



DELIVERABLE D2.1

Selection of biomass feedstocks

DISSEMINATION LEVEL: PUBLIC

*Grant Agreement no 101006656
Research and Innovation Actions (RIA) project
Granted by:
Innovation and Networks Executive Agency (INEA)*

Document Control Sheet

Project	GICO Gasification Integrated with CO ₂ capture and conversion																
Grant Agreement n.	101006656																
Document Title	D2.1 Selection of biomass feedstocks																
Lead Beneficiary	P. N. 6 - CSIC																
WP number	WP2																
Type	Report																
Dissemination level	PU: Public																
	<table border="1"> <thead> <tr> <th>Version</th> <th>Date</th> <th>Description</th> </tr> </thead> <tbody> <tr> <td>1.0</td> <td>11.05.2021</td> <td>Draft version by CSIC</td> </tr> <tr> <td>2.0</td> <td>18.05.2021</td> <td>Draft version integrated by USGM</td> </tr> <tr> <td>3.0</td> <td>27.05.2021</td> <td>Draft version integrated by ENEA and FZJ</td> </tr> <tr> <td>4.0</td> <td>14.07.2021</td> <td>Minor revision from USGM and UNIVAQ</td> </tr> </tbody> </table>		Version	Date	Description	1.0	11.05.2021	Draft version by CSIC	2.0	18.05.2021	Draft version integrated by USGM	3.0	27.05.2021	Draft version integrated by ENEA and FZJ	4.0	14.07.2021	Minor revision from USGM and UNIVAQ
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4.0	14.07.2021	Minor revision from USGM and UNIVAQ															
Date	22/07/2021																
Number of pages	42																
Archive name	D2.1 (Selection of feedstocks and their characterization)																
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EXECUTIVE SUMMARY

This report summarises the selection of biomass wastes with the best prospects as feedstocks for sorption enhanced gasification (SEG) and subsequent CO₂ conversion and oxygen separation (e.g. sorbents, catalyst and membrane). The work corresponds to *WP2- Gasification, sorbents and conditioning, Task 2.1. Feedstock and pre-treatments, Sub-Task 2.1.1. Selection of 20 raw materials*, and has been developed by CSIC, USGM/UNIVAQ and ENEA with FZJ for primary sorbent effect on gasification process.

Based on previous consortium experience and a review of recent bibliography, a large variety of biomasses has been identified in terms of type, availability (t/year in EU), and techno-economic feasibility. On the basis of the combination of a diversity of criteria and taking into account partners' databases and results quoted in the literature, residues (singles or mixtures) with higher potential to be used in gasification have been selected. Such preliminary approach has been subsequently refined by a comprehensive assessment of the physicochemical features of the diverse biomass feedstocks, resulting in the final choice of 10 wastes for direct gasification and 10 residues in which a prior treatment by hydrothermal carbonization could reduce detrimental effects on SEG and CO₂ sorbents and catalysts.

The report is scheduled as follows:

- **Chapter 1, Introduction**, includes a short summary about biomass gasification and subsequent CO₂ conversion and oxygen separation (e.g. sorbents, catalyst and membrane) and the need for suitable feedstocks within the GICO project framework.
- **Chapter 2, Objectives and scope** of the deliverable are presented.
- **Chapter 3, Preliminary assessment of biomass wastes**, summarizes a wide variety of residual biomass and biogenic fraction of wastes classified in terms of category, type, origin, quantity, availability in EU, and describes a preliminary selection of those with greater feasibility for a more efficient use in the energy market.
- **Chapter 4, Analysis of the potential of the selected biomass wastes for enhanced gasification and CO₂ sorbents and catalysts**, compiles the physicochemical features of the feedstocks indicative of profitable gasification and preliminary tests by modelling and HTC as pre-treatment.
- **Chapter 5, Conclusions.**
- **Chapter 6, References.**



1. INTRODUCTION

Biomass is defined as renewable organic matter available that can be converted into energy. This description is different from the one used in ecology where all organic matter in a given habitat is included under this term. Directive 2009/28 / EC of the European Parliament and of the Council, of April 23, 2009, on the promotion of the use of energy from renewable sources defines it in more detail, indicating that biomass corresponds to “the biodegradable fraction of products, waste and residues of 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 of industrial and municipal waste”(1).

Biomass is the fourth largest energy resource in the world (after oil, coal and natural gas) and includes a wide range of materials, such as, among others, wood chips and sawdust, straws, agricultural and forestry residues, municipal organic waste, bagasse generated in the agro-food industry, manures, sewage sludge, digestates, black liquor from the paper mill, etc. Indeed, they display very diverse morphological, structural and physicochemical characteristics.

Biomass has a number of advantages as feedstock for energy generation. It is renewable, safe and clean and produces little waste. It is continuously generated as a result of human, animal and plant activity, so its availability is assured. In addition, its price is lower than that of other fuels and the balance of CO₂ emissions to the environment is neutral. Not least, its use for energy provides additional economic and social benefits by simultaneously disposing degradable and pollutant wastes.

Nevertheless, the energy use of the organic substances is limited, to some extent, by their complexity, poor reliability and low energy density, resulting therefore less efficient than fossil fuels. Additionally, the supply chain presents shortcomings because distribution channels are not yet as widespread as for other fuels. It should not be overlooked that biomass requires more space than other fuels and the storage and high local emissions of pollutants may be limiting drawbacks to be applied for bioenergy (2).

The technical and economic potentials of biomass are higher than the current world energy consumption, thus, the challenge relies on its viable and sustainable utilization (3). The use of biomass residues as feedstock would solve the long-standing drawback associated with the use of biomass as an energy source, i.e. competition with food, and would facilitate the simultaneous disposal and valorisation of highly degradable wastes. To fully exploit the biomass energy, small scale plants offering high reliability and efficiency and low environmental impacts must be developed, to overcome the low energy density and perishability of this fuel.

The gasification of biomass consists of its thermal decomposition (typically above 650 °C) in the presence of gasification agents, e.g. air, oxygen, steam, CO₂ or a combination of these. Such a process transforms the biomass into the so-called bio-syngas containing CO, H₂, CH₄, steam, CO₂, light hydrocarbons and, in case of air gasification, nitrogen (N₂). The fuel gas may contain a certain amount of impurities, e.g. tar, particulates, carbon, hydrogen sulphide (H₂S) and/or hydrogen chloride (HCl) (2).

The type of solid feedstock has a significant impact on the gasification technology: suitable biomass is typically characterised by significant scale availability (a few dozens to thousands t/year) and low cost (negative to maximum 100 €/t), but also by good physical (low water content and high bulk density) and chemical properties (high calorific value and carbon-to-nitrogen ratio, remarkable presence of volatile substances and low ash, chlorine and sulphur content).

New technologies developed at GICO, i.e. *Steam Sorption Enhanced Gasification (Figure 1)*, can treat residual biomass with high moisture content (up to 50%), low ash melting temperature (the optimal gasification temperature, due to CO₂ sorption, decreases from 800 to 650 °C) and higher tar, sulphur and chlorine content (4).

The use of CaO-sorbents in the gasifier will shift the thermodynamic equilibrium towards more H₂ and, thus, the volume fraction of the dry syngas from containing about 40% H₂, 23% CO and CO₂ and 13% CH₄ to being made up of 90% H₂, 5% CO, 2% CO₂ and 3% CH₄). Following GICO process, CaO is converted into CaCO₃ during the gasification of biomass residues and the spent solid sorbent is regenerated by releasing CO₂ in a calcination step at ≥ 900 °C under a CO₂-rich atmosphere.

GICO project raises the possibility of using hydrothermal carbonization to modify certain characteristics of the biomass wastes to make them more suitable for profitable gasification.

In recent years, hydrothermal carbonisation (HTC) has emerged as a very promising technology for the sustainable management of biomass waste (5–9). Without prior drying, the HTC process takes place under temperatures between 160 and 250 °C and the respective autogenous vapour pressure. The lower dielectric constant of subcritical water favours the dissociation of biopolymers by reactions normally catalysed by acids and bases. It provides an excellent medium for the transformation of a wide variety of biomass residues into a C-enriched solid by-product (hydrochar) (5–9).

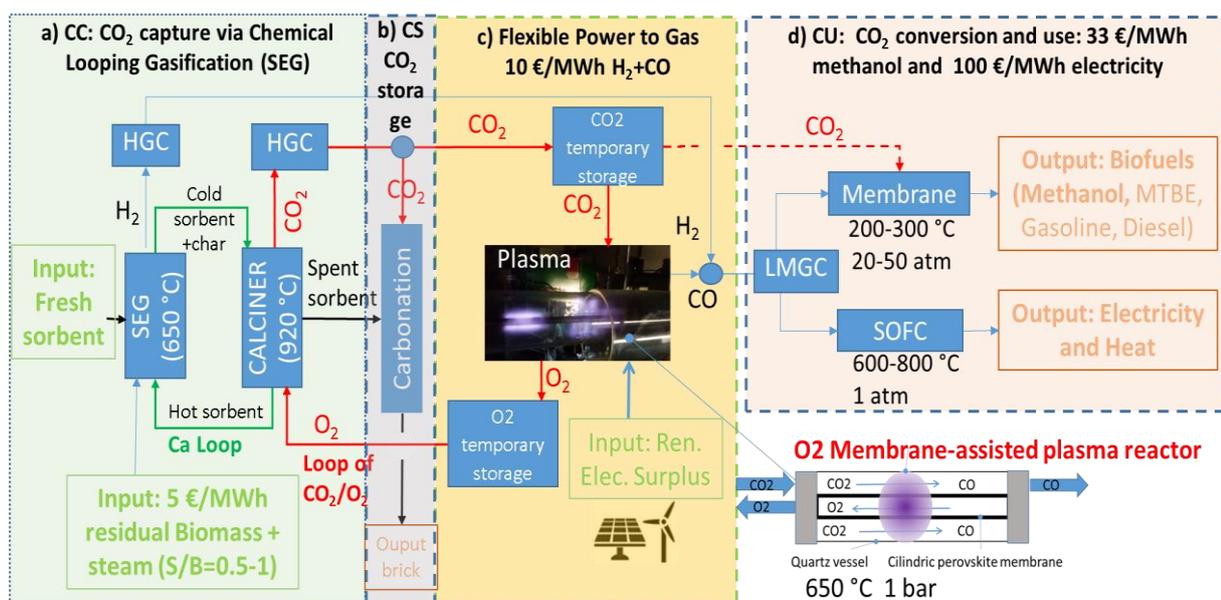
Within the GICO framework, HTC can be used to upgrade a wide variety of biomass and residues for gasification application. On the one hand, HTC produces energy densification (0.7-2) and enhances handling and drying properties of the material, resulting in significant cost savings if compared to the initial biomass. On the other hand, properties of subcritical water and production of organic acids during

hydrothermal treatment increase the solubility of alkali and alkaline earth metals (10,11), leading to partial dissolution of inorganic components. Improved slagging, fouling or alkali indices and combustion properties have been reported for hydrothermally treated biomass wastes (12–14). It has been reported that HTC enables nitrogen and chlorine removal from municipal solid waste (MSW) (15).

