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Abstract

Currently, the production of thermal energy by biomass has shown a clear trend toward densified biofuels (pellets). This is due to their consistent size and shape that can be more easily delivered to homes, businesses, and power plants and can be automatically fed into advanced pellet boilers in a controlled and calibrated way. The use of densified biofuels also reduces the costs associated with handling and transportation, due to the increase in density involved by densification process. Demand for wood pellets is currently growing at a faster rate than supply in Europe. It is estimated that pellet market is growing to 50 Mt year\(^{-1}\) by 2025; however, most wood waste is already committed for pressed wood products and pellets, therefore more supply of raw materials are needed. With the possible shortage of woody raw materials for pellet production and considering the low forestry residues potential in several countries, agricultural residues could be largely used in the future for fuel pellets manufacturing. Agricultural pellets, as well known as “agripellets”, are emerging and promising. However, they have certain differences compared to conventional wood pellets.

Keywords: agripellets, biomass, solid biofuels, agricultural residues

1. Introduction

The growing domestic and industrial demand of biomass for heat and power production in Canada, United States, Europe, and China has resulted in a strong growing global pellet marked during the last decades, and continuous growth of the market is predicted for the next years [1]. It is estimated that the demand for pellets will be triples from 2012 to 2020, rising from 16 to 46 million metric tons per year [2]. In the pellet production, there is a shortage of woody raw materials, and the price of the wood raw material increases. Considering that only
woody pellets from forestry residues have already successfully established technologies and markets for production and consumption in these countries, it is necessary to focus on studying the pelletization of new sources of raw materials. Agricultural residues can be one of the potential alternative feedstock since it is abundantly available and at low cost. In the near future, agricultural residues have a tremendous potential in biomass pellets industry. It is therefore of great interest to study the characteristics of this new category of raw material, paying special attention to the problems that they may trigger both at production and utilization level. At a technical level, the main difference between wood pellets and agripellets is the somehow higher friability, the slightly lower energy content and the higher ash content of the latter.

The future of agripellets as a carrier of energy from biomass appears to be promising. This is influenced by many factors. Popularity of biomass is motivated by aspects of various types, such as:

- Economic: energy production from biomass is the least capital intensive process compared with other forms of renewable energy. Besides, the production of pellets can help to stimulate economic activity and reduce unemployment.
- Policy: European Union defines the share of renewables in the energy balance of the Member States, and also in the United States, pellet is expected to significantly increase its importance.
- Social: the growing environmental awareness of citizens contributes to the popularization of biofuels in industrial and individual scale.
- Environmental: biomass is characterized by carbon neutrality and lower emissions of harmful elements in comparison with the use of fossil fuels.
- Energy: a large and stable technical potential of biomass as energy source.

2. Agricultural residues for energy purposes: agripellets

Nowadays, fuel pellets are mainly made from sawdust, wood chips, and wood shavings. The supply of wood materials can be limited because producers of fiberboard, particleboard, and oriented strand board compete for the same forestry and mill residues as pellet producers [3]. This competition and the current increased demand for wood pellets, both for residential and industrial use, have led to a shortage of sawdust and wood shavings. If demand and prices continue to rise, other biomass wastes than sawdust, wood chips, and wood shavings should be considered for pellet production. Agricultural residues are among those future new raw materials. Agricultural residues refer all the organic materials which are produced as by-products from harvesting and processing of agricultural crops. These residues can be further categorized into primary residues and secondary residues. Primary or field-based residues are those generated in the field at the time of harvest (e.g., straw, stalks, and leaves that are left over after harvest), whereas those coproduced during processing are called secondary or processing-based residues (e.g., sugar beet pulps, cotton mill wastes, peanut shells).
Availability of primary residues for energy application is usually low since collection is difficult, and they have other uses as fertilizer, soil conservation, animal feeding, and litter. The amount of secondary residues varies widely depending on the crop and processing methods used [4].

Currently, large amounts of agricultural residues are left in the field to rot or are burned in the open air, ultimately releasing carbon dioxide to the atmosphere. This biomass could be used to produce pellets which are a form of solid fuel. The most important reason for using agricultural residues for energy purposes is that it is carbon neutral, that is, the carbon emitted during their combustion is taken up in the regrowth of the biomass used to produce them and therefore does not add to greenhouse gas emissions. Further, any consumption of fossil fuels replaced by biomass will lower CO\textsubscript{2} emissions.

