DELIVERABLE D2.1

Biomass selection and characterization for small-to-medium scale gasification-SOFC CHP plants

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TABLE OF CONTENT

LIST OF FIGURES

LIST OF TABLES

1 EXECUTIVE SUMMARY

This report summarise the work made in order to understand the potential waste **biomass** in Europe and to select among them the waste biomass most suitable for gasification considering <u>availability</u> on significant scale (t/year), good technical (<u>physical</u> (low water content and high bulk density) and <u>chemical</u> (high Caloric Value, high volatile substances, low ash, high Carbon to Nitrogen ratio, low Chlorine and Sulphur content)) and <u>economic</u> (selling cost at production site plus transport cost) characteristics and to <u>characterise</u> (proximate and ultimate analysis, elements determinations, ignition and burn-out temperatures, ashes characterization) the waste biomass selected as representative. In particular, this report, shows the work undertaken under the <u>Task 2.1, Biomass supply</u> led by USGM and the <u>Task 2.2, Feedstock characterisation</u> led by ENEA of the <u>WP2, Gasification & conditioning tests</u>, of the BLAZE project by USGM (5 MM), ENEA (4 MM), EUBIA (4 MM) and UNIVAQ (1MM).

This report is composed of the following parts:

- **Chapter 2, Introduction**, quotes a brief introduction on biomass and gasification definitions and related characteristics;
- **Chapter 3, Biomass specifications for gasification,** quotes a short description of the main biomass specifications for gasification;
- **Chapter 4, Biomass feedstock**, describes the biomass availability and cost on the EU 28 countries by groups and subgroups and regions;
- **Chapter 5, CHP potential**, summarises CHP plants widespread over EU in the capacity range from 25-100 kWe (small scale) to 0.1-5MWe (medium scale);
- **Chapter 6, Supply chain cost**, describes the supply cost for different biomass category;
- **Chapter 7, Biomass selection**, selects 10 samples and 5 mixtures representative of the most available European biomass species that will be characterized in chapter 8 and gasified in Task 2.3 (D2.2) in order to asses syngas composition and contaminants that affect SOFC and related gasifier parameters and bed materials to reduce SOFC hazardous effects;
- **Chapter 8, Biomass characterization**, quotes the chemical and physical characterization of the waste biomass selected, illustrating the protocols used, the proximate/preliminary and ultimate/elemental analysis, the elements determinations, ignition and burn-out temperatures, ash melting behaviour and thermophysical characterization;
- **Chapter 9, Conclusions**, quotes a comprehensive discussion and outlook;
- **Chapter 10, References**, quotes the references of all the report.

At the end there are 15 pages that quotes, as **Annex I and II**, the experimental results on ignition/burn out temperatures and TGA of ashes.

2 INTRODUCTION

The general definition of **biomass** (from dictionary, i.e. from first documents in 1930-1980) is "**organic matter (available on a renewable basis) that can be converted into energy**" (different from biomass in ecology where it encompass all the organic matter in a given habitat). More in detail, Directive (EU) 2001/77/EC on the promotion of the use of energy from renewable sources (always Article 2 Definitions, after repeated in Directives 2003/54/EC repealed by 2009/30/EC on biofuels and used by 2014/94/EU on alternative fuels infrastructure; and repeated in Directives 2003/54/EC repealed by 2009/28/EC and amended by 2018/2001 on RES [1]) states that biomass refers to "the **biodegradable fraction of products, waste and residues from biological origin** from agriculture including vegetal and animal substances, from forestry and related industries, including fisheries and aquaculture, as well as the biodegradable fraction of waste, including industrial and municipal waste of biological origin" ("biological origin" and "fisheries and aquaculture" added in 2009). According to these definitions, biomass resources include a wide range of materials, e.g. wood chips, straw, miscanthus, poultry waste, sewage sludge, etc., which have diverse physical and chemical properties.

Biomass is the fourth world-wide energy resource (following oil, coal and natural gas) but the energy use of the organic substances is limited by their low energy density, complexity of the supply chain (often in competition with the main uses of organic matter, as food and materials), low reliability and efficiency (owing to the use of a complex substance) and high local emissions of pollutants [2]. Indeed, the technical and economic potentials of biomass are higher than the current world energy consumption, thus, the challenge is in its viable and sustainable use and not in its availability (as long as there is life there will be availability of organic material, used "directly" by living organisms as their own source of energy and materials (food) or used "indirectly" like a source of external energy (biomass) and materials: (clothing, furniture, buildings, chemicals, etc.) [3]. To really exploit the biomass energy potential, reliable, high efficiency and low environmental impacts small scale plants have to be developed, to follow the low energy density and perishability of this fuel. Using biomass wastes as feedstock in reliable, efficient and low emissions micro to medium plants (as gasification-fuel cells) would solve all the old-actual drawbacks associated to biomass utilization as energy source (i.e. competition with food and materials avoided owing to the waste nature; low energy density and perishability not important owing to the micro to medium scale; low cost and missions owing to the high efficiency and low emissions gasification-fuel cells coupling) [4].

Gasification, which is the thermal decomposition (typically above 650 °C) of biomass in the presence of gasification agents, e.g. air, oxygen, steam, CO_2 or a combination of them that transforms biomass into so-called bio-syngas that contains CO, H_2, CH_4, steam, CO_2, light hydrocarbons and, in case of air gasification, nitrogen (N_2). The fuel gas may contain a certain amount of impurities, e.g. tar, particulate matter, char, hydrogen sulphide (H_2S) and/or hydrogen chloride (HCl) [2].

The type of solid feedstock has a significant impact on the technology for gasification: biomass suitable is typically characterised by an availability on significant scale (from few dozens to few thousands t/year) and by low cost (e.g. from negative to maximally 100 €/t) but also by overall good physical (low water content and high bulk density) and chemical (high calorific value, high volatile substances, low ash, high carbon to nitrogen ratio, low chlorine and sulphur content) properties. The new technologies applied in BLAZE, i.e. Double Bubbling Fluidised Bed gasifier (DBFBG) with inserted sorbent and catalysts, can in addition treat material with high humidity content (up to 50%), low ash melting temperature, high tar, sulphur and chlorine content. Thus, the integration of DBFBG, hot gas conditioning and SOFC will allow the conversion of a greater variety of low cost biomass wastes at almost zero emissions to heat and power with high efficiencies, largely improving both the environmental impacts and its social acceptance.

Individuating availability and cost of sustainable biomass feedstock is necessary for large scale deployment of bioenergy technologies: thus according to the aim of task T2.1 "Biomass supply", most promising residual feedstock, biomass and biogenic fraction of wastes, were selected based on an initial assessment of biomass availability at European level (EUBIA data). Representative samples of each kind of selected feedstock were then collected and submitted by ENEA to physical and chemical characterizations within Task 2.2 "Feedstock characterisation". The considered specific analysis were selected in order to provide the data relevant to evaluate their potential exploitation and performances in processes of thermochemical gasification. Specifically, the selected feedstock were submitted to proximate and ultimate analysis, including S and Cl, HHV and LHV measurements. Since the properties of the produced ash at high temperature is relevant to the proper operation of a gasification reactor, additional studies were carried out in order to assess the potential risks of ash softening/melting and fly ash production, respectively possible causes of loss in fluidization of the gasification bed inventory and pipes, and downstream equipment fouling.

Analysis of major and minor chemical elements was included in order to get preliminary feedback on the presence of elements that, in particular in combination with Cl, could lead to formation of inorganic vapors (e.g. metal halides) dangerous for the smooth operation of the SOFC. Finally, such analysis was also included in view of successive and more general assessment on the subject of waste management, with the aim of evaluating how to consider the solid streams, such as ash and dust, expected to be produced at the BLAZE gasification plant.

3   BIOMASS SPECIFICATION FOR GASIFICATION

In general, the first element to consider in assessing viable biomass uses is the energy and economic feedstock production costs. The first one is evaluated by Energy Return On Energy Investment, EROEI, in GJ/GJ while the second one is evaluated by the production cost in mass (€/t) divided by the useful Heating Value (HV in GJ/t), thus is expressed in €/GJ. The feedstock price is the largest component of the operating costs in a biomass plant and varies from negative price of some waste biomass (e.g. -100 €/t of particular biomass contaminated waste) to high price of some dedicated crops (e.g. 500 €/t of particular crops). Considering an average energy yield value of 100 GJ/ha (e.g. average yield of 10 t/ha and average heating value of 10 GJ/t), for a value of 10 GJ/ha for cultivation and harvesting, the energy production cost is 0.1 (EROEI of 10 because I used 10 GJ to have 100 GJ) while a mean economic cost (e.g. HV 10 GJ/t and 40 €/t) is about €4/GJ. These average optimistic values include, among other items, transport energy and its economic costs of 0.5 MJ/km and 0.02 €/km per ton [5]. Lower yield and lower HV biomass do not have proportionally lower costs meanwhile it is possible to have higher energy and economic cost; therefore, the energy and economic returns could become negative (i.e. EROEI less than 1 and production cost higher than the one of fossil fuels) [6]. For this reason (that include also less environmental impacts because only a portion of the impacts can be attributed to the waste) and for not competing with food and biomaterial organic matter uses, it is preferable to use low cost residual biomass. The main residual biomasses are:

1. Forestry, arboricoltural and agricultural residues (i.e. organic matter produced on the ground as tree pruning, straw);
2. Agro-industrial residues (i.e. organic matter produced in farm/industry plants as fruit shells);
3. OFMSW (waste paper, etc.);
4. Sludge and manure.

In some documents residue and waste are synonym but in others residue is more associated to by-product (so has a higher economic value but always inelastic supply respect to elastic supply of product and by-product) meanwhile waste has no or negative economic value. Thus, in this report we consider residue and waste as synonym eve if, normally, OFMSW (Organic Fraction of Municipal Solid Waste) and sludge/manure, are more considered as biomass waste meanwhile forestry and agro and industrial organic residues as biomass residues. Of course, regarding CHP use, the agro-industrial residues (or OFMSW or sludge and manure) that can be used in the plant where are produced that, on average, needs heat and power, are preferred. Among agro-industrial residues, we can mention food, textile and wood and paper industrial residues like shells, husks, pomace, bagasse, sugar beet pulp, textile and dyeing residues, sawdust and black liquor. Among fruit shells the main used are the shells of pine, hazelnut, walnuts and almonds. Among forestry, arboricoltural and agricultural residues the main pruning are of beech, oak, spruce, poplar, willow, eucalyptus, grape and olives; meanwhile the main

straw are of wheat, corn, rye, barley, rice. In every energy conversion process, because of energy needs in terms of efficiency and power density, fuels with a high LHV are favourites. Thus in the thermochemical processes as gasification, in particular, this meaning that biomass with lower humidity is preferable. Seasoning can reduce the moisture content, or the excess of heat produced by the power plant could be exploited to dry biomass in order to use also biomass with 50% of moisture. The density affects significantly any freight and storage. Furthermore, in fluidized bed gasifier to have a good mixing between fuel and bed material, the biomass density should be comparable with that of the bed. Another important feature that must be considered is the size and shape of the biomass feeding the gasifier. Biomass must be processed to a uniform size or shape to feed into the gasifier at a consistent rate and to ensure homogeneous and efficient gasification. This can lead to significant costs for the shredding: chip size (1-2 cm) is at the moment the right compromise. The chemical composition (C, O, H, N, S, Cl) is another important aspect that must be considered. For lignocellulosic biomass the chemical composition (expressed on a dry and ash free basis) is generally more constant (C around 40-50%, O 30-45%, H 5-6%, N 0,1-1%, S and Cl 0,01-0,2%) than that of other solid fuels (MSW, coal). Furthermore, more than 80% of the biomass is volatile the remaining 20% is charcoal. Coal is typically only 20% volatile, while the remaining 80% is unreactive coke, which is more difficult to gasify than charcoal. Generally, lignocellulosic biomass has very low Sulphur and Chlorine content compared to coal and MSW. Finally, ash and TAR contents are one of the main obstacles to economical and viable applications of biomass gasification technologies. Fuels with a high ash content require greater attention because ash brings sintering, agglomeration, deposition, erosion and corrosion problems. Furthermore, they are elutriated by the producer gas, thus more is the ash content and much more problematic will be the gas cleaning procedures. TAR condenses as the temperature decreases, causing clogging and damage to the downstream equipment [7]. To sum up, the most suitable biomass for gasification must have availability on significant scale (t/year) and a good physical (low water content and high bulk density) and chemical characteristics (high Caloric Value, high volatile substances, low ash, high Carbon to Nitrogen ratio, low Chlorine and Sulphur content). The focus so can be assumed initially on lignocellulosic biomass waste like "shells" (of pine, hazel, walnuts and almonds); "pruning" (of wood/forestry/agricultural "threes", thus: beech, oak, spruce, poplar, willow, eucalyptus, grape, olives); "straws" (of wheat, corn, rye, barley, rice); agro-industrial residues (e.g. dry exhausted olive). Among these, shells have the more suitable characteristics (low humidity content not great variable, high density, low ash content, high calorific value). Prunings have a greater variation of the characteristic. Straws/agro-industrial residues not only have a larger characteristic variation, but also a higher ash content that in many cases bring to a melting temperature lower than the gasification temperature and thus clog the reactor. Regarding the C, H and O chemical composition, as already written, the lignocellulosic biomass has almost the same wt percentage (respectively 40-50, 5-6, 30-45). N, Cl, S accounts for very low percentages that vary depending on the biomass typologies and cultivation characteristics (soil, fertilizers, etc.). In summary,

lignocellulosic waste as the almond shell, with heating value of 18 MJ/kg and a price of 75 €/t (an average lignocellulosic price between the low cost agro-industrial residues and pruning and the higher cost of energy cultivation at the sizes considered, i.e. 0,1-10 MWth input) can be surely one of the representative biomass to be considered for gasification process in BLAZE.

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4 BIOMASS FEEDSTOCK

4.1 Methodology (EUBIA)

The potential availability of biomass from agriculture, forestry and waste has been investigated by many past and recent studies and many references are available in the scientific literature for this subject. For the scope of this document both the datasets and the elaborated results provided by the S2Biom project were used [8]. S2Biom was a collaborative research project supported by the European Commission under the 7th Framework Programme which run between 2013 and 2016, to develop an integrated design and evaluation of optimal biomass delivery chains and networks at European, national, regional and local scale. In this context the S2Biom project carried out a thorough data collection and an estimation of sustainable biomass potentials based on the adoption of an advanced methodological approach and on the use of a computerised toolset. The toolset contains fully populated databases at local, regional and pan European levels. The data were assessed for the years 2012, 2020 and 2030 and different scenarios of biomass potentials were created. For this study, the data of the "base potential" of biomass were used, for which the quantification of the available biomass potential take into account the agreed sustainability standards in the Common Agricultural Policy (2014-2020) for agriculture, land management and forestry management plans for forests, as well as the restrictions to biomass use resulting from the sustainability criteria introduced by the Renewable Energy Directive (EC Directive 28/2009). The data and figures included in this document and presenting the estimation of the regional distribution of biomass energy potential expressed in GJ/km2 were elaborated using the biomass supply viewer tool developed by Wageningen University of Research and available at the S2Biom project website0F[1]

4.2 Biomass availability

Here are presented the data extracted by the S2biom database (www.s2biom.eu) about biomass availability by feedstock at European level for EU28. All the biomass has been categorized in the following:

- – Primary residues from forest
- – Agricultural residues
- – Secondary residues from wood industries
- – Secondary residues of industry utilising agricultural products
- – Municipal waste
- – Waste from wood

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[1] https://s2biom.wenr.wur.nl/home

－ Digestate from biogas production1F[2]

The total biomass potential availability is equal to 678,878 kton/year (dry mass basis).
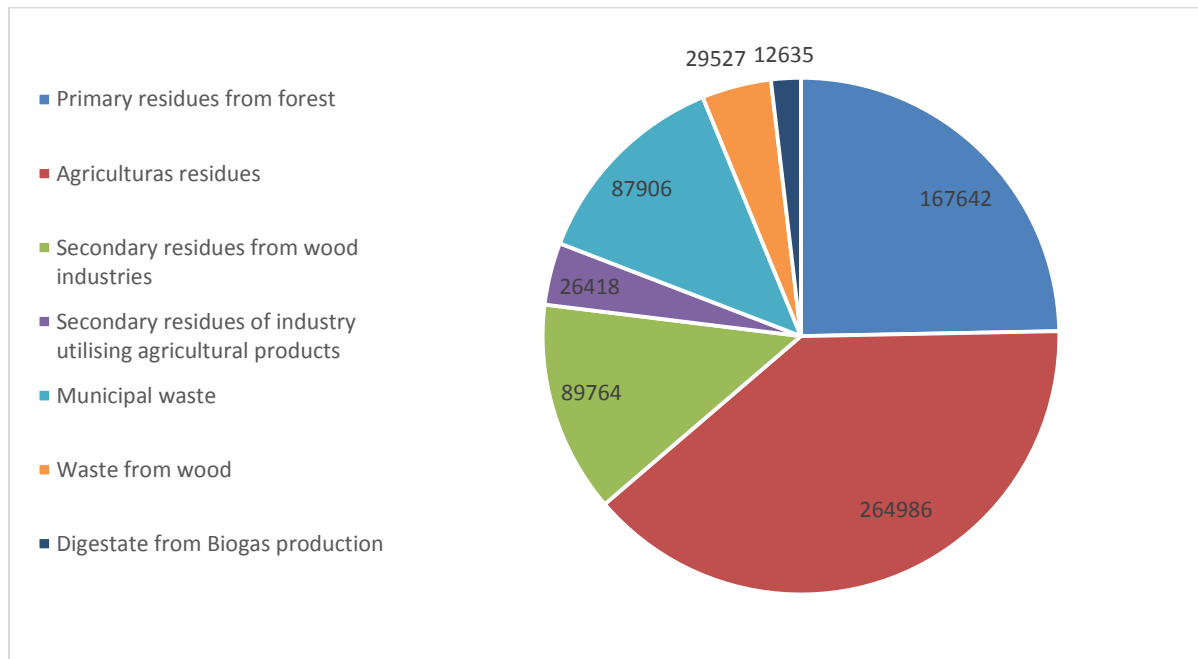
Figure 1. Biomass potential availability repartition per category (Kton/year on dry mass basis)

As shown in Figure 1, the major biomass availability is provided by <u>agricultural residues</u> (265 Mt/y), <u>primary residues from forest</u> (168 Mt/y), secondary residues from wood industries (90 Mt/y) and MSW (88 Mt/y) respectively.