The behaviour of biomass ash during hydrothermal treatment depends on the type of feedstock and the conditions under which the process takes place. In general, hydrochars from wood and algae, herbaceous and agricultural residues, compost and faecal waste showed lower ash content than those derived from municipal solid waste (MSW), digestate and municipal and industrial sludge (16). In addition, the ash yield for the first biomass set is lower, indicating differences in both the chemical composition and the solubility of the inorganic components. Generally, hydrochars derived from maize stubble, miscanthus, switch grass, rice husks and olive, artichoke and orange residues and empty fruit bunches have higher contents of K, Mg, S and Si compared to those obtained from industrial sludge. On the other hand, Al, Fe, P, Ca and Si frequently show low solubility.

Along this initial period (6M), a large variety of parameters quoted in the literature as relevant for a successful gasification of biomass, as well as results obtained by CSIC and ENEA were compiled. This was used as a preliminary assessment of the potential of the different wastes as GICO feedstocks.

Figure 1. GICO Concept



2. OBJECTIVES AND SCOPE

The main objective was the selection of 20 biomass wastes, belonging to different categories, as potential feedstocks for GICO.

Taking into account the large scale of the gasification technology, a first selection of biomass waste was made based on its availability in Europe and its cost. It has also been considered that, although some wastes are not the most generated, they do have a high environmental impact because they degrade rapidly and require management beyond landfill or anaerobic digestion.

The data obtained by CSIC and ENEA on their physicochemical characteristics (moisture, content and composition of inorganic impurities, volatile matter, calorific value, thermal behaviour of ashes, etc.), complemented with the information cited in the bibliography, made it possible to establish the advantages and limitations of each of them for the GICO process and, therefore, the selection or rejection as raw material for this project.

Despite belonging to the same category, certain biomass residues, whether with a single compound or a mixture of several materials, can present great heterogeneity in their characteristics. Most of them depend to a large extent on the generation process, the country of origin, seasonality, climatic conditions, etc. For this reason, special efforts have been made to collect data from different sources in order to obtain a more reliable picture of each waste.

On the other hand, it was not necessary to carry out a full characterisation of each material, as some characteristics, such as excess moisture, inappropriate particle size and shape, unsuitable contents of K, Na, Si, etc., fusibility of ashes at low temperature, etc., allowed some candidates to be discarded without further testing.

3. PRELIMINARY SELECTION OF BIOMASS WASTES

Availability in Europe was the first criterion that was agreed to be used to start the selection process. Based on the datasets and the elaborated results provided by the S2Biom project (17), a variety of residual biomass and biogenic fraction of wastes within the following categories has been considered as potential candidates (*Table 1*):

- Primary residues from industrial forestry activities
- Agricultural wastes
- Secondary wastes from the woodworking industries

- Secondary residues from industrial processing of agricultural products
- Municipal waste
- Wood waste
- Digestate generated in biogas production
- Livestock Manures

Although a large-scale availability of all the wastes shown in *Table 1* is assured, their technical characteristics as well as cost, reliability, complexity of the supply chain, environmental impact of their transport and processing, cost-effective routes currently operating for their valorisation, etc. compromise their efficient use and market applicability.

Table 1. Main biomass waste categories and potential availability in EU

Biomass category	Biomass type	Made of	Quantity (kton/year) [dry basis]	Candidate
Primary residues from forestry	1211 -Logging residues from final fellings from non-conifer trees	Branches, leaves, chips, bark, sawdust and other residues from chestnut trees fellings	23,348.37	
	1212 - Logging residues from final fellings from conifer trees	Branches, leaves, chips, bark, sawdust and other residues from pine trees fellings	35,757.92	☐
	1213 - Logging residues from thinnings from nonconifer trees	Branches, sticks and leaves from chestnut trees thinnings	11,960.00	☐
	1214 - Logging residues from thinnings from conifer trees	Branches, sticks and leaves from pine trees thinnings	24,244.88	
	1221 -Stumps from final fellings from nonconifer trees	Stumps and other woody residues produced in the stump removal from chestnut trees	27,797.37	☐
	1222 -Stumps from final fellings from conifer trees	Stumps and other woody residues produced in the stump removal from pine trees	44,533.38	☐

Table 1. (Continued)

Biomass category	Biomass type	Made of	Quantity (kton/year) [dry basis]	Candidate
Agricultural residues	2211 - Rice straw and husk		3,218.15	
	2212 - Cereals straw	Spelt wheat straw, wheat straw	167,181.94	☐
	2213 - Oil seed rape straw	Rape straw	18,029.48	☐
	2214 - Maize stover		43,370.94	☐
	2215 - Sugarbeet leaves		8,044.03	
	2216 - Sunflower straw		12,389.47	☐
	2221 - Residues from vineyards	Leafs, sticks, unripe or overripe grapes and any other residue from grape recollection	2,818.70	☐
	2222 - Residues from fruit tree plantations	Leafs, sticks, unripe or overripe apples and any other residue from apple plantations	3,091.60	
	2223 - Residues from olives tree plantations	Leafs, sticks, unripe or overripe olives and any other residue from olive plantations, Fruit Pruning	5,897.37	☐
	2224 - Residues from citrus tree plantations	Leafs, sticks, unripe or overripe oranges and any other residue from orange tree plantations	944.66	
Secondary residues from wood industries	4111 - Sawdust (conifers)	Sawdust from pine trees, wood sawdust	11,302.45	☐
	4112- Sawdust (nonconifers)	Sawdust from chestnut trees, wood chips	1,579.12	
	4113 - Other residues (conifers)		21,040.79	☐
	4114 - Other residues (non-conifers)		3274.37	
	4121 - Residues from industries producing semi-finished wood based panels	Sawdust, scrap wood pieces and rejects	3,503.86	
	4122 - Residues from further wood processing	Residues from carpentry manufactures	16,068.34	☐
	4131 - Bark	Bark from pine trees or eucalyptus trees	5,465.81	
	4132 - Black liquor	Black liquor from paper mill	25,671.72	☐

Table 1. (Continued)

Biomass category	Biomass type	Made of	Quantity (kton/year) [dry basis]	Candidate
Secondary residues from industrial processing of agricultural products	4211 - Olive-stones	Olive-stones from green and black olives, olive pomace	1,187.14	<input checked="" type="checkbox"/>
	4213 - Rice husk		630.68	<input checked="" type="checkbox"/>
	Empty shells of dried fruit	Almond/Hazelnut/Walnut/Pistachio shells	500 (18)	<input checked="" type="checkbox"/>
	4214 - Pressed grapes dregs	Remains from the first grape pressing, such as seeds, stems, bits of grape skin and any other residue derived from this stage of the process	484.50	
	4215 - Cereal bran	Spelt wheat bran	27,224.78	
Municipal waste	5111 – Bio-waste non-separately collected	MSW and Digestate from MSW	54,101.43	<input checked="" type="checkbox"/>
	5112 – Bio-waste separately collected	remains of vegetables, fruits, pasta, legumes, meat, fish, eggs, etc	35,662.09	<input checked="" type="checkbox"/>
Waste from wood	5211 - Hazardous post-consumer wood		4,044.82	
	5212 – Non-hazardous post-consumer wood		22,373.40	
Digestates from biogas production	Digestate from Biogas production		12,634.60	<input checked="" type="checkbox"/>
Livestock manures	Bovine dry matter		139,079	<input checked="" type="checkbox"/>
	Swine manure		9,247	<input checked="" type="checkbox"/>
	Poultry manure		24,892	<input checked="" type="checkbox"/>

In a second step, interest focused on materials of each category that are generated in industrial processes (e.g. forestry, agricultural and livestock activities, carpentry manufacturing) and from daily activities (municipal solid waste). Alternatively, attention was also paid to wastes that are not produced in such large quantities or with unpromising physicochemical characteristics for gasification, but which, due to their high environmental impact, are worth exploring the possibility of making them feasible through pre-treatment. For example, a waste with a high moisture and/or ash content, which can be reduced by hydrothermal carbonization.

As a result, the following biomass materials were considered as potential candidates for gasification feedstock:

1. Branches, leaves, chips, bark, sawdust and other residues from pine trees fellings
2. Branches, leaves, chips, bark, sawdust and other residues from non-conifer trees fellings
3. Wood chips
4. Wheat straw
5. Oil seed rape straw
6. Maize stover
7. Rice husk
8. Sugarbeet leaves
9. Sunflower stalk
10. Olive tree pruning
11. Vine pruning
12. Almond and hazelnut shells
13. Bagasse, stalks and seeds from grapes
14. Olive pomace
15. Residues from canning industry: broccoli and thistle
16. Whey
17. Wood sawdust
18. Out-of-use wood
19. Black liquor from paper mill
20. Bio-stabilized municipal solid waste (MSW)
21. Organic fraction of municipal solid waste (OFMSW)
22. Digestate from biogas production
23. Bovine, swine and poultry manures
24. Sewage sludge

4. ON THE PHYSICOCHEMICAL CHARACTERISTICS OF THE SELECTED BIOMASS FOR ENHANCED GASIFICATION

4.1. Biomass specifications for efficient gasification

Among the many characteristics to be taken into account in biomass processing, moisture, size and shape and density are some of the most relevant parameters for efficient gasification.