Agricultural residues are available in large quantities and can be utilized for sustainable heat and power production, when used as fuel. However, they have low energy density (MJ m\textsuperscript{-3}) and low yield per unit area (dry tons ha\textsuperscript{-1}) [5]. Often, long distances have to be bridged between the biomass place of origin and the place of its utilization, resulting in expensive handling and transportation. Transportation costs of low-density and high-moisture agricultural residues which increase the total biomass-processing cost are a major constraint to their use as an energy source [6]. To increase the density of the biomass, it can be compressed into pellets using a mechanical process in which pressure is applied to the biomass to crush its cellular structure, and thereby increasing its density. Densified biomass, especially pellets, has drawn attention due to its superiority over raw biomass in terms of its physical and combustion characteristics [7]. Many materials originated by agriculture could be used for the production of densified biomass fuels: straw, grain hull waste, tree pruning, fruit stones, dry fruit waste, grain, cork, cotton, and other wastes.

The main characteristics of some selected agripellets are summarized in Table 1. The higher heating value (HHV) of agripellets is high, being even higher than pine sawdust pellets (in the case of pellets made of olive pomace and tomato peels and seed). The ash content confirms the necessity of blending agricultural residues with sawdust or other woody material. In fact, the ash contents for agripellets (3.3–12%) are significantly higher comparing to pine sawdust (2.5%).

According to Colley [14], pellets durability is regarded as high if exceeding 80%, medium if measured as 70–80%, and low if values do not reach 70%. Therefore, agripellets show high quality in terms of durability.

2.1. Olive mill residues

The olive oil industry produces significant quantities of solid olive residues (pieces of skin, pulp, and stones) which due to their characteristics can be utilized for the production of cleaner energy [15]. According to Barbanera et al. [16], it can be assumed that 1 ha of olive tree produces about 2500 kg of olives and about 35 kg of olive pomace. Several studies have been conducted during the last two decades that examined the thermochemical characteristics and performance of solid olive residues [17–21]. The results obtained from these studies suggest that these
solid residues constitute a promising biomass resource because their thermochemical characteristics provide the opportunity for their potential utilization for energy purposes, offering at the same time a solution to the management problems [20].

<table>
<thead>
<tr>
<th>Residue</th>
<th>HHV (MJ kg⁻¹)</th>
<th>Ash content (%)</th>
<th>Pellets durability</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vineyard pruning</td>
<td>17.8</td>
<td>4.4</td>
<td>98.8</td>
<td>[8, 9]</td>
</tr>
<tr>
<td>Olive pomace</td>
<td>22.0</td>
<td>5.6</td>
<td>91.4</td>
<td>[10]</td>
</tr>
<tr>
<td>Peels and seeds of tomato</td>
<td>27.1</td>
<td>4.9</td>
<td>91.2</td>
<td>[11]</td>
</tr>
<tr>
<td>Grape marc</td>
<td>19.5</td>
<td>12.0</td>
<td>85.8</td>
<td>[9, 12]</td>
</tr>
<tr>
<td>Olive pruning</td>
<td>19.6</td>
<td>3.3</td>
<td>91.7</td>
<td>[13]</td>
</tr>
<tr>
<td>Wheat straw</td>
<td>18.3</td>
<td>9.1</td>
<td>94.4</td>
<td>[9]</td>
</tr>
<tr>
<td>Pine sawdust</td>
<td>19.7</td>
<td>2.5</td>
<td>97.2</td>
<td>[9]</td>
</tr>
</tbody>
</table>

Table 1. Characteristics of some agripellets.

The solid fraction combustion of olive residues indicates good combustion behavior of olive kernels and the residual olive pomace, with suitable efficiency and a reduced presence of unburned fraction. However, lower combustion efficiencies are observed during pulp processing [10]. The olive pomace, once it has been subjected to a drying process, can be used as a fuel. However, their oleaginous characteristics limit the densification during the pelletizing process. Moreover, their high concentrations of certain components such as nitrogen and ashes exceed the specifications given by pellets quality standards [20]. Therefore, it is necessary to blend the olive oil by-products with other biomass residues that must present suitable characteristics for an ideal pelletization [22]. Barbarena et al. [16] reported that adding olive tree pruning to olive pomace, the chemical composition of pellet blends respects the standard requirements in terms of mechanical durability and N and Cu content. In addition, the bulk density was enhanced allowing a reduction of transport and storage economic cost. On the other hand, Brlek et al. [23] suggest that limitations regarding combustion of olive pomace pellets can be established due to elevated nitrogen content and higher percent of abrasion. These constrains can possibly be diminished by adding wood biomass to pelletization blend.

