DOI: https://doi.org/10.14256/JCE.2074.2017



Primljen / Received: 12.4.2017.
Ispravljen / Corrected: 13.3.2018.
Prihvaćen / Accepted: 14.4.2018.
Dostupno online / Available online: 10.6.2018.

# Possibilities of bioash application in road building

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Subject review

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## Possibilities of bioash application in road building

Bioashes are inevitable product of meeting the demands to satisfy the increased use of renewable resources in energy production. Ecological and economic problems of bioash disposal, due to its appropriate chemical and physical properties, can be reduced by its application in the construction industry as raw materials. The paper therefore provides an research overview on various aspects of the bioash application in road construction, in compliance with a range of properties depending on the type of biomass and the conditions of combustion. Also shown is current state of research of bioash generated in the domestic thermal power plants.

Key words:
bioash, alternative materials, road building, renewable resources, ecological impact

Pregledni rad

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## Mogućnosti primjene biopepela u cestogradnji

Biopepeli su neizbježan proizvod ispunjavanja zahtjeva za sve većom primjenom obnovljivih izvora u proizvodnji energije. Ekološki i ekonomski problemi zbrinjavanja biopepela, zbog prikladnih kemijskih i fizikalnih svojstava, mogu se smanjiti njegovom primjenom kao sirovine u građevinarstvu. U radu se daje pregled istraživanja mogućnosti primjene biopepela pri gradnji cesta, uzimajući u obzir velik raspon svojstava koja ga karakteriziraju ovisno o porijeklu biomase i uvjetima izgaranja. U radu je također dan pregled istraživanja biopepela nastalog kao proizvod izgaranja biomase u termoelektranama na području Republike Hrvatske.

Ključne riječi:
biopepeo, alternativni materijali, cestogradnja, obnovljivi izvori, ekološki utjecaj

Übersichtsarbeit

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## Möglichkeit der Verwendung von Bioasche beim Straßenbau

Bioasche ist aufgrund der Erfüllung der Forderungen nach immer größerer Verwendung von erneuerbaren Quellen bei der Energieerzeugung ein unvermeidliches Produkt. Die ökologischen und wirtschaftlichen Probleme bei der Entsorgung von Bioasche können wegen der angemessenen chemischen und physikalischen Eigenschaften durch dessen Verwendung als Rohstoff im Bauwesen verringert werden. Die Abhandlung gibt eine Übersicht über die Untersuchungen der Möglichkeiten der Verwendung von Bioasche beim Straßenbau, unter Berücksichtigung der großen Bandbreite an Eigenschaften, die sie abhängig von der Herkunft der Bioasche und den Verbrennungsbedingungen charakterisieren. Die Abhandlung gibt auch eine Übersicht über die Untersuchungen der Bioasche, die als Produkt der Verbrennung von Biomasse in Wärmekraftwerken auf dem Gebiet der Republik Kroatien entstanden ist.

Schlüsselwörter:
Bioasche, alternative Materialien, Straßenbau, erneuerbare Quellen, ökologischer Einfluss

## 1. Introduction

In recent years, a steadily growing demand for energy, and the necessity for reducing greenhouse gas emissions, have resulted in an increased energy production from renewable sources. Energy production from renewable sources is becoming increasingly important as the European Directive 2009/28/EC [1] requires EU member states to produce energy from renewable sources. According to this Directive, it is expected that energy from renewable sources (solar energy, wind energy, energy from watercourses, hydrogen energy, and biomass energy) will account for 20 % of the total energy consumed by 2020.

The Republic of Croatia is faced with an increase in energy consumption and energy prices, while the availability of conventional energy sources is decreasing. In comparison with most Western European countries, Croatia uses energy less efficiently: the country's current use of primary energy per unit of GDP exceeds the average consumption in the European Union by 16.5 % (according to Croatia's Energy Development Strategy, NN 130/2009). The analysis of the existing situation reveals that technical and technological innovations are still insufficiently used in the segments of transformation and final use of energy, which has also affected the construction sector.

Biomass, as a renewable source of energy, is considered one of the most diverse and most valuable sources in the world [2]. According to Directive 2009/28/EC, biomass is a biodegradable fraction of products, waste and residues from agriculture (including vegetal and animal substances), forestry and related industries including fisheries and aquaculture, as well as biodegradable fraction of industrial and municipal waste.

One of the steps towards achieving the objectives set in Directive 2009/28/EC is to release the energy stored in biomass by its combustion or through other technological processes. As a result of this process, a gradual increase is expected in the number of thermal power plants that use biomass to generate heat and electricity. For the production of energy, apart from large generators of energy such as thermal power plants, biomass can also be used in a smaller degree for the thermal energy of individual buildings [3].

