Acids	2.71	5.53	20.13	3.15	–	3.2
Ethers	4.47	1.20	–	–	1.65	–
Esters	4.43	0.72	9.18	0.88	–	16.9
Furans	–	3.24	–	1.66	–	–
Ketones	2.12	6.85	6.40	11.72	2.00	10.1
Nitriles	2.59	2.37	5.47	8.18	–	24.3
Phenols	2.04	17.85	7.00	15.28	1.48	39.5
Pyrroles	11.94	3.82	–	4.04	–	4.6
Saccharides	–	2.66	–	–	–	–

[a] concentration is expressed is area% except stated otherwise;
[b] concentration is expressed in wt%;
[c] concentration is expressed as mg/g biosolids (dry ash-free)

impacts the component distribution in the bio-oil differently. The wet mixing of chemical solvents such as acid, alkalis and metal salts with biosolids affect the formation and distribution of aliphatic and aromatic hydrocarbons, nitrogen, and oxygen-containing compounds, mainly nitriles, amides, heterocyclics amines, ketones, ester, alcohols, and carboxylic acids (Fig. 4(A)). For example, acid (H₂SO₄, H₃BO₃) increases the content of ketones, nitriles and heterocyclics but did not improve hydrocarbon yield, while KOH increases alkanes and monoaromatic hydrocarbons relative to the control (Fig. 4(A)). Acid treatment of biosolids can reduce metal contents as well as passivate the catalytic functions of inherent ash-forming minerals, thereby reducing their cracking ability for aromatic production. On the other hand, KOH can hydrolyse recalcitrant organic compounds in biosolids without reducing the metal oxides content, which aids the secondary cracking reactions to produce aromatics [220]. The catalytic pyrolysis of biosolids using metal oxides and HZSM-5 was observed to considerably improve aromatic hydrocarbons (Fig. 4(B)). HZSM-5 is an effective catalyst material for aromatisation, deoxygenation and denitrogenation reactions via the reaction routes illustrated in Fig. 5. Compared to the non-catalysed bio-oil, HZSM-5 increase aromatic hydrocarbon and decrease oxygenated and nitrogenated compounds, whereas metal oxides such as CaO and Al₂O₃ increase aromatic hydrocarbons, but they did not decrease the content of nitrogenated and oxygenated compounds similarly to biochar catalysts (Fig. 4(B)). This suggests that the mechanism of aromatic formation for HZSM-5 and metal oxides are different. Metal oxides facilitate the secondary cracking of aliphatic hydrocarbon to aromatics [227].

The effect of co-feedstock on bio-oil chemical components distribution is largely related to the type of feedstock, mixing ratio and the synergistic interactions between the feed materials (Fig. 4(C) and (D)). Generally, co-pyrolysis with lignocellulosic biomass appeared to enhance phenols and carboxylic acid production with little improvement in hydrocarbon production (Fig. 4(C)). This is because biomass feedstocks contain higher oxygen content than biosolids due to the biochemical composition difference (Table S3). There is a clear influence of the mixing ratio on the evolution of chemical components during biosolids and sawdust co-pyrolysis (Fig. 4(D)). At 20% sawdust addition, the co-pyrolysis bio-oil composition was similar to that of 100% biosolids pyrolysis, with only a slight increase in phenol and decrease in aldehydes content. There was an obvious turning point in the chemical components' distribution at 40 wt% sawdust addition – aliphatic hydrocarbon became the dominant compound with traces of aldehydes and ester in the bio-oil (Fig. 4(D)). The synergistic interaction was profound when a proper ratio of the two feed materials was achieved.
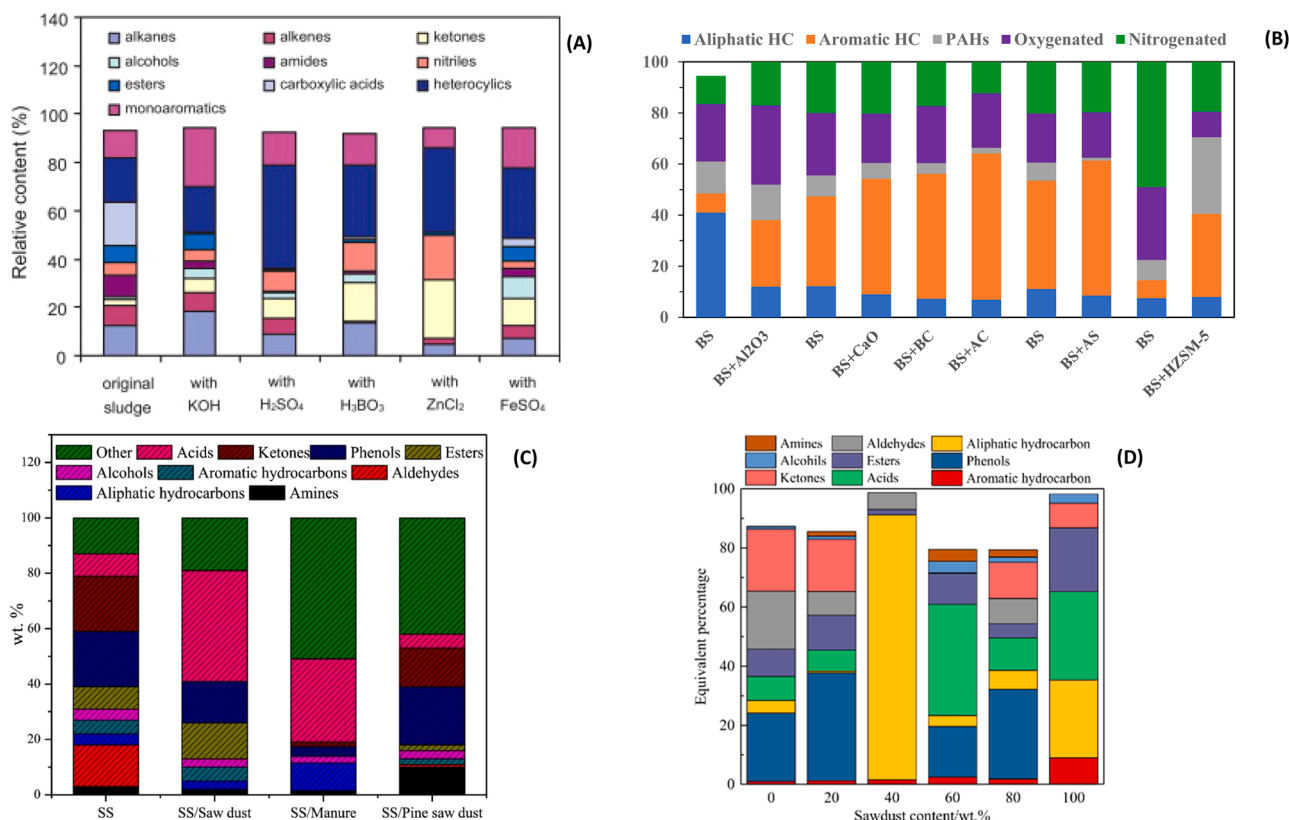
Fig. 4. Effects of pre-treatment, catalysts and co-feed on the distribution of chemical components in biosolids-derived liquid (A) influence of various chemical additives [220]; (B) influence of various catalysts materials: BC – Biochar of biosolids origin, AC – Activated char of biosolids origin, AS – Alum sludge (data obtained from [5,81,219,221]); (C) influence of various feedstocks [65]; (D) influence of mixing ratio of sawdust with biosolids during co-pyrolysis [283].

