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Research Paper

Ashes from challenging fuels in the circular economy

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ABSTRACT

In line with the objectives of the circular economy, the conversion of waste streams to useful and valuable side streams is a central goal. Ash represents one of the main industrial side-products, and using ashes in other than the present landfilling applications is, therefore, a high priority. This paper reviews the properties and utilization of ashes of different biomass power plants and waste incinerations, with a focus on the past decade.

Possibilities for ash utilization are of uttermost importance in terms of circular economy and disposal of landfills. However, considering its applicability, ash originating from the heat treatment of chemically complex fuels, such as biomass and waste poses several challenges such as high heavy metal content and the presence of toxic and/or corrosive species. Furthermore, the physical properties of the ash might limit its usability. Nevertheless, numerous studies addressing the utilization possibilities of challenging ash in various applications have been carried out over the past decade. This review, with over 300 references, surveys the field of research, focusing on the utilization of biomass and municipal solid waste (MSW) ashes. Also, metal and phosphorus recovery from different ashes is addressed.

It can be concluded that the key beneficial properties of the ash types addressed in this review are based on their i) alkaline nature suitable for neutralization reactions, ii) high adsorption capabilities to be used in CO_2 capture and waste treatment, and iii) large surface area and appropriate chemical composition for the catalyst industry. Especially, ashes rich in Al_2O_3 and SiO_2 have proven to be promising alternative catalysts in various industrial processes and as precursors for synthetic zeolites.

1. Introduction

Thermal conversion, i.e., combustion, gasification, and pyrolysis of solid fuels, has three primary purposes: recovering fuel-bound energy, producing gases, and reducing waste from side streams without further use. Thermal conversion of challenging biomass waste fuels and other waste side streams plays an increasingly important role in the circular economy. Toxic wastes without further use must be stored in the final disposal following the laws and directives. On the other hand, thermal conversion enables recovering fuel-bound energy and significantly reduces waste, thereby minimizing or even eliminating the need for disposal. From heterogenous ashes, for example, glass and metals can be recovered. Ashes can be used for soil amendment (Pathan et al., 2003), fertilizers (Schiemenz and Eichler-Löbermann, 2010), secondary building materials, additives to cement and cement substitutes (Rajamma et al., 2009), and selective leaching (Steenari et al., 1999) in order to recover valuable elements.

In the thermal conversion of solid fuels drying, and devolatilization occur, leaving a char residue. After oxidation or gasification of the char, ash remains. Numerous studies have investigated various aspects of the chemistry of ashes from coals, biomasses, and other waste fuels. The formation of ash is a very complex process (Zevenhoven-Onderwater et al., 2001; Vassilev et al., 2013). Some inorganic ash compounds remain stable throughout the process, while others form during specific thermal conversion stages. In industrial thermal conversion, ashes can be divided into bottom and fly ashes. Both bottom ash and fly ashes may also include other residues, e.g. cyclone ashes or air pollution control (APC) residues (De Boom and Degrez, 2012). The reactor type, temperature, atmosphere, residence time, fuel composition, and particle size influence the split bottom ash/fly ash, the ash particle size distribution, and the bottom and fly ash compositions (Hupa, 2012). In biomass combustion and combustion of various waste streams or side streams, the bottom ash/fly ash split is generally difficult to predict with a few exceptions: for example, in municipal solid waste incineration, the bottom ash/fly ash split is around 10. Also, it is important to point out that APC residues may be added to fly ashes, influencing the amount and

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composition of the fly ash. However, based on release studies (Van Lith et al., 2006), harmful and volatile elements such as Cl, Pb, and Zn are more likely to be found in the fly ash, while less volatile elements are more likely found in the bottom ash. To the authorś knowledge, no scientific studies report how the split bottom ash/fly ash is distributed in biomass and waste combustion. In contrast, it is well-known that there is typically significantly more fly ash than bottom ash in pulverized fuel combustion and significant amounts of fly ash and bottom ash in grate-fired combustion. At the same time, the split is strongly dependent on fuel and operation in fluidized bed combustion. Also, metal distribution in municipal waste incineration has been studied (Brunner and Mönch, 1986; Morf et al., 2002). Metal recovery efficiencies from bottom ashes emanating in Denmark were investigated and estimated by (Allegrini et al., 2014).

Biomasses often have ash contents between 0.1 and 10 % (Hupa et al., 2017), while ash in coal can exceed 30 % (Essenhigh, 1981). Waste ash contents range from 0 % (pure plastics) to nearly 100 %, although in such a case, the waste cannot be considered as a combustible fuel. Coal ashes are chemically more stable than biomass ashes. Biomass ashes range from stable to very unstable ashes. The unstable ashes may dissolve almost entirely in water (Vassilev et al., 2013). In addition, many waste ashes are corrosive (Enestam et al., 2013) and may consist of water-soluble harmful elements such as Ba and Sr and valuable elements such as P, Co, and Cu (Vassilev et al., 2013).

Coals, biomasses, and especially waste fuels are heterogeneous. The chemical composition of waste fuels and resulting ashes may vary significantly depending on the day or time of year the waste is generated. It may even be impossible to reproduce identical ashes from the same waste source. There is an urgent need for detailed physical and chemical characterization of various waste ashes (Vassilev et al., 2013).

Several review studies on the chemistry of ashes and the general utilization of ashes have been published (e.g., Vassilev et al., 2013; Hupa, 2012). The present study reviews the most recent findings on ashes from challenging biomasses and biomass waste fuels. Challenging in this context refers to heterogeneous fuels with chemically unstable ashes enriched in harmful elements.

When considering the utilization of ashes in value-added applications, all efforts must follow valid legislation and the best available technologies. One of the first steps to define is to assess whether the ash is classified as hazardous waste or not (EU Waste Directive, 2008/98/EC). According to van Dijen and Pels (2019), for biomass ashes the starting criteria in classification are the fuel composition, combustion technology, additives used, and the EU legislation. Additionally, the content of unburned carbon, CaO and phosphorus contents can be used to specify the actions need to valorize and utilize the ash. They considered several potential biomass ash applications as kind of landfilling applications, e.g., fertilizers in agriculture and forestry, additives for compost production, liming agents in agriculture and forestry, soil stabilization, geopolymers, forest road construction and stabilization of dredging sludge.

The EU Fertiliser directive (EU Fertilizer Regulation, 2019/1009) provides limits for heavy metals and other harmful elements or compounds for ashes in fertilizers or soil-related applications. In the EU, the Waste Act (646/2011), decision 2014/955/EU, and notice on technical guidance (2018/C 124/01) provide guidelines for classifying waste and waste management (Waste act, 2011). In Finland, degree 843/2017 is applied to the professional use of waste, such as various ashes in earth constructions (Finlex, 2017). It should be noted that several other local laws, acts and degrees besides those mentioned above provide additional guidelines for the transport, treatment, and utilization.

2. Biomass and biomass ash composition

Comprehensive reviews by Hupa (2012) and Vassilev et al. (2013) discuss and emphasize the characterization and chemistry of biomass ashes. Biomass ashes are complex, mainly inorganic mixtures with heterogeneous and variable compositions. Table 1 shows typical elemental compositions of ash-forming matter in eight different biomasses (Åbo Akademi University, 2021). In addition, the table lists the ash compositions of typical sewage sludge, peat, and coal. It should be noted that Table 1 only lists selected ones of biomass fuel ashes. Other important biomass ashes include for example waste wood ashes (Martínez-García et al., 2022) sometimes rich in zinc and lead (Enestam et al., 2011). The compositions are given as the most common oxide of each element. However, some elements, such as Ca and P, are frequently present in the ash as more complex compounds, e.g., $Ca_3(PO_4)_2$. Nevertheless, expressing the ash compositions as oxides enables an easy comparison of different biomass ashes and a reasonable estimation of oxygen content in the ash. If all relevant elements have been included, the sum of the oxides is often close to 100 %.

3. Municipal solid waste (MSW) ash

With the drastic increase in urbanization and industrialization during the last few decades, the global municipal solid waste (MSW) generation rate reached approximately 1300 Mt/year (Hoornweg and Bhadat-ata, 2012). MSW generation is projected to grow by 9 % annually (Zhang et al., 2015a), which poses severe environmental and economic concerns. Waste incineration is the conventional method for managing the increasing generation of MSW. However, ashes produced by the incineration of MSW still bring severe environmental problems to groundwater and soil if managed through landfilling (Yan et al., 2019a). Toxic elements might be leached from MSW incineration (MSWI) ashes that contain heavy metals and organic contaminants (Luo et al., 2019).

3.1. Types of MSWI ashes

MSW incineration can be divided into refuse-derived fuel and mass-burning processes. In the first, metals and glass are separated, followed by shredding and incineration, while in the second, the MSW is thermally converted as received without waste separation or shredding. The MSW is transformed physically and chemically as a result of incineration. The generated ash amount varies significantly depending on the process and source fuel: from < 1 to > 30 % by wet weight percentage. The split between the bottom and fly ash is strongly affected by the fuel and thermal conversion system. Fly ashes between 3 and 10 % of the initial MSW (dry basis) have been reported (Yao et al., 2014). Fig. 1 illustrates the partitioning of the two types of MSWI ashes and their treatments.

Chemical partitioning of heavy metals is accelerated by the temperature and presence of chlorine in different waste types. Fly ash often contains a higher concentration of heavy metals and sometimes also organics (Guo and Zhang, 2020; Peng et al., 2020; Wang et al., 2018), although the organic fraction should optimally be destructed in the high-temperature oxidation processes. Dioxins and Furans are forming in the combustion chamber and are hazardous issues in many countries as the concentrations in MSWI fly ash are often above the threshold limit for landfill (Wu et al., 2016). The formations of dioxins and furans via the de novo mechanism are catalyzed by the presence of halides like CuCl (Tesfaye et al., 2022). Song et al. characterized ashes from different spots in the MSW incinerator and reported that most of the heavy metal concentrations are higher in fly ashes than those in bottom ashes (Song et al., 2004). When exposed to landfills, fly ash poses environmental threats due to heavy metal and toxic organic matter leaching (Nowak et al., 2021). Consequently, some EU27 countries, the USA, and China have introduced policies for properly controlling and managing MSWI fly ash (Zhan et al., 2018). One essential step is the stabilization of the MSW fly ash before landfilling. Some researchers have suggested methods for the immobilization of toxic heavy metals in MSWI fly ashes through physical encapsulation, isomorphic substitution (the replacement of an atom by another of similar size in a crystal lattice), chemical compounds, and formation of alkaline surroundings (Tian et al., 2020;

Table 1
Typical oxide compositions (wt%) of biomass, sewage sludge, peat, and coal ash (Åbo Akademi University, 2021). The compositions have been determined with inductively coupled plasma optical emission spectroscopy (ICP-OES).