By burning biomass, large amounts of ash (the so called bioash) are produced that need to be adequately disposed of or recovered. It is assumed that the fulfilment of obligations imposed by Directive 2009/28/EC by 2020 will result in an annual production of 15.5 million tonnes of bioash in EU-28 [4], [5]. The resulting ash has to be recycled as its improper handling can cause environmental pollution and human health problems [6], while disposal at landfills reduces landfill capacity and leads to higher disposal costs [5, 7, 8]. According to the European Waste Catalogue [9], bioash is classified as a non-hazardous waste [9], and is currently largely treated as waste and disposed of without adequate control at landfills, agricultural surfaces, or in forests [10, 11].

## 2. Bioash formation and properties

Biomass can be divided into wooden biomass and herbaceous biomass. It is produced through the action of man and nature and includes wood, by-products of wood industry, waste from forestry, agriculture and food industry (straw, olive residue, rice husk, sunflower seed hull). During combustion the ash is generated in the course of complex chemical and physical processes from inorganic substances contained in the fuel [12]. It consists of bound inorganic materials that are part of the organic structure of biomass, and of mineral particles introduced during the collection, transport or processing of biomass [10]. The ash content obtained by combustion of various types of biomass may vary considerably, cf. Table 1.

**Table 1. Ash content by combustion at 550 °C [10]**

| Type of biomass | Ash content [%] |
|---|---|
| Bark | 5.0-8.0 |
| Woodchips with bark | 1.0-2.5 |
| Woodchips without bark | 0.8-1.4 |
| Sawdust | 0.5-1.1 |
| Waste wood | 3.0-12.0 |
| Straw and grains | 4.0-12.0 |
| Miscanthus (Chinese grass) | 2.0-8.0 |
| Olive waste | 2.0-4.0 |

Biomass can be combusted in two types of furnaces: furnaces with grate combustion system, and furnaces with combustion in the fluidized bed. Grate furnaces are suitable for combustion of biomass with high moisture content, varying particle sizes, and high ash content. Fluidized bed furnaces have a larger boiler capacity and allow combustion of different combinations of biomass, but with prior processing so as to reduce the size of particles, and to eliminate impurities. Fluidized bed combustion usually generates larger amounts of ash, as the ash is mixed with the bed material, which is most often either siliceous sand or dolomite [10].

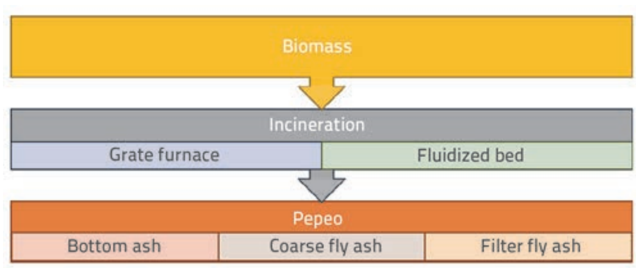


**Figure 1. Types of biomass combustion and bioash fractions**

Three different ash fractions (Figure 1) are produced in the process of biomass combustion: bottom ash, cyclone fly ash, and filter fly ash [10]. Bottom ash is the largest ash fraction,

**Table 2. Distribution of ash fractions in case of grate combustion of various biomass types [10]**

| Ash fraction [%] \ Biomass | Bark | Woodchips | Sawdust | Straw and grains |
|---|---|---|---|---|
| **Bottom ash** | 65-85 | 60-90 | 20-30 | 80-90 |
| **Cyclone fly ash** | 10-25 | 10-30 | 50-70 | 2-5 |
| **Filter fly ash** | 2-10 | 2-10 | 10-20 | 5-15 |

**Table 3. Chemical content of various bioashes**

| Chemical composition [%] \ Type of ash | Beech wood [21] | Sawdust [22] | Rice husk [21. 22] | Corncob [21. 22] | Sugar cane straw [22] | Wheat straw [21. 22] | Sunflower husk [21. 23] |
|---|---|---|---|---|---|---|---|
| $SiO_2$ | 12.33 | 67.20 | 93.2-94.38 | 27.65-66.38 | 59.06 | 4.99-54.24 | 23.46-26 |
| $Al_2O_3$ | 0.12 | 4.09 | 0.21-0.4 | 2.49-7.48 | 4.75 | 1.15-4.55 | 2.23-8.67 |
| $Fe_2O_3$ | 1.09 | 2.26 | 0.1-0.22 | 1.55-4.44 | 3.18 | 0.95-1.05 | 1.19-4.23 |
| CaO | 67.80 | 9.98 | 0.97-1.1 | 11.57-13.19 | 19.59 | 12.54-25.44 | 15.18-17 |
| MgO | 11.43 | 5.80 | 0.1-0.19 | 2.05-2.06 | 2.25 | 2.39-4.63 | 6.65-7.27 |
| $Na_2O$ | 0.89 | 0.08 | 0.1-0.16 | 0.41-1.26 | 0.73 | 1.28 | 0.22-0.79 |
| $K_2O$ | 2.59 | 0.11 | 1.3-2.29 | 4.92-35.46 | 4.75 | 24.72 | 17.1-28.29 |