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[2] The S2Biom dataset does not provide data on digestate. For this type of feedstock the estimation is based on a correlation between available data of digestate from rural biogas plants in Italy and the number and size of rural biogas plants available in Europe.

Primary residues from forest furtherly divided into these biomass type:

- Logging residues from final fellings from non-conifer trees
- Logging residues from final fellings from conifer trees
- Logging residues from thinnings from non-conifer trees
- Logging residues from thinnings from conifer trees
- Stumps from final fellings from non-conifer trees
- Stumps from final fellings from conifer trees
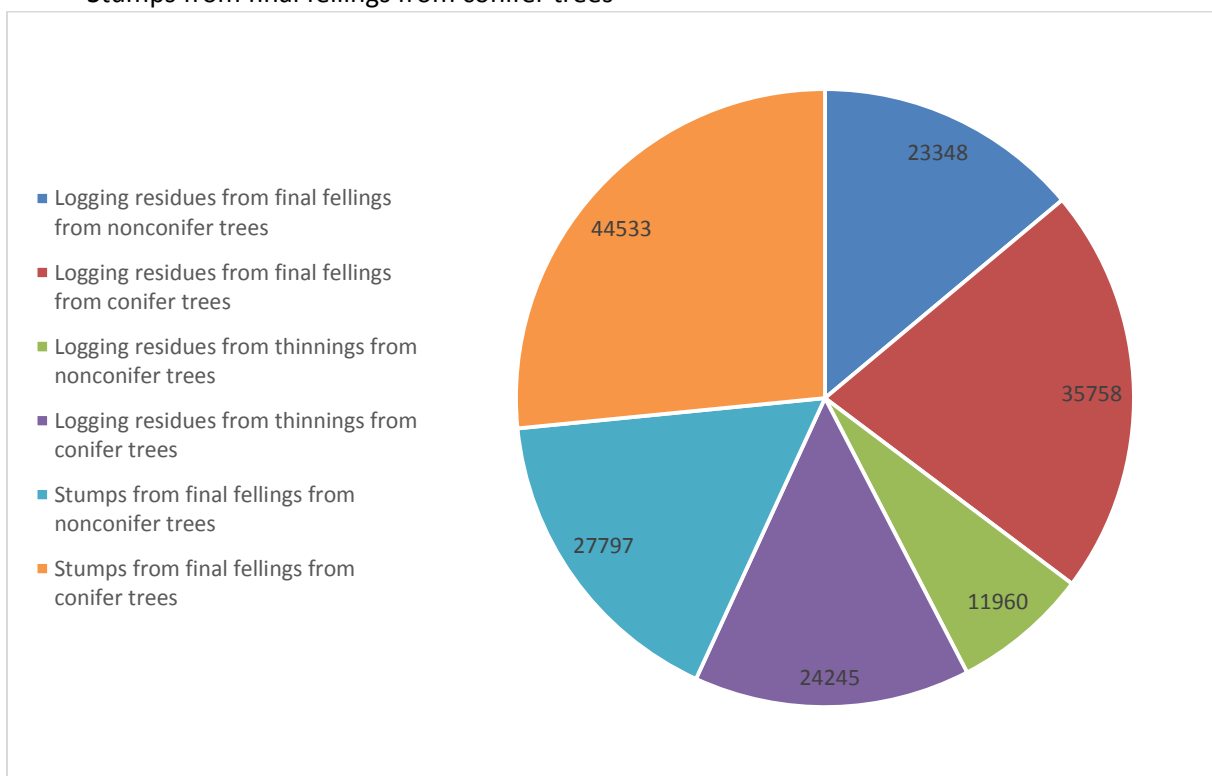
Figure 2. Primary residues from forest potential divided per biomass type (kton/year on dry mass basis)

As shown in Figure 2, the major biomass availability for this category is represented by stumps and logging from final fellings from conifer trees (44 and 36 Mt). These are particularly distributed in Scandinavian regions and in the UK, but are scarce in the rest of Europe. On the other hand, other types of primary residues are more evenly distributed, or at least available in significant quantities in several regional clusters (28 and 23 Mt). For example, this is the case of residues from broadleaved trees (abundant in central Italy, Portugal, France: e.g. quercus, fraxinus, hulmus) and from conifers (abundant in East Germany, Slovakia, Czech Republic and Austria). See fig. 3 and 4.
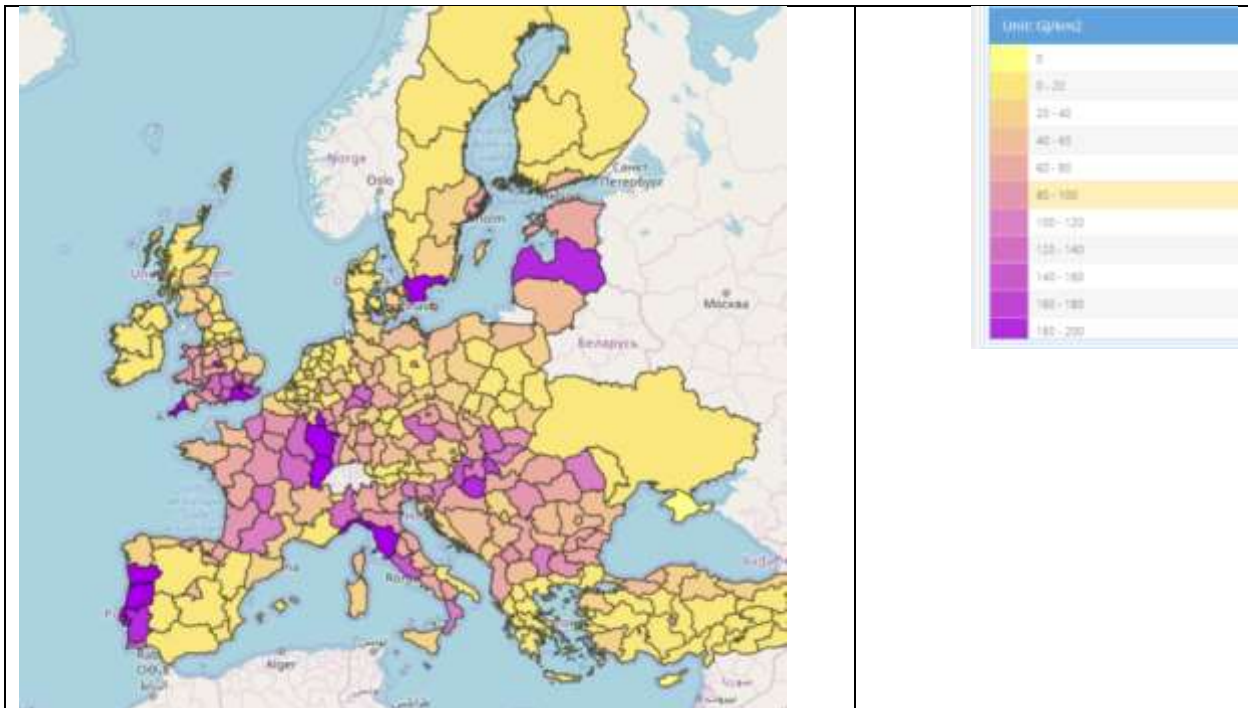
Figure 3. Estimated potential of logging residues from non-coniferous thinnings GJ/km^2 : Source S2biom.eu
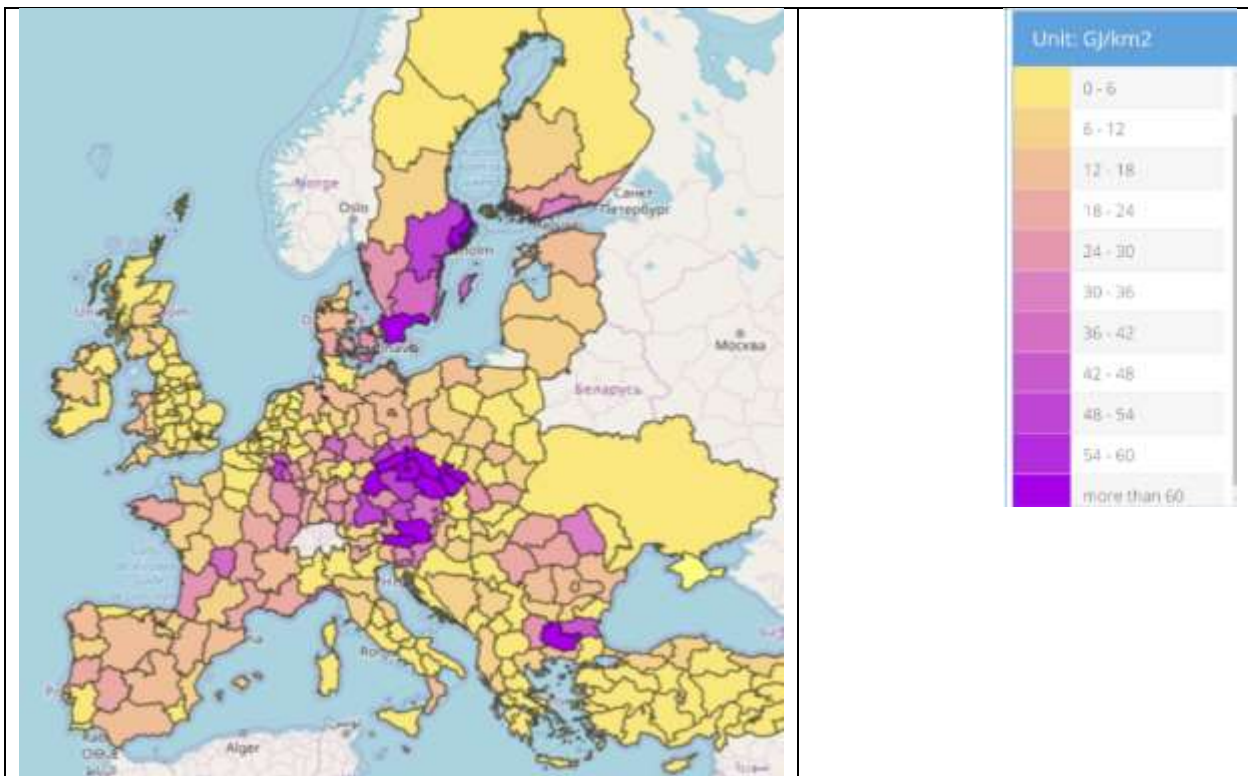
Figure 4. Estimated potential of logging residues from coniferous thinnings. Source: S2Biom.eu

In terms of cost-supply, the roadside cost of biomass from thinnings (conifers and broadleaved species) is estimated in a range comprised between 10 €/m^3 and over 20 €/m^3; with an intermediate cost (12-18

€/m³) for the majority of central European regions and Spain, while for most regions in Italy, Portugal and in the Scandinavian countries, the cost is estimated in the higher end of the range [3]. Figures 5 and 6 below.
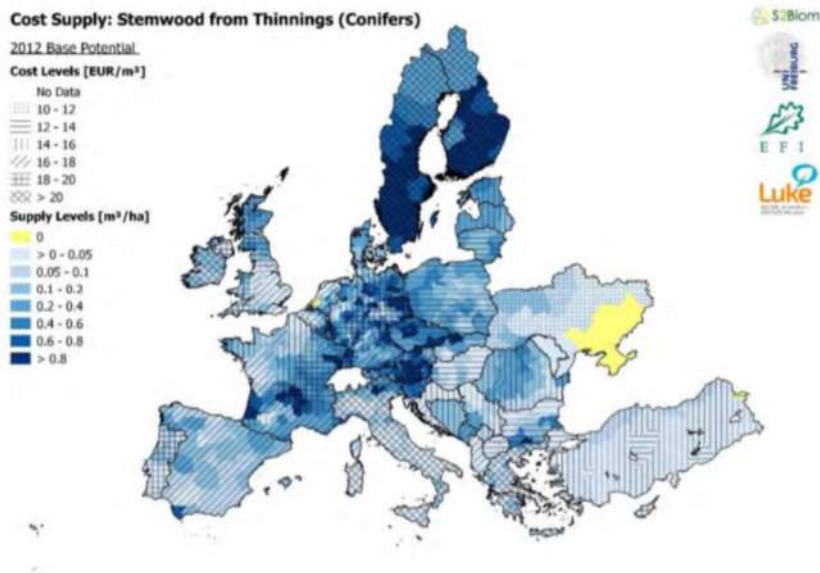
Figure 5. Cost and supply levels of stemwood from conifer thinnings. Source: S2Biom.eu
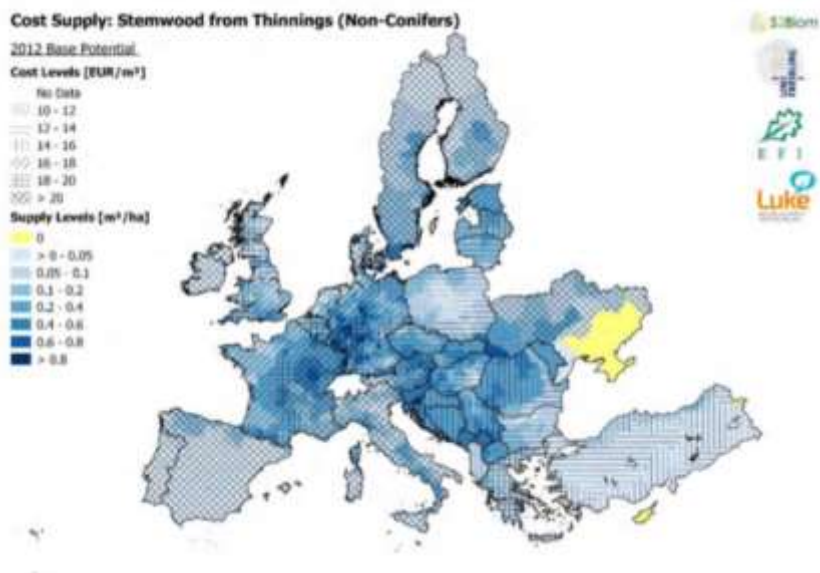
Figure 6. Cost and supply levels of stemwood from broadleaved thinnings. Source: S2Biom.eu

Agricultural residues furtherly divided into these biomass type:
   − Rice straw

- Cereals straw
- Oil seed rape straw
- Maize stover
- Sugarbeet leaves
- Sunflower straw
- Residues from vineyards
- Residues from fruit tree plantations
- Residues from olives tree plantations
- Residues from citrus tree plantations
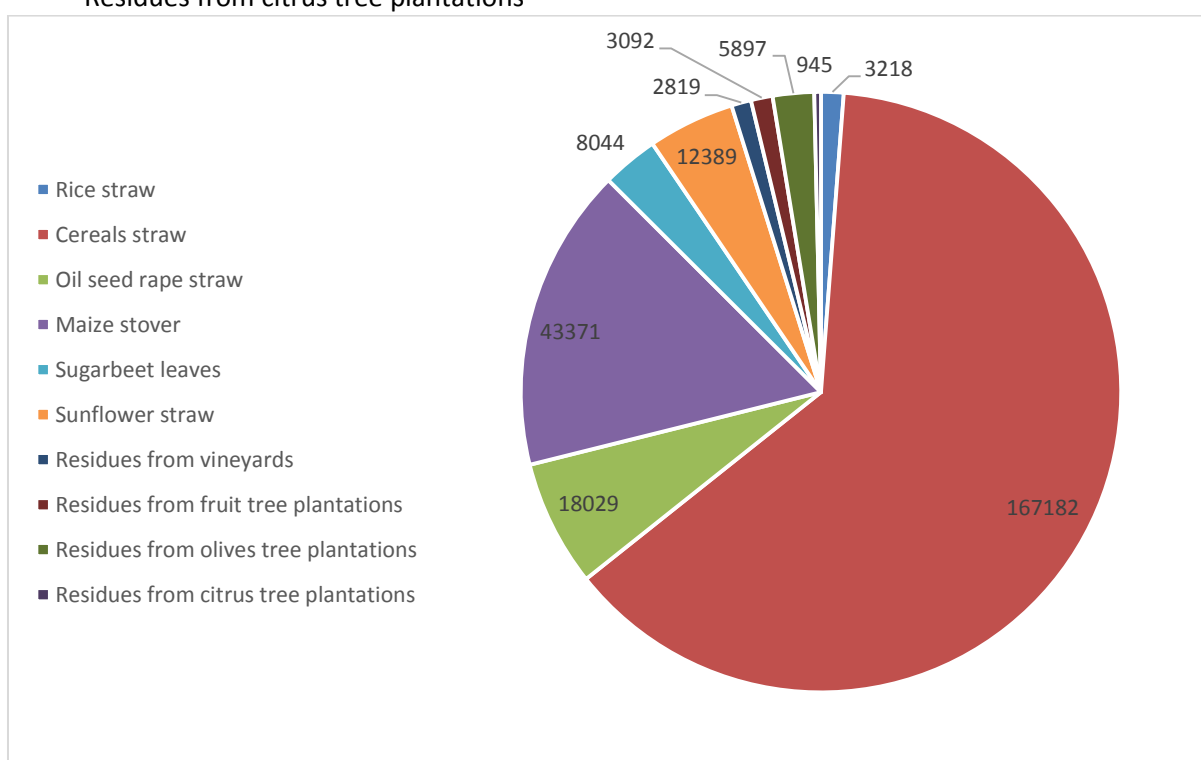
Figure 7. Agricultural residues divided per biomass type (Kton/year on dry mass basis)

As shown in Figure 7, the major biomass availability for this category is represented by cereal straw followed by maize stover. Straw is an abundant residual feedstock all over Europe, however the highest density in terms of energy potential from this source is located in the central and central-east regions of Europe. As shown in Figure 8 some regions in northern France, Germany and Poland offer a potential in the order of 700 to 900 GJ/km$_2$ while the majority of Mediterranean regions have a much lower potential, in the range of 100-200 GJ/km$_2$.