Biomass ash	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MnO	CaO	MgO	P_2O_5	Na_2O	K_2O	Sum
almond shells	6.22	0.98	0.66	0.06	0.05	36.32	3.01	1.6	0.38	30.66	79.95
bagasse	72.96	4.97	2.53	0.29	0.19	11	2.06	0.96	0.34	3.86	99.15
bark	10.74	3.2	4.96	0.14	1.77	60.16	5.82	5.24	0.67	8.69	101.38
eucalyptus bark	0.01	0.14	0.07	0	4.21	77.43	3.12	1.95	0.36	16.07	103.38
forest residue	36.75	5.81	1.91	0.22	1.46	37.14	2.93	3.17	0.2	7.72	97.32
grape seeds	3.44	0.57	0.56	0.03	0.05	52.97	3.12	11.81	0.18	17.52	90.24
rice husk	95.41	0.1	0.05	0	0.12	0.74	0.28	0.53	0.01	1.84	99.09
rice straw	69.88	0.28	0.24	0.01	0.57	6.16	1.55	1.53	0.4	15.26	95.88
straw	58.49	0.39	0.33	0.03	0	21.1	2.13	3.53	0.25	13.59	99.84
sewage sludge	17.86	9.89	36.65	0.75	0.08	13.28	1.12	19.61	0.53	0.82	100.59
peat	20.2	23.09	26.21	0.44	0.22	19.42	2.07	4.1	0.15	0.64	96.56
coal	46.48	24.6	8.43	0.98	0.16	6.83	2.62	0.48	1.36	2.34	94.28

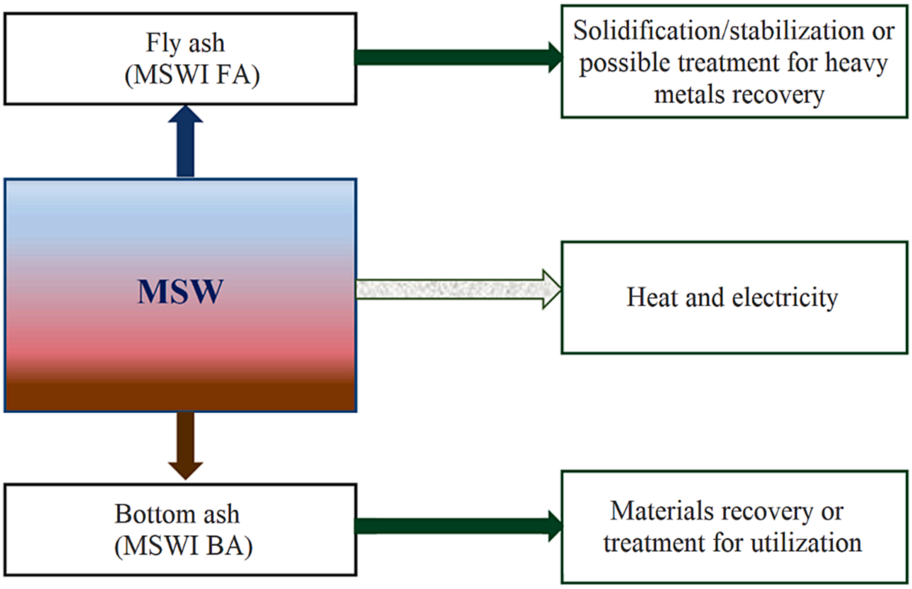

Fig. 1. Schematic process flow sheet showing the two ashes in MSW incineration.

Wan et al., 2018; Zheng et al., 2011; Zheng et al., 2016). MSWI fly ash is currently primarily treated through solidification/stabilization techniques (Zhang et al., 2023).

In some waste incineration plants, the fly ash is mixed with water and bottom ash. For instance, in the USA, the ash streams are commonly combined (Xinghua et al., 2016), while in the European Union, most facilities manage the bottom ash and fly ashes separately, as illustrated in Fig. 1. The bottom ash may consist of glass, ceramics, ferrous and nonferrous metals, and minerals. The amount of fly ash depends on the types of waste, incineration conditions, incinerating plants, and flue gas treatment. The fly ash amount can be up to 3 % of the untreated MSW prior to incineration (Xinghua et al., 2016).

Ashes from a boiler, scrubber, and precipitator or baghouse consist of particulates originating from the primary combustion zone area and are subsequently entrained in the off-gas stream (Pan et al., 2008). As the flue gas passes through the boiler, scrubber, and precipitator or baghouse filter, the entrained particulates (fly ash) stick to the boiler tubes and walls or are collected in the air pollution control equipment (i. e., fly ash), which consists of the scrubber (in the case where SO_2 content is high), electrostatic precipitator, or baghouse. Ash extracted from the flue gas consists of fine particles, with one size-fraction measuring less than 0.1 mm in diameter. In grate-fired waste combustion, baghouse or precipitator ash may comprise up to 25 % of the total combined ash stream (Pan et al., 2008).

MSW incineration fly ash is typically contaminated with water-leachable chloride and sulfate compounds of critical or toxic elements such as Pb, Zn, Cd, and Cr. Table 2 lists potential heavy metals and phosphorus sources in MSW, while typical compounds found in MSWI fly ash are given in Table 3. The content of the critical and toxic elements

Table 2
Potential sources of heavy metals and phosphorus in MSWI fly ash (Jupp et al., 2020; Loginova et al., 2019; Mertoglu-Elmas, 2017; Xinghua et al., 2016; Spreadbury et al., 2023).

Substance	Source
P	Food wastes, wood, paper, textiles, and agricultural biomasses
Pb	Gasoline additives, ammunition, solder, paint, pesticide, electronic waste, glass, ceramic, concrete, and slag
Hg	Electrical manufacturing, pharmaceuticals, paints, plastics, paper, batteries, coal, mercury smelters, fluorescent lamps and mercury preparation plants
Cd	Plastic additives, pigments, electroplating, metal covering and batteries
Cr	Mining industry, smelting plant, electroplating factory, chrome tanning system, metal residues
As	Atmospheric dust, tailings and pesticides, leather, chemicals pharmaceuticals, metallurgy, decolourants, glass, ceramic, concrete, and slag
Sb	Mining industry, smelting plant, glass, ceramic, concrete, and slag
Cu	Paints, pigments, machinery manufacturing, steel production, wires
Zn	Pigments, galvanized steel, smelting, machinery manufacturing, organic synthesis, mining industry

Table 3
Examples of forms of heavy metals and phosphorus in MSWI fly ash (Jupp et al., 2020; Ohenoja et al., 2019; Qian et al., 2008; Weibel, 2017).

Substance	Form of existence
P	$AlPO_4$, P_2O_5, $CaHPO_4$, $Ca_4H(PO_4)_3$
Pb	$PbCl_2$, $PbCO_3$, PbO, Pb_3SiO_3, Pb_3SiO_4,$Pb_3O_2SO_4$, $Pb_3Sb_2O_7$
Cd	$Cd(OH)_2$, CdO, $CdSO_4$, $CdCl_2$, $CdSiO_4$
Zn	$ZnCl_2$, ZnO, $Zn(OH)_2$, $ZnCO_3$, $ZnSO_4$, K_2ZnCl_4
Fe	Fe_2O_3, Fe_3O_4
Cu	$Cu(OH)_2$, CuO, $CuCO_3$

must be reduced before the reuse or disposal of the ash to fulfill the requirements set by legislation (Loginova et al., 2019; Xinghua et al., 2016; Weibel et al., 2021).

Heavy metals and other hazardous substances like dioxins and furans are enriched in MSWI fly ashes. Accordingly, MSW fly ash is classified as a hazardous waste due to the high concentration of leached heavy metals and equivalents of dioxins.

Treatments for MSWI fly ash include chemical stabilization (Zhou et al., 2015), cement solidification (Guo and Shi, 2013), heat treatment (Zhong et al., 2013), recovery of heavy metals (De Boom et al., 2011: Weibel et al., 2021; Quina et al., 2018; Wolffers et al., 2021;), minerals recovery for building industry (Quina et al., 2018), recovery of deicing salts (Quina et al., 2018) and utilization for different applications (Jia et al., 2015). Raw materials such as coal ash and slag are widely used in the cement industry. Due to the similarities between the chemical compositions, MSWI fly ash can partly replace coal ash and slag in cement and concrete manufacturing (Pan et al., 2008; Saikia et al., 2007). More importantly, the unique environment of high temperature up to 1450 °C and alkaline atmosphere in rotary kilns enables the stabilization or complete decomposition of hazardous species such as heavy metals, dioxin, furan, and other toxic substances (Ginés et al., 2009). However, possible high concentrations of metal chlorides at high temperatures might challenge the normal kiln operation and affect the cement quality (Morel et al., 2000). In some countries, the reuse is difficult as the ash quality may, in some cases, not meet the environmental regulations high requirements.

3.1.1. MSW ashes characterization and treatment

When addressing energy recovery as heat and electricity, incineration plays an increasingly significant role in MSW treatment in reducing waste mass and volume by up to 70 % and 90 %, respectively (Yan et al., 2019b; Luo et al., 2019). The characteristics of the incineration byproducts, ashes, can be divided into physical and chemical properties. Grain size distribution, moisture content, dry density, BET Surface area, and compressive strength are essential physical or engineering properties, which have to be taken into account when considering MSWI ash utilization. Examples of chemical characteristics include chemical composition, ignition loss, organic contents, heavy metals, and leachability.

Changes in climate, usage of available materials, and the type of recycling process in a particular area affect MSW's chemical, physical, and biological composition. The major elements in MSW ashes are Al, Ca, Cl, Fe, K, Mg, Na, and Si. Table 4 lists the chemical compositions of selected MSW fly ashes (Jung et al., 2004; Kamon et al., 2000; Wiles, 1996). The average contents of CaO, SiO_2, Cl, and SO_3 make up about 75 wt% of the fly ash, with CaO constituting up to 36 wt%. For comparison, Table 5 lists the average amounts of the same elements found in MSW bottom ashes (Hjelmar et al., 2013). Similar to fly ashes, calcium is also the most abundant element in bottom ashes. However, the next elements are (in decreasing content order) Si, Fe, Al, and Na.

MSW ashes may also be utilized, e.g., as a raw material in tiles (Fan et al., 2019; Ponsot et al., 2015), bitumen (Yan et al., 2019b), and concrete (Ashraf et al., 2019; Caprai et al., 2018). Furthermore, fly ash has attracted much attention as a valuable raw material in geopolymer production (Venkatesan et al., 2019), fired ceramics (Karayannis et al., 2017), and sintered bricks (Leiva et al., 2018). Due to the high contents of CaO, SiO_2, and Al_2O_3, the MSW fly ashes have the potential to be used as siliceous and calcareous raw materials in wall blocks (Silva et al., 2017).

Table 4
Summary of selected chemical composition of MSWI fly ash samples (Chen et al., 2016; Jianguo et al., 2009; Qian et al., 2008; Yan et al., 2019b; Zhang et al., 2016).

Substance	Composition in wt%					
	(Chen et al., 2016)	(Qian et al., 2008)	(Zhang et al., 2016)	(Yan et al., 2019b)	(Jianguo et al., 2009)	Average
CaO	23.12	42.55	40.55	38.12	38.79	36.63
Cl	–	20.11	–	17.99	13.95	17.35
SO_3	17.50	12.73	10.2	–	8.63	12.26
SiO_2	18.64	5.44	15.98	5.80	12.58	11.70
Al_2O_3	9.86	3.1	11.15	2.79	4.06	6.20
K_2O	3.04	4.31	–	8.56	4.92	5.21
Na_2O	2.33	4.82	–	1.32	6.87	3.83
Fe_2O_3	5.45	1.69	4.73	1.03	3.82	3.34
MgO	3.78	1.83	–	–	2.34	2.65
P_2O_5	1.18	1.62	–	–	1.14	1.31
TiO_2	1.79	0.92	–	–	1.05	1.25
ZnO	–	1.17	–	–	0.71	0.94
PbO	0.25	0.42	–	0.78	0.28	0.35
Br	–	0.39	–	–	0.17	0.28
BaO	–	0.15	–	0.57	0.0904	0.27
Sn_2O_3	–	0.35	–	–	0.16	0.25
CuO	–	0.13	–	–	0.17	0.15
Sb_2O_3	–	0.15	–	–	–	0.15
Cr_2O_3	–	–	–	–	0.1388	0.14
MnO	–	–	–	–	0.1164	0.12
SrO	–	–	–	–	0.0774	0.08
NiO	–	–	–	–	0.0188	0.02

Table 5
Summary of selected chemical composition of MSWI bottom ash samples. All data is taken from (Hjelmar et al., 2013).

	Content in mg/kg			
Substance	Average	Median	Min	Max
Ca	130,833	125,586	50,825	198,289
Cl	9211	5943	3644	37,633
S	3862	3475	1310	16,808
Si	82,713	84,180	61,060	96,078
Al	47,232	44,627	30,527	75,089
K	7748	7595	4854	12,722
Na	21,379	22,270	12,308	34,791
Fe	58,714	56,703	34,216	118,220
Mg	12,429	11,242	6377	34,372
P	5633	5049	2531	12,556
Ti	6.7	3.8	3.4	27.5
Zn	3241	2871	1142	9370
Pb	1309	1058	197	6441
Br	44.7	42	23	95
Ba	1102	958	760	2970
Sn	181	154	52	737
Cu	3275	2510	738	17,620
Sb	73	63	18	250
Cr	353	315	115	852
Mn	1173	1104	644	2248
Sr	271	270	267	369
Ni	185	153	38	850

4. Ash utilization during the past decade

4.1. Biomass ashes in acid mine drainage

Mining and mineral processing affect natural waters at mining sites, resulting in mine drainage. Depending on the pH, mine drainage is classified as acid, neutral, or basic. Of these, acid mine drainage (AMD) poses the most significant environmental hazard (Silva et al., 2017). AMD occurs when material containing sulfides (for example, pyrite, FeS_2) is oxidized, forming acid and liberating metal- and sulfate-containing compounds into natural waters. As several metals are soluble in acidic water, additional elements from subterranean ores might leach. Thus, the AMD process can lead to considerable amounts of heavy metals (Fe, Cu, Pb, Zn, Cd, Co, Cr, Ni, Hg), semi-metals (As, Sb), and other elements (Al, Mn, Si, Ca, Na, K, Mg, Ba, F) in natural waters (Heviánková et al., 2014). As a result, typical for AMD is a pH below 5.5, moderate to high metal and metalloid concentrations, and an elevated sulfate concentration (Pettersson et al., 2008). Although not as hazardous as AMD, contaminated neutral drainage (CND) can also be considered an environmental threat. CND refers to an effluent with pH ranging between 6 and 9, containing metals (Cd, Cr, Co, Cu, Fe, Hg, Mn, Mo, Ni, Se, U, and Zn), metalloids (As and Sb), and sulfate that are soluble in the pH range and present in concentrations exceeding local regulatory limits (Calugaru et al., 2018; Pettersson et al., 2008).