collected under the grate, often mixed with impurities, such as sand, soil, or bed material, during the fluidized bed combustion. Cyclone fly ash is a coarser, mostly inorganic, fraction of fly ash transferred by flue gas into the secondary combustion zone. Filter fly ash is the finest fraction collected on electrostatic and fibrous filters or as condensation sludge.

The particle size range, and the grading of individual biomass ash fractions, depend on the ash separation and collection technology, and on the origin of biomass undergoing combustion [13]. Particles larger than 5 μm can be collected by cyclone dust collectors. These particles make a larger fly ash fraction and their size can be up to 100 μm. All smaller particles, the size of an aerosol, of the order of magnitude from 1 to 5 μm, make the filter ash [12, 14]. The largest fraction, the bottom ash, is usually composed of particles larger than 100 μm. However, some studies indicate that this fraction can sometimes contain particles of up to 10 mm in size [15-17]. In a fluidized bed, bottom ash accounts for only 20-30 % of the bed content, while the rest is fly ash [10]. As opposed to that, the distribution of ash fractions in case of grate combustion is shown in Table 2.

Physical and chemical properties of bioash depend on the origin of biomass and part of the plant from which it originates (Table 3), the content of mineral impurities, biomass source location, type of biomass collection and processing, combustion technology, and combustion temperature [10, 18, 19]. Chemical composition of ash depends on the inorganic composition of biomass, while the mineral composition depends on the type of combustion [3, 16]. Therefore, even if the same type of biomass is combusted, the resulting ash properties may vary to a great extent [20].

Bioash produced by grate combustion has a higher content of free (Ca) or bound calcium (CaO) compared to bioash produced by combustion in a fluidized bed, which can be attributed to higher combustion temperatures on the grate [24]. Large content of $SiO_2$ can usually be found in ash produced by combustion in a fluidized bed, where the bottom ash mostly consists of inert bed material (sand), while fly ash is mixed with that material [24].

Differences in ash composition arise not only from biomass origin, but also from combustion temperature. For example, combustion of agricultural biomass needs to be operated at lower temperatures compared to wood biomass, because excessively high temperatures can cause melting and sintering of ash, which causes furnace operation problems [25]. The share of CaO in bioash from agricultural biomass is considerably lower than that in wood ash, but the content of $SiO_2$, alkali, and Cl is higher. At the same time, the share of heavy metals in ash from agricultural biomass is lower compared to that in wood ash [26]. The rice husk biomass is a notable example of biomass types the ash of which exhibits a high $SiO_2$ content (> 90 %). The content of $SiO_2$ is significantly lower in other agricultural and herbaceous biomass, and is very low in wood biomass (Table 3).

Bioash typically also contains a certain amount of harmful compounds, such as heavy metals. Some studies have revealed that the concentrations of Ag, Au, B, Be, Cd, Cr, Cu, Mu, Ni, Rb, Se, and Zn in bioash are higher than the average concentrations in coal ash [21]. Large content of harmful compounds in some ashes, heavy metals in particular, limits the extent of their use, especially in agriculture where ashes are used as a soil amendment enhancing plant growth [27]. Regardless of the type of biomass, the content in heavy metals is higher in fly ash than in bottom ash

[2]. Due to its volatile nature, fly ash combines with flue gases and binds itself to the ash particles collected at filters. The share of heavy metals in fly ash produced by combustion in fluidized bed is lower than that in the ash produced by grate combustion, which is due to combustion technology that causes the mixing of bed material (sand) with the ash [24]. Furthermore, the content of organic admixtures that are harmful to the environment can be a limiting factor in the utilisation of bottom ash. The content of organic material is higher in biomass with a higher percentage of water, and it greatly depends on the technology and efficiency of combustion [28].

From the above mentioned it is apparent that physical and chemical properties of bioash vary significantly, and that it is not possible to generalize its application possibilities. Instead, the existing research results on bioash use should be taken into account when making decisions on its application, and then further research should be carried out. An overview of recent research reveals that bioash belongs to the group of waste materials that can be used in construction, either in their original form or after additional processing. Two basic uses of bioash, depending on its properties, can be differentiated. Thus it can be used:

- as a binding component, when the introduction of ash unchains certain chemical reactions as a result of pozzolanic activity or hydraulic binding of the ash (indirect type of ash use), or
- as a filler, when it is necessary to improve physical properties of mixtures by increasing the proportion of fine particles, or replacing small aggregate fractions (direct type of ash use).