The cost supply curves of straw also indicate that for the majority of regions in Wester Europe the roadside cost of this resource is comprised between 25 and 50 €/per ton (dry mass basis), while in some Eastern European regions the same feedstock could be sourced at a price lower than 25 €/ton (Fig. 9)
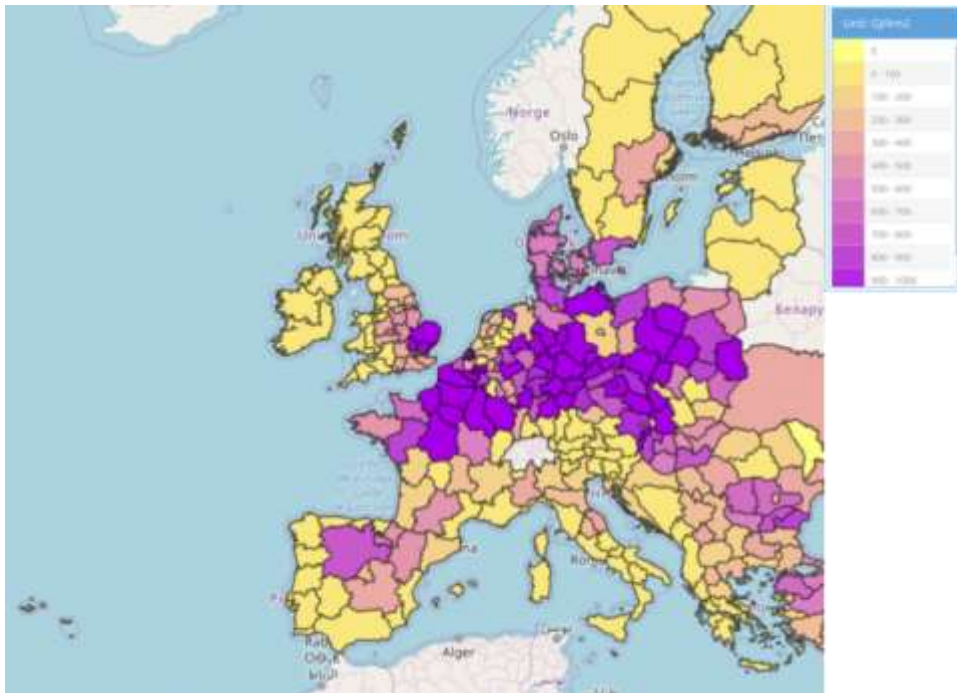
Figure 8. Estimated biomass potential from cereal straw in 2020 (GJ/km2): Source S2biom.eu
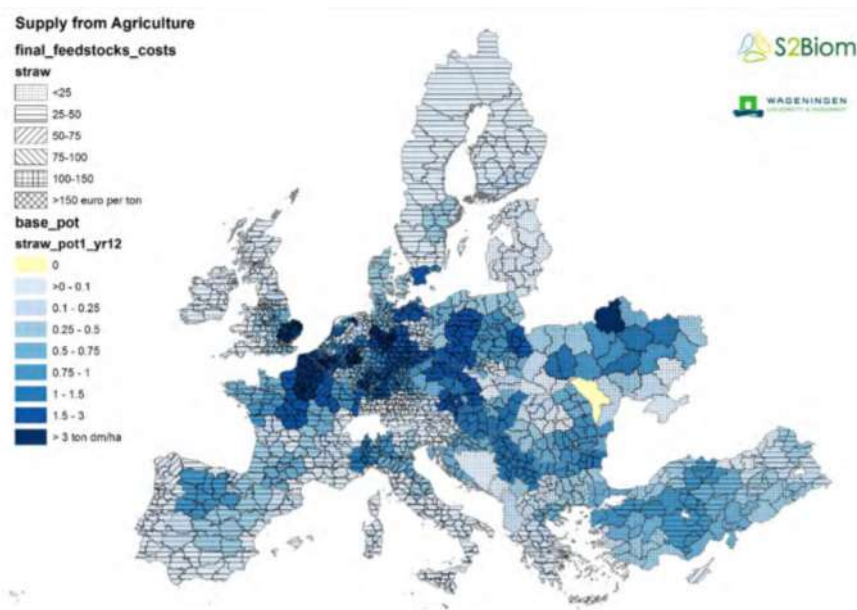
Figure 9. Cost and supply levels for straw and stubbles. Source: S2Biom.eu

Secondary residues from wood industries can be furtherly divided into the following biomass types:

- Sawdust (conifers)
- Sawdust (non-conifers)
- Other residues (conifers)

- Other residues (non-conifers)
- Residues from industries producing semi finished wood based panels
- Residues from further wood processing
- Bark
- Black liquor
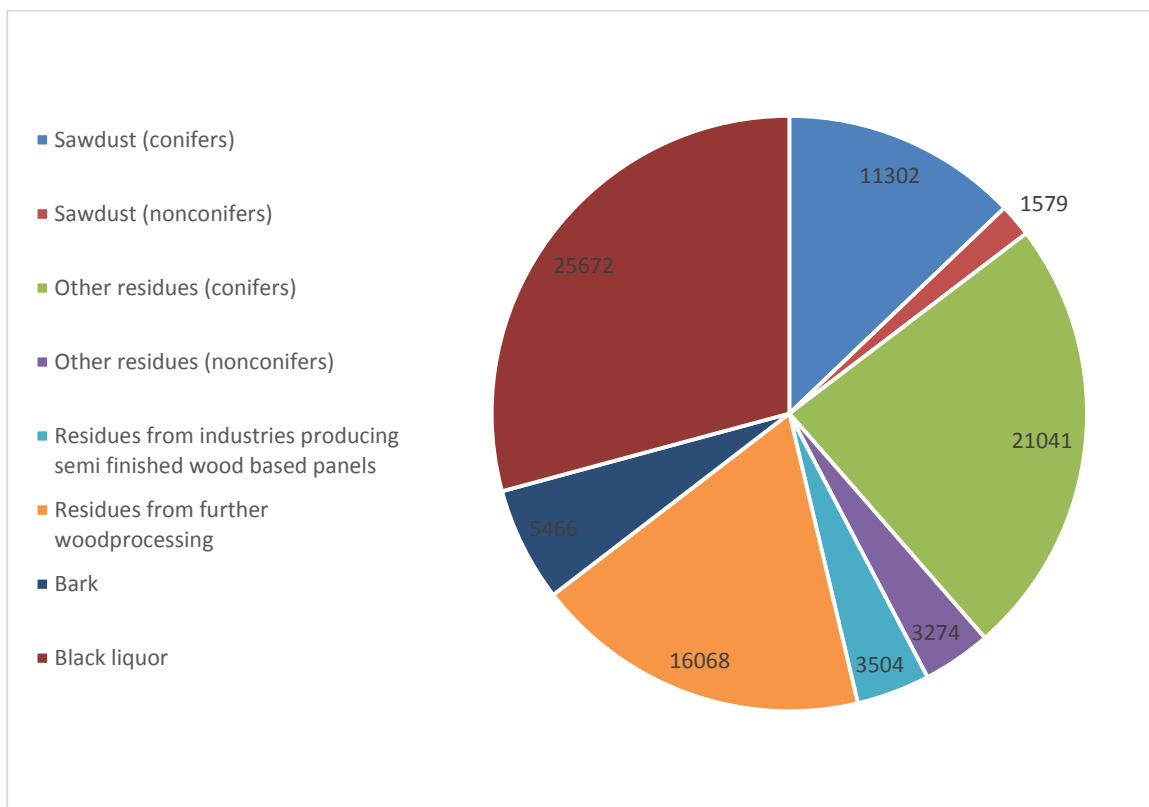
Figure 10. Secondary residues from wood industries divided per biomass type (Kton/year on dry mass basis)

In the secondary residues from wood industries category the major biomass availability is represented by the black liquor (Fig.10) that is the waste product obtained from the kraft process when digesting pulpwood into paper pulp removing lignin, hemicelluloses and other extractives from the wood to free the cellulose fibers. It's followed by other residues (conifer) how it was predictable according to data reported in Figure 2. Sawdust is another abundant residual resource in Europe, and its main end-use is the production of wood pellets. The main biomass potential is represented by the sawdust obtained from coniferous trees, and is mainly located in central and norther Europe (fig. 11)
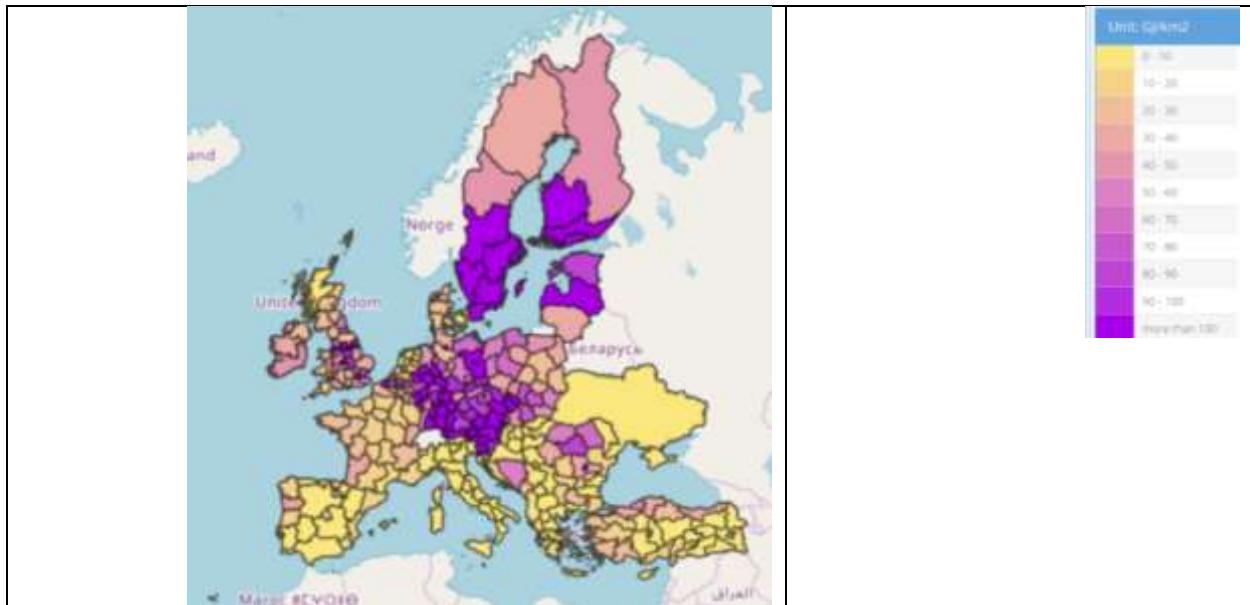
Figure 11. Estimated biomass potential of sawdust residues from coniferous trees in 2020 GJ/km^2. Source S2biom.eu

Secondary residues of industry utilising agricultural products furtherly divided into these biomass type:

- Olive-stones
- Rice husk
- Pressed grapes dregs
- Cereal bran

Looking at Figure 12 is obvious that in this category the major biomass availability is represented by cereal bran. However, several other types of secondary residues suitable for gasification present a significant potential at regional scale, even though they are less in absolute values. This is the case of olive stones from olive milling, largely available in many regions in Greece, central and southern Italy and in southern Spain, as well as the residues from nuts plantations, which are abundant in some specific regions of Italy, Germany and Spain (fig. 13 and 14 below).
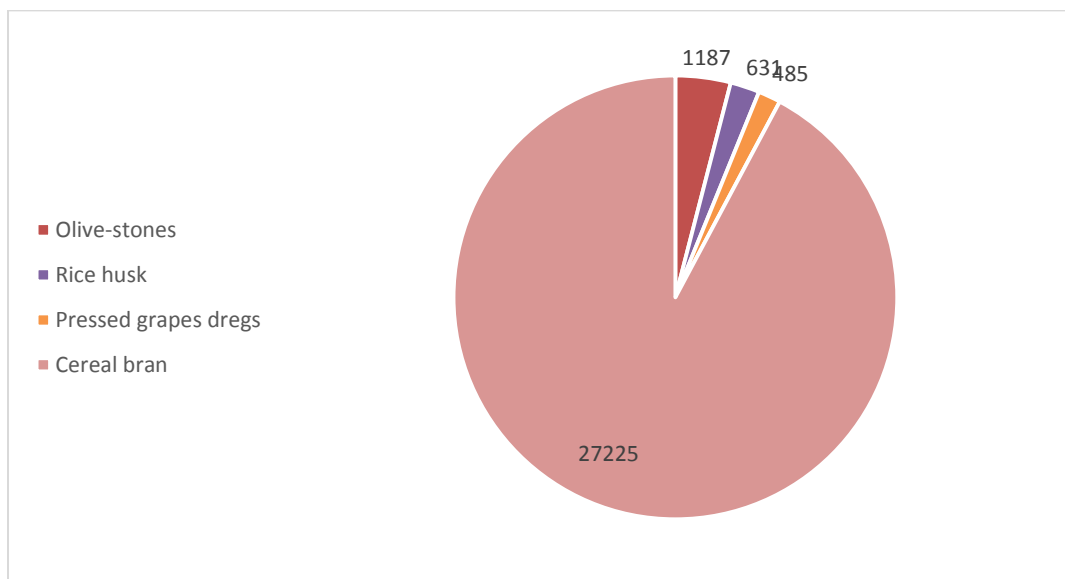
Figure 12. Secondary residues of industry utilising agricultural products divided per biomass type (Kton/year on dry mass basis)
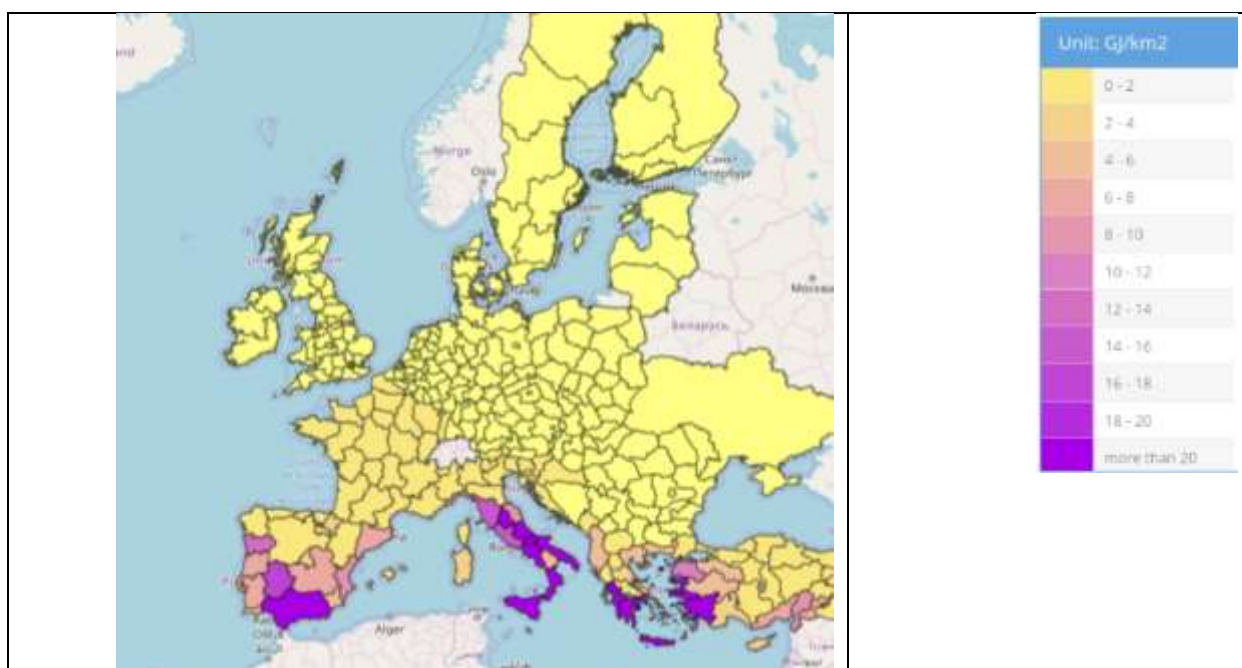
Figure 13. Estimated potential of olive stones in 2020. GJ/km2. Source S2biom.eu
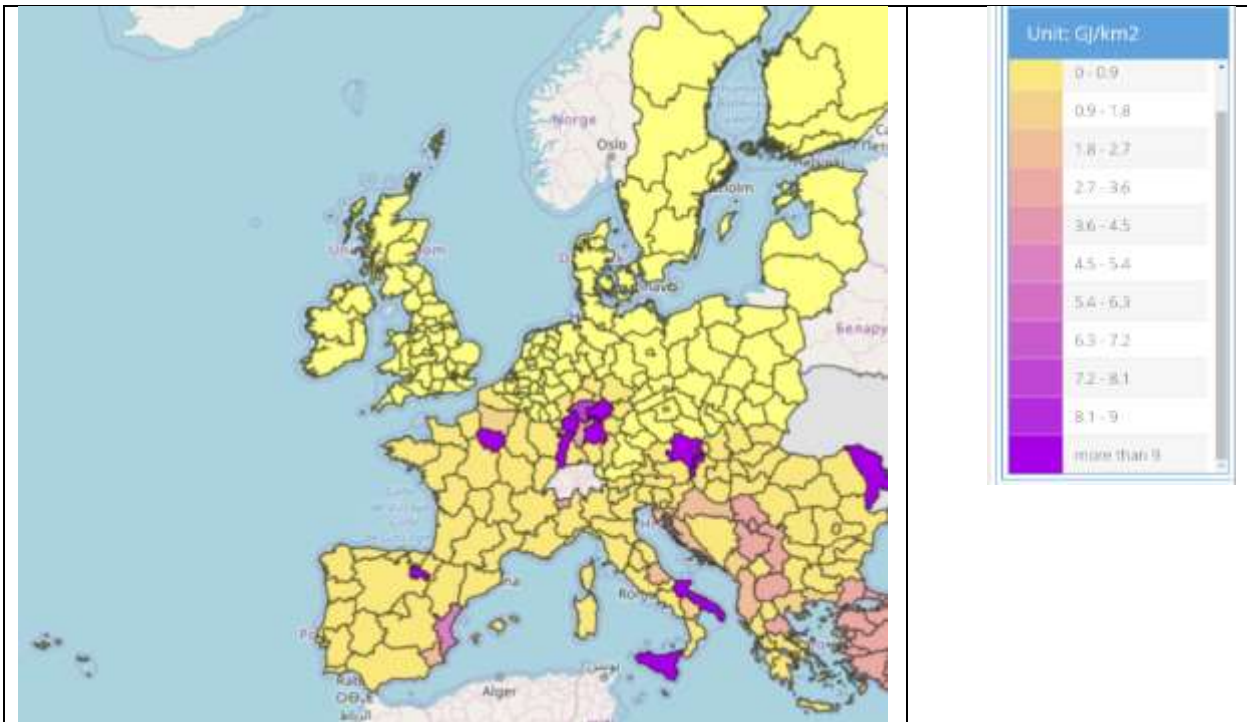
Figure 14. Estimated potential of residues from nuts plantations in 2020 GJ/km2. Source S2biom.eu