In every energy conversion process, fuels with a high calorific value are favourites, because of energy needs in terms of efficiency and power density. In the context of thermochemical processes as gasification, this implies that moisture affects both the quantity and quality of the feedstock and biomass with lower humidity is preferable. In case of too high moisture percentage, the material may be partly dried by using the excess of heat produced by the power plant. On the other hand, climate and seasonality will also affect the water content of biomass.

The real and apparent densities vary considerably depending on the biomass morphology and have an impact on their application in gasification processes. Density significantly affects any freight and storage. Furthermore, in the fluidized bed gasifier, the density of the biomass must be comparable to that of the bed material for achieving a good mixing.

The wide variety of sizes and shapes of the various biomasses determines their suitability for subsequent gasification. The biomass must be processed to a uniform size and shape to feed the gasifier at a suitable rate and to ensure homogeneous and efficient thermochemical transformation and energy generation. This may involve a significant cost for shredding, a chips size of 1-2 cm being currently the right compromise.

Chemical composition (C, O, H, N, S, Cl) is another important aspect that must be considered. In lignocellulosic biomass, the contents (expressed on a dry and ash-free basis) are usually around 40-50 wt% C, 30-45 wt% O, 5-6 wt% H, 0.1-1 wt% N, and 0.01-0.2 wt% S and Cl. The composition of lignocellulosic materials has been found to be more steady than that of other solid fuels (MSW, coal).

Furthermore, more than 80 wt% of the biomass is volatile matter, the rest corresponding to charcoal. For comparison, coal contains typically only 20 wt % of volatile compounds, while 80 wt% accounts for unreactive coke, which is more difficult to gasify than charcoal.

Although lignocellulosic biomass has very low sulphur and chlorine content compared to coal and MSW, ash and tar contents are one of the main obstacles to economical and viable applications of biomass



gasification technologies. Feedstocks with a high ash content require greater attention because inorganic impurities bring sintering, agglomeration, deposition, erosion and corrosion problems. In addition, they are elutriated by the production gas, so the higher the ash content, the more problematic the gas cleaning procedures will be. On the other hand, tar condenses as the temperature decreases, causing clogging and damage to the downstream equipment (2).

To sum up, the most suitable biomass for gasification must have availability on significant scale (t/year) and suitable physical characteristics in terms of low water content and high bulk density, and chemical features, e.g. high calorific value, volatile substances, and C/N ratio and low ash, chlorine and sulphur contents.

In this context, the search for optimal gasification feedstocks can be initially focused on lignocellulosic waste, such as "shells" (from pine, hazelnut, walnuts and almonds), "straws" (from wheat, corn, rye, barley, rice), and agro-industrial residues (e.g. dry exhausted olives), as well as those generated in "prunings" from forestry/agricultural such as beech, oak, spruce, fir, poplar, willow, eucalyptus, grapes, and olives.

Besides the physicochemical properties, the energy and economic feedstock production costs constitute key parameters in assessing the feasibility of the biomass use. As previously reported by BLAZE project (19), the largest impact on the operating costs in a biomass plant comes from the price of the feedstocks. It generally ranges between negative price of some waste biomass (e.g. -100 €/t of certain contaminated waste) and some valuable crops (e.g. 500 €/t of high-performance 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 (Energy Return On Energy Investment (EROEI) of 10 because 10 GJ are used to have 100 GJ). On the other hand, a mean economic cost (€/GJ), estimated by the production cost (€/mass) (40 €/t) divided by the useful Heating Value (10 HV in GJ/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 (20). Lower yield and lower HV biomass do not have proportionally lower costs meanwhile it is possible to have less competitive energy and economic cost. Therefore, the energy and economic returns could become negative (i.e. EROEI less than 1 and production cost above than that of fossil fuels) (21).

The above reasons and others that include lower environmental impact, coupled with the need not to compete with the uses of food organic matter and biomaterial, make the use of low-cost residual biomass more preferable for gasification.

Subsequently, considering a maximum limit of 100 €/t 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 (*Table 2*) (22) .

Table 2. Summary of all the biomasses

Biomass Category	Roadside Average Price (€/t)	Roadside Average Price + 100 km of transport (€/t)	Other biomass processes maximum cost (€/t)
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 ¹	68	98

The situation is different for MSW. Although the mean prices of MSW as a feedstock are mostly negative, they can be set at 0 on average. 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 €/t 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 €/t: an average price of 140 €/t was considered. The treatment of MSW and the generation of bio-stabilized material in MBT is supported by the “gate fee”, i.e. what the manager charges for treating the waste. There is no return on the sale of these materials, but they could reach negative values as feedstock in SEG as the municipalities are keen to remove it from the landfill site. The costs of transport and treatment for bioenergy use have to be added. It has been estimated 60 €/t for municipal waste including supply chain cost. Nevertheless, owing to the cost of disposal, higher transport and treatments cost can be sustained.

4.2. Requirements for CO₂ sorbents and catalysts

In relation to the SEG process, where a mixture of two solids (sorbent and reforming catalyst) with different chemical and physical properties is used in gasification and regeneration reactor and where the

¹ 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.

catalyst undergoes attrition, the integration of the catalyst within the structure of a sorbent would constitute a breakthrough for the industrial development of SEG technology.

The high temperature and the CO₂ atmosphere during the calcination imposes requirements on the sorbent, e.g. it must be resistant to the grain sintering over a prolonged number of cycles. However, the sintering of the CaO grains happens after a number of cycles (23,24). Therefore, the sorbents in both the SEG and the regeneration steps must show a high stability and steady sorption capacity throughout multiple cycles. Further important properties for a high-performance sorbent are: low-cost manufacture, fast reaction kinetics, mechanical stability and sintering resistance. Stable combined materials (catalyst, sorbent and support) would improve the cycling properties of the solids during the continuous H₂ production. The CaO loading is adjusted to avoid grains sintering and the decrease in the multi-cycle performance of the material. As previously reported (25,26) a reasonable amount of active CaO in the solid sorbent has been determined to be between 30 and 60 wt%.

With regards to the chemical stability, Satrio et al. (27) and Albrecht et al. (28) have succeeded in developing core-in-shell structured particles with reactive CaO as core material coated by an Al₂O₃-supported Ni catalyst. Nevertheless, kinetic data have not been reported and the material shows reduced activity during multi-cycling. Martvaltzi et al. (29) also prepared a hybrid CaO-Ca₁₂Al₁₄O₃₃-NiO material for SER application. Materials with different Ni loadings were tested for hydrogen production by SEG under fixed bed conditions, showing an optimum loading around 16 wt%.

To overcome the aforementioned limitations of solid sorbents that hinder the exploitation of sorption-enhanced gasification processes, GICO will focus on the development of synthetic materials capable of maintaining a very high sorption capacity over a larger number of sorption/regeneration cycles and compatible with use in a fluidized bed reactor and rotary drum reactor. Multi-cycle capacity of the combined sorbent-catalyst powder is an important criterion for the SEG process, concerning both the sorption capacity and the catalytic activity of the material.

Ideally, to be competitive, the lifetime of the materials developed in GICO process should match the lifetime of a commercial reforming catalyst (maximum 5 years). During the project, an initial minimum number of 200 cycles of CO₂ capture and regeneration has to be considered as acceptable to assess the use of these materials. The sorbent-catalyst item will be used in a fluidized bed reactor and in a rotary drum reactor where mechanical attrition is always taking place to some extent and results in fines production. The mechanical properties of the sorbent and catalyst are, therefore, important to avoid a high loss of fines and an uneconomical high material consumption. The measurement of the air jet

attrition index will quantify the relative loss of fines in standard attrition conditions following an ASTM standard (ASTM D5757) by using FCC-catalyst as reference material. In this test, the material fraction is exposed to high velocity air jets causing impacts and friction between particles and simulating the conditions over the fluidized bed distribution plate. The air jet attrition index is expressed as the percentage attrition loss after 5 hours test. A maximum value of 15 wt% is proposed, with reference to previous tests with reforming catalysts (25,30). Two classes of supports will be under investigation in the GICO project. Mayenite ($\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$), with high oxygen mobility, has been tested as support for catalytic hydrocarbon combustion (31) or can be modified by substitution of Ca^{2+} by transition metals for the combustion of diesel soot (32), with very positive results in both approaches (*Table 3*). Another class of combined catalytic and sorbent materials that will be investigated is CaO/Ru supported on perovskite CaZrO_3 (calcium zirconate). Then, most of the new developed sorbents use calcium aluminate (mayenite) and calcium zirconate (perovskite) as support and show enhanced mechanical stability, which results in higher resistance to attrition when used in fluidized bed and rotary drum systems.

Table 3. Performance criteria of the sorbent-catalyst material for biomass gasification

Criteria	Target	Unit	Comments
Excess of CaO percentage in the sorbent system	30-60	wt%	Values for avoiding sintering and loss of sorption capacity during multi-cycling
Max percentage of catalytic metal in combined sorbent and catalytic system	15 (Ni) 5(Ru)	wt%	This value should not exceed the max percentage of Ni in commercial catalysts
Minimum sorption capacity	8.5	$\text{gCO}_2/100\text{g CSCM}$	Calculated for a reference limestone with 10g $\text{CO}_2/100\text{g}$ sorbent capacity, containing 15 w/w% Ni
Minimum cycle stability	200	cycles	Without loss of sorption capacity
Maximum air jet attrition index	15	wt% material loss	ASTM test-Reference material: FCC catalyst or crushed reforming catalyst
Maximum particle density	2100	kg/m^3	Calculated for calcined limestone (1750 kg/m^3) + 15 wt% Ni
Minimum particle size	150	μm	Suitable for particle types A or B (easily fluidizable). Terminal velocity around 1 m/s for maximum defined particle density

4.3. Physicochemical features of the selected biomass wastes

With regard to the chemical features of biomass, they are also highly variable, depending to a great extent on the origin, seasonality, processing, storage, etc. In view of the heterogeneity of biomass materials, it has been considered important not to limit the data collection to those obtained from analyses accomplished on specific biomass samples by CSIC and ENEA, but great effort has also been made to gather data quoted in the literature. In this way, a more reliable and consistent picture is available, which allows a more accurate assessment of the true potential of each waste.