## 3. International research on bioash use in road construction

In accordance with the above mentioned, the use of bioash in construction industry has been the subject of a number of studies conducted in all parts of the world. These studies examine various bioashes, which significantly differ by their origin and properties, but also by application method and intended use. According to bioash origin, bioashes from wood biomass and rice husk are most frequently studied. Available research results on the use of bioash in road construction are outlined and described in the following subsections.

### 3.1. Stabilization of soil and base layers of pavement structures

For the stabilization of soils with low bearing capacity, the use is traditionally made of lime for coherent materials, while cement is used for non-coherent materials and materials representing a transition from coherent to non-coherent materials. It is understandable that extensive research has so far been made on various possibilities for using these materials. The use of alternative materials, such as bioash, is of recent date, and so the research and results published about bioash are not so abundant. Stabilizing properties of ash depend on the chemical content and reactivity of certain compounds and, obviously, on the type of base material that is to be stabilised. Considering the energy savings and environmental concerns, and taking into account stabilizing properties of ash, the application of an appropriate type of bioash would reduce the costs of soil stabilization in cases when the binder accounts for 50-70 % of the cost [29].

According to Sarkkinen et al. [29] and Bohrn et al. [30], when bioash is applied as binder for the stabilization of various materials, it must contain at least 20 % of CaO to demonstrate good binding properties. If the CaO content is lower than that, it is necessary to use activators (cement or lime). In addition to the CaO content, binding properties are also influenced by the size of ash particles, while greater reactivity and strength development is associated with the large specific surface of smaller particles. According to European standard EN 450-1, ashes with satisfactory pozzolanic properties are those that cumulatively contain 70 % of $SiO_2$, $Al_2O_3$, and $FeO_3$ [31]. For example, the ash of rice husk contains more than 90 % of $SiO_2$. In addition to the content of the above mentioned oxides, good pozzolanic properties of bioash also depend on whether their structure is amorphous or crystalline [29], which is related to combustion technology and the size of particles.

#### 3.1.1. Stabilization of coherent soils

Coherent soils are stabilized by addition of lime (calcium hydroxide). The lime reacts with clay minerals dissociating into Ca+ and OH- ions. At that, certain types of ions that envelop colloidal clay particles are replaced in soil (cationic exchange), and calcium is introduced in the clay composition, altering the clay soil properties. This correction is fast and the improvement of soil workability, compacting properties, and initial strength, is almost instantaneous. The reaction is followed by a long lasting reaction of lime with active silicates and clay minerals, which is known as pozzolanic reaction. Silicates decompose and a new crystalline phase forms, whereby calcium and silicate hydrates are produced that bind the soil particles, thereby increasing soil strength. The reaction of bioash components as a stabilizing agent with clay minerals occurs in the same way. Therefore, ashes with high CaO content and, consequently, with high pH value, such as wood biomass ash or ash from olive oil production, are considered suitable [32-34]. These ashes, when introduced, create an alkaline environment in soil, which allows development of pozzolanic reactions. Due to introduction of these ashes, soil also undergoes cationic changes and soil structure changes as a result of particles agglomeration, which results in smaller dry density and greater optimal moisture content of the mixture. This effect is also due to lower density of bioash and more porous particles of larger specific area that require larger amounts of water, and so the same effect can also be seen in ashes with higher SiO2 content, such as the ash from rice husk [35, 36] and ash from sawdust [37]. The introduction of bioash into coherent soils often reduces the plasticity index [33-36]. Almost all authors have determined through their research that bioash can reduce swelling of coherent soils [32-35].

Bearing capacity and strength values of stabilizing mixtures vary in accordance with variation of properties of bioash and soil. Supancic and Obernberger [24] examined a combination of wood bottom ash and coarse fly ash produced by grate combustion, and a combination of coarse and filter fly ash produced by combustion in the fluidized bed. They concluded that various combinations of wood bioash can be used as binder for stabilization of clay and silt soils. The same authors also compared stabilization of clay with wood ash and lime on experimental sections and discovered that, when bioash was adequately proportioned, the compressive strength and bearing capacity values measured by dynamic plate load test were similar for both binders 28 days after stabilization. The improvement of CBR by 103.11 % and compressive strength by 26.35 % was determined by Butt et al. for low plasticity clay containing 4 % of sawdust ash [37]. Emeh and Igawe [33] achieved a strength of 1.59 MPa by adding wood ash (18 %) to high plasticity clay. The effect was improved by adding 4 % of lime to the mixture, which ultimately resulted in the strength of 2.50 MPa.