The C-C/C=C bonds in alicyclic hydrocarbons were cracked by the biosolids ash components to produce C_{10}-C_{17} chain compounds [283]. The further increase of sawdust ratio in the mixed feed produced bio-oil whose composition is similar to 100% sawdust pyrolysis. The bio-oil obtained after improving the pyrolysis process through chemical additives, catalysts, or co-feeding is still highly heterogeneous containing several chemical components suggesting that the selectivity of the added materials is relatively weak. The detailed insight into the production and formation routes of attractive chemical components such as hydrocarbons, phenols, ammonia, and levoglucosan from biosolids pyrolysis liquid is provided in Section 7.4.

7.4. Most attractive high-value chemical components in biosolids bio-oil

7.4.1. Hydrocarbons

Generally, biosolids materials are hydrogen deficient, negatively impacting hydrocarbon production during pyrolysis [242]. Hence, improving hydrocarbons production from biosolids would require process or feed modifications through catalysis and/or pre-treatment [55]. Also, co-processing biosolids with feedstocks with high effective hydrogen index (EHI), such as plastics, could improve hydrocarbon yield [242]. The EHI is an indicator of H/C ratio after debiting the compound's hydrogen content for the complete conversion of heteroatoms to NH_3, H_2S and H_2O, and it is expressed by Eq. (3) [285].

$$EHI = (H - 2O - 3N - 2S)/C \qquad (3)$$

Where: H, O, N, S and C is the number of moles of hydrogen, oxygen, nitrogen, sulphur, and carbon in the biomass, respectively. The EHI of plastic is around 2, while biosolids and other organic biomass are < 1 [242].

Hydrocarbons, particularly paraffins and olefins, may originate from

the direct devolatilization of biosolids carbohydrates and the decomposition of other components, such as fatty acids, triglycerides, and steroids, while aromatics are mainly generated through secondary reactions and proteins decompositions [272]. Several works have demonstrated biosolids pyrolysis to bio-oil rich in hydrocarbons (typically aliphatic, monoaromatics, and polyaromatic) through catalysts, co-feeding and pre-treatment. Liu et al. [55] investigated the combined effects of acid pre-treatment and catalyst on the pyrolysis conversion of biosolids to hydrocarbons. The catalytic pyrolysis of digested biosolids using HZSM-5 at a ratio of 20:1 (catalyst/biosolids) produced bio-oil dominated by aromatics (benzene, toluene, xylene, C9 and C10 + aromatics), olefins (ethylene, butene, and propylene), and alkanes (butane, propane, ethane, and methane). The selectivity of the catalyst ranges from 15% to 45% for olefins, 9–33% for aromatics, and 15–38% for alkanes. In the pyrolysis temperature range tested (450–750 °C), the hydrocarbons yield (wt% C) was ranked as aromatic (17.7–24.8%) > olefins (8.5–13.5%) > alkanes (3.3–11.8%), and the yield increased with increasing pyrolysis temperature [55]. At 650 °C, the total hydrocarbon yield in catalytic pyrolysis was 45.3% compared to 10.4% in non-catalytic pyrolysis. Although the high catalyst to biosolids ratio is unattractive, further optimisation studies may be required. Mass transfer and conversion kinetics is usually limited between two solids materials during the dry mixed feed catalytic process; wet-impregnation of the catalyst with the feed could overcome the mass transfer barrier. HZSM-5 acidity and porous structure promote deoxygenation reactions leading to C_2-C_4 olefins condensation into aromatics enhancing hydrocarbons production during pyrolysis [286]. On the other hand, HY zeolite catalyst is less favourable for deoxygenation reactions; rather, the catalyst promotes olefins oligomerisation and hydrogen transfer reactions to maximise paraffin production [287].