Municipal waste furtherly divided into these biomass type:

  − Biowaste non-separately collected
  − Biowaste separately collected

Figure 15. Municipal waste divided per biomass type (Kton/year on dry mass basis)
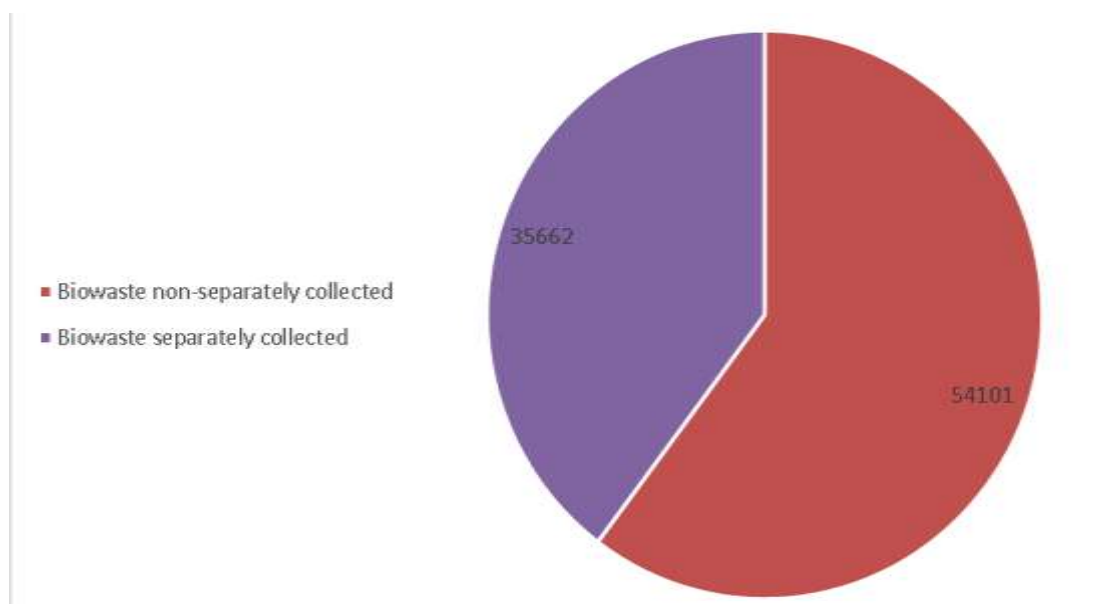
Waste from wood furtherly divided into these biomass type

- Hazardous post-consumer wood
- Non-hazardous post-consumer wood
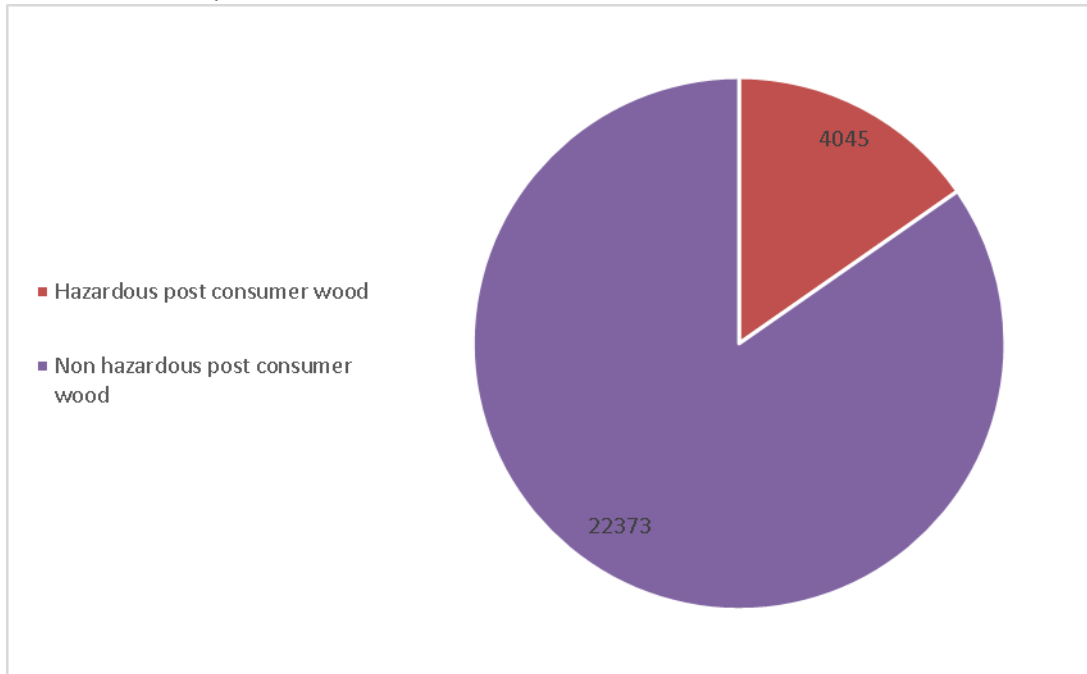
Figure 16. Waste from wood divided per biomass type (Kton/year on dry mass basis)

As shown in Figure 15 and 16, the major biomass availability for municipal waste and waste from wood are biowaste separately collected and non-hazardous post-consumer wood respectively. Unlike the hazardous post-consumer wood, the non-hazardous wood could theoretically represent an interesting feedstock for the BLAZE CHP system, and it is concentrated in the most urbanized regions with the highest population density, where also the energy demand for both heating and power is higher (fig. 17 below)
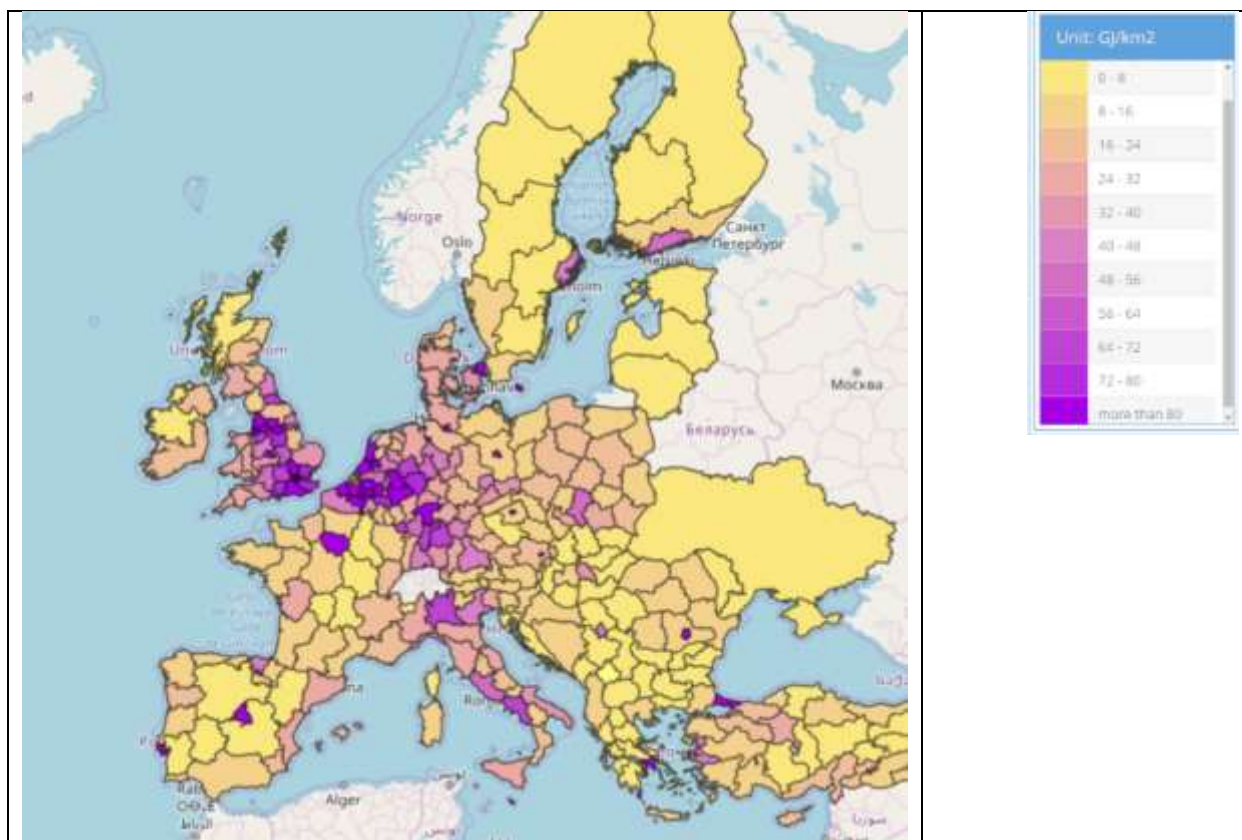
Figure 17. Estimated potential of non-hazardous post-consumer wood in 2020. GJ/km^2. Source S2biom.eu

In conclusion, in Figures 18 and 19 is shown the total biomass availability in EU28 countries: can be easily found that the main producers are Germany and France (104.895 and 100.861 of kton/year respectively), followed by Spain, Poland, Sweden and Italy which produce a quantity between 52.293 and 47.088 of kton/year.
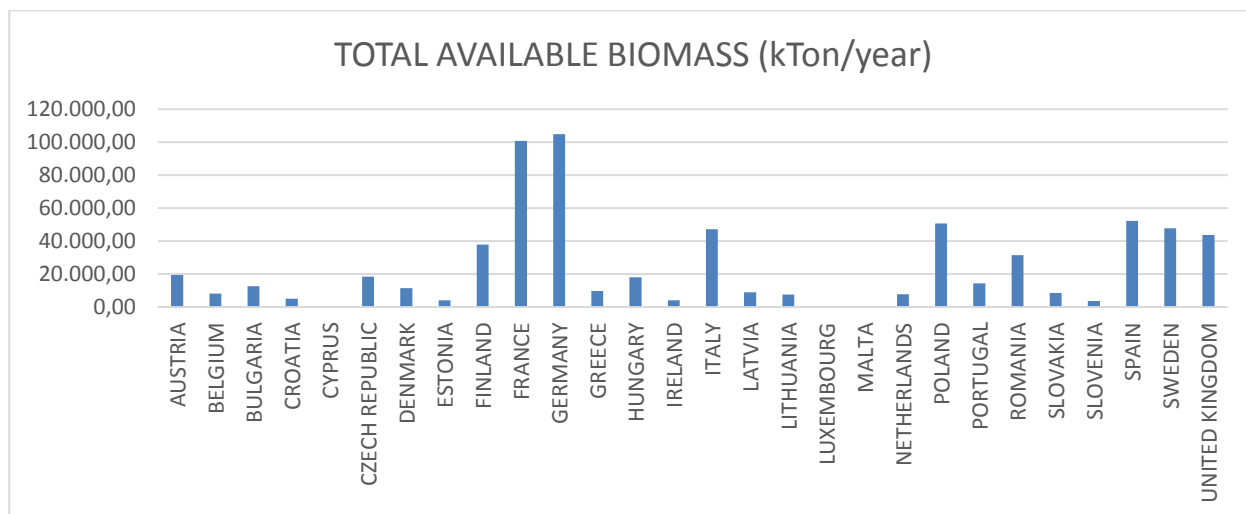
Figure 18. Total biomass availability in EU28 (kton/year). Source S2biom.eu
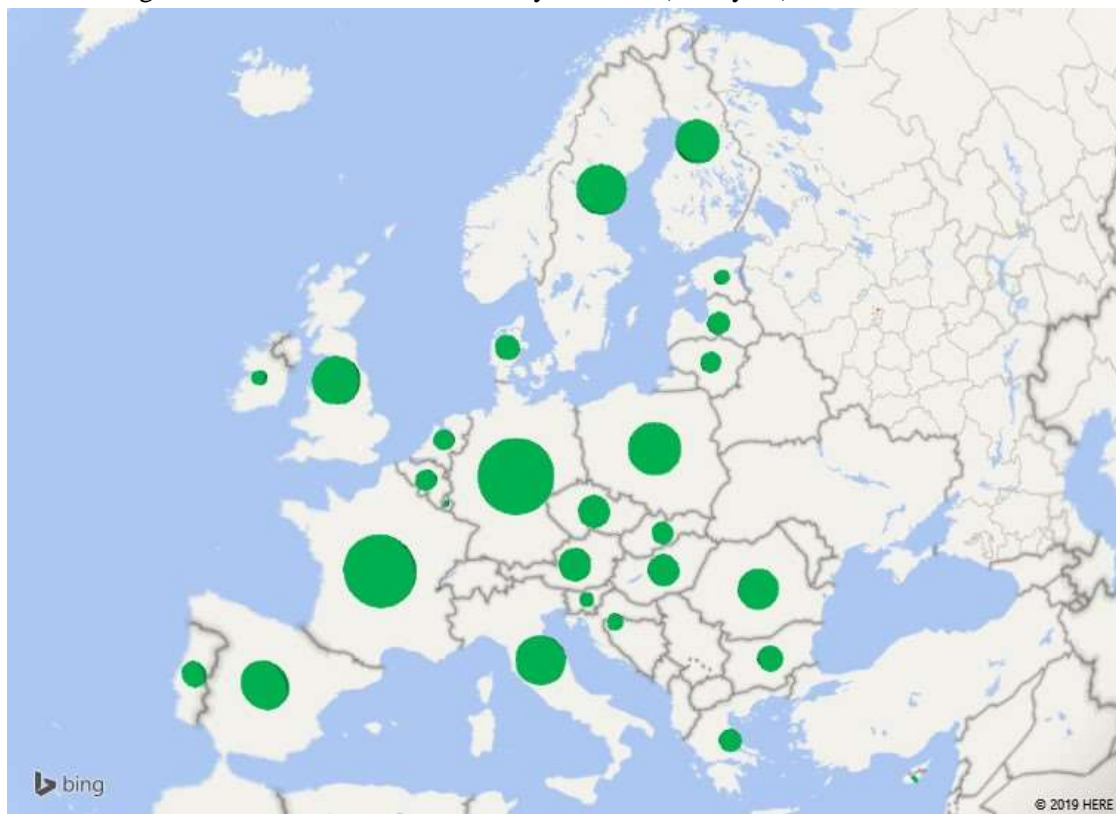
Figure 19. Map of biomass distribution in EU28. Source S2biom.eu

Similarly, in figures 20 and 21 is shown the total lignocellulosic biomass availability in EU28 countries: in particular it can be noted that the main producers, along with France and Germany as in the previous case, are Sweden and Finland.
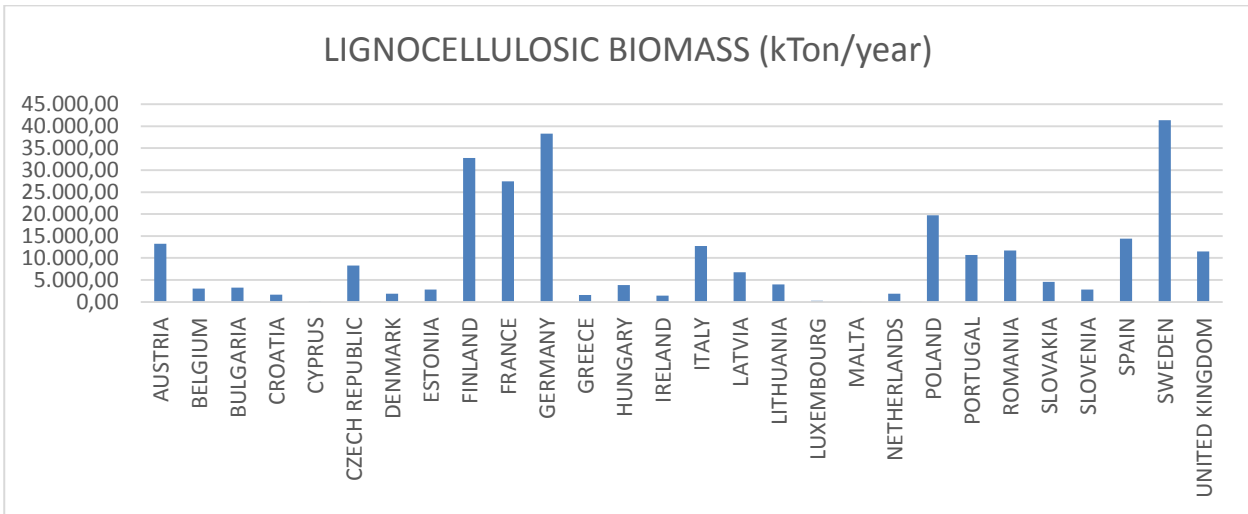
Figure 20. Total lignocellulosic biomass availability in EU28 (kTon/year). Source S2biom.eu
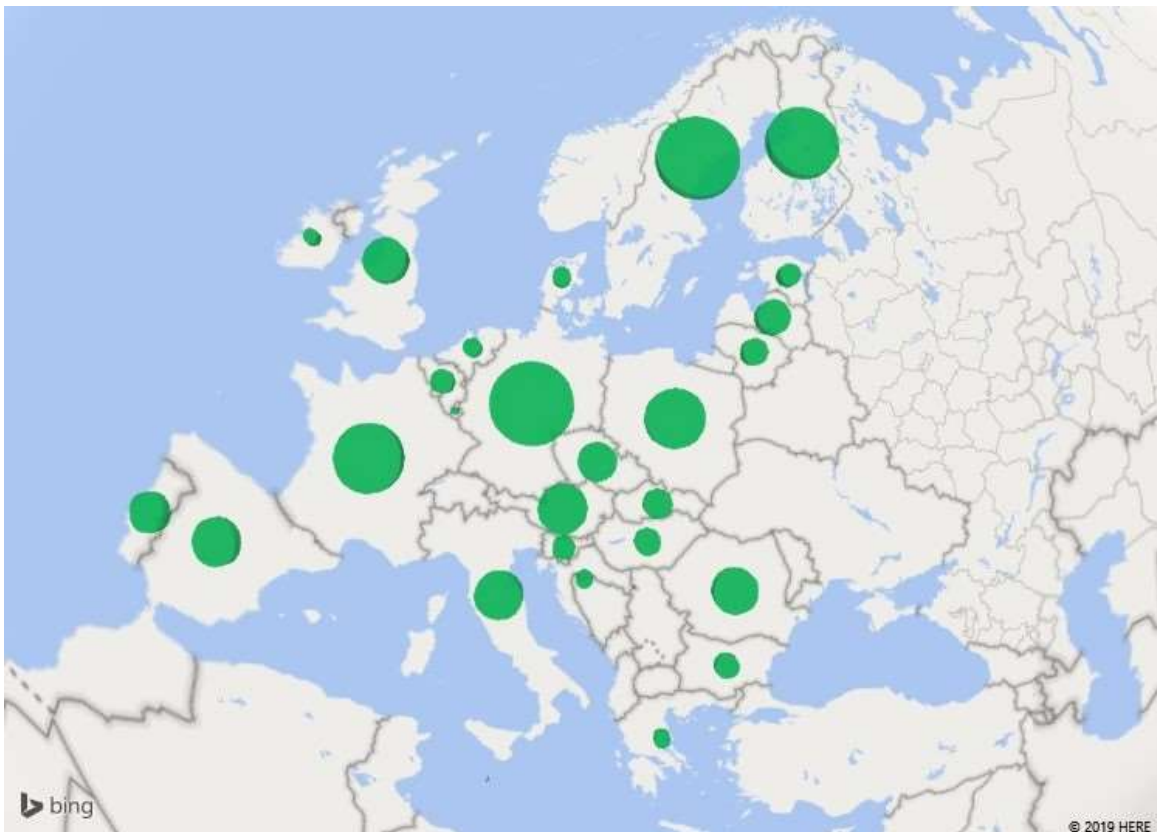
Figure 21. Map of lignocellulosic biomass distribution in EU28. Source S2biom.eu

5 CHP POTENTIAL

The theoretical potential for applying BLAZE technology is seen as the 100% fuel switch to bio-fuels in existing CHP systems – in district heating (DH) as well as in industry. The aim of this study is to project the EU specific penetration rate of biomass fuelled BLAZE system in the CHP markets by 2030. According to "European report on potential of BIO-ENERGY CHP in EU27 ", (Projected) heat demand from bio-energy CHP and DH (Fig. 22) in 2030 is equal to 17.664 ktoe or 205.432 GWh$_{th}$.