The introduction of rice husk ash reveals a somewhat weaker effect on the improvement of mix properties, which can however be further enhanced by cement. By adding rice husk ash, Sarkar et al. [36] improved compressive strength of low plasticity clay and achieved an optimum value of 0.255 MPa in mixtures containing 10 % of ash. Rahman et al. [36] noted an improvement in compressive and shear strength of mixtures after introduction of rice husk ash (0, 5, 10 and 20 %) to stabilize silty sand and clay soils. An 8 % improvement of compressive strength was also observed by Khan et al. [38]. The highest compressive strength and CBR values of 74 % were achieved by combining rice husk ash with cement. As related to use of bioash as stabilising agent, numerous laboratory research results reveal that an optimum share of bioash that improves mix properties should be determined with accuracy, as an increase in bioash proportion above an optimal level can lead to poorer results.

### 3.1.2. Stabilized base layers

In base layers it would be possible to use fine fly ash and coarser bottom ash due to two mechanisms: improvement of bearing capacity through mechanical stabilization and improved grading, or due to bioash action as a hydraulic binder. Laboratory testing of wood ash and ash produced by combustion of waste from paper mills reveal satisfactory values, and the use of such ash is significant [39-41]. However, contradictory results were obtained by field tests related to stabilization of layers of the existing (often forest) roads [30, 41, 42]. Stabilization effect of the addition of 10 % and 20 % of wood ash to mixtures with sand was examined by Škels et al. [39]. Their results revealed a multiple increase in the CBR value in both stabilized mixtures, without significant swelling. The authors described the wood ash as a good hydraulic binder for sand stabilization. However, given the research methodology presented in the paper, the effect is probably the result of mechanical stabilization.

Finnish authors Sarkkinen et al. [40] examined a mixture of bioash and waste rock as material for the construction of stabilized base layers. The waste dolomite rock was stabilised by introducing 20 % of ash produced by burning wood, peat and paper mill waste in a power plant. The compressive strength of the mixture after 28 days amounted to 9.1 MPa. After subjecting samples to 10 cycles of freezing and thawing, the compressive strength of the mixture was 9.5 MPa, which is fully compliant with requirements applicable in Finland for mixtures intended for construction of base layers of road pavements [40].

Vestin et al. [41] examined the possibility of using ash from a paper mill and from burning wood bark and sludge for stabilization of a gravel base layer. In the laboratory part of the research, mixtures containing 20 % and 30 % of ash had approximate initial strengths of 4.7 and 4.4 MPa, respectively. The increase in compressive strength in the mixture containing 20 % of ash was 2 MPa, while it was 5.3 MPa in the mixture containing 30 % of ash. The compressive strength measured after 12 cycles of freezing and thawing decreased in the mixture containing 20 % of ash, and increased in the mixture containing 30 % of ash. The same authors reported stabilization of test section with the mixture containing 30 % of ash [41], which over time resulted in an increase in the load bearing capacity. Visual inspection of test sections conducted two years later after snow melting revealed no visual changes, while longitudinal cracking was observed at control sections.

Bohrn and Stampfer [30] reported a 20 MN/m$^2$ increase in elastic modulus E after having stabilized the bearing layer of the existing forest road with bottom ash from wood biomass, as compared to values obtained by mechanical stabilization of soil. Stabilization by ash from wood biomass produced by combustion in fluidized bed proved to be inadequate.

Possibilities of improving bearing capacity of a gravel forest road by adding wood ash were investigated by Kaakkurivaara et al. [42]. Improvement of bearing capacity of the mentioned forest road was actually achieved, but the results proved less significant than expected. The authors explain that this is due to insufficient compaction during construction, poor mixing technology, and uneven bioash storage time for individual sections. More precisely, bioash reacts with moisture and begins to bind, which is why it should be properly stored in dry environment if it is to be used as binder at a later time.

Bottom bioash can also be used as a replacement for aggregate if its grading is adequate. For cement-bound base course mixtures, Cabrera et al. [16] used ash obtained by combusting 40 % of residues from olive oil production, and 60 % of wood biomass, with particle size in the range of 0 - 10 mm, containing a smaller share of finer particles (< 0.063 mm) compared to natural aggregate. Testing mechanical properties of mixtures revealed an increase in compressive strength, indirect tensile strength, and elastic modulus in all mixtures containing 15 % of ash, compared to mixtures containing only natural aggregate or recycled aggregate from mixed construction waste. Mixtures of recycled aggregate containing 30 % of ash revealed a decrease in indirect tensile strength, while all mixtures containing 30 % of ash revealed a reduction in elastic modulus E compared to mixtures containing only natural or recycled aggregates.