Hydrocarbon production from biosolids with or without additive material is influenced by pyrolysis temperature. Table 9 summarises the
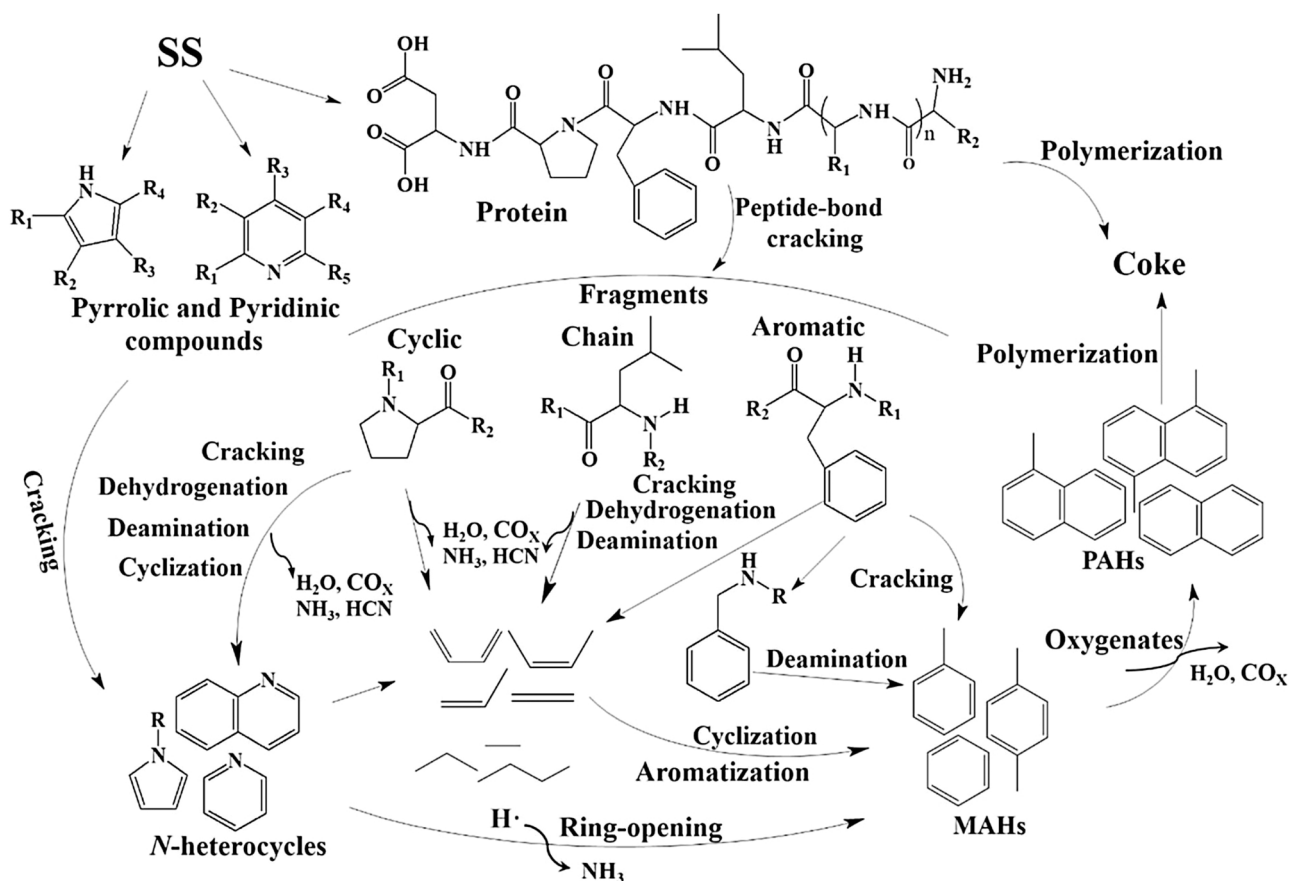
Fig. 5. Pyrolytic reaction pathway of biosolids (SS) for the formation of aromatics and denitro-oxygenation in the presence of HZSM-5 catalysts [284].

effects of pyrolysis temperatures and additive materials on the aliphatic, monoaromatic and polyaromatic hydrocarbon yields. Generally, aliphatic hydrocarbon decreases with increasing temperature, whereas aromatic hydrocarbon increases with increasing temperature up to around 700–800 °C. However, the increase in aromatic hydrocarbon with temperature is accompanied by an increase in polyaromatic hydrocarbon (PAHs). The addition of catalysts such as metal oxides and biochar can increase monoaromatic production while at the same time suppressing the increasing production of polyaromatic (Table 9). Microwave-assisted catalytic fast pyrolysis of mixed biosolids (catalyst to feed ratio of 2) using HZSM-5 zeolite produced hydrocarbons (aromatic, aliphatic and PAHs) whose proportion increased with increasing pyrolysis temperature up to 550 °C [221]. At this temperature, the proportion of the hydrocarbon groups in the bio-oil was 33%, 30% and 8% for aromatic, PAHs and aliphatic, respectively. The absence of catalyst and change in catalyst to feed ratio was inconsequential on aliphatic yield but was significant for aromatics increasing from 7% (no catalyst) to 16% (1:2 catalyst/feed), 24% (1:1 catalyst/feed) and 33% (2:1 catalyst/feed). The increase in PAHs (~7.5–30%) was profound only at the maximum catalyst loading. In another study [288], fast microwave pyrolysis of biosolids in the presence of HZSM-5 increased the proportion of hydrocarbons in the bio-oil. Aliphatic, aromatics, and PAHs reached a maximum of 31.2% at 500 °C, 8.4% at 550 °C and 1.6% at 550 °C, respectively. Higher pyrolysis temperature (550–600 °C) favours the formation of aromatic and PAHs owing to the activation of the Diels-Alder reaction followed by decarbonylation and dehydration reactions [288]. This also explains why the yield of aliphatic hydrocarbons is reduced at higher pyrolysis temperatures (Table 9). HZSM-5 possesses high acidity and is highly selective for producing aromatic hydrocarbons due to its three-dimensional shape-selective micropore structure with pore diameters ca. 0.5 nm [213,289]. However, the microporous

structure can hinder the diffusion of large molecular weight intermediates compounds to the inner pores of the catalyst where the active acidic sites are situated. Mesoporous materials with larger pore sizes (2–10 nm), such as Al-MCM-41 and Al-SBA-15, can alleviate the challenge of high molecular weight cracking [290].

The catalytic pyrolysis of 0.5 mmol/g sulphuric acid-infused biosolids at 650 °C had negligible effects on the yield of hydrocarbons. However, at higher acid loading (1 mmol/g), the yield of aromatic, olefins and alkanes increased by 10.8%, 11.9% and 24.1%, respectively. Similarly, the catalytic pyrolysis of acid-washed biosolids obtained higher hydrocarbons yields but with less improvements than acid-infused biosolids. The improvement in hydrocarbon production with acid infusion could be due to the catalytic functions of residual acid in suppressing the formation of low molecular weight oxygenates [84].