Figures (projections)	2010	2020	2030
Final heat demand from CHP and DH (PRIMES, IEA, UBA), ktoe	56.233	69.056	74.465
(Projected) heat demand from bio-energy CHP and DH (after score card), ktoe	10.967	14.015	17.664
Bio-energy penetration rate in CHP markets (2009: EEA, Eurostat)	19,5% (2009)	20,3%	23,7%
Biomass availability, share heating (sust., cost-eff.), final energy (Biom. Futures), ktoe		129.756	117.868
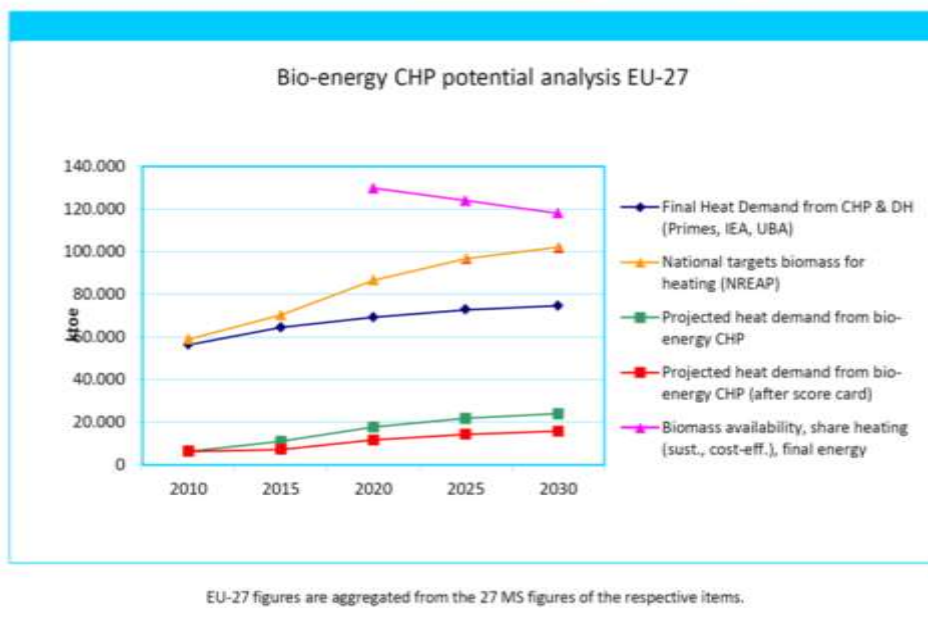
Figure 22. (Projected) heat demand from bio-energy CHP and DH in EU27. Source CODE2 project

To satisfy this heat demand, considering Blaze technology thermal conversion efficiency equal to 40% and assuming a medium value of 3.500 working hours of the plant (considering the number of hours per year in which heat demand is required at residential level) the maximum theoretical peak thermal power (referring to gasifier biomass feeding) that can be installed is 146.637 MW$_{th}$. Starting from this assumption is possible to estimate the number of CHP power plants based on BLAZE technology, in 2030, for different capacity range and scale referring to electrical nominal power output (Fig. 23 and 24).
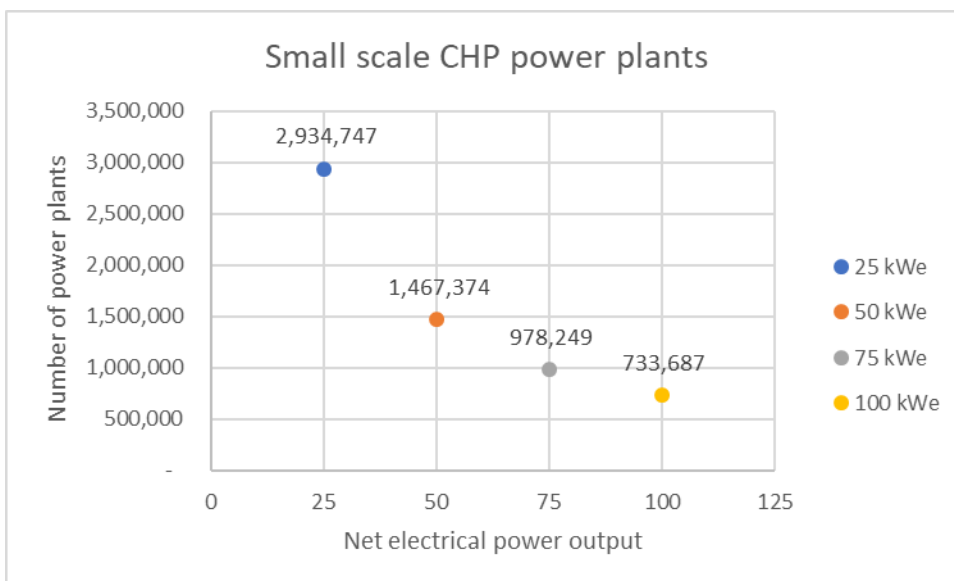
Figure 23. Theoretical numbers of power plants based on BLAZE technology in 2030 for small scale (25-100 kW$_e$)
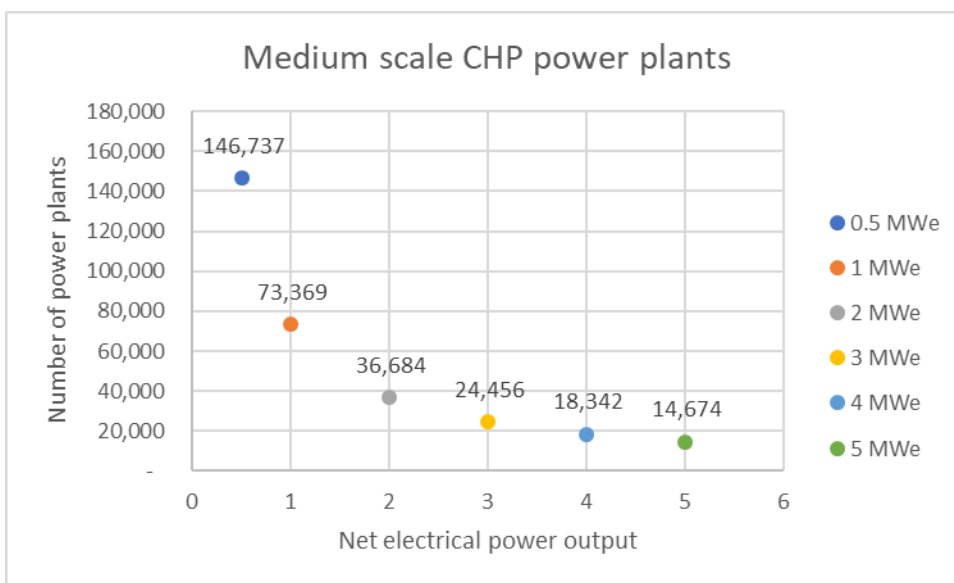
Figure 24. Theoretical numbers of power plants based on BLAZE technology in 2030 for medium scale (0.5-5 MW$_e$)

From the figures above is easy to understand that the potential market of BLAZE technology in EU27 it's very important: considering just the CAPEX, around 4000 €/kW$_e$, the potential market is around 293,474.74 k€. Moreover if we consider the number of hours per year in which heat demand is required at industrial level, equal to 7000, clearly the values reported in the figures would be reduced by half but at the same time also the pay-back time of the plants will be reduced by half.

6 SUPPLY CHAIN COST

"Supply chain management is the management of the flow of goods and services and includes all processes that transform raw materials into final products. It involves the active streamlining of a business's supply-side activities to maximize customer value and gain a competitive advantage in the marketplace." Both the logistics of biomass and its supply are likely to be complex and potentially problematic. Logistics costs is crucial to determine the total delivered cost of biomass.

The biomass supply chain is made up of a range of different activities that affect the **economic** sphere. These can include ground preparation and planting, cultivation, harvesting, handling, storage, in-field/forest transport and road transport. Given the typical locations for biomass sources (farms or forests) the transport is the only mode for collection, it tend to be relatively short to ensure the convenience. In order to supply biomass from its point of production to a conversion plant the following activities are often necessary:

• Harvesting of the biomass in the field/forest.

• In-field/forest handling and transport to move the biomass to road transport.

• Storage of the biomass. Many types of biomass will be harvested at a specific time of year but will be required on annual basis, storage is therefore necessary. The storage point can be located on the farm/forest, at the conversion plant or at an intermediate site.

• Loading and unloading road transport vehicles. Once the biomass has been moved to the roadside it will need to be transferred to road transport vehicles for conveyance to the conversion plant. At the station the biomass will need to be unloaded from the vehicles.

• Transport by road transport vehicle. Using heavy vehicles for transport to the station is likely to be essential due to the average distance from biomass production sites to conversion plant, and the carrying capacity and road speed of such vehicles has to be taken into account.

• Processing of the biomass to improve its handling efficiency and the quantity that can be transported. This can involve increasing the bulk density of the biomass (i.e. processing forest fuel or coppice stems into wood chips) or unitising the biomass (i.e. processing straw or miscanthus into bales). Processing can occur at any stage in the supply chain but will often precede road transport and is generally cheapest when integrated with the harvesting.

Biomass logistic costs typically account for 20–40% of delivered fuel costs and restrict the competitiveness of biomass against other energy sources. A cost-efficient design of the biomass supply chain is critical to overcome these challenges. Biomass parameters that affect the technical and economic feasibility of using it are its quality attributes, its availability and procurement cost. Biomass quality attributes are energy content, moisture content, particle size, ash and contaminant contents. These attributes influence the selection of pre-processing operations (sorting, chipping and drying), the selection of conversion technologies and the transportation costs. The amount of biomass that can be

sustainably procured determines the scale of the project, and the variation of biomass supply over time drives the need for storage operations to ensure a reliable supply over the lifetime of the project. [9–16]

The **environmental** impact of biomass fuel supply is of great importance as the reason of using biomass fuel is that it is less harmful to the environment than traditional fossil fuels. Biomass supply chain can be responsible for a number of environmental impacts, these can include: noise, fossil fuel use and emissions, visual intrusion, health and safety issues, water pollution and traffic generation. Other environmental considerations that must be made concern the role of biomass in supporting the ecosystem from which it is taken: sustaining the soil, regulate water flows, provide food to various organism. [17–19]

From the **social** point of view, it is important to underline instead how the triggering of a biomass supply chain has a positive effect on local autonomies and creates employment. The particularity of the biomass supply chain is that it is extremely determined by the context and case-specific, and so are all the decisions. The supply chains for wood, forest and agricultural waste are short chains, which implies proximity between the places of energy consumption and production. The short supply chain has several advantages in the agro-energy sector: from an environmental perspective, it minimizes transport emissions; from an economic perspective, it reduces the number of operators involved (reduce labour cost). In Europe, there are great difficulties to produce harmonized biomass assessments due to the lack of geo-referenced databases of forests and agricultural field residues covering the whole continent and made with standardized procedures. In general, to get a more realistic overview, the slope of the terrain must also be considered. Additional equipment may be required on more sloping grounds (cableways that carry whole trees to the landing). In a study carried out by L.S. Esteban and J.E. Carrasco in 2011 [20] it is possible to find the costs of biomass (agricultural and forestry waste) including many necessary processing, for biomass of different nature. The study takes place in Spain and then summarizes data about many European countries. The finished product will be considered "on the roadside". To go into more detail on some of the processes that make up the supply chain, the study investigates the following processes about the woody crops in Spain:

Basic costs of harvesting and forwarding woody crops in Spain (Orchard, Olive Vineyard)				
	alignment machine	crushing	forwarding (15 km)	total
	€/ton	€/ton	€/ton	€/ton
Orchard	6	15	9	30
Olive	6	24	7,2	37,2
Vineyard	6	24	7,2	37,2
AVG	6	21	7,8	34,8

Table 1 Basic costs of harvesting and forwarding woody crops in Spain [20]

Another example that is important to report concerns the high tree-covered forest (conifers, broadleaves and mixtures) and the various operations related to the processing of forest residues.

Basic cost used in high tree-covered forest (conifers, broadleaves and mixtures) in Spain.			
	piling up	forwarding	baling	total
	€/ton	€/ton	€/ton	€/ton
slope lower that 20%			
Cleaning	11,21	17,18	17,57	45,96
Thinning	11,21	17,18	17,57	45,96
Final Felling	5	14,47	17,57	37,04
slope higher that 20%			
Cleaning	15	24	24	63
Thinning	15	24	24	63
Final Felling	11,95	16,63	17,57	46,15
AVG	11,56	18,91	19,71	50,19

Table 2.cost items in the processing of tree-covered forest residues [20].

It is important to note that the slope of the land is also taken into consideration and that, an increase in costs is detected for sloped grounds. In fact, even if the sloping lands often offer large quantities of available biomass, the greater difficulty of procurement and processing inevitably affects the cost. Similarly, the following table analyses the costs of some forest waste processing of different nature. Also here it can be noted that the slope of the land plays an important role in determining the cost.

Basic cost used in coppiced forest, dehesas and shrubs for different operations in Spain.			
	piling up	forwarding	baling	total
	€/ton	€/ton	€/ton	€/ton
slope higher that 20%			
Quercus	23,77	16,63	17,57	57,97
Shrubs	24,27	19,9	17,57	61,74
Dehesas	23,77	16,63	17,57	57,97
slope lower that 20%			
Quercus	16	10,66	17,57	44,23
Shrubs	24,27	19,9	17,57	61,74
Dehesas	16	10,66	17,57	44,23
AVG	21,35	15,73	17,57	54,65

Table 3. cost items in the processing of coppiced forest, dehesas and shrubs residues [20].

Given the reasonable and more than acceptable nature of the results for Spain, the data of the same study relating to other European countries are also given below.

The lowest price for agricultural and forestry biomass was found in Poland, highlighted in blue.

COUNTRY	AGRICULTURAL	FORESTAL
	€/ton	€/ton
Sweden	30,24	22,37
Finland	29,62	23,64
Germany	31,97	23,64
Norway	37,65	27,85

Austria	29,78	22,03
Poland	15,57	11,5
Denmark	33,99	25,14
France	24,23	64,13
Spain	23,03	49,7
Italy	33,22	74,03
Greece	22,77	43,77
Portugal	21,37	27,38
AVG	28	35

Table 4. Average costs of agricultural and forest biomass in several European countries [20].

Another aspect to consider is that there is always a difference between the costs related to the production and processing of biomass (considered delivered on the roadside) and the selling price of the same, which includes the seller's profit margin. A case found in literature [21] shows the production costs of wood chips and the price at which it is sold at "the mouth of the plant" (table 5).

ITALY CASE STUDY	
class B wood chips	€/ton
Labor cost	2,4
Energy cost	11,4
Other costs	4,78
Total production cost	18,58
selling price	53
class A1 wood chips	€/ton
Labor cost	32,94
Energy cost	17,32
Other costs	19,83
Total production cost	70,09
selling price	100
AVG	71,5

Table 5. case analysis of wood chips in Italy [21].

The selling price varies between € 53 and € 100/ton, respectively for class B and class A1 wood chips. It is in line with € 74 / ton, that is obtained as an average between several types of forestry biomass.

As regards the municipal solid waste (that is another of the investigated categories) supply chain, it is difficult to determine the average price of the resource. On the final report of the European commission "Costs for Municipal Waste Management in the EU", are reported data regarding the collection of MSW, which is only a part of the entire supply chain, that also includes sorting and transport, on which it is not possible to find separated data. Prices for MSW as raw material are set at 0 (on average they are negative) as they are seen as waste for which the municipalities has to find ways to get rid of at lowest possible cost. At the roadside these potentials are set to have a price of 0, but as soon as they are used in some conversion to energy, cost have to be made for transporting and treating the waste. Even if the cost of collecting waste is among the highest among the different categories of biomass taken into

consideration, the cost charged to the municipalities for disposal is very high, so the profit margin increases and the margins of use are greater. Thus the table below quotes the cost of MSW collection from [22].

COUNTRY	Residual Waste Collection	
	URBAN	RURAL
	€/ton	€/ton
Austria	70	70
Belgium	65	65
Denmark	126	126
Finland	15	32
France	60	70
Germany	67	71
Greece	30	55
Ireland	65	65
Italy	75	75
Poland	45	45
Spain	60	60
Sweden	65	65
United Kingdom	42	60
AVG	60	66

Table 6. Cost of RW collection in EU.

In this case it is also interesting to assume that the conversion plant is near the waste storage site. This can lead to savings on transportation, as the process of sorting can often be expensive.

For what concerns the "waste from wood", the categories of wood processing waste that interest the energy production are the following (classification made by Wood Recyclers Associations (WRA)):

- Grade B: industrial waste wood;
- Grade C: municipal waste wood;
- Grade D: hazardous waste wood.