2.2. Vine residues

The wine industry produces huge amounts of residues every year. Marculescu and Ciuta [24] estimate that for every kilogram of grape processed for wine, more than 20% is residue. The current use of the wood residues produced by the annual pruning activity is generally eliminated through crushing in the vineyard and then spread along the soil, in order to reduce erosion and recycle nutrients that can be incorporated into the soil [25].
Another important residue generated in the production of wine is grape marc. This residue is the skins and pips that remain after the grapes have been crushed. These residues are highly wet (more than 60% of moisture content on wet basis) and have low pH. Also, they present high contents of phosphorous (P), potassium (K), organic matter, phytotoxic, and antibacterial phenolic substances, which make them resistant to biological degradation. These wastes have high contents of lignin and tannin. Hence, they are not appropriate as a nutritional supplement for animals [26]. In addition, due to their high C/N ratio, their recovery as soil fertilizer presents difficulties. Another important constraint related to the management and disposal of wineries and distilleries processing industries is the generation of large quantities in which discharges are usually centralized and seasonal in a short period of the year (3–4 months).

Fernandez-Puratich et al. [8] studied the use of vine wastes for the production of pellets and concluded that the use of these biomass residues is a viable alternative option in terms of economy as well as energy.

Marculescu and Ciuta [24] studied the thermal degradation of grape marc in a laboratory furnace. They found that grape marc has high energy content (19.7 kJ kg\(^{-1}\)) and they have recommended for energy production.

Kraiem et al. [12] recommend blending these residues with pine sawdust. They found that a blend with sawdust leads to the decrease of ash contents while densification leads to the increase of the energy densities. Combustion tests of pellets prepared from these residues indicate that boiler and combustion efficiencies are comparable to wood pellets. However, gaseous and particulate emissions are higher and are strongly affected by the operating parameters of the domestic boilers.

2.3. Industrial tomato residues

The industrial processing of tomato leads to a great variety of output products. Large volumes of residual biomass (mainly peels and seeds) are generated by tomato industrial processing plants. Currently, industrial tomato residues do not generate so many benefits for industries, in particular for storage and preservation issues. The accumulation of these residues, predominantly in the warm periods, promotes uncontrolled anaerobic fermentations leading to environmental problems [27]. In this way, fast consumption is advised in order to prevent fermentation processes, which are favored by high temperatures during the industrial processing period. Those residues have a high moisture content, which leads to some storage difficulties, and are generated in large quantities in which discharges are usually centralized and seasonal in a short period of the year. Also, important costs are derived from transport of wastes with significant moisture content, thus impeding their reasonable use. To avoid added costs related to disposal process, tomato manufacturing companies often give their production residues for free to other companies that generally use them for feeding livestock [11] or as soil amendment [28]. However, Rossini et al. [29] found that tomato waste could be suitable for combustion, but the relatively higher nitrogen content can generate environmental problems in terms of NO\(_x\) emissions. In addition, the high chlorine and sulfur contents may lead to the corrosion of the combustion systems. Therefore, as a solution, the authors proposed to separate tomato waste into peels for combustion and seeds for vegetable oil production.
González et al. [30] studied the tomato waste combustion in a mural boiler. They found that tomato residues give higher boiler efficiency than other biomasses (forest residues, sorghum, almond pruning, and reed). Ruiz-Celma et al. [11] studied tomato seeds and peels pellets. They reported a high heating value of these pellets and an energy density (approaching 8 GJ/m$^3$) similar to that of other biomass pellets, regardless their low bulk density values.

3. Techniques for biomass densification

Biomass is densified via two main processes: pelletizing (mechanical densification) and torrefaction. Pelletizing involves applying pressure to mechanically densify the material, while torrefaction involves heating the biomass in the absence of oxygen.

3.1. Pelletizing

The low density of agricultural residues poses a challenge for the handling, transportation, storage, and combustion processes. Those problems are mainly related to the high bulk volume, which results in high transportation costs and demands for large storage capacities, and to the high moisture content which results in freezing and blocking the in-plant transportation systems, as well as in biological degradation. In addition, variations in moisture content make difficult optimal plant operation and process control. All these problems may be addressed through densification, a process that produces solid fuel with denser and more uniform properties than the raw biomass [31].