Although active treatment methods, which require a chemical treatment system to buffer acidity and remove metals, are commonplace during mine operations, they are rarely used at inactive or abandoned sites. Passive treatment systems are preferred at these sites because they use natural or waste materials and have low operating and maintenance costs (Genty et al., 2021). Biomass-based ash might provide an ecological and cost-efficient solution for drainage neutralization and pollutant removal for such applications. The key characteristics of the applied ash are high CaO content for increasing pH and high levels of SiO_2, Al_2O_3, and Fe_2O_3 (Alinnor, 2017). The role of these oxides is metal removal by adsorption onto the fly ash particles due to electrostatic attractions or precipitation/co-precipitation of metals as the pH of the effluent increases (Alinnor, 2017; Calugaru et al., 2018).

Due to their high acid neutralization capacity, some ashes can replace more expensive neutralizing agents such as limestone or lime-based materials (Barbu et al., 2012). For example, wood ash has been reported to remove Ni (>97 % removal over 56 days) effectively (Richard et al., 2020), As (>96 % removal over 56 days) (Braghiroli et al., 2020), and several other pollutants (Fe, Hg, Cr, Cd, Co, Cu, Pb, Al, Mn, Zn, Mg, and SO_4^{2-}) (Heviánková et al., 2014). Also, ash originating from straw, meat and bone meal, and poultry litter (effectively) adjusted pH and removed pollutants with high removal efficiencies for Al, Fe, Mn, and Zn (Silva et al., 2017). Their study also showed that it is possible to make accurate predictions for the suitability of untested ash types by comparing their chemical composition to known chemical classifications of biomass ashes. The pollutant removal efficiency of ash can be further improved, for example, by modifying the pH, cation exchange capacity, and concentrations of potential contaminants of the ash before utilization. With an alkaline fusion-modified wood ash compared to untreated ash, the sorption capacity for Ni and Zn increased, the reduction in efficiency became lower, and the stability of Zn was enhanced (Calugaru et al., 2017). Zeolites, a group of aluminosilicates that can be produced from biomass ash, possess potent sorption capacities, which might be applicable to AMD treatment.

A mixture of soil, biomass, and coal fly ashes was studied for its applicability as a flow-through reactive barrier (Penney et al., 2013). The idea of the barrier was to place it in the soil close to an inactive mine site, where it would passively treat AMD-contaminated groundwater as the water flows through the barrier. The studied mixture buffered the effluent pH to meet mine effluent regulations with minimal change in hydraulic conductivity. Furthermore, regulated metal concentrations were reduced by up to three orders of magnitude. However, after passing the mixture, the measured Al concentrations of the effluents increased above the regulatory limits as a function of the ash content due to Al dissolution. Therefore, the possible dissolution of hazardous elements from ash or pH increase to too high a level needs to be studied and known before ash utilization. Also, coating/passivation (loss of reactivity) and clogging (loss of permeability) caused by precipitated minerals during treatment might limit the applicability of biomass ash. Mineral precipitation can be avoided by using biomass ash-containing pre-treatment units, which remove acidogenic metals such as Fe and Al before their reactions with water decrease effluent's pH value to a level where precipitation of other metals is hindered (Ayora et al., 2013; Rakotonimaro et al., 2016). Such a pre-treatment unit containing wood ash removed Fe with an efficiency close to 100 % and other pollutants such as Al, Zn, Pb, Mn, and SO_4^{2-} to a lesser extent (Rakotonimaro et al., 2016). If clogging is not an issue, the Fe sorption unit can also be placed after a sulfate-reducing biofilter unit in a system, where most of the sulfate is removed first, followed by an effective Fe and additional sulfate removal (Genty et al., 2021). Furthermore, biomass ash can stabilize inorganic contaminants in biofilters for their safer disposal (Lounate et al., 2020).

4.2. *Biomass ashes in catalysts*

Biomass ash can be applied to various industrial processes as a catalyst. High concentrations of alkali and alkaline earth metals (AAEMs) together with low silica content make biomass ash a suitable and cost-efficient catalyst for petroleum coke, low-rank, and bituminous coal gasification (He et al., 2020; Huang et al., 2014; Rizkiana et al., 2014; Wei et al., 2019). Biomass ashes rich in Al_2O_3 and SiO_2 are promising alternative catalysts and adsorbents in various industrial processes (Sayehi et al., 2020). For example, Al_2O_3/SiO_2-rich ashes promoted methanol degradation in hydrogen production (Assad Munawar et al., 2021; Chen et al., 2010). The catalytic properties of these ashes are based on a group of zeolites: $M_{x/n}(SiO_2)(AlO_2)_x{\cdot}mH_2O$, where M stands for a cation. A recent review comprehensively summarized different types of zeolites and their syntheses from biomass ashes e (Li et al., 2021a). In addition, SiO_2-rich ashes, such as rice husk ash, can be utilized as catalyst support, improving the physicochemical properties of bio-oils through esterification when sulfonated (Sutrisno and Hidayat, 2017).

Due to their high alkalinity, CaO-rich ashes may be used as catalysts for biodiesel production (Boey et al., 2011; Chen et al., 2013; Ho et al., 2012; Sharma et al., 2012). Furthermore, CaO-containing biomass ashes can be used as additives in fluidized bed combustion to lower emissions through catalytic oxidation of noxious species such as CH_4, CO, and HCN (Loffler et al., 2002). Interestingly, in oxygen-free atmospheres of char hydrogasification, CaO-rich ashes have been shown to improve the CH_4 yield of the reaction $C(s) + H_2(g) \rightarrow CH_4(g)$ (Wang et al., 2019a).

Carbon-based ashes from woody biomass combustion have been reported to catalyze several reactions, such as the crosslinking reaction of epoxy resins with amines (Stasi et al., 2019), the oxidation of hydrogen sulfide (H_2S) and methanethiol (CH_3SH), volatile organic sulfur compounds and propanol (Kastner, et al., 2003; Kastner, et al., 2005; Kastner, et al., 2008), as well as 2-methylbutanal and hexane vapors (Kolar and Kastner, 2010). Owing to their significantly larger specific surface area compared to coal ashes, the utilization of wood ashes results in improved conversion rates. Consequently, such ashes may be considered an ecological substitute in the catalyst industry. An entirely different source of ash, namely rendering industry waste, produces large quantities of hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$), which can be converted to tri-calcium phosphate ($Ca_3(PO_4)_2$) and used as a catalyst in biodiesel production (Chakraborty et al., 2015).

Other reported industrial processes, for which the applicability of biomass-derived ashes as catalysts has been addressed, contain low-temperature (600–800 °C) gasification of biomass (Nanou et al., 2013); tar reforming during biomass gasification (Buentello-Montoya et al., 2019; Pio et al., 2018); and NO_x reduction in flue gases (Tran et al., 2009).

4.3. *Biomass ashes in cement, concrete, and mortars*

The cement industry consumes significantly large quantities of natural resources (limestone) and energy while generating remarkable amounts of CO_2. Lowering the use of virgin raw materials and decreasing CO_2 emissions have encouraged scientists to study the applicability of locally produced biomass ash to replace aggregates used by the cement and concrete industry. Biomass utilization would i) decrease the need for ash landfilling, ii) reduce the CO_2 emissions of cement production (about 0.63 tons of CO_2 is emitted for each ton of Portland cement produced (Lounate et al., 2020), and iii) preserve the natural resources involved in cement production, with further beneficial effects on the environment.

The cementitious components of the most common type of cement, Portland cement, are calcium silicates (C_2S and C_3S), tricalcium aluminate (C_3A), and tetracalcium aluminoferrite (C_4AF) (Wang et al., 2016). When reacting with water, according to Eqs. 1–4, all components form a (C-S-H) complex, which is the key hydration product that contributes to the strength of cementitious products. The addition of ash provides a secondary phase of pozzolans, mainly SiO_2, which enables additional/different pozzolanic reactions, resulting in enhanced concrete strength (Fig. 2) (Yin et al., 2018).

$$C_3S + H_2O \rightarrow (CaO)_x \cdot (SiO_2)_y \cdot (H_2O)_z + Ca(OH)_2 \quad (1)$$

$$C_2S + H_2O \rightarrow (CaO)_x \cdot (SiO_2)_y \cdot (H_2O)_z + Ca(OH)_2 \quad (2)$$

$$C_3A + H_2O \rightarrow (CaO)_x \cdot (Al_2O_3)_x \cdot (H_2O)_x \quad (3)$$

$$C_4AF + H_2O \rightarrow (CaO)_x \cdot (Al_2O_3)_y \cdot (Fe_2O_3)_z \cdot (H_2O)_w \quad (4)$$

Biomass ashes contain varying amounts of amorphous silica, and, therefore, the silica-containing ashes might be applicable to the cement industry as a partial replacement for conventional compounds. Amorphous silica is reactive, making it necessary for the reactions described above and, therefore, an interesting pozzolan candidate for the cement construction industry.

Rice husk contains around 10 % silica, providing around 90 % silica in rice husk ash (RHA) (Chandrasekhar and Pramada, 2016; Sua-Iam and Makul, 2015). Since a particularly high amount of this silica is amorphous, the feasibility of RHA as pozzolanic material has been comprehensively covered in several reviews (e.g., Fapohunda et al., 2017; Jittin et al., 2020; Khana et al., 2014; Liu et al., 2016; Moayedi et al., 2019; Nguyen et al., 2019; Sharma et al., 2020; Sua-Iam and Makul, 2015). An extensive list of beneficial effects of rice husk ash on the mechanical and chemical properties of concrete can be found in (Khan et al., 2015). On a general level, the beneficial effects of RHA on concrete properties have been summarized as improved shrinkage properties, increased resistance towards sulfate attacks and water absorption, and, if ground to ultrafine particles, reduced chloride ingress and better mechanical properties (Pandey and Kumar, 2020; Sua-Iam and Makul, 2015). The reduced chloride ingress depends on a discontinuous and tortuous pore structure caused by biomass ash (not only RHA) (Demis et al., 2015). Such pore refinement results in lowered conductivity and thus hinders electrochemical transportation processes. However, there is an upper limit of RHA addition, above which the mechanical properties begin to weaken (Pandey and Kumar, 2020). Rice husk ash can be used in self-compacting concrete (SCC), a special type of concrete that can be placed and consolidated without any vibration effort (Sua-Iam and Makul, 2015). Because of the coverage of the review articles, only a concise summary focusing on more recent publications will be given in this sub-chapter.

The reasons for partial replacing clinker in cement production with sugarcane bagasse ash (SBA) are similar to those with RHA: reductions in CO_2 emissions and need for landfilling, improved strength properties, reduced water permeability, and decreased chloride penetration (Amin, 2011; Rukzon and Chindaprasirt, 2012). Even though SBA can be considered a pozzolanic material, its pozzolanic activity depends significantly on the size and fineness of the ash particles (Cordeiro et al., 2008). Furthermore, the amount of added SBA affects the properties of the cement significantly (Sua-Iam and Makul, 2013).