Table 4 summarizes some relevant chemical characteristics of the selected biomass materials. Although the values in *Table 4* can only be taken as a rough estimate because the lack of details in the literature does not allow them to be normalized, it is clearly observed that the different materials fit into the general patterns found for biomass. They present C, H, N, O contents that vary in relatively narrow ranges, being essentially made up of 40-50 wt% of C and O. Additionally, 75-85% of the biomass is volatile matter and the fixed carbon rarely surpasses 20%.

At a glance, the main difference lies in the moisture content and the percentage of inorganic matter. *Table 4* highlights the high moisture of vegetable residues, such as broccoli and thistle, and the same applies for whey and swine manure.

It is worth noting the different moisture values found for the same residue. As an example, the moisture content of branches and leaves from pine trees varies between 10 and 70 wt% and those of poplar trees between 6 and 60 wt%. Large divergences are also detected in the moisture contents of wood sawdust (5-25 wt%), black liquor (4-21 wt%), MSW and MSW-digestate (3-60%), OFMSW (2-57%), digestate (2-71%). On the contrary, the values for this parameter reported in a number of papers for wheat straw, oil rape straw and maize stover are quite similar and do not exceed 5-11%.

Based on the ash content, a clear distinction is made between the set involving lignocellulosic materials and that containing MSW, OFMSW, digestate and manure. The latter group have much higher ash contents as well as S and Cl.

In terms of moisture and ash content, lignocellulosic biomass residues such as pine, hazelnut, walnut and almond shells and pruning wood (beech, oak, spruce, poplar, willow, eucalyptus) appear more competitive candidates for gasification. Straws and agro-industrial (oil and wine production) wastes also present potential for SEG, but the melting temperatures of the ashes in some of these materials may be a great concern with regard to reactor clogging and bed agglomeration.

Table 5 summarises the content of minor elements, such as K, Na and P, whose presence could result detrimental to the SEG plant operation. The table also includes the values of ignition temperature (T_i) and burn-out temperature ($T_{\text{burn-out}}$), which were determined by Thermo-Gravimetric Analysis. T_i corresponds to the temperature at which major decompositions of the biomass samples begin to take place and reveals the decomposition region of volatile matter. $T_{\text{burn-out}}$ is the temperature at which there is no noticeable weight loss over time and, then, the combustion can be considered completely achieved.

Taking into account that a profitable operation of the reactor requires that the biomass ashes do not soft/melt at the gasification temperature, information on the thermal behaviour of the inorganic matter is highly relevant to avoid reactor damages and downstream equipment fouling.

According to protocol CEN/TS 15370-1:2006, it is evaluated on the basis of:

- “Shrinkage Starting Temperature” (SST): temperature at which the area of the test piece falls below 95% of the original test piece area at 550 °C;
- “Deformation Temperature” (DT): temperature at which the first signs of rounding of the edges of the test piece occurs due to melting;
- “Hemisphere Temperature” (HT): temperature at which the test piece forms a hemisphere, that is the height of the sphere becomes equal to half its base diameter;
- “Flow Temperature” (FT): temperature at which the ash is spread out over the supporting tile in a layer, and the height of the layer is half of the test piece at HT.

All data summarized in *Table 4* and *Table 5* will be used for a detailed evaluation of each material in Section 5.

Table 4. Proximate, ultimate analyses, S and Cl contents and calorific value of biomass wastes

Biomass		Moisture (%)	Ash (%)	VM (wt %)	FC (wt %)	C (wt%)	H (wt%)	N (wt%)	S (wt%)	Cl (wt%)	O (wt%)	HHV (kJ/kg _{dry})	Ref
Woods	Branches and leaves from pine tree	30.3-70.2	0.05-0.69			48.3-55.4	5.2-7.8	0.16-2.06	0.14-0.66		35.3-44.1	19364-21713	(33)
		31.8										17133	(34)
		50-56	0.4-2.2			51.8	6.1	0.3	0.01	0.004	41.2		(35)
				79.4-85.7	14.0-18.7	46.5-48.6	6.7-6.9	0.13-0.74	0.03-0.86		42.1-46.4		(36)
		10.4-51.4	17.1-29.9	66.3	16.6	40.7-44.3	5.2	1.8-2.7	0.20-0.29	0.72	31.4	17700	CSIC
	From fir	0.7	82.1	17.2	51.1	6.14	0.41	0.09		41.56	20000	CSIC	
		010	87.30	12.60	50.64	6.18	0.06	0.02		43.0	20370	(37)	
		44.2	2.86	85.1	14.9	49.4	5.5	0.16	0.03		44.8		(38)
		24-60	0.62-1.14	80.9-83.8	15.6-18.1	49.3-50.5	6.0-6.1	0.33-0.77	0.01-0.03		41.8-43.5	19640-19960	(39)
		6.0-6.5	1.70-2.18	76.0-76.9	15.3-15.4	45.1-45.7	6.3	0.11-0.15	0.14-0.16		47.7-48.3	18386-18420	(40)
			1.43			48.5	5.9	0.47	0.01		43.7	19380	(41)
			21	76.8	1.4	36.2	4.3	1.1	1.2		51.6		(42)
			2			48	6.2	0.4	0.03	<0.01	43	19800	(43)
			0.55	83.7	15.75	46.73	5.88	0.4	0.04		46.8		CSIC
			0.79	82.55	16.66	49.66	6.02	0.37	0.08		42.95	19600	CSIC
			1.26	80.98	17.76	51.1	6.09	0.54	0.06		42.39	19500	CSIC
			1.12	83.94	14.94	48.93	6.06	0.43	0.02		43.44	19500	CSIC
		7.37	2.77	79.31	17.92	49.41	5.7	0.6	0.04		41.48	19580	CSIC
		5.0	0.9	83.3	15.8	49.3	6.4	0.14	0.08	0.015	43.2	19600	ENEA
	From Oak	10.5	2.1	81.6	16.3	48.5	6.3	0.25	0.03	0.04	42.8	19020	ENEA
From beech	5.90	0.82	84	15.40	48.26	5.80	0.29	0.03		44.80	18690	(44)	
Wood chips (from industry)	8.9	0.5	81.2	18.3	45.81	5.85	0.1	<0.01	<0.01	47.69	18090	ENEA	

Table 4. (Continued)

	Biomass	Moisture (%)	Ash (%)	VM (wt %)	FC (wt %)	C (wt%)	H (wt%)	N (wt%)	S (wt%)	Cl (wt%)	O (wt%)	HHV (kJ/kg _{dry})	Ref	
Straws	Wheat straw	8.5	4.99	65.6	21.0							17250	(45)	
		6.4	8.1			41.8	4.8	0.5	0		38	17000	(46)	
		7.5	4.4	75.6		47.1	5.7	0.75	0.07	0.07		18610	(47)	
		7.5	6	79	15	47.2	6.6	0.25	0.03		40.3		(48)	
		9.2	5.9	77.7	16.4	39.5	4.4	1.7	0.64	0.290	53.8	17014	CSIC	
		9.4	6.4	77.3	16.3	39.7	4.4	1.7	0.64	0.27	53.6	17014	CSIC	
		7.6	9.22	72.69	18.09	42.89	5.81	0.98	0.05	0.12	40.93	17250	(19)	
		7.6	13.29	69.10	17.61	41.93	5.79	0.91	0.08	0.21	37.79	16660	(19)	
	Oil Rape straw	9.8	6.6	75.6	17.8	46.1	5.3	0.34	0.09	0.06	41.7	17700	ENEA	
		10.5	5.6	80.2	3.7	42.9	5.8	0.87	0.58		49.9		(49)	
			6.1	74.6	19.3	43.8	5.8	0.83	0.61		42.9	17700	(50)	
		9	3.5	69.6	17.9	37.8	4.6	0.76		0.04	44.3	16960	(51)	
	Maize stover		6.2			47.1	5.9	0.84	0.27	0.47	40	18100	(52)	
			7.6		95.5					0.134		17900	(53)	
		5.5	7.4	71.6	15.6						16714	(54)		
		8	5.7	76.8	17.5	48.8	6.2	0.5	0.1		44.4	18450	(55)	
		5	7.0	74.2	13.8	44.2	5.5	0.53	0.1	0	37.7	18050	(56)	
				90.6				1.21					(57)	
		6.8	5.5	75.7	16.9	33.5	5.7	0.52	0.07		54.7	17310	(58)	
		7.5	9.1	74.5	16.4	44.5	5.0	0.5	0.23	0.44	40.2	17900	ENEA	
Agricultural wastes	Sugarbeet leaves	9.4	2.3	71.9	16.5	40.8	5.9	1.3	0.19		45.7	17005	(59)	
		6.1	3	74.2	16.7	43.4	6.3	1.4	0.2		48.7	16100	(60)	
				79	16.9	45.7	6.8	1			46.7	18700	(61)	
		12.5	9	76	15	38.9	5.7	1.2	0.51		47.5	15095	(62)	
		9.5	12.7-13.9	72.3		41.0	5.0	0.97	0.24	0.002	40.2	15900	(63)	
	Sunflower stalk			11.95		46.77	5.51	1.89	0.21	0.52	33.15	19120	(64)	
				11.14		42.74	5.03	0.99	0.11	0.78	39.21	16320	(65)	
				8.82		45.51	5.03	0.31	0.03	0.68	39.62	17040	(66)	
	Olive tree pruning			2.9				1	0.15	0.02			(67)	
		3.8	1.7	72.6	21.9	51.2	6.7	1.12			39.3	19830	(68)	
		0.8	77.9	21.3	48.5	5.3	0.7			44.7	19100	(69)		
		5.3			44.5	5.8	0.84	0.02	0.02		17320	(70)		
		0.37	84.8	14.83	52.11	6.04	0.23			40.91		CSIC		
Vine pruning	14.9	1.55	80.8	17.66	49.57	5.96	0.10	<0.01	<0.01	42.80	19060	(19)		
Almond shell	3.67	1.42	77.80	19.58	46.28	6.28	0.54	0.0185	0.0005	46.89	18950	(71)		
Hazelnut shell	3.3	0.6	80.3	15.8	50.5	6.6	0.21	0.006	0.05		18200	(72)		
Almond	12.9	5.3					0.22	0.01	0.008			(73)		
	10.0	1.31	80.35	18.33	48.79	6.14	0.51	<0.01	<0.01	43.24		ENEA		
Residues from industrial process involving agriculture materials	Bagasse	58.70	6.0	62.2	31.8	47.2	5.8	0.8			46.1	19917	CSIC	
	Grape Stalks	7.01	3.5	58.4	38.1	55.4	6.2	1.4			37.0	17698	CSIC	
	Grape seeds	7.6	2.3	69.58	20.5	49.9	6.3	1.3	0.18		32.3	21290	(74)	
	Rice husk	5.2	14.7	67.7	17.6	43.7	5.3	0.1	0.02	0.03	36.1	16350	ENEA	
	Oil free-seeds	11.32	3.5	76.5	20.0	55.4	6.2	1.4			37.0	22663	CSIC	
	Olive pomace		10	3.9			51.3	5.9	0.95	0.11			(75)	
				1.9-3.8	77.6-78.0	18.6-20.1	53.2-53.5	8.9-9.2	0.6-1.0			36.3-37.3	21700-22300	(76)
			5.5-10	2.6-9.0	43.2-80.2	9.9-44.3	46.8-54.9	5.7-8.2	0.7-2.2	0.0-0.3		33.6-46.2	19500-25460	(77)
			6.9	5.2	71.9	16.1	47.9	6.1	1.8	0.1	0.39	32.0	20520	(78)
			5.5-10	0.56-5.60	77.8-80.9	15.3-18.5	52.3-55.2	7.5-8.2	0.06-2.22	<0.1	0.09-0.80	34.0-40.1	20610-23390	(79)
			0.37	82.41	17.22	51.62	5.97	0.25	0.01		41.78	20500	CSIC	
		36.3	5.95	73.01	21.04	51.84	7.14	2.79	0.06	0.08	32.14	21350	(19)	
Broccoli	91.6	8.9	70.2	20.9	48.1	6.2	4.2	0.71	<0.13	40.8	17800	CSIC		
Thistle	91.8	9.1	88.6	2.3	44.9	5.8	2.9	0.09	2.85	46.3	16100	CSIC		
Whey	94.2	10.0	70.2	19.8	44.0	6.8	2.8	0.22		46.1	16200	CSIC		