Compared to zeolite-based catalysts, the hydrocarbon and aromatic selectivity of metal oxides-based catalysts are very low [291]. The influence of these catalysts on hydrocarbon production from biosolids pyrolysis has been inconsistent due to their diverse types (alkali and alkaline earth, metalloids, transition, noble metals). For example, Ni-based oxides such as NiO and NiO_3 lowered the formation of aromatic hydrocarbon by ~70%; however, MoO_3 was observed to increase aliphatic hydrocarbons by 36% relative to the non-catalytic process [227]. CaO reduced aliphatic hydrocarbon at 500 °C by 18%, and at higher temperatures (700–900 °C), the reduction increased to 26% [5]. In another study, [215], Fe_2O_3 and CaO increased aliphatic hydrocarbon yield by 34% and 72%, respectively, whereas only CaO improved aromatic hydrocarbon considerably by 91% relative to the control process. Lastly, blending MgO and CaO with biosolids delayed the release of olefins and alkanes [76]. Alkanes production was severely suppressed by both mineral additions, whereas the reductions in the release order of alkenes were more significant for MgO than CaO but were

Table 9
Effects of temperature and various additives on hydrocarbons production.

Materials (Mixing ratio)	Pyrolysis Temp (°C)	Relative Distribution (Peak Area%)*			Refs
		Aliphatic HC	Monoaromatics HC	PAHs	
BS+ CaO (1:1)	500	24.4 (29.6)	26.5(20.2)	3.4 (2.4)	[5]
	700	9.0(12.2)	45.2(35.2)	6.2 (8.2)	
	900	9.6(13.1)	45.5(34.6)	0.0 (0.0)	
BS+SiO₂ (10:1)	600	26.4 (26.3)	25.3(22.4)	5.4 (8.7)	[99]
	800	4.5(0.6)	16.8(29.2)	37.8 (31.6)	
	900	0.3(0.2)	11.6(16.5)	48.6 (42.2)	
BS+Al₂O₃ (10:1)	600	21.9 (26.3)	35.5(22.4)	6.8 (8.7)	[99]
	800	0.75(0.6)	15.8(29.2)	39.4 (31.6)	
	900	0.0(0.2)	6.8(16.5)	53.3 (42.2)	
BS+Fe₂O₃ (10:1)	600	30.4 (26.3)	27.7(22.4)	5.6 (8.7)	[99]
	800	0.0(0.6)	10.3(29.2)	45.0 (31.6)	
	900	0.0(0.2)	7.6(16.5)	53.5 (8.7)	
BS+ Biochar (1:1)	500	21.3 (29.6)	30.8(20.2)	2.1 (2.4)	[5]
	700	7.3(12.2)	48.9(35.2)	4.2 (8.2)	
BS+ Activated Char (1:1)	500	19.3 (29.6)	35.8(20.2)	1.1 (2.4)	
	700	6.9(12.2)	57.3(35.2)	2.2 (8.2)	
BS + alum sludge (1:1)	500	9.0(22.4)	48.2(22.6)	0.4 (7.6)	[81]
	700	8.5(11.1)	52.9(42.5)	1.1 (7.1)	
	900	3.5(12.5)	52.3(43.1)	1.0 (1.3)	
BS +CaO (10:1)	500	8(5)	6.5(8.8)	–	[215]
	600	9(6.8)	13.5(6.8)	–	
	800	12(8.5)	17(12.5)	–	
	900	16(9.0)	14(7.5)	–	
BS + Fe₂O₃ (10:1)	500	6.5(5)	7.2(8.8)	–	[215]
	600	6.7(6.8)	13(6.8)	–	
	800	11(8.5)	15(12.5)	–	
	900	12.5(9.0)	9(7.5)	–	
BS+Al₂O₃ (7.5:1)	450	75(80)	25(20)	–	[219]
BS+Al₂O₃ (5:1)		77(80)	23(20)	–	
BS+Al₂O₃ (2.5:1)		63(80)	37(20)	–	
BS+Al₂O₃ (1:1)		60(80)	40(20)	–	

* the values in parenthesis are the yield during 100% biosolids pyrolysis

inconsequential on the amount of the minerals added. The in-situ catalytic pyrolysis of biosolids using metal oxides can have varying reaction mechanisms driven by pyrolysis temperature and metal species [292]; hence the wide differences observed in chemical components formation during pyrolysis.

Catalytic slow pyrolysis of biosolids at 500–900 °C in the presence of lime, biochar and activated char reduced aliphatic hydrocarbon and PAHs but increased aromatics yield [5]. At all the pyrolysis temperatures, activated char outperformed all other bed materials with respect to the effects on hydrocarbon production in the bio-oil. Biosolids biochar was used as a catalyst for the pyrolysis of biosolids, and the content of hydrocarbon (alkane and alkene) increased from 18% in non-catalysed bio-oil to 39% in char-catalysed bio-oil [73]. Adding carbon-based residue as catalysts has advantageous effects on hydrodeoxygenation of organics and remove chlorine-bearing compounds, leading to improved

bio-oil dominated by hydrocarbons [293]. The microwave pyrolysis of KOH-impregnated biosolids increased alkanes and monoaromatic contents in the bio-oil by 8 area% and 10 area% respectively, relative to the raw biosolids bio-oil, whereas H_2SO_4 and $ZnCl_2$ impregnation did not promote hydrocarbons production [220]. Chen et al. [294] found that pressurised pyrolysis (1–7 MPa) of dried biosolids increased aromatic hydrocarbon (62.7 area%) and alkanes (8.2%) but decreased alkenes (2.6%) proportion in the bio-oil compared to atmospheric pyrolysis bio-oil.