Besides rice husk and bagasse ashes, wood-derived ash is more common in the Northern Hemisphere and, is considered for cement production. However, woody biomass ash may contain heavy metals, which should not leach out from the cement. Berra et al. published a leaching study of Portland cement mixed with wood ash, showing that Cd, Cr, Cu, Ni, Pb, and Zn release stayed below the regulatory limits for a simulated 100-year period (Berra et al., 2019). However, the ash needs to be pretreated prior to its use in cement to remove chlorine. The impact of wood ash addition on concrete properties is summarized in (Cheah and Mahyuddin, 2011). In general, wood ash does not improve concrete characteristics remarkably – the question is more about how much wood ash can be added to concrete to pass regulatory limits. Even when wood ash addition reduces the drying shrinkage of concrete and improves corrosion resistance against monobasic acids, wood ash-blended concrete requires more water for acceptable workability and a longer time to set. Furthermore, wood ash addition results in lower bulk density, decreased mechanical properties (compressive, flexural, and splitting tensile strength), and lower corrosion resistance against dibasic acids. The amount of added ash also plays a role: ash (Eucalyptus tree bark, forest residues, and black liquor) addition of 15 wt% resulted in higher concrete porosity, which enables chloride ingress through increased electrical conductivity (Velay-Lizancos et al., 2017). However, certain properties such as durability, corrosion current resistance, and resistance against chloride diffusion can be improved by blending wood ash with rice husk, sugarcane bagasse, or coal ash. A mixture of coal and wood ashes can be used as a precursor for geopolymers with similar properties as pure coal ash (Shearer et al., 2016). Wood ash does not improve gel formation kinetics or mechanical properties, but unnecessary landfilling is avoided with wood ash addition.

It is important to note that the terms “wood ash” or “woody biomass ash” cover a broad group of ashes in terms of chemical composition, for example. The amounts of SiO_2 and CaO, essential for concrete formation, may vary between 6 and 68 % and 6–83 %, respectively (Vassilev et al., 2010). However, the high SiO_2 content alone does not

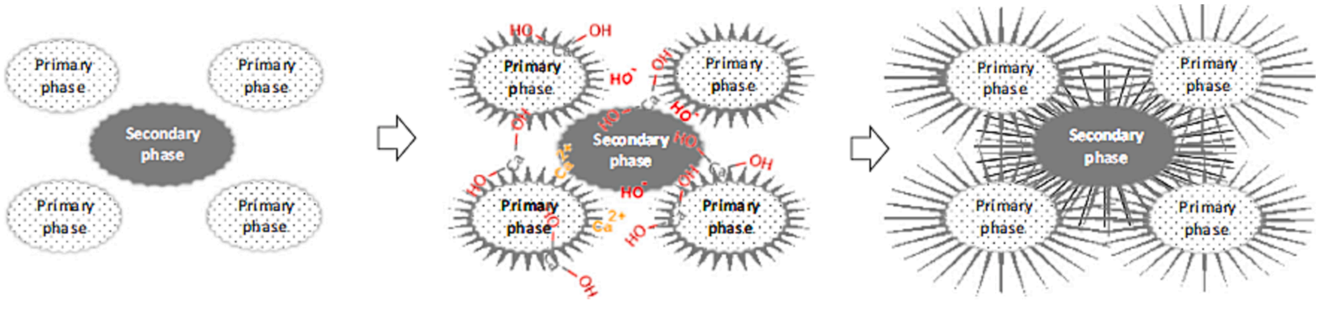

Fig. 2. A schematic presentation of the step-wise reactions associated with the primary and secondary phases in the hybrid cement with combustion ashes (Yin et al., 2018). Reprinted from Waste Management 78, 2018 401–416, Environmental perspectives of recycling various combustion ashes in cement production - A review Yin, K., Ahamed, A., Lisak, G., Fig. 3, with kind permission from Elsevier.

automatically result in improved pozzolanic activity, for the amounts of Al_2O_3, Fe_2O_3, and CaO also play an important role (Demis et al., 2015).

Like other ashes reviewed in this chapter, the silica content of palm oil fuel ash (POFA) is high, ranging between 43 % and 71 % (Hamada et al., 2018). In Malaysia, one of the largest palm oil producers, the annual POFA production is approximately 10 million tons (Safiuddin et al., 2011), so the availability of POFA for the local cement industry is high. Summaries focusing on the applicability of POFA as a pozzolan are presented, for example, in (Hamada et al., 2018; Mazenan et al., 2017; Safiuddin et al., 2011; Thomas et al., 2017). POFA has been found to improve the properties of concrete in several ways, for example, (i) by increasing the density and durability of cement mortars when applied with Ca, (ii) by increasing the compressive strength and decreasing water absorption when applied with nano-sized silica, (iii) by improving resistance for chloride and sulfate attacks, (iv) by lowering the specific gravity of cement, and (v) by reducing the drying shrinkage of concrete. Also, POFA is applicable for SCC production.

Although considered rather waste ash than biomass ash, waste paper sludge ash (WPSA) can also be used as a supplementary cementitious material in concrete. In recent studies, an optimum ash addition of 5 % has been reported to increase both the compressive and flexural strength of the material (Fauzi et al., 2016; Kumar and Rani, 2016; Keerthana Devi et al., 2023). Furthermore, WPSA additions improved the durability of concrete with different acids (Bui et al., 2019; Keerthana Devi et al., 2023). However, the WPSA addition comes with a cost of slightly decreased workability. WPSA has also been successfully added to a less energy-intensive concrete mix containing glass cullet without compromising the mechanical properties of the material (Mavroulidou and Awoliyi, 2018). Another potential application of WPSA in the cement industry lies in super-hydrophobic powders, which are formed when WPSA is ground with stearic acid (Spathi et al., 2015; Wong et al., 2015). With a partial replacement of cement with super-hydrophobic PSA, the water absorption and sorptivity were decreased by more than 80 %, which also decreased the electrical conductivity of the material through reduced internal moisture content (Wong et al., 2015). Although a decrease in the workability of the material was observed, compressive strength and hydration properties stayed at an acceptable level.

The utilization of biomass ash can also be considered as a follow-up step in the local conservation of the environment. Ash from *Arundo donax*, a native Asian plant considered an invader species elsewhere, is applicable as such to be used in non-steel-reinforced concrete (Paya et al., 2018). However, due to the high chlorine content of the ash, its utilization for steel-reinforced concrete would require a pretreatment step such as washing. Biomass ash can also be mixed with other industrial wastes to avoid the unnecessary landfilling of both or all components. For example, when mixed with silica gel by-products, biomass ash can be used in alkali-activated binders of materials considered an ecological alternative to ordinary Portland cement (OPC) (Vaičiukynienė et al., 2012).

In addition to silica, high Ca contents of ash benefit brick production. Calcium is known to increase the condensation and polymerization reactions through aluminosilicate dissolution and incorporate it into the geopolymer pore structure as a counter-balancing cation, resulting in a quick-setting and strong geopolymer material (Canfield et al., 2014). When a mixture of coal fly ash and high-calcium wood ash was applied to mortar block production, the produced geopolymer mortar blocks could be considered a normal weight solid load-bearing unit based on a 28-day compressive strength experiment (Cheah et al., 2017).

4.4. Biomass ashes in CO_2 capture

Among anthropogenic emissions, carbon dioxide (CO_2) has been identified as the most predominant greenhouse gas responsible for climate change (Ochedi et al., 2020). In the U.S., the primary sources of CO_2 are transportation, power production, and industrial processes, which produced altogether around 81 % of CO_2 emissions in 2018 (United States Environmental Protection Agency, 2021). One approach is to capture formed CO_2 and either store it safely or convert it into a less harmful form, which has raised interest in the implementation of CO_2-capturing technologies. One of the feasible technologies is called carbon capture and storage by mineralization (CCSM), which is based on the reaction of CO_2 with a solid divalent metal oxide (MO) in the ash, forming a metal carbonate (MCO_3) (Sanna et al., 2012). Although the technology is not yet cost-competitive with geological storage, the high CaO content of woody biomass ash (24 – 45 %) (Gunning et al., 2010) makes them a potential future alternative for ecological and environmental carbon storage. The challenges and possibilities of CCSM have been summarized recently (Sanna et al., 2012). Altogether, the possibility to utilize cheap and reusable waste materials like biomass ash as adsorbents has gained attention in circular economy awareness.

The key feature common for effective adsorbents is a large specific internal surface area. Besides, the chemical composition of biomass ash plays an important role in CO_2 capture capacity. When eight different biomass ashes were compared, it turned out that the ashes rich in Ca, Mg, K, and Na were the best potential candidates for CO_2 capture (Vassilev and Vassileva, 2020). This is based on the solid–gas interactions, where CO_2 is captured in its reactions with alkaline earth and alkaline oxyhydroxides. Although biomass fly ash, generally meets the requirement of high porosity, its other physicochemical properties make it less competitive than commercial sorbents. Untreated wood biomass ash, for example, can reach 20–30 % of the CO_2 capture capacity of a commercial sorbent (Guo et al., 2015). The adsorption efficiency of biomass fly ash can be improved through activation by KOH (Plaza et al., 2012), H_3PO_4 (Heidari et al., 2014) or other suitable additives. Rice husk ash with 20 wt% magnesium oxide showed excellent CO_2 uptake due to the beneficial surface texture and basicity of the adsorbent (Guo et al., 2020). In addition, the uptake stability remained unaltered for ten test cycles, showing the environmental and economic potential of modified ash-based adsorbents. Modification of wood ash with polyamines resulted in an improved CO_2 capturing capacity with an excellent regeneration conversion (Wang et al., 2017). The increase in temperature, initial CO_2 concentration in the gas phase, and/or in the gas flow rate will further increase the CO_2 adsorption rate of amine-modified ash through easier diffusion within the pores and channels (Guo et al., 2019). The beneficial effect of increased CO_2 concentration and gas flow rate was confirmed in another study, but the increase in the temperature led to a decreased sorption rate (Zhao et al., 2019). According to the study, the amount of added amine affects the sorption capacity, peaking at 25 % of added amine. The amine-based enhanced adsorption capacity originates from the increased number of active sites for chemisorption. When the amine content is further increased, the adsorption efficiency decreases through the limited porosity of ash. Ash can also be treated with lithium carbonate (Li_2CO_3), forming lithium orthosilicate (Li_4SiO_4), which is a very effective CO_2 sorbent with excellent properties for cyclic CO_2 sorption/desorption (Eq. (5) (Essaki et al., 2005; Kimura et al., 2005). However, the ash should be prewashed before reacting with Li_2CO_3, to achieve a high adsorption capacity, which remains stable after several sorption/desorption cycles (Wang et al., 2015).

$$Li_4SiO_4(s) + CO_2(g) \leftrightarrow Li_2CO_3(s) + Li_2SiO_3(s) \quad (5)$$

Aluminum- and silicon-rich ashes can be utilized as precursors for zeolites, which can be used for CO_2 adsorption due to their morphology, electrostatic interactions, and capability to include alkali metal cations (Zhang et al., 2008). For example, bagasse fly ash can be used to produce zeolites, resulting in a high porosity and an ion exchange capacity comparable to similar commercial products (Purnomo et al., 2012). Agricultural biomass ash can also enhance existing CO_2 capture technologies as an additive. Chemical looping combustion (CLC) is a relatively new thermal conversion technology based on direct oxygen transfer between an oxygen carrier and fuel. Iron ore is, for instance, a natural oxygen carrier, which, however, suffers from a relatively low reactivity, making it less attractive for CLC technology. Interestingly, after being combined with biomass ash, the reactivity of iron ore improved (Zhang et al., 2019). However, the chemical composition and added ash amount are critical to optimal reactivity. Another alternative is adding biomass ash to $Ca(OH)_2$-based pellets for a more porous sorbent structure (Ridha et al., 2015). Where biomass ash is responsible for higher porosity, CaO reacts with CO_2, binding it as calcium carbonate ($CaCO_3$). After 20 test cycles, the $Ca(OH)_2$-based biomass-templated pellets captured around 33 % more CO_2 than biomass-free pellets. This is a promising example of a low-cost application of biomass ash, reducing greenhouse gas emissions and the need for ash disposal in landfills. Before becoming a realistic, environmentally friendly technology, CLC still has obstacles to overcome. Nevertheless, this technology has already shown its potential in pilot-scale experiments. The gains, challenges, and future of biomass ash utilization in CLC have been recently reviewed (Zhao et al., 2017).

The fact that waste paper sludge ash (WPSA) is alkaline and has a very small particle size as well as high calcium content, makes it a noteworthy candidate for indirect carbonation (a carbonation process taking place in more than one stage). In fact, with additional treatments such as pH swing of the leachate from WPSA or CO_2 dose adjustment, 29.1–324 kg of CO_2 could be stored per ton of WPSA (Kim and Kim, 2018). The study provides an example of waste utilization in carbon capture and particularly if the applied solvents can be recovered, the economic feasibility of the process would be further improved.