Table 4. (Continued)

Biomass		Moisture (%)	Ash (%)	VM (wt %)	FC (wt %)	C (wt%)	H (wt%)	N (wt%)	S (wt%)	Cl (wt%)	O (wt%)	HHV (kJ/kg _{dry})	Ref	
Residual woods	Wood sawdust	4.8	1.27	78.3	15.6	46.5	5.8	0.1	0.01	0.03	41.4	19260	(80)	
		16.4	0.37	81.0	18.6	48.6	5.8	2.39	3.56	0.4	43.2	15100	(81)	
			0.13	81.6	18.4								20581	(82)
		11.2	0.41	81.8	17.8	49.40	5.84	0.43	<0.01	<0.01	43.92	20160	(19)	
		8.9	0.54	81.20	18.26	45.81	5.85	0.1	<0.01	<0.01	47.69	18090	(19)	
		6.6	0.43	84.66	14.91	47.07	6.15	0.1	<0.01	<0.01	46.24	18480	(19)	
	24.5	1.45	81.50	17.05	49.88	5.80	1.06	0.02	<0.01	41.79	19140	(19)		
	Out-of-use wood from furnitures	10.1	4.0	81.6	17.3	48.3	5.9	2.9	0.04		42.9	19501	CSIC	
Black liquor from paper mill		8.6	32.5	50.8	8.04	23.5	4.8	0.08	4.4	0.08	34.8	10550	(83)	
		3.81	32.4	45.7	18.9	31.07	2.96	0.55	0.93		29.09		(84)	
						34-39	3-5	0.05-0.2	3-7	0.2-2	33-38		(85)	
			9.4			6.3			4.9				(86)	
Municipal wastes	MSW	20.6	48.28	43.54	8.18	33.27	3.87	0.15	0.74	0.12	13.57	12080	(19)	
		6.2	15.8	68.1	9.9	46.2	7.7	1.7	0.23		22.3	19220	(87)	
		3.3	9.1	79.7	7.2	63.6	8.1	0.4	0.11		27.1	15978	(88)	
		60.6	4.0	31.9	3.6	55.2	5.3	2.6	0.29	0.07	34.8	12420	(89)	
		4.6	5.3	77.9	16.7									(90)
		59.6	15.5	21.6	3.4	14.6	2.1	0.4	0.09		7.6			(91)
		25	18.5-22.6			41.2-42.3	5.4-5.5	1.2-1.3	0.18-0.23	0.45-0.71	28.9-32.3			(92)
		48.9	35.5	59.1	5.4	54.1	6.5	2.9	0.81	0.76	35.7	25788	CSIC	
		23.0	47.01	40.32	12.67	32.65	4.43	2.37	0.2	0.4	12.94	11190	(19)	
	OFMSW	10.8	7.7	76.9	15.4	52.3	6.5	2.7	0.3		38.3	19900	(93)	
		2.1	12.9	68.8	16.3	58.6	6.7	2.2	0.3		17.1			(94)
										1.2				(95)
	57.0	15.0	74.3		39.8	5.1	1.6			40.5	14900	CSIC		
Digestates			15.7-35.8	78.4-85.1	14.9-21.6	34.3-42.6	4.0-5.0	1.9-2.1	0.2-0.4		23.9-34.3	13400-17000	(96)	
			12.4	67.0	20.6	42.5	5.9	1.8			49.8	19740	(97)	
		6.8	25.7	55.5	18.8	35.8	9.5	3.2	0.3		25.5		(98)	
		2.3	54.8	33.0	9.9	21.8	2.6	1.3	0.54	0.34	18.6	8920	(99)	
			16.0-55.5	36.2-70.2	2.1-13.8	24.1-44.1	1.7-5.1	1.5-3.2	0.2-1.5		16.4-31.3	14900-17800	(100)	
		<2.5 – 2.9	23.1-38.8	68.0		35.5-43.1	6.1	3.8-6.3	0.80-0.86	0.24	21.9	18707	CSIC	
		71.2	23.3-44.6	52.4		30.0-44.5	4.4	3.6-4.3	0.63-1.60	<0.13	15.8	12891	CSIC	
	71.2	25.81	63.97	10.22	32.22	4.51	3.07	0.97	0.1	33.32	13700	(19)		
Manure of bovine, swine and poultry	Bovine dry matter					25.9		0.7	0.58				(101)	
						30.5-35.1		2.2-2.3					(102)	
		84.3	12.0	77.0	11.0	6.9	6.8	0.4					(103)	
		9.5	32.2	45.8	12.5	41.1	5.9	2.7	0.37		49.9	13426	(104)	
	Swine manure			17.1	82.9		41.2	5.7	3.9					(105)
				12.6	64.8	22.6	44	5.1	2.9	0.2		35.7	15800	(106)
		6.9- 8.6	25.2-26.4	58.9-60.2	7.2-7.7	54.3-58.4	7.5-7.9	4.3-5.1	1.7-1.9		26.8-31.5			(107)
			21.2	69.5	9.3							19500		(108)
			19.9	73.8	6.4					1.2	1.4			(109)
		98.0	0.52			0.8		<1.00	0.05	2.43				CSIC
	Poultry manure	12.8-62.5	10.6-15.4	26.6-64.4		14.8-36.0	5.7-8.2	1.9-2.4					11552-14587	(110)
			24.4			37.8	4.8	1.9	0.1		31	15100	(111)	
		18.1-70.9	12.0-44.4	50.4-69.9	5.2-18.1	21.9-42.9	2.5-5.6	1.7-5.5	0.28-0.68		29.2-34.1	8577-16546	(112)	
						44.7		24.3	0.1		23.9			(113)
		90	32	67		41		4.6	0.46					(114)
							2.8	1.18	0.71			11552-14587	(115)	