These results confirmed the possibility of using bottom ash for the production of base layers stabilized with cement, in full compliance with requirements specified in Spanish regulations.
Apart from usual materials, such as gravel and sand, Pavšić et al. [43] suggest that bioash from paper mills (wood, bark, paper manufacturing sludge) can be used to stabilize sewage sludge and recycled mixed aggregates, through creation of a controlled low strength material. The study revealed that adding bioash from wood biomass effectively inhibits microbial activity in the sludge mixture, and that an inert and environmentally acceptable material can thus be obtained, with a 28-day compressive strength of about 1.6 - 1.8 MPa, that meets quality requirements for stabilized road layers, for bedding of service ducts, as well as requirements for trench filling material.

### 3.2. Asphalt layers

Fly ash generated by combustion of coal in thermal power plants is used in asphalt layers as a substitute of mineral filler. This type of ash has been studied much more extensively compared to bioash. An increase in the amount of coal-based fly ash in asphalt mixtures results in an increase of indirect tensile strength and in higher resistance to fatigue and low temperature, but also in lower resistance to rutting [44].
Compared to conventional mineral fillers, bioash properties cover a much wider range and significantly differ from ash obtained by burning coal. It is often necessary to conduct appropriate preliminary actions to make sure that ash meets requirements for fillers as specified in relevant standards. Melotti et al. [20] investigated physical and chemical properties of 21 bioashes from 12 thermal power plants produced by combustion of woodchips, rice husk, straw, bark, etc. They discovered that initial size of particles of virtually all bioashes used was too large, and that it exceeded the size prescribed for fillers. Similar findings were published by Sargin et al. [45] and Xue et al., [46], while Pasandin et al. [47] established that the grain size distribution is satisfactory. Consequently, to achieve the desired grading, it is necessary to subject ash to milling and sieving, and to provide for separate storage of individual ash fractions. Furthermore, the water content of some biomass ash is higher than permitted [20], [47] and, therefore, attention should be paid to proper storage and transport of ash when it is to be used in asphalt mixtures.
Bioash differs by shape of its particles from spherical particles of coal-based fly ash, i.e. bioash shape is usually more irregular [20, 47, 48]. Such particle shape results in higher absorption of bituminous binder and in lower workability of asphalt mixtures [47]. However, the shape of particles can also have a positive effect, i.e. it increases shear strength and rigidity, thereby increasing resistance to plastic deformation [48].
According to literature data, the ash from rice husk is most often used in hot asphalt mixtures, while other types of ash are either considered inappropriate [47] or their usability has not as yet been explored. Studies have revealed that the use of rice husk ash can increase the Marshall stability and indirect tensile strength in comparison to mixtures with conventional filler [45], [48]. That type of ash also exhibits a positive effect on water resistance, but it negatively affects density of mixtures and air void content [48]. Therefore, a special attention should be paid to ash dosage, e.g. by resorting to partial replacement of standard material, so as to achieve positive effects and to keep adverse effects within acceptable limits.
Apart from use of rice husk ash as mineral filler, authors Xue et al. [46] showed that rice husk ash and wood sawdust ash can be used to modify bituminous binder. In this case, the desired effect was not achieved by chemical reactions with bitumen, but rather modification of bituminous binder occurred by mechanical agitation. It was discovered that bioash used in asphalt mixtures has a negative effect on stability during storage and that it increases viscosity, which is why it is necessary to carefully control volume of bioash in order to achieve desired properties. When properly dosed, bioash improves the resistance to rutting and behaviour of bitumen at high temperatures, with rice husk ash usually producing better results [46].