Wang et al. [226] performed ex-situ catalytic pyrolysis of wastewater biosolids by passing generated pyrolysis vapours over HZSM-5 catalyst (0.5 mg feed/10 mg catalyst). Hydrocarbon yield varies 34.1–43.5% at 400–800 °C pyrolysis and 500 °C catalysis temperatures. The influence of pyrolysis temperature was not profound on hydrocarbon yield and selectivity. On the contrary, catalysis temperature caused a significant increase in hydrocarbon yield. At a pyrolysis temperature of 500 °C, the yield of olefins increased from 12.9%, reaching a maximum of 26.3%, and aromatics increased from 8.7% to 18.8% as catalysis temperature increased from 400 °C to 800 °C. Azuara et al. [1] observed that two-stage catalytic pyrolysis of sewage biosolids using γ-Al₂O₃ did not improve the yield of aliphatic hydrocarbon. However, the presence of γ-Al₂O₃ decreased aromatic and increased the PAHs contents in the bio-oil organic phase. Both pyrolysis and catalysis temperatures impact the hydrocarbon proportions in the oil. γ-Al₂O₃ catalyst influences hydrocarbons yields (in area%) from 17.9 to 22.1–18.2–19.3 for the aliphatic fraction, from 7.9 to 11.8–1.9–9.8 for the aromatics and from 1.2 to 7.8–14.8–26.1 for PAHs.

Blending waste tires with biosolids (at a 2:1 ratio) increased the hydrocarbon contents in the co-pyrolysed oil significantly. Paraffins increased from 3.5% (in raw biosolids bio-oil) to 21.2% (in blended biosolids bio-oil), olefins increased from 6.6% to 25.3% while aromatic increased from ~0–7.1% [248]. The high production of hydrocarbons in the blended feed bio-oil could be partly attributed to improved hydrodeoxygenation and hydrocracking reactions catalysed by hydrogen transfer in the presence of waste tire and partly to the chemical make-up of tire (styrene-butadiene). Co-blending biosolids with pinewood sawdust (at equal weights) produced bio-oil whose hydrocarbon contents increased by over 100%, equivalent to 0.56 wt% in biosolids-bio-oil and 1.25 wt% in blended feed bio-oil [62].

7.4.2. Phenols

Phenols and their derivatives are important chemical building blocks and may originate from biosolids pyrolysis through the decomposition of polysaccharides (e.g., tyrosine-containing peptides) and proteins [272,282]. The main phenolic compounds in biosolids-based bio-oil are phenol, methyl phenols and 4-ethylphenol, guaiacols and isoeugenol [295]. Generally, phenols are not prone to deoxygenation over acidic catalysts such as HZSM-5, so they are not significantly reduced by catalytic effects [296]. The catalytic cracking of biosolids pyrolysis vapours over γ-Al₂O₃ facilitated the production of methyl phenol due to the enhanced cracking of protein-derived intermediates [272]. Alvarez et al. [297] obtained 14.4–18.0 wt% bio-oil as phenolic compounds (alkyl-phenols, benzenediols and guaiacols) from non-catalytic fast pyrolysis of biosolids at 450–600 °C. Phenols were the main component identified in the water-free bio-oil. Arazo et al. [281] also observed that phenols are the largest components (15.3 area%) in biosolids bio-oil behind hydrocarbons (42.2 area%). On the contrary, the atmospheric pyrolysis of dried biosolids produced bio-oil dominated by hydrocarbons and nitriles, and no phenolic compounds were detected; however, pressured pyrolysis (3 MPa) at the same temperature enhanced phenols production reaching 13.6 area% [294]. Phenols yields were strongly dependent on the pyrolysis temperature, and an increase in pyrolysis temperature from 350 °C to 950 °C decreased phenols proportion from 23,990 ppm to 10,919 ppm [266]. Pyrolysis of torrefied pre-treated biosolids increased phenols proportion in the bio-oil relative to the raw biosolids bio-oil [298]. The influence of various co-feed, catalysts and chemical

pre-treatment on phenol yield during biosolids pyrolysis are summarised in Table 10. Compared to chemical pre-treatment and catalysts, co-feeding enhances phenol production through synergistic interactions. Phenols are common components reported in biosolids-derived oil; however, like other oxygenates compounds, their presence could lower bio-oil heating value. Therefore it is necessary to extract phenolics using appropriate solvents such as DCM, and when extracted could be used as a low cost renewable resin [272].

7.4.3. Ammonia

One of the unique characteristics of biosolids compared to lignocellulosic biomass is the relatively high nitrogen content (Table S3). The nitrogen in biosolids can be present as protein-N (P-N), pyridine-N (N-6), pyrrole (N-5), quaternary-N (N-Q), and nitrogen oxides (N-X). P-N

Table 10
Effects of catalysts, co-feed and chemical additives on phenol production.

Feed Materials	Pyrolysis condition	Phenol yield (area%)*	Remarks	Refs
BS[a]+ZSM-5	Py-GC/MS, 3 mg feed, 1:1 BS to cat ratio, 600 °C, 30 °C/min, 10 s vapour r.t.	19.8 (20.2)	ZSM-5 catalysis did not impact phenol yield compared to the metal oxides.	[227]
BS+NiO		16.8 (20.2)		
BS+MoO₃		14.8 (20.2)		
BS+KOH	Microwave pyrolysis, 400 °C, 53–82 g catalysts/kg biosolids	0.52 (1.25)	H₂SO₄ slightly improved phenol production, whereas KOH significantly suppressed the formation of phenol similar to ZnCl₂	[220]
BS+H₂SO₄		1.83 (1.25)		
BS+ZnCl₂		0.58 (1.25)		
BS+FeSO₄		1.21 (1.25)		
BS+ Pinewood sawdust	Fast pyrolysis, 1 g/min feed rate, 500 °C, vapour r.t < 1 s, char r.t. 2 min	20.12 (17.85)[b]	Alkyl-phenols and benzenediols are the major phenolic compounds in co-pyrolysis oil from the secondary dissociation of methoxy phenols	[62]
BS+ digested manure	525 °C, 600 g feed, 8 °C/min, 30 min (1:1 ratio)	31.1 (10.0)[c] 7.5(1.7)[d]	Phenol partitioned more into the organic phase and originated from the high lignin and protein content of the co-feed	[238]
BS+ alum sludge	500 °C, 35 °C/min, 60 min 700 °C 900 °C	2.88(0.0) 3.56(0.0) 0.0(0.0)	The high alumina content of alum sludge increased aromatisation reactions to enhance phenol yield. Increasing the ratio of alum sludge further increases phenol to 11.9%	[81]
BS+Y-zeolite	0.3 g catalyst/g BS 300–400 °C 400–500 °C 500–600 °C 600–700 °C	15.4 (13.4) 14.7 (13.9) 11.2(6.7) 11.4 (4.1)	Pyrolysis temperature affects phenol production, and the optimum temperature was around 500 °C. The catalyst enhances phenol yield, particularly at higher temperatures	[299]