Table 5. Presence of inorganic elements and thermal behaviour of the biomass ash

Biomass		K (wt %)	Na (wt %)	P (wt %)	T _i (°C)	T _{burn-out} (°C)	SST (°C)	DT (°C)	HT (°C)	FT (°C)	Ref	
Woods	Branches and leaves from pine tree	0.18- 0.60		0.04-0.16			1125	1210	1250	1275	(35)	
		1.85	0.121	0.19	283-318	475 - 533					(116)	
	Branches and leaves from poplar tree				167-207							(38)
		0.24	0.01	0.06								(41)
		0.03	0.4				754	> 1500	> 1500	> 1500		(42)
		1.97	1.82	0.62								CSIC
	Poplar	8.94	0.49	10.1								CSIC
		0.10	0.004								>1400	ENE A (117)
	Oak											ENE A (118)
		1.24	0.004					1360			1380	
Wood chips	0.10	0.004		309.1	556.0	1110	>1385	>1385	>1385		ENE A (119)	
Straws	Wheat straw						748	839	1105	1244	(119)	
		1.4	0.0524	0.14			894	934	999	1096	CSIC	
		0.85	< 0.0005	0.12			943	1054	1177	1328	CSIC	
		1.06	0.23		295.3	541.0	1030	1065	1195	1315	(19)	
		0.23	1.06		265.7	561.5	1100	1135	1185	1300	(19)	
	Oil Rape straw	0.67	0.054									ENE A (50)
		0.85	0.521		264	455			1380	1400	1420	(51)
								1213				(52)
	Maize stover	0.50	0,025	0,025								(53)
					263	402	1204 - 1206	1187 - 1196	1210 - 1213	1218-1225		(54)
							1277	1500	1500		(55)	
1.25		0.023									ENE A (56)	
Agricultural wastes	Sugarbeet leaves				230	500-590					(59)	
					183	750					(62)	
	Sunflower stalk	0.30	0.09	0.05					1224	1241	1267	(63)
							820	920	1640	1650		(64)
							700	780	1750	1800		(65)
	Olive tree pruning						620	630	670	700		(66)
		1.14	0.01									(67)
					258	517						(69)
								1299				(70)
	Vine pruning	9.43	3.38									CSIC
0.18		0.005		276.8	558.2	1360	1380	>1385	>1385		(19)	
Almond or Hazelnut Shells	8.24	0.0428	0.11			882	1527	1576	1584		(120)	
Rice husk	0.50	0.02	0.02								(73)	
	0.41	0.03		269.1	604.1	915	1000	1180	1210		(19)	
	0.58	0.052		299.9	554.2	920	990	>1385	>1385		ENE A (75)	
Residues from industrial process involving agriculture materials	Olive pomace	1.28									(75)	
					227-241	527-558					(76)	
					181-220	509-530	1165-1185	1185-1320	1195-1335	1330-1350		(79)
	0.64	0.06		277.1	649.6	1280	1290	1300	1345		(19)	
	Broccoli	0.34	< 0.10	< 0.05							CSIC	
	Thistle	2.64	2.43	0.27							CSIC	
Whey	0.17	< 0.10	0.07							CSIC		

Table 5. (Continued)

Biomass		K (wt %)	Na (wt %)	P (wt %)	T _i (°C)	T _{burn-out} (°C)	SST (°C)	DT (°C)	HT (°C)	FT (°C)	Ref	
Residual woods	Wood sawdust	0.05	0.01	0.06				1215	1252	1271	(121)	
		3.23	90.9	0.38							(80)	
												(81)
					270	500						(82)
		0.05	0.01		322.6	580.7	1250	1300	>1385	>1385	>1385	(19)
		0.10	0.004		309.1	556.0	1110	>1385	>1385	>1385	>1385	(19)
	0.09	0.01		315.6	556.8	1225	>1385	>1385	>1385	>1385	(19)	
	0.17	0.01		297.4	517.7	1335	1370	>1385	>1385		(19)	
	Out-of-use wood from furniture	0.11	0.15	0.02			1146	1154	1160	1257	CSIC	
Black liquor from paper mill		1.35	17.4	0.01							(83)	
		0.1-2	17-25								(85)	
		1.3-2.1	15-18								(86)	
		4.87	13.24		253.6	480.1	675	680	705	730	(19)	
Municipal Wastes	MSW							1180	1195	1210	(87)	
					220	560					(88)	
				0.14								(89)
								1340	1400	1425		(91)
		0.12- 0.20	0.06- 0.10									(92)
		0.86	1.12	0.57			1182	1190	1190	1192	CSIC	
		1.21	1.02		286.4	547.0	1210	1220	1240	1300	(19)	
	OFMSW					224	828					(122)
			1.14	0.69	0.58							(123)
								1035	1153	1230	(94)	
		0.76	1.12								(95)	
Digestate		1.80-3.67	0.08-0.66	0.39- 0.94							(96)	
					240	540					(97)	
		0.80	0.78	0.37							(99)	
		0.7-1.6	0.3 – 0.9	0.7-2.7							(100)	
		0.49	0.23	0.94-1.17							CSIC	
		0.47	< 0.10	1.25							CSIC	
Manure of bovine, swine and poultry	Bovine dry matter			0.18							(101)	
			0.92-1.08		0.72-2.49						(102)	
						172	453					(104)
	Swine manure		1.21	0.14	1.52			1260	1320	1380	1500	(106)
			0.34	<0.10	0.06							(108)
	Poultry manure								1113	1179	1368	CSIC
							249	637				(124)
			0.7		0.4							(111)
			2.15	0.43	2.27							(113)
			4.74	0.09	2.07							(114)
										(115)		

4.4. Preliminary assessment by modelling

Due to the scatter and complexity of the experimental data, an approach was accomplished by modelling. As a first approximation to the impact of different parameters such as temperature and CaO on the main gas components (H₂, CO, CO₂, CH₄, H₂O) and on alkali, sulphur and chlorine species in the syngas, some preliminary calculations were performed by using FactSage 8.1. FactSage can calculate multiphase and multicomponent equilibria using Gibbs energy minimization routines. Biomass data provided by CSIC were used as starting inputs.

Because FactSage is only able to calculate equilibria which might deviate widely from realistic values, the following three steps were carried out:

Determination of the necessary amount of water (gasification medium) for the complete conversion of graphite (C) to carbon monoxide (CO) and carbon dioxide (CO₂) at 600 °C and 1 atm to maximize the amount of gas and thus the resulting amount of H₂ (primary and secondary water gas reaction).

Gasification of the various biomasses with the amount of water found in point 1 at 600 °C, 650 °C, 700 °C and 1 atm.

Addition of CaO in excess to the resulting gas phase from 2, so that the maximum amount of carbon dioxide can be absorbed by CaO.

The data (see *Table 6* and *Table 7*.

Table 7) obtained can, therefore, only be interpreted as limiting values of an ideal (in thermodynamic equilibrium) working gasification plant. A SimuSage-model adapted to experiments would be provided during the project.

The effect of gasification temperature on syngas generation was investigated varying from 600 to 700 °C. The results are shown in *Table 6*. As could be seen, the six major components (H₂, H₂O, CO, CO₂, CH₄, N₂) make up over 99.9 mol% of the syngas. Moreover, temperature had a significant negative effect on hydrogen production. The hydrogen fraction decreased for all investigated biomasses with increasing temperatures between 600–700 °C. The mole fraction of H₂ in an H₂-CH₄-CO-CO₂-gas equivalent, referred to as A in *Table 6*, decreased from approximately 90 mol% to 80 mol%.

Table 6. Effect of temperature on the main components of the syngas at atmospheric pressure

Biomass	T(°C)	H ₂ O (g)	CaO (g)	X-H ₂	X-CH ₄	X-N ₂	X-H ₂ O	X-CO	X-CO ₂	A
Thistle	600	70	160	0.79	0.08	0.02	0.11	0.01	0.003	0.89
Whey	600	80	170	0.79	0.06	0.01	0.13	0.01	0.003	0.92
Bio-stabilised of MSW	600	110	190	0.79	0.07	0.01	0.11	0.01	0.003	0.90
Broccoli	600	90	190	0.78	0.08	0.02	0.11	0.01	0.003	0.90
Sewage Sludge	600	120	200	0.78	0.07	0.03	0.11	0.01	0.003	0.90
Green Waste	600	110	200	0.79	0.06	0.01	0.12	0.01	0.003	0.92
Digestate	600	150	240	0.79	0.07	0.02	0.11	0.01	0.003	0.91
OFMSW	600	80	170	0.79	0.07	0.01	0.11	0.01	0.003	0.90

Table 6. (Continued)

Biomass	T(°C)	H ₂ O (g)	CaO (g)	X-H ₂	X-CH ₄	X-N ₂	X-H ₂ O	X-CO	X-CO ₂	A
Thistle	650	70	160	0.76	0.06	0.01	0.11	0.04	0.01	0.87
Whey	650	80	170	0.77	0.05	0.01	0.13	0.03	0.01	0.89
Bio-stabilised of MSW	650	110	190	0.77	0.06	0.01	0.11	0.04	0.01	0.88
Broccoli	650	90	190	0.76	0.06	0.02	0.11	0.04	0.01	0.87
Sewage Sludge	650	120	200	0.76	0.06	0.03	0.11	0.04	0.01	0.88
Green Waste	650	110	200	0.77	0.05	0.01	0.12	0.04	0.01	0.89
Digestate	650	150	240	0.76	0.06	0.02	0.11	0.04	0.01	0.88
OFMSW	650	80	170	0.77	0.06	0.01	0.11	0.04	0.01	0.88
Thistle	700	70	160	0.68	0.03	0.01	0.12	0.12	0.04	0.79
Whey	700	80	170	0.68	0.02	0.01	0.14	0.11	0.04	0.81
Bio-stabilised of MSW	700	110	190	0.68	0.02	0.01	0.13	0.12	0.04	0.80
Broccoli	700	90	190	0.68	0.02	0.02	0.13	0.12	0.04	0.79
Sewage Sludge	700	120	200	0.67	0.02	0.02	0.13	0.12	0.04	0.79
Green Waste	700	110	200	0.68	0.02	0.01	0.14	0.11	0.04	0.81
Digestate	700	150	240	0.68	0.02	0.02	0.13	0.12	0.04	0.80
OFMSW	700	80	170	0.68	0.02	0.01	0.13	0.12	0.04	0.80

An increase of the amount of CaO in the gasification unit leads to a reduction in H₂S- and COS-concentrations due to sulfiding. Above that, no more H₂S and COS can be reduced after CO₂ is converted completely (CaO in excess).

For 650 °C the amount of the sulphur-containing gas components can be so reduced to <40 ppm (H₂S) and <0.1 ppm (COS), respectively. The syngas from all examined biomasses has NaCl and KCl concentrations in the lower double digit ppm range, while the syngas from digestate reaches high HCl-concentrations (200 ppm). The concentrations for the alkali chlorides can be found in *Table 7*.