Regarding UK it was possible to find the gate fees for high grade (clean, untreated wood waste along with some non-hazardous lower grade solid wood waste) and low grade (non-hazardous treated) wood waste. The Hazardous wood waste price can vary in a wide range, because it is strongly dependent on the nature of possible contaminants and necessary processing operations (source: "Wood waste: A short review of recent research UK 2012" [23]:

WOOD WASTE	
	€/ton
Hazardous	125
NON HAZARDOUS	
High Grade	5
Low Grade	25
AVG	15

Table 7. Wood waste gate fees (UK).

As regards the category of "secondary residues from wood industry", sawdust was the type of biomass with very high potential, for this reason its costs were analyzed in several European countries (source: "The JRC-EU-TIMES model. Bioenergy potentials for EU and neighbouring countries" [24]):

Residues from wood industry (sawdust)		
	€/GJ	€/ton
UK	2,2	37,4
Finland	2	34
Germany	2,5	42,5
Norway	2,1	35,7
Austria	2,5	42,5
Poland	1,7	28,9
Denmark	2,5	42,5
France	2,4	40,8
Spain	2,7	45,9
Italy	2,8	47,6
Greece	2,2	37,4
Portugal	2,1	35,7
AVG	2	39

Table 8. cost of the residues from wood industry.

The calculation was carried out considering the LHV of sawdust 17 MJ/kg. Within the category "secondary residues of industry utilizing agricultural products", the available economic data were found expressed in €/GJ.

secondary agricultural residues	
	€/GJ
UK	5,4
Finland	5,4
Germany	4,7
Norway	5,1
Austria	7,5
Poland	3,1
Denmark	5,4
France	3
Spain	3,8
Italy	3,8
Greece	4,8
Portugal	3,6
AVG	5

Table 9. Secondary agricultural residues [24].

The data are found by the average values of: stubbles, OSR and sunflower, cereal straw, rice straw, sugar beet, cherries and other soft fruits, apples and pears, citrus, olives and olives pits, vineyards, grass and maize.

Based on the available data in literature [24] and the high potential of this type of biomass, the cost of olive pits was also investigated:

secondary agricultural residues: OLIVE PITS	
	€/ton
Europe AVG	55

Table 10. Olive Pits cost.

All the costs are considered for the resource on the roadside.

Table 11 summarizes the prices of the different biomass categories, which were subsequently analyzed. In addition to the roadside cost of biomass, transport costs were considered. A 100 km limit was set because, with a consumption of 0.5 MJ/kg ton it would be counterproductive from the energetic point of view. The price of transport itself was considered 0,02 €/km.

Subsequently, considering a maximum limit of € 100 / ton introduced previously, a cost ceiling to be allocated for other processes (i.e. milling, drying, etc.) aimed at preparing biomass for gasification was calculated as a first approximation.

BIOMASS CATEGORY	Roadside AVG PRICE	Roadside AVG PRICE + 100km of transport	Biomass other processes maximum cost
	€/ton	€/ton	€/ton
Primary residues from forest	35	37	63
Agricultural residues	28	30	70
Secondary residues from wood industries	35	37	63
Secondary residues utilising agricultural products	55	57	43
Waste from wood (no Hazardous)	15	17	83
Digestate (collection)	66[3]	68	98

Table 11. summarizing table of all the biomasses.

The situation is different for MSW. In this case the maximum limit to be allocated to further processing can be raised considering the cost of disposal (i.e. landfill taxes) per ton of waste.

This value has been investigated and is more than 100 € / ton for most European countries, and this fact widens the profit margin. For example, in some Italian regions such as Campania, Veneto, Sardegna and Basilicata can be up to € 130-150 / ton: an average price of 140 €/ton was considered.

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[3] The digestate, as a waste, can be considered as a resource at cost 0, as it is often used as agricultural fertilizer. In fact, in the table the same cost is attributed to the MSW, that is the one related to the collection.

BIOMASS CATEGORY	AVG PRICE	AVG PRICE + 100km of transport	Post Processing maximum cost
	€/ton	€/ton	€/ton
Municipal waste (collection)	60	62	78

Table 12. summarizing table of MSW costs.

7 BIOMASS SELECTION

In order to select 10 sample and 5 mixtures representative of the most available European biomass species suitable for gasification which will be characterized to assess their main physical and chemical properties we'll consider 3 main parameters:

- Biomass availability
- Biomass repartition per typology in terms of energy available
- Biomass cost

All the biomass has been categorized in the following main groups:

- Primary residues from forest
- Agricultural residues
- Secondary residues from wood industries
- Secondary residues of industry utilising agricultural products
- Municipal waste
- Waste from wood
- Digestate from biogas production
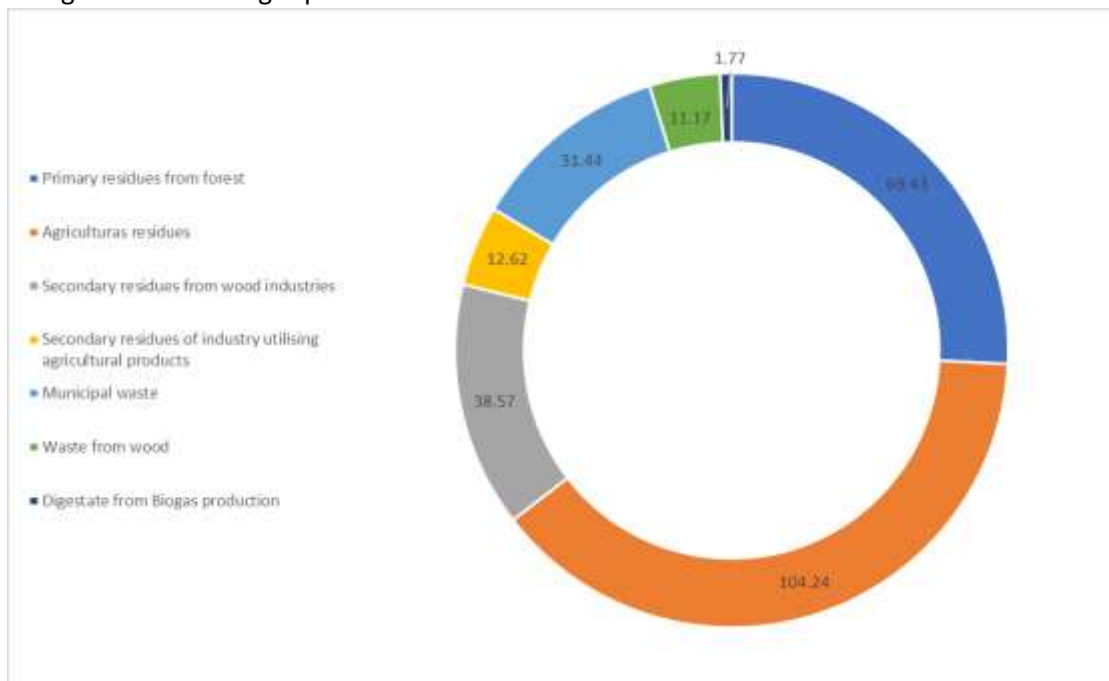
Figure 25. Biomass repartition per typology in terms of energy available (MTOE)

As it can see in Figure 25, the major energy is provided by agricultural residues, primary residues from forest and secondary residues from wood industries respectively: these categories are also the ones that have a greater amount of biomass available (see par. 4.2).

According to previous assessments (biomass availability, biomass repartition per typology in terms of energy available, biomass cost) 10 single residual biomass and 5 mixes of biomass and wastes listed in Table 13 were selected and submitted to chemical-physical characterizations.

Type of feedstock			Sector of production	Main Group
1	Single Material	Olive pomace pitted	Food Industry	Secondary residues of industry utilising agricultural products
2	Single Material	Almond shells	Food Industry	Secondary residues of industry utilising agricultural products
3	Single Material	Corn cobs	Agricultural	Agricultural residues
4 [a)]	Single Material	1- Wheat Straw (pellets 10 mm) 2- Wheat Straw (pellets 6 mm)	Agricultural	Agricultural residues
5	Single Material	Rice husk	Agricultural	Secondary residues of industry utilising agricultural products
6	Single Material	Olive pruning	Agricultural	Agricultural residues
7	Single Material	Arundo donax	Wild crops	Primary residues from forest
8	Single Material	Wood chips	Forestry management	Primary residues from forest
9	Single Material	Sawmill waste	Joinery	Secondary residues from wood industries
10	Single material	Black Liquor	Paper mills	Secondary residues from wood industries
1	Mix	Swarf and sawdust	Wood industries	Secondary residues from wood industries
2	Mix	Multi-essence wood chips	Forestry management	Waste from wood
3	Mix	Subcoal	Waste management	Municipal waste
4	Mix	Municipal solid waste	Waste management	Municipal waste
5	Mix	Digestate	Waste management	Digestate from biogas production

a) For this type of residues, samples of two different pellet diameters were supplied for characterization.

Table 13. List of the residual feedstocks selected within BLAZE

8 BIOMASS CHARACTERIZATION

Different chemical and physical characterizations were carried out on residual biomass feedstocks, 10 single materials and 5 mixes, as selected by the assessment carried out in the previous chapters.

Aim of the activity was to collect their main relevant properties, and thus preliminary evaluate about their performances, as a fuel to be used in a process of gasification for power production via SOFC in accordance with the overall goal of the BLAZE projects.

Based on the whole data set collected, with the exception of corn cobs and black liquor (BL), it appears that all woody and herbaceous biomass feedstocks can potentially be used as fuel in a process of gasification with a BFB reactor. However, for most parts of these feedstocks, the contents of S and Cl found could lead to levels of gaseous products containing S and Cl (e.g. H_2S, HCl and alkali halides) too high for a use of the product gas in a SOFC. A first gas cleaning to reduce their concentrations at level consistent with the SOFC specification need to be considered for all these matrices. Corn cobs and BL need to be excluded mainly due to their rather low ash melting temperatures compared to the typical values adopted in BFB gasification (i.e. slightly above 600 °C vs 800-850 °C).

As far as MSW and digestate is concerned, with respect to their performance in gasification, these feedstocks should be further assessed from an energy viewpoint due to their significantly low heating calorific values compared to all the other considered matrices. Their exploitation in a gasification process appears challenging also based on the results coming from the analysis of major and minor metal elements. From these data in fact MSW and digestate has revealed a rather high content of K, Na, Pb and Zn which in combination with the high content of Cl could lead to the formation of their respective chlorides, present in the form of vapors in the product gas. Although depending on concentration in the gaseous flow and time of exposure, KCl and NaCl are known to have a negative effect on SOFC performances. As far as the presence of $PbCl_2$ and $ZnCl_2$, and their effect on SOFC, is concerned the reference literature is instead missing. The presence of these two species in the producer gas must nonetheless be considered because of their environmental related issues. Together with subcoal, for MSW and digestate, on the basis of the ultimate analysis, a producer gas with relatively high contents of H_2S and HCl is also plausible.

8.1 Standard protocols

The characterization for the acquisition of the most relevant data for biomass feedstocks exploitation via gasification were all carried out on samples prepared from a sub-sample representative of the original material. Sub-sampling and sample preparations were carried out in accordance with the relative UNI EN protocols. Before analysis, each feedstock was milled in a knife mill at 1 mm and dried at 105 °C up to constant weight, in accordance with CEN/TS 14780 and UNI EN 14774-1 protocols.

In Table 14 a list of the protocols of reference adopted for each carried out measurement is presented.

Characterization	Parameter	Ref. Method
Sample preparation	Size of particles, after representative sample grinding	UNI EN 14780
Humidity	Amount of water in the as received sample	UNI EN 14774-1 (ASTM E203)
Bulk density	Mass of sample per occupied volume by the "as received" sample	UNI EN 15103
Proximate Analysis	Ash content	UNI EN 14775 – TAPPI T211 om93
	Volatile Matter (VM)	UNI EN 15148, mod. ASTM modif. D3175
	Fixed Carbon (FC)	
Ultimate Analysis	Elemental analysis (C, H, N, O)	UNI EN 15104
	Sulfur (S), Chlorine (Cl)	UNI EN 15289
Major metal elements	Content of Al, Ca, Fe, Mg, K, Si, Na, Ti	UNI EN 15290
Minor metal elements	Content of Cd, Cr, Cu, Mn, Ni, Pb, V, Zn	UNI EN 15297
Calorific value	Higher Heating Value (HHV) Lower Heating Value (LHV)	UNI EN 14918, ISO 1928 DIN 51900 – TAPPI Test T684
Ash melting	Melting Temperatures	CEN/TS 15370-1, ISO 540: 1995 and DIN 51730: 1998.

Table 14. Methods of reference for the most relevant characterizations of the residual feedstocks selected within BLAZE.

In the case of Black Liquor sample, for some of the determinations TAPPI Standard procedures were adopted. Specifically, the ash value was determined according to the TAPPI T211 om 93, the Solid content (corresponding to humidity content) with the TAPPI Test T650, and the Heating Values with the TAPPI Test T684.

To complete the assessment of the selected residues about thermal decomposition of ash and reactivity under oxidizing conditions (i.e. TGA of ash, temperature of ignition and burn-out), procedure in accordance with literature were adopted.

8.2 Humidity content

The determination of humidity was performed directly on the as received samples, before their further reduction, in accordance with CEN/TS UNI EN 14774-1 protocols. In short, on each feedstock three samples of about 300 g each were kept in an oven at 105 °C up to constant weight. Each value was obtained as a mean value of at least three measurements.

In the case of black liquor, nominal humidity content indicated by the supplier was around 20 %-wt; due to its slurry consistence, for the humidity value acquisition of this sample the TAPPI Test T650 protocol, specifically design for weak and strong black liquors samples, was adopted.

8.3 Proximate analysis

This set of analysis gives data on ash, volatile matter (VM), and fixed carbon (FC) of a solid biofuel. Ash and VM are both experimentally quantified, while FC is calculated by mass balance.

The experimental measurements were carried out on a 105 °C dried specimen and were expressed as a percentage by weight, on a dry basis. Each value was obtained as a mean of at least three measurements.

8.3.1 Ash

According to UNI EN 14775, ash content is defined as the mass of inorganic residue remaining after combustion of a biomass under specified conditions, the value is expressed as a weight percentage of the dry matter in the biomass. The sample combustion is carried out in air under controlled heating rate to reach a final temperature of 550 °C (± 10 °C). The sample is then kept at this temperature up to constant weight.

8.3.2 Volatile Matter (VM)

This determination is based on the standard protocol UNI EN 15148 and is applicable to all solid biofuels; it represents the loss in mass when solid dry biofuel is heated out of contact with air, under defined conditions. To the aim, about 1 g of the dried sample is transferred in a crucible of inert material, covered with a well-fitting lid and weighed. Then the dish is placed in a muffle heated at 900 °C (± 10 °C) and kept at this temperature for 7 min. To prevent oxidation of the material, the sample is heated out of contact with ambient air. The crucible is then extracted from the muffle, allowed to cool down and then weighted. The percentage of volatile matter is calculated from the loss in mass.

8.3.3 Fixed Carbon (FC)

Fixed carbon (FC) is an indirect determination. It is calculated by difference from VM and ash amounts, dry basis, as in the equation below:

$$FC\ (\%\text{-wt}) = 100 - [VM\ (\%\text{-wt}) + Ash\ (\%\text{-wt})]$$

The complete set of proximate analysis for the biomass feedstocks selected in the project, and related humidity content of the «as received» samples, are summarized in Table 15:

Feedstock	Humidity (%-wt, as received)	(%-wt, dry basis)		
		Ash	VM	FC
Olive pomace pitted	36.3	5.95	73.01	21.04
Almond shells	10.0	1.31	80.35	18.33
Corn cobs	9.0	3.04	78.99	17.97
1- Wheat Straw (pellets 10 mm)	7.6	9.22	72.69	18.09
2- Wheat Straw (pellets 6 mm)	7.6	13.29	69.10	17.61
Rice husks	5.2	14.70	67.70	17.60
Arundo Donax	10.1	3.43	79.50	16.22
Sawmill waste	11.2	0.41	81.8	17.8
Wood chips	8.9	0.54	81.20	18.26
Olive Prunings	14.9	1.55	80.8	17.66
Black Liquor	20.6	48.28	43.54	8.18
Swarf and sawdust	6.6	0.43	84.66	14.91
Multi-essence wood chips	24.5	1.45	81.50	17.05
Subcoal	3.2	15.60	72.52	11.88
Municipal solid waste	23.0	47.01	40.32	12.67
Digestate	71.2	25.81	63.97	10.22

Table 15. Humidity content and Proximate analysis of the residual feedstocks selected in BLAZE.

The collected data drawn attention on the results concerning the produced ash and in particular on all those samples producing a quite significant amount, higher than 5-6 %-wt, since such values suggests issues related to ash removal from the gasification bed material and their disposal.

8.4 Ultimate analysis

This analysis gives data on the content of elements such as carbon, hydrogen, nitrogen, oxygen, sulfur and chlorine, present in the considered feedstocks. All these elements are the most relevant in mass balances and process modelling of a gasification process. Moreover, chemical species generated during the gasification process from some of them (i.e. S, Cl, N) can be responsible of poisoning effects on the plant components devoted to catalytic stages. Measurements about these last elements are carried out also because their products can have environmental impact.

8.4.1 Elemental analysis (CHN/O)

According to the procedures of reference C, H, and N are measured by elemental analyzer. Oxygen is calculated by mass balance. For the aim of the present activity, data were acquired with the Vario MICRO Cube CHN/O elemental analyzer, by Elementar. The analytical principle is based on a complete combustion reaction in which a known amount of dry sample is burned to convert the material into ash

and flue gas products; the produced gas stream is then analyzed quantitatively through the specific instrumental gas-analysis procedure, which is based on a thermal conductivity detector (TCD), to evaluate C, H and N elements as CO_2, H_2O and N_2. To the CHN/O determinations of the BLAZE feedstocks, amounts of about 500 mg of sample from each selected feedstock were used.

