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Dissemination level		
PU	Public	x
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Content

This is a public report.

For this deliverable D6.4.1, another full version for confidential use is available.

Executive summary

Description of the deliverable objective and content

The aim of this work is to analyse and screen the different sources of biomass from the Eurobioref project. According to various criteria, we have selected different biomasses and biomass wastes as candidates for carbonization application and production of activated carbon.

In the general document of WP6.4's description of work, some criteria like for instance biomass composition and ash content are clearly suggested for biomass selection. These criteria will of course, although not sufficient, be of good help for the selection. Agronomical and Economical criteria, for instance, will also be considered.

In addition to these, a first series of carbonisation/activation trials is needed to get a clearer idea on the suitability of each biomass for activated carbon production.

The study is therefore divided into three main parts:

- Part one is a bibliographic work on biomasses to gather information on different aspects like agronomical, economical or environmental issues.
- A second part dedicated to biomass sample collection followed by their chemical and physical analysis.
- In the third part, a literature study on the biomass transformation is carried out and used to guide us on a first series of exploratory carbonization and activation tests.

Finally, all these elements lead us to define the suitability of each biomass for activated carbon production.

In order to simplify the screening and take into account the availability issues of certain biomasses, all the studied biomasses are categorized into four main classes as follows:

- Lignocellulosic biomasses: includes all the perennial grasses with the use of the whole plant or a part of it.
- Woody materials: includes all the trees, even in short rotation coppice, for production of wood.
- Oils crops: includes all the plants grown for the production of oils by crushing their seeds and the use of their press cake and shells.
- Exotic materials: includes all the plants and trees native from southern hemisphere and particularly from tropical countries.

Of course, other sources of biomass not tested within this project, might be promising for the activated carbons. In general a "promising" biomass should have the following preliminary characteristics prior to getting actual testing results for activated carbon production:

- Low ash content;
- Good agronomical data such as adaptability, little water and chemical aid requirement, high density in harvesting, little moisture, etc;
- It should preferably be associated have mild environmental and toxicity issues;
- Being able to bring it to different granulometry.

Introduction:

The suitability of a certain type of activated carbon to be used in an application will depend on the precursor, on the activation method and on the adsorbate.

The type of biomass, the shape and the size of the particles play a significant role in the formation of pores. The distribution of the different porous sizes influences the way the molecules are adsorbed in the material. Besides technical criteria, biomass availability and cost are other important parameters to take into account for the biomass selection.

Although the texture of the activated carbon is very important, activated carbons with similar texture may also present different adsorption capacities due to variations of the amount and nature of the surface groups. The chemistry of the surface groups on an activated carbon may influence the hydrophobic/hydrophilic character and the basic/acidic character of the material which consequently reflects on the major adsorption mechanism: physisorption or chemisorption.

The activation method is also very important and it is categorized in two groups:

- The physical activation involves the thermal treatment of pyrolysis to remove volatiles and carbonize the product and the development of a porous network with an oxidising agent (steam, carbon dioxide or air).
- The chemical activation involves the carbonization of the raw material with a chemical agent (KOH, NaOH, $ZnCl_2$, H_3PO_4).

Different activation methods give raise to different properties and structures. Before the activation, pretreatment procedures should take place according to the method chosen and the form of the raw material.

According to the activation method followed, special consideration should be given to the conditions of the heat rates, the initial and final temperature, the flow rates and the pressure in the reactors. The physical activation requires the use of two kilns and the chemical activation the use of a single kiln. The adsorption capacity measured depends highly on the type of the adsorbate and the interactions with the adsorbent in certain conditions.

Part one: Description of the bibliographic work

In this part we have gathered agronomical, economical, environmental and toxicological information on biomasses. Main sources of information were other Eurobioref partners, reports from agricultural and environmental institutes as well as articles from scientific publications.

Data from different sources were verified and cross checked. Economical data were collected from energetic crops research programs and from current practices for more conventional crops.