* the values in parenthesis are the yield during 100% biosolids pyrolysis;
[a] the feed is a mixture of biosolids and sawdust at 1:2 mass ratio;
[b] yield is expressed as wt% of water-free bio-oil;
[c] phenol content in the organic phase of the bio-oil,
[d] phenol content in the aqueous phase of the bio-oil

and N-6 constitute about 80% of the total-N in biosolids, and ammonia (NH₃) is the main product of P-N transformation, while N-6 is mostly transformed into HCN during pyrolysis [300]. The nitrogen in biosolids can transform into a range of compounds in solid, liquid and gaseous product fractions such as Char-N, NH₃, HCN, N₂, amines, pyrroles, and amides [67]. Nitrogenated compounds are highly undesirable in bio-oil and require denitrogenation (DeNOx) refining. The formation of NH₃ during biosolids pyrolysis may be favourable, as the production of NH₃ is considered a DeNOx process [5]. However, the formation of NH₃ is usually accompanied by HCN, a highly poisonous gas. Both NH₃ and HCN are precursors of NOx, and monitoring these N-containing products will be useful for pollution control during biosolids pyrolysis [237,301]. NH₃ is mainly concentrated in the aqueous phase of biosolids bio-oil and can be a major specific value-added chemical produced in the pyrolytic aqueous fraction. The NH₃ content in biosolids pyrolysis oil varies from study to study [272]. Kaminsky and Kummer [21] reported 35–39 g/l NH₃ in biosolids pyrolysis liquid obtained at 620–750 °C. NH₃ content ranging from 22 to 42 g/l in biosolids pyrolysis oil at 450–650 °C was reported in another study [13]. The catalytic (γ-Al₂O₃) post-treatment of biosolids pyrolytic vapour yielded an aqueous phase containing 4.5–5.5 wt% NH₃ [1]. There is potential to recover NH₃ from biosolids pyrolysis liquid or use it directly as liquid fertiliser.

Ammonia evolution during biosolids pyrolysis is a function of pyrolysis temperature. Labile proteins in biosolids are responsible for the formation of HCN and NH₃ at low pyrolysis temperature (<400 °C) [55, 302]. The decomposition of N-containing volatiles (nitrile-N and heterocyclic-N compounds) in the tar contributes to HCN and NH₃ release at higher temperatures (>500 °C) [303]. Pyrolysis of biosolids with metal-loaded HZSM-5 catalyst promoted the devolatilisation of biosolids nitrogen, mostly as NH₃ and traces of HCN [55,302]. Liu et al. [55], during HZSM-5 catalytic pyrolysis of biosolids, reported that pyrolysis temperature affects biosolids' nitrogen release as NH₃. At 450 °C, 30.6% of N was converted to NH₃, and 49.7% was retained as char-N, and at 750 °C, 63.4% N was released as NH₃, 13.2% as HCN and 18.6% as char-N. An increase in pyrolysis temperature from 400° to 700°C in the presence of HZSM-5 facilitated N release as NH₃ from 15 mol% to 50 mol%, but it was complemented by higher HCN release from 3 mol% to 9 mol% while char-N and coke-N decreased considerably [284]. The ex-situ catalytic pyrolysis of biosolids using HZSM-5 released about 32% as NH₃ and 2% as HCN, while the balance was char-N [226]. HZSM-5 promoted the cleavage of C-C bonds in nitriles to improve NH₃ formation, while the cracking of N-containing heterocycles at temperatures above 500 °C was responsible for the high yield of HCN [284] (see Fig. 5). Ex-situ catalytic pyrolysis of biosolids compared to in-situ catalysis hindered the formation of HCN but did not improve NH₃ evolution. Several studies have found that catalytic pyrolysis of biosolids improves NH₃ formation. For instance, Patel et al. [5] observed that NH₃ increased in the presence of bed materials during the slow catalytic pyrolysis of biosolids. The order of the bed materials for NH₃ formation was activated char > biochar > lime > empty bed. In another study, the addition of CaO promoted the conversion of HCN to NH₃, and CaO further reacted with HCN to produce N₂ (non-polluting gas) which is the final product of denitrogenation reactions [225]. Shan et al. [304] demonstrated that Ca and Na acetate addition lowered NH₃ emission during biosolids pyrolysis due to the production of acetone (from acetates decomposition) which reacted with NH₃ to produce amines. The co-pyrolysis of biosolids with bagasse decreased NH₃-N yield due to increased conversion of N to other volatile N-compounds [237]. Wei et al. [160] observed that NH₃ was the dominant gaseous product (equivalent to 37.4% of total N in biosolids) while HCN was the minor gaseous nitrogen product (<5%) during biosolids pyrolysis. Demineralisation of biosolids lowered the NH₃ and increased HCN yields at the same pyrolysis conditions as the untreated biosolids. This suggests that mineral matter promotes N conversion to NH₃ during pyrolysis, which corroborates the higher NH₃ evolution observed in metal oxides blended biosolids pyrolysis [225]. The higher HCN yield from untreated

biosolids indicates that mineral matter inhibits the conversion of bio-solids N to HCN. CaO usually catalyses the hydrolysis of HCN to form NH_3 (Eq. 4). Since acid pre-treatment reduce Ca content in biosolids, it can explain the major cause of lower NH_3 and higher HCN yields in demineralised biosolids than in untreated biosolids [160,305]. A scheme summarising the role of mineral matter on N transformation in biosolids is depicted in Fig. 6 [160].