So far, this sub-chapter has addressed various alternatives for capturing gaseous CO_2. However, the concept of CO_2 capture can be broadened to include the capture and immobilization of carbon as carbonates in calcareous soils when biomass ash is used as a fertilizer (Lopez et al., 2018; Buss et al., 2019). Based on the results, it was calculated that after ash amendment, 14.5 g CO_2 remained fixed per kg of fly biomass ash, 16.5 g CO_2 per kg of bottom biomass ash with plant cultivation, and 19.7 g CO_2 per kg of bottom biomass ash without plant cultivation (Lopez et al., 2018). In the life cycle of biomass, from its cultivation to utilization, carbon capture can positively affect the carbon balance of the biomass-based power production process.

4.5. Biomass ashes in the composting process

Composting is a clean and sustainable method of managing waste by degrading and stabilizing organic matter. The applicability of various biomass ashes to composting has been studied to some extent, and so far, the results have been promising. Bottom ash from the combustion of wood chips, sod peat, residues from plywood industries, and waste-derived fuel was used to boost the composting of catering waste (Koivula et al., 2004). The studied ash increased the mineralization rate of the compost, accelerated the formation of humic acids, and decreased the formation of odorous gases, particularly H_2S. In addition, nitrogen loss decreased, allowing larger compost amounts to be utilized in cultivation or green area construction. Odor control of composts is also achievable with woody biomass ash with a high carbon content (Rosenfeld et al., 2002; Rosenfeld et al., 2004). Alkaline ashes, such as woody biomass ash, can adjust or buffer the pH value of acidic composts. The benefits manifest themselves in enhanced heat production and microbial activity (Kurola et al., 2011), decreased number of pathogenic bacilli (Fernandez-Delgado Juarez et al., 2015a), and increased decomposition of lignocellulose in green waste (Karnchanawong et al., 2017). Additional positive effects of wood and agro-industrial ash on composting are accelerated organic matter degradation, resulting in improved humification, increased water holding capacity, and nutrient content (Asquer et al., 2017; Asquer et al., 2019; Fernandez-Delgado Juarez et al., 2015b).

Despite the applicability of biomass ash-containing composts to implement the circular economy concepts, hazards, such as the environmental risk of heavy metal contamination, need to be considered carefully.

4.6. Biomass ashes in fertilizers

Biomass ashes may contain a variety of macro- and micronutrients, which should not be misplaced in landfills. Therefore, the applicability of biomass ash as a fertilizer on fields or forests is of increasing interest. When considered as a soil fertilizer, biomass ash typically contains high enough nutrients (P, Ca, Mg, and K) and relatively low concentrations of potentially toxic elements (As, Cd, Cr, Cu, Ni, Pb, and Zn). The ash may not contain all the important/essential nutrients. A study addressing the suitability of eight different wood ashes as fertilizers concluded that six contained sufficient CaO to be used as calcium fertilizers, but none met the minimum concentration limits for other essential elements (Maschowski et al., 2016). Similarly, biomass ash usually lacks sufficient nitrogen; thus, nitrogen needs to be added, e.g., as bio-solids (Brännvall and Kumpiene, 2016; Månsson et al., 2009). This kind of combined fertilization has been reported to expand the crown growth of Scots pines (*Pinus sylvestris* L.) (Ozolincius et al., 2007). Long-term soil improvement is achievable with a suitable ash-based fertilizer: according to a 7-year experiment, wood ash can promote the long-term productivity of short-rotation woody crops (Sartori et al., 2007). The applicability of wood ash on forest ecosystems (i) to mitigate nutrient depletion and soil acidity, (ii) to increase soil microbial biomass and its activity, and (iii) to replace lime has been addressed especially in northern Europe (Aronsson and Ekelund, 2004; Brunner et al., 2004; Pitman, 2006; Zimmermann, 2002).

In order to prevent dust problems, improve logistics, and lower storage costs, biomass fly ash can be granulated before application. The porous structure of granules may also improve the water sorption properties and resistivity to wind erosion (Vincevica-Gaile et al., 2019). Slow release of certain elements, e.g., potassium, into the soil is desirable to avoid pH/nutrient shock and reduce fertilizing frequency. For this purpose, the release rate of a pressed ash tablet is much slower than that of powder ash (Zhang et al., 2018a). Despite the low nitrogen content of granules, the heavy metal and nutrient contents are reported to meet the limits set by legislation (Pesonen et al., 2016). Compared to unprocessed fly ash, granulation reduces significantly the bioavailability of nutrients bound in biomass fly ash, lowering the fertilizing effect of fly ash (Pesonen et al., 2017). Luckily, adding ammonium sulfate to the granulation process increases the recoveries of the bioavailable nutrients to the same level as with the unprocessed fly ash. In addition to the chemical composition, the applied amount of biomass fly ash in granules affects fertilization efficiency. When the crop yield improvement by granules containing varying amounts of wood ash was compared, granules with 30 % of ash resulted in the largest yield (Buneviciene et al., 2020).

In addition to forestry, wood ash can similarly benefit the agroecosystems by i) increasing the pH of acid soils, ii) improving the electrical conductivity of the soil, iii) augmenting microbial activity, and iv) optimizing the dissolved organic carbon (DOC) level (Cruz et al., 2017; Perucci et al., 2008). Similar results have been observed in pot experiments, where lettuce and spinach were fertilized with wood and peat ash (Huang et al., 2017).

The fertilizing properties of biomass ash can be enhanced by mixing it with other types of waste, such as municipal sewage sludge (MSS) (Wójcik et al., 2017; Wójcik et al., 2019; Wójcik, et al., 2020). Such mixtures were reported to increase the yield of a grass-legume crop through increased K and Ca uptake of the plants (Antonkiewicz et al., 2020). The yield and uptake levels generated by the mixture were higher than those of the single components. Furthermore, the mixture optimized the Ca-to-Mg ratio of the crop when considered to be used as fodder. However, other optimal macronutrient levels were not met, and, therefore, additional mineral fertilization might be required. Regarding the chemical composition of the crop as biofuels, the crop grown in soil fertilized with biomass ash alone contained the most optimal composition.

Due to the heterogeneous composition of biomass, a way to predict the chemical composition of biomass ash and its suitability for fertilizing purposes would be of high value. For this purpose, a descriptive factor termed the "potassium utilization potential factor" has been introduced (Vakalis et al., 2017). This factor combines the initial potassium concentration in the fuel with the potassium concentration or dilution during combustion. As a result, a value reflecting the utilization potential of the fuel feedstock is given. The calculations are carried out using statistical entropy analysis, which showed that Mg, for example, remained mainly in the solid fraction (ash), regardless of the combusted biomass. The K content, on the contrary, fluctuated significantly, and biomass with the highest initial K content did not have the K-richest ash among the studied biomasses.

Although not originating from Plantae, ash from rendering product streams (meat and bone meal, cattle tissues) can also be considered biomass ash. Animal-derived ash is rich in calcium (30.7 %) and phosphate (56.3 %) in the forms of $Ca_{10}(PO_4)_6(OH)_2$ and β-$Ca_3(PO_4)_2$ (Deydier et al., 2005). Both Ca and P are fertilizers, making animal-derived ash a low-cost mineral source with no heavy metal content.

When using biomass ashes as fertilizers, attention needs to be also paid to the overall ash composition. If the ashes contain high levels of toxic organic compounds or heavy metals, their use might become limited in agricultural soils, despite the possibly high nutrient content. For example, when ash from a domestic woodstove firing of different types of biomass was used as a fertilizer, the macronutrient levels in the soil increased. However, plant growth was inhibited, and the Al content in plant tissues increased (Ribeiro et al., 2017). The pH of the soil can affect the leaching of toxic and growth-promoting compounds, and, therefore, soil characteristics need to be taken into account when constituting an ash-spreading strategy (Jagodzinski et al., 2018). The chemical composition of the ash can be affected, among other factors, by applied process parameters. Increasing the calcination temperature from 500 to 815 °C resulted in lower Cd and Pb contents in the formed ash (Wei et al., 2020). Unfortunately, the potassium content followed the same trend. It is well-known that potassium volatilization is significant in the combustion of biomasses and coal above 600 °C (Cao et al., 2021; Johansen et al., 2011). In another study, a lower combustion temperature for grass and corn-stover pellets resulted in a higher portion of soluble nutrients in ash. The share of insoluble nutrients increased as a function of temperature between 500 °C and 800 °C (Zhang et al., 2018b). These few examples do not cover all the challenges related to biomass ash utilization. However, they show that biomass composition and combustion parameters have a complex effect on ashes used as fertilizers.

4.7. *Waste ashes utilization: Geotechnical and other applications*

MSWI bottom ash from fluidized bed firing and grate firing has been successfully used in various applications over the past few decades. One main utilization area is in earth construction after the mechanical separation of valuable metals (Holm et al., 2018). Particular emphasis has been paid to understanding the behavior of heavy metal leaching in landfilling (Li et al., 2021b; Wang et al., 2021).

In contrast, MSWI fly ashes have mainly been landfilled. Several toxic metals are volatile and thus enriched in the fly ashes (Haberl et al., 2018; Ruth, 1998).

The separation of harmful and critical elements from fly ashes through leaching and thermal treatments has been reported by several research groups (Lindberg et al., 2015; Lane et al., 2020; Nowak et al., 2010; Zhang et al., 2021).

Utilizing MSWI fly ash can decrease the need for virgin materials and thus save natural resources while partly solving waste disposal problems. Ashes can help achieve green construction goals by reducing the greenhouse gases and energy consumption associated with producing and transporting processed raw materials. However, the geotechnical and environmental properties of MSWI fly ash and bottom ash must first be assessed to encourage beneficial use. Some waste products like fly ash and bottom ash can be utilized as additives to conventional construction materials, road construction, and embankments. The high strength and low compact density of MSWI fly ashes suggested their suitability in mixtures to stabilize soft marine clay (Goh et al., 1993). Initial leaching of cadmium and chromium exceeded the limits for drinking water but decreased after 28 days to acceptable levels. Heavy metals did not leach from the fly ash stabilized with lime or cement.

When it comes to the utilization of municipal solid waste incinerator (MSWI) bottom ash for road construction, two separate features need to be considered; 1) the applicability of ash in terms of its physical properties and 2) the leachability of hazardous compounds from the ash. Addressing the physical properties, the major constituents of MSWI bottom ash are typically Ca, Si, and Al, which are also found in conventional aggregates for road construction. Furthermore, physical properties such as particle size distribution (PSD), abrasion resistance, and strength of MSWI bottom ash have been reported to be close to those of naturally mined aggregates (e.g. Forteza et al., 2004; Vegas et al., 2008). Izquierdo et al. (2001) characterized MSWI bottom ashes in road construction. Physical and geotechnical properties suggested that the ashes were well-graded, highly compactable, and conformed to the technical requirements. The geotechnical properties together with a very low and acceptable risk of collapsibility of a French MSWI bottom ash make it a potential candidate as a raw material for the road construction industry (Le et al., 2018). Further improvement of the properties may occur through a blending strategy: when MSWI bottom ash from Florida was blended with natural and recycled aggregate sources, the PSD and bearing strength properties of the blend were improved (Townsend et al., 2020).

In addition to the major constituents of MSWI bottom ash, it usually contains heavy metals and contaminants of potential concern (COPC) such as As, Ba, Cr, Cu, Pb, Sb, and Zn, which often exceed accepted thresholds (Schafer et al., 2019; Zhu et al., 2020). Earlier, the applicability of various MSWI bottom ashes for road construction with respect to the related environmental regulations has been addressed (Birgisdóttir et al., 2006; Hjelmar et al., 2007; Izquierdo et al., 2008; Dabo et al., 2009; Toller et al., 2009; De Windt et al., 2011). The results demonstrate nicely the challenges when discussing the applicability of MSWI bottom ash from an environmental point of view: depending on the ash, the country in question, and the local legislation, leachate levels were acceptable whereas others weren't. However, with appropriate pretreatments such as natural aging or blending of MSWI bottom ash with natural and recycled road base aggregates, the leaching concentrations of hazardous elements can be kept below the limit values, making MSWI bottom ash a feasible alternative for road construction raw material (Schafer et al., 2019; Zhu et al., 2020). Regarding the removal of Cl^- and SO_4^{2-} from MSWI bottom ash, wet processing can be applied for transferring soluble salts as chlorides and sulfates in a fine fraction (Holm and Simon, 2017). This method has been reported to effectively reduce Cl^- and SO_4^{2-} concentrations in leachates (Kalbe and Simon, 2020).