The main advantages of densified compared to non-densified fuels are the following:

- Reduced cost of transportation due to increased bulk density (from 80–200 to 600–700 kg m$^{-3}$).
- An increased energy density, resulting higher energy efficiency.
- Simplified mechanical handling and feeding.
- Uniform combustion in boilers resulting in lower emissions during combustion.
- Reduced dust production.
- A lower moisture content (lower than 10%), favoring a long conservation and less loss of product during storage.
- Reduced possibility of spontaneous combustion in storage.
- Simplified storage and handling infrastructure, lowering capital requirements at the combustion plant.

All these factors make pellets one of the more attractive forms of biomass-based energy. The major disadvantage to biomass densification technologies is the relative high energy cost for the pelleting process, increasing the price of the end product. In addition, it is important to have in mind that agricultural residues are highly dispersed and may be over long distances.
from the pelleting facilities. An appropriate solution could be to carry the pelleting mill to the raw material. A few mobile pelleting mills already exist. Such a pelleting mill can meet a specific demand, for instance several farmers wanting to share the investment cost of a pelleting equipment which after can be moved from a place to another [32].

The process of pellet manufacturing was first developed for the livestock feed industry. The process consists of a few basic sub-processes: comminuting of the raw material, drying, pelleting, and cooling. The raw material is first cleaned of contaminant such as rocks, metals and other foreign material, and then grinded in a hammer mill or a chipping machine. The particle size is adjusted to a uniform maximum dimension and should have proper size and be consistent. The moisture content in the raw material can be considerably high and are usually up to 50–60% which should be reduced. Rotary drum dryer is the most common equipment used for this purpose, where the moisture content of the uniformly dimensioned particles is reduced to about 10–15% (w.b.). Drying increases the efficiency of biomass, and it produces almost no smoke on combustion. The feedstock should not be over dried, as a small amount of moisture helps in binding the biomass particles. The drying process is the most energy intensive process and accounts for about 70% of the total energy used in the pelletization process. Thereafter, raw material can be conditioned according to legal specifications (i.e., steam or organic binding agents can be added). The particles are then moved by conveyor to a pellet mill, where the pellets are compressed against a heated metal plate (known as die) using a roller. Due to the high pressure, frictional forces increase, leading to a considerable rise in temperature (90–100°C), and are immediately air quenched down to 25°C. High temperature causes the lignin, and resins present in biomass to soften which acts as a binding agent between the biomass fibers. This sets up the lignin and hardens the product, and contributes to maintain its quality during storage and handling. On the outer side of the latter, a knife cut off the pellets at the desired length. Residual moisture in the feedstock turns to steam during compression and helps to lubricate the compression die [33].

Finally, the pellets are packed into bags using an overhead hopper and a conveyor belt. Pellets are then ready for storage (in a silo) or for automatic packing (in 25 kg bags or big bags—1 to 1.5 m$^3$). Commercial pellet mills and other pelleting equipment are widely available worldwide.

3.2. Torrefaction

Torrefaction is a very promising technology for improving the fuel properties of solid biomass (e.g. pellets). This technology is a version of slow pyrolysis processes that comprise the heating of biomass in the absence of oxygen and air [30, 34] in which the goal is to dry, embrittle, and waterproof the biomass. This is accomplished by heating the biomass in an inert environment at temperatures of 200–320°C. During the treatment, biomass starts to decompose and releases combustible volatile matter, mainly composed by organic compounds, together with moisture. Biomass loses most of the low-energy content material in the form of gaseous and condensable liquids. Common events that occur during torrefaction include drying, depolymerization and recondensation, limited devolatilization and carbonization, and extensive devolatilization and carbonization [35]. Several studies have been conducted to evaluate a combined torrefaction-
pelletization process possible in a commercial scale. Reed and Bryant [36] first considered the combination of torrefaction and pelletization to produce a new type of high energy density and water-resistant pellets. Bergman [37] proposed and demonstrated a combined torrefaction and pelletization process for the production of high energy density wood pellets. The addition of pelletization to torrefaction would potentially create a bio-based fuel with similar energy density to coal, prompting the adoption of this product for replacing coal in heat and power facilities. Currently, a number of torrefaction pilot plants have been designed, under construction, or publicly announced [38]. Carapeda [35] reports that if the biomass is torrefied before being densified, the energy consumption during the pelleting process is reduced by a factor of 2 and the throughput is increased, also by a factor of 2.