$$HCN + H_2O \xrightarrow{CaO} NH_3 + CO \qquad (4)$$

7.4.4. Levoglucosan and anhydrosugars

Levoglucosan (LG) is a primary product of the thermal decomposition of cellulose and is usually present in substantial amounts (10–50 wt %) in the bio-oil obtained from lignocellulosic biomass [306]. LG is a highly valued platform chemical with potential in many applications [307]. Biosolids are not structured lignocellulose biomass and have not been extensively explored as a feedstock for LG production. Nevertheless, LG has been reportedly identified in biosolids bio-oil from the studies of Alvarez et al. [62,297], where the flash pyrolysis of biosolids was performed in a conical spouted bed reactor optimised for liquid production at 450–600 °C. The authors detected the highest LG concentration of 3.90 wt% in the whole liquid at 450 °C. At 500 °C, LG yield reduced to 1.78 wt%, further reducing to 1.29 wt% at 600 °C. While this observation is consistent with extant literature on the influence of temperature on LG yield [279,308], the low LG yield from biosolids is partly due to its low cellulose content aggravated by the 'single pot' traditional pyrolysis approach employed. Moreover, biosolids contain substantial amounts of metals and minerals, which interferes with the thermal decomposition of cellulose to LG [5]. AAEMs are known to have drastic effects in suppressing the LG formation pathway during pyrolysis [78,309,310]. When biosolids were co-fed with pinewood sawdust at a 1:1 mass ratio, a slight improvement in the LG yield was observed. LG concentration in 100% biosolids bio-oil obtained at the same conditions was 1.78 wt% bio-oil and increased to 2.40 wt% in the oil obtained from the co-pyrolysed liquid, which was a 35% decrease from the yield in 100% pinewood sawdust bio-oil. LG in minute concentration was also detected in the whole pyrolysis liquid of biosolids obtained at 450 °C in another study [29]. Mild pyrolysis temperature and a good choice of reactor configuration can favour the formation of anhydrosugars in the biosolids bio-oil. Continuous mode of operation, low char residence time, and very short vapour residence time (<2 s) during the pyrolysis

process would prevent significant volatiles-volatiles and char-volatiles interactions that would otherwise enhance the formation of more secondary reaction products [311,312]. Although the few studies are not optimised for LG production, the obtained yields are comparable to that from the fast pyrolysis of untreated biomass [279,313]. Hence, high LG yield could be obtained from the liquid product of demineralised biosolids fast pyrolysis in a well-optimised process.

The co-pyrolysis of biosolids with cellulose-rich biomass can bring about positive interactions in improving LG yield. This interaction can be bettered if both feedstocks and the process are optimised for LG production via fast co-pyrolysis. Feed pre-treatment for the removal of AAEMs or passivating AAEMs catalytic functions and delignification followed by pyrolysis at 350–450 °C have been shown to enhance LG formation in many feedstocks [87,308,314]. Careful selection of lignocellulose biomass feed with desired features (high cellulose and low ash contents) can neutralise potential antagonistic effects on LG production during the fast co-pyrolysis process. However, besides the feed cellulose and ash contents, other process factors influence many competing pyrolytic pathways [315].

7.4.5. Others

A range of other platform chemicals can be recovered from biosolids pyrolysis liquid. Carboxylic acid is one of the main components in the pyrolysis aqueous fraction. It is generated from the hydrolysis of the acetyl ester groups present in polysaccharides and fatty acids [272]. Acetic acid is a major component of carboxylic acids in many bio-oils; however, Fonts et al. [29] found butyric acid and lactic acid as the main components in biosolids-derived pyrolytic liquid. Acetamide is another potential value-added chemical and may have different origins in biosolids pyrolysis liquids. It could come from the pyrolysis of microbial cell walls, thermally labile proteins containing glycine [76], or acetic acid and ammonia reaction [295]. Acetonitrile could be formed by the dehydration of acetamide and constitute another important chemical component in biosolids pyrolysis liquid [13,272].

8. Conclusions and future research perspectives

Biosolids are unavoidable waste products of the wastewater treatment process and require a sustainable approach to their management. While land application and incineration remain dominant biosolids management routes in many countries, thermochemical conversion via pyrolysis is gaining intense research attention in tackling many challenges with the traditional management methods. Despite the promising ability of the pyrolysis technique for biosolids treatment, it is still limited by low product quality, such as highly concentrated HMs-containing biochar and nitro-oxygenated bio-oil. The unstructured and heterogenous biosolids compositions and the 'one-pot' pyrolysis approach have been identified to aggravate these challenges. In order to alleviate biosolids pyrolysis of the many limitations, several process developments involving the use of catalysts, pre-treatment, and co-feeding have been deemed beneficial to a larger extent. Acid pre-treatment of biosolids for demineralisation, hydrolysis and HMs removal can enhance the pyrolytic conversion of biosolids to high-quality products. Metal oxides catalysts play significant roles in suppressing pollutants release from N, S, and Cl-bearing compounds in biosolids during pyrolysis, while HZSM-5 catalysis benefits the cracking of PAHs and oxygenates in the tar as well as improves aromatic yields. Lastly, co-pyrolysis of biosolids with a range of feedstocks can lower pyrolysis activation energy, increase bio-oil yields, improve biochar physicochemical and surface properties, and lower HMs contents in the char. Repositioning the traditional 'one-pot' pyrolysis approach to biosolids conversion into an integrated pre-treatment pyrolysis, pyrolysis-catalysis and co-pyrolysis or any combinations can improve biosolids valorisation to high-quality end materials such as high-value chemical, biochar and bio-oil. However, the influence of these process/feed modifications in achieving several beneficial improvements has not
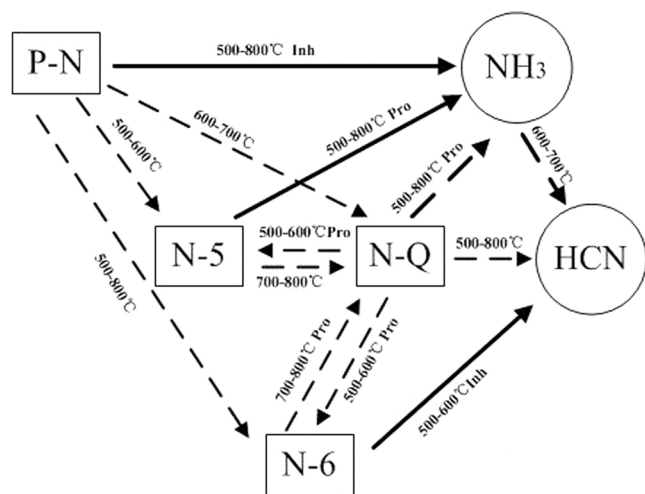

Fig. 6. Influence of organic matter on the transformation of N compounds during biosolids pyrolysis; protein-N (P-N), pyridine-N (N-6), pyrrole (N-5), and quaternary-N (N-Q) "Inh" denote pathway inhibited by mineral matter and "Pro" denotes pathways promoted by mineral matter, solid lines denote main routes, and broken lines denote secondary routes.
Adapted from [160].

been largely consistent, and many issues require debottlenecking. Challenges and perspectives for future research are highlighted below.