These paragraphs addressing MSWI bottom ash present examples of studies, showing promising results regarding the potential of MSWI bottom ash recycling as a road construction material. However, it must be kept in mind that, prior to usage, bottom ash must be in accordance with environmental requirements, which vary from country to country, as does the chemical composition of the MSWI bottom ash. Therefore, it is impossible to state that MSWI bottom ash, generally speaking, could or could not be utilized in road construction in a certain country. One approach to survey, whether a certain type of MSWI bottom ash meets the national legislative requirements, is to carry out a risk assessment (e.g. Van Praagh et al., 2018).

Show et al. (2003) studied the use of MSWI fly ash in stabilizing marine clays. They found the MSW fly ash suitable as a partial cement replacement in soil stabilization due to its physical and chemical properties. Calcium and silicon in the ash favored the pozzolanic reactions needed for the stabilization. The leaching of chromium was within acceptable limits. In contrast, the leaching of nickel and lead initially exceeded the drinking water limits but decreased to acceptable levels after a longer time. Forteza et al. (2004) studied the suitability of MSWI bottom ash in road construction applications. The ash's chemical composition and several physical properties of relevance for road construction applications were measured. Also, the leaching of elements from the bottom ash stored for various times and cylinders made of mixtures of the ash stored for one month, sand, cement, and gravel were analyzed. MSWI bottom ash was suitable for base and sub-base granular layers in road construction after a refined particle-size distribution. They concluded that the MSWI bottom ash is feasible in gravel-cement bases and concrete pavements if the poor abrasion resistance is solved. In addition, the leaching of harmful elements did not exceed the limits for ashes stored for a minimum time of one month.

Due to the high CaO content, and cementitious as well pozzolanic properties of waste paper sludge ash (WPSA), it can be considered self-cementing with no need for additional activators. When testing the compressive strength and California Bearing Ratio of WPSA-stabilized clay, it was concluded that an optimum amount of 10 % of WPSA enhanced the clay soil strength for long periods (Khalid et al., 2012). The beneficial effect of WPSA addition on treated soil properties was also observed when parameters such as plasticity characteristics, UCS (unconfined compressive strength), water retention, and volumetric stability of the soil were addressed (Mavroulidou, 2018).

Mohamedzein et al. (2006) studied the effect of MSWI ash on the stabilization of desert sand. Fine-grained, poorly graded desert sand with a low amount of silt and relatively high permeability challenges its use to support structures and roads or to construct landfill liners and covers. The fly ash studied was from the combustion of municipal waste consisting mainly of paper and paper board. The incorporation of the MSWI fly ash positively affected the unconfined compressive strength, shear strength, and permeability of the desert sand mixtures. No leaching tests of heavy metals from the mixtures were carried out. Aubert et al. (2006) found that MSWI-treated fly ash could be added to cement-based materials. Shi and Kan (2009) investigated the characteristics of MSWI fly ash–cement materials and the effect of mineral admixtures. Their investigated MSWI fly ash contained high contents of heavy metals, requiring solidification or stabilization of the ash. The potential of MSWI fly ash to replace cement was low, potentially delaying hydration reactions. They also tested ground granulated blast furnace slag, which showed better compressive strength results.

Lam et al. (2010) conducted experiments on MSW incineration bottom ash, highlighting the potential to use these ashes in road pavement applications. Zekkos et al. (2010) carried out a study, in which the MSW for geotechnical purposes was characterized. The emphasis was on quantifying the two main factors influencing the geotechnical behavior of the ash, namely the moisture and organic content. In addition, four-phase characterization techniques were developed. These techniques can be used in various future MSW studies addressing the mechanical properties of the ash.

Alhassan and Tanko (2012) also characterized the components and contents of various MSW bottom ashes. Based on various test results, the geotechnical properties indicated that these ashes could be applied to various fields as a filling material, for improvement of grading properties, and as a free-draining material. Adedokun et al. (2013) have done work on the MSW obtained from an active dumping site. They considered these materials suitable for landfilling material and pavement construction, where replacing virgin raw materials with waste-based materials would improve economic efficiency. In their studies, Bhavya et al. (2015) demonstrated the positive effect of MSW incineration bottom ash on the stabilization and strength development of clayey soils. Based on their various experiments, the optimum MSW incineration bottom ash content in the clayey soil was around 25 %. When the feasibility of incinerated MSW ash as soil replacement in the road construction sector was addressed by Patil et al. (2016), the optimum quantity of replacement of MSW incineration ash was 15 % based on strength development. From the economic viewpoint, the replacement was executable without compromising the soil properties. Lynn et al. (2017) assessed the characteristics of municipal incineration bottom ash (MIBA) and its performance in road pavement applications through systematic analysis and evaluation based on experimental data reported in the literature. MIBA was identified as a granular material, which usually meets the grading requirements for unbound materials after standard processing. Good compaction is achievable at maximum dry density (MDD) and optimum moisture content (OMC) after processing. In addition, features such as bearing capacity and abrasion resistance were reported to be typical for lightweight aggregate and sufficient for use in lower-strength applications such as embankment, fill, and subbase materials. Furthermore, the dry density and compressive strength of the mixtures decreased as a function of an increasing MIBA content. Nonetheless, the requirements for all subbase and road base applications can be met with suitable binder content adjustments.

Singh and Kumar (2017a) studied the compaction and strength behavior of mixed cement and MSWI ash. The addition of cement resulted in a decreased MDD and an increased OMC. Furthermore, the strength increased as a function of added cement. They concluded that MSWI ash and cement mixtures can be used as lightweight filling material in structures like embankments and road construction.

Singh and Kumar (2017b) studied the applicability of MSWI ash mixed with fiber for cement. Le et al. (2017) characterized the behavior of MSW ashes and studied their mechanical properties so that they can be applied for engineering purposes. According to their study, bottom ash had better shear strength and stability than sand and gravel. Also, the elastic behavior was close to typical materials that are used to construct embankments and road pavements. MSWI ash contains many impurities, which are not suitable for construction purposes. The currently available techniques are not sufficient to remove all the impurities completely. Also, these processes are costly. This limits the use of MSWI bottom ash in concrete construction (Le et al., 2017). Xuan et al. (2018) studied using MSWI bottom ash as a replacement for sand in concrete construction along with supplementary cementitious materials like fly ash, ground granulated blast-furnace slag, and waste glass powder. They concluded that the dry mix method is effective in controlling the bulging of mortar specimens made with MSWI ash.

4.8. *Metals recovery/valorization*

4.8.1. *Metal recovery from MSWI fly ash*

The annual production of MSWI residues is worth noting; an amount of up 58 Mt has been estimated to originate from the waste incinerated in Europe (Eurostat, 2013). Due to their high content of valuable materials, MSW incineration residues have the potential to become an important resource. Therefore, recovery activities regarding MSWI solid residues are drawing attention through the possibilities to increase the sustainability of waste-to-energy systems (Allegrini, 2014; Allegrini et al., 2014a).

Fly ashes may have significant contents of heavy metals (e.g., Cd, Cu, Pb, and Zn) and can therefore be considered to be a hazardous waste requiring proper treatment prior to its disposal. MSW ashes may however be a potential source of heavy metals. Zinc, lead, cadmium, and copper can be relatively easily removed during thermal treatment of fly ash, e.g. in the form of chlorides (Kuboňová et al., 2013). In return, wet extraction methods could provide promising results for these elements including chromium and nickel. Hydrometallurgical processes can be used to recover the metals from MSWI fly ash. For example, in Switzerland, most MSWI fly ashes are treated with the acid fly ash leaching process to recover heavy metals before deposition (Weibel et al., 2021). Research on the recovery of metals from ashes is focused on finding the optimal leaching parameters (Allegrini et al., 2015; Tang et al., 2019).

Zinc recovery from waste incineration residues was studied by (Fellner et al., 2015). They reported that the highest economic recovery of zinc to be from filter ashes generated at grate incinerators that are equipped with wet air pollution control. According to the investigation of (Purgar et al., 2016), 50 % of Zn (i.e., 400 t Zn per annum) that pass-through Austria's capital city, Vienna, waste incineration system can be found in fly ashes. In Switzerland, a process that recovers pure zinc (>99.99 %) as well as a mixed fraction of lead, copper, zinc and cadmium out of waste incineration fly ash has been recently implemented at full scale (Purgar et al., 2016).

4.8.2. Metal recovery from MSWI bottom ash

MSWI bottom ash often contains valuable metals (Allegrini et al., 2014b). The Advanced Dry Recovery (ADR) dry separation technology one option to separate and recover valuable metals, thus decreasing the need for landfilling. The separation of the sticky and moist mineral fraction surrounding the coarser bottom ash particles enables the recovery of metal particles in all sizes. For example, after being treated with the ADR dry separation technology, approximately 10 % of a bottom ash consisted of ferrous metals and 4–6 % of non-ferrous metals, such as Al, Cu, and Pb. State-of-the-art technologies for non-ferrous metals recovery from MSWI bottom ash was summerized by (Šyc et al., 2020). In addition to the metals recovery after dry treatments, the authors described the the usage of eddy current separation technology for the non-ferrous metals recovery. Magnetic separation technique for material recovery from MSWI boiler fly ashes was reported by (De Boom et al., 2011).

In addition to metals, bottom ash may contain minerals with a grain size distribution and technical properties very close to natural sand and gravel. The high separation efficiency of minerals enables the partial replacement of virgin raw materials in road construction and concrete products (Suomen erityisjäte, 2021).

4.9. Other applications: Biomass ashes in miscellaneous applications

In the previous sub-chapters, the utilization of biomass ash is/was addressed one industrial application at a time. This sub-chapter collects applications that did not fit elsewhere in this review. In addition, rarely studied ash types are included here. The survey strives to give an overview of the versatility of biomass ash utilization.

In India, spice residues are combusted in the oleoresin industry, generating several tons of ash daily. Based on the physicochemical properties of spice residue ash, the ash is used i) in concrete production, ii) as an adsorbent in pollution control, food industry, and wastewater treatment, iii) in polymer composites, iv) in SO_2 capture, and v) for soil amendment (Barbu et al., 2012). Ashes from wood pulp soft tissue and printing paper have been applied to humidity sensors, showing good stability and excellent selectivity against different gases (Sun et al., 2018). A solid sound absorbent was produced from coconut coir and spent coffee grounds ashes by mixing the ashes with epoxy resin (Teng et al., 2020). Although the samples with ashes had higher sound absorption coefficients than reference samples without, the improvement was insignificant.

As mentioned above, biomass ash usually contains high levels of silica, which can be extracted and modified to high add-value silicon nanoparticle materials (Liang et al., 2020; Liou and Yang, 2011). The high silica contents of peanut shell ash make it a promising candidate for glass and/or concrete production (Yao et al., 2016). Another application for SiO_2-rich ash could be as an extender filler in a photochromic pigment for an increased bulk volume (Chindaprasirt and Rattanasak, 2020). That study revealed that silica from sugarcane bagasse ash can be blended at different silica-to-pigment mass ratios for either thick-layer painting or thin-layer screen-printing on fabrics. The pigment blends showed very good color fastness when washed. In addition, silica can be extracted from sugarcane bagasse ash with a lower chemical and energy consumption than in the traditional silica production from molten quartz sand. Also, the paint industry may benefit from biomass ash-based fillers. Woody biomass fly ash has been successfully utilized as a filler for the resin adhesive used in plywood manufacturing (Fukui et al., 2020) and in reinforcing composite materials (Stasi et al., 2021). When addressing the applicability of ash-based SiO_2, rice husk ash (RHA) has been studied extensively. One study showed that RHA contained over 60 % silica, 10–40 % carbon, and minor other mineral composition, making RHA a valuable feedstock for silica nanoparticles (Shen et al., 2014). In addition to silica nanoparticles, the carbon content of rice husk ash enables the fabrication of other small-size products, such as super-microporous carbon materials (SMC) with a high specific surface area and pore volume (Yakovlev et al., 2007). Silica and porous carbon-containing composites can be used, for example, in the cleaning of gases and liquids, storing of gases (including the challenging hydrogen), reinforcing rubber extenders and rubber-based elastomer composites, as absorbents for pollution control and environmental preservation, thermal insulators, catalyst supports, release controllers in biomedical applications, and as biosensors (Dishovsky et al., 2018; Foo and Hameed, 2009; Liu et al., 2016; Shen et al., 2014; Toda et al., 2018). A comprehensive summary of the utilization of rice husk ash can be found in (Shen et al., 2014).