### 3.3. Concrete

Concrete is used in road construction for the realisation of pavement structures, as a bedding or cover for various elements, and for construction of various drainage elements, curbs, and road structures. In addition to the pressing need for large quantities of natural building materials, there is also a considerable demand for cement, the production of which contributes to global $CO_2$ emissions. In accordance with requirements to reduce generation of $CO_2$, a part of cement used in concrete could be replaced with bioash.
European standard EN 450-1 [31], which prescribes properties for coal-based ash to be used as a type II mineral additive in cement mixtures, specifies that biomass ash can be used as a part of that ash (up to 30 %). In their study, Hosseini et al. [22] indicate that, due to large content of amorphous silicon, the ash produced by burning agricultural crop residues can be used as raw material for the production of cement (so called biocement) or as a partial replacement of cement. This type of ash contains at least 70 % of amorphous $SiO_2 + Al_2O_3 + Fe_2O_3$ for pozzolanic reactions, and can be improved by additional operations such as ash milling. In case this ash is used in concrete, it is necessary to make sure that combustion is complete in order to limit the content of organic substances. Replacing cement with small quantities of ash (10-20 %) can improve properties of hardened concrete (strength, durability, resistance to ambient conditions) [22] and behaviour of fresh concrete [49]. Depending on its source and properties, bioash can have a negative effect on the strength and workability of concrete, as was determined by Senas et al. for sunflower husk ash [50].
According to EN 450-1 [31], ash from wood biomass does not meet requirements for use as mineral admixture due to its insufficient pozzolanic activity, as described by Berra et al. [51] and Luz Garcia and Sousa-Coutinho [3]. In paper [51] this ash had an excessive chloride and sulphate content, unlike the ash in paper [3] that contained no components with adverse effect on concrete. Due to

**Table 4. Possible use of bioash in road construction**

| Application | Function | Type |
|---|---|---|
| **Stabilization of coherent material** | Partial or complete replacement for binder | Wood ash<br>Ash from olive oil production<br>Rice husk ash |
| **Mechanical stabilization of unbound material** | Fine grained aggregate | Ash from wood, peat and waste from paper mills |
| **Bound base courses** | Binder | Bottom ash from wood and residues from olive oil production |
| | Aggregate | Rice husk ash |
| **Hot mix asphalt** | Filler | Ash from agricultural crops (straw) |
| **Structural concrete** | Partial replacement for cement | Rice husk ash |
| **Unreinforced and lower quality concrete** | Filler or replacement for aggregate | Ash from wood, olives and other biomass |

excessive size of particles and insufficient pozzolanic properties, this ash can only be used as filler or partial replacement for sand in low strength concrete and unreinforced concrete.

As to bottom ash (from olives and other biomass), it can be used in concrete and blinding mortar (bedding for curbs, drains, etc.) as reported by Beltrán et al. [17, 52]. A large content of organic matter in this ash can be limited by sieving and using only finer fractions (up to 2mm), but organic matter content and high ash porosity still have a negative effect on mechanical properties and durability of concrete and mortar. Application is therefore recommended only in smaller quantities or for non-structural concrete.

Table 4 provides a summary of potential use of bioash in road construction as based on literature data.

## 3.4. Environmental impact of bioash

Despite satisfactory mechanical properties of mixtures in which bioash is used, the environmental impact can be a limiting factor with regard to its wider application. It should not be forgotten that it is a waste material of variable chemical and mineral composition, and that its uncontrolled use could have negative effects on human health, the surrounding soil, and water. According to Chesner et al. [6], the environment and human health can be endangered by the presence of volatile and heavy metals (As, Cd, Cu, Cr, Hg, Pb, Zn, etc.), organic substances (benzene, phenols, etc.), and fine dust containing toxic and organic elements.

When assessing the negative impact of bioash on the environment, it is important to consider data on the position of the layer (soil or pavement), its designed thickness, type of primary binder (bitumen or cement), and quantity applied. The permeability of bound materials is significantly lower as ash particles are surrounded by a bitumen or cement layer preventing passage of water. An intensive penetration of harmful elements from the constructed layer into the surrounding soil and water may occur during construction when the surface of the layer is unprotected and exposed to rain.

Apart from examining properties of mixtures containing bioash, some authors also examined its potentially negative environmental impacts. Thus Supancic and Obernberger [24] investigated the application of different fractions of wood ash produced by grate combustion and by combustion in the fluidized layer for soil stabilization. Their results revealed that the heavy metal content in fly ash produced by grate combustion is beyond the limits allowed according to Austrian regulations, which is why this material is not considered suitable for soil stabilization.

Vanhanen et al. [18] conducted field research to test environmental impact of road strengthening using a combination of gravel and wood fly ash. Their research also revealed that the concentrations of Cr, Mo, F, and $SO_4$ are too high for the reuse of this waste material in soil, although it could be used in structures with surfacing. Vestin et al. [41] concluded that initial leaching of K, Na, Cl, and $SO_4$ was present in gravel roads stabilized with fly ash originating from combustion of wood bark and sludge in the fluidized bed. The observed leaching had a tendency to decrease over time and, after two years, the concentrations were similar to those of the reference ash-free section.

Melotti et al. established that ash to be disposed in the environment exhibited excessive leaching of Cr and sulphate. However, they noted that the leaching test was conducted on pure ash. In its planned application in asphalt, the coating of ash particles with bitumen should reduce the release of harmful substances and, therefore, potential application of bioash should not be discarded simply based on eluate analysis.