1. ***Biosolids compositional modifications:*** Reducing the compositional complexity of biosolids by increasing the volatile matter and decreasing the inorganic constituents would help enhance the pyrolytic conversion of biosolids to high-quality bio-oil having low water and oxygenates contents and produce biochar with low ash and HMs content. Benchmarking biosolids suitable for pyrolysis with respect to their volatile and ash contents as well as HHV could be beneficial in increasing value capturing from biosolids pyrolysis products.

2. ***Biosolids pre-treatment:*** Despite numerous benefits of pre-treatment integrated with pyrolysis in a biorefinery context, the application of this process remains inadequately explored in biosolids pyrolysis. One of the limiting drawbacks of biosolids pre-treatment is the non-competitive composition with typical lignocellulosic biomass, for which most pre-treatment techniques have been developed. The mechanisms of most of the pre-treatment methods are not known for biosolids hydrolysis, fractionation and demineralisation and are usually inferred from observations with lignocellulosic feedstocks. Fundamental investigations into the reaction mechanisms and kinetics between biosolids constituents and many pre-treatment agents are imperative. Expanding the scope of pre-treatment in biosolids processing is necessary to optimise the full benefits of integrated biosolids processing. Existing pre-treatment methods such as acid, thermal and alkali hydrolysis need to be fully developed to suit biosolids' physicochemical peculiarities, and new techniques, including organosolv, ionic liquids, ozonolysis, biochemical, amongst others, need to be widely tested on biosolids for several goals. There is a great prospect with biosolids pyrolysis integrated with combined pre-treatment and catalysis or co-feeding, but more fundamental studies are needed.

3. ***Choice of catalysts materials:*** HZSM-5 zeolite and metal oxides have been extensively used as catalyst materials for biosolids pyrolysis. HZSM-5 is a proven catalyst for catalytic cracking to improve aromatic hydrocarbon yield, while metal oxides are well studied for pollutants degradation and char cracking. Cation exchange zeolite materials such as Y-zeolite, USY, and MCM-41 have not been widely tested on biosolids pyrolysis, and they are likely to behave differently from the conventional HZSM-5. Similarly, metal salts of nitrates, sulphates, and chlorides such as $ZnCl_2$, KNO_3, and $FeCl_3$ have a very limited investigation on biosolids pyrolysis. Given the relatively higher mobility of metal salts than metal oxides, their catalytic effects on product distribution and compositions are unclear and require investigation. Lastly, various catalyst materials can mitigate pollutant release during pyrolysis; they could cause deleterious effects on product yields and chemical composition, which have not been well studied. Therefore, identifying robust additive materials that can produce largely desired effects during biosolids pyrolysis is necessary.

4. ***Functionalising biosolids biochar:*** Biosolids biochar in its raw form is limited by compositional and physicochemical attributes and requires substantial modifications for many applications. Demineralisation and solvents impregnation are insufficient to produce application-specific biochar; therefore, several advanced developments are required to tailor biosolids biochar for targeted applications. Rather than the end of pipe treatment/modification of biosolids biochar, attention should shift to functionalising biosolids feed before pyrolysis, for which advanced pre-treatment will play the leading role.

5. ***Extraction of chemical components in biosolids bio-oil:*** The whole pyrolysis liquid composition is still complex and highly heterogeneous despite several efforts around biosolids pre-treatments, catalysis, and co-feeding focus on improving the chemcial value of the bio-oil. Also, the improvement in the energy value of the final bio-oil obtained from such processes is still inferior to conventional diesel and gasoline grade fuel. The interest in recovering value-added chemicals from the bio-oil would require detailed qualitative and quantitative analysis of the liquid product to the greatest possible extent. Exhaustive determination of the chemical composition of the pyrolysis liquid from biosolids will be instrumental in assessing its potential as a source of valuable chemicals. Research is warranted in the bio-oil analytical techniques, liquid fractionation techniques, components separation, extraction, and purification to maximise value-added chemical production potential from biosolids-derived oil.

6. ***Joint pre-treatment, catalysts and co-processing strategy:*** several works have demonstrated the effectiveness of catalysts and co-feeding as an individual process in improving biosolids pyrolysis. Only a few works have examined the combined effects of adding catalysts during biosolids co-pyrolysis, termed catalytic co-pyrolysis. For example, co-pyrolysis of biosolids with woody biomass can effectively lower HMs in the resultant biochar, while catalytic pyrolysis is effective for tar cracking and deoxygenation of bio-oil. Combining these two benefits in one process may be obtained via catalytic co-pyrolysis approach. However, more studies are needed to establish these mutual benefits on biosolids pyrolysis. There are barely any reported works on catalytic and co-pyrolysis of treated biosolids which is a step further in the pyrolysis process and product improvement. Combining at least two of pre-treatment, catalysts, or co-feeding will be a step away from the conventional standalone catalytic and co-pyrolysis process. However, thorough investigation on how the intended synergistic benefits can be captured from the integrated biosolids pyrolysis system is needed.

CRediT authorship contribution statement

Ibrahim Gbolahan Hakeem: Conceptualisation, Methodology, Formal analysis, Investigation, Writing – original draft. **Pobitra Halder:** Validation, Visualisation, Writing – review and editing. **Charles Chinyere Dike:** Data curation, Writing – review and editing. **Ken Chiang**: Validation, Writing – review and editing. **Abhishek Sharma**: Writing – review and editing. **Jorge Paz-Ferreiro:** Supervision, Writing – review and editing. **Kalpit Shah:** Conceptualisation, Validation, Supervision, Project administration.

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.

Acknowledgements

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jaap.2022.105608.

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