All these studies are innovative examples of high-quality, cost-efficient, and eco-friendly approaches to utilizing and recycling ash from various types of biomass.

4.10. Biomass ashes in the road (and other) construction

Increased traffic volume and the expansion of transportation networks on less accessible and suitable terrains rcalls for new approaches to road construction. Soil hardness is a criterion for road construction that isnot met with soft silt and clay soil. The soil strength can be improved through soil stabilization with binders such as lime (CaO), which, when reacting with water, results in the formation of a strengthening calcium silicate (CHS) (Eqs. (6) and (7).

$$\mathrm{CaO(s)} + \mathrm{H_2O(l)} \rightarrow \mathrm{Ca(OH)_2(s)} \tag{6}$$

$$\mathrm{Ca(OH)_2(s)} + \mathrm{H_4SiO_4(s)} \rightarrow \mathrm{CaH_2SiO_4{\cdot}2H_2O(s)} \tag{7}$$

Similar to the cement industry, the pozzolanic and hydraulic characteristics make biomass ash a good candidate for soil stabilization. On a general level, the positive effect of ash addition can result in the reduction of soil plasticity and expansion as well as in the increase of compressive strength and optimal moisture content. These effects have been documented for various biomass ashes such as olive (Dishovsky et al., 2018), rice husk (Basha et al., 2005), sugarcane bagasse ash (Yadav et al., 2017), barley, sunflower seed shells, and wheat fly ash (Barisić et al., 2019). Even though wood ash decreased the plasticity and maximized the dry density of clay soil while the strength increased, such modifications were not permanent, and the increased strength was not sustained for more than two weeks (Liu et al., 2016). Therefore, wood ash alone may not be suitable as a soil modifier for construction purposes, regardless of the high CaO content. However, mixing wood ash with sewage sludge has given encouraging results for producing composite construction material for various applications (Pavšič et al., 2014). Depending on the ash/sludge mixing ratio, a controlled low-strength composite construction material with a desired compressive strength was achieved. The mesoporous material disabled water access to the pollutants within the composite matrix, making the material environmentally inert. Sewage sludge is not the only industrial residue that can be combined with biomass ash for a higher-quality product. A mixture of rice husk ash and calcium carbide residue (CCR) from acetylene plants improved soil properties remarkably by increasing compressive strength, cohesion, and internal friction angle (Liu et al., 2019). At the same time, curing time, initial water content, swelling potential and pressure, crack quantity, and fineness of expansive soil decreased significantly.

When possessing the characteristics of a “Controlled Low Strength Material” (Trejo et al., 2004), a biomass ash-containing material could be used, in addition to road construction, in daily or intermediate landfill covers, or as low flow fill material, as bedding material for pipes and cables, or the backfilling of utility trenches. It should be kept in mind that the ash compositions vary dramatically; for example, the strength characteristics of ash-stabilized soil are highly dependent on the chemical composition of the ash. Therefore, studies addressing locally available biomass ash are urgently needed. Such studies are still scarce, but for example, in Southern Europe, ash of vine shoots and grape husks from a local vineyard demonstrated favorable properties for road construction (Vamvuka et al., 2017).

In addition to high Ca content, biomass ashes may possess characteristics that make them suitable for brick production. Amorphous silica-rich rice husk can be used as pozzolan for rural building applications (Nair et al., 2006). Olive pomace ash has a high content of K_2O, which is used in glazing as a fluxing oxide due to its low melting point. Because of this, olive pomace ash could be used in brick production to reduce firing temperatures. When the correlation between ash amount and brick characteristics was addressed, an amount of 10 wt% of olive pomace ash resulted in an optimum melting behavior and pore formation of the bricks (Eliche-Quesada et al., 2016). Larger ash additions increased water absorption and lowered compressive strength, so attention needs to be paid to the amount of added ash. Similar trends were observed with rice husk and wood ashes: wood ash can be used in ceramic bricks for up to 20 wt% and rice husk ash for up to 10 wt% to fulfill still the technological standards and mechanical properties of bricks. Higher ash additions produced bricks that did not meet the standards established for water absorption (Eliche-Quesada et al., 2017).

Although not considered biomass ash, but waste ash, waste paper sludge ash (WPSA) can also be used to partly replace fly ash and lime in fly ash/lime/gypsum bricks. When several parameters such as compressive strength, water absorption, weight density, percentage voids, efflorescence, drying shrinkage, dynamic modulus of elasticity, and impact energy were addressed, an ash replacement of 2.5–15 wt% (fly ash replaced) and of 2.5–5 wt% (lime replaced) satisfied the Indian building brick requirements (Govindan and Kumarasamy, 2023). The possibility for partial replacement of raw materials may result in more sustainable brick production, more effective waste management, and thus, reduced need for landfills.

4.11. Phosphorus recovery from ash

Phosphorus (P) is crucial for all living organisms and performs essential functions for nourishment, growth, and plant development. It is one of the key ingredients of fertilizers. The shortage of P in the soil can affect the plant metabolism severely and, consequently, their production. The demand for P is increasing considerably (Van Vuuren et al., 2010). For instance, ~27 Mt of pure phosphorus is added to farmland as fertilizer annually, of which only 3 Mt/y is consumed through our diet, and the rest is dissipated (van Enk and van der Vee, 2011). This transfer is expected to intensify with an increasing population.

Today, most of the P is obtained from phosphate rock, which is non-renewable and limited (Cordell et al., 2009). Consequently, the EU identified P in 2020 as one of the 30 economically significant materials with high supply risk (European Commission, 2020). The prevailing primary phosphorus deposits are estimated to be exhausted by 2070, with unidentified but presumed phosphorus reserves in the earth’s crust running out between 2100 and 2150. Consequently, as shown in Fig. 3, closing the phosphorus loop through recoveries from secondary feedstock is essential. Municipal wastewater is one of the major secondary sources of phosphorus, and the extraction of phosphorus from sewage has been extensively studied and implemented on some sites (Havukainen et al., 2016.; Kelessidis and Stasinakis, 2012; Wilfert et al., 2015).

A study of phosphorus flows for the EU and Japan recently showed that solid waste and its incineration residues contain similar amounts of P as the sewage sludge (Kalmykova and Karlfeldt Fedje, 2013; Matsubae-Yokoyama et al., 2009; Ott and Rechberger, 2012). Food and food processing wastes constitute a significant source of P in solid waste (4.0 g P/kg TS, total solid). Other P sources in solid waste are wood, paper, and textile (0.2–0.3 g P/kg TS). Therefore, solid waste contains a considerable amount of P even in the foreseeable future (Kalmykova and Karlfeldt Fedje, 2013).

After high-temperature incineration or other forms of thermal conversion of municipal solid wastes, the formed ashes can be potential sources for soil fertilizer in case they contain appropriate nutrients such as phosphorus (P). However, the direct utilization of ashes in agricultural land is restricted since they also contain heavy metals, pathogens, and toxic compounds. Ash treatments can partly remove organic pollutants and partly volatilize the heavy metals, but the ideal method is to recover the essential nutrients such as P and utilize them to produce fertilizers and other chemicals.

4.11.1. Composition of P in different ashes and recovery methods

The P content in biomass ashes can vary from almost none to 17 wt%. To enable more efficient P recovery from combustion ashes of sewage sludge and biomass blends, Falk et al. (2020a) examined the fate of P in fluidized and fixed bed combustion of the fuels. Differences in the P speciation through the different combustion technologies originated from differences in the combustion temperatures. Compared to fluidized bed combustion, fixed bed combustion favored the formation of (Ca, Mg)–K-phosphates rather than Ca-phosphates for the two tested fuel blends (Falk et al., 2020b). Moreover, Hedayati et al. (2021a) studied

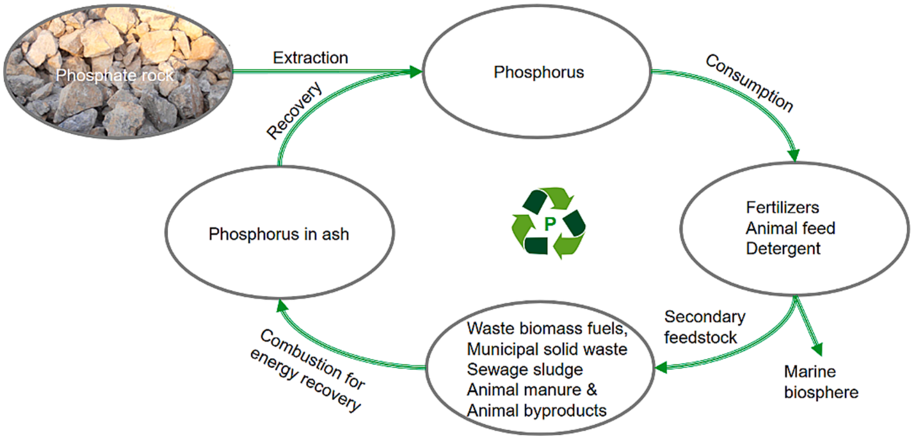

Fig. 3. Conceptual overview of closing the loop of phosphorus via recovery from ashes.

the fate of P in single-pellet thermal conversion of forest residues between 600 and 1000 °C, focusing on char composition. The majority of P in all forest residues remained in residual char/ash, and hydroxyapatite ($Ca_5(PO_4)_3OH$ (apatite)) was the predominant P crystalline compound in all studied ash residues. At 950 °C, P was also reported to exist in the form of $Ca_{10}(PO_4)_{5.65}(CO_3)_{0.64}(OH)_{3.452}$ (Hedayati et al., 2021b).

When investigating fly ashes from the co-combustion of sewage sludge with wood in a circulating fluidized bed combustor (CFB), Pettersson et al. (2008) claimed that P was more concentrated in the fly ash than in the bed ash. Up to 98 % of the phosphorus leaving the CFB boiler was retained in the fly ash, suggesting P recovery technologies from ashes should focus on the fly ash as the main secondary raw material.

The methods used to extract P from different ashes include electro-kinetic (Sturm et al., 2010), thermochemical (Adam et al., 2009); bioleaching and accumulation (Zimmermann and Dott, 2009), and wet chemical methods, such as acid leaching (Biswas et al., 2009; Donatello et al., 2010; Kalmykova and Karlfeldt, 2013; Pettersson et al., 2008) and acid or acid-base leaching with subsequent precipitation (Kaikake et al., 2009; Levlin et al., 2005; Petzet et al., 2011). The wet chemical methods have higher efficiency and faster processing time than the other methods. The P recovery through the electro-kinetic method reported by (Sturm et al., 2010) yielded less than 1 %, while bioleaching and bioaccumulation required more than ten days for completion, which could be an obstacle for potential up-scaling to an industrial scale. In contrast, the acid dissolution–alkali precipitation method could yield up to 92 % P recovery from chicken manure ash (Kaikake et al., 2009), whereas acid leaching can be applied for P recovery in the case of ashes from co-combustion of sewage sludge and wood (Pettersson et al., 2008). Petzet et al. (2011) reported that a two-step acid-base leaching of a sewage sludge ash (SSA) showed 50–80 % and 60–80 % of phosphorus release, respectively. Thermo-chemical treatment of SSA at different temperatures showed a consistent increase in the phosphorous solubility in citric acid (Adam et al., 2009). Pettersson et al. (2008) investigated the recovery of P by acid leaching of fly ashes from the co-combustion of sewage sludge with wood in a circulating fluidized bed combustor. Their results, for a pH between 0.5 and 1, showed that a significant fraction of phosphorus could be recovered from the ashes without precipitation of secondary phosphates. They also reported a correlation between the recovery rate of phosphorous and the type of flocculation agent used in the wastewater treatment plant where the sludge is formed. For instance, when $Fe_2(SO_4)_3$ was used as a flocculating agent, they observed that P recovery was more difficult. Nevertheless, even in those cases, the recovery of phosphorus from these fly ashes by acid leaching was reported to be between 50 and 80 %.