8.4.2 *Analysis of Sulphur and Chlorine*

Chlorine and sulfur were determined via combustion in an oxygen bomb and subsequent absorption of the acidic gas components in a $NaHCO_3$/Na_2CO_3 buffer solution. After vapor absorption, the solution was analyzed via *DIONEX DX 500* ion chromatographic system for Cl, and S content (Figure 26).
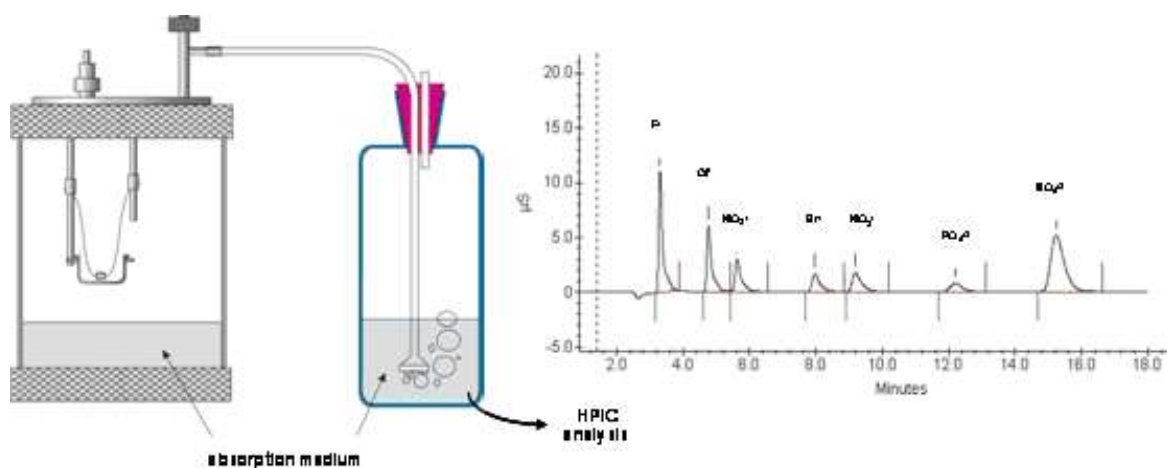
Figure 26. Biomass preparation for Cl, and S analysis via HPIC chromatography (absorption medium: Na_2CO_3/$NaHCO_3$ buffer, pH= 9.5).

Oxygen was ultimately calculated by mass balance, according to the equation below:

$$O \ (\%\text{-wt}) = 100 - [C(\%\text{-wt})+H(\%\text{-wt})+N(\%\text{-wt})+Cl(\%\text{-wt})+S(\%\text{-wt})+Ash(\%\text{-wt})]$$

The results of elemental analysis for all the feedstocks selected in BLAZE are summarized in Table 16.

Feedstock	%-wt, dry basis					
	C	H	N	S	Cl	O
Olive pomace pitted	51.84	7.14	2.79	0.06	0.08	32.14
Almond shells	48.79	6.14	0.51	<0.01	<0.01	43.24
Corn cobs	45.73	6.24	0.44	0.03	0.44	44.08
1- Wheat Straw (pellets 10 mm)	42.89	5.81	0.98	0.05	0.12	40.93
2- Wheat Straw (pellets 6 mm)	41.93	5.79	0.91	0.08	0.21	37.79
Rice husks	43.73	5.31	0.1	0.02	0.03	36.11
Arundo Donax	45.05	6.17	0.55	0.11	0.29	44.40
Sawmill waste	49.40	5.84	0.43	<0.01	<0.01	43.92
Wood chips	45.81	5.85	0.1	<0.01	<0.01	47.69
Olive Prunings	49.57	5.96	0.10	<0.01	<0.01	42.80
Black Liquor	33.27	3.87	0.15	0.74	0.12	13.57
Swarf and sawdust	47.07	6.15	0.1	<0.01	<0.01	46.24
Multi-essence wood chips	49.88	5.80	1.06	0.02	<0.01	41.79
Subcoal	53.74	9.04	2.25	0.1	1.0	18.27
Municipal Solid Waste (MSW)	32.65	4.43	2.37	0.2	0.4	12.94
Digestate	32.22	4.51	3.07	0.97	0.1	33.32

Table 16. Elemental analysis of the residual feedstocks selected within BLAZE.

data collected in the case of elemental analysis draw attention in particular on those samples having a relatively high content in S and Cl elements (e.g. corn cobs, wheat straw, black liquor, subcoal ecc.), because of their potential negative effects on the operation of the SOFC unit. According to the BLAZE project scheme, a SOFC is in fact the end user to produce power from the produced syngas. Their relatively high content then emphasize the need of very effective solutions to be implemented, such as sorbents and guard beds, to reduce the content of related gaseous products (e.g. HCl, H_2S, vapors of alkali halides), in case of use of these materials as feedstocks for gasification, and thus reduce the risk that the gaseous product containing these elements could reach the SOFC unit.

8.4.3   Calorific Value (HHV and LHV)

These parameters are relevant for assessing the energy balance and energy efficiency of a gasification process. The higher heating value (HHV) was measured in an adiabatic bomb calorimeter, at constant volume and at a reference temperature of 25 °C. Lower heating value (LHV) was instead calculated from HHV according to the equation:

$$LHV(kJ/kg) = HHV(kJ/kg) - 212.2(kJ/kg) \times H(\%\text{-wt}) - 0.8(kJ/kg) \times [O(\%\text{-wt}) + N(\%\text{-wt})]$$

HHV values were measured using an *IKA Calorimeter C4000*, calibrated by combustion of certified benzoic acid.

The results for the heating value determination for all the feedstocks of relevance in BLAZE are summarized in 17.

Feedstock	MJ/kg$_{Feedstock}$, dry basis	
	HHV	LHV
Olive pomace pitted	21.35	19.79
Almond shells	19.02	17.68
Corn cobs	17.98	16.62
1- Wheat Straw (pellets 10 mm)	17.25	15.98
2- Wheat Straw (pellets 6 mm)	16.66	15.40
Rice husk	16.35	15.19
Arundo Donax	17.70	16.25
Sawmill waste	20.16	18.89
Wood chips	18.09	16.74
Olive Prunings	19.06	17.76
Black Liquor	12.08	11.20
Swarf and sawdust	18.48	17.14
Multi-essence wood chips	19.14	17.88
Subcoal	23.65	21.68
Municipal solid waste	11.19	10.22
Digestate	13.70	12.69

Table 17. Higher and lower heating values of the of the residual feedstocks selected within BLAZE.

From these data the main considerations concern the feedstocks with relatively low heating values, such as black liquor, municipal solid waste and digestate, which could have negative effect on the overall energy process integrations and thermal self-sustainability.

8.5 Determination of major and minor elements

The UNI EN 15290 and 15297 standards describes methods for the determination of the content of major (i.e. Al, Si, K, Na, Ca, Mg, Fe, Ti) and minor (i.e. Cd, Cr, Cu, Mn, Ni, Pb, V, Zn) elements in solid biofuels.

The procedure is based on the process of acid digestion of solid biofuel samples carried out in a closed vessel heated by means of an electrical resistance.

In a typical test of feedstock digestion, an amount of 500 mg of milled sample is mixed with H_2O_2, HNO_3

and HF in a closed vessel to allow the decomposition reaction. The vessel is left at ambient conditions for at least 5 minutes, during which the mix of reagents start the reactions, then it is closed and heated up to 134 °C to complete the process of chemical digestion and dissolution of any inorganic produced salts.

The quantification of each element of interest is then carried out by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) on the solution obtained at the end of the acid digestion, or on those obtained from it after proper dilution. All these analysis were carried out using an ICP-OES 700 S instrument, by Agilent Technology.

The values acquire on the feedstocks selected for the aim of the BLAZE project presented in 18 and 19.

Feedstock	mg/kg$_{Feedstock}$							
	Al	Ca	Fe	Mg	K	Si	Na	Ti
Olive pomace pitted	1934.0	11522.9	1154.7	336.3	6374.7	11830.8	583.5	492.0
Almond shells	98.0	610.0	178.0	280.0	4100.0	2650.0	250.0	10.0
Corn cobs	19.7	271.6	121.4	230.2	9784.7	1918.2	111.3	4.7
1- Wheat Straw (pellets 10 mm)	2228.9	6525.9	2288.3	1246.4	10584.4	21787.2	2267.6	53.3
2- Wheat Straw (pellets 6 mm)	4308.2	12878.4	2267.6	4421.3	2288.3	23857.0	10584.4	115.0
Rice husk	230.1	2856.2	156.0	336.2	5789.0	56322.0	522.0	5.0
Arundo donax	74.3	1183.7	722.1	834.8	8965.0	8907.4	256.9	5.0
Sawmill waste	190.3	1181.5	112.1	222.2	498.0	150.4	53.3	33.0
Wood chips	6.2	830.6	<2	303.9	1030.5	56.9	43.0	<3
Olive pruning	41.2	4272.3	52.3	210.0	1788.7	1365.4	49.9	<3
Black liquor	517.9	938.2	50.5	230.0	48654.5	533.7	132364.9	<3
Swarf and sawdust	44.7	1181.4	4.5	342.3	860.8	101.6	56.5	<3
Multi-essence wood chips	58.3	5529.0	125.9	542.5	1694.0	872.6	133.8	<3
Subcoal	14386.1	32172.4	16904.3	2576.8	3296.9	3835.0	2333.4	61.6
Municipal solid waste	24409.5	92839.2	12202.2	9160.9	12124.1	65764.7	10222.7	467.7
Digestate	18000.0	41200.0	7880.0	5600.0	3200.0	54550.0	3500.0	450.0

Table 18. Content of the major inorganic elements in the residual feedstocks selected within BLAZE.

Feedstock	mg/kg_Feedstock							
	Cd	Cr	Cu	Mn	Ni	Pb	V	Zn
Olive pomace pitted	<0.5	<2	33.5	26.2	7.3	16.2	2.6	16.3
Almond shells	<0.5	<2	5.1	56.2	<3	<3	7.8	18.9
Corn cobs	<0.5	19.9	2.4	3.7	8.4	<3	<3	13.9
1- Wheat Straw (pellets 10 mm)	<0.5	18.8	13.5	66.2	8.8	8.5	4.1	15.5
2- Wheat Straw (pellets 6 mm)	<0.5	19.2	9.5	120.9	8.5	8.0	7.2	32.0
Rice husk	8.1	2.1	5.6	185.2	<3	<3	<3	12.2
Arundo donax	2.3	14.9	3.2	33.1	12.7	4.8	<3	107.8
Sawmill waste	<0.5	3.0	<3	35.5	1.0	3.8	<3	6.4
Wood chips	<0.5	<2	<3	1.8	0.4	<3	<3	2.9
Olive pruning	<0.5	2.3	<3	4.3	<3	4.3	3.3	2.8
Black liquor	<0.5	<2	<3	64.2	2.0	3.4	3.8	10.1
Swarf and sawdust	<0.5	4.3	<3	38.0	1.8	<3	<3	<2
Multi-essence wood chips	<0.5	6.3	12.0	7.2	3.8	5.3	3.2	22.4
Subcoal	<0.5	<2	42.2	39.3	<3	23.3	9.2	202.2
Municipal solid waste	<0.5	<2	414.7	583.9	20.3	249.5	10.4	943.1
Digestate	5.6	45.5	78.2	201.2	11.2	55.0	13.2	389.4

Table 19. Content of the minor inorganic elements in the residual feedstocks selected within BLAZE.

The analytical data on the major metal elements show homogeneity in their contents for all woody and herbaceous biomass feedstocks and almost in line with the typical value can be expected for solid biofuels, as in the ISO/FDIS 17225-1 international standard. For Na and K very high values are found in the case of Black Liquor, this in accordance with the origin of the material that comes from a treatment of woody material with *chemicals* containing Na and K. Subcoal, MSW and digestate, with the exception of Ti, are characterized by a content of all the major considered elements significantly higher, from one to two orders of magnitude, thus confirming the result anticipated by the proximate analyses on the related ash. Based on these results in fact, these feedstocks resulted to be those with the highest ash content.

By recalling the results about Cl content determined in the elemental analysis (Table 16), the data presented in Table 18 for corn cobs, wheat straw, arundo donax, black liquor, subcoal, MSW and digestate, due to the relatively high K and/or Na contents, lead to predict the presence of vapors of KCl and/or NaCl in the produced gas, if these materials will be fed to the gasification reactor. This aspect should be taken into account in relation to the fact that vapors of alkali halides could be dangerous for

the SOFC if they reach the unit at concentration higher than a few ppm-v. The integration between the results from ultimate analysis and major metal elements hence suggests to give attention to the possible presence of relatively high concentration of alkali halides in the producer gas when coming from the gasification of the above mentioned materials. In such cases, the integration of very effective solutions in the BLAZE process aimed at reducing their content at levels compliant with the SOFC technical specifications will be crucial to guarantee the unit smooth operation.

With regards to the content of minor elements, the contents measured in all woody and herbaceous biomass feedstocks is also for this set of elements consistent with ISO/FDIS 17225-1. Such consistency can be extended to the woody-related black liquor sample, as well.

Regarding the sample of subcoal, MSW and digestate the alignment with the same standard is observed for most part of the minor inorganic elements. Exceptions are observed for Cu in MSW, Pb in MSW and digestate. In the mentioned standard for this element the maximum value reported are 190 mg/kg (dry feedstock) and 30 mg/kg (dry feedstock), respectively. The higher values can clearly have effect on the final concentrations of these elements in the ashes, both bottom and fly, that would be produced during gasification if these kind of feedstocks are be fed to the gasification reactor. Moreover, as indicated by the elemental analysis for the same matrices, due to the high Cl content formation of $PbCl_2$ vapors can be expected. The same possibility can be suggested also on Zn, for which although the values found in the matrices are not out of range, formation of $ZnCl_2$ and presence as vapor in the produced gas is to be expected, as well.

8.6   Additional measurements and characterization

To better characterize the behaviour of the selected feedstocks, in view of their possible subsequent use in the thermochemical process of gasification, determinations to investigate their reactivity and occurrence of problems associated with the content of certain chemical elements and the nature of the ashes were carried out. Specifically, the additional assessments concerned:
- combustion parameters: ignition and burn-out temperature

thermal behaviour of the produced ashes.

8.6.1   Combustion parameters: ignition and burn-out temperatures

The *ignition* temperature (T_i) is the temperature at which major decompositions of the biomass samples begin to take place, it corresponds to the decomposition region of volatile matter. The *burn-out* temperature ($T_{burn-out}$) is defined as the temperature at which the combustion can be considered complete, that is there is no noticeable weight loss over time.

These two key temperatures are estimated by *Thermo-Gravimetric Analysis* (TGA) technique. Specifically, given a TGA curve, T_i corresponds to the onset of the thermogram, while $T_{burn-out}$

corresponds to the temperature from which the rate of weight loss on DTG curve is less than 1%/min [26]

Usually, low values of T_i and $T_{burn-out}$ are indicative of a greater reactivity and a faster burning of the solid biofuel [27]. These values are indicative of a corresponding relative reactivity also in the gasification processes.

To determine the T_i and $T_{burn-out}$ parameters, TGA thermograms were acquired under oxidizing atmosphere on grinded samples of each selected feedstocks. The curves were acquired with a *TGA 7 Perkin Elmer* instrument operated under air.

TGA and derivative thermogravimetric (DTG) curves of wheat straw and woodchips samples are presented in Figure 27 and 28, respectively, as examples. The entire set of acquired curves is presented in Annex I.

According to the curve trends, as exemplified by the two mentioned biomass feedstocks, three step weight losses can be recognized.

The first step accounts for moisture evaporation, the second is due to oxidative degradation and the last one regards the combustion of the char material produced during the thermogravimetric analysis [28].

Such stages can be better recognized in the DTG curve especially with regard to the processes of degradation/oxidation. In general, the higher the depth and sharpness of the peak, the greater the reactivity of the samples during the related reaction stage [28, 29].

In 20 the estimated T_i and $T_{burn-out}$ values from the whole set of TGA thermograms are summarized:

Feedstock	Combustion temperatures (°C)	
	T_i	$T_{burn-out}$
Olive pomace pitted	277.1	649.6
Almond shells	269.1	604.1
Corn cobs	257.7	542.4
1- Wheat Straw (pellets 10 mm)	295.3	541.0
2- Wheat Straw (pellets 6 mm)	265.7	561.5
Rice husks	299.9	554.2
Arundo Donax	265.9	529.4
Sawmill waste	322.6	580.7
Wood chips	309.1	556.0
Olive Pruning	276.8	558.2
Black Liquor	253.6	480.1
Swarf and sawdust	315.6	556.8

Multi-essence wood chips	297.4	517.7
Subcoal	296.8	554.0
Municipal solid waste	286.4	547.0
Digestate	268.0	549.5

Table 20. T_i and $T_{burn-out}$ for the residual feedstocks selected within BLAZE.

By comparing the collected data, it appears evident that for all the selected materials, the ignition temperature is higher than 250 °C. The specific feedstocks with the relatively low T_i are black liquor and corn cobs, for these materials the data suggest the opportunity to lend attention to the phase of feedstock feeding to the reactor since possible pre-decomposition could already occur in the feeding system if the temperature profiles in this system are not properly addressed.

Concerning the data of temperature burn out, with exception of the black liquor, all the considered feedstocks have values higher of 500 °C. The materials with the highest $T_{burn-out}$ values are olive pomace and almond shells. By using these feedstocks, a less efficient gasification process can be foreseen due to a minor reactivity of the produced char which in turn could result in a higher residual char rate production.

8.6.2 Ash melting behaviour

This determination allows to collect characteristic temperature data that can be used to compare the tendency of the ashes from different solid biofuels to form deposits or in causing bed material agglomeration due to heating. CEN/TS 15370-1:2006 is the most recent protocol currently available for studying the softening and melting behavior at high temperatures of ash produced by solid fuels. The material used for the test is a homogeneous ash sample prepared from the related solid biofuel according to UNI EN 14775. The determination is performed at a defined heating rate in a controlled atmosphere; test specimen made from the ash is heated and continuously observed.

All acquisition have been carried out using a Heating Microscopes Misura® HSML Mod. 1400-3002 by Expert System Solutions.

To the aim, the key temperatures to be acquired are the "shrinkage starting temperature" (SST), the "deformation temperature" (DT), the "hemisphere temperature" (HT) and the "flow temperature" (FT).

According to the mentioned protocol:

➢ SST is defined as the temperature at which the area of the test piece falls below 95% of the original test piece area at 550 C (this process may be due to a number of factors, including the release of carbon dioxide by carbonate decomposition, volatile alkali compounds, and/or sintering);

- DT is the temperature at which the first signs of rounding of the edges of the test piece occurs due to melting;

- HT is the temperature at which the test piece forms a hemisphere, that is the height of the sphere becomes equal to half its base diameter;

- FT is the temperature at which the ash is spread out over the supporting tile in a layer; at this stage the height of the layer is half of the test piece at the hemisphere temperature.