The aim is to obtain a global, though not exhaustive, overview for each biomass. For some not-widespread biomasses, the available data are indeed still limited.

1) Agronomical information:

a) Botanical description:

The essential elements to identify properly each biomass were collected: botanical and common name, botanical family (*e.g.*, Gramineae, Poaceae, …).

b) Biological lifecycle:

The knowledge of the biological lifecycle gives some important information on the different steps of growth and the time of development of a crop. Thanks to these points, it's possible to value the production duration, the potential yield and the frequency of harvest. These elements are decisive in the determination of the crop management (field production, short rotation coppice, forest, etc…) and the associated cost, especially the calculation of the pay-off for the crop establishment and the maintenance cost.

c) Cultural conditions:

The crop cultural conditions gather a set of data from the type of soils, the water requirement and the climates adapted for the crop, until the possible need in fertilizer and agro-chemical treatment. Their compilation enables to define the best production areas for each biomass and is an essential information to evaluate the associated logistic costs. The economic cost of the chemical inputs (fertilisers, pesticides,…) will be calculated thanks to these data.

d) Harvest (period, density, yields):

The study of harvesting conditions as well as their frequency is essential because they will have a real impact on the cost structure and on the availability of the crops.
The period of harvest will depend on both weather and biological lifecycle which cannot be easily controlled, and will also depend on the future utilization of the crop which may require a limited moisture content for example.

For lignocellulosic crops and woody materials for instance, it is generally necessary to wait until the end of the vegetative period, mostly the beginning of the winter, to start the harvest. This increases the risk of having to work on soft and waterlogged ground, which may complicate the access of fields to harvesting machines and thus prolong the harvest period. For short rotation coppice in particular, it is necessary to carefully wait this rest period to allow a vigorous resumption of the culture after cutting.

For the crops harvested during the good season, other issues may happen such as the availability of harvesting machines and workers too busy with others food crops harvest. Some toxicity issue with exotic materials like Castor and Jatropha, as explained in a following paragraph, should be taken in account for the harvest of these crops.

The utilization of specific equipment for planting and harvesting may induce additional costs. An important issue is that, for the moment, some machines only exist in a prototype stage and would need larger crop surfaces and more developped markets to be built on a large scale.

Finally, the density of the crops in kg/m^3 has to be considered as it will have an impact on logistic cost. It will be necessary to find the adapted form (e.g. pellets, bales, loose,…) of the raw material for transport and storage.

e) Disease and pest sensitivity:

Crops threatened by disease and pest will require more attention; sometimes the use of natural bio-control or agrochemical treatment to protect the crop will be necessary thus generating additional expenses.

Especially for crops newly planted on area different from their native habitat, some tests shall be carried out to assess the disease and pest pressure.

2) Economical Information:

a) Crop cost per ton:

The crop cost is the consequence of two main types of costs:

- The crop establishment cost, calculated from the following costs: soil preparation before planting, Seedling- or seed- costs, planting operation (machines, labour), possible additional costs (fertilizers, insecticides, weed killers);

- The annual cost, calculated from the following costs: crop maintenance to keep a clean plot (mechanical or chemical weeding, fertilizer), annualized cost of harvesting (mowing, silage, grinding, …).

In order to calculate the cost per ton, one must also take into account the production time and the total yield.

$$\textbf{Cost per ton} = \frac{\textbf{(Crop establishment cost + (Annual cost x Production time)}}{\textbf{Total Yield}}$$

The data found in literature were sufficient enough to be able to make a cost per ton evaluation for almost each crop**.**

When values found in different pieces of literature for the same crop differed to much we used an average in our calculation.

b) Logistics:

Logistics costs include all the costs relative to the transport of the raw materials from the harvest site through the storage areas until the place of use. The type of transport (trucks, train, boat, …) and the density of the biomass are the two significant parameters for the calculation. Thus, if a local production is not possible, the packaging of the material in the form of loose goods, bale, chips, sawdust, or even pellets must be considered in terms of relative costs.

c) Storage:

The storage of these biomasses is very important because the possibility of using a year-round material harvested only once or twice a year means that one has to store it and keep it stable in the time with its desired properties. Large storage areas representing a real economic investment may be required, especially when the raw material has a low density.