4.12. Biomass ashes in soil amendment other than fertilizing

Adding biomass ash to soil has several beneficial effects: improvements in soil texture, aeration, water-holding capacity, and salinity (Wójcik, 2018). Ashes from different wood species increase the soil pH for various soils (Gomez-Rey et al., 2013; Huang et al., 2017; Moilanen et al., 2012; Park et al., 2012). Similar trends of increasing pH after ash application also apply to straw ash (Mercl et al., 2016). This broadens the spectrum of ash sources for the remediation of acidic soils. The pH increase is beneficial, especially for acidic soil, as nutrient availability improves with increasing pH (Ochecova et al., 2016). Such improvement originates from the increased availability of base cations and is mainly associated with enhancing the soil's effective cation exchange capacity (Gomez-Rey et al., 2012). The effect of ash application can be long-lasting: higher pH values were recorded from soil 13 years after ash application (Moilanen et al., 2012). In addition to neutralizing acidic soils, increasing pH can decrease the mobility of potentially toxic elements, thus limiting their plant uptake (Ochecova et al., 2014). For example, silicon, abundantly present in biomass ashes, can alleviate Cd accumulation and toxicity in plants by improving oxidative stress and suppressing Cd availability, mobility, and plant uptake (Chen et al., 2019; Lei et al., 2020). Biomass ash can also function as a precursor for zeolites, which are discussed more thoroughly in the sub-chapter addressing catalysts. Potassium-based zeolites (K-zeolites) possess relatively high Cs^+ adsorption capacity (Fukasawa et al., 2017). Moreover, when absorbing Cs^+, K-zeolites release K^+ ions, which promote plant growth. This is a clear advantage compared to industrially produced Na-zeolites, which might inhibit the water and mineral absorption by plants because of the released sodium ions.

In addition to low pH and contaminants, soil can become vulnerable to erosion due to inappropriate fertilization and overutilization of land. Consequently, rainfall, tillage, and mechanical cultivation can damage the soil. Owing to the high water-holding capacity of wood ash, its addition to degraded clay loam soil enhanced the stability of soil against externally driven forces from intensive raindrops and irrigation disturbance (Ahirwal et al., 2017; Huang et al., 2017).

Biomass ashes can also be applied to the remediation of heavily contaminated soils, such as reclaimed mining soils. These soils suffer from low levels of soil fertility, low contents of organic matter and nutrients, low pH, high concentrations of toxic elements (Ahirwal et al., 2017; Feng et al., 2019; Yuan et al., 2018), low concentrations of cations, and therefore, a low cation exchange capacity (Asensio et al., 2019; Zhen et al., 2019). The main goal for such soils is to ameliorate the soil before revegetation rather than improve the plant yield. Biomass ash has shown potential in cases with severely contaminated soils. When oil palm shell and rice husk ash were applied to reclaim mining soils' carbon mineralization and soil microbial biomass carbon, the two most broadly applied variables for measuring the effect of, for example, ash addition on soil microbial processes, increased significantly (Saidy et al., 2020). Furthermore, the pH of contaminated mining soils can be increased with wood ash to a level recommended by national legislation (Cruz et al., 2017).

4.13. Biomass ashes in wastewater treatment

Depending on the wastewater source and technologies, wastewater treatment can be divided into several different steps. Adsorption of various harmful compounds is typically applied in various wastewater treatment plants, and in some cases, biomass ash adsorption properties can be considered adequate for this purpose. For instance, sugarcane bagasse is a widely used energy source, resulting in large amounts of bagasse ash: in 2012–2013, the annual generation of bagasse fly ash was around 12 million tons (Maschowski et al., 2016). Due to the large production quantities, high carbon content, and porosity, the adsorption characteristics of bagasse ash are extensively addressed. Bagasse ash can be applied as an adsorbent, among other industrial applications, to brine water treatment in sugar factories (Ngasan et al., 2019), removal of metalloids, metals, and heavy metals (Gupta et al., 2003; Leechart et al., 2016; Ruangchuay et al., 2007; Taha, 2006; Yadav et al., 2014), phenols (Attia, 2007; Gupta et al., 1998; Jain and Singh, 2022; Srivastava et al., 2006), and dyes (Gupta et al., 2000; Khosla et al., 2015; Mall et al., 2005; Mane et al., 2006; Sharma, 2014). Zeolites have already been addressed in this review in the sub-chapter for ash utilization in catalysts. However, it is worth mentioning that zeolites produced from bagasse fly ash or sugarcane straw ash can also be used as adsorbents for phenols and dyes (Fungaro et al., 2014; Shah et al., 2011a; Shah et al., 2011b; Tailor et al., 2012). A recent review article (Patel, 2020) gives a more comprehensive summary of bagasse ash valorization.

Due to its porosity and high basicity, wood ash can have a high capacity to adsorb Mg, a typical contaminant in industrial effluents and mine waters (Mosoarca et al., 2020). Interestingly, after the adsorption process, exhausted wood ash enriched in Mg has been reported to increase specific growth plant parameters of barley crops. Such an approach is a promising example of multilateral utilization of biomass, fitting well in the circular economy strategy.

Ash of Eucalyptus trims, chips, and rice husks show potential as dye remover from wastewater compared to coal fly ash (Pengthamkeerati et al., 2008). All kinds of biomass fly ashes might not be effective in the remediation of dye-contaminated water, but their properties can be improved by adding suitable functional groups. For example, a convenient silanization method is applicable to produce BFA functionalized with 3-aminopropyltriethoxysilane (APTES) (Dogar et al., 2020). The absorption capacity of the functionalized BFA for two anionic dyes was reported to be 2–3 times higher than that of a non-functionalized BFA. Furthermore, after the desorption of the dyes, the same batch of the functionalized BFA could be used for several adsorption cycles, making it a low-cost alternative for remediation applications. Cd is another pollutant that can be effectively removed by APTES-functionalized agricultural ash (Xu et al., 2017). Ash from agricultural and forest residues can also be functionalized with hydrogen peroxide, iron, and alkalies or refined further to geopolymers to create very effective dye (methylene blue) removers (Ikhlaq et al., 2020; Liu et al., 2018; Novais et al., 2019; Pengthamkeerati and Satapanajaru, 2015). Rice husk ash is an effective precursor material in synthesizing photocatalytic nanocomposites, which are excellent removers of textile dye pollutants (Adam et al., 2013). The suitability of rice husk ash originates from characteristics such as high adsorption capability, high ion-exchange capacity, significant specific surface area, and high reusability, which are all covered in greater detail in a recent review article focusing on ash-based photocatalytic nanocomposites (Lum et al., 2020).

Ash from agricultural and forest residues is also applicable for P removal from livestock and sewage treatment wastewaters (Barbosa et al., 2013; Carricondo Anton et al., 2020; Wang et al., 2019b, c; Leng et al., 2019), and for treating the effluent of the thermomechanical pulping process (Cave and Fatehi, 2018; Chen et al., 2017). Furthermore, the ash is applicable in biofilm carriers for organics and ammonia removal from municipal wastewater (Li et al., 2019) and for the removal of hazardous species such as lead (Novais et al., 2020), fluorides (Dobaradaran et al., 2015; Zdunek et al., 2019), mercury (Imla and Yussof, 2018), boron (Ulatowska et al., 2020), phenols (Gholizadeh et al., 2013), and chromium (Vaid et al., 2014).

4.14. Biomass ashes in waste treatment

The organic fraction of municipal solid waste (OFMSW) is a complex mixture consisting of organic residues (e.g. food residues, feces, paper) and impurities (e.g. plastics). So far, OFMSW has been mainly treated by composting, but there is an increasing interest in using OFMSW for biogas production through anaerobic digestion (AD) (Leechart et al., 2016). Compared to composting, the energy recovery through biogas production in AD combined with the further utilization of the digestate makes the method more resource-efficient and climate-friendly. However, there are certain challenges in digesting OFMSW, the most important being inhibition through ammonia, sulfur, or acidification (Ariunbaatar et al., 2016; Moestedt et al., 2016). Another notable challenge is the deficiency of micronutrients such as minerals and trace elements (TE), leading to process instability due to the increased inhibition by volatile fatty acids (VFA) and foaming, resulting in reduced efficiency in biogas production (Vintiloiu et al., 2012; Zhang et al., 2015b). In AD, TEs have several roles: they promote microbial aggregation and sulfide precipitation, bind carrier-proteins and nutrients, and function as micronutrients for enzymatic reactions Ariunbaatar et al., 2016; Choong et al., 2016). The importance of TE originates from them improving CH_4 production and accelerating methanogenesis, which is the most critical phase of AD., The key TEs for biogas production are Fe, Co, Mn, Mo, W, Ni, and Se (Choong et al., 2016), are often found in biomass ash. Still, the impact of biomass ash on TE concentrations, biogas yield, and process stability in AD of OFMSW has barely been addressed. Ash from landscape management material and forest residues on AD in batch tests showed promising results (Leechart et al., 2016). Ash additions raised the pH values, suppressing acidification. Additionally, the metal oxides in ash precipitated CO_2 as mineral carbonates, which reduces efforts for biogas purification. It is also expected that when fed continuously, ash supplementation optimizes methanogenesis, resulting in lower VFA accumulation and, thus, increased CH_4 yields.

The utilization of biomass-enhanced sewage sludge as fertilizer is discussed in the sub-chapter addressing fertilizers, but other possibilities for biomass ash utilization with sewage sludge are discussed here. It might not be feasible in all cases to refine sewage sludge into biogas, whereupon it can be incinerated or used in fertilizers and landfills. Especially in the case of disposal, the high water content of sewage sludge becomes an issue due to the large volume of waste, resulting in increased transportation and disposal costs (Wójcik, 2018).

The effectiveness of sewage sludge conditioning with ash results from the electrostatic interactions enabling floc formation as sludge particles congregate around the ash microspheres (Wójcik et al., 2020). Biomass ash acts as a skeleton in this structure, forming a water-binding permeable and rigid lattice structure, which also keeps the sludge porous under high pressure.

On a general level, the moisture content of sewage sludge decreases as a function of increasing ash dosage. Ash addition also reduces the compressibility factor and specific filtration resistance, making the sludge filtration process faster (Wójcik, 2018). Furthermore, ash application reduces the number of pathogens in sludge, increasing its hygienity and making further treatment safer (Wójcik et al., 2020). However, the effectiveness of dewaterability and pathogen reduction depends on the source of ash and dosage optimization (Wójcik et al., 2018; Wójcik et al., 2020). Despite the promising results of biomass ash as a dewatering agent for sewage sludge, a few things should be kept in mind, as pointed out by Wójcik (2018). First, high ash doses in the dewatering process increase the mass of treated sludge, in transportation, and disposal costs. Second, the mechanical parts of the dewatering devices are not designed for treating ash-conditioned sludge. This could accelerate the wear of certain parts, such as pumps, valves, and pistons.

5. Concluding remarks

Possibilities for ash utilization are of uttermost importance in terms of circular economy and disposal of landfills. However, considering its applicability, ash originating from the heat treatment of chemically complex fuels such as biomass and waste poses several challenges, such as high heavy metal content and the possible presence of toxic and corrosive species. Furthermore, the physical properties of the ash might limit its usability. Nevertheless, numerous studies have been carried out over the past decade addressing the utilization possibilities of challenging ash in various applications. This review with over 300 references surveys the field of research, focusing on the utilization of biomass and municipal solid waste (MSW) ashes. Also, metal and phosphorus recovery from different ashes was addressed.

The key beneficial properties of the various ashes addressed in this review were (i) alkaline nature suitable for neutralization reactions, (ii) high adsorption capabilities to be used in CO_2 capture and waste treatment, and (iii) large surface area and appropriate chemical composition for the catalyst industry. Especially, ashes rich in Al_2O_3 and SiO_2 are promising alternative catalysts in various industrial processes and as precursors for synthetic zeolites.

It should be kept in mind that the chemical composition and physical properties of the ash depend on its source in terms of feedstock and geographic location. Therefore, the suitable industrial applications for ash utilization are dictated to some extent by the origin of the ash. However, as this review conveys, there are promising targets where such ashes find local utilization globally. With appropriate applications and low-cost pretreatment solutions, ash from various biomasses and waste may be recycled and utilized in high-quality, cost-efficient, and eco-friendly processes. Finally, all utilization must follow valid legislation.

CRediT authorship contribution statement

Juho Lehmusto: Conceptualization, Funding acquisition, Investigation, Writing – original draft, Writing – review & editing. **Fiseha Tesfaye:** Conceptualization, Funding acquisition, Investigation, Writing – original draft, Writing – review & editing. **Oskar Karlström:** Conceptualization, Funding acquisition, Investigation, Writing – original draft, Writing – review & editing. **Leena Hupa:** Conceptualization, Funding acquisition, Investigation, Supervision, Writing – original draft, Writing – review & editing.

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.

Data availability

No data was used for the research described in the article.

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