Table 7. Alkali, sulphur and chlorine species in the syngas at 650 °C and atmospheric pressure

Biomass	H ₂ O (g)	CaO (g)	X-H ₂ S	X-COS	X-HCl	X-NaCl	X-Na ₂ Cl ₂	X-Na ₃ Cl ₃	X-KCl	X-K ₂ Cl ₂
Thistle	70	160	3.03E-05	7.74E-08	5.41E-06	1.18E-05	6.29E-06	6.04E-08	2.36E-05	1.12E-05
Whey	80	170	3.61E-05	7.74E-08						
Bio-stabilised of MSW	110	190	3.25E-05	7.74E-08						
Broccoli	90	190	3.09E-05	7.74E-08	5.22E-06	1.18E-05	6.29E-06	6.04E-08	2.36E-05	1.12E-05
Sewage Sludge	120	200	3.12E-05	7.74E-08	5.25E-05	1.18E-05	6.29E-06	6.04E-08	8.75E-08	
Green Waste	110	200	3.52E-05	7.74E-08	1.05E-05	6.37E-06	1.85E-06	9.59E-09	2.36E-05	1.12E-05
Digestate	150	240	3.24E-05	7.74E-08	1.98E-04	1.18E-05	6.29E-06	6.04E-08	8.94E-08	
Min			3.03E-05	7.74E-08	5.22E-06	6.37E-06	1.85E-06	9.59E-09	8.75E-08	1.12E-05
Max			3.61E-05	7.74E-08	1.98E-04	1.18E-05	6.29E-06	6.04E-08	2.36E-05	1.12E-05
Median			3.24E-05	7.74E-08	1.05E-05	1.18E-05	6.29E-06	6.04E-08	2.36E-05	1.12E-05

The gas release calculation described in this section will be further used to choose decent sorption materials, which are adapted to the needs of the different syngases (compositions, temperature, pressure). Various oxides (ZnO, ZnTiO₃, FeO, MnO, CuO, ...) are considered for sulphur sorption.

4.5. Pre-treatment by hydrothermal carbonization

As a first approximation to the possibilities of using HTC to improve the properties of wastes with less advantages for gasification, a set of 6 materials with different characteristics was involved in hydrothermal carbonization studies at laboratory scale. Broccoli, thistle, whey, organic fraction of municipal solid waste (OFMSW), bio-stabilized material derived from mechanical–biological treatment of municipal solid waste (MSW) and out-of-use wood from furnitures were subjected to HTC. The experiments were carried out in a 3-liter reactor at temperatures of 180 and 230 °C with operating times of 2 and 4 hours, and biomass/water ratios of 1:4.

The broccoli and thistle and whey are representative of agro-food wastes generated in the canning industry, which frequently display a moisture content > 90%. OFMSW and bio-stabilized MSW (49 wt%) are largely produced daily worldwide and beyond landfill and incineration, its most advanced management is limited to composting and anaerobic digestion. They correspond to waste mixtures and their moisture (~ 50 wt%) and purity are lower than that of broccoli and thistle. In the bio-stabilization process, some C is lost, but also volume is reduced (which is beneficial for transport) and moisture is decreased (less degradability and better storage), which results more interesting for gasification than MSW.

Finally, the list includes the remains of cuttings, stumps, straw, shells, etc., which constitute fairly pure streams within waste materials. They could still be recycled to obtain materials prior to energy recovery.

Currently, there is a problem in the recycling of out-of-use wood from furniture because it contains glues and polymers, and composting is not an option for them and recycling into boards is eventually exhausted. If bioenergy is needed, these materials are much cheaper and pre-treatment by HTC could increase their interest for gasification.

As a brief summary, it has been found that hydrochar yield tends to decrease with HTC severity (*Figure 2*). The calorific value (*Figure 3*), generally increases as the temperature and the reaction time increase as a consequence of the carbon enrichment of the resulting solid. However, bio-stabilised MSW does not follow such a trend. Although there is an increase in carbon content of the respective hydrochar, HTC on MSW also concentrates ashes (*Figure 4*), and the calorific value drops. At a glance, ash content can be

reduced under mild HTC (*Figure 4*), but the final result greatly depends on the raw feedstock and the process conditions.

Figure 2. Evolution of solid yield by HTC at different conditions

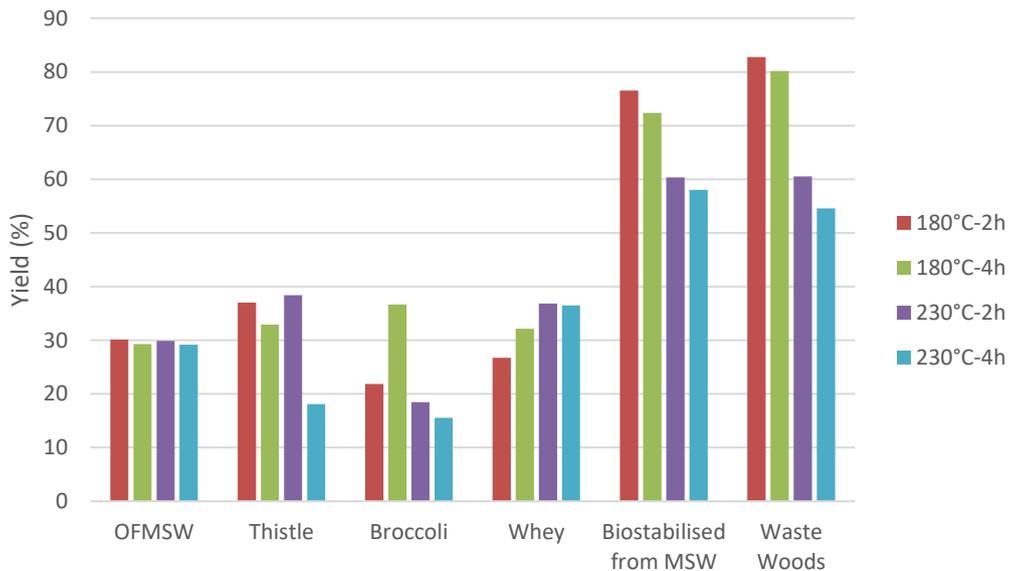


Figure 3. Effect of HTC operational conditions on the HHV of different biomass wastes

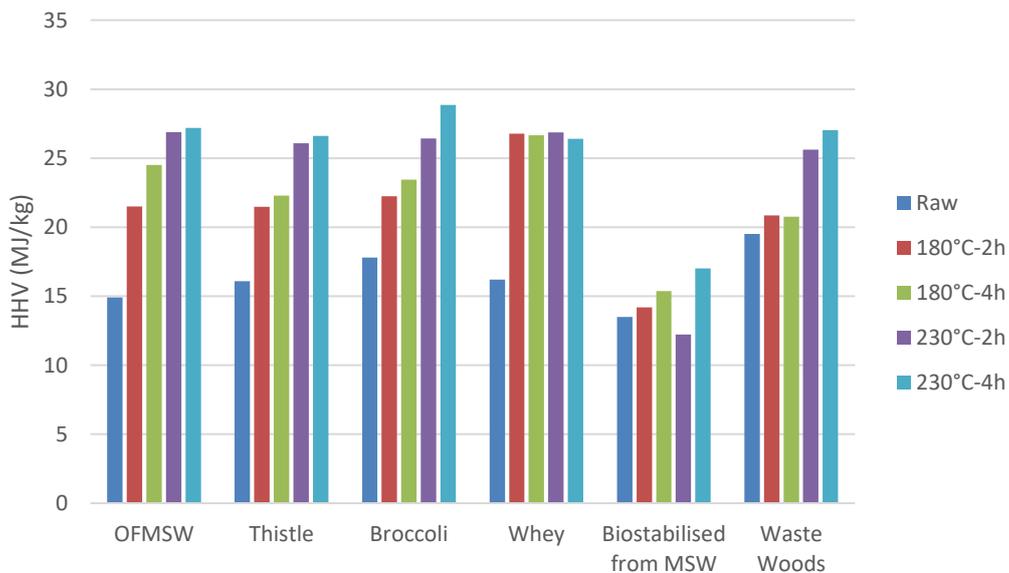
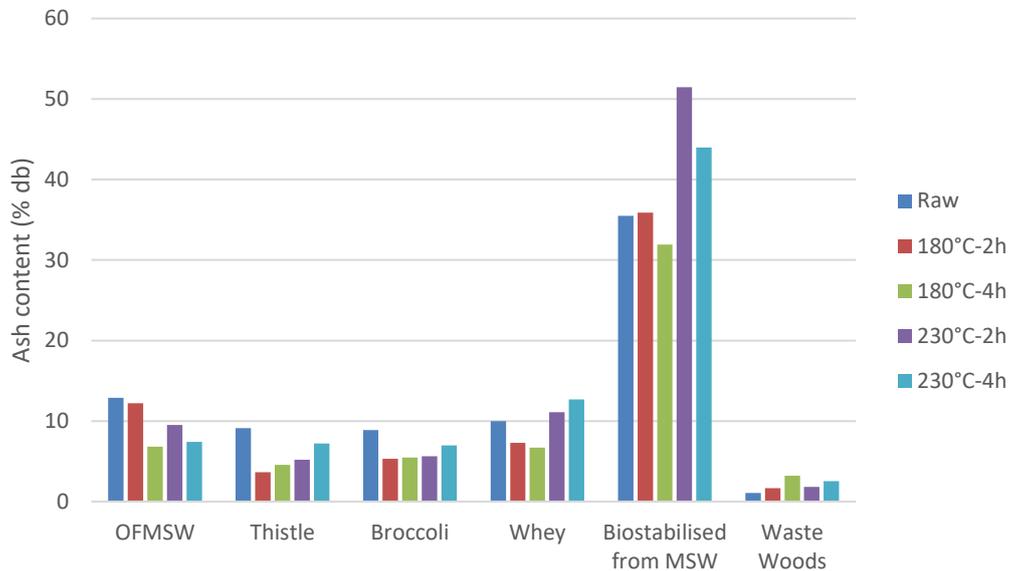


Figure 4. Ash content of hydrochars obtained from diverse biomass wastes under different conditions



5. ASSESSMENT OF THE POTENTIAL OF THE DIVERSE BIOMASSES AS FEEDSTOCKS IN GICO

The objective of the activity was to select 10 simple residuals (pure or mixed) to use without pre-treatment and 10 residual raw materials of "low quality" that need to be pre-treated by HTC. Based on the classification of the residual biomass in terms of availability, cost and suitability of its most relevant characteristics, a preliminary evaluation of the potential as feedstock in the gasification process addressed by the GICO project has been carried out. *Table 8* summarizes a set of 10 wastes with potential to be used for direct gasification and 10 residual raw materials (in Roman numerals) that need to be pre-treated through HTC. In particular, Wheat straw and OFMSW (due to the large availability in Europe), will be selected for both direct gasification and pre-treatment to evaluate the effect of HTC on the same feedstock.