The main advantages of torrefaction of raw biomass feedstock include:

- Increase in energy content and heating value of the final torrefied product by reducing O/C and H/C ratios.
- Decrease in moisture content, which provides two main benefits: (i) reduced transportation costs associated with moving unwanted water and (ii) the prevention of biomass decomposition and moisture absorption (biomass becomes hydrophobic) during storage and transportation, which in turns helps in preserving the quality of the product.
- Improved grindability and friability (80–90% less energy consumption for grinding).
- Torrefied pellets have more strength (1.5–2 times impact load and does not disintegrate easily during handling and storage).
- Overall improvement in the chemical composition of the biomass (smoke-producing compounds removed).

The main disadvantage of torrefaction of raw biomass feedstock includes additional cost, energy, and equipment required for processing. In addition, ash content is not removed so ash content would likely increase per unit of weight [35]. Therefore, torrefaction can be considered as one of the major pretreatment technologies for improving the properties of agricultural residues, in order to deal with such problems as high bulk volume, high moisture content, and poor grindability.

4. Combustion of agripellets

Physical and chemical properties vary significantly within and between the different agricultural raw materials. Depending on the type of application, these variations may be critical and may affect the performance of the system. Physical properties, such as bulk density, moisture content, particle size and distribution, and durability, are important for the choice of processes and equipment. On the other hand, chemical properties are of great importance for the energy efficiency, environmental pollution, and ash-related operating problems.

Agripellets combustion triggers several major obstacles regarding emissions (gas, dust, and aerosols), deposit formation (slagging, fouling), and corrosion. Another problem is that the
ash content of agripellets is higher than wood pellets (about 2–10 times higher than that of wood pellets). All those problems not only depend on the fuel characteristics but also on the design of the combustion equipment and the way it is operated. Recently, Kraiem et al. [12] reported that silicon (Si), potassium (K), calcium (Ca), magnesium (Mg), phosphorous (P), and aluminum (Al) are the major elements of agripellets. Compared to wood pellets, a typical feature of agripellets is their higher content in nitrogen (N), sulfur (S), chlorine (Cl), and K, increased by the use of fertilizers and pesticides/herbicides in agriculture. The presence of those elements leads to relatively important emissions of NOx, SOx, and HCl compared to wood pellets. In addition, K influences both particulates emission and slagging (by lowering the softening temperature of the fuel) of an increased ash volume. Besides, a high Cl content results both in corrosion problem on the surfaces of the boiler and in formation of dioxins and furans. Finally, for a large-scale use, in relation with the high ash content and the low melting point, it has been stated that straw pellets could present better results with grate combustion or fluidized bed systems. Those problems can be overcome by the use of multi-fuel boilers in the range of 10–60 kW which is more suitable for burning agripellets; co-firing of agricultural residues with fossil fuel; cleaning the agricultural residues before pelletizing them into agripellets to make them with less ash content; and to add in specific anti-slagging agents (e.g., kaolin) or mix in some sawdust to change the fuel characteristic.

Environmental and technical features of combustion technologies indicate that pellets made from agricultural residues should be used primarily in large-scale combustion plants equipped with sophisticated combustion control systems and flue gas cleaning systems, whereas wood pellets should be preferred for small-scale heating systems. In the future, the main technical challenges regarding agripellets are the production of a high-quality fuel, and technological improvement for small-scale combustion devices.

4.1. Emissions

During combustion, N, S, and Cl in the fuel (present in higher proportion in agripellets than in wood pellets) may lead to atmospheric pollutants such as nitrogen oxides (NOx), sulfur dioxide (SO2), hydrogen chloride (HCl), and chlorinated hydrocarbons. Moreover, Cl favors the formation of dioxins and furans. The incomplete combustion of agripellets is mainly the result of low combustion temperatures, short residence times, oxygen shortage, or combinations of these effects. Incomplete combustion results in emissions of carbon monoxide (CO) and volatile organic compounds (VOC), particles, tar, and polycyclic aromatic hydrocarbons (PAH). Zeng et al. [39] demonstrated that the emission of NOx, SO2, HCl, and total particulate matter can be reduced by blending agricultural raw materials with woody biomass though substantial reduction potential was only observed for blends with at least 50 wt% wood.