Netinger Grubeša and Barišić [53] discovered that ash from sunflower husk contains excessive amounts of Zn and Cu, and so, according to Croatian regulations, it can not be used in agriculture. However, an alternative use of this bioash in construction industry is to be investigated.

Data from various studies on potential negative effects of bioash have revealed that it can contain harmful substances in quantities beyond those allowed for the disposal in the environment, or for the application on agricultural soils. Studies were most often conducted by analysing concentrations in the ash itself or in the eluate obtained from it. A smaller number of studies focusing on eluates collected in situ show that the concentrations of harmful compounds are lower, and that they tend to decrease over time. Therefore, when dealing with potentially harmful bioash

Figure 2. a) First private biomass power plant in Croatia; b) woodchips used, c) combustion of biomass [55]

(determined solely by ash or eluate analysis), its possible use must be carefully analysed and determined, and any potential harmful effects should be tested on mixtures.

## 4. Application of bioash in Croatia

As a member of the European Union, Croatia has accepted the obligation to increase the use of renewable energy sources as required by European Directive [1], in which it is specified that the share of renewable energy at the EU level should be at least 20 % by 2020. The potential of biomass use as a source of renewable energy is very high in Croatia since forests cover 48 % of its territory [4], and it is also possible to use part of agricultural residue such as straw, sunflower husks, olive cakes, and waste from the pruning of vineyards and orchards [5]. While the use of biomass for energy is constantly increasing in the world, first biomass power plants have only recently been built in Croatia (Figure 2). Wood biomass from wood processing industry, and waste from forest industry, are used in these biomass power plants, where combustion is mostly carried out in grate furnaces. However, it is planned to increase the use of energy from biomass, and to commission 55 power plants with an installed power of 93.97 MW [54]. Such an increase in capacities entails the need to find an acceptable way of handling greater quantities of ash.

The use of ash produced in Croatia in mortars was tested using ash generated through combustion of forest and wood waste in grate furnaces of the Lika Eko-Energo plant [4]. Coarse fly ash was used in mortar production as partial replacement of cement and sand (the proportion of ash ranged from 0 to 30 %). However, although the ash used contains clinker minerals, suggesting that it can be used in the cement replacement, it did not meet the requirements specified in EN 450-1 for the application of fly ash in concrete [31]. Reasons for that are excessively large particles, insufficient amount of pozzolanic oxides ($SiO_2$, $Al_2O_3$ i $Fe_2O_3$), and high amounts of alkaline metals and reactive CaO and MgO. These properties could be improved by pre-washing and mechanical treatment of bioash. In the mortars tested, an increase in cement replacement had a negative effect on hydration mechanisms, and it significantly reduced the workability, compressive strength and flexural strength. However, mortars with 5 % cement replacement and 3.3 % sand replacement fulfilled the requirements for use in structural mortars and concrete.

Figure 3. a) Sunflower seed hull; b) bioash from combustion of sunflower seed hull

Apart from the mentioned study, Faculty of Civil Engineering in Zagreb plans to conduct a study on the application of bioash from wood biomass in construction industry [5]. Studies on the possibilities of using ash from agricultural cultures are currently under way at the Faculty of Civil Engineering in Osijek [56] (Figure 3).

## 5. Conclusion

The share of biomass as a renewable source in the production of total energy is steadily increasing. The combustion of biomass in thermal power plants generates large amounts of ash that need to be disposed of or recycled. The resulting ash is most often stored at landfills and, given the trend of increasing the share of renewable sources in the total energy production, the quantities of ash are increasingly accumulating. Favourable physical and chemical properties of coal ash, as well as positive experience on its application in construction industry, have inspired an ever-growing number of studies on bioash application. Studies conducted so far have revealed that bioash considerably varies as to its composition and properties, depending on the origin of biomass, biomass handling, and combustion technology and temperature. A wide range of properties means that numerous possibilities are available for the use of bioash in road construction as a substitute for traditional materials. The chemical composition of bioash, primarily the share of CaO and pozzolan, suggests the possibility of partial or complete replacement of traditional binders, cement and lime, in the stabilization of soils with low bearing capacity, in base layers of road pavements, or in concrete. In the absence of binding properties, ash can be used as a replacement for mineral fillers and aggregates (sand or gravel) in asphalt mixtures, concrete, and other pavement layers, depending on ash fraction. A very important aspect in the use of ash is its environmental impact, and so the quantity of its harmful elements must be studied before ash use. Due to its wide range of properties, bioash offers numerous application possibilities, but that same wide range of properties also points to the fact that adequate application of bioash in road construction can not be determined without prior detailed research and analysis.

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