Besides, the moisture of the product and its health condition (notably moulds or other micro organisms) must be controlled to avoid a degradation of the product. In this regard, a natural or artificial drying step may allow a better conservation of the materials, but will raise the price.

d) Production area, amount:

To evaluate the biomass potential, it's necessary to seek for production data to get an idea of the amount produced and currently available on the market. For some crops, however, as they are not widespread yet, we only have a limited access to reliable data, which prevents us from having an accurate view of the market.

e) Uses and current valuations:

To evaluate the biomass potential, it is also necessary to seek for current uses and prospective projects (other than activated carbon production) around each crop.

The number and the type of uses will have a great influence on the market price. Indeed, the use of a biomass to make product with high added value and in large amount, will induce a raise on the market price if the available amount of biomass is low.

Thus, the gap between demand and supply for one crop will have a positive impact on the market price and act as a driving force for the development of production areas resulting in a subsequent increase in production supported by a technical cultivation improvement as , for instance, the decrease of the seedlings production cost.

3) Environmental and Toxicity issues:

a) Poisonous plant for human:

Some of the biomass analysed in this screening present some toxicity issues for human. Although, these toxins will be destroyed during the thermochemical treatment, some risks exist for the people who have to handle these materials. The crop production area must clearly warn about the risk. The harvest, transport and processing conditions must be adapted to prevent the people's exposure to the risk. Additional CAPEX costs will have to be taken into account.

b) Invasive species:

The invasive potential of each plant should be studied, and notably if a plant is introduced into an environment different from its native habitat that can lead to an unwanted spread. Indeed, an invasive plant is an exotic species, imported for its ornamental value or economic interest and by its proliferation, transforms and degrades the natural environment in a more or less reversible manner.

These plants generally have the following characteristics:

- They have a rapid development and are very competitive;
- They have no known pests or consumers in invaded areas;
- They preferentially colonize disturbed habitats (rapid invasion of artificial environments, degraded or depleted in species).

In this study, plants with rhizome propagation could have an invasive character and must be watched closely to avoid issues, especially if rivers are present near the cultivation area which can permit the transport of the rhizome.

c) Impacts on the environment:

The influence of each crop on its environment will depend on its cultural conditions. The increase of cultivation area to the detriment of forest as well as culture standardization can have a strong negative impact on biodiversity (destruction of the habitat of some species not compensating the environmental benefit of producing Activated Carbon from these biomasses).

On the opposite, in the case of degraded or polluted areas, the crop establishment may allow an increase in biodiversity by creating a vegetal cover, which can be a shelter for some species of birds and insects, or even animals, but also a protection against runoff and soil erosion.

d) Agrochemical requirement:

A balance must be respected between toxicity and costs of chemical treatments, and their interests for the crop cultivation. In our study, a crop requiring too much chemical treatment won't have a sustainable character. Furthermore, it will loose of its interest, not only because of the costs, but also because of the risk to have some chemical traces polluting the activated carbon.

Part two: Chemical and physical analysis of biomass samples

1) Proximate, ultimate and trace analysis:

These analyses were performed by CERTH. Please find hereafter a summary of the findings.

a) Moisture

The moisture content of all materials analyzed did not exceed 15%. Dried materials are more effective for thermal processes.

b) Ash

The total ash content of a material is a first indication of its purity. Ash content will be more ore less annoying, depending on its composition. If the ash is constituted of inert silica, it will only have a negative impact on production yield and activation level, but if the ash contains significant amounts of heavy metals like for instance Cadmium, Lead or Arsenic its use to produce food-grade Activated Carbon shall be prohibited.