In addition, ashes formed during agripellets combustion can generally be divided into bottom ashes, coarse fly ashes, and aerosols (fine fly ash). These fractions differ significantly concerning their particle size and chemical composition as well as their formation mechanisms. The bottom ash is the ash fraction remaining in the furnace after combustion of the fuel and is then removed by the de-ashing system. Coarse fly ashes are particles entrained from the fuel bed with the flue gas. They mainly consist of refractory species (such as Ca, Mg, Si as well as
small amounts of K, Na, and Al), and their particle sizes can vary between some μm and 100 μm. Particles that are small enough to follow the flue gas on its way through the furnace and the boiler finally form the coarse fly ash emission at the boiler outlet. Aerosols are formed by gas-to-particle conversion processes in the furnace and in the boiler. Some of the aerosol particles coagulate with coarse fly ashes due to collisions [33]. During combustion of agripellets, part of the volatile compounds is released from the fuel to the gas phase: aerosols are then formed by condensation or nucleation of these volatile compounds. Aerosols are much smaller than coarse fly ash (typical particle size significantly <1 μm). Aerosol emissions present high concentrations of heavy metals and sometimes of organic compounds. By their dimension, they can remain suspended in the air for long period of time and enter into the inner parts of lungs. In small-scale pellet furnaces and boilers, the main ash fraction is bottom ash. Furnace and boiler ash form the major share of coarse fly ash, which is usually precipitated and mixed with the bottom ash. A small amount of course fly ash is emitted with the flue gas [33].

4.2. Deposit formation

Biomass boiler issues regarding slagging, fouling, and corrosion are related to alkali species present in agricultural residues. These alkali species are released as gaseous alkali chlorides, hydroxides, and/or sulfates during combustion. Alkali chlorides/sulfates later condense on cold boiler surfaces enhancing fouling and corrosion. This is referred to as slagging when the deposits are in a molten or highly viscous state, or fouling when the deposits are built up largely by species that have vaporized and then condensed. Slagging is often found in the radiant section of the furnace, while fouling occurs in the cooler furnace regions where the heat exchanger equipment is located [40]. The negative effects of slagging and fouling are high furnace material wear, heat transfer efficiency reduction with pressure drop, and increased corrosion of the boiler.

Potassium and sodium compounds are present in all agricultural residues. During combustion, these alkali compounds combine with silica and causes slagging and fouling problems in conventional combustion equipment designed for burning wood at higher temperatures. Volatile alkali also lowers the fusion temperature of ash; combustion of agricultural residue causes slagging and deposits on heat transfer surfaces. In order to overcome this problem, special boilers have been designed with lower furnace exit temperatures or low operation temperature. These designs can reduce slagging and fouling from combustion of agripellets.

Hence, this underlines the necessity of a careful treatment of raw materials so as to avoid mineral contamination. Deposit formation related problems affecting agripellets deserve a special attention because they lead to reduced accessibility of the appliances, and also to bad publicity for the agripellet market.

4.3. Corrosion

The presence of even a small concentration of Cl in fuel will result in the formation of alkaline chloride compounds on boiler surfaces. Chlorine can influence the corrosion of superheater tubes in many ways. Gases containing Cl₂, HCl, NaCl, and KCl may cause a direct corrosion
by accelerating the oxidation of the metal alloys. Such gases may also influence the corrosion caused by other mechanisms, such as molten alkali sulfate corrosion of superheater alloys and sulfidation of water walls. In addition, Cl may also deposit on superheater tubes and thereby influence its corrosion [41]. Chlorine corrosion could be prevented by co-firing aluminum silicates containing fuel, such as coal or peat. When those fuels are co-fired with agricultural residues, chloride formation can be avoided. In addition, a parameter that has been often referred to is the sulfur-to-chlorine atomic ratio (S/Cl) in fuel or fuel blend. It has been suggested that if this ratio in fuel is less than two, there is a high risk for superheater corrosion. When the ratio is at least four, the blend could be regarded as noncorrosive. However, the best way to prevent the molten phase corrosion is to keep superheater metal temperature below the first melting temperature of deposits, in practice below 500°C when firing agripellets [32]. Several field studies have shown that the main contributor to superheater corrosion in boilers is Cl, in particular alkali chlorides (NaCl, KCl). The relatively low sulfur content in most agricultural residues may introduce corrosion problems in the superheaters.

### 4.4. Ash recycling for agricultural applications

The rapidly growing number of pellet heating installations illustrates an increased interest in environmentally friendly heating systems. The problems associated with the use of agripellets are essentially linked to the ash management. Thus, the recycling or storage of agripellets ash deserves a special attention.

Ash is the inorganic uncombustible part of fuel left after complete combustion and contains the bulk of the mineral fraction of the original biomass [42]. In wood pellets, ash represents less than 2%, while in agripellets, it can be 5–10% and up to 30–40% in rice husks and milfoil [43].