In Figure 29 a representation of these key temperatures is shown.
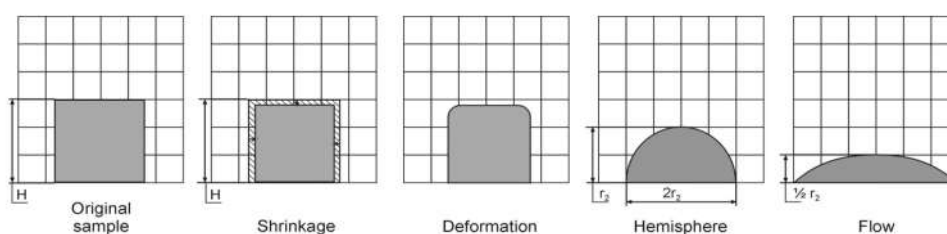
Figure 27 Key temperatures in the ash melting process.

The key temperatures for all the feedstocks selected in BLAZE are summarized in Table 21.

Feedstock	Ash melting temperatures (°C)			
	SST	DT	HT	FT
Olive pomace pitted	1280	1290	1300	1345
Almond shells	915	1000	1180	1210
Corn cobs	625	645	760	995
1- Wheat Straw (pellets 10 mm)	1030	1065	1195	1315
2- Wheat Straw (pellets 6 mm)	1100	1135	1185	1300
Rice husks	920	990	>1385	>1385
Arundo Donax	1005	1185	1290	>1385
Sawmill waste	1250	1300	>1385	>1385
Wood chips	1110	>1385	>1385	>1385
Olive Prunings	1360	1380	>1385	>1385
Black Liquor	675	680	705	730
Swarf and sawdust	1225	>1385	>1385	>1385
Multi-essence wood chips	1335	1370	>1385	>1385
Subcoal	1240	1250	1254	1300
Municipal Solid Waste	1210	1220	1240	1300
Digestate	1020	1245	1260	1300

Table 21. Characteristic ash melting temperatures for the residual feedstocks selected within BLAZE.

According to the acquired data, for most of the selected feedstocks no problems of ash melting are expected to arise during the process of gasification, except in the case of black liquor and corn cobs.

For these two materials in fact the SST and DT data indicate that ash melting starts to occur at temperatures significantly lower than those typically used in gasification processes, which are around 800 °C. Potential issues of bed material defluidization could then be expected if such feedstocks are not used in a gasification process of rather low temperature. To still exploit these two feedstocks throughout a gasification process, a use in an entrained flow gasifier operated in slugging regime, rather than in a BFB gasifier, perhaps would be preferable.

Although characterized by SST and DT above 900°C, the ash melting data on almond shells and rice husks draw attention, as well. This is due to the fact that though feedstock gasification is nominally expected to occur at temperature lower than 900 °C, in a real process hot spots can take place inside the bed material. In this area ash fusion phenomena could be triggered, with consequent agglomeration of the bed material and loss of fluidization.

8.7 Evaluation of the thermophysical characteristics of ashes

8.7.1 Thermogravimetric analysis of ash

Thermogravimetric analysis (TGA) of ash samples of each feedstocks was performed to determine further parameters regarding their thermal behavior. Specifically, from the analysis of the TGA and DTG (Derivative Thermo-Gravimetric) curves, thermal decomposition and evaporation stages, occurring during the heating of the samples, can be highlighted [30].

Based on data available in literature [32, 33, 34], the peaks contained in the temperature ranges 350÷400 °C and 600÷800 °C can be recognized as the thermal decomposition of $MgCO_3$ to MgO, and $CaCO_3$ to CaO, respectively. In the higher temperature range, typically 700÷950 °C, KCl evaporation can also be observed.

The whole set of acquired thermograms is presented in Annex II. Based on the TGA and DTG curves acquired on the feedstocks considered under the present BLAZE Task, with the exception of Corn cobs, in all ashes from the considered feedstocks, the area of $CaCO_3$ decomposition was recognizable. $MgCO_3$ decomposition was well evident only in samples from woody residues, wheat straw, municipal solid waste and digestate. These results were also in accordance with the relatively high content of the two elements shown by the ICP-OES data analysis (Table 18). The signal due to KCl vapors was also evident in particular in the case of subcoal, wheat straw and corn cobs. For these feedstocks, this result highlights that, in case of use in gasification, KCl presence in the produced syngas can be expected.

8.7.2 Fouling tendency

Several inorganic constituents present in the fuel can be causes of the onset of fouling issues [30, 31] in plants involving thermochemical processes for energy conversion of solid fuels. The major elements leading to such ash behavior are alkali metals (K, Na), alkaline earth metals (Ca, Mg) and silicon [31, 32]. In the presence of aluminosilicates, alkali and alkaline earth metals lower the ash fusion temperature resulting in an increase in fouling tendency [33], as well as in slagging.

In the literature several studies are proposed to have a prediction on the thermal behavior of ashes. Two of the most important parameters for this assessment are the basic-acidic compounds ratio index ($R_{b/a}$) [34, 35] and the index of fouling (Fu). They are respectively defined as:

$$R_{b/a} = \frac{\%(Fe_2O_3 + CaO + MgO + K_2O + Na_2O)}{\%(SiO_2 + TiO_2 + Al_2O_3)} \qquad (1)$$

$$Fu = R_{b/a} \cdot \%(Na_2O + K_2O) \qquad (2)$$

Where the % values are calculated as relative content with respect to the determined ash amount.

Based on the index of fouling, characteristic range of values can be identified. A summary of such ranges is presented in Table 22.

Fouling index	Tendency to fouling
Fu < 0.6	Low
0.6 < Fu < 40	Medium
Fu ≥ 40	High

Table 22. Evaluation of fouling tendency of ashes from biomass feedstocks.

In Table 23 evaluation of the fouling tendency is estimated for all the feedstocks considered in the BLAZE project, together with the related expected tendencies.

Feedstocks	Fu[a)]	Tendency to fouling
Olive pomace pitted	12.8	Medium
Almond shells	47.0	High
Corn cobs	121.8	High
1- Wheat Straw (pellets 10 mm)	4.1	Medium
2- Wheat Straw (pellets 6 mm)	8.9	Medium
Rice husks	0.5	Low
Arundo Donax	25.8	Medium
Sawmill waste	48.4	High
Wood chips	205.5	High
Olive prunings	41.2	High
Black liquor	5528.7	High

Swarf and sawdust	282.4	High
Multi-essence wood chips	85.3	High
Subcoal	10.4	Medium
Municipal Solid Waste (MSW)	6.2	Medium
Digestate	1.8	Medium

a) calculated on the basis of amount of minor and major chemical elements measured via ICP-OES analysis (Table 18 and Table 19).

Table 23. Fouling tendency for all the residual feedstocks selected within BLAZE.

Within the terms of the qualitative value of the fouling index approach, the results of the assessment presented in Table 23 indicate that, with the exception of the rice husk, all the considered samples can give rise to fouling issues, with a probability ranging from *Medium to High*. Although the entity of the phenomenon will depend on the specific amount of the produced ash, this aspect should be taken into account in order to avoid the risk of inorganic vapor condensation in the piping and equipment present along the transfer of the producer gas to SOFC, as well as in the SOFC itself.

9 CONCLUSION

The general objective of this report was the selection and collection of preliminary information on the types of feedstocks in order to evaluate their potential use in the BLAZE gasification process. In this perspective, based on the experimental data collected on the received representative samples, and on their respective ashes, some first evaluations can be accomplished.

Mainly based on the results from the ash melting study, corn cobs and black liquor do not appear very promising as possible feedstock for biomass gasification in a bubbling fluidized bed (BFB) reactor. That is because of their low melting temperature compared to that typically used in this type of gasifiers. Still based on data from ash behavior, almond shells and rice husks needs some attention, as well. Control of the temperature profiles inside the reactor is a very important aspect to keep present in the use of this type of feedstocks. Hot spots should be avoided because, according to the SST and DT temperatures, phenomena of ash melting and bed agglomeration may occur.

From the data about proximate and elemental analysis, subcoal, municipal solid waste and digestate appear as difficult feedstocks for application in gasification due to the high amount of ash produced and high Cl and S contents. Moreover, taking in to account the quite high content in K and Na elements, as well as in Pb and Zn, presence of vapors of KCl, NaCl, $PbCl_2$ and $ZnCl_2$ in the producer gas can be expected. Depending on the concentration in the gaseous flow and time of exposure, KCl and NaCl are known to have a negative effect on SOFC performances. As far as the presence of $PbCl_2$ and $ZnCl_2$, and their effect on SOFC, is concerned the reference literature is instead missing. Nonetheless, the presence of these two species in the producer gas must be considered because of their environmental related issues.

For all the other remaining feedstocks, all of which are woody and herbaceous biomass types, no special issues are foreseen with regard to their use as feedstocks in a process of gasification in a BFB reactor. However, for most of them attention is lead from the relatively high content of S and Cl because during gasification they will give rise to production of S and Cl containing products (e.g. H_2S, HCl and alkali chlorides) that can be noxious to any catalytic downstream equipment and to the SOFC unit.

For all these feedstocks, the chemical analysis then support the need to properly address issues related to the presence of inorganic gas contaminants with effective solutions for gas cleaning, able to allow their reduction to levels consistent with the technical specifications of any plant component, downstream of the gasifier, that could be damaged by their presence.

An overview of recommendations for each of the 15 considered feedstocks is presented in Table 24.

Feedstocks	Overall recommendations
Olive pomace pitted	Feedstocks with overall characteristics **suitable** to its use in gasification according to the BLAZE BFB reactor. H_2S, HCl and KCl in the producer gas are expected; use of solutions to reduce their content would be required to preserve the smooth operation of the SOFC.
Almond shells	Feedstocks with overall characteristics **suitable** to its use in gasification according to the BLAZE BFB reactor. **Attention** should be led to the gasification temperature in the reactor due to a process

	temperature quite close to the expected process value. H$_2$S, HCl, KCl in the producer gas are expected.
Corn cobs	**NOT** indicated for use in a BFB gasification process due to low ash melting temperatures.
1- Wheat Straw (pellets 10 mm)	Feedstocks with overall characteristics **suitable** to its use in gasification according to the BLAZE BFB reactor. **Attention** should be led to the relatively high ash content. H$_2$S, HCl, KCl and NaCl in the producer gas are expected; use of solutions to reduce their content would be required to preserve the smooth operation of the SOFC.
2- Wheat Straw (pellets 6 mm)	Feedstocks with overall characteristics **suitable** to its use in gasification according to the BLAZE BFB reactor. **Attention** should be led to the relatively high ash content. H$_2$S, HCl, KCl and NaCl in the producer gas are expected; use of solutions to reduce their content would be required to preserve the smooth operation of the SOFC.
Rice husks	Feedstocks with overall characteristics **suitable** to its use in gasification according to the BLAZE BFB reactor. **Attention** should be led to the gasification temperature in the reactor due to a process temperature quite close to the expected process value. H$_2$S, HCl, KCl in the producer gas are expected.
Arundo Donax	Feedstocks with overall characteristics **suitable** to its use in gasification according to the BLAZE BFB reactor. H$_2$S, HCl, KCl in the producer gas are expected; use of solutions to reduce their content would be required to preserve the smooth operation of the SOFC.
Sawmill waste	Feedstocks with overall characteristics **suitable** to its use in gasification according to the BLAZE BFB reactor. H$_2$S and HCl in the producer gas are expected; use of solutions to reduce their content would be required to preserve the smooth operation of the SOFC.
Wood chips	Feedstocks with overall characteristics **suitable** to its use in gasification according to the BLAZE BFB reactor. H$_2$S and HCl in the producer gas are expected; use of solutions to reduce their content would be required to preserve the smooth operation of the SOFC.
Olive prunings	Feedstocks with overall characteristics **suitable** to its use in gasification according to the BLAZE BFB reactor. H$_2$S, HCl and KCl in the producer gas are expected; use of solutions to reduce their content would be required to preserve the smooth operation of the SOFC.
Black liquor	**NOT** indicated for use in a BFB gasification process due to low ash melting temperatures.
Swarf and sawdust	Feedstocks with overall characteristics **suitable** to its use in gasification according to the BLAZE BFB reactor. H$_2$S and HCl in the producer gas are expected; use of solutions to reduce their content would be required to preserve the smooth operation of the SOFC.
Multi-essence wood chips	Feedstocks with overall characteristics **suitable** to its use in gasification according to the BLAZE BFB reactor. H2S, HCl and KCl in the producer gas are expected; use of solutions to reduce their content would be required to preserve the smooth operation of the SOFC.
Subcoal	Feedstocks with overall characteristics **suitable** to its use in gasification according to the BLAZE BFB reactor. **Attention** should be led to the relatively high ash content. H$_2$S, HCl, KCl and NaCl in the producer gas are expected; use of solutions to reduce their content would be required to preserve the smooth operation of the SOFC.
Municipal Solid Waste (MSW)	Feedstocks with overall characteristics **suitable** to its use in gasification according to the BLAZE BFB reactor. **Attention** should be led to the quite high ash content and low heating values. H2S, HCl, KCl and NaCl in the producer gas are expected; use of solutions to reduce their content would be required to preserve the smooth operation of the SOFC. Presence of PbCl$_2$ and ZnCl$_2$ are also expected.
Digestate	Feedstocks with overall characteristics **suitable** to its use in gasification according to the BLAZE BFB reactor. **Attention** should be led to the quite high ash content and low LHV value. H$_2$S, HCl, KCl and NaCl in the producer gas are expected; use of solutions to reduce their content would be required to preserve the smooth operation of the SOFC. Presence of PbCl$_2$ and ZnCl$_2$ are also expected.

Table 24. Overall recommendations on the exploitation of the fifteen selected residual matrices as feedstocks in the BLAZE gasification process.

In order to select the biomass to test in the gasification process in the next deliverable here follows the strengths and weaknesses of each type of biomass, considering availability, supply cost and chemical-physical characterization.

The following table presents all the types of biomass and it shows the most important characteristics. The biomass is ordered by the low heating value:

Feedstock	CATEGORY	Humidity (%-wt, as received)	LHV MJ/kg	Ash %wt, dry basis	S %wt, dry basis	Cl %wt, dry basis	Ash melting T (DT) (°C)
Subcoal	Municipal waste	3,20	21,68	15,60	0,10	1,00	1250,00
Olive pomace pitted	Secondary residues of industry utilising agricultural products	36,30	19,79	5,95	0,06	0,08	1290,00
Sawmill waste	Primary residues from forest	11,20	18,89	0,41	<0.01	<0.01	1300,00
Multi-essence wood chips	Waste from wood	24,50	17,88	1,45	0,02	<0,01	1370,00
Olive Prunings	Secondary residues from wood industries	14,90	17,76	1,55	<0.01	<0.01	1380,00
Almond shells	Secondary residues of industry utilising agricultural products	10,00	17,68	1,31	<0.01	<0.01	1000,00
Swarf and sawdust	Secondary residues from wood industries	6,60	17,14	0,43	<0.01	<0.01	>1385
Wood chips	Primary residues from forest	8,90	16,74	0,54	<0.01	<0.01	>1385
Corn cobs	Agricultural residues	9,00	16,62	3,04	0,03	0,44	645,00
Arundo Donax	Agricultural residues	10,10	16,25	3,43	0,11	0,29	1185,00
1- Wheat Straw (pellets 10 mm)	Agricultural residues	7,60	15,98	9,22	0,05	0,12	1065,00
2- Wheat Straw (pellets 6 mm)	Agricultural residues	7,60	15,40	13,29	0,08	0,21	1135,00
Rice husks	Secondary residues of industry utilising agricultural products	5,20	15,19	14,70	0,02	0,03	990,00
Digestate	Digestate from biogas production	71,20	12,69	25,81	0,97	0,10	1245,00
Black Liquor	Secondary residues from wood industries	20,60	11,20	48,28	0,74	0,12	680,00
Municipal solid waste	Municipal waste	23,00	10,22	47,01	0,20	0,40	1220,00

Table 25. Biomass types and technical characteristics.

The tables 26 and 27 instead, show the categories of biomass that have been analysed, sorted according to their estimated potential in Europe and their supply chain cost:

CATEGORY	potential (Kton dry mass/y)
Agricultural residues	264986,32
Primary residues from forest	167641,91
Municipal waste	89763,53
Secondary residues from wood industries	87906,47
Secondary residues of industry utilising agricultural products	29527,11
Waste from wood	26418,22
Digestate from biogas production	12634,60

Table 26. Biomass categories sorted for their potential.

CATEGORY	cost €/ton
Waste from wood	15
Agricultural residues	28
Primary residues from forest	35
Secondary residues from wood industries	35
Secondary residues of industry utilising agricultural products	55
Municipal waste	60
Digestate from biogas production	66[4]

Table 27.Biomass categories sorted for their cost.

Among the types of biomass with the highest LHV there are some that have some disadvantages, such as the high ash content and humidity and a considerable content of contaminants (subcoal and olive pomace), as shown in the table 25.

In the tests to carry out in lab scale, it is therefore suggested to analyse subcoal and olive pomace, to better test and assess the functionality of the sorbents.

Among the types penalized by a high ash content we find rice hust, digestate, MSW and black liquor. The latter can cause problems in gasification also because of the low ash melting temperature (680 °C), which would exclude it a priori from a process that is normally held at higher temperatures. The digestate is not to be considered particularly favoured also due to the high levels of humidity, sulphur and its scarce availability.

The agricultural residues, although not presenting the higher LHV values, have low values of ash, humidity and contaminants. Almond shells (Secondary residues of industry utilizing agricultural products) also presents very good technical values such as low contaminants, high ash melting temperature, high LHV and low ashes content.

It is possible to see from table 26 and 27 how the waste from wood has the lower price but is very scarce in terms of potential. The biomasses that may seem more interesting are the agricultural residues, this category has low price and the higher potential in Europe.

Considering the technical and economic aspects, it is therefore suggested, in the context of the experimentation that sees the coupling of gasification and SOFC (100 kWth gasifier and 25 kWe of SOFC, WP6), to test and investigate one of the following biomass:

- Agricultural residues: Arundo Donax or similar.
- Primary residues from forest: Sawmill, Wood Chips.
- Secondary residues from wood industry: Sawdust.
- Secondary residues of industry utilizing agricultural products: almond shell or similar.
- Waste from wood: Wood Chips.

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[4] Even in this case the price for MSW and digestate was set considering the collection and not the raw material, that can be considered 0 as it is a waste.

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