Biomasses with the highest ash content were olive kernel (the particular material analyzed) and cardoon, which exceeded 10 % ash as received. For cardoon this is rather common due to inclusion of dust and dirt from the harvesting process.

c) Proximate

Dry proximate analyses for Arundo Donax, cardoon, Jatropha capsule, and sunflower cake exhibited the higher fixed carbon content.

d) Sulphur

Switchgrass showed a high sulphur content of 0.41 % dry compared to other materials having almost half of the sulphur. Sunflower derived materials also had somehow higher sulphur content. A too high sulphur content may have a negative impact on the environment as some sulphur containing molecules may be released in the atmosphere.

e) Ash elements

The most abundant elements in all the biomass samples were K, Na, Ca, Mg, Fe, and Si.

According to Certh's experience, Alkali metals in particular, but alkaline earths as well, have been proven to aid char formation. This is of interest for the production of activated carbons, in order to maintain a high yield during carbonization. Additionally these metals appear to lower the biomass pyrolysis temperature by 50°C or more, depending on the concentration. This could be of economical interest for the process.

Olive kernel, sunflower cake pellets, castor, jatropha, willow exhibit the higher Ca content. Similarly olive kernel, sunflower cake pellets, castor and jatropha had the higher Mg content. Materials olive kernel, sunflower cake, arundo donax, castor, and jatropha had high alkali content (K, Na).

The absence of heavy metals from all the biomass samples is important for maintaining the possibility of utilizing the resulting activated carbon in applications of the food or pharmaceutical industry or water-treatment.

Indeed elements Co, As, Cd, Sb, Pb, Se, and V were practically non-existing. Only sunflower cake pellets contained trace amounts of Cd and V probably due to a contamination during pelletizing.

Heavier elements such as Cr, Co, Ni, Ti, Mn were also scarce in all samples.

2) Granulometry and Impregnability

a) Impregnability test

An impregnability test has been developed in order to have a first idea of the impregnation capacity of each raw material before starting chemical activation process. The impregnation rate evolution with water and phosphoric acid follow the same trend carrying out the impregnation test allows to determine whether a material is or difficult to impregnate.

b) Pelletizing

The particle size of biomass is subject to special attention because it influences the behaviour of the material during the steps of carbonization and activation. In this sense, the shaping of the finer raw materials into pellets could lead to better results, compared to using free forms.

Part three: Biomass transformation

1) Bibliographic information on biomass transformation:

The analysis of scientific articles about production of activated carbon from biomasses gives us a better understanding of their behaviour in the steps of carbonization and activation, and especially allows us to:

- identify opportunities for pre-treatment to, for instance, influence grain size distribution of raw materials;
- gather some first indications on carbonization and activation conditions;
- observe and compare the yields and porous surfaces obtained.

2) First series of carbonization tests:

Within the framework of "Task 6.4.2 Batch Carbonization" CECA has started a first series of exploratory carbonization and activation tests on the gathered biomass samples using a standard set of conditions.

Whenever possible, both steam and chemical activation with phosphoric acid were trialled. A whole series of parameters were followed, these will be explained in full detail in deliverable **D6.4.3 (R,M36,CO)**.

Switchgrass straw before…

…and after chemical activation

Switchgrass pellets before…

…and after steam activation

The results are not exhaustive and not final but, as already mentioned in the introduction, we do at this stage consider that they give the clearest idea on the suitability of each biomass for activated carbon production.

Synthesis of results and Conclusion

We have established a ranking of the biomasses based on information and results.

One biomass is disqualified as the product is really not adapted for carbon production. It is not possible at this stage to completely exclude any other biomass as a sample of better quality or an appropriate pre-treatment may lead to an acceptable carbon in the future. We will therefore go on evaluating all the samples proposed by the partners in the coming 2 years.

The efforts put on each biomass will from now on be weighted according to the ranking. This ranking will evolve throughout the project, other biomasses will be step-by-step disqualified and our work will be more and more focused.