The first and direct consequence for small scale stoves and boilers of the increased ash residue with agripellets is that there the ash storage under the furnace will have to be emptied more frequently, which is quite negative as far as the convenience of users is concerned. Considering that the ash storage should normally be emptied once every 5–15 days with wood pellets depending on the consumption, agripellets would oblige to remove ashes more frequently (almost daily). On the other hand, James et al. [43] suggest that inefficiencies in boilers and furnaces result in high percentages of unburned organic matter in ash. This carbon content may be recycled to the boiler or furnace to improve energy output and increase the process efficiency.

Part of the ash is taken out in the bottom of the boiler and is called bottom ash while the remainder is composed of the fine particles that are driven out of the boiler with the flue gases. This part of the ash is called fly ash. Each ash fraction has different composition. Filter fly ash tends to accumulate the largest part of heavy metals. Ashes from agripellets are produced in higher quantities, but the content in heavy metals for each fraction seems to be lower.

The collected bottom ash and fly ash from the combustion of agripellets should be disposed of in a safe way. These ashes contain nutrients, primarily potassium, and other soil-fertilizing elements like magnesium, phosphorus, and calcium and can therefore be applied in agriculture.
as fertilizer. It seems that ash is strongly alkaline (pH of 11–12) and could cause sharp increase of pH and ion concentration in the soil after spreading [32]. Thus, ash should not be used unless a soil pH test has been done. Such a phenomenon would be harmful with respect to plant growth. Consequently, ash could be treated (e.g., granulated) in some way to reduce impact on soil. In regard to acidic soil correction, agripellets ashes as a garden amendment are a much more convenient means than the traditionally used ground limestone, bearing in mind that it is an absolutely costless resource.

In order to utilize the nutrients from the fly ash, a utility owned plant has developed a method for washing them leaving heavy metals behind in a fraction to be stored. The product is a valuable fertilizer, and the process could be carried out centrally using fly ash from both utility owned plants and district heating plants.

According to Gomez-Barea et al. [44], the utilization of ash has also seen its application in the construction industry. Fly ash can be used as a cement replacement in concrete, for soil stabilization, as a road base, structural filler in asphalt and asphalt base products, lightweight bricks and synthetic aggregate.

5. Pellets quality standards

The combustion of densified biomass fuels in fully automatic heating systems for residential sector and small-scale furnaces requires high fuel quality. However, high quality is not necessary if these fuels are used in larger industrial furnaces because they are equipped with more sophisticated flue gas cleaning, combustion, and process control systems. Pellets are a standardized fuel, which simplifies construction and operation of burners. For pellets, producers are very important to have quality standardization because it increases the customer confidence. However, the quality of the pellets should be defined in terms of the heating technology, since different heating systems require different fuel qualities. For example, large heating plants are not demanding in terms of pellets durability or amount of fines. In contrast, pellets stoves require an extremely durable pellet, which does not produce too much dust in the storage bunker, and do not cause technical problems in the feeding and combustion unit. From this perspective, the different quality of agripellets would suggest a different use, preferentially in large-scale systems [45].

In the present, the development of quality standards for wood pellets is set on five different levels in Europe: (1) European Commission and European Committee for Standardization; (2) EU member state governments; (3) European Biomass Association and European Pellet Council (which represent the European biomass sector); (4) Wood Pellet Buyers Initiative (which represents end users of biomass); and (5) standards developed by individual private companies [46]. Standards exist on national (e.g., DIN), European (EN), and on international level (ISO).

Usually, standards developed by standards organizations are voluntary but can become mandatory if adopted by a government or business contract.
According to European Standard ENplus which is related to wood pellets for nonindustrial use and which will gradually supersede all national standards (e.g., ÖNORM M1735, or DINplus), wood pellets can be classified into three basic categories: ENplus A1, ENplus A2, and ENplus B. The quality requirements of ENplus are based on an international standard: ISO 17225-2. This international standard has replaced the European Standard EN 14961-2. The ENplus certificate requires stricter quality criteria. This quality seal stands for low emissions and trouble-free heating with high energy value.

Class A1 includes wood pellets originating from stem wood, without chemical additives and with low ash and Cl content. Class A2 considers wood pellets with slightly higher ash and/or Cl content. Wood pellets derived from reused wood, residues, or bark are included into class B. Table 2 shows the specifications of the three wood pellet classes according to ENplus in comparison with German (DIN-plus) and Austrian (ÖNORM M7135) standards.