Table 8. Feedstock selection

Category	Biomass	Potential and suitability for SEG
Primary residues from forest	1 <u>Branches, leaves, chips, bark, sawdust and other residues from conifer trees fellings</u>	According to <i>Table 4</i> , this class of feedstock has similar characteristics (ash, VM, FC, C, H, N, S, Cl, O, HHV) among the various types (e.g. pine, fir, cypress). Thus fir ("abete") is selected as representative of the primary residues from conifer forestry residues owing to its greater availability (<i>Table 1</i>), low cost (<i>Table 2</i> -primary residues from forestry) and suitable characteristics (low ash and sulphur and chlorine contents) that allow to use it without pre-treatments
	2 <u>Branches, leaves, chips, bark, sawdust and other residues from non-conifer trees fellings</u>	Based on the similarity of the characteristics (ash, VM, FC, C, H, N, S, Cl, O, HHV) of the different types, e.g. beech, poplar, oak (<i>Table 4</i>), beech chips ("faggio") are selected as a representative of the primary non-coniferous forestry residues due to their greater availability (<i>Table 1</i>) and low cost (<i>Table 2</i> -primary forestry residues). Their suitable characteristics (low ash, S and Cl contents) allow it to be used without pre-treatments
Agricultural residues	3 & I-HTC <u>Wheat straw</u>	Wheat straw is selected as a representative straw, based on its high availability (<i>Table 1</i>) and low cost (<i>Table 2</i> -Agricultural waste), although a somewhat relevant presence of ash and a high content of sulphur and chlorine may negatively affect its performance. This
	4 <u>Maize stover</u>	Maize stover is a good representative of straw with high availability (<i>Table 1</i>) and low cost (<i>Table 2</i> -agricultural residues). Medium ash content and high sulphur and chlorine percentages somewhat reduce their suitability.
	5 <u>Olive tree pruning</u>	Olive tree pruning is widely available (<i>Table 1</i>) at low cost (<i>Table 2</i> -agricultural residues) and display appropriate features (low ash and sulphur and chlorine contents, high HHV and SST)
	6 <u>Vine pruning</u>	Vine pruning is selected on the basis of great availability (<i>Table 1</i>), low cost (<i>Table 2</i> -agricultural residues) and suitable characteristics (low ash, sulphur and chlorine contents, high HHV and medium SST)
	II - HTC <u>Rice husk</u>	Based on its large availability (<i>Table 1</i>) and low cost (<i>Table 2</i> -agricultural residues), rice husk is worth studying as potential feedstock. However, its poor characteristics make it a candidate to be subjected to pretreatment by HTC, at least to reduce its ash content and increase its calorific value

Table 8. (Continued)

Category	Biomass	Potential and suitability for SEG
Secondary residues from wood industries	7 <u>Wood sawdust</u>	Wood sawdust has the main advantages of great availability (<i>Table 1</i>), slow cost (<i>Table 2</i> -secondary residues from wood industries) and appropriate features (low ash, sulphur and chlorine contents, high HHV and SST), but the material have to be densified for optimizing performance
Secondary residues from industrial processing of agricultural products	8 <u>Olive pomace</u>	Olive pomace is selected attending to great availability (<i>Table 1</i>), low cost (<i>Table 2</i> -agricultural residues) and interesting characteristics in terms of high HHV and high/medium SST. Its potential is somewhat limited by high moisture content and medium ash and sulphur and chlorine percentages.
	III - HTC <u>Winery wastes</u>	Wet residue consisting of seeds and stalks that is highly heterogeneous and ferments rapidly due to its high sugar content. It is generated by winery activities in large areas of the EU, but only seasonally. Winery wastes are usually managed by landfilling, composting and anaerobic digestion and there are also already alternatives for chemical valorisation by extraction of compounds for nutrition and cosmetics. Ash content in the range 3.5-6 wt% and HHV of 12663-19917 kJ/kg. Hydrothermal carbonisation may reduce the presence of ashes to 2-3 wt% and significantly improve the calorific value. It could be selected as a potential candidate for pre-treatment by <u>HTC</u>
	9 <u>Almond and hazelnut shells</u>	Based on their proximate and ultimate analyses, they appear of good prospects for gasification. However, the thermal behaviour of the ash, with SST values around 900 °C, suggests the need for a careful control of the calciner temperature
	IV- HTC <u>Broccoli</u> V - HTC <u>Thistle</u>	Secondary residues of industry utilising agricultural products account for 29527 kton dry mass/year and broccoli and thistle have been selected as representative of vegetable waste from canning industry. They are generated seasonally as they depend on the particular cycle of each specimen. Their management relies mainly on composting. They can exceed 90% moisture values, so their direct recovery “as it is” by SEG is rather unfeasible due to extremely low matter content. Their properties are enhanced by hydrothermal carbonization, but the yield is not competitive. Potential application in SEG after being used in HTC as component of mixtures, thus taking advantage of their moisture to facilitate the <u>HTC</u> reaction with less added water.
	VI - HTC <u>Whey</u>	It contains an extremely low matter content. It may be valorised by being used as <u>HTC</u> liquid in place of water. Hydrothermal carbonization of mixtures of wood waste and whey leads to solid with enhanced fuel properties

Table 8. (Continued)

Category	Biomass	Potential and suitability for SEG
Municipal waste	10 & VII - HTC <u>Organic fraction of municipal solid waste (OFMSW)</u>	Mixture of materials very heterogeneous in composition and physical properties. Its characteristics depend on the habits of consumers in each country, the season of the year, appropriate selective collection, etc. Its recovery by SEG would compete with the profitability of composting and anaerobic digestion. As main shortcomings for SEG, this type of waste display high contents of ash, moisture, K, sulphur and chlorine. HTC pre-treatment at temperatures of 180-230 °C and times of 2 and 4 hours gives a hydrochar yield of 30 wt% regarding to the mass of the initial residue (dry basis). As shown in <i>Figure 3</i> and <i>Figure 4</i> , this process significantly increases the calorific value and reduces the percentage of ash. The decrease in ash content indicates a remarkable solubilisation of inorganic impurities by HTC.
	VIII - HTC <u>Out-of-use wood</u>	Heterogeneous material (both in terms of texture and chemical composition) that is available throughout the year, their demand fluctuates greatly in the market. They have reached an average price of 15 €/t in Spain, but demand fell and the cost reached 0 €. The composition C-H-N-O-S is similar to that of forestry wood but the ash content is generally higher. It accounts for around 4 wt% at 550 °C and 1 wt% determined at 810 °C, indicating a relevant presence of carbonates, among others. Management is highly required because the stockpiles ferment and volatile emissions associated with the presence of glues, paints, waxes, etc. have also been detected. The latter could be a drawback for its use in SEG as it may increase emissions. Previous studies have shown that HTC pre-treatment could remove, at least partially, the added polymeric compounds. The HTC yield at 200 °C was around 80% and the calorific value increased to 21000-22000 kJ/kg. The presence of ash is not substantially modified after HTC treatment indicating a partial solubilisation during the process.
Digestate and sewage sludge	IX - HTC <u>Digestate from biogas production</u>	It corresponds to a heterogeneous material, widely available and in need of an end use. It is estimated a potential of 12635 kton dry mass/year in EU, but one should be aware that the characteristics range widely. They are highly dependent on the feed source used in anaerobic digestion, as well as on the operating conditions. As key detrimental parameter, it is worth noting the very high ash content. Depending on the origin of the feedstock subjected to anaerobic digestion, the corresponding digestate contains from 12.4 to 54.8 wt% of ash. Moreover, the presence of S and Cl is significant and some samples do not achieve adequate calorific value. Candidate to be upgraded by HTC
	X - HTC <u>Sewage sludge</u>	Despite the unsuitable characteristic for gasification (high ash content and low HHV), it has been selected owing to the large availability and polluting behaviour as a potential candidate to be upgraded by HTC .

6. CONCLUSIONS

The general objective of this report was the collection of relevant features of a large diversity of biomass wastes to select (via tables that classify the residual biomass respect to availability, cost and characteristic suitability) 10 plain (pure or mixture) residual to be used without pretreatments and 10 residual feedstocks that need to be pre-treated (via HTC) pure or mixture coming from “low grade” feedstock.

Based on the data concerning availability, physicochemical features (i.e. ultimate and proximate analysis, inorganic elements and ash thermal behaviour), calculation via FactSage software, as well as evaluation on favourable aspects, versus adverse one, for exploitation in GICO, a preliminary screening on the biomass feedstocks/wastes of higher interest for the project was carried out. According to the integrated assessment, 20 feedstocks have been therefore identified (*Table 8*). Of these, 10 are plain residual feedstocks, 10 are considered for HTC pretreatments.

Considering the preliminary results obtained for hydrochars derived from wastes, it is suggested to subject OFMSW, out-of-use wood and green waste from parks and gardens to HTC at the pilot plant. Vegetable residues or those derived from dairy industries, with an extremely high moisture percentage, present the potential to be incorporated into waste mixtures and, thus, reduce the amount of water required for the HTC process.

The HTC as pre-treatment would also be valid to sanitise and stabilise the waste, thus favouring its storage. According to the DoA of GICO project, each sample will undergo specific characterizations, as indicated in “T2.1.2. Feedstocks for sorption enhanced gasification (SEG) campaign: characterization of untreated and HTC pretreated biomass”.

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