<table>
<thead>
<tr>
<th>Property</th>
<th>DIN plus</th>
<th>ÖNORM M 7135</th>
<th>ENplus A1</th>
<th>ENplus A2</th>
<th>ENplus B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter (mm)</td>
<td>4 ≤ d ≤ 10</td>
<td>4 ≤ d &lt; 10</td>
<td>6 (±1)</td>
<td>6 (±1)</td>
<td>6 (±1)</td>
</tr>
<tr>
<td>Length (mm)</td>
<td>≤5 × d</td>
<td>5 × d</td>
<td>3.15 ≤ L ≤ 40</td>
<td>3.15 ≤ L ≤ 40</td>
<td>3.15 ≤ L ≤ 40</td>
</tr>
<tr>
<td>Ash content (wt%)</td>
<td>&lt;0.5*</td>
<td>&lt;0.5*</td>
<td>≤0.7</td>
<td>≤1.5</td>
<td>≤3.0</td>
</tr>
<tr>
<td>Ash melting behavior (°C)</td>
<td>Not specified</td>
<td>Not specified</td>
<td>≥1200</td>
<td>≥1100</td>
<td>≥1100</td>
</tr>
<tr>
<td>Moisture (%)</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>≤10</td>
<td>≤10</td>
<td>≤10</td>
</tr>
<tr>
<td>Net calorific value (MJ kg⁻¹)</td>
<td>≥18</td>
<td>&gt;18*</td>
<td>≥16.5</td>
<td>≥16.5</td>
<td>≥16.0</td>
</tr>
<tr>
<td>Fines (wt%)</td>
<td>≤1</td>
<td>Not specified</td>
<td>≤1</td>
<td>≤1</td>
<td>≤1</td>
</tr>
<tr>
<td>Mechanical durability (wt%)</td>
<td>≥97.7</td>
<td>Not specified</td>
<td>≥97.5</td>
<td>≥97.5</td>
<td>≥95.5</td>
</tr>
<tr>
<td>Chlorine (wt%)</td>
<td>≤0.02</td>
<td>Not specified</td>
<td>≤0.02</td>
<td>≤0.03</td>
<td>≤0.03</td>
</tr>
<tr>
<td>Arsenic (mg kg⁻¹)</td>
<td>Not specified</td>
<td>Not specified</td>
<td>≤1</td>
<td>≤1</td>
<td>≤1</td>
</tr>
<tr>
<td>Cadmium (mg kg⁻¹)</td>
<td>Not specified</td>
<td>Not specified</td>
<td>≤0.5</td>
<td>≤0.5</td>
<td>≤0.5</td>
</tr>
</tbody>
</table>

* dry mass

Table 2. Comparison of regulations related to pellet quality.

Generally, limit values for ash content, moisture, net calorific value, and chlorine are fairly similar. All standards prohibit the use of binding agents. Austrian and German standards do not mention the amount of fines, while in Enplus, fines must not be more than 0.5–1.0%. German and Austrian standards do not define durability or mechanical stability despite the importance of these attributes. This is because during transport in tankers and the pneumatic filling of storage bunkers, mechanical strain on pellets is high. In addition, pellets with poor mechanical stability produce large amounts of dust. Hence, small heating systems require very high pellet quality. In these systems, the amount of fines in fuel pellets is of special importance. In contrast, combustion units in large heating systems are not affected by the amount of fines. The different requirements of small and large combustion systems make necessary definition of different groups of standards [32].
6. Conclusions

The increasing competition for solid biomass, such as wood pellets, will create space for relatively novel biomass sources to enter the market, among which agricultural residues have the greatest potential. In comparison with wood, agricultural residues present high ash, N, K, and Cl content. The underlying problems are higher related emissions, deposit formation and corrosion. Many techniques are currently used, while others are under improvement stage to overcome the inherent drawbacks of agripellets composition. These techniques include agricultural practices, fuel preparation, combustion technologies, flue gas cleaning systems, and the possibility of co-combustion of agripellets with solid fossil fuels. ENplus quality certification is a major step toward establishing biomass pellets as a widely used energy source. However, the high nitrogen and ash contents strongly limit the certification of pure agripellets. In this regard, several studies have shown that blending agricultural residues with sawdust before pelleting could help to meet ENplus certifications.

Consequently, the use of agripellets in the residential heating sector cannot be recommended at present, because small-scale pellet furnaces are not specially designed for this kind of fuel. Therefore, for small-scale heating systems, which require high-quality fuels, the use of wood pellets is recommended. Agripellets should be used primarily in large-scale combustion plants equipped with sophisticated combustion control systems and flue gas cleaning systems.

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References


